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Reactivity and Structure of (η^6-$C_6(CH_3)_6$)$Mn(CO)_2H$: Stable Alkylrhenium Analogues

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The reactivity of Mr′H (**2**; Mr′ = (η^6-$C_6(CH_3)_6$)$Mn(CO)_2$) with protic acids, Lewis bases, and transition-metal organometallics is reported. Reaction of **2** with triflic acid or $HBF_4 \cdot Et_2O$ generates H_2 and $[Mr'(S)]^+$ (S = CH_2Cl_2, OEt_2, $CF_3SO_3^-$). Treatment of **2** with $CpW(CO)_3X$ (X = Cl, I), $CpFe(CO)_2X$ (X = Cl, I), and $Mn(CO)_5Br$ results in metathesis to give Mr′X and $CpW(CO)_3H$, $CpFe(CO)_2H$, and $Mn(CO)_5H$, respectively. Reaction of **2** with $[CpFe(CO)_2]_2$ produces $CpFe(CO)_2H$ and the new complex $Mr'Fe(CO)_2Cp$. The reaction of $[Rr'CO]PF_6$ (Rr′ = (η^6-$C_6(CH_3)_6$)$Re(CO)_2$) with $(CH_3)_3NO$ and $(n\text{-}Bu)_4NCl$ results in the formation of Rr′Cl (**5a**). Reaction of **5a** with *t*-BuLi produces $Rr'(C(CH_3)_3)$, while reaction with $K(C_2H_5)_3BH$ yields $Rr'C_2H_5$. The structures of **2** and **5a**, determined by single-crystal X-ray diffraction studies, are reported here. Compound **2** crystallizes in the space group $Pna2_1$ with unit cell dimensions $a = 11.918(1)$ Å, $b = 10.826(2)$ Å, $c = 10.465(1)$ Å, $Z = 4$, $V = 1350.2$ Å^3, $R_1 = 0.042$, and $R_2 = 0.043$. Compound **5a** crystallizes in the space group $Pbca$ with unit cell dimensions $a = 13.689(0)$ Å, $b = 13.573(0)$ Å, $c = 15.298(0)$ Å, $Z = 8$, $V = 2842.4$ Å^3, $R_1 = 0.085$, and $R_2 = 0.18$.

Introduction

The centrality of transition-metal hydrides in organometallic chemistry[1] and catalytic processes[2] has been extensively investigated and is well established. These hydrides are known to play many significant roles as stoichiometric reagents and as intermediates in, or catalysts for, numerous reactions of significance, including hydrogenations, olefin isomerizations, and hydroformylations. They can be used for hydrometalation of numerous organic substrates, including olefins,[3] alkynes,[4] aldehydes,[5] ketones,[5] COS,[6] CS_2,[6] CO_2,[6,7] and CO.[8] Their ability to metathesize metal halides to metal hydrides, not readily accessible by other methods, is an indication of the strength of their hydridic character. Surface hydrides are postulated to take part in Fischer–Tropsch catalysis[9] and metal-catalyzed hydrogenations of numerous organic functionalities.[10] The behavior of metal–hydride bonds on surfaces and similar bonds in transition-metal complexes[10] would provide assistance for better understanding the different reactivities of metal catalysts.

Reactions of $[Mr'CO]^+Y^-$, (**1**: Y = PF_6; Mr′ = (η^6-$C_6(CH_3)_6$)$Mn(CO)_2$) with $(CH_3)_3NO$ and $(n\text{-}Bu)_4NX$ (X = Cl, Br, I) have been reported to afford neutral complexes of the form Mr′X (X = Cl (**3a**), Br (**3b**), I (**3c**)).[11] Borohydrides react with **1** to deposit hydride on the arene ring, producing (η^5-cyclohexadienyl)manganese tricarbonyl complexes.[12] Treatment of **3a–c** with hydride sources results in the formation of the transition-metal hydride, Mr′H (**2**).[11] The formation of $[(\eta\text{-arene})Re(CO)_3]^+$ and (η^5-cyclohexadienyl)$Re(CO)_3$ complexes has been reported, but little metal-centered chemistry of rhenium with coordinated hexacarbocycles has appeared in the literature.[13] We have previously reported the synthesis of the analogous (arene)rhenium dicarbonyl iodide compound Rr′I, but no reaction chemistry was presented.[11b] The two new (η-arene)rhenium dicarbonyl alkyls described herein are the first reported members of this class of compounds.

The pK_a of the non-methylated analogue of **2**, (η^6-C_6H_6)$Mn(CO)_2H$ (MrH) (26.8),[14a] is the highest value reported using the pK_a scale established for transition-

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[1] For reviews see: (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (c) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231 and references therein.

[2] Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629 and references therein.

[3] Wilford, J. B.; Stone, F. G. A. *Inorg. Chem.* **1965**, *4*, 93.

[4] Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1969**, 2766.

[5] (a) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 33 and references therein. (c) Carr, D. B.; Yoshifuri, M.; Shoer, L. I.; Gell, K. I.; Schwartz, J. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 127 and references therein.

[6] (a) Darensbourg, D. J.; Rocicki, A. *Organometallics* **1982**, *1*, 1685. (b) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1983**, *248*, C13.

[7] Slater, S. G.; Schumann, B. F.; Darensbourg, M. *Organometallics* **1982**, *1*, 1662.

[8] (a) Lapinte, C.; Astruc, D. *J. Organomet. Chem.* **1984**, *260*, C13. (b) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (c) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700. (d) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (e) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659. (f) Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 2858.

[9] Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

[10] Albert, M. R.; Yates, J. T., Jr. *The Surface Scientist's Guide to Organometallic Chemistry*; American Chemical Society: Washington, DC, 1987; p 105.

[11] (a) Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1984**, *3*, 1445. (b) Bernhardt, R. J.; Wilmoth, M. A.; Weers, J. J.; LaBrush, D. M.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 883.

[12] (a) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807. (b) Winkhaus, G.; Wilkinson, G. *Proc. Chem. Soc., London* **1960**, 311. (c) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigert, D. A. *Chem. Rev.* **1984**, *84*, 525. (d) Morken, A. M.; Eyman, D. P.; Wolff, M. A.; Schauer, S. J. *Organometallics* **1993**, *3*, 725.

[13] (a) Winkhaus, G.; Singer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1963**, *18*, 418. (b) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754. (c) Kane-Maguire, L. A. P.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700. (d) Calderazzo, F.; Poli, R.; Barbati, A.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1984**, 1059. (e) Rybinskaya, M. I.; Kaganovich, V. S.; Kudinov, A. R. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1984**, 813; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 885.

