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Mini Review

The preparation of imidazolidinone and oxazolidinone chelated carbene complexes

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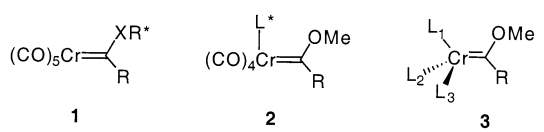
Abstract

The synthesis of several internally chelated imidazolidinone and oxazolidinone Fischer carbene complexes of the type $(CO)_4M=CC(R^1)NCO(CHR^2CHR^3X)$ are reported where the M = chromium, tungsten; R^1 = methyl, ethyl, *iso*-propyl, phenyl, *trans*-propenyl, *iso*-propenyl, *iso*-butenyl, cyclohexenyl and 1-propynyl; R^2 = H, Ph, Bn, Me, Cy; R^3 = H, Me, Ph; X = O, NMe. Four different methods are used for the synthesis of these complexes. The imidazolidinone complexes are best prepared by adding an imidazolidinone or lithiated imidazolidinone to a methoxy carbene complex or to an in-situ generated acetoxy carbene complex. α,β-Unsaturated imidazolidinone complexes are prepared by aldol condensations of alkyl imidazolidinone complexes or by alkylaltion of these complexes with bromomethyl methyl ether and then elimination of methanol. The oxazolidinone complexes are best made by a two-step procedure that involves the addition of an β-aminoalcohol to a methoxy or acetoxy complex followed by closure of the resulting amino carbene complex to the oxazolidinone complex with phosgene. © 2001 Published by Elsevier Science B.V.

Keywords: Carbene complexes; Chromium; Tungsten; Imidazaolidinone; Oxazolidinone; Chelated Fischer carbene complexes

1. Introduction

The utilization of Fischer carbene complexes in organic synthesis has been actively pursued since their discovery [1] in 1964 and is a field that has seen rapid growth in recent years [2]. In the thirty three years of their history, a considerable number of reactions of Fischer carbene complexes have been discovered that have made possible the diversity of the applications in organic synthesis to which these complexes can now be employed. Only a small percentage of various known reactions of Fischer carbene complexes have been investigated in their asymmetric versions with a chiral complex [3]. In principle, a chiral center could be introduced into a Fischer carbene complex at three positions. Chiral complexes of the type **1** could be prepared in which the stabilizing heteroatom X could be embodied in a chiral alcohol [3,4] or amine [2c,3,5]. A chiral complex could also be generated by replacing a carbon monoxide ligand with a ligand containing a chiral center as indicated by the structure **2** [6]. Finally, a third possibility is to incorporate a chiral center at the metal center by employing a pseudo-tetrahedral arrangement of ligands as indicated in structure **3** [7]. In reality, only the reactions of complexes of the type **1**



1 2 3

Scheme 1.

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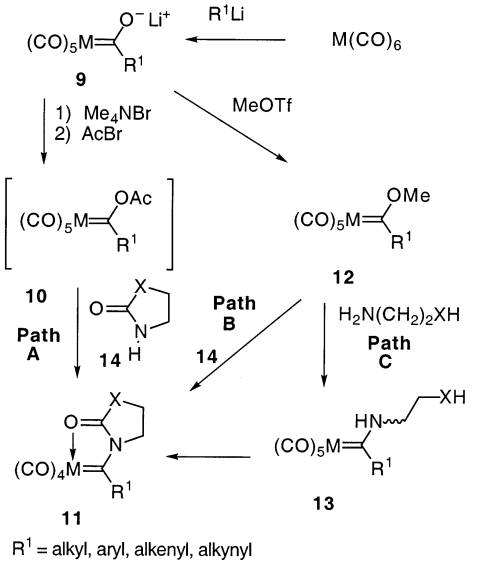
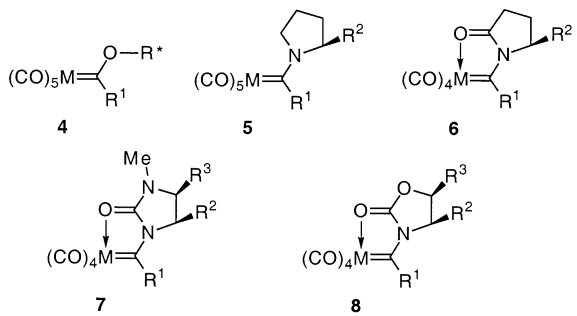


Scheme 2.



Scheme 3.

have been explored to any extent up to this point in time, however, the results of these studies are just beginning to come in and it is far too early to be able to access just what the impact of complexes of this type will have on the actual asymmetric applications (see Scheme 1).

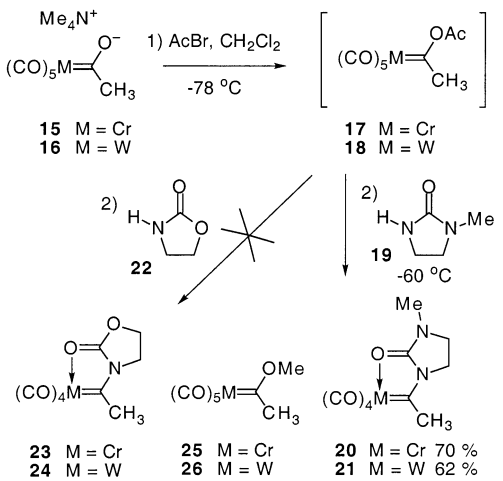
One of the reasons that complexes of the type **2** have not been actively pursued is that complexes of this type (L*-phosphine) are known to undergo relatively facile *cis*/*trans* isomerization which would lead to a loss in control of asymmetric induction [8]. A limitation associated with the development of chiral complexes of the type **3** is that a resolution would be required after the complex was synthesized and this has not yet been achieved despite the fact that some investigations on complexes of this type have been pursued [7]. While the majority of investigations of the reactions of chiral Fischer carbene complexes have been associated with members of the type **1** complexes, these complexes also have drawbacks. Complexes of the type **1** derived from chiral alcohols suffer from the fact that there are likely to be multiple low energy conformers possible. Specifically, the two carbon–oxygen single bonds in complex **4** provide two degrees of freedom for rotation of the chiral center in the alcohol relative to the carbene carbon. One of these degrees of freedom can be removed if amino complexes of the type **5** are employed since nitrogen is trivalent and the chiral center can be embedded in a ring preventing free rotation about the carbon–nitrogen bond to which the chiral center is appended. One of the drawbacks of complexes of the type **5** is that a dialkyl amine substituent on carbene complexes reduces the reactivity to the point where the complex would loose its generality to many reactions of interest [9]. It was found that much of this reactivity can be restored to amino complexes if the nitrogen atom is destabilized by conjugation to a carbonyl group [9,10]. An additional advantage of *N*-acyl carbene complexes is that the carbonyl oxygen usually chelates to the metal by expulsion of a carbon monoxide ligand and removes the remaining degree of freedom associated with rotation about the carbene carbon–nitrogen bond [11]. This would suggest that a complex of the type **6** would be ideal for asymmetric synthesis since the chiral center in the pyrrolidine ring would be securely anchored by the chelation of the carbonyl group. However, our experience with complexes of this type suggests that complex **6** would not be stable enough to be handled without special precautions [9]. For these reasons, we initiated a program into the preparation and evaluation of the imidazolidinone and oxazolidinone carbene complexes **7** and **8** for use in asymmetric synthesis [12] (see Scheme 2).

2. Synthesis of non-chiral imidazolidinone and oxazolidinone complexes

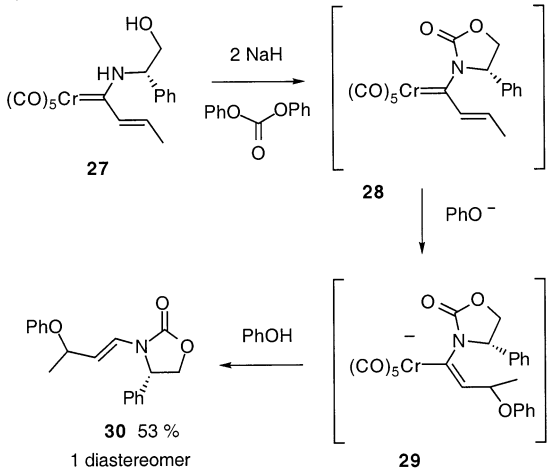
The complexes presented in this work have been prepared by four different procedures three of which are summarized in Scheme 3. Path A and B are related in that they both involve the introduction of the intact imidazolidinone or oxazolidinone **14**. For some complexes this can be accomplished by direct replacement of a methoxyl group in the complex **12** and in others this approach requires the utilization of the more active acetoxyl complex **10** which is not readily isolable and for convenience is generated and reacted in-situ [13]. The third approach outlined in Scheme 3 involves a two-step procedure that begins with the aminolysis of the methoxyl complex **12** (or acetoxyl complex **10**, not shown) with either an β-amino ethanol derivative or a 1,2-diaminoethane derivative to give the amino complex **13**. The second step requires the formation of the cyclic urea or cyclic carbamate and then loss of a carbon monoxide ligand to give the chelated imidazolidinone or oxazolidinone complex **11**. The relative advantage of these three methods will be evaluated for

the preparation of alkyl, aryl, alkenyl and alkynyl complexes of the type **11**. The fourth method involves the interconversion of the chelated complexes **11** and in this work this will be illustrated by alkylation and aldol addition and elimination reactions.

The chromium and tungsten imidazolidinone complexes **20** and **21** could be prepared in good yields by the addition of 2-methylimidazolidinone **19** to the acetoxyl carbene complexes **17** and **18**, respectively. The methoxyl complexes **25** and **26** were unreactive to the imidazolidinone **19**. A reaction was observed upon addition of the N-lithio derivative of **19** but no significant amount of either **20** or **21** was formed in this reaction. The oxazolidinone complexes **23** or **24** could not be prepared in significant amounts by the addition of oxazolidinone **22** to the acetoxyl complexes **17** and **18**. These reactions lead to the formation of a complex mixture of products, which were not carefully characterized. In some instances a small amount of a compound could be obtained whose spectral data were



Scheme 4.

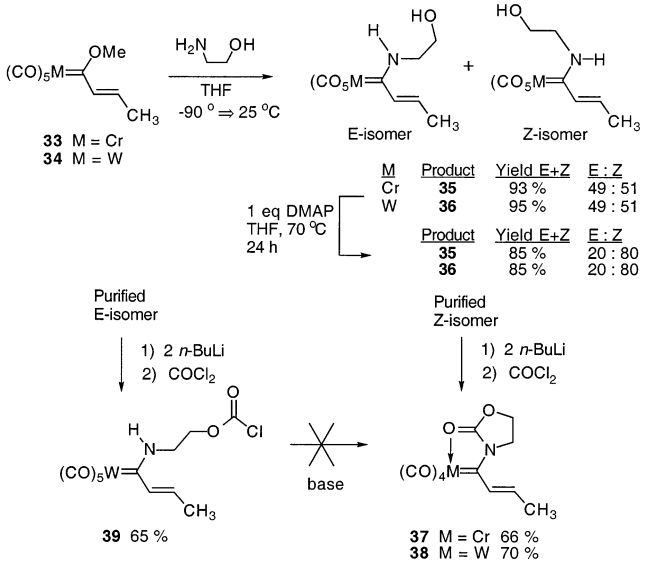


Scheme 5.

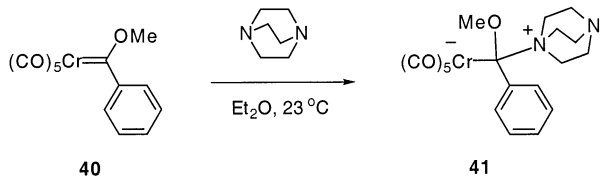
consistent with **23** or **24** but these compounds were not particularly stable and tended to decompose in short periods when handled in air with no special precautions. The instability of these complexes would appear not to permit any general applications of their reactions in asymmetric synthesis. We were thus delighted to find that the imidazolidinone complexes **20** and **21** presented no special difficulties in handling in the presence of air or water and could be purified by silica gel chromatography in the normal manner. These complexes were found to be comparable in stability to their corresponding methoxy complex **25** or **26**. A solution of the chromium imidazolidinone complex **20** in ether when allowed to stand open to the air and room light was observed to persist for six days compared to seven days for the methoxy complex **25**. Complexes **20** and **21** could be chromatographed on silica gel in air with no (see Scheme 4) significant loss of material. For storage, these complexes are best kept as crystalline materials in a vial under nitrogen in the freezer.

All attempts to prepare the oxazolidinone complexes **23** and **24** by the two-step procedure outlined in Scheme 3 were unsuccessful. Similar observations have been made before and disclosed in a report which revealed that attempted closure of amino complexes of the type **13** (X = O) leads to a process in which the metal is lost and which leads to the ultimate formation of ene carbamates [14]. The example from this work shown in Scheme 5 illustrates the formation of the ene carbamate **30**. The oxazolidinone carbene complex **28** could not be isolated from reactions which generated the oxazolidinone ring either from triphosgene or diphenyl carbonate as phosgene equivalents. In the case of the latter reagent, it was surmised that the desired *trans*-propenyl oxazolidinone carbene complex **28** underwent Michael addition of phenoxide ion and then protonation of the enolate **29** at the metal center and reductive elimination lead to the observed product **30**, which was interestingly formed as a single diastereomer. We have observed that β-amino ethanol will add to the methoxyl complex **25** in near quantitative yield but we were not able to close the oxazolidinone ring in the second step (i.e. **13** to **11** in Scheme 3). This closure was attempted with several reagents including phosgene (vide infra) but, the instability of the product suspected of being **23** for the reasons discussed above, dissuaded us from an extensive search for conditions to generate the methyl oxazolidinone complexes by Path C.

As summarized by the information in Scheme 6 it is possible to prepare and isolate the oxazolidinone carbene complexes **37** and **38** which bear a *trans*-propenyl group on the carbene ligand by the two step procedure involving aminolysis and then closure of the oxazolidinone ring. The aminolysis with β-aminoethanol is carried out on the chromium and tungsten methoxyl complexes **33** and **34** and in each case a very high yield



Scheme 6.

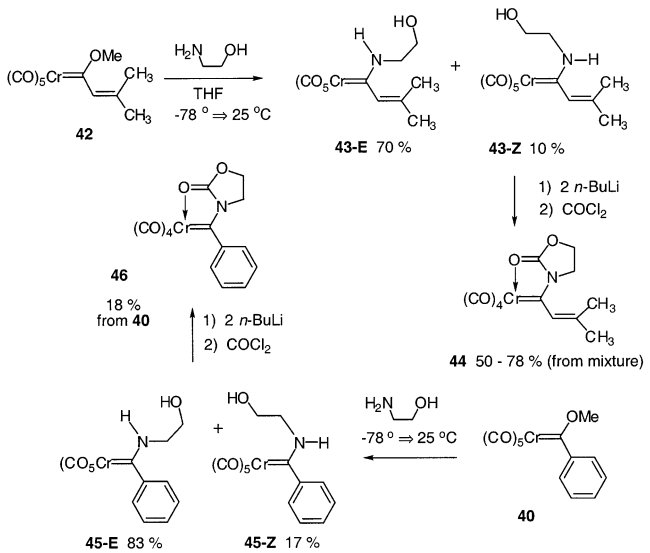


Scheme 7.

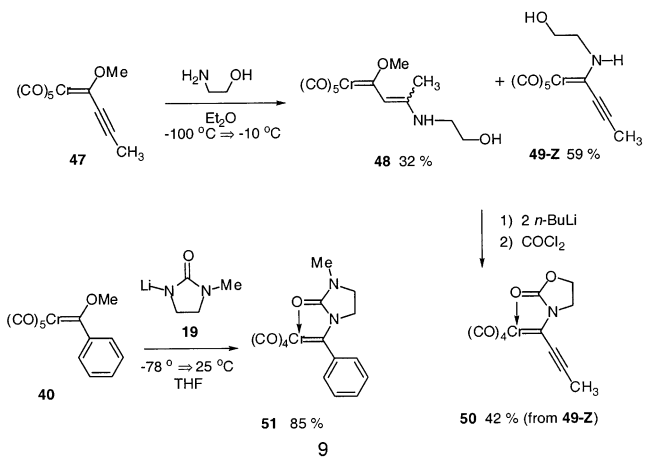
of the amino complex is obtained as a 1:1 mixture of rotamers. The two rotamers are easily separable by silica gel chromatography and the stereochemistry is assigned by ^{1}H-NMR according to the method by Fischer [15] and by X-ray analysis (vide infra). Many failed attempts were registered in an effort to close the oxazolidinone ring. Neither the E or Z-isomer of **35** or **36** would undergo closure upon reaction with either dimethylcarbonate, methyl chloroformate, carbonyldiimidazole or triphosgene in the presence of base. Success was achieved when the Z-isomer was treated with two equivalents of butyllithium and then 1.5 equivalents of phosgene. The chromium and tungsten complexes **37** and **38** were both obtained in good yields as deep purple solids that once obtained in the solid form could be stored at -30°C for several days. However, both complexes are sensitive to water and thus an aqueous workup was avoided but silica gel chromatography in air at ambient temperatures was tolerated. It was rather interesting to find that while the Z-isomer could be closed with phosgene, the E-isomer was totally resistant to the same procedure. Instead, the chloroformate complex **39** was isolated from the reaction with the E-isomer in 65% yield. This compound could not be coaxed to close to the oxazolidinone complex **38** either by heating at 70°C for 24 h or by treating with either one or two equivalents of butyllithium at -78°C. Finally, it can be mentioned that extensive investigation revealed that Path C is far superior to Path A for the preparation of the oxazolidinone complexes **37** and **38**. The only success encountered with experiments on Path A involved the addition of the *n*-lithio derivative of **14** to the reactive intermediate generated by treatment of **9** with triflic anhydride and resulted in **38** only in low yields (5–10%) which were not reproducible.

Confronted with the fact the Z-isomer can be closed and the E-isomer cannot, a method for the isomerization of these complexes was needed if efficient overall yields of the oxazolidinone complexes **37** and **38** were to be realized. Since the dianion of complex **35** (or **36**) is first generated in the successful closure with phosgene, it appears that the nitrogen anion in these complexes cannot undergo inversion. This was confirmed in experiments in which the E-isomer of the tungsten complex **36** was treated with either one or two equivalents of butyllithium and then quenched with water to provide a quantitative recovery of **36** in which no trace of the Z-isomer could be detected. Interestingly, the hydroxyl proton in the E-isomer of **36** is the most acidic proton in the molecule and does not exchange with the amino proton, since upon treatment with one equivalent of butyllithium and then D_2O the hydroxyl proton at $\delta = 2.17$ is absent but the amino proton at $\delta = 8.65$ was still present. The thermal barrier to the interconversion of the tungsten complex **36** is quite high since heating the E-isomer of this complex in THF at 70°C for 24 h lead to a 90% recovery and no detectable formation of the Z-isomer. The high barrier to rotation of an amino carbene complex is due to the significant amount of double-bond characters for the N–Ccarb bond due to the donation of the nitrogen lone pair of electrons into the empty pz orbital of the carbene carbon [16]. One method to overcome this is suggested by an observation made by Fischer that a tertiary amine such as DABCO can form the 1:1 adduct **41** with the chromium carbene complex **40** [17]. This idea was well placed since treatment of a 1:1 mixture of E- and Z-isomers of the tungsten complex **36** with one equivalent of 4-dimethylaminopyridine (DMAP) in THF at 70°C for 24 h lead to a mixture enriched to 80% of the Z-isomer (85% recovery). The yellow solution of complex **36** becomes deep red when DMAP is added and remains this color until the aqueous workup. A ^{13}C-NMR spectrum of this solution did not provide any evidence for a tetrahedral intermediate and thus if involved is likely in an unfavorable equilibrium. Nonetheless, treatment with DMAP does provide a method for isomerization of amino complexes **35** and **36** to the isomer required for closure to the oxazolidinone complexes and as such represents the first amine induced isomerization of an amino carbene complex (see Scheme 7).

