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Agostic Complexes via Nucleophile Addition/Protonation Reactions of (η^6-Benzene)tris(trifluorophosphine)chromium

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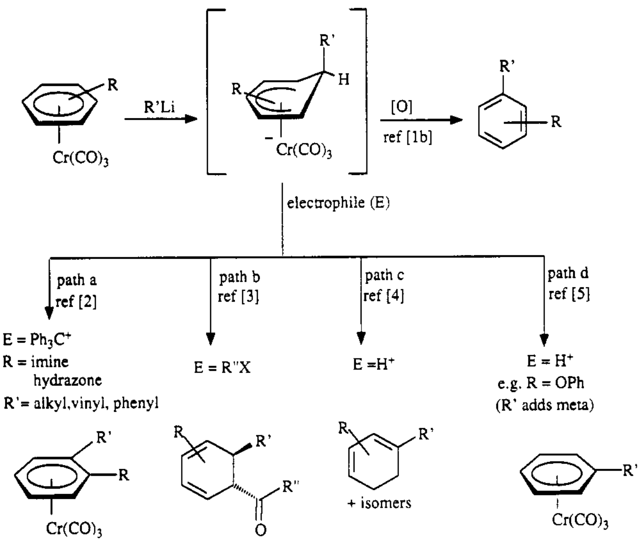
Summary: Sequential nucleophile/proton addition to (η^6-C_6H_6)$Cr(PF_3)_3$ (2) yields the highly fluxional agostic complexes 3 and 4. The mechanism of isomerization has been elucidated by variable-temperature NMR studies and the agostic structure confirmed by an X-ray analysis of 4 (($C_{12}H_{12}$)$Cr(PF_3)_3$, a = 7.608(3) Å, b = 15.259(3) Å, c = 14.490(3) Å, β = 102.92(3)°, monoclinic, $P2_1/c$, Z = 4).

The readily accessible, stable $Cr(CO)_3$ complexes of arenes prove increasingly useful as reagents for organic synthesis. A variety of reactions not possible with the free arene can be carried out with often high regio- and stereochemical control.[1] A typical example is the efficient addition of carbanions to the exo face of the arene which affords η^5-cyclohexadienyl complexes. *In situ* oxidation releases the substituted arene,[1b] whereas reactions with electrophiles, by appropriate choice of the reagent, can be directed to one of the products shown in Scheme I.[2–5] In path b, a *trans* addition of nucleophile and electrophile, with or without CO insertion, generates two adjacent stereogenic centers.[3] Unfortunately, with acids (path c), the high 1,2-regioselectivity found with C-electrophiles is not attained and the reaction produces mixtures of isomeric cyclohexadienes. In simple systems, the major product is the 1-substituted cyclohexadiene.[4] In some cases, protonation is highly regioselective or equilibration can be used to direct the reaction to a single product.[6,7]

Scheme I



Hydrogen shifts also play a key role in *cine* and *tele* aromatic substitutions in (arene)$Cr(CO)_3$ complexes (path d).[5]

The mechanism of the protonation reaction and the hydrogen shifts is not known, and intermediates have eluded isolation.[4b] It was suggested that, presumably *via* protonation at the metal center and reductive elimination, a labile η^4-1,3-cyclohexadiene complex is generated which can readily undergo H-migration to give the more stable 1,3-cyclohexadiene isomer.[1b,5] We were intrigued by the question of the nature of the intermediate. In order to resolve this question, we synthesized the benzene and mesitylene complexes of $Cr(CO)_3$, $Cr(PF_3)_3$, and Mn(CO)(dppe)$^+$ and subjected these complexes to the nucleophilic addition/protonation sequence. In this paper we focus on [(η^6-benzene)$Cr(PF_3)_3$] (2)[8] and show that the mechanism of these hydrogen shifts is associated with the 1,2-H-exchange and 1,5-H-migration in the agostic complexes shown in Scheme II.[9]

[(η^6-benzene)$Cr(PF_3)_3$] (2), synthesized *via* photolytic ligand exchange in [(η^6-benzene)$Cr(CO)_3$] (1),[10] was treated first with $LiEt_3BH$[11] and then with HBF_4 to give 3 as a thermally unstable orange oil which was purified by column chromatography at −50 °C.[12]

The ^1H NMR spectrum of 3 at different temperatures is shown in Figure 1.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

[1] For recent reviews see: (a) Davies, S. G.; Donohoe, T. J. *Synlett* **1993,** *5,* 323. (b) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 4, p 517. (c) Uemura, M. *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, 1991; Vol. 2, p 195.

