Inorganica Chimica Acta 364 (2010) 205–219

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Origin of the regioselectivity in an intramolecular nucleophilic addition to arene chromium tricarbonyl complexes

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ARTICLE INFO

Article history:
Available online 4 August 2010

Dedicated to Arnold L. Rheingold

Keywords:
Arene chromium tricarbonyl
Aromatic nucleophilic addition
X-ray diffraction
Solid-state ^{13}C NMR spectroscopy
Solution ^{13}C NMR spectroscopy
Regioselectivity

ABSTRACT

The source of the regioselectivity in the intramolecular nucleophilic addition of nitrile-stabilized carbanions to arene chromium tricarbonyl complexes was investigated for seven different substitution patterns on the arenes. All of the arenes are 1,4-dioxygenated and the substitution varies in the oxygen substituent and in the substituents of the arene carbons (hydrogen and alkyl). The regioselectivity is correlated with the preferred conformations of the chromium tricarbonyl group which in turn was determined by solution and solid-state ^{13}C NMR spectroscopy, ^{1}H NMR spectroscopy in solution as well as X-ray diffraction. In the four complexes analyzed by X-ray diffraction and the three complexes analyzed by solid-state ^{13}C NMR spectroscopy, there was only one complex where it was found that the preferred conformation of the $-Cr(CO)_3$ is different in solution than it is in the solid-state.

1. Introduction

Two of the most important synthetically significant chromium (0)-mediated organic transformations were both first reported in the literature in 1975 [1,2]. Both of these reactions made use of organometallic compounds first synthesized in the laboratories of Fischer [3,4]. In early 1975, the Semmelhack group described the successful nucleophilic addition to benzene chromium tricarbonyl with net substitution for hydride by a wide variety of carbanions [1,5]. Latter the same year, Dötz reported that chromium Fischer carbene complexes would react with alkynes to give arene chromium tricarbonyl complexes in which the new arene ring was the result of a formal [3+2+1] cycloaddition involving the assembly of the alkyne, the carbene ligand and a carbon monoxide ligand [2,6]. Since an arene chromium tricarbonyl complex is a product of the reaction of a carbene complex with an alkyne, it seemed only natural that these two reactions should be combined.

This did not happen until 1992 when our group investigated the reaction of a number of chromium carbene complexes of the type **1** with 6-cyano-1-hexyne and other alkynes bearing carbanion stabilizing groups [7]. The coupling of these reactions could not have happened until methods were developed for the in situ protection of the phenol function in the phenol chromium tricarbonyl complexes that are the primary products of the reactions of Fischer carbene complexes with alkynes [8]. As indicated in Scheme 1, silyl triflates are one of the electrophiles that can be used to trap the phenol complexes to give hydroquinone silyl ether complexes of the type **3** in an efficient manner and in good yields. Treatment of these arene chromium tricarbonyl complexes with LDA leads to deprotonation alpha to the nitrile and subsequent addition of the resulting nitrile-stabilized carbanion to the coordinated benzene ring at either of the two carbons originally derived from the alkyne to give the η^5-dienyl complexes **4** and **5**. Oxidation of the η^5-chromium tricarbonyl anionic intermediates **4** and **5** leads to a mixture of the spirocyclic cyclohexadienone **6** and the tetrahydronaphthalene **7**. The distribution between these two products depends on the nature of the substituents R^1 and R^2 and the temperature of the reaction. In fact, in some cases the major product obtained at room temperature differs from that obtained at −78 °C indicating that the anionic η^5-dienyl complexes **4** and **5** can interconvert and that the kinetic and thermodynamic products are not the same.

We have previously reported the product distributions from the intramolecular nucleophilic addition reactions of the six arene chromium tricarbonyl complexes **8**–**14** and they are summarized in Scheme 2 [5]. Treatment of the complex **8** with 1.2 equivalents of LDA at −78 °C and then after 1.5 h quenching the reaction with

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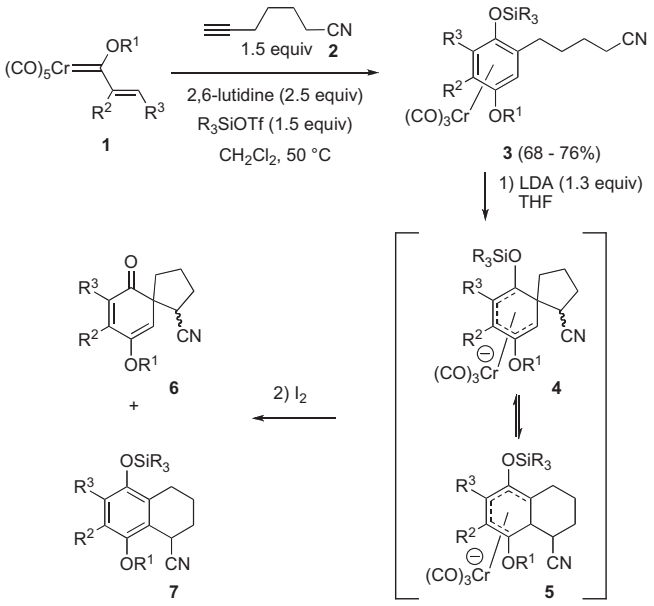
doi:10.1016/j.ica.2010.07.037



Scheme 1.

iodine at −78 °C gave to the spirocyclic dienone product **15** resulting from ipso-addition in 73% yield. On the other hand, if the reaction temperature was allowed to rise to 0 °C after the addition of LDA and the reaction quenched with iodine after an hour at 0 °C, the dienone **15** was not detected and instead the fused tetralin **16** resulting from vicinal addition was isolated in 67% yield. This was interpreted to mean that complex **4** (Scheme 1) is the kinetic η^5-dienyl complex and that it is completely converted to the thermodynamic η^5-dienyl complexes **5** when the temperature is raised to 0 °C.

The kinetic and thermodynamic products are less clear-cut for many of the other arene complexes. For the TBS substituted complex **9**, the spirocyclic product **17** was also formed in good yields at −78 °C; however, when the temperature was raised to 0 °C, the ^{1}H NMR spectrum of the reaction mixture indicated the absence of both of the products **17** and **18** and the presence of two other compounds (∼30% each), one of which was identified as the metal free arene derived from complex **9**. Interestingly, while the TBS complex **9** gave the spirocyclic product **17** at −78 °C, the TIPS complex **10** gave the isomeric vicinal substituted product **18** at −78 °C. The 6-methyl substituted arene complex **11** displayed a different behavior, giving the vicinal substituted product **20** whether the intramolecular nucleophilic addition was carried out at −78 °C or at 0 °C. It was thought the regiochemistry could be reversed for steric reasons by employing cyclohexyl substituted arene complex **12**, but instead the reaction gave dramatically reduced yields of the same regioisomer. The regioselectivity of the 6-methyl complex **11** was reversed at −78 °C for the 5-methyl complex **13** which gave the spirocyclic product **21** in 73% yield. Raising the temperature to 0 °C led to a switch in preference for the vicinal substituted product **22a** but only in very low yield. Unlike, the reactions of the arene complexes **9** and **10**, there was no significant effect of TBS versus TIPS groups in the complexes **13** and **14** since both led to the spirocyclic product **21** at −78 °C. The reasons for the regioselectivity outcomes for the reactions in Scheme 2 are not entirely readily evident and is the subject of the present work.

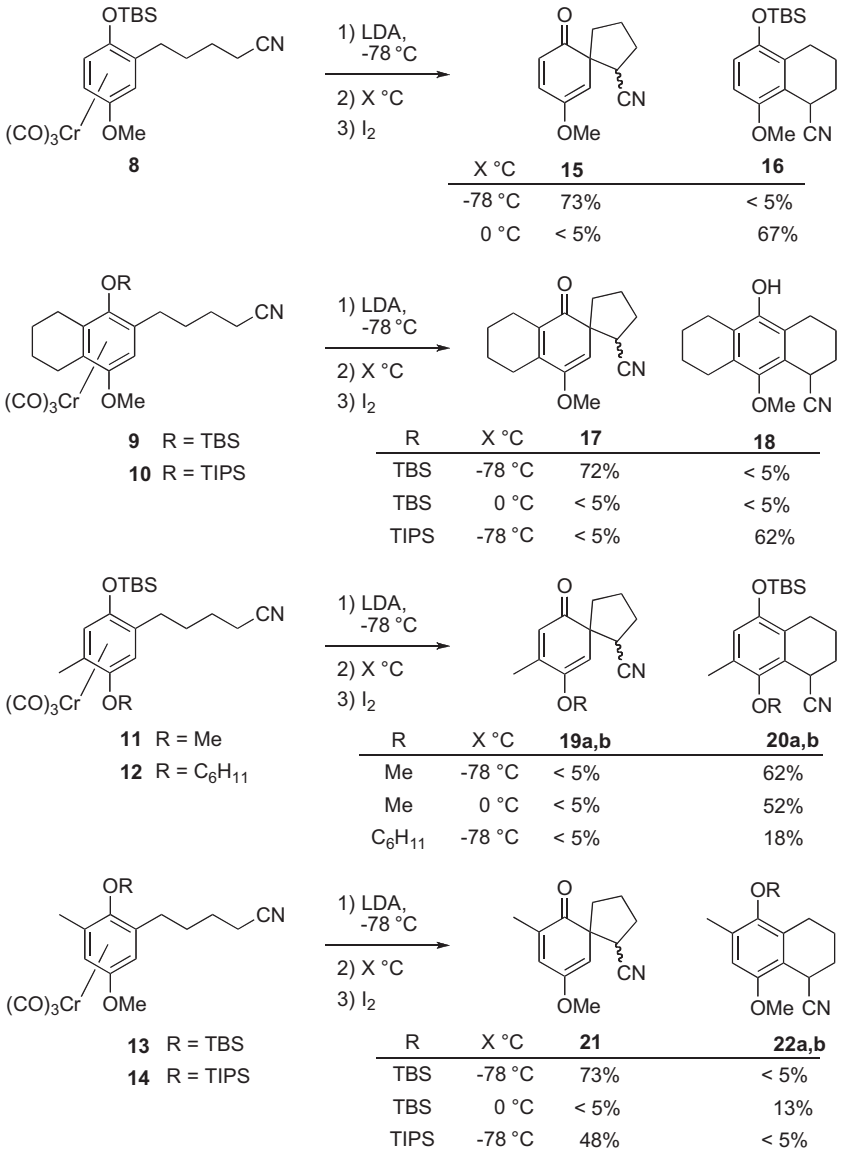
The regioselectivity seen in the addition of nucleophiles to substituted benzene chromium tricarbonyl has been extensively investigated in the past [5]. Factors which effect the position of nucleophilic substitution include the electronic nature and substitution pattern of ring substituents which can function as either strong resonance donors or acceptors [9], avoidance of adverse steric interactions [10], maximization of favorable HOMO–LUMO interactions [11], direction by total charge density [12] and activation of specific ring positions by a conformationally restricted $Cr(CO)_3$ fragment [13]. Complicating the picture even more is the fact that several types of carbanions add to various arene–$Cr(CO)_3$ complexes reversibly, so that products obtained can be the result of either kinetically-controlled attack or of equilibration to a thermodynamically favored position [9h,14]. The emerging consensus regarding the position of intermolecular kinetic attack by nucleophiles on $Cr(CO)_3$-complexed arenes is to see the metal fragment as exerting a major influence on the total charge distribution of the complexed arene which directs attack to carbons eclipsed by carbonyl ligands. Intramolecular nucleophilic additions of carbanions to arene chromium tricarbonyl complexes have not been examined to as great an extent [9b,15].

As has been shown by the work of Jackson et al. [13a,b], Uemura et al. [16], Ullenius and co-workers [9h] and Rose [13c], in systems in which the –$Cr(CO)_3$ fragment adopts a preferred configuration, carbons eclipsed by a CO ligand are preferentially attacked. Though still rotating, if the metal fragment adopted a preferred average position, it would lead to either the 1,3,5 or 2,4,6 carbons being relatively electron poor and, hence, relatively activated for nucleophilic attack. In our system this would translate to activation of either ipso or vicinal attack. "Thermodynamically-restricted rotation", as defined by Mislow and co-workers [17], has been used to explain the behavior of substituted arene–$Cr(CO)_3$ complexes in the past. Unlike "kinetically-restricted rotation" [18] where conformers of the same relative energy are impeded from interconverting by a high rotation barrier, "thermodynamically-restricted rotation" is used to describe the phenomenon in which conformers of different relative energy that are able to interconvert kinetically are present in unequal amounts, with the lower energy conformer predominating. In this case thermodynamically-restricted rotation would be caused by the electron-releasing ability of the alkyl substituents to stabilize the relatively positively-charged eclipsed ring carbons, inducing one of the two possible eclipsing conformations of the metal fragment to be of lower energy.

