Examination of the slightly discolored solution by ^{29}Si NMR showed that only starting material was present.

Photolysis of $IsHSi(SiMe_3)_2$. A pentane (15 mL) solution of $IsHSi(SiMe_3)_2$ (100 mg) was photolyzed for 18 h at −60 °C. Examination of the slightly colored solution by ^{29}Si NMR showed that only starting material was present.

Photolysis of $IsFSi(SiMe_3)_2$ (8) and Is(1-pyrrolyl)Si-$(SiMe_3)_2$ (9). A pentane (15 mL) solution of 8 or 9 (100 mg) was photolyzed for 18 h at −60 °C. Examination of the colored solutions by ^{29}Si NMR showed only hexamethyldisilane. The signals in the ^1H NMR spectrum were broad, even at elevated temperatures.

Thermolysis of $IsClSi(SiMe_3)_2$ (7). Trisilane 7 (115 mg) was heated in refluxing benzene (20 mL) for 2 days. No change was noted. Examination of the solution by ^{29}Si NMR indicated that only trisilane 7 was present.

X-ray Data Collection. Single crystals of (*E*)-1 were grown by slow cooling of a saturated solution in C_6D_6 to 10 °C. Single crystals of (*E*)-2 were grown by heating a concentrated solution of (*Z*)-2 in hexane for 1 week, followed by slow cooling of this solution to 10 °C. Suitably sized crystals of (*E*)-1 and (*E*)-2 were taken from the solution under argon and immediately mounted on a thin glass thread with cyanoacrylate cement. Single crystals of 3 were grown by slow cooling of a saturated solution in hexane to 0 °C and mounted similarly. A thin coat of this cement was used to seal the surface of all the crystals. All studies were carried out on a Siemens P3F diffractometer equipped with Cu Kα radiation (except Mo Kα for 3) and a graphite-crystal monochromator. Unit cell parameters were obtained from least-squares refinements based on the setting angles of 25 reflections. For 3 the space group was uniquely determined by the systematic absences in the data; for (*E*)-1 and (*E*)-2 $P\bar{1}$ was assumed and confirmed by successful structure solution and refinement. Data collection and refinement parameters used for the structure determinations are summarized in Table I. Throughout data collection standard reflections were measured every 100 reflections to monitor stability. The structures were solved by direct methods using Siemens SHELXTL PLUS (VMS). *E* maps revealed the positions of the silicon and carbon atoms. For (*E*)-2, the *p*-isopropyl group is disorded. Further electron density difference maps revealed the hydrogen atoms. In the final cycles of refinement all non-hydrogen atoms were assumed to vibrate anisotropically and all hydrogen atoms were assumed to vibrate isotropically.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. AFOSR-89-0004 and the National Science Foundation (Grant No. CHE-8922737) with financial aid (Y.v.d.W.) from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Tables of crystal data, bond lengths, bond angles, atomic coordinates, equivalent isotropic dispacement coefficients and occupancies, anisotropic displacement coefficients, and hydrogen atom coordinates for compounds (*E*)-1, (*E*)-2, and 3 (24 pages). Ordering information is given on any current masthead page.

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^{13}C NMR Spectroscopic and EHMO Study of Slowed Tripodal Rotation in $[(Benzyl)Cr(CO)_3]^+$ and $(Fulvene)Cr(CO)_3$ Systems: Metal-Stabilized Nonplanar Cations

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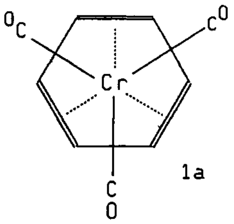
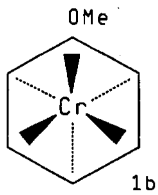
The variable-temperature ^{13}C NMR spectra of a series of methyl- and methoxy-substituted $(benzyl)Cr(CO)_3$ cations and neutral $(fulvene)Cr(CO)_3$ complexes reveal that the metal carbonyl resonances are split at low temperature; the barriers to tripodal rotation are rationalized in terms of the degree of localization of charge at the aromatic or fulvene carbons. It is shown that primary benzyl cations require greater stabilization by the tricarbonylchromium fragment than do analogous secondary or tertiary benzyl cations. These experimental results are complemented by molecular orbital calculations at the extended Hückel level.