The synthetic route developed for the synthesis of the *trans*-propenyl oxazolidinone complexes **37** and **38** shown in Scheme 6 can be extended to the synthesis of the phenyl and *iso*-butenyl complexes **46** and **44**, respectively. Aminolysis of the iso-butenyl methoxyl complex **42** with β-aminoethanol gives an 80% yield of a mixture of stereoisomers in which the E-isomer is predominant in an 88:12 ratio. The major E-isomer could be obtained in pure form by silica gel chromatography but the minor Z-isomer could only be obtained in pure form with repeated elutions. Treatment of the E-isomer of **43** with two equivalents of *n*-butyllithium and then phosgene lead to the oxazolidinone **44** which is in contrast to the *trans*-propenyl complex **36** for which only the Z-isomer could be closed. The aminolysis of the phenyl complex **40** with β-aminoethanol also gave predominantly the E-isomer of the expected amino carbene complex. The combined yield of the E- and Z-isomers of **45** vary between 90–100%. The isomers of **45** cannot be separated by silica gel chromatography and thus the crude reaction mixture was taken on to the oxazolidinone **46** in 18% overall yield from **40**. The 18% overall yield of phenyl complex **46** suggests that only the Z-isomer will undergo ring closure to form an oxazolidinone ring as is the case for the *trans*-propenyl complex **38**. To confirm this pure or enriched samples of the E- and Z-isomers of **45** would be required. While no separation at all could be achieved by silica gel chromatography, the major E-isomer of **45** could be crystallized from the mixture to give a 35% yield of pure compound. The best purity for the Z-isomer that was obtained in a mother liquor was an enrichment of 78:22. A sample of this enriched Z-isomer was treated to the ring closing conditions with phosgene to give a 60% yield of the oxazolidinone complex **46** and as expected, when the pure E-isomer was treated to the same conditions, no detectable amount of complex **46** was observed. A limitation in the synthesis of the phenyl oxazolidinone complex **46** from **40** by Path C is that the overall efficiency of the conversion could not be improved by isomerization of the E-isomer into the Z-isomer. Heating the E-isomer complex **45** with DMAP under the conditions that were successful for complex **38** lead to significant decomposition with loss of the carbene ligand to give a DMAP complex of chromium pentacarbonyl. The small amount of material that was recovered was still predominately the E-isomer ($\sim$ 2:1). The synthesis of **46** may be better effected by Path B as it is for complex **51** (Scheme 9) but this has not yet been investigated. As was shown in the case of the E-isomer of complex **36**, the E-isomer of **45** could not be isomerized to the Z-isomer with butyllithium. Treatment of **45-E** with 2 equivalents of *n*-butyllithium at -78°C for 30 min and then quenching with water gave a 92% recovery of the carbene complex which was determined by ^{1}H-NMR to be exclusively the E-isomer. In a similar fashion, a sample of **45** with a 1.4:1 E:Z ratio was unchanged when treated in the same way (see Scheme 8).



Scheme 8.



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Scheme 9.

The assignment of the major isomer of **35** as either the E- or Z-isomer was not a straightforward analysis. The stereochemistry of amino carbene complexes can reliably be assigned by the relative chemical shifts of protons on the nitrogen substituents [15]. The protons on the Z-isomer are closer to the metal center and as a result are always shifted downfield relative to those of the E-isomer. This relationship also holds for the proton on nitrogen in secondary amino complexes as can be seen for complexes **43** and **45** (Table 1). This is not true for complex **35** in which the most downfield shifts for both the NH proton and the methylene protons are found in the same isomer (Z). Adding to the confusion are the observations that the Z-isomer, but not the E-isomer, of complexes **35** and **45** can be converted to the oxazolidinone complex. This is to be compared to

Table 1
E and Z-isomers of β-aminoethanol carbene complexes

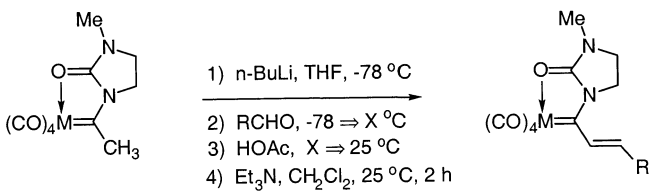
Complex	Isomer	N–H chemical shift	N(CH2)20 chemical shift	Close to oxazolidinone
35	E-isomer	8.90	3.64–3.97	no
	Z-isomer	8.98	4.01–4.14	yes
43	E-isomer	9.21	3.60–3.85	yes
	Z-isomer	8.88	4.06–4.17	
45	E-isomer	9.49	overlap	no
	Z-isomer	9.00	overlap	yes

the observation that the E-isomer of **43** can be converted to the oxazolidinone complex **44**. These discrepancies were resolved by solving the solid state structure of the E-isomers of chromium complexes **35**, **43** (as its acetate derivative) and **45**. As a result it was found that the use of the chemical shift of the NH proton was unreliable in the assignment of the stereochemistry of **35,** whereas**,** the chemical shift of the methylene protons would allow for the correct prediction of the stereochemistry of **35**. The reason for the fact that the Z-isomers of **35** and **45** can be closed to oxazolidinone complexes and the E-isomers cannot is not understood at this time. Also not understood, is the reason that the E-isomer of **43** will undergo closure to an oxazolidinone while the E-isomers of **35** and **45** will not. The ring closing reactions with phosgene require the dianion of the complex be generated with two equivalents of *n*-butyllithium and it is possible that the dianion of **43** can isomerize while those of **35** and **45** can not. To test for this, a sample of **43** with an E:Z ratio of 6.0:1 was treated with two equivalents of butyllithium in THF at −78°C for 30 min followed by a water quench to give an 87% recovery of complex **43** with an E:Z ratio that was unchanged. As described above, the same observations were made for **35** and **45**. Thus the origin of this difference can not be identified as this time.

The alkynyl oxazolidinone complex **50** is prepared in a manner similar to complexes **35**, **43** and **45** except in this case the aminolysis must be carried out at −100°C to minimize the formation of the Michael adduct which is known to be a serious side reaction in the aminolysis of alkynyl complexes [18]. Even at −100°C, the reaction of the alkynyl complex **47** with aminoethanol gives substantial amounts of Michael adduct **48** along with the desired amino complex **49** which is obtained as one isomer that is tentatively assigned as the Z-isomer. At higher temperatures, small amounts of the E-isomer can be observed. Treatment of **49-Z** with two equivalents of butyllithium and then phosgene gives the alkynyl oxazolidinone complex **50** in 42% yield. The phenyl imidazolidinone complex **51** was most easily prepared by Path C (Scheme 3) involving the addition of the lithiated imidazolidinone **19** to the methoxy carbene complex **40** to give the desired product directly in 85% yield. Complex **51** was a robust orange solid that in the crystalline form is stable in air at room temperature (r.t.) for extended periods without decomposition.

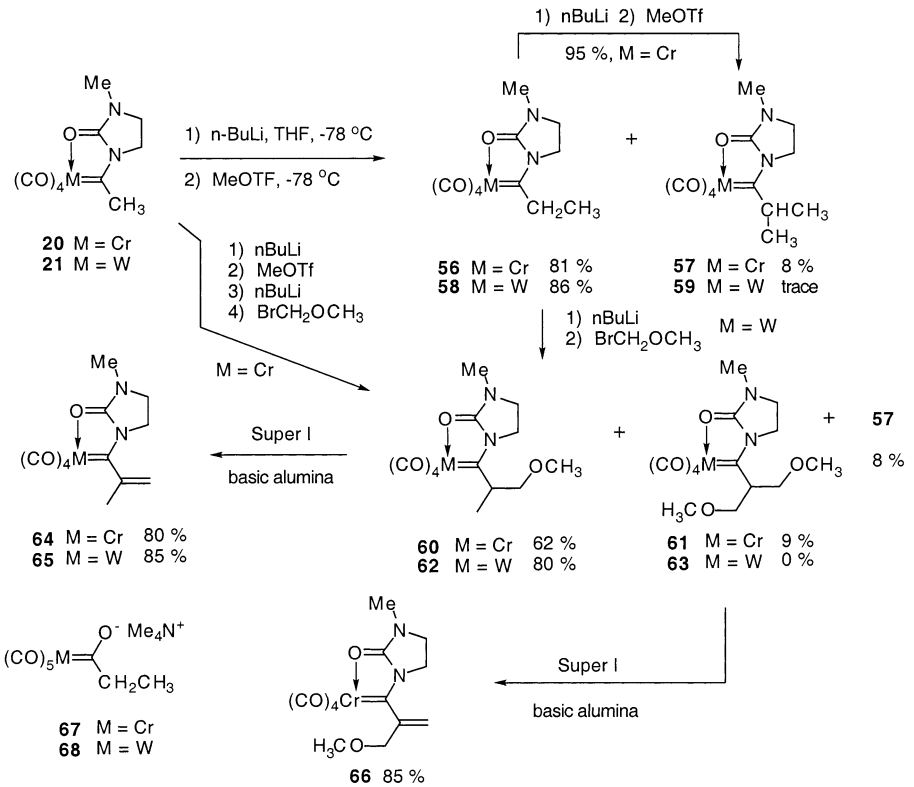
In contrast to the α,β-unsaturated oxazolidinone complexes **37** and **38**, the corresponding imidazolidinone complexes could only be efficiently obtained by an aldol condensation [12b] of the methyl imidazolidinone complexes **20** and **21** (Scheme 10). Attempts to prepare complex **52** by the addition of the lithiated imidazolidinone **19** to the methxoy complex **33** via path B in Scheme 3 or the protonated imidazolidinone **19** to in-situ generated acetoxy or trifloxy complexes according to path A in Scheme 3 did not result in the formation of significant amounts of complex **52**. The aldol addition adducts were isolated but not purified prior to elimination with triethylamine with the exception of the tungsten styryl complex **55** which underwent elimination during the isolation of the aldol adduct. The *trans*-propenyl complexes **52** and **53** were isolated as reddish–purple solids and the styryl complexes were obtained as deep Prussian blue solids. The imidazolidinone complexes are more stable than the oxazolidinone complexes. When a sample of **52** was dissolved in ether and shaken with water and then the bilayer allowed to stand exposed to room light and at r.t. the color of the complex did not visibly fade until after 2 days whereas a sample of complex **37b** began to fade after 2 h when treated in the same manner.

The imidazolidinone complexes can be alkylated in good yields with methyl triflate and bromomethyl methyl ether as illustrated in Scheme 11. Treatment of



Complex	M	R	Et_3N	Temp	Product	Yield
20	Cr	Me	yes	-40	**52**	60
21	W	Me	yes	0	**53**	62
20	Cr	Ph	yes	0	**54**	76
21	W	Ph	no	0	**55**	65

Scheme 10.

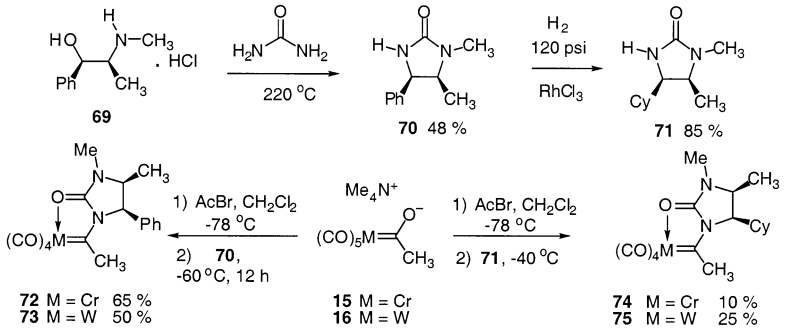


Scheme 11.

complex **20** with butyllithium and then methyl triflate gave an 81% yield of the ethyl complex **56** and an 8% yield of the iso-propyl complex **57** along with a 9% of the starting material. The ethyl complex **56** could not be separated from **20** or **57** but subsequent alkylation of the mixture with additional methyl triflate gave the iso-propyl complex **57** in 95% yield which was one compound. The same alkylation of the tungsten methyl complex **21** was more selective giving only trace amounts of the over alkylated product **59** and only trace amounts of starting material unreacted. The tungsten complex **58** could be further alkylated with bromomethyl methyl ether to give the complex **62** in 80% yield with no over alkylation. The corresponding chromium complex **60** could be prepared by the sequential double alkylation of **20** with methyl triflate and then with bromomethyl methyl ether to give complex **60** in 62% yield which could be separated from the over-alkylated products **61** and **57**. The elimination of methanol could be achieved from complexes **60** and **62** to give the iso-propenyl complexes **64** and **65** in high yields. In a similar fashion, methanol could be eliminated from the purified complex **61** to give the 1-methoxyl-2-propenyl complex **66** in 85% yield. The ethyl complexes **56** and **58** could not be prepared by the direct method indicated in Scheme 4 that was successful for the methyl complexes **20** and **21**. Reaction of the imidazolidinone **19** with acetoxy complexes generated in-situ from the ammonium salts **67** and **68** gave the ethyl complex **56** and **58** in 7 and 10% yields, respectively.

3. Synthesis of chiral imidazolidinone and oxazolidinone complexes

The chiral methyl substituted imidazolidinone complexes **72**–**75** were prepared by Method A in the same manner as the non-chiral methyl complexes **20** and **21** (Scheme 4). All of the complexes are derived from (4R, 5S)-1,5-dimethyl-4-phenyl-2-imidazolidinone **70** which was prepared by the fusion of urea with (-)-ephedrine hydrochloride **69** by the method of Close [19]. The use of the imidazolidinone auxiliary **70** has the attractive feature that both enantiomers of ephedrine **69** are commercially available and therefore both enantiomers of **70** can be easily prepared by the Close method. The corresponding cyclohexyl substituted imidazolidinone **71** can be prepared by hydrogenation of the phenyl ring with hydrogen in the presence of rhodium chloride according to the method of Drewes, Malissa and Roos [19c]. Hydrogenolysis of the benzylic carbon–nitrogen bond was not observed. Complexes derived from both imidazolidinones **70** and **71** were prepared by Method A according to the procedure developed for the non-chiral complexes **20** and **21** (Scheme 4). As indicated in

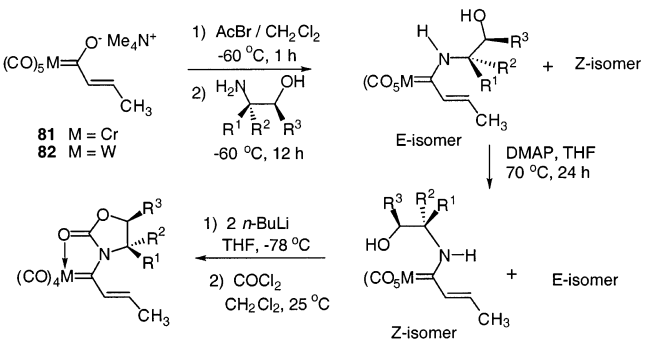


Scheme 12.

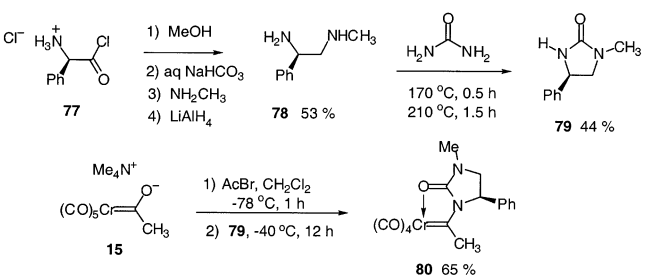
Scheme 12, the yields of the methyl carbene complexes were lower for both the chromium and tungsten series with the cyclohexyl auxiliary **71**, however, the yields for the phenyl substituted auxiliaries **72** and **73** were essentially the same as for the non-chiral analogs **20** and **21**.

The unknown imidazolidinone **79** was prepared from the diamine **78** which in turn was prepared from the commercially available (R)-phenylglycine chloride hydrochloride **77** as indicated in Scheme 13. The imidazolidinone **79** can be prepared in excellent yields from the diamine **78** by reaction with phosgene in the presence of aqueous potassium hydroxide. It was interesting to find that imidazolidinone **79** could also be prepared from the diamine **78** by fusion with urea utilizing the same procedure that was developed by Close for the preparation of the imidazolidinone **70** from the amino alcohol **69** [19]. The attachment of the imidazolidinone auxiliary **79** to a chromium carbene complex proceeded smoothly to give complex **80** following the method developed for complex **72**.

The procedure for the preparation of the chiral oxazolidinone carbene complexes **91**–**95** was slightly modified from that used for the preparation of the non-chiral complexes **37** and **38** (Scheme 6). Due to the increased steric bulk of the chiral amines, the aminolysis of the *trans*-propenyl methoxy complex **33** was sluggish and the yields of the corresponding amino complexes were low. This problem was circumvented by adding the chiral amines to the acetoxy complex generated in-situ from the ammonium salts **81** and **82** (Table 2). The yields of the aminolysis reaction were good but unfortunately mixtures of rotamers were obtained with the major rotamer as the undesired E-rotamer. As was found to be the case with the non-chiral amino complexes **35** and **36**, only the Z-rotamers of **86**–**90** could be cyclized to the oxazolidinone complex with phosgene. The stereochemistry of the rotamers of complexes **86**–**90** was assigned by ^{1}H-NMR correlation with complexes **35**, **43** and **45** whose structures were determined by X-ray diffraction (Table 1). Isomerization of the E-rotamers was effected using DMAP as described earlier affording decent overall yields of complexes enriched in the Z-isomer. With the exception of complex **95**, the rotamers of both the tungsten and chromium complexes could be easily separated by chromatography and multigram quantities of the Z-rotamers were obtained as stable, yellow crystalline solids. The oxazolidinone complexes **91**–**95** were prepared in good yields from the Z-rotamers and phosgene with the procedure developed for the non-chiral complexes **37** and **38**. These complexes were obtained as deep purple solids, which in crystalline form, could be stored under argon in a freezer for several weeks without significant decomposition. However, these complexes are most conveniently used immediately after preparation.



The preparation of cyclohexenyl substituted imidazolidinone carbene complexes was not possible by either method A or B in Scheme 3 and the synthesis of the corresponding oxazolidinone complexes proved difficult and was achieved via method C as outlined in Scheme

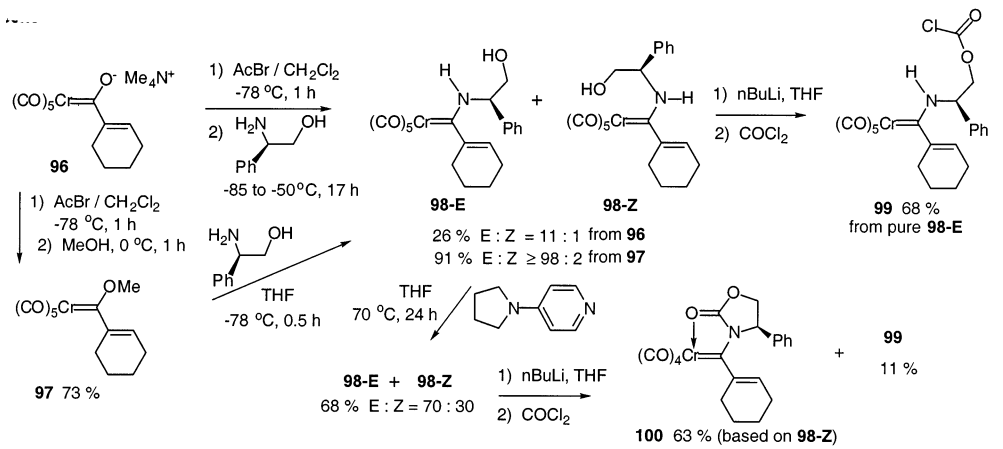


Scheme 13.