[14] (a) Kristjansdottir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983. (b) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (c) Jordan, R. F.; Norton, J. R. *ACS Symp. Ser.* **1982**, *No. 198*, 403. (d) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (e) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

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metal hydrides by Norton and co-workers.[14] This makes it the least acidic, most hydridic compound characterized to date using this scale. π-Carbocyclic ring permethylation of $CpFe(CO)_2H$ ($CpFe(CO)_2$ = Fp) is reported to increase the pK_a on the Norton scale from 19.4 to 26.3, an average of 1.4 pK_a units per added methyl group. These results suggest that permethylation of the arene in MrH would be expected to increase the pK_a to a value in the range 33–35. This pK_a value, similar to those reported for anionic metal hydrides,[1a,15] can be used to predict the very hydridic nature of **2** reported here.

We have previously described the synthesis of the manganese hydride **2**,[11] its deprotonation with strong bases to give Li[Mr′] (**4**),[11] and its reaction with CS_2 to form Mr′SC(S)H.[16] We have also reported that the carbonylation of **2** leads to the formation of *endo*-(η^5-$C_6(CH_3)_6H$)-$Mn(CO)_3$.[17] We report here a more convenient synthesis of **2**, an overview of its hydridic reactivity, and its solid-state structure.

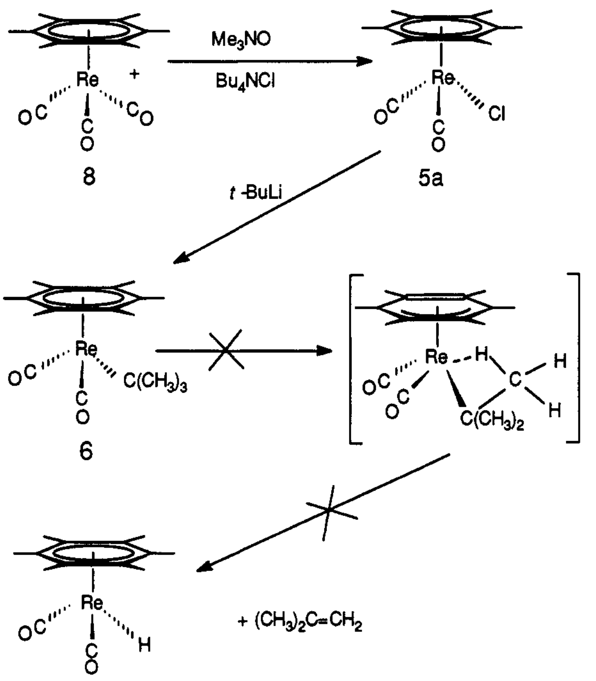
The interesting nature of **2** has led us to attempt the synthesis of the rhenium analogue via Rr′Cl. Rr′Cl (**5a**: Rr′ = (η^6-$C_6(CH_3)_6$)$Re(CO)_2$) was synthesized using the same method we reported for **3a–c** and Rr′I (**5b**).[11] The solid-state structure of **5a**, while highly disordered, was found to be essentially the same as that of Mr′Cl.[11] The similarity in the syntheses and structures of Mr′Cl and Rr′Cl led us to predict that the synthesis of Rr′H might be possible using the same procedures reported for the synthesis of Mr′H.[11] Because the reactions of **3c** with either *t*-BuLi or $K(C_2H_5)_3BH$ had been successfully used to synthesize **2**, it was expected that reaction of **5a** with these reagents would produce Rr′H. Surprisingly, *t*-BuLi reacted with **5a** to produce Rr′($C(CH_3)_3$) (**6**) and $K(C_2H_5)_3BH$ gave Rr′C_2H_5 (**7**).

Results and Discussion

Improved Synthesis of 2. The synthesis of hydride **2** by reduction of **3c** with $NaBH_4$ in THF was previously reported by our group.[11] Using (n-Bu)$_4$NBH$_4$, a more soluble borohydride, results in shorter reaction times. FTIR spectroscopic evidence has established that **2** can be formed in good yields by the reaction of **3c** with *t*-BuLi or at low temperature (−63 °C) by the reaction of **1** with (n-Bu)$_4$NOH in a solution of acetone/water (50%, v/v). When this solution is warmed, Mr′$_2$ is also observed. In contrast, we have reported that the room-temperature reaction of **1** with (n-Bu)$_4$NOH in a solution of THF results in complete conversion to Mr′$_2$.[12d] The difficulty of isolation of **2** in the procedures outlined here makes reduction of **3c** with (n-Bu)$_4$NBH$_4$ the method of choice.

We have attempted to synthesize the rhenium analog of **2** by methods that were successful with manganese. Compound **5a** was formed by reaction of [Rr′CO]$^+$ (**8**) with (n-Bu)$_4$NCl and Me$_3$NO. Attempts to synthesize Rr′H by addition of (n-Bu)$_4$NBH$_4$ to **5a** gave no observable reaction, suggesting that a more hydridic reagent should be used. Reaction of **5a** with (n-Bu)$_4$NOH in acetone/water resulted in quantitative displacement of the arene ring, as evidenced by ^{1}H NMR. This is apparently due to the oxophilic nature of rhenium compounds.[18]

Scheme I



We were surprised to observe that reaction of **5a** with $K(C_2H_5)_3BH$ resulted in the production of **7** instead of the expected rhenium hydride. Upon addition of $K(C_2H_5)_3BH$ to a solution of **5a** in THF, two new carbonyl bands were seen at 1884 and 1817 cm^{-1} in the IR spectrum of the reaction mixture, suggesting an anionic species. Sublimation of the crude product resulted in the formation and isolation of the product **7**, which had ν_{CO} bands at 1926 and 1868 cm^{-1}. We postulate on the basis of the results of Herrmann,[19] Ting,[20] and Bercaw,[21] that the intermediate product may be an anionic rhenium borohydride complex. Herrmann found that reaction of Cp′ReCl$_4$ with NaBH$_4$ and NaCp resulted in evidence for a borohydride complex,[19] while Ting[20] and Bercaw[21] have isolated and characterized $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_2(B_2H_6)$ (R = Me, Et; X = Cl, Br) and Cp′$_2$NbBH$_4$, respectively. Ethyl complexes formed by reaction of a metal chloride with $LiB(C_2H_5)_3H$ have been reported for iron,[22] germanium,[23] and rhodium.[24]

The reaction of **5a** with *t*-BuLi did not lead to the expected hydride complex but led instead to the formation of the new compound **6** (Scheme I). Complex **6** may be analogous to an intermediate anticipated in the formation of **2**, when **3a–c** react with *t*-BuLi. It is assumed that Mr′($C(CH_3)_3$) is converted to **2** by β-hydride elimination of $(CH_3)_2C{=}CH_2$. This process would be facilitated by the facile ring slippage of the η^6-arene at room temperature to produce the η^4-arene, 16-electron analog, which would have an empty metal-centered orbital required for the β-hydride elimination. The proposed ring slippage in the

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(15) (a) Krumholz, P.; Stettiner, H. M. A. *J. Am. Chem. Soc.* **1949**, *71*, 3035. (b) Venerable , G. D., II; Halpern, J. *J. Am. Chem. Soc.* **1971**, *93*, 2176.

(16) Schauer, S. J.; Eyman, D. P.; Bernhardt, R. J.; Wolf, M. A.; Mallis, L. M. *Inorg. Chem.* **1991**, *30*, 570.