Introduction

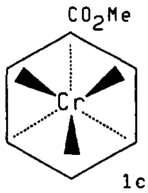
In complexes of the type $(arene)Cr(CO)_3$, the question of slowed tripodal rotation on the NMR time scale has aroused much controversy for nearly 20 years.[1] The favored conformations in the solid state were enunciated by Carter, McPhail, and Sim as the result of a series of X-ray crystallographic determinations.[2] While the staggered isomer **1a** is found for $(benzene)Cr(CO)_3$ itself,[3] incorporation of electron-donating or electron-withdrawing substituents yields the eclipsed rotamers **1b** and **1c**, respectively. The rationale offered to account for structure **1b** is that the electron-donating group, e.g., Me_2N or MeO, polarizes the charge distribution in the ring so as to render the ortho and para carbons relatively electron-rich. This makes the C(2), C(4), and C(6) positions better donors to the metal atom and, maintaining the preferred octahedral geometry at chromium, the carbonyl ligands are found to eclipse the C(1), C(3), and C(5) sites.[4] Conversely, com-



1a



1b



1c

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[1] McGlinchey, M. J. *Adv. Organomet. Chem.* **1992**, *34*, 285.

[2] Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1967**, 228.

[3] Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *5*, 1314.

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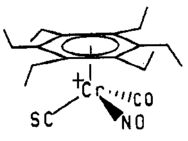
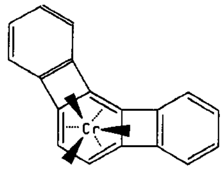
plexes bearing electron-withdrawing substituents, as in $(C_6H_5CO_2Me)Cr(CO)_3$, adopt conformation **1c**.[5]

Extended Hückel molecular orbital calculations by Albright, Hoffmann, and Hofmann have shown that, in the absence of overwhelming steric or electronic factors, the energy barrier which must be surmounted to spin the $Cr(CO)_3$ moiety about the Cr–ring-centroid axis is tiny;[6] thus, the chances of detecting slowed tripodal rotation in solution on the NMR time scale in such a system are remote. Nevertheless, it has been established that the barrier to tripodal rotation in sterically hindered systems such as $(C_6Et_6)Cr(CO)L'L''$, **2**, where L′ and L″ are CO, CS, or NO^+, is approximately 9.5 kcal mol^{-1}.[7] Moreover, the elegant studies of Siegel[8] and of Hunter[9] have demonstrated the existence of other molecular systems where bulky groups hinder rotation of $Cr(CO)_3$ moieties.



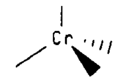
2

The calculatory approach also suggested two scenarios in which electronic influences might be brought to bear.[6] The first possibility raised was that bond fixation in an arene ring would impose a substantial barrier to tripodal rotation. This concept was brilliantly exploited by Nambu and Siegel who synthesized the terphenylene complex **3**.[10]



3

The crucial factors here were (a) the partial bond fixation caused by the presence of the benzocyclobutadiene moieties and (b) the lowering of the symmetry from C_{3v} to C_s which resulted in a 2:1 splitting of the $Cr(^{13}CO)_3$ resonance at low temperature. Hoffmann et al. also proposed that $[(benzyl)Cr(CO)_3]^+$ would preferentially adopt structure **4**, analogous to **1c**, which would be approximately 6.8 kcal mol^{-1} more stable than the rotamer **5**. Moreover, it was suggested that the exocyclic methylene group should bend down by 11° toward the metal atom so as to optimize the overlap between the vacant p_z orbital on carbon and a suitable filled d orbital on chromium.[6] (X-ray crystallographic data on the closely analogous ferrocenyl cation **6** revealed a methylene bend angle of 20°;[11] moreover NMR data on the tricobalt cluster **7** have confirmed that the $C{=}CR_2$ moiety leans toward a $Co(CO)_3$ vertex.[12])



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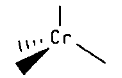

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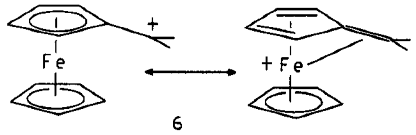

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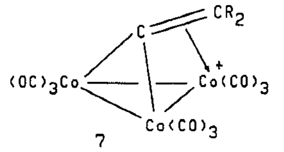

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To investigate further these phenomena, we have synthesized a series of cationic $[(benzyl)Cr(CO)_3]^+$ complexes and recorded their variable-temperature ^{13}C NMR spectra. These data are complemented by studies on the closely analogous $(fulvene)Cr(CO)_3$ systems, and the barriers to tripodal rotation have been evaluated both by experimental means and by use of EHMO calculations.