Table 2
Preparation of *trans*-propenyl oxazolidinone complexes

M	R^1	R^2	R^3	Amino alcohol	Aminolysis complex	Aminolris		Isomerization		Chelated complex [a]
						% Yield	Z	% Yield	E:Z	
Me	H	Ph	83	86	74	88:12	87	20:80	91	70%
Me	H	Ph	83	87	70	80:20	85	20: 80	92	68%
Ph	H	H	84	88	73	88:12	85	25: 75	93	68%
Ph	H	H	84	89	71	90:10	87	33:67	94	68%
H	Bn	H	85	90	78	88:12	85	20:80	95 [b] 45%	

[a] Unless otherwise specified, yields are given from purified Z-isomer.
[b] Form a 20:80 mixture of E:Z isomers. Yield based on the amount of Z-isomer.



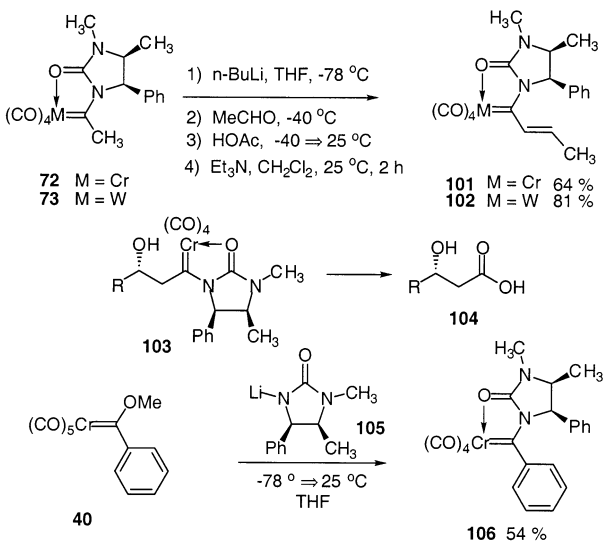
Scheme 14.

14. The preparation of cyclohexenyl imidazolidinone complexes via method C has not yet been explored. The amino alcohol complexes **98** were prepared by aminolysis of the methoxyl complex **97** in yields that were much higher than by aminolysis of an in-situ generated acetoxy complex which was the opposite of the observations made for the *trans*-propenyl complexes **86** (Table 2). The aminolysis of the methoxy complex **97** with (R)-phenylglycidol proceeded in high yields, but to the detriment of the synthesis of complex **100**, the reaction was highly selective for the formation of the E-isomer. As was the case for complex **35** and **45**, treatment of the E-isomer of **98** with butyllithium and then phosgene gave only a chloroformate and none of the desired oxazolidinone complex. Enhanced amounts of the Z-isomer could not be obtained by performing the aminolysis of **97** at r.t. (79% yield, E:Z 19:1) or in methylene chloride at r.t. either in the presence or absence of triethylamine (50–60% yield, E:Z ≥ 80:1). Isomerization of the **98-E** to the Z-isomer with 4-dimethylamino pyridine (DMAP) with the procedure developed for the complexes **35** and **36** gave 44% recovery of the complex with an E:Z ratio of 3.1:1 after 48 h. A 37% yield of pentacarbonyl chromium complex of DMAP was isolated from this reaction. Substitution of diazabicyclooctane (DABCO) for DMAP gave a 62% yield with a 3.5:1 ratio. The best results were obtained with 4-pyrrolidinopyridine which gave a 68% recovery with an E:Z ratio of 2.3:1. Treatment of this mixture to the cyclization conditions developed for the synthesis of complex **37** gave desired oxazolidinone complex **100** in 63% yield based on the Z-isomer of **98**.

The chiral α,β-unsaturated imidazolidinone complexes **101** and **102** were prepared by an aldol condensation with the procedure that was developed for the preparation of the non-chiral analogs **52** and **53** (Scheme 10). The methyl imidazolidinone complexes have been shown to give high asymmetric induction for the formation of the aldol adducts **103** for a variety of aldehydes [3,12a] and also in adducts from the Michael reaction [12c]. They have been shown to be effective chiral synthons for acetate enolates in the aldol reaction since the aldol adduct carbene complexes can be converted to the β-hydroxy acids **104** in high yields. The elimination of the aldol adduct carbene complexes **103** to the aldol condensation carbene complexes of the type **101** is much more facile than for simple alkoxy carbene complexes [20] or simple dialkylamino com-

plexes [21]. For both of these classes of complexes, elimination of the β-hydroxy requires activation as a mesylate, whereas, the imidazolidinone complex **103** can be induced to dehydrate by simple exposure to triethylamine. The reason for this may be related to the acidity of the imidazolidinone complexes. The acidity of these complexes has not been determined but is anticipated to be intermediate between alkoxy [22] and amino complexes [23] and closer to that of water and alcohols. The α,β-unsaturated complexes have been shown to give high asymmetric inductions in exo-selective Diels–Alder reactions [12d]. Finally the chiral phenyl imidazolidinone complex **106** can be prepared in good yield by the addition of the lithiated imidazolidinone **105** to the methoxy complex **40**. Complex **106** has been shown useful in the asymmetric synthesis of silanes and stannanes [12e](see Scheme 15).

Although not all of the permutations have yet been investigated, the present investigation reveals that the aryl and methyl substituted imidazolidinone complexes are best prepared by the direct introduction of an imidazolidinone unit according to path A or B in Scheme 3 and oxazolidinone complexes are best made by the two step procedure involving aminolysis and the ring closure as indicated by path C in Scheme 3. Unsaturated imidazolidinone complexes can be accessed by aldol condensation reactions of alkyl substituted complexes. From the point of view of synthetic utilization, imidazolidinone complexes would appear to be the most attractive since they are far more stable than the oxazolidinone complexes. This difference is manifested in the fact that the methyl substituted oxazolidinone complexes **23** and **24** are too unstable to be isolated. This instability is presumably related to the decreased electron density on nitrogen in the oxazolidinone complexes vs. the imidazolidinone complexes.



Scheme 15.

This leads to greater reactivity for the oxazolidinone complexes for certain reactions such as the Diels–Alder reaction. However, in this case the higher stability of the imidazolidinone complex wins out since the reactions can be performed at higher temperatures where higher overall efficiencies can be achieved. The imidazolidinone complexes can be stored cold in a vial sealed with a rubber septa which has been flushed with nitrogen for prolonged periods without substantial decomposition. The oxazolidinone complexes are best used directly after their preparation but good yields can still be obtained in a number of applications. Further studies on the synthetic applications of both classes of complexes in a number of different reactions of Fischer carbene complexes will be reported.

4. Experimental

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran, ether and benzene were distilled from benzophenone ketyl under nitrogen. Dichloromethane and hexane were distilled from calcium hydride. High-resolution mass spectra were recorded on a VG 70-250 instrument or obtained from the Midwest center for Mass Spectrometry in Lincoln, NE. Elemental analyses were done by Galbraith Laboratories in Knoxville, TN. Optical rotations were obtained on a Perkin–Elmer 141 polarimeter at wavelength of 589 nm (sodium D line) using 1.0 decimeter cells. Specific rotations, $[\alpha]^{D}$ are reported in degrees per decimeter at 25°C and the concentration (c) is given in grams per 100 ml.

*4.1. Preparation of 1-methyl-2-imidazolidinone (**19**) [24]*

A solution of 2-imidazolidinone (15.2 g, 177 mmol) in 200 ml of 1,4-dioxane was prepared in a 500 ml 3-neck flask equipped with a condenser. Sodium hydride (60 wt% in paraffin, 8.33 g, 208 mmol) was added slowly under an atmosphere of nitrogen with vigorous stirring. The milky solution was heated to 65°C and stirred at this temperature for 2 h and then cooled to 0°C. Methyl iodide (20.4 ml, 328 mmol) was added slowly via syringe and the resulting mixture was stirred at r.t. for 14 h. The reaction mixture was filtered through a bed of Celite and the solvent removed in a rotary evaporator. Flash chromatography (10% MeOH in CH_2Cl_2, $R_f = 0.15$) on a $2 \times 15''$ plug of silica gel in a large column (two portions) gave 9.2 g of the title compound as a white solid in 52% yield. Further crystallization from $CHCl_3$–hexane gave **19** as white crystals. Spectral data for **19**: m.p. 112–113°C (lit 114–115°C) [24]; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.75

(s, 3H), 3.39 (s, 4H), 5.20 (br s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.25, 37.68, 47.17, 163.40; IR (neat) 3268 s, 2866 m, 1699 vs, 1503 m, 1452 m, 1404 m, 1280 m, 1257 m cm^{-1}; mass spectrum, m/z (relative intensity) 100 M^+ (100), 85 (5), 78 (7), 71 (23), 65 (3); Anal. Calc. for $C_4H_8N_2O$: C, 47.97; H, 8.06; N, 27.99. Found: C, 47.68; H, 8.14; N, 28.28%.

4.2. Preparation of [methyl-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (20)

Tetramethylammonium (1-hydroxy-ethylidene) pentacarbonylchromium (0) [25] **15** (500 mg, 1.62 mmol) was dissolved in 6 ml of CH_2Cl_2 and cooled to -78°C under an atmosphere of argon. Freshly distilled acetyl bromide (110 ml, 1.49 mmol) was added dropwise and the deep reddish-purple solution was stirred for 1 h after which time a solution of 1-methyl-2-imidazolidinone **19** (149 mg, 1.49 mmol) in 3 ml of CH_2Cl_2 was added dropwise via cannula. The solution was gradually warmed to -60°C over a 30 min period and stirred at this temperature for 12 h. The mixture was quickly warmed to r.t. and concentrated on a rotary evaporator to remove half of the solvent. The remaining dark reddish–brown solution was loaded onto a silica gel column and the product eluted with CH_2Cl_2 ($R_f = 0.39$) to give 221 mg of title compound as a dark red solid in 51% yield. Other runs have given up to 70% yield. Shorter reactions times (-45°C 1 h, -20°C 1 h) also can give yields of $\sim$50%. Spectral data for **20**: m.p. 134°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 3.00 (s, 3H), 3.03 (s, 3H), 3.93 (t, 2H, $J = 6.9$ Hz), 3.95 (t, 2H, $J = 6.5$ Hz); ^{13}C-NMR (500 MHz, acetone-d_6, -50°C) δ 30.49, 33.34, 42.24, 49.34, 162.54, 216.44, 231.87, 232.07, 312.52; ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 31.11, 33.86, 41.43, 48.99, 162.32, 216.10, 231.83, 232.15, 317.33; IR (neat) 1999 m, 1917 vs, 1884 vs, 1830 vs, 1716 m, 1384 m cm^{-1}; mass spectrum, m/z (relative intensity) 290 M^+ (6), 273 (2), 262 (5), 206 (10), 178 (2), 154 (100); Anal. Calc. for $C_{10}H_{10}N_2O_5Cr$, FAB (3-NBA), m/z 289.9994, measured 290.0003. Anal. Calc. for $C_{10}H_{10}N_2O_5Cr$: C, 41.39; H, 3.47; N, 9.65. Found: C, 41.47; H, 3.35; N, 9.64%.

In some reactions, a mixture of two compounds (**20a** and **20b**) was isolated which comprised the front running yellow band ($R_f = 0.40$) just ahead of the deep red band containing **20** ($R_f = 0.39$). The mixture would turn red upon standing at r.t. in air. These compounds are tentatively identified as the two atropisomers of the pentacarbonyl analogs of **20** since it was found that they could be converted to **20**. A mixture of **20a** and **20b** (358.0 mg, 1.13 mmol) was dissolved in 5 ml of CH_2Cl_2 and heated to reflux for 5 min. Then 5 ml of hexane was added and the mixture was heated to reflux again for 5–10 min. Upon cooling, a red precipitate began to form, and was collected via filtration and washed with cold hexane (3×5 ml). The solid was identified as the chelated complex **20** which was obtained in 99% yield (323.0 mg). Complex **20a**: yellow solid, $R_f = 0.40$ (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 2.97 (s, 3H), 3.48 (s, 3H), 3.60 (t, 2H, $J = 7.3$ Hz), 4.64 (t, 2H, $J = 7.3$ Hz). Complex **20b**: yellow solid, $R_f = 0.40$ (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 3.00 (s, 3H), 3.09 (s, 3H), 3.54 (t, 2H, $J = 7.2$ Hz), 4.06 (t, 2H, $J = 7.2$ Hz).

4.3. Preparation of [methyl-[3-(1-methyl-2-imidazolidone)]methylene] tetracarbonyltungsten (0) (21)

Complex **21** was prepared according to the procedure described for **20**. Crystallization from CH_2Cl_2 and hexane afforded 0.29 g of **21** as ruby-red prisms in 62% yield. Spectral data for **21**: m.p. 128°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 2.73 (s, 3H), 3.10 (s, 3H), 3.93 (t, 2H, $J = 8.3$ Hz), 4.03 (t, 2H, $J = 8.3$ Hz); ^{13}C-NMR (75 MHz, acetone-d_6, -50°C) δ 30.97, 34.87, 42.36, 49.43, 165.53, 207.06, 216.66, 221.14, 292.51; IR (neat) 2005 (s), 1864 (vs), 1818 (s), 1382 (m), 1300 (m) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 422 M^+ (10, ^{182}W), 394 (8), 366 (5), 307 (15), 219 (5), 154 (100); Calc. for $C_{10}H_{10}N_2O_5{}^{182}W$, FAB (3-NBA), m/z 420.0073, measured 420.0082.

4.4. Preparation of [trans-propenyl-(2-hydroxyethylamino)methylene] pentacarbonylchromium (0) (35-E) and (35-Z)

Trans-propenyl (methoxy) pentacarbonyl chromium (0) **33** [27] (1.53 g, 5.54 mmol) was dissolved in 12 ml of THF and cooled to -90°C under an atmosphere of argon. Ethanolamine (0.37 g, 6.10 mmol) was dissolved in 6 ml of THF and added to the solution dropwise. After the addition was complete, the yellow solution was immediately warmed to r.t. and concentrated on a rotary evaporator. The resulting oil was chromatographed on silica gel with CH_2Cl_2–Et_2O (2:1) to give 0.77 g of *trans*-propenyl (2-aminoethanol) pentacarbonyl chromium (0) **35-E** (46%, $R_f = 0.58$) and 0.78 g of the **35-Z** (47%, $R_f = 0.51$) as yellow solids in 93% combined yield. The stereochemistry was assigned by ^{1}H-NMR [15] and by X-ray diffraction of the E-isomer (vide infra). Complex E-rotamer was isomerized as described in the general procedure to give a 80:20 ratio of Z to E respectively, in 85% combined yield after chromatography. The O*H* signals for both the E and Z rotamers were not located by ^{1}H-NMR. Spectral data for **35-E**: m.p. 100–102°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.97 (d, 3H, $J = 6.8$ Hz), 3.64–3.67 (m, 2H), 3.90–3.97 (m, 2H), 6.21 (dq, 1H, $J = 15.0$, 6.5 Hz), 6.61 (d, 1H, $J = 15.6$, Hz), 8.90 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.23, 50.34, 60.53, 136.80, 139.22,

218.10, 223.17, 272.92; IR (neat) 3305 (m), 2049 (s), 1906 (shoulder, vs), 1886 (vs), 1529 (m), 1069 (m) cm^{-1}. Spectral data for **35-Z**: m.p. 68–70°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.85 (d, 3H, $J = 6.8$ Hz), 4.01–4.03 (m, 2H), 4.11–4.14 (m, 2H), 5.63 (dq, 1H, $J =$ 15.0, 6.5 Hz) 6.88 (d, 1H, $J = 15.6$), 8.98 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.70, 54.07, 61.08, 124.11, 145.96, 217.83, 223.70, 267.34; IR (neat) 3305 (m), 3287 (w), 2054 (s), 1910 (vs), 1538 (m), 1045 (m) cm^{-1}; mass spectrum (mixture of rotamers), m/z (relative intensity) 305 M^+ (20), 277 (35), 193 (55), 165 (100), 135 (40), 119 (45), 110 (65); Anal. Calc. for $C_{11}H_{11}O_6CrN$ (mixture of rotamers): C, 43.25; H, 3.63; N, 4.59. Found C, 43.93; H, 3.95; N, 4.55.

4.5. Preparation of [trans-propenyl(2-hydroxyethylamino)methylene] pentacarbonyltungsten (0) (36-E) and (36-Z)

Complex **36** was prepared from complex **34** [27] (1.95 g, 4.68 mmol) with the procedure described above for complex **34**. Purification gave 0.92 g of complex **36-E** ($R_f = 0.32$) in 47% yield and 0.93 g of complex **36-Z** ($R_f = 0.26$) in 48% yield as yellow solids. Spectral data for **36-E**: m.p. 115–117°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.02 (d, 3H, $J = 6.3$ Hz), 2.17 (s, 1H, O*H*), 3.60 (q, 2H, $J = 5.3$ Hz), 3.88–3.93 (m, 2H), 6.52 (d, 1H, $J = 15.2$ Hz), 6.61 (dq, 1H, $J = 15.0$, 6.5 Hz), 8.65 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.36, 50.06, 60.29, 137.24, 147.02, 199.11, 202.93, 251.37; IR (neat) 3300 (m), 2056 (s), 1885 (vs), 1527 (m) cm^{-1}. Spectral data for **36-Z**: m.p. 65–67°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.90 (d, 3H, $J = 6.3$ Hz), 3.99–4.01 (m, 4H), 5.94 (dq, 1H, $J = 15.0$, 6.5 Hz) 6.75 (d, 1H, $J = 15.2$), 8.82 (br s, 1H, N*H*) (OH signal not located); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.37, 56.12, 60.80, 130.46, 146.70, 198.26, 203.52, 247.30; IR (neat) 3291 (m), 2062 (s), 1900 (vs), 1540 (m), 1443 (m), 1402 (m), 1049 (m), 958 (m) cm^{-1}; mass spectrum (mixture of rotamers), m/z (relative intensity) 437 M^+ (50, ^{184}W), 409 (30), 381 (30), 353 (85), 295 (85), 267 (100), 240 (65); Calc. for $C_{11}H_{11}NO_6^{184}W$ (mixture of rotamers) m/z 437.0097, measured 437.0074.

A 86:14 ratio of complexes **36-E** and **36-Z**, respectively, were isomerized as described in the general procedure to give a 80:20 ratio of **36-Z** to **36-E**, respectively, in 85% combined yield after chromatography. Attempted isomerization of **36-E** with both one and two equivalents of *n*-butyllithium in THF at −78°C followed by D_2O quench gave exclusive recovery of the E-iomser in 85% yield. The ^{1}H-NMR data for **36-E** obtained from treatment with one equivalent of butyllithium had the O*H* signal (δ 2.17) absent and the spectrum of **36-E** from the experiment with two equivalents had both the O*H* the N*H* signals (δ 8.65) absent.

4.6. General procedure for the isomerization of amino carbene complexes with 4-dimethylamino-pyridine

The appropriate amino carbene complex (1.00 eq) was dissolved in THF to make a 0.20 M solution and 4-dimethylaminopyridine (1.00 eq) was added and the mixture was stirred until all the reactants had dissolved. The reaction flask was then degassed by the freeze-thaw method, backfilled with an atmosphere of argon at r.t. The stopcock was closed and the flask placed in a pre-heated oil bath set at 70°C. The yellow solution was stirred for approximately 24 h upon which the mixture became deep red. After cooling to r.t., the reaction flask was opened and diluted with ether. The mixture was washed with 1 N HCl (3 ×), saturated aqueous NH_4Cl (1 ×), and NaCl (1 ×). The yellow solution was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude products were chomatographed with the appropriate solvent system to afford enrichments of the desired Z-rotamers as described in the individual preparation with >85% recovery of the mass balance in each case. Control experiments have shown that isomerization of the E-rotamers does not occur thermally in the absence of 4-dimethylaminopyridine. However, it remains to be determined whether isomerization occurs with the same efficiency using catalytic amounts of DMAP.