[2] Path a is abstraction of the *ipso* hydrogen by trityl cation; see: Kündig, E. P.; Liu, R.; Ripa, A. *Helv. Chim. Acta* **1992,** *75,* 2657.

[3] Path b is addition/acylation and addition/allylation; see: (a) Kündig, E. P.; Cunningham, A. F., Jr.; Paglia, P.; Simmons, D. P.; Bernardinelli, G. *Helv. Chim. Acta* **1990,** *73,* 386. (b) Kündig, E. P.; Inage, M.; Bernardinelli, G. *Organometallics* **1991,** *10,* 2921. (c) Kündig, E. P.; Bernardinelli, G.; Liu, R.; Ripa, A. *J. Am. Chem. Soc.* **1991,** *113,* 9676. (d) Bernardinelli, G.; Cunningham, A., Jr.; Dupré, C.; Kündig, E. P.; Stussi, D.; Weber, J. *Chimia* **1992,** *46,* 126. (e) Kündig, E. P.; Ripa, A.; Bernardinelli, G. *Angew. Chem.* **1992,** *104,* 1115; *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1071.

[4] Path c is addition/protonation; see: (a) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981,** *37,* 3957. (b) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Barger, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979,** *101,* 3535.

[5] Path d is *cine* substitution (addition *ortho* to the leaving group) and *tele* substitution (addition *meta* (shown here) or *para*); see: (a) Djukic, J. P.; Rose-Munch, F.; Rose, E. *J. Chem. Soc., Chem. Commun.* **1991,** 1634. (b) Rose-Munch, F.; Bellot, O.; Mignon, L.; Semra, A.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1991,** *402,* 1. (c) Rose-Munch, F.; Rose, E.; Semra, A.; Bois, C. *J. Organomet. Chem.* **1989,** *363,* 103. (d) Rose-Munch, F.; Rose, E.; Semra, A.; Filoche, M. *J. Organomet. Chem.* **1989,** *363,* 123.

[6] (a) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.* **1980,** *102,* 5924. (b) Semmelhack, M. F.; Harrison, J. J.; Thebtaranonth, Y. *J. Org. Chem.* **1979,** *44,* 3275.

[7] Kündig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.* **1983,** *105,* 6962.

[8] (a) The formation of 2 upon irradiation of 1 in the presence of PF_3 was reported briefly: Clark, R. *J. Chem. Eng. News* **1964,** *42* (Oct 26), 52. (b) Kruck, Th. *Angew. Chem.* **1967,** *79,* 27; *Angew. Chem., Int. Ed. Engl.* **1967,** *6,* 53. (c) Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973,** 120. (d) Nixon, J. F. *Adv. Inorg. Chem. Radiochem.* **1985,** *29,* 41.

[9] For a review of agostic complexes, see: Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988,** *36,* 1.