The eclipsed conformations for the silyl-protected complexes which differ only by the pattern of arene ring substitution are shown in Scheme 3. Since these complexes are 1,4-dioxygenated both the (1e) (carbons 1,3,5 eclipsed) and (4e) (carbon 2,4,6 eclipsed) conformations have one eclipsed carbon with an ether substituent. For this analysis, the difference in electron-donating ability between the methoxy and silyoxy groups is assumed to be insignificant. For the purposes of this discussion the numbering of the aromatic carbons in all of these complexes will be the same, with the aromatic carbon bearing the methoxy substituent numbered as "1" and the aromatic carbon bearing the tethered nitrile numbered "3".

In looking at the alkyl substituents, the conformations having more eclipsed carbons with alkyl, as opposed to hydrogen substituents, would be expected to be electronically more stable. This would predict conformations **9** (1e) would be preferred over **9** (4e), **13** (1e) would be preferred over **13** (4e), and **8** (1e) would be preferred over **8** (4e). In each of these cases the kinetic product of nucleophilic attack is the result of attack at C-3, or attack at the ring position which by this analysis is activated by being eclipsed with a CO ligand. Because of the para disposition of the ether and alkyl substituents, a prediction for complex **11** cannot be made.

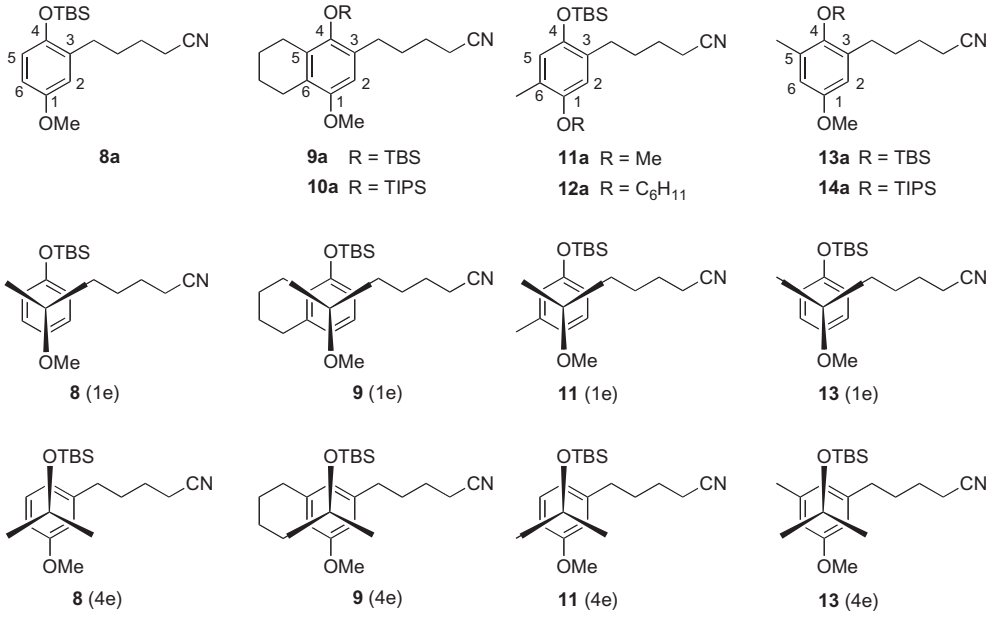
The goal of the present work is to interpret the regioselectivities observed in the reactions outlined in Scheme 2 in terms of the conformation of the chromium tricarbonyl groups in the arene



Scheme 2.

complexes **8**–**14**. The products in Scheme 2 obtained at −78 °C are considered kinetic addition products while those obtained at 0 °C are considered thermodynamic products. Kundig et al. has found that intermolecular addition reactions conducted and quenched below −50 °C, or which use HMPA as cosolvent, give kinetic addition products [14b]. The role of the HMPA is to coordinate to the cation and decrease the interaction between the cation and the carbanions-stabilizing group which is necessary for reversible addition. We did not perform the reactions in the presence of HMPA. In the instance of complex **8**, we did get a clean rearrangement to a thermodynamic product. Warming the reactions of complex **9** led to mixtures from which no addition products could be obtained. With complex **11** warming the reaction afforded the same major product, meaning either the kinetic and thermodynamic products are the same, as was found to be the case with anisole-$Cr(CO)_3$ and the anion of isobutyronitrile [14b] or there is a rapid conversion of a kinetic product to the thermodynamic addition product **20a** [9h]. Because of our results with complex **8** we consider the former possibility more likely. In no instance did we see any signs of formation of spirocycle **19**. Complex **13** also rearranged to a different product upon warming, although not as cleanly as complex **8**.

The conformations of the $Cr(CO)_3$ group in each complex have been determined by a combination of ^{13}C NMR spectroscopy in solution and X-ray structure determination in the solid-state and by the use of ^{13}C NMR spectroscopy in the solid-state to correlate the solution state with the solid-state. It is not often that solid-state ^{13}C NMR spectroscopy has been used to correlate solution and solid-state structures in arene chromium tricarbonyl complexes [18a] and to our knowledge it has not been used, in turn, to interpret regioselectivities in nucleophilic addition to these complexes. Solid-state X-ray structures could be determined for four complexes (**9**–**11** and **14**) and solid-state ^{13}C NMR spectra were obtained for three complexes (**9**, **11** and **14**). To determine the conformations of the $Cr(CO)_3$ in the various complexes by ^{13}C NMR spectroscopy it was necessary to assign all six of the arene carbon atoms in each complex (**8**–**14**, Scheme 2) and also to assign all six of the arene carbon atoms in each of the corresponding free arenes (**8a**–**14a**, Scheme 3). All of the free and complexed arenes examined in this work have six distinct aromatic resonances. The



Scheme 3.

assignment of each arene carbon in the $Cr(CO)_3$ complexes and the free arenes was done by a combination of introducing a ^{13}C label at position 4 and introducing a deuterium at position 2. The former was done be preparing carbene complexes of the type **1** (Scheme 1) with ^{13}C enriched carbon monoxide ligands. The benzannulation reaction with alkyne **2** gave arene complexes enriched in ^{13}C at carbon 4, since this carbon is derived from a carbon monoxide ligand [6]. Carbons C-3 and C-5 can be identified by ^{13}C–^{13}C coupling to C-4. Although when C-5 bears an alkyl substituent, C-3 and C-5 cannot be distinguished in this way, since the $-Cr(CO)_3$ fragment has C_{3v} symmetry, for this analysis, they do not need to be further assigned. Introduction of a deuteron at the 2-position was accomplished by performing the benzannulation reaction with alkyne **2** in which the alkenyl hydrogen had been replaced by deuterium and allowed the assignment of C-2 and C-6.

2. Experimental

2.1. General procedures, methods and materials

Flash column chromatography was performed on EM Science 330–400 mesh silica gel. Hexanes (from bulk) were distilled before use, while other solvents (HPLC grade) were used without further purification. Solvent systems were either ternary mixtures of diethyl ether, dichloromethane, and hexanes, which are referred to in this order (e.g., 1:1:4, diethyl ether, dichloromethane, and hexanes, v/v/v), mixtures of ethyl acetate and hexanes (v/v), or hexanes. Analytical TLC was performed on 3.5 × 7.5 cm Baker-flex IB2-F plastic plates with a mm silica gel layer. Low resolution mass spectra were recorded on a Finnigan 1015 instrument. High resolution mass spectra were recorded on a VG analytical 7070E mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville TN. Solid-state ^{13}C NMR spectra were recorded on a Bruker 300 AM instrument at Argonne National Laboratory with an external reference of tetrakis-trimethylsilylsilane.

Single crystals of compounds **11**, **9**, and **10** were grown at ambient temperatures from 50% saturated ether solutions layered with an equal volume of pentane. Single crystals of **14** were grown at ambient temperatures from a saturated methylene chloride solution layered with twice the volume of pentane. All crystallographic data reported in this paper were obtained nearly two decades ago using scintillation detectors. Various methods not applicable to modern CCD-detector data collections were employed to control the time required to obtain adequate quality data, including restrictions in 2θ to allow only the collection of observed data, minimal redundancy and variable-speed scan times. Alerts found in CHECKCIF output that would be considered serious today were necessary when these data were obtained. Nonetheless, all data reported in this paper are considered fully reliable by modern criteria.

2.2. Synthesis of arene chromium tricarbonyl complex *8* and the free arene *8a*

Carbene complex **1a** [19] (R^1 = Me, R^2 = H, R^3 = TBS) (0.3283 g, 0.872 mmol) and alkyne **2** (0.190 g, 1.77 mmol) were combined in 18 mL CH_2Cl_2 in a 50 mL flame dried pear-shaped single-necked flask in which the 14/20 joint was replaced by a high vacuum T-shaped Teflon value. The system was deoxygenated by the freeze–thaw method and after the third cycle, the flask was back-filled with argon at room temperature. The flask was sealed by closing the Teflon value and the flask was then heated at 65 °C for 11 h. The temperature of the oil bath was then raised to 73 °C and the reaction mixture was heated until it was clear and yellow (4 h). After removal of the solvents, the crude product was purified by chromatography on silica gel with 1:1:6 mixture of ether/methylene chloride/hexane to give arene–$Cr(CO)_3$ complex **8** (0.269 g, 0.590 mmol, 68%) as a yellow solid. Spectral data for **8**: (yellow prisms [ether/pentane] mp 84–85 °C, R_f = 0.24, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.32 (s, 3 H), 0.36 (s, 3 H), 0.98 (s, 9 H), 1.70–1.83 (m, 4 H), 2.32–2.38 (m, 1 H), 2.41 (t, 2 H, J = 6.4 Hz), 2.80–2.88 (m, 1 H), 3.63 (s, 3 H), 5.00 (dd, 1 H, J = 7.0, 2.6 Hz), 5.16 (d, 1 H, J = 7.0 Hz), 5.20 (d, 1 H, J = 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ −4.8, −4.5, 16.9, 17.9, 25.1, 25.3, 29.2, 29.8, 55.9, 75.8 (C-6), 82.1 (C-5), 83.2 (C-2), 104.3 (C-3), 119.2 (-CN), 130.0 (C-4), 137.6 (C-1), 234.1; IR (neat film) 2932w, 2250vw, 1955vs, 1866vs, 1472m, 1258m, 878w, 672w cm^{-1}; mass spectrum *m/z* (rel. intensity) 455 (M^+, 5), 371 (95), 356 (5), 314 (15), 262 (100). *Anal.* Calc. for $C_{21}H_{29}CrNO_5Si$: C, 55.37; H, 6.42; N, 3.07. Found: C, 55.50; H, 6.35; N, 2.89%.

*2.2.1. Assignment of the arene carbons of complex **8***

Heating a CH_2Cl_2 solution of carbene complex **1a** at 65 °C for 24 h under 1 atmosphere of ^{13}CO led to complete decomposition of the carbene complex. Thus the carbon resonances were only tentatively assigned with the aid of analogy to the arene–$Cr(CO)_3$ complexes in which C-4 had been labeled. Assignment of the C-1, C-4, and C-3 resonances were straightforward. In all cases the resonance C-1 (*C*-OMe) is farther downfield than the one for C-4. The resonance for C-3 showed no NOE enhancement and is in the range characteristic of alkyl-substituted aromatic carbons of arene–$Cr(CO)_3$ complexes. Assignment of the Car-H resonances was less simple. The farthest upfield Car-H resonance, 75.8 ppm, was assigned to C-6, since this carbon in the free arene was calculated to have the highest upfield shift, situated *para* to an alkyl substituent. This would mean a $\Delta\delta$ on complexation of 35.7 ppm. It was considered unlikely that the carbon resonance at 111.5 ppm in the free arene would correspond to either of the other Car-H resonances (82.1, 83.2 ppm), since this would lead to a $\Delta\delta$ value of either 29.4 or 28.3 ppm, values well outside the range (32.8–35.1 ppm) seen for the other Car-H $\Delta\delta$ values of the fully assigned complexes **9**–**14**.