(17) Wilmoth, M. A.; Bernhardt, R. J.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 2559.

(18) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111.

(19) Paciello, R. A.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1989**, *28*, 2890.

(20) (a) Ting, C.; Messerle, L. *J. Am. Chem. Soc.* **1989**, *111*, 3449. (b) Ting, C. Ph.D. Thesis, University of Iowa, 1989.

(21) Bell, R. A.; Cohen, S. A.; Doherty, N. M.; Threlkel, R. S.; Bercaw, J. E. *Organometallics* **1986**, *5*, 972.

(22) Balch, A. L.; Corman, C. R.; Safari, N.; Latos-Grazynski, L. *Organometallics* **1990**, *9*, 2420.

(23) Gysling, H. J.; Luss, H. R. *Organometallics* **1989**, *8*, 363.

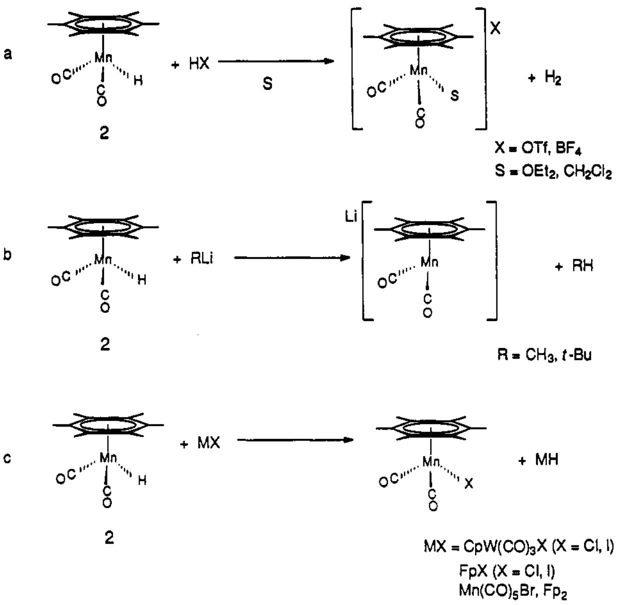
(24) Jones, W. A. Personal communication, University of Rochester, Rochester, NY.

manganese complexes is supported by the observation that Mr′X loses hexamethylbenzene when heated to 114–135 °C (X = Cl (114 °C), Br (126 °C), I (135 °C)), but this proposal is not supported for **5b**, because it melts at 170 °C with retention of the arene ring.[11] The rhenium hydride complex has not been isolated in our laboratory but has been detected as a fragmentation product in the mass spectrum of **6**.

Reaction of 2 with Acids. Transition-metal complexes containing weakly coordinated ligands are important synthetic precursors. This is the basis of the synthetic strategy for the ligand substitution of transition-metal carbonyl complexes using Me_3NO.[25] In these reactions, Me_3N or coordinating solvent molecules are weakly bound to the metal in species which act as intermediates.[25] Recent interest in transition-metal halocarbon complexes is due in part to the fact that unsaturated metal centers can coordinate halocarbons as Lewis bases, activating them to nucleophilic attack.[26] Crabtree[27] has reported cases of second- and third-row halocarbon coordination, which are supported by crystallographic evidence. Gladysz and coworkers[28] have synthesized $[(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(PPh_3)(ClCH_2Cl)]BF_4$ and studied its reaction chemistry.

In addition to halocarbons, oxygen donors often form weakly coordinated complexes with low-valent organometallic species. Sweigart has reported the synthesis of $[Mr'(THF)]PF_6$ and its reaction with alkenes, leading to complexes of the type $[(arene)Mn(CO)_2(alkene)]^+$.[29] Another oxygen donor, OTf^-, is assumed to be a weakly coordinating ligand. In $Cp'Fe(CO)_2OTf$ ($Cp' = C_5(CH_3)_5$), however, there is an unusually short Fe-O bond, and the complex is relatively unreactive to nucleophilic attack.[30]

Scheme II



A compound similar to $Cp'Fe(CO)_2OTf$, Mr′OTf (**9**), has been synthesized by reaction of **2** with CF_3SO_3H (HOTf) (Scheme IIa). This reaction was initially observed in CH_2Cl_2, but the solvent was found to react slowly with **9** to produce **3a**. Compound **1** (Y = OTf) was observed as a minor product of this reaction. The reaction in hexane was monitored by IR spectroscopy, and the new product, **9**, precipitated as a bluish red solid. Upon dissolution in CH_2Cl_2, **9** displayed bands at 1992 and 1940 cm^{-1}, similar to those reported for the red complex $[Mr'(THF)]^+$ (IR (THF) ν_{CO} 1992, 1942 cm^{-1}).[29] During the course of the reaction of **2** with HOTf in hexane, the solution changed from yellow to pale red, suggesting loss of the hydride ligand, due to formation of H_2, and coordination of OTf^-. Compound **9** was found to be stable in air for several hours but decomposed rapidly in THF and CH_2Cl_2.

The synthesis of **9** was undertaken since it was thought that the triflate ligand would be very labile and other ligands could be added to the metal to afford new Mr′L complexes. The addition of I^- to **9** resulted in the known compound **3c**, presumably by nucleophilic displacement of OTf^-. Upon dissolution of **9** in THF, bands in the IR spectrum consistent with the formation of $[Mr'(THF)]PF_6$[29] were observed. Although $[Mr'(THF)]PF_6$ was reported to form $[Mr'(alkene)]^+$ when reacted in CH_2Cl_2 with $(H_3C)_2C{=}C(CH_3)_2$,[29] **9** did not display any evidence for alkene coordination upon addition of $(H_3C)_2C{=}C(CH_3)_2$. These observations suggest that the OTf^- ligand is too strongly coordinated to permit displacement by alkenes. These results stimulated us to search for more weakly coordinating leaving groups. It is interesting to note that dissolution of **9** in THF apparently resulted in displacement of OTf^-, but on dissolution in CH_2Cl_2 compound **9** remained intact, as evidenced by IR, but slowly reacted to give **3a**.

Reaction of **2** with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 resulted in the immediate formation of **3a** and a small amount of **1** (Y = BF_4) (Scheme IIa). These results suggest the intermediacy of CH_2Cl_2 coordinated to the unsaturated metal center.

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(25) (a) Albers, M. O.; Colville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227. (b) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255. (c) Blumer, D. J.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71.