Results and Discussion

Benzyl Complexes. The enhanced reactivity of tricarbonylchromium complexes of benzyl halides toward nucleophilic substitution has been attributed to stabilization of the cationic intermediates by delocalization of the positive charge onto the metal.[13] It has been proposed that such a stabilization would be enhanced if the exocyclic methylene were to bend down through ≈11° toward the metal, thus increasing overlap between the vacant benzylic p_z orbital and a filled orbital on chromium.[6] Earlier INDO calculations by Clack and Kane-Maguire had also led to the conclusion that the methylene fragment would bend toward the metal; these data suggested a bend angle of ≈40° and also that a staggered structure of type **1a** would be favored.[14] By means of EHMO calculations, we find a minimum energy structure **4** when the chromium is displaced by 0.12 Å toward the benzylic carbon and the methylene bend angle is 22°. As shown in Figures 1 and 2, the principal stabilizing interaction allows the delocalization of the positive charge onto the $Cr(CO)_3$ unit via overlap of the vacant p_z orbital of the benzylic carbon with the filled $d_{x^2-y^2}$ orbital on chromium. This orbital is marked with an asterisk (*) in Figure 1 and is seen to be gradually stabilized as the exocyclic methylene fragment bends down toward the tripod. The corresponding out-of-phase combination of benzylic p_z and chromium $d_{x^2-y^2}$ orbitals is the LUMO and, of course, is gradually raised in energy as the Walsh diagram clearly shows. The two highest occupied orbitals are of mostly chromium 3d and carbonyl π^* character and are little affected by geometric changes of the exocyclic methylene moiety. At the optimum position, the overlap population between the benzylic carbon and the chromium is 0.046 and the gain in stability resulting from the bending of the methylene carbon is ≈1.7 kcal

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(4) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1966**, 822.

(5) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1967**, 1619.

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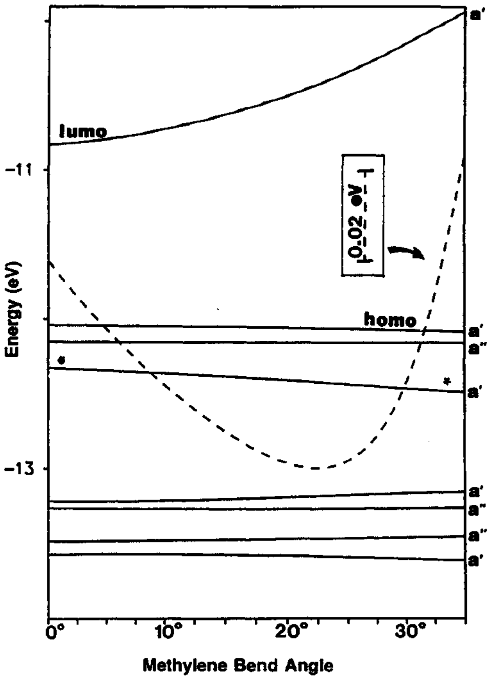
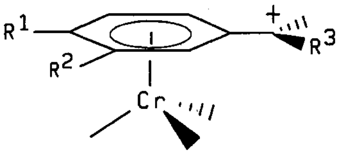


Figure 1. Walsh diagram showing how the orbital marked by an asterisk (*) is stabilized by bending the exocyclic methylene group in 4 toward the Cr(CO)$_3$ moiety (see text). The variation in total energy (dashed line) is plotted on a different scale (which is inset).

mol^{-1}. To the extent that we choose to believe the charge distribution given by the EHMO calculations, the benzylic carbon in the planar cation bears a charge of +0.34 but this is reduced to +0.23 as a result of methylene bending and charge transfer from the chromium center.