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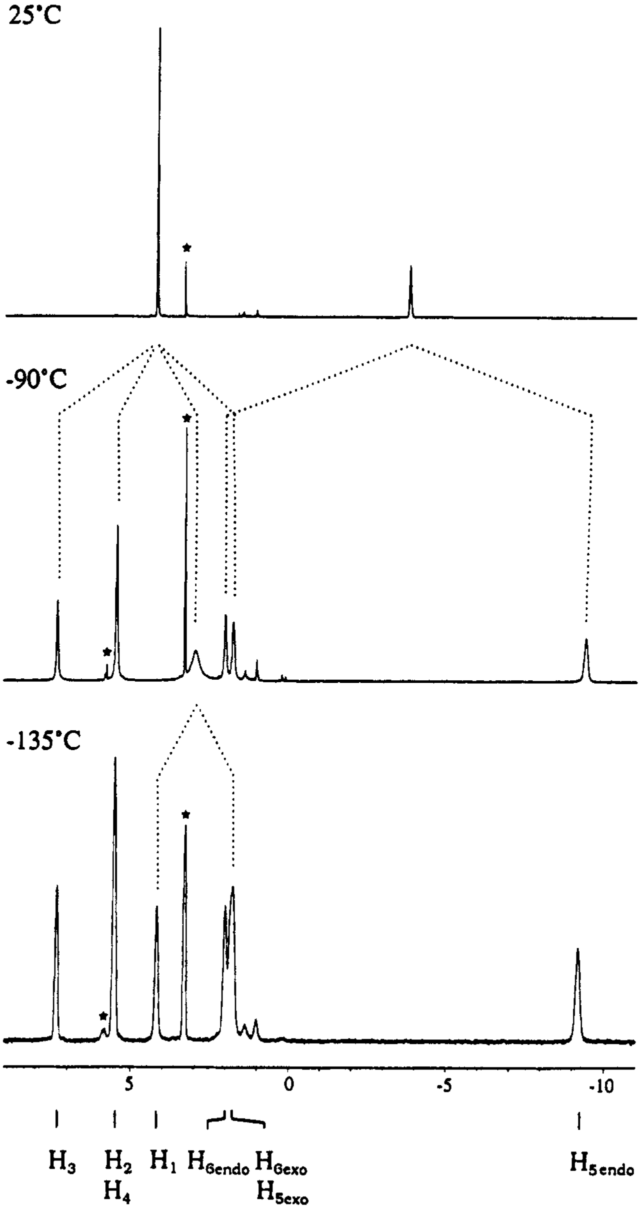
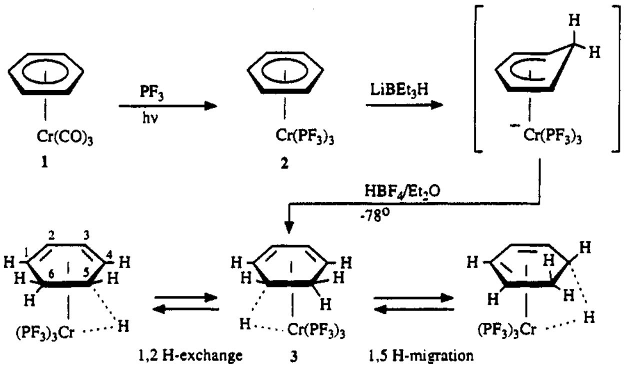


Figure 1. Variable-temperature ^{1}H NMR spectra (400 MHz, $(CD_3)_2O/CD_2Cl_2$) of complex **3**. Asterisks denote solvent peaks.

Scheme II



^{1}H NMR spectra reveal two distinct, degenerate modes of isomerization for complex **3**. The spectrum at 25 °C is exceedingly simple and consists of two singlets at 4.19 and −3.87 ppm in an intensity ratio of 3:1. The two fluxional processes shown in Scheme II account for this behavior. The 1,2-H-exchange and 1,5-H-migration scramble the four vinylic protons and the two *exo* protons, and the 1,2-H-exchange process scrambles the two *endo* protons. The low-field signal is therefore assigned to H–C(1–4) and H_{exo}–C(5,6) and the high-field signal to H_{endo}–C(5,6).

At −90 °C the 1,2-H-exchange process is slow on the NMR time scale. The 1,5-H-migration introduces a plane of symmetry (C(3), C(6), Cr) through the molecule which renders H–C(2) and H–C(4) as well as H–C(1) and H_{exo}–C(5) pairwise equivalent. The latter produce a broad signal at 2.92 ppm. The spectrum corresponding to the frozen structure was obtained only after cooling to −135 °C. This is indicated by the splitting of the signal associated with H–C(1), H_{exo}–C(5) into two distinct signals.