(26) (a) Charbonnier, F.; Faure, R.; Loiseleur, H. *Acta Crystallogr.* **1978**, *34B*, 3598. (b) Murray-Rust, P.; Stallings, W. C.; Monit, C. T.; Preston, R. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 3206. (c) Karipides, A.; Miller, C. *J. Am. Chem. Soc.* **1984**, *106*, 1494. (d) Barcelo, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *J. Chem. Soc., Chem. Commun.* **1985**, 43. (e) Solans, X.; Font-Altaba, M.; Aguilo, M.; Miravitlies, C.; Besteiro, J. C.; Lahuerta, P. *Acta Crystallogr.* **1985**, *C41*, 841. (f) Cotton, F. A.; Lahuerta, P.; Sanau, M.; Schwotzer, W.; Solana, I. *Inorg. Chem.* **1986**, *25*, 3526. (g) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1986**, *25*, 4519. (h) Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, 261. (i) Liotta, F. J., Jr.; Van Duyne, G.; Carpenter, B. K. *Organometallics* **1987**, *6*, 1010. (j) Karipede, A.; Peiffer, K. *Inorg. Chem.* **1988**, *27*, 3255. (k) Colsman, M. R.; Noiret, M. D.; Miller, M. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1988**, *110*, 6866. (l) Barcelo, F.; Lahuerta, R.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *Organometallics* **1988**, *7*, 584. (m) Woska, D. C.; Wilson, M.; Bartholomew, J.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1992**, *11*, 3343. (n) Astruc, D.; Hamon, J.; Roman, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502. (o) Hamon, J.; Astruc, D.; Roman, E.; Batail, P.; Mayerle, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 2431. (p) Hamon, J. R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758. (q) Astruc, D.; Roman, E.; Hamon, J.; Batail, P. *J. Am. Chem. Soc.* **1979**, *101*, 2240.

(27) (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Burk, M. J.; Crabtree, R. H.; Holt, E. M. *Organometallics* **1984**, *3*, 638. (c) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913. (d) Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Inorg. Chem.* **1987**, *26*, 2559. (e) Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Organometallics* **1987**, *6*, 2241. (f) Kulawiec, R. J.; Crabtree, R. H. *Organometallics* **1988**, *7*, 1891.

(28) (a) Winter, C. H.; Gladysz, J. A. *J. Organomet. Chem.* **1988**, *354*, C33. (b) Winter, C. H.; Arif, A. M.; Gladysz, J. A *J. Am. Chem. Soc.* **1987**, *109*, 7560. (c) Winter, C. H.; Arif, A. M.; Gladysz, J. A *Organometallics* **1989**, *8*, 219. (d) Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (e) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766. (f) Agbossou, S. K.; Fernandez, J. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 476. (g) Dalton, D. M.; Fernandez, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198.

(29) Halpin, W. A.; Williams, J. C., Jr.; Hanna, T.; Sweigart, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 376.

(30) Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.

The resulting weakening of the C–Cl bond[31] would lead to facile cleavage to give **3a**. A ^{13}C NMR experiment at low temperature (–85 °C) revealed no signals that could be assigned to a complex with CH_2Cl_2 coordinated to the metal. Because first-row transition-metal complexes of halocarbons are reported to be very labile,[26–28] the above result does not preclude the formation of a methylene chloride coordinated intermediate in these reactions.

Addition of $HBF_4{\cdot}Et_2O$ to a solution of **2** in diethyl ether (0 °C) resulted in the disappearance of the IR bands for the carbonyl frequencies assigned to **2** (IR (diethyl ether) ν_{CO} 1943, 1894 cm^{-1}) and the appearance of new bands corresponding to $[Mr'OEt_2]^+$ (IR (diethyl ether) ν_{CO} 1990, 1935 cm^{-1}) (Scheme IIa). Reaction of the resulting solution with added PMe_3 led to the quantitative formation of $[Mr'PMe_3]BF_4$.[32] This is interpreted as further evidence for the formation of $[Mr'OEt_2]^+$ and demonstration of the weak nature of the diethyl ether–Mn interaction. Several minutes after the addition of the phosphine, the red color of the ether complex was replaced by the bright yellow of $[Mr'PMe_3]BF_4$.[32] The formation of this product (eq 1) was confirmed by IR and ^1H NMR spectroscopy.

$$2 + HBF_4{\cdot}Et_2O \rightarrow [Mr'OEt_2]^+ \xrightarrow{PMe_3} [Mr'PMe_3]^+ \qquad (1)$$

Deprotonation of 2. Reaction of **2** with CH_3Li[11] or *t*-BuLi in THF or hexane results in the formation of Mr′Li (**10**) (Scheme IIb). Reaction in hexane allows precipitation of the insoluble product **10**. However, **2** was not deprotonated by KH in THF. We previously reported[11] that this species can be methylated in THF with CH_3I to give $Mr'CH_3$.[33] Solid compound **10** has not been fully characterized but has been studied in solution because of its high reactivity and sensitivity to air. Reaction of a hexane suspension of **10** with **1** results in the formation of Mr'_2.[34]

Hydride Transfer Reactions of 2. Reaction of **2** with transition-metal organometallic halides (MX) gave quantitative formation of MH and Mr′X (Scheme IIc). This hydrogen–halogen exchange of **2** with $CpW(CO)_3X$ (X = Cl, I) yields $CpW(CO)_3H$ (^1H NMR δ –7.39 ppm) and **3** (X = Cl, I). Reaction with FpX (X = Cl, I) produces FpH (^1H NMR δ –11.99 ppm) and **3** (X = Cl, I), while reaction with $Mn(CO)_5Br$ gives $Mn(CO)_5H$ (^1H NMR δ –7.90 ppm) and **3b**. Fp_2 reacts with **2** to yield FpH (^1H NMR δ –11.99 ppm) and the new complex Mr′Fp, which was isolated and characterized by IR, ^1H and ^{13}C NMR, and MS techniques. No reaction was observed with either $Re(CO)_5Br$ or **5a**.

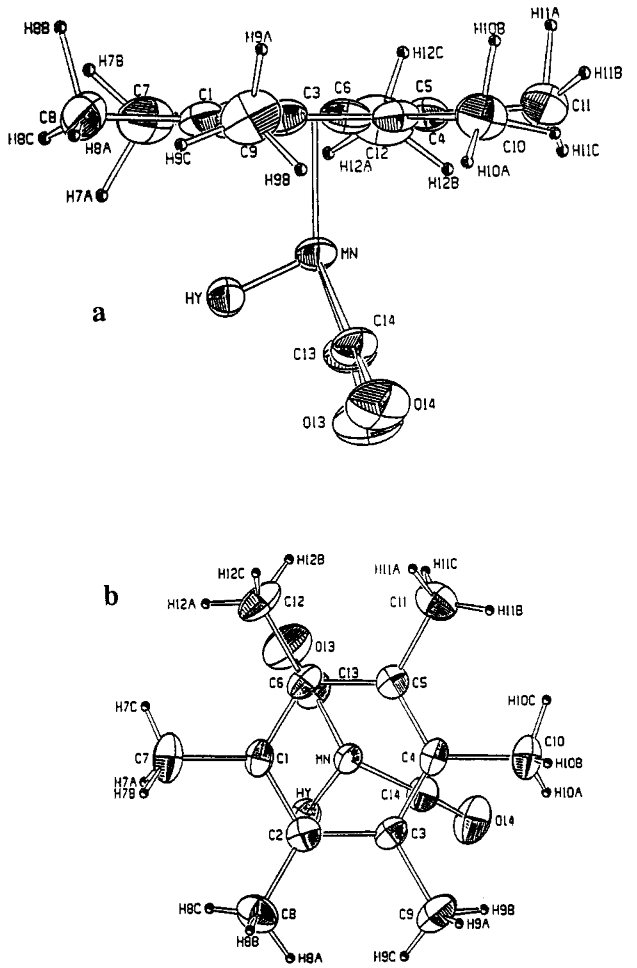

Figure 1. ORTEP drawings of **2**.