8: R^1 = Me; R^2 = H; R^3 = Me
9; R^1 = MeO; R^2 = H; R^3 = H
10; R^1 = H; R^2 = MeO; R^3 = H
11; R^1 = H; R^2 = Me; R^3 = H
12; R^1 = Me; R^2 = H; R^3 = H

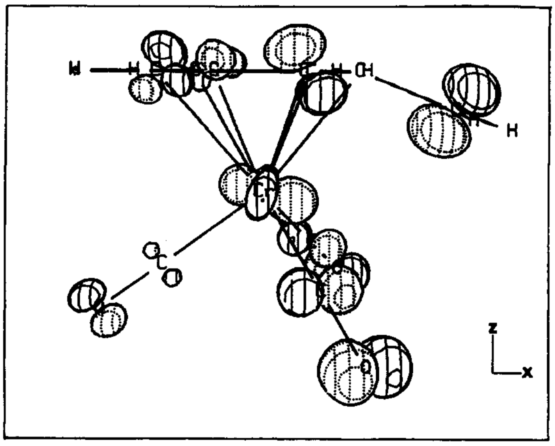


Figure 2. CACAO plot of the orbital in 4, marked with an asterisk (*) in Figure 1, showing the interaction of the vacant p orbital on the electron-deficient carbon with the filled $d_{x^2-y^2}$ orbital on chromium.

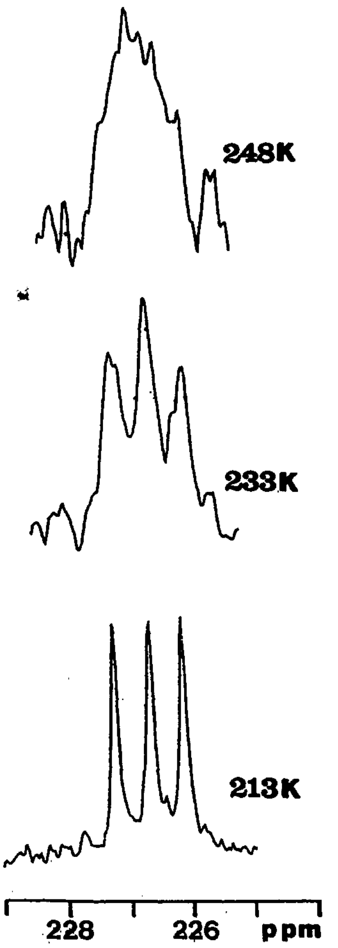


Figure 3. 125.7-MHz ^{13}C variable-temperature NMR spectra of [(4-MeC$_6$H$_4$CHMe)Cr(CO)$_3$]$^+$ (8) in the metal carbonyl region.

As pointed out by Siegel,[10] the barrier to tripodal rotation in 3 can be related to the degree of bond fixation in the central aromatic ring. Likewise, the extent of charge localization in [(benzyl)Cr(CO)$_3$]$^+$ should control the barrier to Cr(CO)$_3$ rotation. We are aware of only one claim of slowed carbonyl exchange in such a system; Ceccon has reported that the 22.6-MHz ^{13}CO spectrum of the cation 8, derived by protonating (methyl-*p*-tolylcarbinol)Cr(CO)$_3$ with FSO$_3$H, shows three carbonyl resonances at low temperature.[15] However, since no spectra were shown nor was an activation energy barrier calculated, we have repeated this experiment to verify the result. Figure 3 depicts the 125.7-MHz ^{13}C spectrum of 8 over the range -60 to -25 °C (at which point the coordinated cation shows clear signs of decomposition) and fully confirms Ceccon's original claim. Simulation of the spectrum yields a $\Delta G^{\ddagger}_{248}$ value of 11.7 ± 0.4 kcal mol^{-1} for the tripodal rotation process. This experimentally determined activation energy presumably includes not only the barrier to rotation of the tricarbonylchromium moiety through 120° but also the bending of the methylene fragment. The EHMO derived barrier for this fluxional process in [(benzyl)Cr(CO)$_3$]$^+$ was calculated to be 7.4 kcal mol^{-1} and is shown in Figure 4.

The incorporation of electron-donating or -withdrawing substituents in the π-complexed phenyl ring should modify the electron density distribution at the ring carbons and so affect the barrier to tripodal rotation. Thus, placement of a methyl or methoxy group para to the benzylic cation should help to localize the relatively electron-rich sites at

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(15) Acampora, M.; Ceccon, A.; Dal Farra, M.; Giacometti, G.; Rigatti, G. *J. Chem. Soc., Perkin Trans. 2* 1977, 483.