Using PhLi as the nucleophile, the above procedure was repeated for the preparation of complex **4**.[14] The X-ray structure analysis (Figures 2 and 3)[15] shows the initially formed complex to have undergone 1,5-H-migration to

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(10) Synthesis and analytical data for **2**: A pressure-resistant glass reactor equipped with an O-ring tap and a magnetic stirring bar and containing a THF (50 mL) solution of **1** (2.141 g, 10 mmol) and PF_3 (50 mmol) was placed in a photochemical reactor (Rayonnet, The Southern New England Ultraviolet Co.) equipped with nine 3500-Å lamps. At intervals of ca. 12 h PF_3 was condensed and displaced CO was vented using standard vacuum-line techniques. The reaction was followed by IR(THF): $[(C_6H_6)Cr(CO)_2(PF_3)]$, ν_{CO} 1941.8, 1889.7 cm^{-1}; $[(C_6H_6)Cr(CO)(PF_3)_2]$, ν_{CO} 1912.4 cm^{-1}; **2**, ν_{PF} 811.0 cm^{-1}. The reaction mixture was taken to dryness and the crude product taken up in ether, filtered over neutral grade Al_2O_3, and recrystallized from toluene/hexane to afford **2** (2.583 g, 66%) as pale yellow crystals. Mp: 195 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 4.24 (q, $^3J_{HP}$ = 2.8 Hz, 6H). MS (70 eV); *m/z* (%): 394 (5) (M^+), 375 (4) ($M^+ - F$), 356 (1) ($M^+ - 2F$), 337 (6) ($M^+ - 3F$), 306 (0.2) ($M^+ - PF_3$), 218 (5) ($M^+ - 2PF_3$), 130 (44) ($M^+ - 3PF_3$), 52 (100) (Cr^+). HRMS: calcd for $C_6H_6CrF_9P_3$ 393.8943, found 393.8947. Anal. Calcd for $C_6H_6CrF_9P_3$: C, 18.29; H, 1.53. Found: C, 18.38; H, 1.62.

(11) For nucleophilic addition of $LiEt_3BH$ to **1** see: Djukic, J. P.; Rose-Munch, F.; Rose, E.; Dromzee, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6434.

(12) Complex **3** was reported to be formed on cocondensation of 1,4-cyclohexadiene, PF_3, and chromium.[13] The ^{1}H NMR spectrum reported bears no resemblance to the one obtained in this work for **3**. We believe that a different complex was isolated in the previous study.

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(14) Synthesis and analytical data for **4**: A solution of **2** (108 mg, 0.27 mmol) in THF (3 mL) at −78 °C was treated with PhLi (1.5 equiv). The temperature of the reaction mixture was raised to −30 °C over a period of 3 h. THF was removed *in vacuo*, and the residue was taken up in ether and cooled to −78 °C. Upon dropwise addition of HBF_4 (54% in ether, 1.5 equiv), the reaction mixture slowly turned from yellow to dark red. After 30 min the mixture was concentrated and then chromatographed at −50 °C (silica gel, degassed under vacuum for 24 h). Apolar materials were first eluted with hexane (200 mL), followed by **4** (118 mg, 91%, red solid), which was eluted with 3:1 hexane/ether. ^{1}H NMR (400 MHz, CD_3OCD_3/CD_2Cl_2): δ 7.57–7.40 (m, 5H, H_{arom}), 4.71 (s, 2H), 4.20 (s, 1H), 4.07 (s, 2H), 0.36 (s, 1H, H_{endo}), −7.26 (s, 1H, H_{endo}). MS (70 eV; *m/z* (%)): 472 (1) (M^+), 296 (1) ($M^+ - 2PF_3$), 206 (20) ($M^+ - 3PF_3 - H_2$), 52 (100) (Cr^+). HRMS: calcd for $C_{12}H_{12}CrF_9P_3$ 471.9412, found 471.9416.