Crystallographic Study of 2. The crystallographic study was performed to establish the molecular structure of **2** and **5a**, in order to compare them to the published structure of **3a**.[11] Because of disorder in **5a** a direct comparison with **3a** is not possible.[35] The solid-state structure of **2** is illustrated in the ORTEP plot in Figure 1. A summary of crystal data is shown in Table I. Selected bond distances and angles for **2** are given in Table II. As illustrated in Figure 1b, the molecule has a "piano stool" arrangement in which the three ligands underneath the (hexamethylbenzene)Mn fragment represent the legs. Unlike the structure of **3a**, which has a mirror plane within the molecule and has its carbonyl ligands staggered with respect to the ring carbons, the structure of **2** does not have a mirror plane within the molecule. When the molecule is viewed from the top, one carbonyl carbon (C13) is eclipsed by one of the ring carbons (C6) and the other carbonyl carbon (C14) bisects ring carbons C3 and C4 (Figure 1b). The manganese atom of **2** is in a pseudooctahedral environment with the hexamethylbenzene ligand occupying three coordination sites. The C13–Mn–C14 angle of 89.8(3)° agrees with a pseudooctahedral symmetry for the manganese atom. As shown in Figure 1a, the Mn–C vectors in **2** subtend angles of 43.5(3)° for Mn–C13 and 40.2(3)° for Mn–C14, which are much more than in **3a** (36.7(2)° for Mn–C17 and 36.5(3)° for Mn–C15). This is probably due to the much smaller steric requirement for the hydride vs that for chloride.[36] The idealized angle in an octahedron is 35.3(0)°. This bending away from the arene ring may influence the overlap of the empty

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[31] Crystal structures of coordinated halocarbon complexes display increased C –X bond distances. This is illustrated by refs 28e and 27e.

[32] Snyder, D. B.; Schauer, S. J.; Eyman, D. P.; Moler, J. L.; Weers, J. J. *J. Am. Chem. Soc.*, in press.

[33] Munro, G. A.; Pauson, P. L. *Isr. J. Chem.* **1976/1977**, *2*, 258.

[34] Schlom, P. J. Ph.D. Thesis, University of Iowa, 1990.

[35] The Re atom position, located from a Patterson map, is at approximately $y = {}^1/_4$, with the hexamethylbenzene (HMB) molecule as a cap above ${}^1/_4$ and the Cl atom and two CO groups as legs below $y = {}^1/_4$. The CO and Cl groups appear to be disordered over the three leg positions. In addition, the whole molecule also appears to be disordered with an alternate orientation of the HMB cap below $y = {}^1/_4$ and the disordered legs above $y = {}^1/_4$. This disordered model could not be refined. Hence, no bond angles or distances from this structure should be considered as truly determined. The idealized HMB rings and reasonable leg distances and angles, equally disordered relative to their location about $y = {}^1/_4$ gives R_1 and R_2 values of 0.085 and 0.18, respectively. Refining with fixed atom positions in the model, but with the isotropic temperature factors on each atom varied, indicated perhaps an unequal disorder, with the HMB located above $y = {}^1/_4$ dominating. This model did not have a significantly lower R value, however.

[36] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

Table I. Crystallographic Data and Refinement Parameters for 2 and 5a[a]

	2	**5a**
formula	$C_{14}H_{19}O_2Mn$	$C_{14}H_{18}O_2ClRe$
color	yellow	yellow
cryst size, mm	0.13 × 0.13 × 0.50	0.41 × 0.42 × 0.12
fw, amu	274.24	439.95
a, Å	11.918(1)	13.689(16)
b, Å	10.826(2)	13.573(2)
c, Å	10.465(1)	15.298(18)
V, Å^3	1350.2	2842.4
space group	*Pna*2$_1$	*Pbca*
Z	4	8
density (calcd)	1.35	2.056
λ(Mo Kα), Å	0.710 73	0.710 73
R_1[b]	0.042	0.085
R_2[c]	0.043	0.18

[a] In this and subsequent tables esd's are given in parentheses. [b] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. [c] $R_2 = [\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/s^2(F)$, where $s^2(F) = s^2(F)' + [(PWT)F]^2$ (PWT = 0.04 (**2**), 0.08 (**5a**)).

Table II. Selected Bond Lengths (Å) and Angles (deg) for 2

	Bond Distances		
Mn–Cl	2.197(6)	Mn–C2	2.184(6)
Mn–C3	2.167(6)	Mn–C4	2.167(6)
Mn–C5	2.208(6)	Mn–C6	2.206(6)
Mn–C13	1.759(6)	Mn–C14	1.755(6)
C13–O13	1.154(8)	C14–O14	1.163(7)
C1–C2	1.429(9)	C2–C3	1.413(9)
C3–C4	1.418(9)	C4–C5	1.401(8)
C5–C6	1.425(9)	C6–C1	1.44(1)
C1–C7	1.50(1)	C2–C8	1.490(9)
C3–C9	1.500(9)	C4–C10	1.518(9)
C5–C11	1.51(1)	C6–C12	1.51(1)
Mn–H	1.37(6)		
	Bond Angles		
C1–C2–C3	120.0(6)	C2–C3–C4	120.3(5)
C3–C4–C5	121.1(5)	C4–C5–C6	119.4(6)
C5–C6–C1	120.4(6)	C6–C1–C2	118.9(6)
Mn–C13–O13	176.8(6)	Mn–C14–O14	176.8(6)
C13–Mn–C14	89.8(3)	C13–Mn–H	76(3)
C14–Mn–H	96(5)		

manganese orbitals with the filled π-symmetry bonding orbitals on the π-carbocyclic ring. This overlap may be maximized if one of the carbonyls (C14–O14) occupies a staggered conformation. This would account for the observed shorter bond distance C1–C6. If the orthogonality of the carbonyls is to be maintained, the other carbonyl (C13–O13) is forced into an eclipsed position with respect to an arene ring carbon. These are apparently the optimal positions for these carbonyls if a pseudooctahedral coordination at manganese is to be maintained.