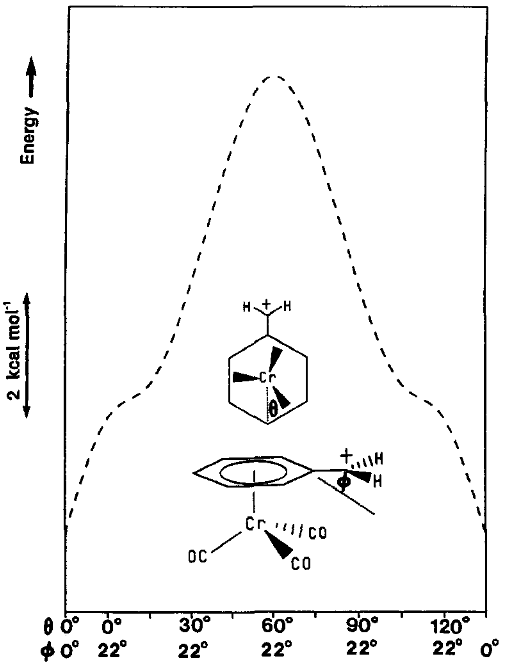

Figure 4. EHMO calculated energy profile showing the changes brought about by initially bending the exocyclic methylene through angle ϕ and then rotating the $Cr(CO)_3$ tripod through angle θ in $[(benzyl)Cr(CO)_3]^+$.

the C(1), C(3), and C(5) positions. In contrast, incorporation of a methyl or methoxy substituent meta to the benzyl cation would be expected to counteract the charge localization and lower the barrier to rotation of the $Cr(CO)_3$ fragment since no single orientation is greatly favored over the others. This picture gains support from EHMO calculations which yield rotational barriers of 7.5 and 5.1 kcal mol^{-1}, respectively, for the *p*- and *m*-methoxybenzyl–$Cr(CO)_3$ cations. Indeed, tripodal rotation in the *p*-methoxybenzyl complex **9** is slowed at −70 °C, but the onset of decoalescence appears only at −100 °C for the analogous *m*-methoxy system **10**. These primary cations are stable only below −40 °C, so there is only a narrow temperature range over which changes in the NMR spectra can be followed. Therefore, our experimental $\Delta G^{\ddagger}$ values ($\approx$ 11 and $\approx$ 10 kcal mol^{-1} for **9** and **10**, respectively) arise from simulations based on rather small changes in rate constants and should not be regarded as precise values.

Interestingly, an EHMO calculation on the tertiary cation $[(C_6H_5CMe_2)Cr(CO)_3]^+$ shows that bending of the α-carbon toward the metal is energetically slightly disfavored.[16] There are no major steric problems, and one might speculate that the tertiary cation has much less need for anchimeric assistance from the chromium than does a primary cation. Such a proposal has been advanced previously with respect to cluster-stabilized cations such as $[Co_3(CO)_9CCR_2]^+$.[17,18] We have also obtained ^{13}C NMR spectra of the primary cations $[(3\text{-methylbenzyl})Cr(CO)_3]^+$ (**11**) and $[(4\text{-methylbenzyl})Cr(CO)_3]^+$ (**12**), which are stable below −50 °C; a spectrum of **11** appears as Figure 5.

Unambiguous assignment of all the aromatic nuclei in these cationic benzyl–chromium complexes would require time-consuming two-dimensional ^1H–^1H COSY and ^1H–^{13}C shift-correlated experiments, and this was not our primary objective. We chose instead to focus on the carbonyl resonances which in each case split at low temperature. With the limited data set available, the rotational barrier in **11** is estimated to be $\approx$12.5 kcal mol^{-1}—perhaps indicating an interaction of the primary cationic center with the electron-rich metal atom slightly stronger than is the case for the secondary cation in **8**. We note also that the observation of 2:1 patterns for the ^{13}CO resonances in the para-substituted complexes supports the eclipsed rotamer **4** originally proposed by Hoffmann et al.[6] rather than the staggered orientation for the tripod suggested previously.[14] The latter scenario should yield three carbonyl peaks at low temperatures, but we only see such 1:1:1 patterns in cases where the arene is unsymmetrically substituted.

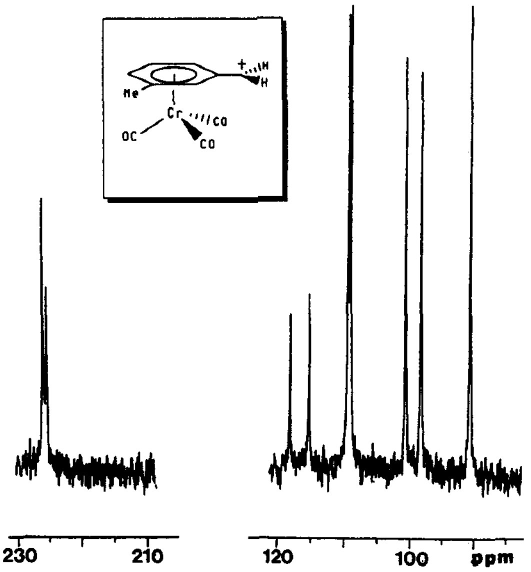

Figure 5. 125.7-MHz ^{13}C NMR spectrum of the cation $[(3\text{-methylbenzyl})Cr(CO)_3]^+$ (**11**) at −90 °C.