The tentative assignment of the C-2 and C-5 resonances is based on the following analysis. The resonances of arene–$Cr(CO)_3$ complex **8** at 82.1 and 83.2 ppm correspond to the resonances of free arene **8a** at 115.7 and 118.9. The resonance at 82.1 ppm is assigned to correspond to that at 115.7 ppm, while that at 83.2 ppm corresponds to that at 118.9 ppm, since this gives $\Delta\delta$ values of 33.6 and 35.7 ppm. The opposite correlation would give $\Delta\delta$ values of 36.8 and 32.5 ppm. The first value is well outside the established range (32.8–35.1 ppm). The assignment of C-2 and C-5 then simplifies to which pair of resonances, [82.1/115.7, $\Delta\delta$ = 33.6 ppm] and [83.2/118.9, $\Delta\delta$ = 35.7 ppm], belongs to C-2 and which to C-5. Simple calculations based on substituent effects [20] on the uncomplexed arene **8a** predicts the C-2 resonance at 114.6 ppm and the C-5 resonance at 115.1 ppm due to a slight upfield shift of C-2 versus C-5 since it is *ortho* to a straight-chain alkyl substituent. This would suggest assigning the more upfield resonances to C-2. However, C-2 and C-6 are related by symmetry to the C3v symmetric metal fragment; the largest difference in a single complex for the C-2 and C-6 $\Delta\delta$ values is 1.4 ppm ($\Delta\delta$ upon complexation = 34.5 and 33.1 for **14**). For **13** the difference in $\Delta\delta$ values for C-2 and C-6 is 0.5 ppm. If the assignment for C-2 is the resonances at 82.1 ppm (**8**) and 115.7 ppm (**8a**), the difference in the $\Delta\delta$ values for C-2 and C-6 would be 2.1 ppm. Assignment of C-2 as the other pair of resonances gives the same value of $\Delta\delta$ for both C-2 and C-6. The assignments of C-2, C-5, and C-6 are reasonable when compared to similar carbons in the fully assigned complexes, especially when looking at the values of $\Delta\delta$ upon complexation. The $\Delta\delta$ value for both C-2 and C-6 (35.7 ppm) is consistent with the values obtained for those carbons thought to be on-average staggered by the –$Cr(CO)_3$ fragment. For complexes **13** and **14**, the $\Delta\delta$ values C-2/6 are 35.1/34.6 and 34.5/33.1 ppm, respectively. In complex **9** the $\Delta\delta$ value for C-2 is 34.4 ppm, while in complex **11** it is 34.7 ppm for C-5. The $\Delta\delta$ value for C-5 (33.6 ppm) is also consistent with those of on-average eclipsed carbons (C-2 of **10**, 32.3 ppm; C-2 of **11**, 32.8 ppm). The ^{13}C NMR spectrum of complex **8** was also investigated at a number of temperatures down to −60 °C in CD_2Cl_2 and the data are presented in Table 1.

Table 1
Variable temperature ^{13}C NMR data for complex **8** (CD_2Cl_2).

Temp (°C)	CO	C-1	C-4	C-3	C-2	C-5	C-6
20	234.22	137.60	130.01	104.62	83.41	82.23	75.92
0	234.19	137.54	129.72	104.67	83.37	82.13	75.61
−25	234.11	137.44	129.29	104.73	83.29	82.03	75.17
−50	234.00	–	128.87	104.80	83.19	82.00	74.69
−60	234.00	137.26	128.71	104.83	83.14	82.00	74.51

*2.2.2. Synthesis of **8a** and the assignment of the arene carbons*

The arene **8a** was isolated as a minor component of a sequential benzannulation/nucleophilic addition reaction (yield not determined). Spectral data for **8a**: (colorless oil, R_f = 0.42, 20% EtOAc/hexanes) ^1H NMR ($CDCl_3$) δ 0.23 (s, 6 H), 1.02 (s, 9 H), 1.68–1.78 (m, 4 H), 2.34 (t, 2 H, J = 6.9 Hz), 2.60 (t, 2 H, J = 7.2 Hz), 3.75 (s, 3 H), 6.60 (dd, 1 H, J = 8.6, 3.0 Hz), 6.65 (d, 1 H, J = 2.8 Hz), 6.68 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ −4.2, 17.0, 18.1, 25.0, 25.8, 28.9, 29.8, 55.5, 111.5 (C-6), 115.7 (C-5), 118.9 (C-2), 119.5 (–CN), 132.6 (C-3), 147.3 (C-4), 153.7 (C-1); IR (neat film) 2248vw, 1498s, 1254m, 1222s cm^{-1}; mass spectrum *m/z* (rel. intensity) 319 (M^+, 95), 304 (40), 293 (10), 276 (5), 263 (100), 247 (15), 234 (90), 220 (45), 207 (40), 183 (95), 165 (80). HRMS calc for $C_{18}H_{29}NO_2Si$ *m/z* 319.1968, meas 319.2003. HRMS on M^+–CH_3 calc for $C_{17}H_{26}NO_2Si$ *m/z* 304.1733, meas 304.1758.

The aromatic carbon resonances were assigned through correlation with shifts calculated using additive substituent effects on carbons of mono-substituted benzenes [20] substituting the values of ethyl and methoxyl for the C-3 tether and the TBS-oxy group, respectively. The calculated values (observed resonance) are as follows: C-1, 152.2 (153.7); C-4, 151.7 (147.3); C-3, 130.7 (132.6); C-5, 115.1 (115.7), C-2, 114.6 (118.9), C-6, 112.5 (111.5). The rationale for assigning the C-2 and C-5 resonances is included in the discussion above of the assignments of the aromatic resonances of arene–$Cr(CO)_3$ complex **8**.

*2.3. Synthesis of arene chromium tricarbonyl complex **9** and the free arene **9a***

A solution of carbene complex **1b** (R^1 = Me, R^2,R^3 = –$(CH_2)_4$–) [21] (0.1213 g, 0.3839 mmol), alkyne **2** (0.062 g, 0.58 mmol), 2,6-lutidine (0.11 mL, 0.96 mmol), and TBSOTf (0.13 mL, 0.58 mmol) in 7.7 mL of CH_2Cl_2 was added to a 50 mL flame dried pear-shaped single-necked flask in which the 14/20 joint was replaced by a high vacuum T-shaped Teflon value. The system was deoxygenated by the freeze–thaw method and after the third cycle, the flask was back-filled with argon at room temperature. The flask was sealed by closing the Teflon value and the flask was then heated at 50 °C under argon for 23 h. After removal of the solvents, the crude product was purified by chromatography on silica gel with 1:1:4 mixture of ether/methylene chloride/hexane to give the arene–$Cr(CO)_3$ complex **9** (0.1403 g, 0.275 mmol, 72%). Spectral data for **9**: (yellow needles [ether], mp 119–120 °C, R_f = 0.30, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.37 (s, 3 H), 0.39 (s, 3 H), 1.01 (s, 9 H), 1.49–1.65 (m, 1 H), 1.69–1.82 (m, 6 H), 1.91–1.98 (m, 1 H), 2.28–2.32 (m, 1 H), 2.41 (t, 2 H, J = 7.0 Hz), 2.49–2.54 (m, 1 H), 2.69–2.80 (m, 4 H), 3.71 (s, 3 H), 4.86 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.24, −1.96, 17.18, 18.74, 21.08, 21.83, 23.71, 25.09, 25.15, 25.93, 29.55, 29.74, 55.90, 73.42 (C-2, *C*-ar-H), 98.87 (C-6), 102.37 (C-3), 106.09 (C-5), 119.19 (CN), 125.61 (C-4), 137.27 (C-1, *C*-ar-OMe), 234.97; IR (neat film) 2247vw, 1946s, 1857s, 1457m, 1429m, 1259m, 1091m cm^{-1}; mass spectrum *m/z* (rel. intensity) 509 (M^+, 10), 425 (45), 41 (10), 373 (15), 316 (100), 288 (10). *Anal.* Calc. for $C_{25}H_{35}CrNO_5Si$: C, 58.92; H, 6.92; N, 2.75. Found: C, 58.77; H, 7.00; N, 2.53%.

*2.3.1. Assignment of the arene carbons of complex **9***

The C-4 ^{13}C, ^2H-labeled arene–$Cr(CO)_3$ complex **9** was prepared by stirring carbene complex **1b** in a minimal amount of hexanes for 24 h at 50 °C under 1 atmosphere of 99% ^{13}CO. The benzannulation reaction was performed as described above for unlabeled complex **9** except that instead of blanketing the reaction with argon, after the final freeze–pump–thaw cycle the reaction vessel was charged

with 1 atmosphere of ^{13}C-labeled CO. In addition the alkenyl proton of the alkyne **2** had been replaced with a deuteron. After 25 h at 55 °C the labeled complex **9** was obtained in 57%. The signal at δ 125.61 was significantly enhanced and was assigned as the resonance for *C*ar -OTBS (C-4). The signal at 137.27 was assigned as *C*-ar-OMe (C-1). The signal at 73.42 was assigned as that for C-2 and this was confirmed when in the ^{2}H labeled complex the intensity of the signal at 73.42 was nearly eliminated. This was further confirmed by a gHMQC experiment in which coupling was established between the proton singlet at 4.86 and the carbon at 73.4 The aromatic signals at 106.09 and 102.37 were surrounded by doublets (J = 57 and 58 Hz, respectively) resulting from ^{13}C to ^{13}C coupling, indicating these were the resonances for C-3 and C-5. The signal at 98.87 was free of any such doublet and was assigned as C-6. The carbons C-3 and C-5 were distinguished by the following experiments. A TOCSY 1D experiment involving irradiation at the triplet at 2.41 (next to nitrile) identified all of the protons in the four carbon aliphatic chain. One of these protons was not overlapped with the others (m, 2.28–2.32) and a gHMBC experiment revealed that this proton is coupled to C-3 but not C-5. The ^{13}C NMR spectrum of complex **9** was also investigated at a number of temperatures down to −60 °C in CD_2Cl_2 and the data are presented in Table 2. Six signals were identified in the aromatic region of the solid-state ^{13}C NMR spectrum that correlated well with the chemical shifts in solution. The assignments made for these carbons are: C-1 (138.6), C-4 (125.4), C-5 (107.3), C-3 (105.2), C-6 (101.1), C-2 (75.7).

2.3.2. Synthesis of ***9a*** and the assignment of the arene carbons

Iodine (5 equiv) was added as a solid to a stirred solution of labeled arene–$Cr(CO)_3$ complex **9** in 10 mL THF under air at rt. TLC showed a clean conversion to the desired free arene. After 1 h, the mixture was washed with 10% $Na_2S_2O_3$ and dried with brine and $MgSO_4$. Chromatography (20% EtOAc/hexanes) through a short silica gel column afforded arene **9a**. Spectral data for **9a**: (pale yellow solid, mp 57–60 °C, R_f = 0.48, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 6 H), 1.02 (s, 9 H), 1.65–1.72 (m, 8 H), 2.33 (t, 2 H, J = 6.9 Hz), 2.59–2.64 (m, 6 H), 3.77 (s, 3 H), 6.41 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.83, 17.07, 18.81, 22.35, 22.60, 23.30, 25.02, 25.62, 26.20, 29.37, 29.98, 55.45, 107.93 (C-2, *C* ar-H), 119.72 (CN), 124.73 (C-6), 127.73 (C-5), 129.90 (C-3), 144.80 (C-4), 151.74 (C-1, *C*-OMe); IR (neat film) 2246vw, 1464m, 1414w, 1230s, 1093m, 883m cm^{-1}; mass spectrum *m/z* (rel. intensity) 373 (M^+, 55), 316 (M-*t*-Bu, 100), 288 (10), 273 (5), 253 (5), 235 (5), 219 (5), 199 (10), 185 (5); HRMS calc for $C_{22}H_{35}NO_2Si$ *m/z* 373.2437, meas 373.2453.

The aromatic carbon signals were assigned on the basis of the following evidence: δ 144.80 (*C*-OTBS, increased signal intensity due to ^{13}C label), 151.74 (*C*-OMe, lack of increased signal intensity), 127.73 and 129.90 (C-3 and C-5, surrounded by ^{13}C–^{13}C doublets, J = 69 and 68 Hz, respectively), 107.93 (*C*ar-H, decrease in signal intensity in ^{2}H-labeled compound), 124.73 (C-6, lack of ^{13}C–^{13}C doublets). Carbons C-3 and C-5 were distinguished by the following experiments. A gCOSY experiment reveals that the triplet at 2.33 next to the nitrile is 3-bond coupled to a proton in the multiplet at 2.59–2.64. In a gHMBC experiment it was shown that this proton is coupled to C3 and the nitrile carbon.

Table 2
Variable temperature ^{13}C NMR data for complex **9** (CD_2Cl_2).

Temp (°C)	CO	C-1	C-4	C-5	C-3	C-6	C-2
20	235.01	137.23	125.44	106.35	102.89	98.71	73.71
0	234.96	137.27	124.99	106.46	102.97	98.48	73.48
−25	234.91	137.29	124.31	106.56	103.05	–	73.16
−50	234.81	137.29	123.66	106.64	103.14	97.78	72.90
−60	234.78	137.27	123.40	106.66	103.15	97.67	72.80

2.4. Synthesis of arene chromium tricarbonyl complex ***10*** and the free arene ***10a***

A solution of carbene complex **1b** (R^1 = Me, R^2, R^3 = –$(CH_2)_4$–) [21] (0.204 g, 0.647 mmol), alkyne **2** (0.133 g, 1.24 mmol), 2,6-lutidine (0.19 mL, 1.62 mmol), and TIPSOTf (0.26 mL, 0.97 mmol) in 13 mL of CH_2Cl_2 was added to a 50 mL flame dried pear-shaped single-necked flask in which the 14/20 joint was replaced by a high vacuum T-shaped Teflon value. The system was deoxygenated by the freeze–thaw method and after the third cycle, the flask was back-filled with argon at room temperature. The flask was sealed by closing the Teflon value and the flask was then heated at 50 °C under argon for 23 h. After removal of the solvents, the crude product was purified by chromatography on silica gel with 1:1:4 mixture of ether/methylene chloride/hexane to give after crystallization the arene–$Cr(CO)_3$ complex **10** (0.257 g, 0.466 mmol, 72%). Spectral data for **10**: (fine yellow needles [ether/pentane], mp 135–136 °C, R_f = 0.28, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 18 H, J = 6.8 Hz), 1.22–1.30 (m, 3 H), 1.55–1.68 (m, 1 H), 1.78–1.98 (m, 7 H), 2.44–2.51 (m, 2 H), 2.57–2.67 (m, 4 H), 2.73–2.78 (m, 1 H), 2.92 (dt, 1 H, J = 16.4, 5.4 Hz), 3.67 (s, 3 H), 5.11 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 17.1, 18.03, 18.06, 21.3, 21.6, 23.0, 25.61, 25.65, 28.3, 29.0, 56.3, 75.5 (C-2, *C*ar-H), 99.4 (C-3/5), 101.1 (C-6), 103.1 (C-3/5), 119.3 (CN), 132.4 (C-4), 134.2 (C-1, *C*-OMe), 235.0; IR (neat film) 2248w, 1943vs, 1901m, 1862vs, 1453m, 1422m cm^{-1}; mass spectrum *m/z* (rel. intensity) 551 (M^+, 22), 467 (100), 415 (45), 372 (85), 340 (15). *Anal.* Calc. for $C_{28}H_{41}CrNO_5Si$: C, 60.96; H, 7.49; N, 2.54. Found: C, 60.62; H, 7.53; N, 2.23%.