4.7. General procedure for the preparation of oxazolidinone carbene complexes

The Z-rotamer of the appropriate amino carbene complex (1.00 eq) was dissolved in THF (0.15 M) and cooled to −78°C under an atmosphere of argon and *n*-butyllithium (2.05 eq, 1.6 M in hexanes) was added dropwise. After stirring for 5 min, a solution of phosgene (1.50 eq, 1.93 M in toluene) was added and the dark red solution was warmed to r.t. over a 30 min period. The dark solution was stirred at r.t. until the solution became deep purple. The mixture was concentrated after ~1.5 h on a rotary evaporator and the purple residue was quickly(!) chomatographed on silica gel with the appropriate solvent system affording the desired complex. The isolated chelated complex was dissolved in a small amount of CH_2Cl_2 and was slowly crashed out of solution by the dropwise addition of pentane. The deep-red micro-crystalline solids obtained though this procedure are stable at −30°C under argon for weeks with only slight decomposition. However, these complexes are best used immediately following their preparation.

4.8. Preparation of [trans-propenyl(2-oxazolidinone)methylene] tetracarbonylchromium (0) (37)

Complex **37** was prepared as described in the general procedure starting with 0.27 g (0.89 mmol) of **35-Z** to

give, after chromatography using CH_2Cl_2–hexane (3:1, $R_f = 0.35$), 0.22 g of **37** in 70% yield as a deep reddish–purple solid. Spectral data for **37**: m.p. 95°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 2.17 (d, 3H, $J = 6.8$ Hz), 4.40 (t, 2H, $J = 7.6$ Hz), 5.08 (t, 2H, $J = 7.5$ Hz), 7.07 (d, 1H, $J = 14.5$ Hz), 7.84 (dq, 1H, $J = 14.4$, 7.6 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, -50°C) δ 21.56, 45.59, 72.75, 138.99, 160.98, 165.48, 217.13, 232.62, 233.17, 302.37; IR (neat) 2007 (vs), 1866(vs), 1816 (vs), 1702 (s), 1615 (s), 1420 (s), 1260 (s), 1226 (s) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 303 M^+ (50), 275 (40), 247 (80), 219 (60), 174 (35), 154 (100), 136 (90), 89 (55); Calc. for $C_{11}H_9NO_6Cr$, FAB (3-NBA), m/z 302.9835, measured 302.9848.

4.9. Preparation of [trans-propenyl(2-oxazolidinone)methylene] tetracarbonyltungsten (0) (38)

Complex **38** was prepared as described in the general procedure starting with 1.13 g (2.58 mmol) of **36-Z** to give 0.65 g of **92** in 58% yield as a deep reddish–purple solid after chromatography using EtOAc–hexane (1:1, $R_f = 0.50$). Smaller scale reactions starting with 0.50 g (1.14 mmol) of **36-Z** led to the isolation of **38** in 70% yield. Spectral data for **38**: m.p. 141–143°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 1.92 (d, 3H, $J = 7.0$ Hz), 4.12 (t, 2H, $J = 8.0$ Hz), 5.07 (t, 2H, $J = 8.4$ Hz), 6.51 (d, 1H, $J = 14.5$ Hz), 8.18 (dq, 1H, $J = 14.4$, 7.1 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, -50°C) δ 21.52, 45.55, 72.31, 139.84, 164.52, 169.66, 207.14, 217.35, 220.34, 278.82; IR (neat) 2007 (vs), 1866 (vs), 1816 (vs), 1702 (s), 1615 (s), 1420 (s), 1260 (s), 1226 (s) cm^{-1}; mass spectrum: no parent ion observed, 351 M^+ (10, $^{184}W(CO)_6$); Calc. for $C_{11}H_9NO_6{}^{182}W$, FAB (3-NBA), m/z 432.9913, measured 432.9902.

The chloroformate complex **39** was isolated in 65% yield as a yellow oil when the procedure described above was used starting with **36-E** instead of **36-Z**. Spectral data for **39**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.05 (d, 3H, $J = 7.3$ Hz), 3.82 (q, 2H, $J = 5.7$ Hz), 4.52 (t, 2H, $J = 5.3$ Hz), 6.49 (d, 1H, $J = 14.7$ Hz), 6.67 (dq, 1H, $J = 15.0$, 6.7 Hz), 8.50 (br s, 1H); IR (neat) 3300 (w), 2062 (vs), 1903 (m), 1816 (vs), 1773 (m), 1512 (w), 1158 (m) cm^{-1}.

4.10. Preparation o [iso-butenyl(methoxy)methylene] pentacarbonylchromium (0) (42)

To a solution of 1-bromo-2-methyl propene (5.00 g, 0.037 mol) in 100 ml of THF at -78°C was added *t*-butyl Lithium (0.074 mol, 43.6 ml of 1.7 M solution in pentanes). After 1.5 h this solution was transferred via cannula to a slurry of chromium hexacarbonyl complex (7.4 g, 0.034 mol) in 200 ml THF at r.t. The resulting yellow solution was stirred for 1.5 h and then stripped of solvent to leave a dark red viscous oil. This oil was dissolved in a minimum amount of water and then a solution of tetramethyl ammonium bromide (5.18 g, 0.051 mol) in 10 ml water was added. The water layer was extracted with three 40 ml portions of methylene chloride. The combined organic layers are dried with $MgSO_4$ and filtered through a plug of Celite. The filtrate was treated with methyl triflate (6 g, 0.036 mol). After 30 min, the solvent was removed and the dark red oil was loaded onto a silica gel column and eluted with hexanes. Fractions containing complex **42** were concentrated and cooled to -78°C. The product crystallized from solution and was collected by fast cold filtration and then dried under vacuum to give 6.8 g (70%) of carbene complex **42** as dark red crystals. Spectral data for **42**: m.p. 33 ~ 34°C, $R_f = 0.28$ (Hexane); ^{1}H-NMR ($CDCl_3$) δ 1.88 (s, 3H), 1.91 (s, 3H), 4.72 (s, 3H), 7.26 (s, 1H); ^{13}C-NMR $CDCl_3$ δ 21.99, 27.62, 66.18, 140.12, 141.50, 216.72, 223.96, 338.90; IR (neat): 2058 s, 1930 brs, 1590 m, 1451 m, 1251 m, 1186 m, 976 m; mass spectrurm, m/z (relative intensity) 290 M^+ (23), 262 (6), 234 (7), 206 (11), 178 (27), 150(100), 135 (10), 120 (23), 107 (16), 91 (13), 82 (17), 75 (5), 67 (5); HRMS calc. for $C_{11}H_{10}O_6Cr$: 289.9882, found 289.9876.

4.11. Preparation of of [iso-butenyl(2-hydroxyethylamino)methylene] pentacarbonylchromium (0) (43)

Methoxy isobutenyl carbene complex **42** (3.5 g, 0.012 mol) was put in flask with 200 ml dry THF. This was cooled to -78°C for 15 min. Ethanol amine (0.74g, 0.012 mol) was added as a 20 ml THF solution. TLC showed immediate product formation (CH_2Cl_2, $R_f =$ 0.3). The solution turned from bright red to light yellow after 10 min. This was stirred at -78°C for 1 h and at r.t. for 30 min. Then the reaction mixture was concentrated and run through a short column (1:1 hexane:CH_2Cl_2 ~ CH_2Cl_2). The crude-NMR showed E:Z 7:1. The major product was isolated as yellow crystals and identified as the E-isomer (1.89 g, 49%). The stereochemistry of the major product was assigned by ^{1}H-NMR [15] and confirmed by X-ray diffraction of the acetate derivative **107** (vide infra). The Z-isomer was obtained as a viscous oil mixed with E-isomer. Spectral data for **43-E**: m.p. 53 ~ 55°C, $R_f = 0.29$, (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 1.52 (s, 3H), 1.83 (s, 3H), 3.60 (s, 2H), 3.85 (s, 2H), 6.18 (s, 1H), 9.21 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ 19.52, 24.51, 51.29, 60.59, 124.02, 133.29, 217.61, 223.49, 279.34; IR (neat) 3357m, 2053 s, 1929 brs, 654 s; mass spectrum, m/z (relative intensity) 319 M^+ (100), 291 (42), 285 (7), 263 (18), 235 (43), 231 (7), 219 (23); HRMS m/z calc. for $C_{12}H_{13}O_6NCr$ 319.0148, found 319.0162. Anal. Calc. for $C_{12}H_{13}O_6NCr$: C, 45.15; H, 4.10; N, 4.39. Found: C, 44.95; H, 4.23; N, 3.92%. Spectral data for **43-Z**: $R_f = 0.33$, (CH_2Cl_2), ^{1}H-NMR ($CDCl_3$) δ 1.62 (s, 3H), 1.69 (s, 3H), 4.06 (s, 2H), 4.17 (s, 2H), 6.53 (s, 1H), 8.88 (s, 1H).

*4.11.1. Equilibration of **43-E**, **Z** via its lithium anion*

A solution of *n*–butyllithium (2.5 M solution in hexanes, 0.44 mmol) was added to a solution of **43** (70 mg, 0.22 mmol, E:Z 6.0:1) in 3 ml of THF cooled to −78°C. The yellow reaction solution was stirred for 30 min and quenched with water. The aqueous solution was extracted with ether, dried over anhydrous $MgSO_4$, and concentrated to yield 61 mg (87%) of **43** with an E:Z ratio of 6.0:1. The above reaction was repeated with **43** (70 mg, 0.22 mmol, E:Z 6.0:1) and was warmed to r.t. for 30 min before quench. The carbene complex was recovered in 77% yield (54 mg) with an E:Z ratio of 3.8:1.

*4.11.2. Acetylation of **43** to give its acetate derivative (**107**)*

The amino carbene complex **43-E** (0.070 g, 0.220 mmol), Ac_2O (0.021 g, 0.241 mmol) and Et_3N (0.0206 g, 0.034 mmol) were dissolved in 5 ml THF. This solution was stirred at r.t. for 5 h until TLC showed the disappearance of starting material ($R_f = 0.20$, CH_2Cl_2). The solution was concentrated and loaded onto a small silica gel column. After flushing with 50% ether in pet ether, the yellow band was collected. The volatiles were removed to leave a bright yellow solid (70 mg, 90%) which was crystallized from ether–pentane at −20°C. The structure of this compound was determined by X-ray diffraction. Spectral data for **207**: ^{1}H-NMR 500 MHz $CDCl_3$ δ 1.49 (s, 3H), 2.12 (s, 3H), 3.69 (m, 2H), 4.27 (m, 2H), 6.17 (s, 1H), 9.06 (brs, 1H); ^{13}C-NMR 300 MHz $CDCl_3$ δ 19.54, 20.61, 24.59, 48.85, 61.67, 124.21, 133.07, 171.00, 217.43, 223.26, 382.51; IR (neat) 1942w, 1900m, 1878s, 661m; mass spectrum *m*/*z* (relative intensity) 361 M^+ (12), 333 (8), 305 (2), 277 (6), 249 (8), 221 (51), 191 (45), 178 (12), 169 (86), 149 (12), 133 (9), 125 (6), 111 (28), 96 (100), 82 (75), 67 (46), 52 (43); HRMS *m*/*z* calc. for $C_{14}H_{15}O_7Cr$ 361.0254, found 361.0242. Greenish yellow plates (Et_2O–Pentane, −20°C); m.p. 48 ~ 50°C; $R_f = 0.54$, CH_2Cl_2.

*4.12. Prearation of [iso-butenyl(2-oxazolidinone)methylene] tetracarbonylchromium (0) (**44**)*

A 250 ml flask was charged with 100 ml THF and carbene complex **43-E** (1.01 g, 3.176 mmol). The bright yellow solution was cooled to −78°C and *n*-BuLi (2.60 ml of 2.5 M in hexanes, 6.51 mmol) was added slowly. The yellow solution was stirred at −78°C for 30 min and then phosgene (1.65 ml of 1.93 M in Toluene, 3.176 mmol) was added dropwise. The solution turned dark brown and TLC showed a dark yellow spot ($R_f = 0.58$, CH_2Cl_2). The reaction mixture was warmed to r.t. for 1 h. The volatiles were removed and the residue was passed through a plug of silaca gel. The fractions containing the dark yellow product (non-chelate product) are stirred at r.t. for 2 h after which time TLC showed a purple spot ($R_f = 0.55$, CH_2Cl_2) grew at the expense of the yellow spot. At this point, IR shows chelate complex formation was complete. After purification on a short silica gel column (CH_2Cl_2) dark purple crystals of **44** were obtained (0.5g, 50%). The highest yield of a series of runs is 78%. The product is somewhat sensitive to air and stored under argon. Spectral data for **44**: m.p. 160 ~ 162°C (dec.), $R_f = 0.55$ (CH_2Cl_2), ^{1}H-NMR ($CDCl_3$) δ 2.07 (s, 3H), 2.30 (1s, 3H), 4.03 (t, 2H, $J = 8.1$ Hz), 4.93 (t, 2H, $J = 8.1$ Hz), 6.51(s, 1H); ^{13}C-NMR (some decomposition occurs during aquisition) (CD_2Cl_2) δ 22.21, 28.25, 44.93, 71.45, 134.53, 152.82, 216. 98, 312.31; IR (neat): 2054 m, 2013 s, 1904 s, 1840 s, 1714 m, 1413 m, 1254 m, 1191 m, 1204 m; mass spectrum, *m*/*z* (relative intensity) 317 M^+ (5), 289 (3), 233 (6), 220 (7), 205 (32), 165 (12), 153 (13), 108 (20), 94 (24), 80 (37), 67 (17), 52 (100); HRMS calc. for $C_{12}H_{11}O_6NCr$ 316.9991, found 316.9983.

*4.13. Synthesis of of [phenyl(2-hydroxyethylamino)methylene] pentacarbonylchromium (0) (**45**)*

A solution of ethanolamine (210 ml, 3.48 mmol) in 1.5 ml of THF was added dropwise to a solution of phenylmethoxy chromium carbene complex **40** [28] (1.122 g, 3.59 mmol) in 10 ml THF cooled to −78°C. Upon completion of the addition the solution changed color from dark red to yellow. The solution was warmed to r.t. and filtered through a 1:1 mixture of Celite and silica gel. The yellow solution was concentrated to yield a thick yellow gum which began to crystallize on standing. The amino carbene complex exists as a mixture of rotamers (E:Z 5.8:1 by ^{1}H-NMR integration of the amine protons at δ 9.49 & 9.0) about the carbene carbon–nitrogen bond. The isomers are inseparable by silica gel chromatography, however, the E isomer may be obtained in 35% yield via crystallization of the crude product from benzene–hexane. The stereochemistry of the major product was assigned by ^{1}H-NMR [15] and by X-ray diffraction (vide infra). Spectral data for **45-E**: Yellow needles (benzene–hexanes), m.p. 81–83°C; $R_f = 0.58$ (1:1 hexane:EtOAc); ^{1}H-NMR ($CDCl_3$) δ 1.77 (br s, 1 H), 3.36 (q, 2 H, $J = 5.4$ Hz), 3.79 (br s, 2H), 6.81 (d, 2 H, $J = 7.1$ Hz), 7.22 (t, 1 H, $J = 7.5$ Hz), 7.40 (t, 2 H, $J = 7.87$ Hz), 9.49 (br s, 1H); ^{13}C-NMR ($CDCl_3$) δ 51.7, 60.8, 119.0, 126.751, 128.6, 149.6, 217.1, 223.4, 283.0; IR (NaCl, neat) 3598 m, 3222 br w, 2056 m), 1985 m, 1947 br s, 1897* br s, 1547 m, 1439 w, 1097 w, 703w, 680 m, 665 m cm^{-1}; mass spectrum *m*/*z* (relative intensity) 341 (M^+, 6), 313 (7), 285 (5), 257 (8), 229 (17), 201 (40), 171 (23), 147 (68), 117 (100), 103 (25), 91 (80), 77 (50), 52 (42). Anal. Calc. for $C_{14}H_{11}NO_6Cr$: C, 49.27; H, 3.25; N, 4.10. Found: C, 49.48; H, 3.25; N, 4.07%. Spectral data

for **45-Z**: In the ^{1}H-NMR ($CDCl_3$) the amine proton appears at δ 9.0 (0.5 ppm upfield from the amine proton in the E isomer). Integration of these two peaks has been the basis for assigning isomer ratios. All of the other ^{1}H-NMR resonances overlap with the E isomer.

*4.13.1. Attempted purification of **45-Z** via its Acetate*

Acetic anhydride (0.39 ml, 4.1 mmol) was added to a solution of a mixture of **45-Z** and **45-E** (1.286 g, 3.8 mmol, E:Z 5.2:1) and TEA (0.58 ml, 4.2 mmol) in 10 ml of THF. The reaction was stirred for 2 h at r.t. and quenched with saturated $NaHCO_3$ solution. The aqueous solution was extracted with ether, dried over anhydrous $MgSO_4$, and concentrated to yield 1.30 g (90%) of the acetate amino carbene complex as a yellow oil. The two isomeric acetates were partially separable with silica gel chromatography using 90:10 (hexane–EtOAc). Sodium methoxide (>5 mg, catalytic) was added to a solution of the acetate (60 mg, 0.157 mmol, E:Z 3.9:1) in 1 ml of methanol. The reaction was stirred for 5 min at r.t. and poured into pH 7.0 phosphate buffer. The aqueous solution was extracted with ether and dried over anhydrous $MgSO_4$. Solvent removal yielded 42 mg (79%) of **45** with an E:Z ratio of 3.4:1. The reaction was repeated with 130 mg of the acetate (0.339 mmol, E:Z 1.4:1) in 2 ml of methanol. This gave a 77% recovery of **45** with an E:Z ratio of 1.34:1.

*4.13.2. Isomerization of **45** with DMAP*

A single-neck flask equipped with a threaded teflon high vacuum stopcock was charged with amino carbene complex **45** (506 mg, 1.48 mmol, E:Z 6.8:1) and DMAP (181 mg, 1.48 mmol) in 8 ml of THF. The flask was sealed, freeze-pump-thawed (3 cycles), back-filled with argon at r.t. and placed on a 75°C oil bath. The reaction turned bright orange. The reaction was stirred for 24 h, cooled, and concentrated to an orange gum. Silica gel chromatography returned 436 mg (86%) of the starting carbene complex along with 34 mg (7%) of the DMAP:$Cr(CO)_5$ decomposition product. The final E:Z ratio was 6.0:1 by ^{1}H-NMR integration. This reaction was repeated with 61 mg of **45** with a starting E:Z ratio of 1.40:1. After 24 h the final ratio was 2.3:1, however the recovery was very low ($\sim$10%). This reaction was repeated again with pure **45-E** (90 mg, 0.235 mmol) in 1.1 ml of THF with 35 mg DMAP (0.286 mmol). After the reaction had stirred for 40 h, an aliquot was withdrawn for ^{1}H-NMR analysis. This showed the rotamer ratio to be 2.2:1. The heating was continued until the total time was 132 h (5.5 days). At this point the carbene complex was recovered (12 mg, 13%) with an E:Z ratio of 1.46:1. This recovered complex was re-subjected to the isomerization conditions for another 204 h (8.5 days). No carbene complex was recovered from this reaction.

*4.13.3. Attempted equilibration of **45-E,Z** via its lithium anion*

A solution of *n*-butyllithium (0.10 ml of a 2.5M solution in hexane, 0.25 mmol) was added to a solution of **45** (34 mg, 0.10 mmol, E:Z 1.40:1) in 1 ml of THF cooled to -78°C. The yellow reaction solution was stirred for 30 min and quenched with water. The aqueous solution was extracted with ether, dried over anhydrous $MgSO_5$, and concentrated to yield 32 mg (94%) of **45** with an E:Z ratio of 1.36:1. The above reaction was repeated with pure **45**-E (102 mg, 0.30 mmol, E:Z $>$ 40:1). The carbene complex was recovered in 92% yield with no interconversion of rotamers as indicated by ^{1}H-NMR. When the reaction was repeated with pure **45-E** and the solution allowed to warm to r.t. for 30 min before aqueous quench, the complex **45** was recovered in 84% yield as a 14:1 mixture of E:Z isomers.