All C–C–C angles in the arene ring are ~120°, and the Mn–C–O angles are both slightly less than 180°. A least-squares plane analysis indicates that the aromatic hexamethylbenzene ring is planar. The Mn to ring-C distances range from 2.167(6) to 2.208(6) Å, and the C–C bond distances range from 1.401(8) to 1.44(1) Å for the aromatic carbon atoms and 1.490(9)–1.518(9) Å for the C–C(methyl) bonds. The Mn–C and C–C bonds found in **2** are nearly identical with those in **3a** and Mr′$_2$.[34] Compound **2** has Mn–CO distances (1.759(6) and 1.755(6) Å) which are shorter than those for **3a** (1.862(3) and 1.843(4) Å); the shorter bond lengths can be attributed to increased π back-bonding from the metal in **2**. The C–O bond lengths in **2** (1.154(8) and 1.163(7) Å) and **3a** (1.029(3) and 1.034(4) Å) are also consistent with increased electron density in the CO antibonding orbital.

Conclusions

The reactions of **2** reported here illustrate its hydridic character. Attempts to synthesize Rr′H from **5a** were unsuccessful but led to the formation of the new complexes **6** and **7**. The chemistry of these complexes may offer some new insight into the mechanisms involved in the reactions of analogous manganese species. Compound **2** is potentially of importance because it is a neutral hydride with a high pK_a value and very high hydridic character. Reaction of **2** with acids leads to protonolysis and the formation of Mr′L species which hold weakly bound L. Reactions with RLi result in abstraction of a proton to produce the anion **10**. One of the most interesting reactions involves hydrogen–halogen exchange with transition-metal organometallic compounds. This reaction may lead to a useful synthetic methodology for transition-metal hydrides. Further examinations of the reactivity of **2** are underway in our laboratory.

Experimental Section

General Procedures. **1**,[12] **3c**,[11,37] CpW(CO)$_3$X (X = I,[38] Cl[38a,39]), FpX (X = Cl,[40] I[39,41]), Fp$_2$,[39] Mn(CO)$_5$Br,[42] Re(CO)$_5$Br,[43] and **8**[13a] were prepared by published methods. Solvents were dried, distilled, and degassed thoroughly with nitrogen or argon prior to use.[44] The reagents *t*-BuLi (1.7 M solution in pentane), $K(C_2H_5)_3BH$ (1.0 M solution in THF), $HBF_4{\cdot}Et_2O$ (85%), and HOTf were purchased from Aldrich and used without further purification. All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk or glovebox techniques. IR spectra were recorded on either an IBM/Bruker IR98 interferometer or a Mattson Cygnus 25 FTIR spectrometer. Microanalyses were performed by Desert Analytics, Tuscon, AZ. The ^{1}H and ^{13}C NMR spectra were recorded on either a JEOL FX90Q or Bruker AC300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported (in ppm) as positive downfield from tetramethylsilane. EI MS spectra were recorded on the VG TRIO 1 instrument with a 70-eV electron beam. All other mass spectra were recorded on a VGZAB-HF in the fast atom bombardment (FAB) ionization mode using xenon as the fast atom source at the University of Iowa High Resolution Mass Spectrometry Facility or at the Midwest Center for Mass Spectrometry, the latter facility having partial support from the National Science Foundation, Biology Division (Grant No. DIR9017262). The reactions, monitored by IR spectroscopy of samples removed from the reaction mixture, were assumed to be complete when the carbonyl bands of the reactants and products ceased to change.

Synthesis of (η^6-$C_6(CH_3)_6$)Mn(CO)$_2$H (2). Method I. In a Schlenk flask was placed **3c** (0.400 g, 1.00 mmol) and $(n\text{-Bu})_4NBH_4$ (0.264 g, 1.01 mmol) as solids, followed by rapid addition of THF (125 mL). The solution was stirred 30–45 min at room temperature, followed by removal of volatiles under reduced pressure. Sublimation of the residual solids at 50 °C yielded **2** (0.178 g, 65% yield) as yellow crystals. ^{1}H NMR and IR spectra confirmed the existence of **2**.

Method II. In a Schlenk flask was placed **1** (0.100 g, 0.220 mmol) followed by rapid addition of acetone/water (50%, v/v)

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(37) Bernhardt, R. J. Ph.D. Thesis, University of Iowa, 1984.

(38) (a) Sloan, T. E.; Wojcicki, A. *Inorg. Chem.* **1968**, *7*, 1268. (b) Although CpW(CO)$_3$I is usually prepared by reaction of CpW(CO)$_3$H and I$_2$, the reaction of CpW(CO)$_3$K with I$_2$ was successfully used in this work to give 60% isolated yield.

(39) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(40) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

(41) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110.

(42) Reimer, K. J.; Shaver, A. *Inorg. Synth.* **1979**, *19*, 159.

(43) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1985**, *23*, 41.

(44) Shriver, D. F.; Drezdon, M. A. In *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

and the solution was cooled to −63 °C. Addition of $(n\text{-Bu})_4NOH$ (0.25 mL, 0.65 mmol) resulted in a slight color change to darker yellow. Spectroscopic yields were 75%, but warming of the solution resulted in a significant amount of Mr'_2, the predominant product observed when the reaction was run in THF.[12d] No isolated yield was determined.

Method III. In a Schlenk flask was placed **3c** (0.041 g, 0.10 mmol) followed by rapid addition of hexane or toluene (75 mL). Addition of *t*-BuLi (2 equiv) resulted in a color change of the solution from dark purple to yellow-green. Examination of the solution by IR spectroscopy revealed loss of **3c** and conversion to **2**. Spectroscopic yields were 80%, but no isolated yield was calculated.

Synthesis of Rr′Cl (5a). In a Schlenk flask was placed **8** (1.16 g, 2.00 mmol), followed by rapid addition of CH_2Cl_2 (50 mL). To this was added a solution of CH_2Cl_2 (20 mL) containing Me_3NO (0.38 g, 5.1 mmol) and $(n\text{-Bu})_4NCl$ (1.11 g, 4.00 mmol). The solution turned yellow as the reaction progressed. The products were adsorbed onto 60–200 mesh silica gel and eluted with CH_2Cl_2. After removal of the solvent by rotary evaporation, the product was recrystallized from CH_2Cl_2/hexane. The isolated yields were found to vary between 10 and 30%.

5a (isolated as yellow crystals): IR (CH_2Cl_2) ν_{CO} 1961, 1902 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (s, 18H, $C_6(CH_3)_6$); ^{13}C NMR (CD_3COCD_3, −75 °C): δ 199.12 (s, CO), 104.81 (s, $C_6(CH_3)_6$), 16.50 (q, CH_3, J = 130.1 Hz); EI MS m/z 440.057 45 (exact M: calcd for $C_{14}H_{18}O_2ClRe$ 440.055 29), 440 $[M]^+$, 405, 403 $[M - Cl]^+$, 384 $[M - 2CO]^+$, 337 $[M - 2CO - Cl]^+$, 279 $[M - (C_6(CH_3)_6)]^+$.