2.4.1. Assignment of the arene carbons of complex ***10***

The ^{13}C, ^{2}H-labeled arene–$Cr(CO)_3$ complex **10** was prepared by stirring carbene complex **1b** in a minimal amount of hexanes for 24 h at 50 °C under 1 atmosphere of 99% ^{13}C-labeled CO. The benzannulation reaction was conducted as above, except that instead of blanketing the reaction with argon, after the final freeze–pump–thaw cycle the reaction vessel was charged with 1 atmosphere of 99% ^{13}C-labeled CO. In addition the alkenyl proton had been replaced with a deuteron. After 25 h at 55 °C the ^{13}C, ^{2}H-labeled **10** was obtained in 56% yield. The signal at δ 132.4 was significantly enhanced and was assigned as the resonance for *C*ar-OTBS (C-4). The signal at 134.2 was assigned as *C*ar-OMe (C-1). The signal at 75.5 had already been assigned as that for C-2 on the basis of its greater intensity in the spectrum of the unlabeled complex. This assignment was confirmed when in the ^{2}H labeled complex the intensity of the signal at 75.5 was nearly eliminated. The aromatic signals at 103.1 and 99.4 were surrounded by doublets (J = 54 and 60 Hz, respectively) resulting from ^{13}C to ^{13}C coupling, indicating these were the resonances for C-3 and C-5. The signal at 101.1 was free of any such doublet and was assigned as C-6. The ^{13}C NMR spectrum of complex **10** was also investigated at a number of temperatures down to −60 °C in CD_2Cl_2 and the data are presented in Table 3.

2.4.2. Synthesis of ***10a*** and the assignment of the arene carbons

Iodine (0.36 g, 1.42 mmol, 7 equiv) was added as a solid to a solution of labeled arene–$Cr(CO)_3$ complex **10** in 3 mL THF stirred in air at rt. TLC showed formation of both the desired free arene and the desilylated uncomplexed phenol. After 45 min, the mixture was washed with 10% $Na_2S_2O_3$ and dried with brine and $MgSO_4$. Chromatography on silica gel (20% EtOAc/hexanes) afforded ^{13}C, ^{2}H-labeled arene **10a** (yield not determined). Spectral data for **10a:** (colorless oil, R_f = 0.54, 20% EtOAc/hexanes) ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 18 H), 1.25–1.35 (m, 3 H), 1.71–1.76 (m, 8 H), 2.35 (t, 2

Table 3
Variable temperature ^{13}C NMR data for complex **10** (CD_2Cl_2).

Temp (°C)	CO	C-1	C-4	C-3/5	C-6	C-3/5	C-2
23	235.7	134.9	133.0	103.9	101.6	100.6	76.5
0	235.6	134.7	132.8	103.9	101.4	100.4	76.2
−40	235.5	134.4	132.5	104.0	101.0	100.4	75.7
−60	235.4	134.3	132.3	104.0	100.7	100.3	75.5
−78	235.4	134.2	132.1	104.1	100.5	100.2	75.3
−90	235.3	134.1	132.0	104.1	100.3	100.2	75.1
−95	235.3	134.1	132.0	104.1	100.3	100.2	75.1

H, J = 6.8 Hz), 2.61–2.67 (m, 6 H), 3.76 (s, 3 H), 6.39 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.3, 17.5, 17.7, 22.3, 22.6, 23.4, 25.3, 25.4, 29.6, 30.3, 55.4, 107.8 (C-2, *C*ar-H), 119.7 (CN), 124.6 (C-6), 127.3 (C-3/5), 129.3 (C-3/5), 146.2 (C-4), 151.5 (C-1, *C*-OMe); IR (neat film) 2246vw, 1464m, 1230m, 883m cm^{-1}; mass spectrum *m/z* (rel. intensity) 415 (M^+, 90), 372 (M–*i*-Pr, 100), 344 (10), 330 (5), 316 (10), 302 (5), 289 (4), 275 (3), 260 (5), 247 (5), 233 (5), 217 (5), 186 (15); HRMS calc for $C_{25}H_{41}NO_2Si$ *m/z* 415.2907, meas 415.2935.

The aromatic carbon signals were assigned on the basis of the following evidence: δ 146.2 (*C*-OTBS, increased signal intensity), 151.6 (*C*-OMe, lack of increased signal intensity) 127.3 and 129.3 (C-3 and C-5, surrounded by ^{13}C–^{13}C doublets, J = 71 and 76 Hz, respectively), 107.8 (*C*ar-H, decrease in signal intensity in ^2H-labeled compound), 124.6 (C-6, lack of ^{13}C–^{13}C doublets).

2.5. Synthesis of arene chromium tricarbonyl complex **11** and the free arene **11a**

A solution of carbene complex **1c** (R^1, R^2 = Me, R^3 = H) [21,22] (0.1284 g, 0.465 mmol), alkyne **2** (0.075 g, 0.699 mmol), 2,6-lutidine (0.14 mL, 1.16 mmol), and TBSOTf (0.16 mL, 0.699 mmol) in 9.5 mL of CH_2Cl_2 was added to a 50 mL flame dried pear-shaped single-necked flask in which the 14/20 joint was replaced by a high vacuum T-shaped Teflon value. The system was deoxygenated by the freeze–thaw method and after the third cycle, the flask was back-filled with argon at room temperature. The flask was sealed by closing the Teflon value and the flask was then heated at 50 °C under argon for 19 h. After removal of the solvents, the crude product was purified by chromatography on silica gel with 1:1:4 mixture of ether/methylene chloride/hexane to give arene complex **11** (0.1596 g, 0.340 mmol, 73%) as a yellow solid. Spectral data for **11**: (mp 96–99 °C, R_f = 0.21, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.31 (s, 3 H), 0.37 (s, 3 H), 0.97 (s, 9 H), 1.67–1.78 (m, 4 H), 2.14 (s, 3 H), 2.20–2.24 (m, 1 H), 2.39 (t, 2 H, J = 6.0 Hz), 2.70–2.74 (m, 1 H), 3.69 (s, 3 H), 5.13 (s, 1 H), 5.25 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.5, −4.4, 15.8, 17.0, 18.0, 25.1, 25.3, 29.6, 29.7, 56.5, 79.3 (C-2, *C*ar-H), 86.3 (C-5), 97.8 (C-6), 100.3 (C-3), 119.3 (CN), 131.4 (C-4), 134.4 (C-1, *C*-OMe), 234.7; IR (neat film) 2248w, 1952s, 1868s, 1484m, 1371m, 1224m, 1019m cm^{-1}; mass spectrum *m/z* (relative intensity) 469 (M^+, 5), 400 (15), 385(45), 370 (8), 333 (15), 276 (100), 248 (15). *Anal.* Calc. for $C_{22}H_{31}CrNO_5Si$: C, 56.27; H, 6.65; N, 2.98. Found: C, 56.14; H, 6.33; N, 2.91%.

2.5.1. Assignment of the arene carbons of complex **11**

The ^{13}C, ^2H-labeled arene–$Cr(CO)_3$ complex **11** was prepared as follows: A solution of carbene complex **1c** (0.27 g, 1.0 mmol) in 5 mL CH_2Cl_2 was degassed by the freeze–pump–thaw method (three cycles). After the final cycle the reaction flask was charged with 1 atm 99% ^{13}CO, sealed, and heated for 18 h at 50 °C. The flask was then charged with alkyne **2** (0.075 g, 0.70 mmol) which had the alkenyl proton replaced with a deuteron, 2,6-lutidine (0.29 mL, 2.5 mmol), and TBS-triflate (0.35 mL, 1.5 mmol). After degassing the reaction flask was again charged with 1 atm of ^{13}CO and sealed. After 24 h at 50 °C normal workup and chromatography (20% EtOAc/hexanes) afforded the labeled complex **11** (yield not determined). The aromatic carbon resonances were assigned on the basis of the following evidence: 131.4 (C-4, *C*-OTBS, increased signal intensity), 134.4 (C-1, *C*-OMe, lack of increased signal intensity), 100.3 (C-3, surrounded by a ^{13}C–^{13}C doublet, J = 59 Hz), 86.3 (C-5, surrounded by a ^{13}C–^{13}C doublet, J = 53 Hz) 79.3 (C-2, *C*ar-H, decrease in signal intensity in ^2H-labeled compound), 97.8 (C-6, lack of ^{13}C–^{13}C doublet). The ^{13}C NMR spectrum of complex **11** was also investigated at a number of temperatures down to −60 °C in CD_2Cl_2 and the data are presented in Table 4. Six signals were identified in the aromatic region of the solid-state ^{13}C NMR spectrum that correlated well with the chemical shifts in solution. The assignments made for these carbons are: C-1 (137.7), C-4 (127.2), C-3 (108.1), C-6 (94.5), C-5 (90.5), C-2 (78.4).

2.5.2. Synthesis of **11a** and the assignment of the arene carbons

Iodine (0.40 g, 1.57 mmol, 5 equiv) was added as a solid to a solution of arene–$Cr(CO)_3$ complex **11** (0.147 g, 0.313 mmol) stirred in 2 mL THF under air. TLC indicated **11** had been consumed in less than 10 min. The mixture was diluted with ether, washed with 10% $Na_2S_2O_3$, 1% HCl, and brine, then dried over $MgSO_4$. Filtration through a short plug of 1:1 silica gel/Celite and removal of solvent afforded arene **11a** (0.084 g, 0.252 mmol, 80%) which was characterized without further purification. Spectral data for **11a**: (colorless oil, R_f = 0.49, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.22 (s, 6 H), 1.02 (s, 9 H), 1.68–1.72 (m, 4 H), 2.15 (s, 3 H), 2.34 (t, 2 H, J = 6.8 Hz), 2.59 (t, 2 H, J = 7.2 Hz), 3.77 (s, 3 H), 6.55 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, 15.9, 17.0, 18.1, 25.0, 25.8, 29.2, 29.7, 55.9, 112.1 (C-2, *C*ar-H), 119.7 (CN), 121.0 (C-5), 124.9 (C-6), 129.0 (C-3), 146.6 (C-4), 151.9 (C-1, *C*-OMe); IR (neat film) 2246vw, 1504m, 1464m, 1398m, 1259m, 1212s, 1030m cm^{-1}; mass spectrum *m/z* (relative intensity) 333 (M^+, 100), 318 (M−CH_3, 30), 277 (100), 248 (85), 233 (50), 219 (90), 207 (70), 195 (90), 183 (100), 163 (25), 151 (85), 138 (40), 124 (85); HRMS calc for $C_{19}H_{31}NO_2Si$ *m/z* 333.2124, meas 333.2134.

The ^{13}C, ^2H-labeled **11a** was obtained by stirring ^{13}C, ^2H-labeled **11** in $CHCl_3$ in air for 24 h. Filtration through 1:1 silica gel/Celite afforded a mixture of the desired free arene and the starting arene–$Cr(CO)_3$ complex. The aromatic carbons of the free arene could be assigned from the spectrum of this mixture based on the following evidence: δ 146.6 (C-4, *C*-OTBS, increased signal intensity), 151.9 (C-1, *C*-OMe, lack of increased signal intensity), 129.0 (C-3, C-H from unlabeled spectrum, surrounded by ^{13}C–^{13}C doublet, $J \sim$ 70 Hz), 112.1 (C-2, *C*ar-H, decrease in signal intensity in ^2H-labeled compound), 124.9 (C-6, lack of ^{13}C–^{13}C doublets), 121.0 (C-5, surrounded by ^{13}C–^{13}C doublet, $J \sim$ 70 Hz).