Olah has reported a marked deshielding of the benzylic carbon when going from $(cumyl\ alcohol)Cr(CO)_3$, $\delta = 71.42$, to $[(C_6H_5CMe_2)Cr(CO)_3]^+$, $\delta = 170.92$; however, the complexed cumyl cation is still shielded by 83 ppm relative to the noncoordinated system, viz., $[C_6H_5CMe_2]^+$ itself.[19] It was suggested that this downfield shift of only 100 ppm could be interpreted in terms of decreased localization of the positive charge on the benzylic site since the electron deficiency could be alleviated by donation from the tricarbonylchromium moiety. Seyferth[20] and Ceccon[15] have noted that transformation of secondary alcohol complexes into secondary carbocations, e.g., the mono- or bis($Cr(CO)_3$) complexes of $[(MeC_6H_4)_2CH]^+$, brings about a deshielding of the benzylic carbon nucleus of $\approx$65 ppm. We see from the present data that protonation of primary alcohols to yield the corresponding primary carbocation complexes, such as **9** through **12**, results in a deshielding of only $\approx$25 ppm. This is a clear indication that the delocalization of positive charge onto the $Cr(CO)_3$ fragment is very considerable in the primary carbocation complexes.

It appears, therefore, that the ^{13}C NMR chemical shifts of the benzylic carbons together with the activation energy barriers toward tripodal rotation are useful probes of the localized nature of the arene-to-chromium interactions.

Fulvene Complexes. As noted above, the ferrocenyl cation adopts a bent geometry[11] such that one extreme

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(16) It may soon be possible to verify this conjecture since we have recently isolated the cation $[\pi\text{-}Cr(CO)_3(C_6H_5)_3C]^+$ and are attempting to grow X-ray-quality crystals: Malisza, K. L.; McGlinchey, M. J. Unpublished results.

(17) Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* 1987, *109*, 5749.

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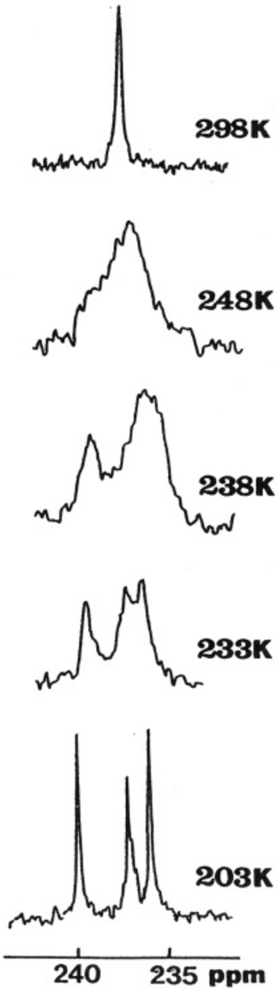
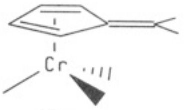
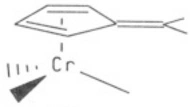


Figure 6. 125.7-MHz ^{13}C variable-temperature NMR spectra of (6-methyl-6-phenylfulvene)$Cr(CO)_3$ (**15**) in the metal carbonyl region.

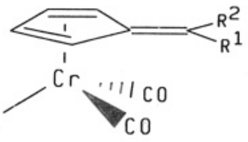
canonical form would represent the cation as a $(C_5H_3)Fe^+$ fragment bonded to a nonplanar fulvene ligand. This concept is buttressed by the X-ray crystallographically determined structure of (6,6-diphenylfulvene)$Cr(CO)_3$ in which the exocyclic carbon is bent down through 30°.[21] Hoffmann et al. have calculated that for (fulvene)$Cr(CO)_3$ the staggered rotamer **13a** should be 7.3 kcal mol^{-1} more stable than the eclipsed rotamer **13b**; this difference is augmented to 9.3 kcal mol^{-1} when the exocyclic methylene is bent down by 30° toward the metal.[6] Preliminary results by Kreiter[22] and by Behrens[23] suggest that tripodal rotation may be slowed on the NMR time scale at low temperature.