(15) Crystal structure determination of **4**: A red crystal (0.13 × 0.20 × 0.35 mm) obtained from a toluene/hexane solution was mounted in a Lindemann capillary under Ar with freshly distilled and dried dodecane as adhesive. Crystal data: $(C_{12}H_{12})Cr(PF_3)_3$, M_r = 472.1; μ = 1.055 mm^{-1}, $F(000)$ = 936, d_{exptl} = 1.91 g cm^{-3}, monoclinic, $P2_1/c$, Z = 4, a = 7.608(3) Å, b = 15.259(3) Å, c = 14.490(3) Å, β = 102.92(3)° from 20 reflections (19° < 2θ < 32°), V = 1639.6(8) Å^3. Cell dimensions and intensities were measured at 200 K on a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å), ω–2θ scans, scan width 1.2° + 0.25 tan θ, and scan speed 0.02–0.14° s^{-1}. Two reference reflections measured every 45 min slowed variation less than $3.1\sigma(I)$. A total of 2573 unique reflections were measured, of which 2326 were observables ($|F_0| > 4\sigma(F_0)$); R_{int} for equivalent reflections was 0.056. Data were corrected for Lorentz and polarization effects and for absorption[16] (A^*(min, max) = 1.141, 1.229). The structure was solved by direct methods using MULTAN 87;[17] all other calculations used the XTAL[18] system and ORTEP[19] programs. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[20] All coordinates of hydrogen atoms were observed and refined with isotropic displacement parameters fixed to 0.05 Å^2. The final R factor was 0.044 (R_w = 0.033, $w = 1/\sigma^2(F_0)$).

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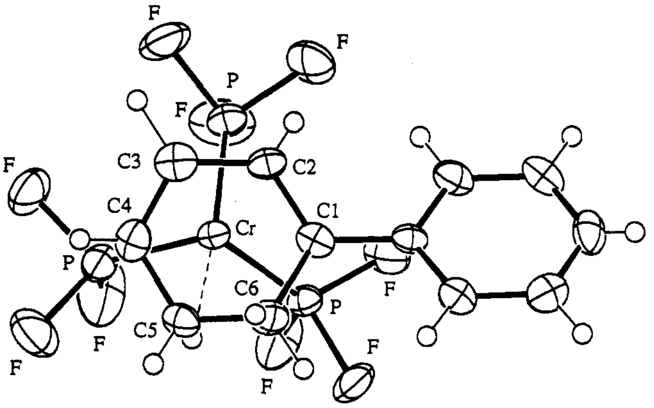

Figure 2. Crystal structure of 4.

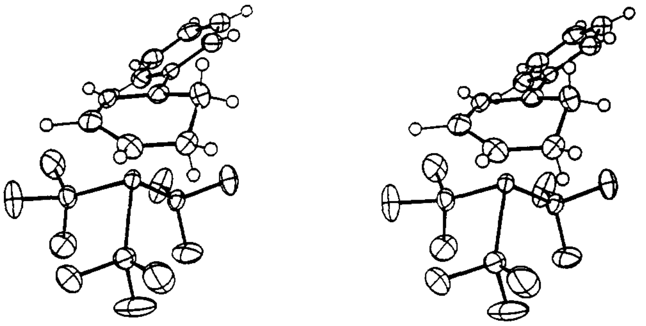

Figure 3. Stereoview of the crystal structure of 4. Ellipsoids are represented with 50% probability.

place the phenyl substituent at an sp^2 center. The coordination geometry of the chromium atom is a distorted octahedron. The agostic hydrogen is *cis* to two phosphorus atoms ($H_{agostic}$–Cr–P(1) = 88(1)°, $H_{agostic}$–Cr–P(3) = 84(1)°) and *trans* to the third ($H_{agostic}$–Cr–P(2) = 171(1)°). The Cr–P_{trans} distance (2.119(1) Å) is shorter than the Cr–P_{cis} distances, which are 2.156(2) and 2.157(2) Å.