2.6. Synthesis of arene chromium tricarbonyl complex **12** and the free arene **12a**

A solution of carbene complex **1d** (R^1 = *c*-C_6H_{11}, R^2 = Me, R^3 = H) [23] (0.5319 g, 1.545 mmol), alkyne **2** (0.248 g, 2.32 mmol), 2,6-lutidine (0.45 mL, 3.9 mmol), and TBSOTf (0.53 mL, 2.3 mmol) in 30 mL of CH_2Cl_2 was added to a 100 mL flame dried pear-shaped single-necked flask in which the 14/20 joint was replaced by a high

Table 4
Variable temperature ^{13}C NMR data for complex **11** (CD_2Cl_2).

Temp (°C)	CO	C-1	C-4	C-3	C-6	C-5	C-2
20	234.80	134.45	131.45	100.66	97.95	86.49	79.59
0	234.80	134.32	131.22	100.57	97.77	86.44	79.39
−25	234.76	134.13	130.90	100.46	97.53	86.34	79.15
−50	234.71	133.93	130.55	100.33	97.26	86.25	78.92
−60	234.68	133.83	130.42	100.28	97.16	86.29	78.85

vacuum T-shaped Teflon value. The system was deoxygenated by the freeze–thaw method and after the third cycle, the flask was back-filled with argon at room temperature. The flask was sealed by closing the Teflon value and the flask was then heated at 50 °C under argon for 23 h. After removal of the solvents, the crude product was purified by chromatography on silica gel with 1:1:10 mixture of ether/methylene chloride/hexane followed by crystallization from ether/pentane to give arene complex **12** (0.6244 g, 1.161 mmol, 75%) as golden yellow prisms. Spectral data for **12**: (mp 87–89 °C, R_f = 0.46, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 3 H), 0.38 (s, 3 H), 0.98 (s, 9 H), 1.30–1.45 (m, 3 H), 1.51–1.61 (m, 3 H), 1.70–1.82 (m, 6 H), 1.88–1.94 (m, 1 H), 1.95–2.00 (m, 1 H), 2.15 (s, 3 H), 2.20–2.25 (m, 1 H), 2.40 (t, 2 H, J = 6.0 Hz), 2.68–2.75 (m, 1 H), 3.98–4.03 (m, 1 H), 5.15 (s, 1 H), 5.19 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.3, −4.2, 16.1, 17.1, 18.1, 23.3, 23.4, 25.27, 25.32, 25.5, 29.8, 29.9, 31.6, 32.0, 78.1, 81.5, 86.5, 98.0, 100.6, 119.2, 131.1, 133.4, 234.9; IR (neat film) 2250vw, 1948vs, 1869vs, 1480m, 1371m, 1222m, 841m, 674m cm^{-1}; mass spectrum *m/z* (rel. intensity) 537 (M^+, 10), 453(95), 401 (15), 370 (55), 344 (5), 313 (5), 262 (100), 231 (10). *Anal.* Calc. for $C_{27}H_{39}CrNO_5Si$: C, 60.31; H, 7.31; N, 2.60. Found: C, 59.94; H, 7.14; N, 2.38%.

2.6.1. Synthesis of the free arene *12a*

Iodine (0.32 g. 1.26 mmol, 4 equiv) was added as a solid to a solution of arene–$Cr(CO)_3$ complex **12** (0.166 g, 0.314 mmol) dissolved in 2 mL THF stirred at rt under air. After 10 min the reaction mixture was diluted with 2 mL $CHCl_3$. After 5 min TLC showed consumption of **12** with the formation of several additional compounds. The mixture was washed with 10% $Na_2S_2O_3$, brine, and dried with $MgSO_4$. Concentration and chromatography (1:1:10) afforded arene **12a** (0.032 g, 0.080 mmol, 26%). Spectral data for **12a**: (colorless oil, R_f = 0.64, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 6 H), 1.02 (s, 9 H), 1.32–1.41 (m, 3 H), 1.52–1.60 (m, 3 H), 1.65–1.82 (m, 6 H), 1.92–1.97 (m, 2 H), 2.17 (s, 3 H), 2.34 (t, 2 H, J = 6.7 Hz), 2.57 (t, 2 H, J = 6.9 Hz), 4.04–4.09 (m, 1 H), 6.55 (s, 1 H), 6.59 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.2, 16.2, 17.1, 18.2, 23.7, 25.0, 25.7, 25.8, 29.2, 29.6, 32.1, 76.7, 116.7, 119.7, 120.8, 126.8, 129.0, 146.9, 149.9; IR (neat film) 2246w, 1501m, 1402m, 1254w, 1208m, 1048w, 967m cm^{-1}; mass spectrum *m/z* (rel. intensity) 401 (M^+, 85), 386 (10), 371 (5), 344 (45), 333 (15), 318 (10), 276 (75), 262 (100), 248 (10), 234 (30), 219 (10), 207 (10), 193 (35), 181 (20), 165 (10), 147 (15); HRMS calc for $C_{24}H_{39}NO_2Si$ *m/z* 401.2750, meas 401.2767.

2.7. Synthesis of arene chromium tricarbonyl complex *13* and the free arene *13a*

A solution of carbene complex **1e** (R^1 = Me, R^2 = H, R^3 = Me) [24] (0.6419 g, 2.326 mmol), alkyne **2** (0.374 g, 3.49 mmol), 2,6-lutidine (0.68 mL, 5.82 mmol), and TBSOTf (0.80 mL, 3.49 mmol) in 25 mL of CH_2Cl_2 was added to a 100 mL flame dried pear-shaped single-necked flask in which the 14/20 joint was replaced by a high vacuum T-shaped Teflon value. The system was deoxygenated by the freeze–thaw method and after the third cycle, the flask was back-filled with argon at room temperature. The flask was sealed by closing the Teflon value and the flask was then heated at 65 °C under argon for 20 h. After removal of the solvents, the crude product was purified by chromatography on silica gel with 1:1:4 mixture of ether/methylene chloride/hexane followed by crystallization from ether/pentane to give the arene–$Cr(CO)_3$ complex **13** (0.7982 g, 1.70 mmol, 73%). Spectral data for **13**: (fine yellow needles [ether/pentane], mp 77–78 °C, R_f = 0.29, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 0.357 (s, 3 H), 0.362 (s, 3 H), 1.01 (s, 9 H), 1.73–1.89 (m, 4 H), 2.24 (s, 3 H), 2.31–2.39 (m, 1 H), 2.42 (t, 2 H, J = 5.9 Hz), 2.77–2.83 (m, 1 H), 3.67 (s, 3 H), 4.943 (s, 1 H), 4.945 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.9, −2.6, 17.1, 17.8, 18.6, 25.1, 25.8, 28.8, 29.9, 55.7, 78.0 (C-2/6), 78.8 (C-2/6), 102.1(C-3/5), 106.0 (C-3/5), 119.2 (CN), 126.4 (C-4), 139.2 (C-1, *C*-OMe), 234.4; IR (neat film) 2247w, 1955s, 1862s, 1546m, 1465s, 1264m, 1050m cm^{-1}; mass spectrum *m/z* (rel. intensity) 469 (M^+, 10), 385 (70), 370 (10), 328 (20), 276 (40). *Anal.* Calc. for $C_{22}H_{31}CrNO_5Si$: C, 56.27; H, 6.65; N, 2.98. Found: C, 56.35; H, 6.82; N, 2.92%. The aromatic carbon signals were assigned on the following evidence. C-1 and C-4 by analogy to the three ^{13}C-labeled complexes **11**, **9**, and **10** in which the C-1 resonance is always higher field than the C-4 resonance and C2/6 by the large signal intensity indicating C_{ar}–H.

2.7.1. Synthesis of the free arene *13a*

Iodine (0.43 g, 1.7 mmol, 5 equiv) was added as a solid to a stirred solution of arene–$Cr(CO)_3$ complex **13** (0.160 g, 0.341 mmol) in 2 mL THF under air. TLC indicated **13** had been consumed in less than 10 min with clean conversion to **13a**. The mixture was diluted with ether, washed with 10% $Na_2S_2O_3$, 1% HCl, and brine, then dried over $MgSO_4$. Filtration through a short plug of 1:1 silica gel/Celite and removal of solvent afforded arene **13a** (yield not determined) which was characterized without further purification. Spectral data for **13a**: (pale yellow oil, R_f = 0.48, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 6 H), 1.03 (s, 9 H), 1.62–1.74 (m, 4 H), 2.20 (s, 3 H), 2.32 (t, 2 H, J = 7.0 Hz), 2.60 (t, 2 H, J = 7.2 Hz), 3.74 (s, 3 H), 6.48 (d, 1 H, J = 3.0 Hz), 6.52 (d, 1 H, J = 3.1 Hz); ^{13}C NMR ($CDCl_3$) δ −3.2, 16.9, 18.1, 18.6, 24.8, 26.0, 29.0, 29.9, 55.3, 112.6 (C-2 or 6), 113.9 (C-2 or 6), 119.6, 129.4, 132.4, 145.4, 153.5; IR (neat film) 2246w, 1606w, 1482sh, 1472s, 1441sh, 1254sh, 1219s, 1066m cm^{-1}; mass spectrum *m/z* (rel. intensity) 333 (M^+, 60), 318 (15), 276 (100), 257 (5), 248 (50), 234 (5), 219 (85), 207 (20), 195 (25), 183 (85), 175 (20), 163 (10), 151 (85); HRMS calc for $C_{19}H_{31}NO_2Si$ *m/z* 333.2124, meas 333.2122.

2.8. Synthesis of arene chromium tricarbonyl complex *14* and the free arene *14a*

A solution of carbene complex **1e** (R^1 = Me, R^2 = H, R^3 = Me) [24] (0.709 g, 2.57 mmol), alkyne **2** (0.413 g, 3.85 mmol), 2,6-lutidine (0.75 mL, 6.42 mmol), and TIPSOTf (1.04 mL, 3.85 mmol) in 40 mL of CH_2Cl_2 was added to a 100 mL flame dried pear-shaped single-necked flask in which the 14/20 joint was replaced by a high vacuum T-shaped Teflon value. The system was deoxygenated by the freeze–thaw method and after the third cycle, the flask was back-filled with argon at room temperature. The flask was sealed by closing the Teflon value and the flask was then heated at 60 °C under argon for 25 h. After removal of the solvents, the crude product was purified by chromatography on silica gel with 1:1:4 mixture of ether/methylene chloride/hexane followed by crystallization from ether to give arene–$Cr(CO)_3$ complex **14** (0.899 g, 1.76 mmol, 69%) as yellow prisms. Spectral data for **14**: (mp 95–97 °C, R_f = 0.40, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.14 (d, 18 H, J = 7.0 Hz), 1.21–1.30 (m, 3 H), 1.80–1.91 (m, 4 H), 2.30 (s, 3 H), 2.41–2.51 (m, 2 H), 2.70 (t, 2 H, J = 6.0 Hz), 3.64 (s, 3 H), 5.02 (d, 1 H, J = 2.5 Hz), 5.10 (d, 1 H, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 14.24, 17.10, 17.93, 18.40, 25.54, 27.42, 28.88, 55.89, 78.62 (C-2), 79.36 (C-6), 99.06 (C-5), 104.36 (C-3), 119.33 (CN), 131.38 (C-4), 137.93 (C-1), 234.41; IR (neat film) 2248vw, 1952s, 1869sh, 1866s, 1546w, 1465m, 1424m, 1235m, 1050w, 882m cm^{-1}; mass spectrum *m/z* (rel. intensity) 511 (M^+, 5), 427 (60), 375 (20), 332 (100), 300 (10), 270 (5). The carbon at C-4 was assigned based on enhanced intensity in the ^{13}C labeled compound and C-3 and C-5 were identified from their coupling to C-4. The rest of the carbons were assigned based on a gHMBC experiment in which the methyl singlet at 2.30 was found to be coupled to C-4, C-5 and C-6, but not to C-1, C-2 or C-3. The ^{13}C NMR spectrum of complex **14** was also investigated at a number of temperatures down to −60 °C in

Table 5
Variable temperature ^{13}C NMR data for complex **14** (CD_2Cl_2).

Temp (°C)	CO	C-1	C-4	C-3	C-5	C-6	C-2
20	–	–	–	–	–	–	–
0	234.43	137.88	131.07	104.95	99.56	78.51	78.48
−25	234.35	137.80	130.73	105.06	99.64	78.67	78.22
−50	234.26	137.71	130.29	105.19	99.74	78.18	77.91
−60	234.22	137.70	130.25	105.26	99.78	77.99	77.99

CD_2Cl_2 and the data are presented in Table 5. Six signals were identified in the aromatic region of the solid-state ^{13}C NMR spectrum that correlated well with the chemical shifts in solution. The assignments made for these carbons are: C-1 (139.8), C-4 (136.6), C-3 (108.5), C-5 (100.2), C-6 (81.1), C-2 (77.0).