Synthesis of Rr′(C(CH₃)₃) (6). In a Schlenk flask was placed **5a** (0.044 g, 0.10 mmol), followed by rapid addition of toluene (30 mL). To this was added 2–4 equiv of *t*-BuLi (1.7 M, pentane) via syringe. The solvent was removed under reduced pressure, and the resulting yellow solids were extracted with hexane. After solvent removal the solids were purified by a two-step sublimation. The first sublimation, done at 50 °C to remove free hexamethylbenzene, was followed by sublimation of the product at 100 °C in 20% yield: IR (THF) ν_{CO} 1924, 1867 cm^{-1}; ^1H NMR (C_6D_6) δ 1.83 (s, 9H, CH_3), 1.78 (s, 18H, $C_6(CH_3)_6$); ^{13}C NMR (CD_3COCD_3, −75 °C) δ 204.84 (s, CO), 105.08 (s, $C_6(CH_3)_6$), 44.07 (q, $\mathit{C}(CH_3)_3$, J = 121.8 Hz), 17.23 (q, $C(\mathit{CH}_3)_3$, J = 127.5 Hz), 8.26 (s, CH_3); EI MS m/z 462.1562 (exact M; calcd for $C_{18}H_{27}O_2Re$ 462.1568), 462 $[M]^+$, 406 $[M - H_2C{=}(CH_3)_2]^+$, 447 $[M - CH_3]^+$, 432 $[M - 2CH_3]^+$, 419 $[M - CH_3 - CO]^+$, 376 $[M - H_2C{=}C(CH_3)_2) - 2CH_3$ or $M - 2CO - 2CH_3]^+$.

Synthesis of Rr′C₂H₅ (7). In a Schlenk flask was placed **5a** (0.044 g, 0.10 mmol), followed by rapid addition of THF (30 mL). To this was added 2–4 equiv of $K(C_2H_5)_3BH$ (1.0 M, THF) via syringe. The solvent was removed under reduced pressure to give $Rr'C_2H_5$: IR (THF) ν_{CO} 1926, 1868 cm^{-1}; ^1H NMR (CD_2Cl_2, −65 °C) δ 2.20 (s, $C_6(CH_3)_6$), 1.68 (t, $CH_2\mathit{CH}_3$, J = 7.42 Hz), 0.65 (q, CH_2CH_3, J = 7.40 Hz); ^{13}C NMR (CD_2Cl_2, −65 °C) δ 204.42 (s, CO), 104.79 (s, $C_6(CH_3)_6$), 24.67 (q, $CH_2\mathit{C}H_3$, J = 122.0 Hz), 16.05 (q, $(C_6(\mathit{CH}_3)_6$, J = 129.4 Hz), −11.12 (t, $\mathit{C}H_2CH_3$, J = 121.6 Hz); EI MS m/z 434.1260 (exact M; calcd for $C_{16}H_{23}O_2Re$ 434.1256), 434 $[M]^+$, 406 $[M - H_2C{=}CH_2 = Rr'H]^+$, 378 $[M - H_2C{=}CH_2 - CO]^+$.

Reaction of 2 with HOTf To Give Mr′OTf. In a Schlenk flask was placed **2** (0.013 g, 0.050 mmol), followed by rapid addition of hexane (75 mL). The solution was heated to 40 °C, and excess (2–4 equiv) HOTf was added in a dropwise fashion. The volatiles were removed under vacuum. Mr′OTf: IR (CH_2Cl_2) ν_{CO} 1992, 1941 cm^{-1}, IR (acetone) 1990, 1936 cm^{-1}.

Reaction of 9 with (*n*-Bu)₄NI. In a Schlenk flask was placed **9** (0.023 g, 0.055 mmol), followed by rapid addition of CH_2Cl_2 (50 mL). To this was added $(n\text{-Bu})_4NI$ (0.040 g, 0.11 mmol). The solution turned color rapidly from dark pink to red-orange. The solvent was removed under vacuum, yielding **3c**. The presence of **3c** was confirmed by IR and ^1H NMR spectroscopy.

Reaction of 9 with THF. In a Schlenk flask was placed **9** (0.027 g, 0.064 mmol), followed by rapid addition of THF (25 mL). The solution went through a rapid series of color changes from bright pink to red to pale yellow. The existence of $[Mr'THF]^+$[29] was confirmed by IR spectroscopy.

Reaction of 2 with HBF₄·Et₂O in CH₂Cl₂. In a Schlenk flask was placed **2** (0.051 g, 0.19 mmol), followed by rapid addition of CH_2Cl_2 (75 mL). The reaction mixture was cooled in an acetone/N_2(l) slurry. Upon addition of $HBF_4{\cdot}Et_2O$ (0.05 mL) the solution turned red. Warming of the solution or prolonged standing resulted in the formation of **3a** and **1**, as evidenced by IR spectroscopy.

Reaction of 2 with HBF₄·Et₂O in Diethyl Ether To Give [Mr′(OEt₂)]BF₄. In a Schlenk flask was placed **2** (0.029 g, 0.11 mmol), followed by rapid addition of diethyl ether (50 mL). The reaction mixture was cooled in an ice bath and was stirred. Upon addition of a solution of $HBF_4{\cdot}Et_2O$ (0.05 mL in 20 mL of ether) the solution turned red. The IR spectrum indicated that formation of $[Mr'OEt_2]BF_4$ had occurred: IR (diethyl ether) ν_{CO} 1990, 1935 cm^{-1}.

Reaction of [Mr′OEt₂]BF₄ with PMe₃. $[Mr'OEt_2]BF_4$, synthesized as detailed above, was combined with an excess of PMe_3 (2–4 equiv). An IR spectrum revealed bands corresponding to the formation of $[Mr'PMe_3]BF_4$[32] and the complete loss of $[Mr'OEt_2]BF_4$. The presence of $[Mr'PMe_3]BF_4$ was also confirmed by an ^1H NMR spectrum.

Reaction of 2 with *t*-BuLi To Give 10. A warm (45–50 °C), nearly saturated solution of **2** (0.137 g, 0.500 mmol) in hexane was prepared. To this solution was added dropwise *t*-BuLi (0.6 mL, 1.7 M in pentane). The solution became red upon contact, and within 2 min **10** precipitated as a red-brown solid. The warm bath was replaced with a cold bath, and the solution was stirred for 30 min. Excess base was removed by washing with hexane. This complex, which was never isolated, was used as quickly as possible due to extreme air and moisture sensitivity. **10**: IR (THF) ν_{CO} 1817, 1686 cm^{-1}.[45]

Reaction of 10 with [Mr′CO]PF₆ To Give Mr′₂. To a solution of **10** (0.040 g, 0.20 mmol) in THF (50 mL) was added a solution of **1** (0.090 g, 0.20 mmol) in 10 mL of THF. The yellow solution turned dark green immediately upon addition, and examination by IR spectroscopy revealed complete conversion to Mr'_2: IR (THF) ν_{CO} 1854, 1692 cm^{-1}.