The two remaining ligand sites are occupied by the diene portion of the cyclohexadiene ring. The cyclohexadiene ligand has five coplanar carbon atoms (maximum deviation of 0.03 Å). The sixth C atom (C(6)) is bent away from the metal, the plane defined by C(1), C(5), and C(6) forming an angle of 44° with the aforementioned ligand plane. Carbon–carbon distances in the diene show an alternating short–long–short pattern (C(1)–C(2) = 1.397(6) Å, C(2)–C(3) = 1.411(7) Å, C(3)–C(4) = 1.383(7) Å). The short C(4)–C(5) and C(5)–C(6) distances (1.445(7) and 1.507(7) Å, respectively), compared to 1.531(6) Å for C(1)–C(6), attest to an appreciable sp^2 character of the agostic carbon (C(5)).

The Cr···$H_{agostic}$···C(5) interaction leads to considerable distortion of the cyclohexadiene ring, as noted by ring angles of 114.9(4)° (C(1)), 123.2(4)° (C(2)), 117.9(4)° (C(3)), 119.9(5)° ((C(4)), 116.1(4)° (C(5)), and 106.0(4)° ((C(6)), which deviate from the almost ideal angles found in the closely related η^5-cyclohexadienyl complex [(η^5-C_6H_5R)Cr(CO)$_3$SnPh$_3$] (R = methyldithianyl).[3a] The metal is unsymmetrically bound, being closest to C(4) (2.143(5) Å) and C(3) (2.187(4) Å) and furthest from C(1) (2.375(4) Å).

The presence of a Cr···H···C interaction is confirmed by bond lengths of 1.82(4) Å (Cr–$H_{agostic}$), 2.243(5) Å (Cr–C(5)), and 1.01(4) Å (C(5)–$H_{agostic}$), the last being 22% longer than the C(5)–H_{exo} distance of 0.83(4) Å. Support for a strained agostic structure comes from J_{C-H} data for 4 where, at −130 °C, the ^{13}C NMR signal associated with C(5) splits into a doublet of doublets with J_{C-H} = 67 and 162 Hz whereas C(6) becomes a triplet with J_{C-H} = 136 Hz (compared with cyclobutane, J_{C-H} = 134 Hz).

Several examples of agostic complexes having the $\eta^{(4:CH)}$-diene–agostic C–H pattern have now been reported,[21-25] and three X-ray structures have been published.[21,24,25] The unprecedented feature of 3 is that the 1,5-H-migration has a lower energy barrier (6.6 kcal mol^{-1}) than the 1,2-H-exchange process (7.8 kcal mol^{-1}).[26] While the latter value falls into the "normal" range, the former is less than half of previously reported values of H-migrations in agostic complexes.[9] Two other features merit attention. In 4, the Cr–C(5) distance is 0.11 Å shorter than the corresponding chromium agostic–carbon bond in cycloheptadiene,[25] cyclooctadiene,[21] and 2,4-dimethylpentadiene[24] analogs. In 4, the $J_{C-H_{agostic}}$ value is 67 Hz, outside the range of values found (82–107 Hz) in the other known $\eta^{(4:CH)}$-diene–agostic C–H complexes.

Both structural and NMR data presented in this article are consistent with an agostic hydrogen in 3 and 4, which undergoes C–H bond cleavage more readily than M–H bond cleavage. In other words, the agostic hydrogen in these compounds is more "hydride-like" than in complexes of this type studied previously. If the behavior of the Cr(CO)$_3$ complex parallels that of the Cr(PF$_3$)$_3$ complex, the formation of double-bond isomers in the nucleophile addition/protonation sequence is readily explained by the low energy barriers between the isomers in the complex intermediate.

Due to their lower stability, compared to the Cr(PF$_3$)$_3$ complexes, the Cr(CO)$_3$ analogs are less amenable to detailed study and we have therefore concentrated our efforts on the former and on the electronically closely related [Mn(dppe)CO]$^+$ [28,29] complexes. We have established, however, that both benzene and mesitylene complexes of the three electrophilic ML$_3$ fragments, when subjected to a nucleophile addition/protonation sequence, form fluxional agostic complexes. Details of these studies will be the subject of a forthcoming full paper.

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Supplementary Material Available: Tables of Crystal data, atomic coordinates, bond lengths, bond angles, torsional angles, displacement parameters, and least-squares planes for 4 (5 pages). Ordering information is given on any current masthead page.

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