*2.8.1. Synthesis of the free arene **14a***

Iodine (0.32 g, 1.28 mmol, 4 equiv) was added as a solid to a solution of arene–$Cr(CO)_3$ complex **14** in 3 mL $CHCl_3$ stirred in air. TLC showed a fairly clean conversion to **14a**. After 15 min the mixture was washed with 10% $Na_2S_2O_3$, then dried with brine and $MgSO_4$. Concentration and chromatography (1:1:10) afforded arene **14a** (yield not determined) as a colorless solid. Spectral data for **14a**: (colorless solid, mp 69–71 °C, R_f = 0.51, 1:1:4) ^1H NMR ($CDCl_3$) δ 1.12 (d, 18 H, J = 7.4 Hz), 1.26–1.33 (m, 3 H), 1.68–1.78 (m, 4 H), 2.25 (s, 3 H), 2.34 (t, 2 H, J = 6.8 Hz), 2.63 (t, 2 H, J = 7.2 Hz), 3.74 (s, 3 H), 6.47 (d, 1 H, J = 2.8 Hz), 6.50 (d, 1 H, J = 2.9 Hz); ^{13}C NMR ($CDCl_3$) δ 14.26, 17.08, 17.99, 18.27, 25.17, 29.27, 30.26, 55.36, 112.41 (C-2), 113.83 (C-6), 119.60 (CN), 128.93 (C-5), 132.00 (C-3), 146.82 (C-4), 153.35 (C-1); IR (neat film) 2245w, 1594w, 1480m, 1466m, 1220s, 1069w, 994m cm^{-1}; mass spectrum *m/z* (rel. intensity) 375 (M^+, 60), 332 (M–*i*-Pr, 100), 304 (20), 290 (10), 276 (5), 262 (5), 246 (5), 234 (5), 219 (8), 207 (10), 193 (10), 179 (5), 166 (15); HRMS calc for $C_{22}H_{37}NO_2Si$ *m/z* 375.2594, meas 375.2566.

The carbon at C-4 was assigned based on enhanced intensity in the ^{13}C labeled compound and C-3 and C-5 were identified from their coupling to C-4. The rest of the carbons were assigned based on a gHMBC experiment in which the methyl singlet at 2.25 was found to be coupled to C-4, C-5 and C-6 with only weak coupling to C-3 and C-2. This was confirmed by gHMBC in that the triplet at 2.63 was coupled to the C-3, C-4 and C-2 but not C-6, C-5 or C-1.

3. Results and discussion

3.1. Correlation of carbon-^{13}NMR and position of kinetic attack

NMR spectra of kinetically-restricted rotational systems can show a set of resonances for each conformer present. Thermodynamically-restricted rotational systems show a single set of resonances which is a weighted average of the conformer population. The effect of –$Cr(CO)_3$ complexation to an arene is a large (20–35 ppm) upfield shift in the aromatic resonances. In systems where there is a preferred –$Cr(CO)_3$ conformation, those carbons that are staggered are shifted upfield (shielded) more than those that are eclipsed. This is consistent with the analysis of Albright [12a] in which the arene HOMO coefficients are larger at ring carbons staggered by the $Cr(CO)_3$ fragment. That the arene–$Cr(CO)_3$ complexes in this study are thermodynamically-restricted rotational systems and, hence, that the –$Cr(CO)_3$ fragment is activating either the *ipso* or vicinal position can be deduced from the ^{13}C NMR spectra of these complexes. This is done by comparing the difference ($\Delta\Delta\delta$) in magnitude of the upfield shift ($\Delta\delta$) in the various aromatic resonances upon complexation of the free arene to the metal fragment.

We chose to look at the differences in shifts between the complexed and uncomplexed arenes to compare arenes with different substitution patterns. Comparison of absolute chemical shift values of differently substituted arene–$Cr(CO)_3$ complexes could be complicated by substituent effects. Bodner and Todd [25] have demonstrated that resonance effects of ring substituents are nearly unchanged by –$Cr(CO)_3$ complexation, while inductive effects are only slightly altered, so differences between the spectra of the complexed and free arenes can be attributed as primarily resulting from the metal fragment. Since the oxygen substituents are *para* any inductive or resonance effects on other ring carbons should be offsetting. It is important to note that the *meta* carbons of toluene-$Cr(CO)_3$ are upfield shifted more than the methyl-substituted carbon (6.3 ppm, 19%), though the *ortho* and *para* carbons are shifted even farther upfield. This means that differences in the amount of upfield shift between similarly substituted 3,6 and 5,2 carbons can be assigned more reliably as the result of the preferred conformation of the metal fragment than it can be for dissimilarly substituted (methyl versus proton) pairs of ring carbons. Because of this, $\Delta\Delta\delta$ values obtained from dissimilarly substituted carbons are either placed in brackets or "corrected" by adjusting the C–ar–H resonance by 6 ppm.

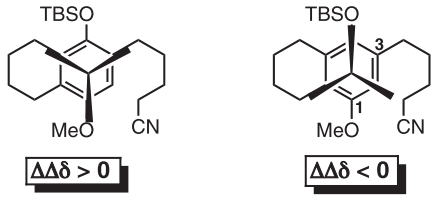
By comparing the differences that result from complexation in the relative positions of carbons *para* to one another, it should be possible to see if the 1,3,5 or 2,4,6 carbons are shifted farther upfield and deduce the average preferred conformation of the metal fragment. The difference in absolute chemical shift ($\Delta\delta$) for carbons *para* to one another is used, since for the complexes in this study carbons *para* to one another tend to be symmetrically substituted with ether, alkyl, or proton substituents, so $\Delta\Delta\delta$ values should be only minimally effected by whatever substituent effects there might be. An equation for obtaining $\Delta\Delta\delta$ values is shown in Eq. (1) [13c]. C_n represents C-1,3 or 5, while C_{n+3} represents a corresponding *para* carbon, C-4, 6 or 2, respectively.

$$\Delta\Delta\delta = \Delta\delta[\text{Arene—Cr(CO)}_3(\delta C_n - \delta C_{n+3})] - \Delta\delta[\text{Arene}(\delta C_n - \delta C_{n+3})] \quad (1)$$

An example of this type of analysis for arene–$Cr(CO)_3$ complex **9** is shown in Table 6. Values for $\Delta\delta$ were obtained from the assigned resonances of the ^{13}C NMR spectra obtained at ambient temperature in $CDCl_3$ for both arene–$Cr(CO)_3$ complex **9** and the corresponding free arene **9a**. As can be seen the $\Delta\delta$ values for the pairs of *para* carbons are generally larger in the –$Cr(CO)_3$ complex than they are in the uncomplexed arene. This means that, for example, C-4 is shifted upfield (shielded) in the arene–$Cr(CO)_3$ complex by more than C-1 is shifted upfield. This can be interpreted as evidence that, on average, C-4 is eclipsed less often by a CO ligand than C-1. This in turn would imply that C-2 would be eclipsed less often than C-3, leaving C-3 more activated for nucleophilic attack than C-2. The $\Delta\Delta\delta$ values for C-5/C-2 is a positive number, while C-3/C-6 is slightly negative. The average of the three $\Delta\Delta\delta$ values is +5.3. This implies that on average there is a preferred eclipsing of the 1,3,5 ring carbons. Even if the value $\Delta\Delta\delta$ C-5/C-2 is adjusted by subtracting the ca. 6 ppm upfield shift to be expected for the unsubstituted C-2, a value of ca. +3.3 is obtained. When the nucleophilic addition reactions are carried out at −78 °C, the only products of cyclization we have isolated are those where attack has occurred at C-3.

As shown in Table 7, similar analysis of the three arene–$Cr(CO)_3$ complexes which differ from **9** only in the pattern of alkyl substituents on the arene ring shows a correlation between the sign of the $\Delta\Delta\delta$ value and the products obtained after −78 °C nucleophilic addition. Complexes **13** and **8** have $\Delta\Delta\delta$ values which would correspond to the configuration of the metal fragment deduced from analysis of the conformers in Scheme 3. Again even after adjusting

Table 6
Analysis of $\Delta\Delta\delta$ values of arene-$Cr(CO)_3$ complex **9**/arene **9a**.



^{13}C NMR δ (ppm)					
Arene $Cr(CO)_3$ complex					
C-1	137.3	C-3	102.4	C-5	106.1
C-4	125.6	C-6	98.9	C-2	73.4
$\Delta\delta$	**+11.7**	**$\Delta\delta$**	**+3.5**	**$\Delta\delta$**	**+32.7**
Uncomplexed arene					
C-1	151.7	C-3	129.9	C-5	127.7
C-4	144.8	C-6	124.7	C-2	107.9
$\Delta\delta$	**+6.9**	**$\Delta\delta$**	**+5.2**	**$\Delta\delta$**	**+19.8**

$\Delta\Delta\delta$ = [Arene–$Cr(Co)_3\Delta\delta[C_{1,3,5}–C_{4,6,2}]$] – [Arene $\Delta\delta[C_{1,3,5}–C_{4,6,2}]$].

	C-1/C-4	C-3/C-6	C-5/C-2
ΔΔδ	**+4.8**	**–1.7**	**[+12.9]**[a]

[a] Uncorrected for difference in $\Delta\delta$ due to asymmetric H vs. alkyl substitution.

the $\Delta\Delta\delta$ values of dissimilarly substituted carbon pairs by ca. 6 ppm, these values remain greater than zero. Since, the labeled carbene complex necessary for the synthesis of ^{13}C-labeled **8** could not be prepared, the values indicated in Table 7 are based on tentative assignments of C-2 and C-5 (see Section 2).

Especially striking is the negative $\Delta\Delta\delta$ value for **11**, the only complex in this series which affords fused-ring products at −78 °C. As mentioned above we could see no *a priori* reason to predict a preferred eclipsing of C-2. Perhaps with the electronic effects of the ring substituents nearly equal, an adverse steric reaction between the C-3 alkyl chain and the –$Cr(CO)_3$ fragment leads to the preferred configuration indicated by these data. It has been shown that the $Cr(CO)_3$ fragment in *neo*-pentylbenzene preferentially eclipses the substituted ring position in solution similarly to toluene-$Cr(CO)_3$ which contrasts *tert*-butylbenzene-$Cr(CO)_3$ [26]. The *neo*-pentyl group is able to avoid interacting with the metal fragment by spending most of its time above the face of the arene opposite the metal. In **11** it is possible that the TBS-oxy-group behaves similarly, but that the relatively smaller C-3 alkyl tether in avoiding this large group is forced to interact with the metal fragment. That alkyl substituents forced *syn* to the metal fragment can effect its preferred configuration has been demonstrated in several systems [13,16,26].

The $\Delta\Delta\delta$ values for complexes **10**, **14**, and **12** (Table 8) show a strong correlation for complex **10**, a possible correlation with **14**, while values for the cyclohexyl complex **12** indicate no clearly preferred configuration for the metal fragment. It is interesting to note that the cyclohexyl complex gave the least efficient nucleophilic addition among those studied in this work. The contrast between the two TIPS-protected complexes helps to explain the difference in the observed position of kinetic attack. It is possible that for **10** ($\Delta\Delta\delta < 0$) the large TIPS-group, certain to be above the plane of the arene and above the face opposite the metal fragment, causes the alkyl tether to spend relatively more time on the same side as the –$Cr(CO)_3$ fragment, interfering with the CO ligands, and leading to a preference of the C-2 eclipsed conformer. This would explain the difference in reactivity of **10** as compared with the TBS-protected **9**.

In contrast, the other TIPS-protected complex **14** ($\Delta\Delta\delta > 0$) has no alkyl substituent at C-6. Despite this proposed effect on the C-3 alkyl tether, the C-3 eclipsed conformation could remain favored, since all three eclipsed carbons have electron-releasing substituents compared to the C-2 eclipsed conformation which has only one such stabilizing interaction. That the TIPS-oxy group itself does not completely control the preferred conformation is analogous to the fact that *neo*-pentyl benzene adopts a preferred configuration of the metal fragment eclipsing the substituted carbon [25]. Of course the actual reasons for the –$Cr(CO)_3$ fragment adopting the preferred configuration it does in each complex are not established. Nonetheless the correlation between the ^{13}C NMR data and the observed position of kinetic attack, pointing to selective activation of either the C-2 or C-3 position by the metal fragment, seems clear.

The population of conformers can be approximated through Eq. (2) [27]. In this equation PA stands for the percentage of the major conformer, θ_{max} represents the maximum change in chemical shift between an eclipsed and staggered carbon, and θ represents the $\Delta\Delta\delta$ value of the compound. This approximation assumes the presence in solution of only the two eclipsed conformers, the staggered pi-bond conformer being seen as a relatively short-lived intermediate. This also assumes a linear relationship between the conformational population and the weighted average in chemical shift.

Table 7
Correlation between $\Delta\Delta\delta$ values and position of kinetic attack.

ΔΔδ = [Arene-Cr(CO)$_3$ Δδ [$C_{1,3,5}$-$C_{4,6,2}$]] - [Arene Δδ [$C_{1,3,5}$-$C_{4,6,2}$]]

Complex	R^2	R^3	$\Delta\Delta\delta$			Position of kinetic attack
			(C1-C4)	(C3-C6)	(C5-C2)	
9	$-(CH_2)_4-$		+4.8	−1.7	[+12.9][b]	C-3
11	Me	H	−2.3	−1.6	−2.0	C-2
13	H	Me	+4.7	[+8.7][b]	[+7.3][b]	C-3
8	H	H	+1.2	[+7.4][a,b]	+2.1[a]	C-3

[a] Based on tentative assignment of C-2 and C-5.
[b] Uncorrected for difference in $\Delta\delta$ due to asymmetric H vs. alkyl substitution.