*4.14. Synthesis of of [phenyl(2-oxazolidinone)methylene] tetracarbonylchromium (0) (**46**)*

The chelate carbene complex is best obtained by reaction of the crude aminolysis product without further purification. The crude yellow gum from the above reaction (complex **45**) was dissolved in 10 ml THF, cooled to -78°C, and treated dropwise with butyllithium (2.9 ml of a 2.5 M solution in hexane, 7.25 mmol). This solution was stirred for 30 min and then cannulated into a solution of phosgene (1.9 ml of a 1.93 M solution in toluene dissolved in 30 ml of THF, 3.67 mmol) at r.t. and stirred for 90 min. The reaction was concentrated and purified via silica gel chromatography using 70:30 hexane:ethyl acetate as the eluting solvent. The dark red gum thus obtained was crystallized from CH_2Cl_2–hexane to yield 239 mg (20%) of the title compound as lustrous bronze colored needles. Spectral data for **46**: Bronze crystals (CH_2Cl_2–hexane), m.p. 130°C (dec.); $R_f = 0.47$ (1:1 hexane:EtOAc); ^{1}H-NMR (CD_2Cl_2) δ 4.07 (br s, 2 H), 4.93 (br s, 2 H), 7.45–7.20 (m, 5 H); ^{13}C-NMR (CD_2Cl_2) δ 45.0, 71.5, 123.6, 128.8, 130.3, 147.0, 163.6, 216.2, 317.6; IR (NaCl, neat) 2015 s, 1901 s, 1840 s, 1710 w, 1257 w, 1220 m, 702 w, 663 w cm^{-1}; mass spectrum m/z (relative intensity), (M^+ not found) 191 (23), 105 (100), 77 (38), 51 (14).

*4.15. Preparation of the of [1-propynyl(2-hydroxyethylamino)methylene] pentacarbonylchromium (0) (**49-Z**)*

Carbene complex **47** (548 mg., 2 mmol) was dissolved in 24 ml of diethyl ether and cooled to -100°C. To this solution was added dropwise a solution of 1-ethanol-2-amine (0.121 ml, 122.2 mg, 2 mmol) in 6.5 ml of diethyl ether. TLC showed that the reaction began

immediately after addition but did not proceed to completion. The formation of a white solid, presumably 1-ethanol-2-amine, was observed. The reaction mixture was allowed to warm up gradually over 30 min. When the mixture was placed in a −10°C bath, the reaction went to completion in 30 min. After concentration, the two major product were purified from the crude reaction mixture by chromatography on silica gel with a 2:1 mixture of hexane and ethyl acetate as eluent to give the Michael adduct **48** (213.1 mg, 0.636 mmol) as a yellow solid in 32% yield and the alkynyl amino complex **49** (335.1 mg, 1.171 mmol) as a yellow solid in 59% yield. The stereochemistry of **49** was tentatively assigned as Z on the basis that it would close to give **50**. Depending on the reaction temperature, small amounts of the E-isomer of **49** can be formed in this reaction. Spectral data for **49-Z**: m.p. 100–101°C; ^{1}H-NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.86–3.88 (m, 4 H), 9.10 (bs, 1 H); ^{13}C-NMR ($CDCl_3$) δ 6.2, 53.8, 60.9, 82.3, 131.6, 217.2, 223.4, 259.2; IR (film) 3595w, 3272w, 2055m, 1915s, 1894s, 1539m; mass spectrum (EI) m/z (relative intensity) 303 M^+ (22), 275 (16), 232 (2), 219 (11), 191 (34), 178 (3), 163 (100), 149 (6), 133 (32), 121 (11), 108 (35), 91 (19), 80 (22), 71 (23), 66 (8), 52 (88), 45 (8); Anal. calc. for $C_{11}H_9NO_6Cr$: C, 43.58; H, 2.99; N, 4.62. Found: C, 43.74; H, 2.70; N, 4.55%. Spectral data for **48**: ^{1}H-NMR ($CDCl_3$) δ 2.04 (s, 3 H), 3.46 (bs, 2 H), 3.84 (bs, 2 H), 4.41 (s, 3 H), 6.18 (s, 1 H), 9.31 (s, 1 H).

*4.16. Preparation of of [propynyl(2-oxazolidinone)-methylene] tetracarbonylchromium (0) (**50**)*

The amino complex **49-Z** (150.0 mg, 0.50 mmol) was dissolved 3 ml of THF [0.15 M] at −78°C, and 411.0 μl of *n*-BuLi [2.47 M in hexane] (1.01 mmol, 2.05 eq) was added dropwise. After 45 min, the dianion solution was transferred dropwise via a cannula to 385.0 μl of a phosgene solution [1.93 M in toluene] (0.743 mmol, 1.5 eq) that was diluted with 40 ml of CH_2Cl_2. The mixture was stirred at −78°C for 20 min and then at r.t. for 15 min. After evaporation of the solvent under reduced pressure (not to dryness), the residue was chromatographed on a silica gel column (size: 1.5 × 30 cm, gradient eluent: 0–100% CH_2Cl_2 in hexane) to provide 62.7 mg of **50** (42%) as a purple red solid. $R_f = 0.65$ (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 2.55 (s, 3H), 4.46 (m, 2H), 4.47 (m, 2H); ^{13}C-NMR was not obtained due to the rapid decomposition in all deuterated solvents; IR (neat) cm^{-1} 2927w, 2179s, 2060s, 1992s, 1924s, 1792s, 1383m, 1348s, 1320s, 1208m, 1175s, 1045m; mass spectrum (EI): m/z (relative intensity) 301 (1) M^+, 272 (1), 257 (1), 239 (1), 220 (100), 209 (1), 192 (19), 164 (19), 136 (26), 108 (100); m/z calc. for $C_{11}H_7CrNO_6$ 300.9678, measured 300.9675.

*4.17. Synthesis of [phenyl-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (**51**)*

A solution of butyllithium (2.2 ml of a 2.5 M solution in hexane, 5.5 mmol) was added dropwise over several min to a stirred solution of 1-methyl-2-imidazolidinone **19** (547 mg, 5.46 mmol) in 30 ml of THF cooled to −78°C. The reaction was stirred for 5 min at −78°C and then allowed to warm to r.t. The anion solution was then again cooled to −78°C and a solution of phenyl-methoxy chromium carbene complex **40** [28] (1.705 g, 5.46 mmol) in 15 ml THF was added via cannula. The transfer was completed upon rinsing with two 5 ml portions of THF. The reaction was stirred 5 min at −78°C. The reaction was then allowed to warm to r.t. and stirred for an additional 60 min. The reaction was concentrated and purified via silica gel chromatography using 1:1 hexane:ethyl acetate as the eluting solvent. The dark red gum thus obtained was crystallized in two crops from CH_2Cl_2–hexane to yield 1.637 g (85%) of lustrous black needles. Spectral data for **51**: Dark purple–black crystals (CH_2Cl_2–hexane), m.p. 137–140°C (dec.); $R_f = 0.22$ (1:1 hexane:EtOAc); ^{1}H-NMR (CD_2Cl_2) δ 3.01 (s, 3 H), 3.85 (m, 4 H, $J = 4.1$ Hz), 7.32 (d, 1 H, $J = 7.6$ Hz), 7.39 (d, 1 H, $J = 7.3$ Hz), 7.42 (d, 1 H, $J = 7.4$ Hz), 7.51 (m, 2 H); ^{13}C-NMR (CD_2Cl_2) δ 31.3, 42.9, 49.2, 123.0, 128.7, 129.6, 146.4, 163.1, 216.4, 231.1, 233.8, 312.3; IR (NaCl, neat) 2005 s, 1887 br s, 1831 s, 1717 s, 1370 m, 1300 m, 1262 w, 1226 w, 704 w, 673 w, 628 w cm^{-1}; mass spectrum m/z (relative intensity, M^+ not found) 220 (65), 108 (92), 80 (100), 52 (100).

*4.18. Preparation of [trans-propenyl-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonyl-chromium (0) (**52**)*

A solution of complex **20** (149 mg, 0.52 mmol) in 5 ml THF was cooled to −78°C under an atmosphere of argon. A 1.6 M solution of *n*-BuLi (0.34 ml, 0.54 mmol) in hexanes was then added dropwise and the resulting yellow solution was stirred for 5 min. Freshly distilled acetaldehyde (44 μl, 0.78 mmol) was added dropwise and the mixture was gradually warmed to −40°C over a 30 min period and the mixture was stirred an additional 30 min at −40°C upon which time the solution became dark red. Acetic acid (31 μl, 0.55 mmol) was injected and the mixture was quickly warmed to r.t. and concentrated on a rotary evaporator. The remaining residue was chromatographed on silica gel with CH_3CN–Et_2O (1:2, $R_f = 0.65$) to give the crude aldol adduct (156 mg, 95%) as a red solid which was immediately taken up in 20 ml of CH_2Cl_2 at r.t. under argon. Triethylamine (28 μl, 0.20 mmol) was then added by syringe and the mixture was stirred for 2

h at r.t. Acetic acid (23 μl, 0.40 mmol) was added and the resulting purple solution was concentrated to about 2 ml and chromatographed on silica gel with CH_2Cl_2 ($R_f = 0.43$) to give 81 mg of **52** as a reddish–purple solid in 60% yield from **20**. Spectral data for **52**: m.p. 130°C (dec.); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.16 (d, 3H, $J = 6.7$ Hz), 3.00 (s, 3H), 3.88 (t, 2H, $J = 8.0$ Hz), 3.98 (t, 2H, $J = 8.0$ Hz), 6.67 (d, 1H, $J = 14.4$ Hz), 7.75 (dq, 1H, $J = 14.4$, 7.1 Hz); ^{13}C-NMR (500 MHz, acetone-d_6, −50°C) δ 20.77, 30.61, 42.75, 48.79,136.80, 159.10, 163.65, 217.20, 231.59, 232.03, 291.83; ^{13}C-NMR (500 MHz, CD_2Cl_2) δ 21.06, 31.27, 41.97, 48.74,136.26, 158.23, 163.38, 217.21, 232.07, 232.54, 297.90; IR (neat) 2001 vs, 1879 vs, 1828 vs, 1712 s, 1376 m, 1384 m cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 316 M^+ (60), 307 (10), 288 (8), 260 (20), 232 (25), 204 (5), 154 (100), 136 (80), 107 (25); Calc. for $C_{12}H_{12}N_2O_5Cr$, FAB (3-NBA), m/z 316.0152, measured 316.0154. Anal. Calc. for $C_{12}H_{12}N_2O_5Cr$: C, 45.58; H, 3.82; N 8.86. Found: C, 45.62; H, 4.05; N, 8.51%.

4.19. Preparation of [trans-propenyl [3-(1-methyl-2-imidazolidone)]methylene] tetracarbonyltungsten (0) (53)

Complex **53** was prepared according to the procedure described above for complex **52** from the methyl complex **21** (207 mg, 0.49 mmol). After addition of triethylamine, the solution was stirred for 45 min and then the purple solution was concentrated to ~2 ml and the crude product was chromatographed with CH_2Cl_2 ($R_f = 0.41$) to give 150 mg of **53** as a reddish–purple solid in 62% from **21**. Spectral data for **53**: m.p. 115°C (dec.): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.04 (d, 3H, $J = 7.2$ Hz), 3.09 (s, 3H), 3.96–4.02 (m, 4H), 6.53 (d, 1H, $J = 14.3$ Hz), 8.00 (dq, 1H, $J = 14.2$, 6.9 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, −50°C) δ 20.92, 30.89, 43.08, 48.70, 137.96, 162.80, 166.77, 217.20, 219.79, 225.83, 272.85; IR (neat) 2002 (s), 1902 (vs), 1864 (vs), 1816 (vs), 1702 (s), 1374 (m), 1299 (m), 1224 (m) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 448 M^+ (^{184}W, 10), 419 (5), 391 (3), 363 (2), 341 (5), 327 (2), 154 (100), 136 (80); Calc. for $C_{12}H_{12}N_2O_5{}^{184}W$, FAB (3-NBA), m/z 448.0256, measured 448.0238.

4.20. Preparation of [trans-β-styryl-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (54)

A solution of complex **20** (150 mg, 0.52 mmol) in 5 ml of THF was cooled to −78°C under an atmosphere of argon. A 1.6 M solution of *n*-BuLi (0.34 ml, 0.54 mmol) in hexanes was added and the yellow solution was stirred for 5 min after which freshly distilled benzaldehyde (79 μl, 0.78 mmol) was added dropwise. The reaction mixture was gradually warmed to 0°C over a 30 min period and stirred at this temperature for an additional 30 min. Acetic acid (0.31 μl, 0.55 mmol) was then added and the reaction mixture was immediately warmed to r.t. and stripped of solvent on a rotary evaporator. The remaining residue was filtered through a short plug of Celite with 20 ml of CH_2Cl_2. Triethylamine (50 μl, 36 mmol) was then injected into this filtrate and the mixture was stirred under nitrogen for 1 h. The solution was concentrated to about 3 ml and was chromatographed on silica gel with CH_2Cl_2 ($R_f = 0.50$) to give 151 mg of the title compound as a deep blue solid in 76% yield. Spectral data for **54**: m.p. 131°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 3.02 (s, 3H), 3.90 (t, 2H, $J = 6.8$ Hz), 4.09 (t, 2H, $J = 7.1$ Hz), 7.36 (d, 1H, $J = 15.0$ Hz), 7.46–7.74 (m, 5H), 8.47 (d, 1H, $J = 15.0$ Hz); ^{13}C-NMR (500 MHz, CD_2Cl_2) δ 31.36, 42.06, 48.83, 129.43, 129.55, 129.76, 130.23, 131.64, 155.58, 160.11, 217.65, 232.42, 233.36, 296.29; IR (neat) 1997 s, 1873 vs, 1815 s, 1709 s, 1363 m cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 378 (42) M^+, 350 (13), 322 (13), 307 (25), 289 (10), 266 (2), 154 (100). Anal. Calc. for $C_{17}H_{14}N_2O_5Cr$: C, 53.98; H, 3.73; N, 7.41. Found: C, 53.98; H, 3.72; N, 7.42%.

4.21. Preparation of [trans-β-styryl-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonyltungsten (0) (55)

Complex **55** was prepared from complex **21** (200 mg, 0.47 mmol) according to the procedure described for **54** except that triethylamine was not used. Purification of the product on silca gel ($R_f = 0.65$, CH_2Cl_2) gave 157 mg of the aldol condensation product **55** in 65% yield as a prussian blue solid. The aldol addition product was also isolated in 10% yield. Spectral data for **55**: m.p. 80°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 3.11 (s, 3H), 4.02 (t, 2H, $J = 7.7$ Hz), 4.09 (t, 2H, $J = 7.7$ Hz), 7.22 (d, 1H, $J = 14.9$ Hz) 7.35–7.56 (m, 3H), 7.80 (d, 2H, $J = 7.6$ Hz), 8.71 (d, 1H, $J = 15.0$ Hz); IR (neat) 1991 (s), 1869 (vs), 1808 (s), 1696 (s) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 510 M^+ (^{184}W, 40), 495 (30), 460 (55), 427 (70), 391 (75), 371 (25), 154 (100); Calc. for $C_{17}H_{14}N_2O_5{}^{184}W$, FAB (3-NBA), m/z 509.9402, measured 510.0403.

4.22. Preparation of [ethyl [3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (56)

4.22.1. Method A

According to the procedure for the preparation of complex **20**, the carbene complex **56** was prepared from the ammonium salt **67** and 1-methyl-2-imidazolidinone

19 in 7% yield as a dark red solid. Spectra data for **56**: m.p. 112°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 1.44 (t, 3H, $J = 7.6$ Hz), 2.98 (s, 3H), 3.18 (q, 2H, $J = 7.6$ Hz), 3.88–3.97 (m, 4H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 12.20, 31.16, 40.34, 41.09, 48.85, 162.54, 216.30, 231.85, 231.97, 322.51; IR (neat) 2006 (s), 1875 (vs), 1816 (vs), 1717 (s), 1364 (m), 1300 (m) cm^{-1}; mass spectrum, m/z (relative intensity) 304 M^+ (10), 276 (25), 220 (25), 192 (10) 154 (100); Calc. for $C_{11}H_{12}N_2O_5Cr$, FAB (3-NBA), m/z 304.0151, measured 304.0153. Anal. Calc. for $C_{11}H_{12}N_2O_5Cr$: C, 43.43; H, 3.98; N, 9.21. Found: C, 43.02; H, 4.21; N, 9.00%.

4.22.2. Method D

Complex **20** (280 mg, 0.97 mmol) was dissolved in 8 ml THF and cooled to −78°C under an atmosphere of argon. A 1.6 M solution of *n*-BuLi (0.63 ml, 1.01 mmol) in hexanes was then added dropwise and the resulting yellow solution was then transfered slowly via cannula to a solution of methyl triflate (115 μl, 1.01 mmol) in 1 ml ether at −45°C. After 30 min, the reaction was warmed to r.t. and the solvent was removed on a rotary evaporator. Flash chromatography on silica gel with CH_2Cl_2 ($R_f = 0.62$) gave 287 mg of alkylated product which consists of 83 mol% of **56** (81% yield) and 8 mol% of **57** (7% yield) and a 9% recovery of the starting material **20** as indicated by ^{1}H-NMR. These three carbene complexes are inseparable on silica gel.

4.23. Preparation of [ethyl[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonyltungsten (0) (58)

4.23.1. Method A

According to the procedure for complex **20**, the carbene complex **58** was prepared from the ammonium salt **68** and 1-methyl-2-imidazolidinone **19** in 10% yield as a dark red solid. Spectral data for **58**: m.p. 121°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 1.45 (t, 3H, $J = 7.5$ Hz), 2.82 (q, 2H, $J = 7.5$ Hz), 3.07 (s, 3H), 3.87–4.04 (m, 4H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 13.40, 31.31, 41.46, 41.95, 48.66, 165.40, 204.45, 216.32, 221.41, 301.97; IR (neat) 2006 (s), 1869 (vs), 1810 (vs), 1714 (s), 1389 (m), 1301 (m) cm^{-1}; mass spectrum, m/z (relative intensity) 436 M^+ (15, ^{184}W), 352 (50), 322 (45), 296 (30) 268 (65), 240 (35), 212 (35), 165 (35), 140 (90); Calc. for $C_{11}H_{12}N_2O_5{}^{184}W$, m/z 436.0256, measured 436.0267.

4.23.2. Method D

According to the Method D for the preparation of complex **56**, the tungsten carbene complex **58** was prepared from complex **21** by alkylation in 86% yield as a dark red solid. The ^{1}H-NMR indicated that trace amount of the dialkylated product **59** was also present.

4.24. Preparation of [iso-propyl [3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (57)

Complex **56** (300 mg, 0.99 mmol) was dissolved in 8 ml THF and cooled to −78°C under an atmosphere of argon. A 1.6 M solution of *n*-BuLi (0.65 ml, 1.04 mmol) in hexane was then added dropwise and the resulting yellow solution was stirred for 5 min. Methyl triflate (117 μl, 1.04 mmol) was then added via syringe and the reaction mixture was allowed to warm to −40°C in 30 min. After stirring at −40°C for 1 h, the reaction was warmed to r.t. and the solvent was removed on a rotary evaporator. Flash chromatography on silica gel with CH_2Cl_2 ($R_f = 0.62$) gave 298 mg of **57** as a red solid in 95% yield. Spectral data for **57**: m.p. 111°C (dec.); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.53 (d, 6H, $J = 6.5$ Hz), 2.96 (heptet, 1H, $J = 6.5$ Hz), 3.02 (s, 3H), 3.92 (t, 2H, $J = 7.1$ Hz), 4.00 (t, 2H, $J = 7.1$ Hz); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 22.13, 31.28, 41.63, 45.35, 48.42, 162.23, 216.37, 231.74, 232.02, 326.58; IR (neat) 2006 (s), 1866 (vs), 1807 (vs), 1728 (s), 1514 (m), 1461 (m), 1399 (m), 1306 (m) cm^{-1}; mass spectrum, m/z (relative intensity) 318 M^+ (27), 290 (8), 262 (5), 234 (23) 206 (98), 191 (15), 164 (24), 164 (24), 151 (99), 139 (67); Calc. for $C_{12}H_{14}N_2O_5Cr$, m/z 318.0308, measured 318.0359.