13a



13b



14: R^1 = Ph; R^2 □ Ph; L = CO

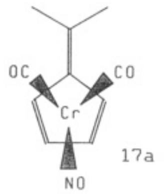
15: R^1 = Ph; R^2 = Me; L = CO

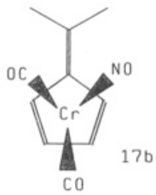
16: R^1 □ Ph; R^2 = Me; L = NO^+

The ^{13}CO NMR spectra of (6,6-diphenylfulvene)$Cr(CO)_3$ (**14**) and of (6-methyl-6-phenylfulvene)$Cr(CO)_3$ (**15**) each show decoalescence behavior at low temperature. The former yields a 1:2 peak pattern, while the latter, as befits a chiral molecule, exhibits three carbonyl resonances; the variable-temperature spectra for **15** are shown in Figure 6. The $\Delta G^\ddagger$ value in each case is 11 ± 0.5 kcal mol^{-1}. These data on tripodal rotation barriers support the concept of parallelism between benzyl and fulvene ligands.

Finally, we note that in his pioneering studies on half-sandwich molecules Rausch reported the ^1H and ^{13}C NMR spectra of a series of $[(C_5H_4CR'R'')Cr(CO)_2NO]^+$ complexes, **16**.[24] It was noted that in some cases the carbonyl ligands gave rise to two resonances even at ambient temperature; this was interpreted in terms of restricted rotation of the ML_3 tripod. In view of the low barriers to $Cr(CO)_3$ rotation observed in the benzyl and fulvene complexes discussed here, the splitting of the CO's in the nitrosyl systems requires an explanation. In fact, we note that the only cations **16** which yield two ^{13}CO peaks are those in which $R' \neq R''$; such molecules are chiral and the CO ligands are rendered diastereotopic. Thus, these carbonyls are always different and one cannot use this observation as a valid argument for restricted rotation *of the tripod*. It does, however, support Rausch's assertion that there is restricted rotation about the C(5)–C(6) bond. Likewise, as shown by Ceccon,[15] rotation about the aryl–CR_2 bond in benzyl systems has a very high barrier. Indeed, the retention of stereochemical integrity in such cations has been exploited synthetically.[25]

EHMO calculations on **16**, where $R' = R'' = H$, show that the symmetric isomer **17a** is favored by 2.7 kcal mol^{-1} over the unsymmetrical rotamer **17b** and also that the barrier to rotation is only 7.3 kcal mol^{-1}. This is consistent with observations that rotation of $Cr(CO)_3$, $[Cr(CO)_2NO]^+$, $Cr(CO)_2CS$, and $[Cr(CO)(CS)NO]^+$ tripods attached to hindered arenes have very similar barriers.[7] The calculated preference for the symmetrical isomer **17a** is related to the ability of the exocyclic double bond to donate electron density to the chromium such that it is trans to the better π-accepting ligand, i.e., NO^+. It is interesting that in the X-ray structure of (η^5-fluorenyl)$Cr(CO)_2NO$ the nitrosyl ligand is sited trans to the unique ring carbon at C(9); in contrast, in (η^5-cyclopentadienyl)$Cr(CO)_2NO$ the nitrosyl and carbonyl ligands are crystallographically disordered.[26]





To conclude, we have described the syntheses and NMR characterizations of a series of tricarbonylchromium complexes of benzylic cations and of fulvenes. The barriers to tripodal rotation may be rationalized in terms of the degree of charge localization at the aromatic or fulvene

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carbons. Perhaps it is appropriate to remind ourselves that EHMO calculations do not take into account charge interactions and the energy variations associated with particular motions are primarily a reflection of the frontier orbital interactions of the two fragments. Thus, when we raise the ground-state energy of one of the fragments, we are increasing the likelihood of observing fluxional behavior. Clearly, a detailed picture of the electron density distribution in these systems would be very valuable. However, not being experts in the field, we defer to our more knowledgeable colleagues for further exegesis.

Experimental Section

All syntheses were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[27] ^{13}C NMR spectra were recorded at 125.7 MHz by using a Bruker AM 500 spectrometer equipped with a 5-mm dual-frequency ^{1}H/^{13}C probe. All spectra were measured in methylene chloride-d_2 and chemical shifts are reported relative to tetramethylsilane. NMR simulations were carried out by using the multisite EXCHANGE program generously provided by Professor R. E. D. McClung (University of Alberta at Edmonton).