Table 8
Correlation between $\Delta\Delta\delta$ values and position of kinetic nucleophilic attack.

ΔΔδ = [Arene-Cr(CO)$_3$ Δδ ($C_{1,3,5}$-$C_{4,6,2}$)] - [Arene Δδ ($C_{1,3,5}$-$C_{4,6,2}$)]

Complex	R^1	R^2	R^3	R^4	ΔΔδ (ppm)			Observed kinetic attack
					(C1–C4)	(C3–C6)	(C5–C2)	
14	Me	H	Me	TIPS	+0.02	[+6.8][a]	[+4.0][a]	C-3
10	Me	–$(CH_2)_4$–		TIPS	−3.5	−2.3	[+4.4][a]	C-2
12	Cyclo-hexyl	Me	H	TBS	−0.7	+0.4	+0.9	C-2

[a] Uncorrected for difference in Δδ due to asymmetric H vs. alkyl substitution.

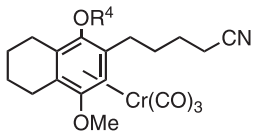
A value of 9 ppm for alkyl substituted carbons can be assigned to θ_{max} from the work of McGlinchy and co-workers [18a]. The $\Delta\Delta\delta$ values for the ambient temperature data for complexes **11**, **13**, **9**, **10**, and perhaps **14** can be approximated as falling in a range between 2 and 4 ppm. This would translate to approximate populations of conformers of between ca. 60:40 and 75:25.

$$PA = 50 + 50(\theta/\theta_{max}) \quad (2)$$

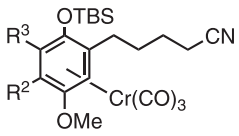
3.2. Low temperature carbon-^{13}NMR study of representative complexes

In complexes with extremely sterically congested arene ligands at low temperature, a splitting of the single ^{13}C resonance of the three CO ligands can become resolved due to rotation of the metal sufficiently hindered for the CO carbons to become magnetically inequivalent. It might also be anticipated that we might see changes in the $\Delta\Delta\delta$ values of the 1,3,5 versus 2,4,6 carbons if, upon cooling, the –Cr(CO)$_3$ fragment rotated through disfavored conformations less frequently. We investigated several of the arene–Cr(CO)$_3$ complexes over a temperature range from 23 to −60 °C in CD_2Cl_2 at 75 MHz. The differences in the ^{13}C resonances observed are listed in Table 9. The aryl resonances of these complexes at 20, 0, −25, −50, and −60 °C are included in the Section 2. In addition the uncomplexed arene **9a** was also examined over a similar temperature range as a control.

Table 9
Changes in chemical shift at low temperature for arene–Cr(CO)$_3$ complexes **8**–**11** and **14** (CD_2Cl_2).



9 (R^4 = TBS)
10 (R^4 = TIPS)



11 (R_2 = Me, R_3 = H)
8 (R_2 = H, R_3 = H)
14 (R_2 = H, R_3 = Me)

Compound	Temp (°C)	Δδ		
		C1–C4	C3–C6	C5–C2
9	20	11.8	4.2	32.6
9	−60	13.9	5.5	33.9
9a	20	7.0	5.3	–
9a	−50	7.2	5.9	–
8	20	7.6	28.7	−1.2
8	−60	8.6	30.3	−1.1
14	20	6.8	26.4	21.1
14	−60	7.5	27.3	22.0
11	20	3.0	2.7	6.9
11	−60	3.4	3.1	7.4
10	23	1.9	2.3	24.1
10	−60	2.0	3.3	24.8

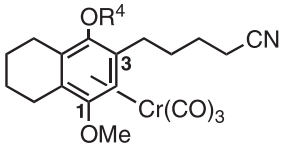
The data in Table 9 are consistent with the analysis presented above for three of the five complexes examined. Complexes **9**, **8**, and **14** all are attacked kinetically at C-3. The resonances for C-1, C-3, and C-5, upon cooling, are shifted downfield relative to the C-4, C-6, and C-2 resonances, respectively. Since staggered carbons are shielded relative to eclipsed carbons, these changes indicate an increase in the population of the C-1,3,5 eclipsed conformation at lower temperature. The amount of change in these resonances is generally greater than that seen for **9a** upon cooling, suggesting the effect is the result of the presence of the metal fragment. The data for complexes **11** and **10** show very little change in the aryl carbon resonances on cooling, suggesting little change in the population of conformers. These two complexes are both attacked kinetically at the C-2 position, though the reasons for the difference between these two complexes and those which are attacked at C-3 are not clear.

The low temperature data from Table 9 can be combined with the $\Delta\Delta\delta$ values from Tables 7 and 8 to give approximate populations of conformers at –60 °C. These approximate values (Table 10) are based on a simple average of the three $\Delta\Delta\delta$ values for each compound and are obtained directly from Eq. (2). The $\Delta\Delta\delta$ values for unsymmetrically substituted pairs of carbons have been corrected by subtracting 6 ppm to correct for the difference in upfield shift of proton versus alkyl substituted carbons. The slight (0.1 ppm) difference in $\Delta\Delta\delta$ values related to use of CD_2Cl_2 versus $CDCl_3$ has not been corrected for. Despite the fact that for **11** and **10** the low temperature spectra showed a shifting away from the C-2,4,6 eclipsed conformation, the data show that in both complexes this remains the more populated conformer. This is consistent with the observed position of nucleophilic attack under conditions favoring formation of kinetic addition products. The reason for the weighted average of the ring carbons for these two complexes to reflect an increase in the population of the C-1,3,5 conformation similar to the other complexes examined is not known.

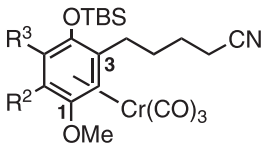
3.3. Correlation between proton NMR and position of kinetic attack

The hypothesis which correlates the ^{13}C NMR data, position of kinetic nucleophilic attack, and the Cr(CO)$_3$ conformation is

Table 10
Approximate population of conformers in solution of arene–$Cr(CO)_3$ complexes **8–11** and **14** (CD_2Cl_2).



9 (R^4 = TBS)
10 (R^4 = TIPS)



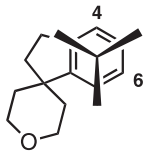
11 (R^2 = Me, R^3 = H)
8 (R^2 = H, R^3 = H)
14 (R^2 = H, R^3 = Me)

Compound	Temp (°C)	ΔΔδ[a]			Avg.	% C1,3,5 eclipsed
		C1–C4	C3–C6	C5–C2		
9	20	+4.9	+1.1	+6.7[b]	+3.4	69
9	−60	+7.0	−0.4	+8.0[b]	+4.9	78
8	20	+ 1.2	+1.6[b]	+2.0	+1.6	59
8	−60	+2.2	+3.2[b]	+2.1	+2.5	64
14	20	+0.3	+2.3[b]	−1.5[b]	+0.4	52
14	−60	+1.0	+3.2[b]	−0.6[b]	+1.2	57
11	20	−2.3	−1.4	−2.0	−1.9	39
11	−60	−1.9	−1.0	−1.5	−1.5	42
10	23	−3.4	−2.4	−1.4[b]	−2.4	37
10	−60	−3.3	−1.4	−0.7[b]	−1.8	40

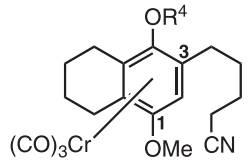
[a] Compared to 23 °C spectra of the corresponding free arene in $CDCl_3$.
[b] Corrected by subtracting 6 ppm for the additional shift of H vs. alkyl substitution.

supported by additional evidence found in a similar analysis of ^1H NMR data. The correlation between the difference in upfield shift ($\Delta\Delta\delta$) of aryl protons, position of nucleophilic attack, and preferred $Cr(CO)_3$ conformation was first proposed by Rose to explain the behavior of the spiroindane complex shown in Table 11 [13c]. As is shown the staggered aryl protons (H-4, H-6) are shifted upfield by an average of 24% more than the upfield shift of eclipsed aryl protons (H-5, H-7). In both complexes **9** and **10** the aryl proton is upfield-shifted slightly less than in the indane complex. This could be because aryl resonances for the uncomplexed indane (δ 7.05, s, 4H) begin so much farther downfield than the more electron-rich uncomplexed hydroquinones **9a** (δ 6.41) and **10a** (δ 6.39). Supporting the idea that in **10** C-2 is preferentially eclipsed, while in **9** it is preferentially staggered, the H-2 proton resonance for **9** is shifted upfield by 17% more than the H-2 resonance of **10**. Unlike the analysis of Rose, this analysis compares proton resonances from different molecules, but the differences in upfield shift do seem to approximate those seen in the spiroindane complex.

Table 11
^1H NMR analysis of $Cr(CO)_3$ conformation.



^1H NMR δ (ppm)



H-4 $\Delta\delta$ = 1.65	H-6 $\Delta\delta$ = 1.82	**9** R^4 = TBS, $\Delta\delta$ = 1.55
H-5 $\Delta\delta$ = 1.38	H-7 $\Delta\delta$ = 1.28	**10** R^4 = TIPS, $\Delta\delta$ = 1.28
$\Delta\Delta\delta$ = 0.27	$\Delta\Delta\delta$ = 0.54	$\Delta\Delta\delta$ = 0.27 (17%)

Average max upfield shift: 1.74 ppm.
Average $\Delta\Delta\delta$ = 0.41 (24%).

*3.4. Preferred conformations of the complexes **9**, **14**, **10**, and **11** in the solid-state*

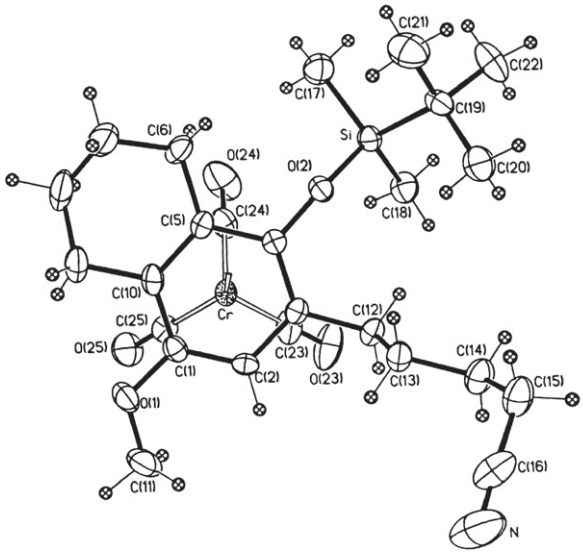
There have been many instances where the position of intermolecular nucleophilic attack has been correlated to the position of the –$Cr(CO)_3$ fragment in the solid-state structures of the arene–$Cr(CO)_3$ complexes. A danger associated with this type of analysis is the fact that the structure observed in the solid-state does not necessarily reflect the configuration of the same complex in solution. The $Cr(CO)_3$ fragment in arene–$Cr(CO)_3$ complexes is susceptible to being twisted from its preferred solution conformation by intermolecular packing forces. For example, in a study involving the determination of a number of crystal structures of arene–$Cr(CO)_3$ complexes with donor substituents, it was reported that the dihedral angles in anisole-$Cr(CO)_3$ and 1,4-dimethoxybenzene-$Cr(CO)_3$ were 8.8° and 18.8°, respectively [9i]. For this reason we were reluctant to obtain solid-state structures of any of these complexes, since information obtained regarding metal fragment geometry can be open to question.

A report from the McGlinchy laboratories showed a close correlation between the ^{13}C solution and solid-state spectra of pentaethylacetophenone-$Cr(CO)_3$ [18a]. We wondered if we would be able to see a similar correlation and be able to define a more secure relationship between the preferred conformation of the $Cr(CO)_3$ fragment in solution and in the solid-state. Single crystals of complexes **9**, **14**, **10**, and **11** were grown and solid-state structures were obtained by X-ray diffraction spectroscopy. In addition solid-state ^{13}C NMR spectra of ca. 120–150 mg each of single crystals of **9**, **14**, and **11** were obtained. The solid-state ^{13}C spectrum of **10** of sufficient quality could not be obtained.