4.25. Preparation of [1-methyl-2-methoxyethyl-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (60) and [1-methoxymethyl-2-methoxyethyl[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (61)

A 264 mg (0.87 mmol) portion of the slightly impure **56** prepared by method D [**20** (9%), **56** (83%) and **57** (8%)] was dissolved in 8 ml of THF and cooled to −78°C under an atmosphere of argon. A 1.6 M solution of *n*-BuLi (0.57 ml, 0.91 mmol) in hexanes was then added dropwise and the resulting yellow solution was stirred for 5 min. Bromomethyl methyl ether [29] (114 μl, 1.04 mmol) was then added via syringe and the reaction mixture was stirred at −78°C for 2 h. The reaction was warmed to r.t. over a 1 h period and the solvent was removed on a rotary evaporator. Flash chromatography on silica gel with CH_2Cl_2 gave 20 mg of **57** ($R_f = 0.62$, 8% overall yield from **20**) and 191 mg of **60** ($R_f = 0.10$, 62% overall yield from **20**), further eluting with ethyl acetate gave 30 mg of **61** ($R_f = 0.34$, 9% overall yield from **20**). Spectral data for **60**: red solid, m.p. 110°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 1.43 (d, 3H, $J = 7.7$ Hz), 2.98 (s, 3H), 3.12–3.19 (m, 1H), 3.31 (s, 3H), 3.69–3.73 (m, 1H), 3.88 (t, 1H, $J = 7.7$ Hz), 3.95–4.11 (m, 4H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 16.90, 31.22, 42.25, 48.33, 50.67, 58.79, 78.57, 162.05, 215.87, 216.38, 231.79 (2C), 323.55; IR

(neat) 2006 (s), 1884 (vs), 1817 (vs), 1721 (s), 1394 (m), 1302 (m), 1106 (m) cm^{-1}; mass spectrum, *m/z* (relative intensity) 348 M^+ (34), 303 (35), 289 (10), 264 (15), 236 (100), 220 (20) 204 (63), 191 (55), 151 (75), 125 (44); Calc. for $C_{13}H_{16}N_2O_6Cr$, *m/z* 348.0414, measured 348.0377. Spectral data for **61**: red solid, m.p. 93°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 2.98 (s, 3H), 3.32 (s, 6H), 3.28–3.42 (m, 1H), 3.87–3.82 (m, 4H), 3.99 (t, 2H, $J = 8.7$ Hz), 4.09 (t, 2H, $J = 7.8$ Hz); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 31.20, 42.60, 48.34, 57.17, 58.97, 74.28, 161.99, 215.92 (2C), 231.57, 231.66, 320.51; IR (neat) 2006 (s), 1885 (vs), 1815 (vs), 1720 (s), 1395 (m), 1301 (m), 1106 (m) cm^{-1}; mass spectrum, *m/z* (relative intensity) 378 M^+ (15), 266 (75), 234 (18), 220 (50) 204 (25), 191 (40), 167 (22), 151 (38), 108 (60); Calc. for $C_{14}H_{18}N_2O_7Cr$, *m/z* 378.0519, measured 378.0477.

*4.26. Preparation of [1-methyl-2-methoxyethyl-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonyltungsten (0) (**62**)*

Carbene complex **62** was prepared from **58** (300 mg, 0.69 mmol) by the procedure described above for the preparation of complex **60**. The product was obtained in 80% yield (263 mg, $R_f = 0.10$) as a red solid. No dialkylation products could be detected. Spectral data for **62**: m.p. 126°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 1.34 (d, 3H, $J = 6.7$ Hz), 2.98–3.06 (m, 1H), 3.07 (s, 3H), 3.28 (s, 3H), 3.65 (dd, 1H, $J = 13.0$, 4.6 Hz), 3.84–4.13 (m, 5H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 17.53, 31.37, 42.68, 48.16, 50.90, 58.81, 79.02, 165.27, 204.00, 204.57, 216.73, 220.94, 303.26; IR (neat) 2005 (s), 1869 (vs), 1806 (vs), 1715 (s), 1450 (m), 1392 (m), 1301 (m), 1258 (m) cm^{-1}; mass spectrum, *m/z* (relative intensity) 480 M^+ (30, ^{184}W), 480 (24), 366 (25), 350 (24), 324 (20), 298 (23), 268 (34), 240 (18), 204 (25), 184 (33), 169 (25), 153 (38); Calc. for $C_{13}H_{16}N_2O_6^{184}W$, *m/z* 480.0518, measured 480.0492. Anal. Calc. for $C_{13}H_{16}N_2O_6W$: C, 32.52; H, 3.36; N, 5.84. Found: C, 32.18; H, 3.80; N, 6.11%.

*4.27. Preparation of [iso-propenyl[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (**64**)*

Carbene complex **60** (175 mg, 0.50 mmol) was dissolved in 3 ml of CH_2Cl_2 and 20 ml of Et_2O under an atmosphere of argon. Alumina (1.54 g, ICN Alumina B-Super 1) was added in one portion and the mixture was stirred at r.t. for 3 h, upon which time the TLC showed that all the starting carbene complex had disappeared. The mixture was filtered and washed with CH_2Cl_2 and the solvent removed in vacuo and the dark residue was chromatographed on silica gel with CH_2Cl_2 to give 127 mg of **64** ($R_f = 0.66$) as a dark purple solid in 80% yield. Spectral data for **64**: m.p. 85°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 2.17 (s, 3H), 2.99 (s, 3H), 3.82–3.96 (m, 4H), 4.69 (s, 1H), 4.97 (s, 1H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 20.77, 31.23, 41.83, 49.02, 105.90, 151.77, 162.44, 216.22, 231.68, 232.92, 314.79; IR (neat) 2007 (s), 1874 (vs), 1823 (vs), 1717 (s), 1375 (m), 1300 (m), 1252 (m) cm^{-1}; mass spectrum, *m/z* (relative intensity) 316 M^+ (13), 288 (6), 256 (11), 232 (12), 220 (100), 204 (73), 192 (7), 164 (27), 154 (24); Calc. for $C_{12}H_{12}N_2O_5Cr$, *m/z* 316.0151, measured 316.0149. Anal. Calc. for $C_{12}H_{12}N_2O_5Cr$: C, 45.58; H, 3.82; N, 8.86. Found: C, 45.20; H, 4.20; N, 8.95.

*4.28. Preparation of [iso-propenyl[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonyltungsten (0) (**65**)*

According to the procedure for complex **64**, the tungsten carbene complex **65** was prepared from complex **62** by dehydration and obtained as a dark brown solid in 85% yield. Spectral data for **65**: m.p. 143°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 2.15 (s, 3H), 3.08 (s, 3H), 3.86–3.99 (m, 4H), 4.76 (s, 1H), 4.99 (s, 1H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 21.32, 31.39, 42.31, 48.94, 107.62, 152.16, 165.71, 204.50, 216.04, 222.29, 292.90; IR (neat) 2008 (s), 1877 (vs), 1820 (vs), 1709 (s), 1371 (m), 1259 (m) cm^{-1}; mass spectrum, *m/z* (relative intensity) 448 M^+ (13, ^{184}W), 420 (5), 352 (77), 336 (43), 296 (65), 270 (100), 240 (70), 212 (70), 198 (24), 184 (47); Calc. for $C_{12}H_{12}N_2O_5^{184}W$, *m/z* 448.0256, measured 448.0221. Anal. Calc. for $C_{12}H_{12}N_2O_5W$: C, 32.17; H, 2.70; N, 6.25. Found: C, 31.80; H, 3.12; N, 6.31%.

*4.29. Preparation of [2-(3-methoxypropene)-[3-(1-methyl-2-imidazolidinone)]methylene] tetracarbonylchromium (0) (**66**)*

According to the procedure for complex **64**, the carbene complex **66** was prepared from complex **61** by dehydration and obtained as a dark brown solid in 85% yield. Spectral data for **66**: m.p. 89°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 3.01 (s, 3H), 3.41 (s, 3H), 3.88 (t, 2H, $J = 8.4$ Hz), 4.01 (t, 2H, $J = 8.0$ Hz), 4.44 (s, 2H), 4.74 (s, 1H), 5.07 (s, 1H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 31.22, 42.26, 49.01, 58.89, 75.85, 105.20, 153.44, 162.32, 215.98, 231.77, 232.80, 312.69; IR (neat) 2007 (s), 1884 (vs), 1825 (vs), 1717 (s), 1377 (m), 1300 (m) cm^{-1}; mass spectrum, *m/z* (relative intensity) 346 M^+ (15), 262 (15), 234 (89), 220 (87), 204 (70), 178 (25), 167 (15), 151 (35), 136 (15), 108 (85); Calc. for $C_{13}H_{14}N_2O_6Cr$, *m/z* 346.0257, measured 346.0221.

*4.30. Preparation of [methyl[(4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidone]methylene] tetracarbonylchromium (0) (**72**)*

Tetramethylammonium(1-hydroxy-ethylidene) pentacarbonylchromium (0) **15** [25] (1.50 g, 4.85 mmol) was

dissolved in 15 ml CH_2Cl_2 under an atmosphere of argon and cooled to −70°C. Freshly distilled acetyl bromide (0.36 ml, 4.85 mmol) was then added dropwise and the remaining solution was stirred for an additional 60 min upon which time a solution of (4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidone **70** [19] (0.92 g, 4.85 mmol) in 10 ml CH_2Cl_2 was added dropwise. The mixture was gradually warmed to −60°C over a 15 min period and was stirred at this temperature for 18 h. The mixture was quickly warmed to r.t. and concentrated on a rotary evaporator to remove two-thirds of the solvent. The resulting reddish–brown solution was loaded onto a silica gel column and the product eluted with CH_2Cl_2 ($R_f = 0.63$) to give complex **72** as a red solid. Further recrystallization from CH_2Cl_2 and pentane afforded 0.84 g of **72** as deep-red prisms in 65% yield. Shorter reaction times (−45°C, 2 h) leads to reduced yields (44%). Spectral data for **72**: m.p. 117°C (dec.); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.85 (d, 3H, $J = 6.7$ Hz), 2.78 (s, 3H), 2.94 (s, 3H), 4.40–4.48 (m, 1H), 5.35 (d, 1H, $J = 8.5$ Hz), 7.08 (br s, 3H), 7.41 (t, 2H, $J = 5.5$ Hz); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 14.84, 28.43, 34.35, 59.98, 61.79, 126.36, 128.35, 129.24, 133.85, 162.32, 215.21, 215.49, 231.62 (2C), 320.87; ^{13}C-NMR (75 MHz, acetone-d_6, −50°C) δ 14.73, 28.45, 30.04, 34.14. 60.45, 62.02, 125.65, 129.41, 129.83, 135.56, 163.12, 216.14, 216.21, 213.74, 232.45, 317.35; IR (neat) 2007 (s), 1982 (shoulder, s), 1900 (vs), 1827 (s), 1711 (s), 1355 (m), 1148 (m) cm^{-1}; mass spectrum, m/z (relative intensity) 380 M^+ (10), 268 (5), 244 (25), 230 (15), 220 (100), 203 (40), 132 (40), 118 (30), 108 (95), 80 (100). Anal. Calc. for $C_{17}H_{16}O_5N_2Cr$: C, 53.68; H, 4.24; N, 7.37. Found: C, 53.31; H 4.24; N, 7.20%.

4.31. Preparaton of [methyl[(4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidone]methylene] tetracarbonyltungsten (0) (73)

According to the procedure for complex **72**, the tungsten carbene **73** was prepared the ammonium salt **16** [26] and (4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidone **70** [19] and obtained in 50% yield as deep-red prisms. Spectral data for **73**: m.p. 115°C (dec.); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.91 (d, 3H, $J = 6.5$ Hz), 2.48 (s, 3H), 3.04 (s, 3H), 4.40–4.55 (m, 1H), 5.33 (d, 1H, $J = 8.5$ Hz), 7.26–7.40 (m, 5H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 15.07, 28.64, 36.16, 60.06, 62.28, 127.97, 128.28, 129.43, 133.36, 165.55, 203.29, 204.30, 216.28, 221.40, 297.68; ^{13}C-NMR (75 MHz, acetone-d_6, −50°C) δ 14.84, 28.70, 30.04, 35.72, 60.62, 62.57, 125.86, 129.59, 129.87, 135.03, 166.14, 204.24, 204.98, 216.39, 221.95, 296.51; IR (neat) 2008 (s), 1974 (shoulder, s), 1909 (vs), 1824 (vs), 1704 (s), 1352 (m) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 512 M^+ (50, ^{184}W), 484 (38, ^{184}W), 456 (80, ^{184}W), 398 (18), 338 (55), 233 (75), 154 (100); Calc. for $C_{17}H_{16}N_2O_5{}^{182}W$, FAB (3-NBA), m/z 510.0542, measured 510.0594. Anal. Calc. for $C_{17}H_{16}O_5N_2W$: C, 39.87; H, 3.15; N, 5.47. Found: C, 39.48; H, 3.50; N, 5.20%.

4.32. Preparation of [methyl[(4R,5S)-1,5-dimethyl-4-cyclohexyl-2-imidazolidinone]methylene] tetracarbonylchromium (0) (74)

According to the procedure for complex **72**, the carbene complex **74** was prepared from the ammonium salt **15** [21] and (4R,5S)-1,5-dimethyl-4-cyclohexyl-2-imidazolidinone **71** [19c] and obtained in 10% yield as a dark red solid. Spectral data for **74**: m.p. 77°C (dec.); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.80–1.25 (m, 5H), 1.41 (d, 3H, $J = 6.6$ Hz), 1.56–2.01 (m, 6H), 2.86 (s, 3H), 3.16 (s, 3H), 4.05–4.46 (m, 2H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 12.61, 25.78, 25.87, 26.61, 27.97, 28.28, 32.29, 35.46, 40.25, 59.66, 63.21, 163.04, 215.24, 215.61, 231.32, 231.74, 318.75; IR (neat) 2934 (m), 2857 (m), 2005 (s), 1882 (vs), 1826 (vs), 1711 (s), 1358 (m), 1141 (m) cm^{-1}; Anal. Calc. for $C_{17}H_{22}N_2O_5Cr$: C, 52.85; H, 5.74; N, 7.25. Found: C, 52.68; H, 6.38; N, 7.10%.

4.33. Preparation of [methyl[(4R,5S)-1,5-dimethyl-4-cyclohexyl-2-imidazolidinone]methylene] tetracarbonyltungsten (0) (75)

According to the procedure for complex **72**, the carbene complex **75** was prepared from the ammonium salt **16** [26] and (4R,5S)-1,5-dimethyl-4-cyclohexyl-2-imidazolidinone **71** [19c] in 25% yield as a dark red solid. Spectral data for **75**: m.p. 75°C (dec.); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 0.86–0.99 (m, 2H), 1.04–1.39 (m, 3H), 1.44 (d, 3H, $J = 6.5$ Hz), 1.51–1.90 (m, 6H), 2.94 (s, 3H), 2.96 (s, 3H), 4.19–4.448 (m, 2H); ^{13}C-NMR (300 MHz, CD_2Cl_2) δ 12.98, 26.30, 26.31, 27.03, 28.39, 29.05, 32.85, 37.31, 40.35, 60.08, 64.16, 164.49, 213.44, 206.61, 216.89, 221.10, 297.80; IR (neat) 2933 (m), 2856 (m), 2006 (s), 1874 (vs), 1818 (vs), 1704 (s), 1358 (m) cm^{-1}. Anal. Calc. for $C_{17}H_{22}N_2O_5W$: C, 39.40; H, 4.28; N, 5.41. Found: C, 39.00; H, 4.34; N, 5.41%.

4.34. Preparation of (4S)-phenyl-1-methyl-2-imidazolidone (79)

Compound **79** was prepared according to the procedure that has been published for the synthesis of imidazolidinone 70 [19] The fusion of urea (1.34 g, 22.25 mmol) and (4R)-phenyl-3-methyl-ethylenediamine **78** [30] (1.38 g, 7.41 mmol) to gave 567 mg of **79** in 44% yield as a white solid after chromatography with 9:1 EtOAc/MeOH ($R_f = 0.44$). Spectral data for **79**: m.p. 124–27°C; $[\alpha]_D$ −33.0° (c 1.00, MeOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.77 (s, 3H), 3.17 (t, 1H, $J = 7.7$ Hz), 3.73 (t, 1H, $J = 8.8$ Hz), 4.69 (br t, 1H, $J = 7.8$

Hz), 4.88 (br s, 1H), 7.25–7.32 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.02, 53.01, 55.54, 125.55, 127.34, 128.25, 141.58, 162.42; IR (neat) 3253 (m), 1699 (vs), 1493 (m), 1442 (w), 1254 (w) cm^{-1}; mass spectrum, m/z (relative intensity) 176 M^+ (100), 132 (15), 118 (7), 104 (35), 9 (12), 91 (14), 77 (17). Anal. calc for $C_{10}H_{12}N_2O$: C, 68.15; H, 6.87; N, 15.90. Found: C, 67.38; H, 7.13; N, 16.50%.

4.35. Preparation of [methyl[(4R)-phenyl-2-imidazolidone]methylene] tetracarbonylchromium (0) (80)

The ammonium salt **15** [25] (352 mg, 1.14 mmol) was dissolved in 7 ml CH_2Cl_2 under an atmosphere of argon and cooled to −60°C. Freshly distilled acetyl bromide (84 μl, 1.14 mmol) was then added dropwise and the remaining solution was stirred for an additional 30 min upon which a solution of imidazolidone **79** (150 mg, 1.14 mmol) in 5 ml CH_2Cl_2 was added dropwise. The mixture was gradually warmed to −40°C over a 15 min period and was stirred at this temperature for 6 h. The mixture was quickly warmed to r.t., filtered through a plug of Celite, and concentrated on a rotary evaporator. The resulting reddish–brown residue was chromatographed silica gel with CH_2Cl_2 ($R_f = 0.64$) to give complex **80** as a red solid. Further recrystallization from CH_2Cl_2 and pentane afforded 271 mg of **80** as deep-red prisms in 65% yield. Spectral data for **80**: m.p. 94°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 2.79 (s, 3H), 2.99 (s, 3H), 3.59 (dd, 1H, $J = 10.0$, 3.4 Hz), 4.29 (t, 1H, $J = 9.6$ Hz), 5.28–5.32 (m, 1H), 7.14 (d, 2H, $J = 7.1$ Hz), 7.37–7.41 (m, 3H); ^{13}C-NMR (75 MHz, acetone-d_6, −50°C) δ 30.66, 34.05, 57.51, 58.41, 126.40, 129.32, 130.11, 140.13, 162.98, 216.29, 218.30, 231.73, 237.46, 317.30; IR (neat) 2008 (s), 1879 (vs), 1825 (vs), 1717 (s), 1363 (m), 1251 (w) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 366 M^+ (20), 307 (15), 289 (10), 154 (100), 136 (72), 107 (25); Calc. for $C_{16}H_{14}O_5N_2Cr$, FAB (3-NBA), m/z 366.0307, measured 366.0300.