The (benzyl alcohol)(CrCO)$_3$ and (fulvene)Cr(CO)$_3$ complexes were prepared by heating the appropriate benzyl alcohol or fulvene with chromium hexacarbonyl in dibutyl ether/tetrahydrofuran according to the method of Top and Jaouen[28] or Mahaffy and Pauson.[29] The complexes were purified by flash chromatography on silica gel and identified by comparison of their mass spectra, infrared and NMR spectra, and melting points with the literature data.[15,30-35]

Preparation of Benzyl Cations. In a typical preparation, (3-methoxybenzyl alcohol)Cr(CO)$_3$ (50 mg) was dissolved in CD$_2$Cl$_2$ (1 mL) and carefully filtered through glass wool into an NMR tube inside a nitrogen-filled glovebag. The sample was cooled in a dry ice/acetone bath, and a few drops of CF$_3$SO$_3$H were slowly added; the initially yellow solution became red-violet upon protonation and the NMR spectrum was immediately recorded at −70 °C. The cations decomposed slowly over a period of a few hours or more rapidly above −40 °C.

[(4-MeC$_6$H$_4$CHMe)Cr(CO)$_3$]$^+$ (8). ^{13}C NMR data at −60 °C: δ 227.0 [1], 226.6 [1], 226.1 [1] (Cr–CO's), 127.3 (benzylic C), 107.0, 103.4, 102.1, 101.4 (aromatic CH's), 106.2 (C(1)), 115.5 (C(4)), 21.0 (ring Me), 16.7 (Me).

[(3-MeOC$_6$H$_4$CH$_2$)Cr(CO)$_3$]$^+$ (10). ^{13}C NMR data at −80 °C: δ 226.9 [3] broad peak (Cr–CO's), 144.7 (C(3)), 116.0 (C(1)), 106.3, 99.5, 89.7, 86.3 (aromatic CH's), 89.1 (benzylic C), 57.9 (MeO).

[(3-MeC$_6$H$_4$CH$_2$)Cr(CO)$_3$]$^+$ (11). ^{13}C NMR data at −60 °C: δ 225.9 [2], 225.2 [1] (Cr–CO's), 118.0 (C(1)), 115.2 (C(3)), 109.3, 108.8, 100.6, 98.6 (aromatic CH's), 90.6 (benzylic C), 20.7 (Me).

[(4-MeC$_6$H$_4$CH$_2$)Cr(CO)$_3$]$^+$ (12). ^{13}C NMR data at −70 °C: δ 226.1 [2], 225.2 [2] (Cr–CO's), 118.2 (C(1)), 113.0 (C(4)), 109.1 [2], 102.3 [2] (aromatic CH's), 91.7 (benzylic C), 21.0 (Me).

[(Ph$_2$C=C$_5$H$_4$)Cr(CO)$_3$] (14). ^{13}C NMR data at −80 °C: δ 240.8 [1], 236.5 [2] (Cr–CO's), 141.2 [1] (ipso-phenyl), 128.5 [2], 128.2 [2], 128.1 [1] (phenyl), 128.2 (C(6)), 107.7 (C(5)), 94.1 [2] (C(2), C(3)), 89.5 (C(1), C(4)).

[(Ph(Me)C=C$_5$H$_4$)Cr(CO)$_3$] (15). ^{13}C NMR data at −80 °C: δ 240.2 [1], 236.7 [1], 235.5 [1] (Cr–CO's), 141.8 [1] (ipso-phenyl), 129.4 [2], 128.0 [2], 126.9 [1] (phenyl), 130.5 (C(6)), 104.3 (C(5)), 95.2, 92.4 (C(2), C(3)), 90.4, 87.4 (C(1), C(4)), 25.4 (Me).

Extended Hückel Molecular Orbital Calculations. Molecular orbital calculations were performed via the extended Hückel method[36,37] with use of weighted H_{ij}'s.[38] These were accomplished by using the program CACAO (Computer Aided Composition of Atomic Orbitals)[39] which also generated the Walsh diagrams and orbital pictures. The parameters used are taken from ref 40. The following distances were used: Cr–arene ring centroid = 1.73 Å, Cr–CO = 1.84 Å, C–O = 1.14 Å, C–C = 1.41 Å, C–H = 1.09 Å.

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