ORTEP diagrams of complexes **9**, **14**, **10** and **11** and the relevant dihedral angles are presented in Figs. 1 and 2. For complex **9**, ^{13}C NMR analysis in solution (CD_2Cl_2) correctly predicts that attack should occur preferentially at C-3 with a $\Delta\Delta\delta$ of +4.9 at –60 °C (Table 10). The X-ray structure of complex **9** (Fig. 1) reveals that, although one of the CO ligands is not directly eclipsing the C-3 carbon, it comes close with a dihedral angle of 9.7°. The closest CO ligand to the C-2 carbon of complex **9** has a dihedral angle of 34.7°. Likewise ^{13}C NMR analysis in solution (CD_2Cl_2) correctly predicts that attack should occur preferentially in complex **14** at C-3 with a $\Delta\Delta\delta$ of +1.2 at –60 °C (Table 10). The X-ray structure of complex **14** (Fig. 1) is consistent with this prediction since one of the CO ligands has a dihedral of 16.1° with C-3 while another has a dihedral angle of 27.8° with C-2. In contrast to complexes **9** and **14**, the ^{13}C NMR data in solution predicts that attack in complex **10** with a $\Delta\Delta\delta$ of −1.8 at −60 °C (Table 10) should occur with C-2 and this is what is observed (Scheme 2). This is supported by the crystal structure of **10**, albeit not strongly, since one of the CO ligands have a smaller dihedral angle with C-2 (21.0°) than with C-3 (26.0°). The most interesting structure is of complex **11** where the conformation of the metal fragment in the solid-state as determined by X-ray diffraction is contrary to what was deduced in solution. The ^{13}C NMR spectrum of complex **11** in solution correctly predicts that attack should occur at C-2 since, as indicated in Table 10, $\Delta\Delta\delta$ is negative (−1.5 at −60 °C).

However, the X-ray structure of complex **11** (Fig. 2) shows that in the solid-state that a CO ligand is much closer to C-3 (dihedral angle 16.8°) than to the C-2 carbon (dihedral angle 31.2°).

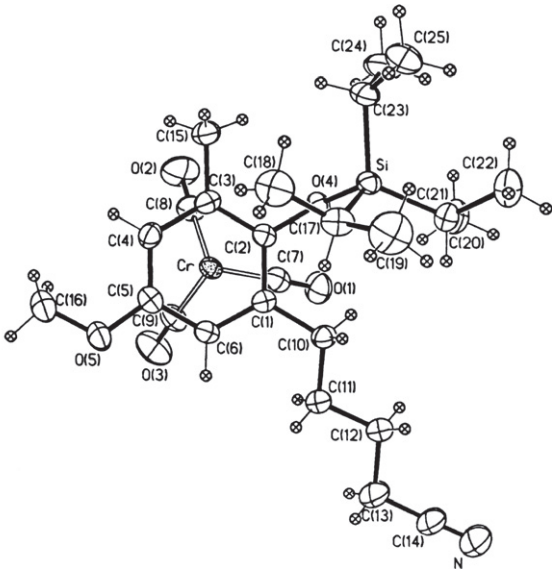
The results from the ^{13}C NMR spectra of complexes **9**, **11** and **14** in both the solution and solid-state are presented in Table 12. Complexes **9** and **14** (Fig. 1), while adopting somewhat staggered positions with respect to the C-2 and C-3 positions (numbering as above C1-OMe, C3-tethered nitrile) are still relatively close to eclipsing C3, the conformer deduced from their solution spectra to be more heavily populated. We expected that the solid-state ^{13}C NMR spectra of complexes **9** and **14** to be fairly similar to their



arene-$Cr(CO)_3$ complex **9**

C_{23}-Cr-C_3-C_{12}	9.7°	C_{23}-Cr-C_2-H	34.7°
C_{25}-Cr-C_1-O_1	9.0°	C_{25}-Cr-C_{10}-C_9	33.4°
C_{24}-Cr-C_5-C_6	10.8°	C_{24}-Cr-C_4-O_2	31.9°
Average	9.8°	Average	33.3°

Dihedral Angles (Crystallographic numbering)

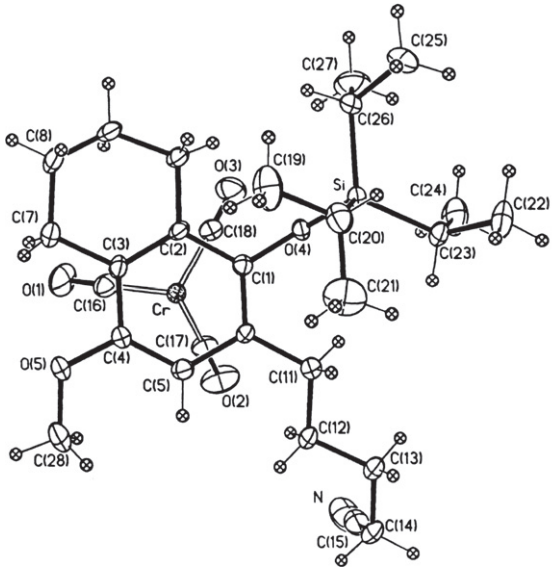


arene-$Cr(CO)_3$ complex **14**

C_7-Cr-C_1-C_{10}	16.1°	C_7-Cr-C_2-O_4	32.5°
C_9-Cr-C_5-O_5	10.5°	C_9-Cr-C_6-H	27.8°
C_8-Cr-C_3-C_{15}	14.2°	C_8-Cr-C_4-H	32.2°
Average	13.6°	Average	30.8°

Dihedral Angles (Crystallographic numbering)

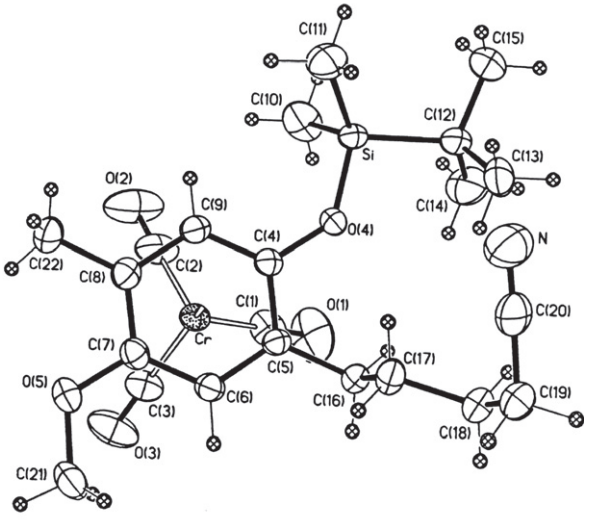
Fig. 1. ORTEP diagrams of arene–$Cr(CO)_3$ complexes **9** and **14**.



arene-$Cr(CO)_3$ complex **10**

C_{17}-Cr-C_5-H	21.0°	C_{17}-Cr-C_6-C_{11}	26.0°
C_{16}-Cr-C_3-C_7	16.3°	C_{16}-Cr-C_4-O_5	21.5°
C_{18}-Cr-C_1-O_4	22.2°	C_{18}-Cr-C_2-C_{10}	25.3°
Average	19.8°	Average	24.3°

Dihedral Angles (Crystallographic numbering)



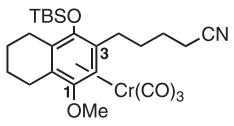
arene-$Cr(CO)_3$ complex **11**

C_1-Cr-C_5-C_{16}	16.8°	C_1-Cr-C_4-O_4	27.0°
C_3-Cr-C_7-O_5	19.5°	C_3-Cr-C_6-H	31.2°
C_2-Cr-C_9-H	16.3°	C_2-Cr-C_8-C_{22}	31.4°
Average	17.5°	Average	29.9°

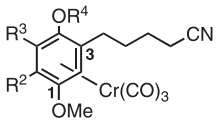
Dihedral Angles (Crystallographic numbering)

Fig. 2. ORTEP diagrams of arene–$Cr(CO)_3$ complexes **10** and **11**.

Table 12
Comparison of solid-state and solution ^{13}C NMR $\Delta\Delta\delta$ values for arene–$Cr(CO)_3$ complexes **11**, **9** and **14**.



9



11 (R^2 = Me, R^3 = H, R^4 = TBS)
14 (R^2 = H, R^3 = Me, R^4 = TIPS)

Compound	Conditions	$\Delta\Delta\delta$[a]			Avg.
		C1–C4	C3–C6	C5–C2	
9	20 °C, CD_2Cl_2	+4.9	−1.1	+6.7[b]	+3.4
9	−60 °C, CD_2Cl_2	+7.0	−0.4	+8.0[b]	+4.9
9	solid	+6.3	+1.0	+3.6[b]	+3.6
14	20 °C, CD_2Cl_2	+0.3	+2.3[b]	−1.5[b]	+0.4
14	−60 °C, CD_2Cl_2	+1.0	+3.2[b]	−0.6[b]	+1.2
14	Solid	+1.7	+3.3[b]	+0.6[b]	+1.9
11	20 °C, CD_2Cl_2	−2.3	−1.4	−2.0	−1.9
11	−60 °C, CD_2Cl_2	−1.9	−1.0	−1.5	−1.5
11	Solid	+5.2	+9.4	+3.2	+5.9

[a] Compared to 23 °C spectra of free arenes **9a**, **14a**, **11a** in $CDCl_3$.
[b] Corrected by subtracting 6 ppm for the additional shift of H vs. alkyl substitution.

low-temperature solution spectra and they are (Table 12). The X-ray structure of complex **11** indicated that a different conformation of the -$Cr(CO)_3$ is preferred in the solid-state than in the solution state as determined by ^{13}C NMR analysis in CD_2Cl_2. Thus it was anticipated that the solid-state spectrum of **11** would be significantly different from that taken in solution with $\Delta\Delta\delta$ values greater than zero. Indeed, this was found to be the case. The average $\Delta\Delta\delta$ value for the ^{13}C NMR spectrum of complex **11** in solution is −1.5, whereas, the average $\Delta\Delta\delta$ for the ^{13}C NMR spectrum of complex **11** in the solid-state is +5.9 (Table 12). Thus, the example of complex **11** indicates the shortcomings associated with predicting the position of nucleophilic attack from the solid structure of an arene chromium tricarbonyl complex.

3.5. Regioselectivity from additive electronic effects

The selectivity of kinetic nucleophilic attack seen with several of the complexes discussed above was very good. The intramolecular nucleophilic addition for complexes **11**, **13**, **9**, **10**, and **8** was carried out at −78 °C so that the minor addition product was not seen. Only with complex **14** was a fraction isolated which could have contained a significant amount (12–15%) of a minor addition product, which would have a selectivity of ca. 3:1. With the other complexes selectivity was at least 12:1 (60%:5%) in favor of the main product. This type of selectivity implies a difference in free energy between the transition states ($\Delta\Delta G^*$) leading to the major and minor products of at least 1.5–2.0 kcal/mol. The conformational preferences indicated from the spectral data, primarily the result of electronic effects do not seem sufficiently large to be the only factor controlling the position of kinetic attack. The difference in the ground state energy of the two eclipsed conformers is probably greater than 0.5 kcal/mol, but less than 1.0 kcal/mol and with a rotational barrier roughly equivalent to that value [28].

Semmelhack and co-workers [10] have suggested that the transition states in nucleophilic addition of stabilized carbanions to arene–$Cr(CO)_3$ complexes are "late" or more product-like in nature. If the relative stability of "product-like" transition states is considered, it can be seen that the effects would be additive, allowing for a sufficiently large $\Delta\Delta G^*$ to lead to the observed level of selectivity [29]. Since it has been established in the intramolecular reaction that the eclipsed carbons of the predominant conformer are those which suffer nucleophilic addition, it seems reasonable to propose that in the intramolecular reactions the more favored conformer is also the more reactive (lower energy transition state) since the carbons eclipsed by CO should be more electron depleted. The resulting $\Delta\Delta G^{\ddagger}$ would reflect the sum of the two energy differences (ΔG_{rot} and $\Delta G^{\ddagger}$) thereby telescoping the influence of the relative energy differences of the two conformers with the result that the differences of the energies of the transition states leading to the two products could be sufficiently large (~2 kcal) to account for the selective formation (>12:1) of the addition products observed in this work under kinetic conditions.

4. Conclusions

In a series of 1,4-dioxygenated arene chromium tricarbonyl complexes, the position of kinetic attack by a nitrile-stabilized carbanion tethered at C-3 by a three methylene tether was examined for four patterns of alkyl substitution at the 5 and 6 positions. Generating and maintaining the carbanion at −78 °C for between 1 and 1.5 h, followed by addition of iodine at the same temperature afforded good selectivity for generating addition products resulting from addition at either C-2 or C-3. The position of kinetic attack were correlated with ambient and low temperature ^{13}C NMR spectra, solid-state ^{13}C NMR and crystallographic data, and ^{1}H NMR spectra. All of these data indicate an average preferred configuration of the $Cr(CO)_3$ fragment. It has been established that when the $Cr(CO)_3$ fragment adopts a preferred configuration, it is the predominate force in directing addition by nucleophiles. However, it is the conformation of the $Cr(CO)_3$ in solution that correlates with the regioselectivity, not the conformation in the solid-state. We have proposed that the high degree of regioselectivity in the intramolecular addition reaction is the result of an additive electronic effect of the alkyl substituents which both favors a preferred conformation of the $Cr(CO)_3$ fragment and lowers the energy of activation for addition to the major conformer relative to the minor conformer.

Acknowledgment

This work was supported by a Grant from the National Science Foundation (CHE-0750319).

Appendix A. Supplementary material

CCDC 790425, 790426, 790427, and 790428 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.037.

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