4.36. Preparation of [trans-propenyl[(2R,1S)-phenylmethyl-2-aminoethanol]methylene] pentacarbonylchromium (0) (86-E) and (86-Z)

The ammonium salt **81** (1.00 g, 3.62 mmol) was dissolved in 10 ml of CH_2Cl_2 and cooled to −60°C under an atmosphere of argon. Acetyl bromide (267 μl, 3.62 mmol) was injected dropwise over a 5 min period and the resulting deep purple solution was stirred for an additional 45 min. A solution of (1R,2S)-(−)-norephedrine (0.55 g, 3.62 mmol) in 5 ml of CH_2Cl_2 was then added dropwise and the solution was warmed to −40°C and stirred an additional 10 h. The yellow–brown solution was quickly warmed to r.t. and filtered though a plug of Celite. The solution was concentrated on a rotary evaporator and the remaining residue was chomatographed with CH_2Cl_2 to give 0.93 g of complex **86-E** (65%, $R_f = 0.51$) and 0.13 g of complex **86--Z** (9%, $R_f = 0.42$) as yellow solids in 74% combined yield. Complex **86--E** was isomerized as described in the general procedure to give a 80:20 ratio of **86--Z** to **86--E**, respectively, in 87% combined yield after chromatography. The O*H* signal was not located by ^{1}H-NMR for either **86--E** or **86--Z**. Spectral data for **86--E**: m.p. 110–113°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.17 (d, 3H, $J = 6.6$ Hz), 1.96 (d, 3H, $J = 6.5$ Hz), 4.26–4.28 (m, 1H), 4.87 (br s, 1H), 6.10 (dq, 1H, $J = 15.4$, 6.7 Hz), 6.52 (d,1H, $J = 15.4$ Hz), 7.40–7.30 (m, 5H), 8.82 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 15.44, 19.86, 59.87, 76.36, 126.46, 126.77, 129.37, 129.60, 137.37, 140.02, 218.77, 224.01, 271.80; IR (neat), 2053 (vs), 1970 (shoulder, vs), 1908 (vs), 1507 (s) cm^{-1}. Spectral data for **86--Z**: m.p. 105–108°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.23 (d, 3H, $J = 6.6$ Hz), 1.87 (d, 3H, $J = 6.5$ Hz), 4.66–4.68 (m, 1H), 5.16 (br s, 1H), 6.10 (dq, 1H, $J = 15.2$, 6.7 Hz), 6.90 (d, 1H, $J = 15.1$ Hz), 7.34–7.42 (m, 5H), 9.07 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.04, 17.59, 62.98, 75.23, 123.17, 125.64, 128.24, 128.74, 139.86, 146.14, 217.84, 223.43, 262.54; IR (neat) 2054 (w), 1972 (shoulder, vs), 1917 (vs), 1529 (s), 1450 (m), 1394 (w) cm^{-1}; mass spectrum, (mixture of rotamers), m/z (relative intensity) 395 M^+ (15), 367 (25), 283 (45), 255 (100), 237 (15), 220 (10), 188 (15), 170 (25), 160 (35); Calc. for $C_{18}H_{17}NO_6Cr$, FAB (3-NBA), m/z 395.0461, measured 395.0465.

4.37. Preparation of [trans-propenyl[(2R,1S)-phenylmethyl-2-aminoethanol]methylene] pentacarbonyltungsten (0) (87-E) and (87-Z)

Carbene complex **87** was prepared from the ammonium salt **82** (1.00 g, 2.14 mmol) according to the procedure above for the preparation of complex **86**. The product was purified by chromatograpy on silica gel with CH_2Cl_2:Et_2O:hexane (1:1:2) to give 0.63 g of complex **87-E** (56%, $R_f = 0.54$) and 0.16 g of complex **87-Z** (14%, $R_f = 0.46$) as yellow solids in 70% combined yield. Complex **87-E** was isomerized as described in the general procedure to give a 80:20 ratio of **87-Z** to **87-E**, respectively, in 85% combined yield after chromatography. The O*H* signal was not located by ^{1}H-NMR for either **87-E** or **87-Z**. Spectral data for **87-E**: m.p. 116–119°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.20 (d, 3H, $J = 6.6$ Hz), 2.01 (d, 3H, $J = 5.4$ Hz), 4.22 (dq, 1H, $J = 6.0$, 3.2 Hz), 4.88 (br s, 1H), 6.50–6.53 (m, 2H), 7.34–7.42 (m, 5H), 8.60 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.68, 19.48, 58.82, 75.45, 125.72, 126.04, 128.70, 128.90, 136.84, 147.02, 199.19, 203.20, 248.84; IR (neat) 3351 (w), 2061 (vs), 1968 (shoulder, vs), 1905 (vs), 1504 (s), 1452 (m) cm^{-1}. Spectral data

for **87-Z**: m.p. 82–85°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.21 (d, 3H, $J = 6.7$ Hz), 1.93 (d, 3H, $J = 6.5$ Hz), 4.60–4.62 (m, 2H), 5.89 (dq, 1H, $J = 15.0$, 6.7 Hz), 6.81 (d, 1H, $J = 15.2$ Hz), 7.34–7.42 (m, 5H), 8.90 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.13, 19.46, 58.82, 75.43, 125.72, 126.04, 128.82, 128.88, 139.83, 146.99, 198.38, 203.29, 242.70; IR (neat) 3280 (w), 2061 (vs), 1969 (shoulder, vs), 1909 (vs), 1534 (s), 1451 (m) cm^{-1}; mass spectrum (mixture of rotamers), m/z (relative intensity) 527 M^+ (20, ^{184}W), 499 (15), 443 (40), 415 (40), 387 (75), 267 (40), 117 (100); Calc. for $C_{18}H_{17}NO_6^{184}W$ (mixture of rotamers) m/z 527.0569, measured 527.0545.

4.38. Preparation of [trans-propenyl[(2R)-phenyl-2-aminoethanol]methylene] pentacarbonylchromium (0) (88-E) and (88-Z)

Carbene complex **88** was prepared from the ammonium salt **81** (0.69 g, 2.05 mmol) and (R)-(−)-phenylglycinol (0.28 g, 2.05 mmol) according to the procedure above for the preparation of complex **86**. The product was purified by chromatography on silica gel with CH_2Cl_2–Et_2O–hexane (1:1:2) to give 0.50 g of complex **88-E** (64%, $R_f = 0.33$) and 70 mg of complex **88-Z** (9%, $R_f = 0.21$) as orange oils in 73% combined yield. Complex **88-E** was isomerized as described in the general procedure to give a 75:25 ratio of **88-Z** to **88-E**, respectively, in 85% combined yield after chromatography. The O*H* signal was not located by ^{1}H-NMR for either **88-E** or **88-Z**. Spectral data for **88-E**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.85 (d, 3H, $J = 7.0$ Hz), 3.97 (br d, 1H, $J = 10.4$ Hz), 4.06 (br d, $J = 10.1$ Hz, 1H), 4.97–5.00 (m, 1H), 6.24 (dq, 1H, $J = 15.2$, 6.7 Hz), 6.43 (d, 1H, $J = 14.3$ Hz), 7.25–7.43 (m, 5H), 9.32 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.84, 64.06, 66.34, 126.92, 127.16, 129.25, 130.10, 137.88, 141.34, 218.80, 223.92, 275.08; IR (neat), 3360 (w), 2053 (s), 1971 (shoulder, vs), 1913 (vs), 1496 (m), 1062 (w) cm^{-1}. Spectral data for **88-Z**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.87 (d, 3H, $J = 6.6$ Hz), 4.18–5.29 (m, 2H), 5.58–5.64 (m, 2H), 6.99 (d, 1H, $J = 15.6$, Hz), 7.34–7.44 (m, 5H), 9.35 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.56, 65.67, 66.31, 122.90, 126.50, 128.44, 129.15, 136.70, 146.41, 217.42, 223.35, 268.57; IR (neat) 3275 (w), 2054 (s), 1973 (shoulder, vs), 1910 (vs), 1521 (m), 1054 (w) cm^{-1}; mass spectrum, m/z (relative intensity) 381 M^+ (10), 353 (15), 269 (30), 241 (35), 137 (40), 104 (100), 77 (30); Calc. for $C_{17}H_{15}NO_6Cr$ m/z 381.0304, measured 381.0257.

4.39. Preparation of [trans-propenyl[(2R)-phenyl-2-aminoethanol]methylene] pentacarbonyltungsten (0) (89-E) and (89-Z)

Carbene complex **89** was prepared from the ammonium salt **82** (1.00 g, 2.14 mmol) and (R)-(−)-phenylglycinol (0.31 g, 2.25 mmol) according to the procedure above for the preparation of complex **86**. The product was purified by chromatography on silica gel with CH_2Cl_2–Et_2O–hexane (1:1:2) to give 0.72 g of complex **89-E** (57%, $R_f = 0.30$) and 87 mg of complex **89-Z** (14%, $R_f = 0.21$) as yellow–orange oils in 71% combined yield. Complex **88-E** was isomerized as described in the general procedure to give a 67:33 ratio of **89-Z** to **89-E**, respectively, in 87% combined yield after chromatography. The O*H* signal was not located by ^{1}H-NMR for either **89-E** or **89-Z**. Spectral data for **89-E**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.94 (d, 3H, $J = 6.8$ Hz), 4.00 (dd, 1H, $J = 11.5$, 4.5 Hz), 4.11 (dd, 1H, $J = 11.3$, 2.9 Hz), 4.96–4.99 (m, 1H), 6.39 (d, 1H, $J = 15.4$ Hz), 6.66 (dq, 1H, $J = 15.0$, 6.6 Hz), 7.28–7.47 (m, 5H), 9.16 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 19.08, 63.59, 65.59, 126.37, 128.61, 129.46, 136.95, 137.94, 147.10, 199.17, 202.96, 253.07; IR (neat), 3358 (w), 2061 (vs), 1968 (shoulder, m), 1909 (vs), 1497 (s), 1064 (m) cm^{-1}. Spectral data for **89-Z**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.89 (d, 3H, $J = 6.4$ Hz), 4.11–4.15 (m, 2H), 5.46–5.49 (m, 1H), 5.88 (dq, 1H, $J = 15.0$, 6.8 Hz), 6.92 (d, 1H, $J = 15.1$, Hz), 7.32–7.44 (m, 5H), 9.20 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.49, 65.39, 68.43, 126.70, 127.82, 128.51, 129.20, 136.72, 147.74, 198.12, 202.88, 249.07; IR (neat) 3400 (w), 2061 (s), 1970 (shoulder, m), 1908 (vs), 1531 (m) cm^{-1}; mass spectrum, m/z (relative intensity) 513 M^+ (75, ^{184}W), 485 (30), 446 (20), 429 (95), 390 (40), 375 (90), 304 (40), 269 (100), 242 (90); Calc. for $C_{17}H_{15}NO_6^{184}W$ m/z 513.0409, measured 513.0448.

4.40. Preparation of [trans-propenyl[(2S)-amino-3-phenyl-propanol]methylene] pentacarbonyltungsten (0) (90-E) and (90-Z)

Carbene complex **90** was prepared from the ammonium salt **82** (3.80 g, 8.31 mmol) and (S)-(−)-2-amino-3-phenyl-1-propanol (1.23 g, 8.31 mmol) according to the procedure above for the preparation of complex **86**. The product was purified by chromatography on silica gel with CH_2Cl_2–Et_2O–hexane (1:1:2, $R_f = 0.23$) to give 3.34 g of complexes **90-E** and **90-Z** as an inseparable mixture of rotamers (7:1, respectively) as a yellow solid in 78% combined yield. This 7:1 mixture of **90-E** and **90-Z** was isomerized as described in the general procedure to give a 80:20 ratio of **90-Z** to **90-E**, respectively, in 85% combined yield after chromatography. The O*H* signal was not located by ^{1}H-NMR for either **90-E** or **90-Z**. Spectral data for **90-E**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.94 (d, 3H, $J = 6.4$ Hz), 3.00 (dd, 1H, $J = 13.8$, 5.8 Hz), 3.08 (dd, 1H, $J = 13.9$, 5.9 Hz), 3.84–3.92 (m, 2H), 4.27–4.29 (m, 1H), 6.21 (d, 1H, $J = 15.1$ Hz), 6.33 (dq, 1H, $J = 15.1$, 6.7 Hz), 7.23–7.40

(m, 5H), 8.62 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.88, 37.31, 61.31, 63.27, 127.26, 128.98, 129.32, 129.44, 137.39, 143.21, 199.15, 203.08, 252.18. Spectral data for **90-Z**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.89 (d, 3H, $J = 6.7$ Hz), 3.13 (d, 2H, $J = 7.6$ Hz), 3.77–3.81 (m, 2H), 4.56–4.61 (m, 1H), 5.77 (dq, 1H, $J = 15.2$, 8.4 Hz), 6.79 (d, 1H, $J = 15.1$ Hz), 7.26–7.35 (m, 5H), 8.70 (br s, 1H, N*H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.58, 36.77, 62.44, 65.82, 127.28, 127.82, 128.99, 129.46, 135.97, 147.66, 198.41, 202.82, 246.40; IR (neat) 3400 (w), 2061 (s), 1970 (shoulder, m), 1908 (vs), 1531 (m) cm^{-1}; mass spectrum (mixture of rotamers), m/z (relative intensity) 527 M^+ (12, ^{184}W), 499 (10), 443 (20), 415 (20), 387 (40), 270 (27), 162 (20), 114 (100); Calc. for $C_{18}H_{17}NO_6^{182}W$ (mixture of rotamers) m/z 525.0539, measured 525.0529.

4.41. Preparation of [trans-propenyl[(4R)-methyl-(5S)-phenyl-2-oxazolidinone]methylene] tetracarbonylchromium (0) (**91**)

The oxazolidinone complex **91** was prepared as described in the general procedure with phosgene starting with 0.68 g (1.42 mmol) of **86-Z** to give 0.47 g of **91** after chromatography using EtOAc–hexane (1:1, $R_f =$ 0.43) in 70% yield as a deep purple solid. Spectral data for **91**: m.p. 68°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 0.97 (d, 3H, $J = 6.2$ Hz), 2.17 (d, 3H, $J = 5.9$ Hz), 4.81–4.83 (m, 1H), 6.17 (d, 1H, $J = 6.2$ Hz), 6.83 (d, 1H, $J = 14.0$ Hz), 7.26–7.49 (m, 5H), 7.85 (dq, 1H, $J = 13.8$, 6.9 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, -50°C) δ 16.08, 21.09, 57.55, 87.95, 126.78, 129.32, 129.77, 133.47, 138.26, 160.01, 163.56, 212.55, 216.68, 232.27, 233.34, 305.07; IR (neat) 2010 (vs), 1907 (s), 1835 (s), 1714 (w), 1388 (s), 1239 (s) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 393 M^+ (3), 337 (10), 309 (23), 281 (20), 255 (3), 219 (10), 186 (12), 154 (100); Calc. for $C_{18}H_{15}NO_6Cr$, FAB (3-NBA), m/z 393.0305, measured 393.0290.

4.42. Preparation of [trans-propenyl[(4R)-methyl-(5S)-phenyl-2-oxazolidinone]methylene] tetracarbonyltungsten (0) (**92**)

The oxazolidinone complex **92** was prepared as described in the general procedure starting with 0.75 g (1.42 mmol) of **87-Z** to give 0.51 g of **92** after chromatography using EtOAc–hexane (1:1, $R_f = 0.43$) in 68% yield as a deep purple solid. Spectral data for **92**: m.p. 78–81°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 1.07 (d, 3H, $J = 6.9$ Hz), 2.04 (d, 3H, $J = 6.7$ Hz), 4.91–4.94 (m, 1H), 6.33 (d, 1H, $J = 7.3$ Hz), 6.77 (d, 1H, $J = 14.6$ Hz), 7.35–7.53 (m, 5H), 8.23 (dq, 1H, $J = 14.1$, 7.0 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, -50°C) δ 16.01, 21.45, 57.97, 88.05, 126.88, 129.30, 129.83, 133.45, 139.48, 163.91, 168.34, 204.64, 204.88, 217.26, 220.60, 280.64; IR (neat) 2012 (vs), 1897 (vs), 1824 (vs), 1699 (s), 1393 (s), 1224 (s) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 525 M^+ (20, ^{184}W), 469 (10), 367 (45), 307 (35), 230 (40), 154 (100); Calc. for $C_{18}H_{15}NO_6^{182}W$, FAB (3-NBA), m/z 523.0382, measured 523.0372.

4.43. Preparation of [trans-propenyl[(4R)-phenyl-2-oxazolidinone]methylene] tetracarbonylchromium (0) (**93**)

The oxazolidinone complex **93** was prepared according to procedure starting with 200 mg (0.52 mmol) of **88-Z** to give 135 mg (68%) of **93** as a reddish–purple solid after purification by chromatography on silica gel with EtOAc–hexane (1:1, $R_f = 0.19$). Spectral data for **93**: m.p. 70°C (sub.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 1.96 (d, 3H, $J = 7.2$ Hz), 4.86 (dd, 1H, $J = 9.4$, 4.3 Hz), 5.27 (t, 1H, $J = 10.0$ Hz), 5.52 (dd, 1H, $J = 9.1$, 4.2 Hz), 6.62 (d, 1H, $J = 14.9$ Hz), 7.16–7.21 (m, 2H), 7.40–7.49 (m, 3H), 7.71 (dq, 1H, $J = 14.6$, 6.4 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, -50°C) δ 21.09, 60.19, 79.95, 126.71, 129.44, 130.07, 138.78, 139.26, 160.18, 216.55, 216.70, 231.98, 233.32, 305.30; IR (neat) 2011 (vs), 1909 (vs), 1835 (vs), 1713 (m), 1409 (m), 1205 (m) cm^{-1}.

4.44. Preparation of [trans-propenyl[(4R)-phenyl-2-oxazolidinone]methylene] tetracarbonyltungsten (0) (**94**)

The oxazolidinone complex **94** was prepared according to procedure from the Z-rotamer of **89** (140 mg, 0.27 mmol). The product was purified by rapid chromatography on silica gel with EtOAc–hexane (1:1, $R_f = 0.26$) to give **94** (89 mg, 68% yield) as a deep purple solid. The isolated chelated complex **94** was dissolved in a small amount of CH_2Cl_2 and was slowly crystallized by the dropwise addition of pentane. The deep-red micro-crystalline solid obtained though this procedure can be stored at -30°C under argon for weeks with only slight decomposition. However, this complex is best used immediately following its preparation. Spectral data for **94**: m.p. 73°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 1.74 (d, 3H, $J = 7.0$ Hz), 4.82 (dd, 1H, $J = 8.9$, 4.0 Hz), 5.36 (t, 1H, $J = 8.8$ Hz), 5.54 (dd, 1H, $J = 8.8$, 5.0 Hz), 6.49 (d, 1H, $J = 14.9$ Hz), 7.16 (d, 2H, $J = 7.1$ Hz), 7.42–7.49 (m, 3H), 8.05 (dq, 1H, $J = 14.4$, 7.1 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, -50°C) δ 21.47, 60.73, 79.91, 126.76, 129.63, 130.08, 138.08, 138.72, 140.18, 169.34, 204.32, 204.75, 216.98, 220.79, 280.78; IR (neat) 2013 (vs), 1898 (vs), 1824 (vs), 1698 (m), 1413 (m), 1217 (s) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 511 M^+ (35,^{184}W), 460 (20), 367 (5), 307 (75), 273 (5), 230 (5), 154 (100); Calc. for $C_{17}H_{13}NO_6^{(182)}W$, FAB (3-NBA), m/z 509.0226, measured 509.0214.

4.45. Preparation of [trans-propenyl[(4S)-methylphenyl-2-oxazolidinone]methylene] tetracarbonyltungsten (0) (**95**)

The oxazolidinone complex **95** was prepared as described in the general procedure starting with a 4:1 mixture(1.00 g, 1.89 mmol) of **90-Z** to **90-E**, respectively, to give 0.45 g of **95** after chromatography using EtOAc–hexane (1:1, $R_f = 0.26$) in 45% yield (based on starting amount of **90-Z**) as a deep purple solid. Spectral data for **95**: m.p. 58°C (dec.); ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 1.95 (d, 3H, $J = 6.4$ Hz), 3.05 (dd, 1H, $J = 10.9$, 3.0 Hz), 3.21 (dd, 1H, $J = 9.0$, 5.3 Hz), 4.81–4.93 (m, 3H), 6.72 (d, 1H, $J = 14.2$ Hz), 7.10–7.41 (m, 5H), 8.21 (dq, 1H, $J = 14.3$, 6.9 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, −50°C) δ 21.53, 29.78, 58.13, 75.89, 128.23, 129.49, 130.52, 134.66, 139.64, 164.05, 168.96, 204.54, 205.08, 217.06, 220.31, 281.00; IR (neat) 2011 (vs), 1896 (vs), 1825 (vs), 1700 (s), 1415 (s), 1349 (s), 1249 (s), 1222 (s) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 525 M^+ (35, ^{184}W), 460 (15), 367 (5), 307 (80), 273 (5), 230 (5), 154 (100); Calc. for $C_{18}H_{15}NO_6^{182}W$, FAB (3-NBA), m/z 523.0382, measured 523.0380.

4.46. Preparation of [1-cyclohexenyl[(2R)-phenyl-2-aminoethanol]methylene] pentacarbonylchromium (0) (**98-E**) and (**98-Z**)

4.46.1. Method C

A solution of **97** [31] (0.60–0.90 mmol) in 40 ml of CH_2Cl_2 was cooled to −78°C and transferred to a solution of 1.0 eq of (R)-(−)-2-phenyl glycinol in 20 ml of CH_2Cl_2 at −78°C. The reaction mixture was stirred at −78°C for 1 h, −40°C for 1h, and at 25°C for 1 h, and was closely monitored with TLC analysis (CH_2Cl_2, PMA). After the TLC analysis showed the complete consumption of the starting material, the reaction mixture was concentrated under reduced pressure, and the residue was chromatographed on a silica gel column (size: 1.5 × 30 cm, gradient eluent: 0–80% CH_2Cl_2 in hexane) to provide the desired amino complex **98** as a yellow oil in 50–60% yield with E:Z ratio ≥80:1. When the reaction was carried out in the presence 10 drops of Et_3N, the yield and ratio remained the same. When the reaction was carried out with **97** (0.20–1.1 mmol) in 2–3 ml THF at r.t., **98** was obtained in 79% yield with a E:Z ratio of 19:1. At −10°C, the yield was 80–84% and the ratio was 21:1. At −78°C, the yield was 91% and the ratio was ≥50:1. At −100°C, the yield was 90% and the ratio was ≥50:1. Spectral data for **98-E**: $R_f = 0.43$ (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 1.56 (m, 3H), 1.62 (t, 1H, $J = 5.8$ Hz), 1.81 (t, 1H, $J = 5.4$ Hz), 2.04 (m, 3H), 3.97 (m, 2H), 4.86 (m, 1H), 5.00 (m, 1H), 7.20 (d, 2H, $J = 8.2$ Hz), 7.30 (t, 1H, $J = 6.8$ Hz), 7.37 (t, 2H, $J = 7.3$ Hz), 9.41 (brs, 1H); ^{13}C-NMR ($CDCl_3$) δ 21.7, 21.8, 23.9, 25.8, 63.7, 65.7, 114.8, 126.2, 128.5, 129.3, 137.7, 147.5, 217.8, 223.1, 285.9; IR (neat) cm^{-1} 3345w, 2935w, 2885w, 2861w, 2053s, 1972s, 1914s, 1502m, 1456w, 1056w, 755w; mass spectrum (EI): m/z (relative intensity) 421 (3) M^+, 393 (16), 365 (4), 337 (8), 321 (1), 309 (48), 303 (1), 292 (1), 281 (100), 274 (2), 263 (4), 257 (2), 249 (23), 241 (6), 227 (44), 220 (7), 213 (16); m/e calc. for $C_{20}H_{19}CrNO_6$ 421.0617, measured 421.0619. Spectral data for **98-Z**: $R_f = 0.22$ (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 1.72 (m, 2H), 1.80 (m, 2H), 2.14 (m, 2H), 2.35 (m, 2H), 4.16 (m, 2H), 5.26 (m, 1H), 5.51 (m, 1H), 7.20 (d, 2H, $J = 8.2$ Hz), 7.29–7.43 (m, 3H), 9.20 (brs, 1H); ^{13}C-NMR (CD_2Cl_2) δ 22.2, 22.8, 25.0, 28.3, 66.2, 67.1, 117.5, 127.3, 128.9, 129.6, 137.6, 142.2, 218.3, 224.1, 285.8; IR (neat) cm^{-1} 3343w, 2935m, 2053s, 1972s, 1915s, 1506m, 1499m, 1456w, 1449w, 1437w, 1072w, 1060w, 1056w, 756w.

4.46.2. Method C

A solution of the ammonium salt **96** (187.7 mg, 0.50 mmol) was dissolved in 5 ml CH_2Cl_2 under an atmosphere of argon and cooled to −70°C. Freshly distilled acetyl bromide (one equivalent) was then added dropwise and the remaining solution was stirred for an additional 60 min. to give a deep red solution. A prechilled (at −100°C) solution of 68.6 mg of (−)-(1R)-1-phenyl-1-amino-2-hydroxyethane [(R)-(−)-2-phenyl glycinol] (0.50 mmol, 1.0 eq) in 2 ml of CH_2Cl_2 was added dropwise via a cannula to the acetoxy solution at −78°C. After stirring at −50°C for 3 h, the reaction mixture was concentrated under reduced pressure and chromatographed on a silica gel column (size: 1.5 × 30 cm, gradient eluent: 0–100% CH_2Cl_2 in hexane) to provide 72.5 mg of **98** (34%) as a yellow oil with a E:Z ratio of 13.0:1. When the reaction time was extended to 17 h instead of 3h, **98** was obtained in 26% yield with a E:Z ratio of 11.4:1.

4.46.3. Isomerizations of (**98-E**) to (**98-Z**)

A solution of **98** (E:Z 20–50:1) (0.12–0.43 mmol) and 1.0 eq of the base in THF (0.20 M in **98**) was deoxygenated using freeze-pump-thaw method (3 cycles, at −196/25°C), and was sealed under a blanket of argon at the end of the last cycle. The mixture was heated at 70°C for 24–72 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column (size: 1.5 × 30 cm, eluent: CH_2Cl_2) to provide the pure **98**. The ratios were determined from ^{1}H-NMR analysis. In the presence of DMAP, **98** was recovered in 44–51% yield with new E:Z ratios of 3.1–3.4:1. Also isolated was $Cr(CO)_5$-DMAP in 37–40% yield: yellow solid, decomposition at 106–108°C, $R_f = 0.90$ (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 2.99 (s, 6H), 6.31 (d, 2H, $J = 6.6$ Hz), 7.96 (d, 2H, $J = 6.6$ Hz); ^{13}C-NMR ($CDCl_3$) δ 39.2, 107.4, 153.9, 154.5, 214.8,

220.9; IR (neat) cm^{-1} 2922w, 2917w, 1916s, 807m; mass spectrum (EI): m/z (relative intensity) 314 (56) M^+, 286 (19), 281 (13), 270 (6), 258 (24), 253 (8), 243 (44), 229 (83), 218 (16), 211 (18), 202 (100), 192 (28), 187 (26). In the presence of DABCO at 38 h, the yield was 62% and the ratio was 3.5:1, and at 72h, the yield was 75% and the ratio was 5.0:1. In the presence of 4-pyrrolidine-pyridine at 48 h, the yield was 23% and the ratio was 1.96:1, and at 24 h, the yield was 68% and the ratio was 2.3:1.

*4.47. Preparation of [1-cyclohexenyl[(4R)-phenyl-2-oxazolidinone]methylene] tetracarbonylchromium (0) (**100**)*

The oxazolidinone complex **100** was prepared as described in the general procedure starting with 107.5 mg of **98** (0.255 mmol, E:Z 2.3:1) to give 17.7 mg of **100** (51% based on the amount of **98-Z** isomer) as a dark red film after chromatography on a silica gel column (size: 3 × 18cm, gradient eluent: 0–50% CH_2Cl_2–hexane). Spectral data for **100**: $R_f = 0.20$ (50% CH_2Cl_2–hexane); ^{1}H-NMR ($CDCl_3$) δ 1.12 (m, 1H), 1.33 (m, 1H), 1.42 (brt, 2H, $J = 5.2$ Hz), 2.02 (m, 2H), 2.12 (m, 1H), 2.56 (m, 1H), 4.70 (dd, 1H, $J = 4.6$, 9.1 Hz), 5.20 (t, 1H, $J = 9.0$ Hz), 5.29 (m, 1H), 5.51 (dd, 1H, $J = 4.6$, 8.8 Hz), 7.06 (d, 2H, $J = 7.5$ Hz), 7.20–7.46 (m, 3H); ^{13}C-NMR was not obtained due to the rapid decomposition in all deuterated solvents; IR (neat) cm^{-1} 2935w, 2931w, 2053s, 2017s, 1910s, 1848s, 1713m, 1408w, 1181m; mass spectrum (EI): m/z (relative intensity) 419 (7) M^+, 393 (2), 363 (3), 335 (8), 307 (76), 281 (40), 271 (47), 257 (100), 249 (5), 227 (10), 220 (13), 213 (6), 198 (20), 184 (21), 177 (7); m/z calc. for $C_{20}H_{17}CrNO_6$ 419.0461, measured 419.0457.When the E:Z ratio of the starting complex was 3.0:1, the yield of **100** was 64% (based on Z-isomer). When the ratio was > 20:1, only the chloroformate **99** was found in 30–68% yield. Spectral data for **99**: yellow oil, $R_f = 0.76$ (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 1.63 (m, 4H), 2.11 (m, 4H), 4.50 (dd, 1H, $J = 4.1$, 11.7 Hz), 4.65 (dd, 1H, $J = 2.6$, 11.7 Hz), 4.97 (brs, 1H), 5.29 (brt, 1H, $J = 5.0$ Hz), 7.21 (d, 2H, $J = 7.1$ Hz), 7.42 (m, 3H), 9.00 (brs, 1H); ^{13}C-NMR ($CDCl_3$) δ 21.7, 21.8, 23.9, 26.0, 61.3, 71.5, 115.6, 126.0, 129.4, 129.8, 134.8, 147.1, 198.2, 217.3, 224.7, 286.1; IR (neat) cm^{-1} 3342w, 2933w, 2054s, 1974s, 1919s, 1773m, 1497m, 1457w, 1139m; mass spectrum (EI): m/z (relative intensity) 483 (18) M^+, 455 (66), 399 (27), 381 (27), 371 (100), 354 (11), 343 (54), 335 (13), 318 (4), 307 (51), 292 (9), 281 (38); m/z calc. for $C_{21}H_{18}ClCrNO_7$ 483.0177, measured 483.0172.

*4.48. Preparation of [trans-propenyl[(4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidone]methylene] tetracarbonylchromium (0) (**101**)*

Complex **101** was prepared according to the procedure described above for complex **52** from the methyl complex **72** (715 mg, 1.88 mmol). The crude product was purified on a silica gel column and eluted with EtOAc/hexane (1:1, $R_f = 0.37$) to give 488 mg of **101** as a reddish–purple solid in 64% yield from **72**. Spectral data for **101**: m.p. 73–74°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.87 (d, 3H, $J = 6.7$ Hz), 1.90 (d, 3H, $J = 6.7$ Hz), 2.94 (s, 3H), 4.41 (br t, 1H, $J = 7.4$ Hz), 5.39 (d, 1H, $J = 8.4$ Hz), 6.49 (d, 1H, $J = 14.5$ Hz), 7.03 (br s, 2H), 7.36–7.38 (m, 3H), 7.58 (dq, 1H, $J = 14.4$, 7.3 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, −50°C) δ 14.65, 20.85, 28.55, 60.05, 62.21, 125.93, 129.32, 129.60, 136.37, 137.27, 159.08, 164.44, 213.81, 217.24, 231.48, 232.65, 296.31; IR (neat) 2003 (vs), 1886 (vs), 1819 (vs), 1708 (vs), 1358 (s), 1287 (s), 1225 (m) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 406 M^+ (20), 378 (10), 322 (100), 294 (55), 241 (22), 154 (70); Calc. for $C_{19}H_{18}N_2O_5Cr$, FAB (3-NBA), m/z 406.0621, measured 406.0617. Anal. Calc. for $C_{19}H_{18}N_2O_5Cr$: C, 56.16; H, 4.47; N, 6.89. Found: C, 56.52; H, 4.74; N, 7.00%.

*4.49. Preparation of [trans-propenyl[(4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidone]methylene] tetracarbonyltungsten (0) (**102**)*

Complex **102** was prepared according to the procedure described above for complex **52** from the methyl complex **73** (146 mg, 0.29 mmol). The product was purified on a silica gel column and eluted with CH_2Cl_2 ($R_f = 0.53$) to give 118 mg of **102** as a reddish–purple solid in 81% yield from **73**. Spectral data for **102**: m.p. 115°C (dec.): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.90 (d, 3H, $J = 6.8$ Hz), 1.80 (d, 3H, $J = 7.0$ Hz), 3.02 (s, 3H), 4.48–4.51 (m, 1H), 5.35 (d, 1H, $J = 8.9$ Hz), 6.35 (d, 1H, $J = 14.5$ Hz), 6.99 (br s, 2H), 7.33–7.38 (m, 3H), 7.83 (dq, 1H, $J = 14.3$, 7.0 Hz); ^{13}C-NMR (75 MHz, acetone-d_6, −50°C) δ 14.72, 21.08, 28.76, 60.06, 62.78, 126.05, 129.47, 129.57, 129.71, 135.94, 138.50, 163.72, 204.92, 205.75, 217.03, 220.18, 275.62; IR (neat) 2003 (vs), 1875 (vs), 1808 (vs), 1700 (s), 1360 (m), 1287 (m), 1228 (m) cm^{-1}; mass spectrum, FAB (3-NBA), m/z (relative intensity) 538 M^+ (10, ^{184}W), 510 (5), 482 (8), 460 (3), 426 (5), 307 (20), 154 (100); Calc. for $C_{19}H_{18}N_2O_5^{182}W$, FAB (3-NBA), m/z 536.0698, measured 536.0710.

*4.50. Preparation of [phenyl[(4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidinone]methylene] tetracarbonylchromium(0) (**106**)*

A 100 ml flask was charged with 400 mg (2.1 mmol) (4R,5S)-1,5-dimethyl-4-phenyl-2-imidazolidinone **70** and dissolved in 20 ml THF at −78°C. A solution of *n*-BuLi (2.5 M in hexane, 0.84 ml, 2.1 mmol) was

Table 3
Crystallographic data for **45**, **107**, **35** and **106**

(a) Crystal Parameters				
Compound	**45**	**107**	**35**	**106**
Empirical formula	$C_{14}H_{11}CrNO_6$	$C_{14}H_{15}CrNO_7$	$C_{11}H_{11}CrNO_6$	$C_{22}H_{18}CrN_2O_5$
Formula weight	341.24	361.3	305.21	442.38
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P21/c$	$P\bar{1}$	$P2_12_12_1$
a (Å)	7.9192(11)	16.928(3)	8.026(l)	9.3248(7)
b (Å)	8.4451(10)	8.447(l)	9.257(7)	13.1515(12)
c (Å)	12.185(2)	12.746(2)	10.538(l)	17.098(2)
α (°)	99.375(13)		70.082(9)	
β (°)	97.677(10)	105.45(l)	69.473(8)	
γ (°)	99.656(10)		70.298(8)	
V Å^3	781.7(2)	1756.8(6)	667.96(12)	2096.8(4)
Z	2	4	2	4
Crystal color	Yellow	Yellow–green	Yellow	Dark red
D_{calc}(g cm^{-3})	1.450	1.366	1.517	1.401
μ(Mo$-$K$_\alpha$), cm^{-1}	7.58	6.82	8.77	5.81
Temperature (K)	296	298	297	298
(b) Data Collection				
Diffractometer	Siemens P4			
Monochromator	graphite			
Radiation (Å)	Mo$-$K$_\alpha$($\lambda = 0.71073$)			
2θ scan range (°)	5–50	7-45	4-60	4-60
Reflections collected	3389	2900	3314	4324
Independent reflections	2745	2148	2644	4108
Standard/reflections	3/197	3/1 97	3/197	3/197
(c) Refinement [a]				
$R(F)$ %	4.01 [a]	7.89 [b]	3.82 [a]	5.05 [b]
$R(wF^2)$ %	11.06	9.98	11.69	10.47
Δ/δ (max)	0.03	0.00	0.03	0.04
$\Delta(\rho)$ eÅ^{-3}	0.28	0.53	0.41	0.35
N_o/N_v	14.7	6.4	15.3	15.1

[a] Quantity minimized $= \Sigma\, w\Delta_2$; $R = \Sigma\, \Delta/\Sigma\, (F_o)$; $R(w) = \Sigma\, w\Delta^{1/2}/\Sigma\, (F_o \cdot w^{1/2})$, $\Delta = |(F_o - F_c)|$
[b] Quantity minimized $= R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\, \Delta/\Sigma\, (F_o)$, $\Delta = |(F_o - F_c)|$

added via syringe, and the yellow solution of anion was stirred for 10 min. A solution of phenylmethoxy pentacarbonyl chromium(0) **40** [28] (624 mg, 2.0 mmol) in 20 ml THF was then added via cannula. The reaction was stirred for an additional 20 min at -78°C, then allowed to warm to r.t. while stirring for 15 h. The product was obtained by concentrating the solution to a black oil on the rotovap, then purifying the oil by flash chromatography on silica gel (CH_2Cl_2 eluent). The black band was collected and concentrated to a black powder. The powder was recrystallized from CH_2Cl_2–pentane to give the product as black needle-like crystals. The structure of this complex was confirmed by X-ray diffraction. Yield: 479 mg (54%). Spectral data for **106**: ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 0.83 (d, 3H, $J = 6.7$ Hz), 3.00 (s, 3H), 4.46 (quintet, 1H, $J = 6.9$ Hz), 5.35 (d, 1H, $J = 8.4$ Hz), 7.18–7.24 (m, 10H); ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 14.34, 28.15, 59.64, 62.34, 121.50, 127.09, 127.45, 127.98, 128.24, 128.36, 134.35, 146.72, 163.07, 215.35, 216.12, 230.45, 233.97, 316.08; IR (thin film on NaCl): 2007 (m), 1892 (s), 1833 (s), 1707 (m), 1351 (m), 1220 (w), 698 (w), 671 (w), 607 (w) cm^{-1}. Anal. Calc. for $C_{22}H_{18}N_2O_5Cr$: C, 59.72; H, 4.10; N, 6.33; Cr, 11.75. Found: C, 58.95; H, 4.21; N, 6.40; Cr, 12.59. m.p. 140°C (dec.); $R_f = 0.85$ (CH_2Cl_2), 0.15 (1:1:4 CH_2Cl_2:Et_2O:hexane); black needles.

5. Crystallograghic structural determination for compounds 45, 107 (acetate of 43), 35 and 106

Crystallographic data for **45**, **107**, **35** and **106** have been collected in Table 3. Crystals of **107** were very weakly diffracting which considerably reduced availability of data. Crystals were photographically characterized and those of **45** and **35** were found to be triclinic, those of **107** were monoclinic and those of **106** were orthorhombic. The two triclinic samples were shown to be centrosymmetric by the successful solution and refinement of the structure in $P\bar{1}$; the monoclinic and orthorhomibic space groups were uniquely determined from the systematic absences. No absorption corrections were performed as the transmission ratio was less than 1.15 in all cases. All non-hydrogen atoms

were anisotropically refined except for C(1) to C(5) in **107** to conserve data. Hydrogens atoms were treated as idealized contributions. Various versions of SHELXTL 4 and 5 were used in the solution and refinement (G. Sheldrick, Siemens XRD, Madison, WI).

6. Supplementary material

Crystallographic data for the atomic coordinates, thermal parameters, bond distances and bond angles has been deposited with the Cambridge Crystallographic Data Centre, CCDC. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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