Reaction of 2 with CpW(CO)₃X (X = Cl, I). In a Schlenk flask was placed **2** (0.027 g, 0.10 mmol), followed by rapid addition of THF (75 mL). This solution was added dropwise to a solution of $CpW(CO)_3X$ (0.10 mmol) in 50 mL of THF. Analysis by IR and ^1H NMR spectroscopy revealed spectra identical with the known products $CpW(CO)_3H$[14b] and **3c**[11,37] or **3a**.[11,37]

Reaction of 2 with FpX (X = Cl, I). In a Schlenk flask was placed **2** (0.027 g, 0.10 mmol), followed by rapid addition of THF (75 mL). This solution was added dropwise to a solution of FpX (0.10 mmol) in 50 mL of THF. Analysis by IR and ^1H NMR revealed spectra identical with the known products FpH[46] and **3a**[11,37] or **3c**.[11,37]

Reaction of 2 with Mn(CO)₅Br. In a Schlenk flask was placed **2** (0.027 g, 0.10 mmol), followed by rapid addition of THF (75 mL). This solution was added dropwise to a solution of $Mn(CO)_5Br$ (0.027 g, 0.10 mmol) in 50 mL of THF. Analysis by IR and ^1H NMR revealed spectra identical with the known products $HMn(CO)_5$[47] and **3b**.[11,37]

Reaction of 2 with Fp₂: Synthesis of Mr′Fp. In a Schlenk flask was placed **2** (0.027 g, 0.10 mmol), followed by rapid addition of THF (75 mL). To this solution was added a solution of Fp_2 (0.035 g, 0.10 mmol) in 50 mL of THF. The products observed were FpH and the new compound FpMr′: IR (THF) cis, ν_{CO} 1959, 1929, 1895, 1736 cm^{-1}, trans, ν_{CO} 1928, 1895, 1736 cm^{-1}; IR (hexane) cis, ν_{CO} 1962, 1936, 1903, 1744 cm^{-1}, trans, ν_{CO} 1936, 1903, 1744 cm^{-1}; ^1H NMR (C_6D_6) δ 4.567 (s, 5H), 1.738 (s, 18H), 0.284 (s, 5H); ^{13}C NMR (CD_3COCD_3) δ 288.1, 287.6 (CO bridge), 231.6, 229.6 (CO terminal), 109.5 (arene C), 108.7 (arene C), 89.1

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(45) The stretching frequencies of Mr′Li were reported incorrectly in ref 11.

(46) Green, M. L. H.; Street, C. N.; Wilkinson, G. *Z. Naturforsch., B* **1959**, *14*, 738.

(47) Hieber, W.; Wagner, G. *Z. Naturforsch., B* **1958**, *13*, 339.

(Cp ring C's), 18.0, 16.6, 15.2, 13.8 (C arene), cis and trans isomers; LREI MS *m/z* 451 [M + H]$^+$, 450 [M]$^+$, 394 [M − 2CO]$^+$, 339 [M − (4CO + H)]$^+$, 329 [M − (Cp + 2CO)]$^+$, 301 [M − (Cp + 3CO)]$^+$, 245 [M − CpFe(CO)$_3$]$^+$, 217 [M − CpFe(CO)$_4$]$^+$, 176 [M − Mr′]$^+$, 148 [M − Mr′CO]$^+$. The instability of this complex precluded a satisfactory elemental analysis.

X-ray Data Collection, Solution, and Refinement of 2 and 5a. Crystals of **2** were obtained as yellow needles by sublimation under reduced pressure. Crystals of **5a** were obtained by slow recrystallization from CH_2Cl_2/hexane. A summary of the crystal data and refinement parameters for **2** and **5a** is given in Table I. A crystal of **2** was sealed in a glass capillary tube under dinitrogen and mounted on the diffractometer. Graphite-monochromated Mo Kα radiation (average wavelength 0.710 73 Å) was used to collect data at 295 K on an Enraf-Nonius CAD4 diffractometer, using the ω scan range 0.80 + 0.35 tan θ, with background at 25% below and above the range; the horizontal aperture was varied from 2.0 to 2.5 mm, depending on the angle. The scan speed ranged from 1 to 7° min^{-1} for a hemisphere with θ ranging from 1 to 25°. Lorentz and polarization corrections were made (μ = 9.3 cm^{-1}). Three standards used to monitor crystal decay indicated a maximum decline in F of 2.4%; intensity corrections for decay were not made. A total of 9459 reflections were measured for the hemisphere ($\pm h, \pm k, \pm l$) in reciprocal space for 2θ ranging from 2 to 50°. A total of 1255 independent reflections greater than 3σ above background were used in the least-squares refinement.

The position of the manganese was located by Patterson methods. Positional parameters are reported in Table III. Subsequent cycles of least-squares refinement and difference Fourier calculations were used to locate all non-hydrogen atoms and half the hydrogens. During the final stages of refinement, the remaining hydrogen atom positions were calculated by assigning C–H distances of 0.95 Å and normalizing their positions with respect to located hydrogen atoms. A density peak in the difference electron maps indicated a possible position for the hydride ligand.[48] All other hydrogen atoms were found in the difference maps and placed in idealized positions. No solvent molecules were found. Anisotropic refinement on all non-hydrogen atoms (185 variables, including scale and extinction) gave R values of $R_1 = 0.042$ and $R_2 = 0.043$; the standard deviation of an observation of unit weight was 1.28, the maximum parameter shift/estimated error was less than 0.03, and the maximum peak height on the final electron density difference map was 0.56 e/Å^3. Weights used in refinement are $1/s^2(F)$, where $s^2(F) = s^2(F)' + [(\mathrm{PWT})F]^2$ (PWT = 0.04) is the estimate of the propagated error due to counting error plus the estimated error based on agreement of equivalent reflections (F = 0.013). The data were processed using scattering factor tables provided in the Enraf-Nonius SDP software on a MicroVax 2.[49]

Table III. Positional Parameters[a] and Their Estimated Standard Deviations for 2

atom	x	y	z	B (Å^2)
Mn	0.22209(6)	0.03341(7)	0.25000(8)	2.74(1)
C1	0.2142(5)	0.0982(6)	0.4490(5)	3.7(1)
C2	0.1269(5)	0.1553(6)	0.3761(6)	3.6(1)
C3	0.0522(5)	0.0819(6)	0.3041(6)	3.4(1)
C4	0.0630(5)	−0.0486(6)	0.3037(6)	3.3(1)
C5	0.1463(5)	−0.1074(6)	0.3760(6)	3.4(1)
C6	0.2230(5)	−0.0347(6)	0.4486(5)	3.5(1)
C7	0.2945(6)	0.1750(8)	0.5256(7)	5.7(2)
C8	0.1143(7)	0.2922(6)	0.3815(7)	5.3(2)
C9	−0.0386(5)	0.1432(7)	0.2282(7)	5.7(2)
C10	−0.0174(5)	−0.1253(6)	0.2241(7)	4.8(2)
C11	0.1538(7)	−0.2460(7)	0.3841(7)	5.3(2)
C12	0.3166(6)	−0.0983(8)	0.5208(7)	5.9(2)
C13	0.3600(5)	−0.0182(7)	0.2223(6)	4.3(1)
O13	0.4517(4)	−0.0464(6)	0.2022(5)	6.7(1)
C14	0.1935(6)	0.0206(6)	0.860(5)	3.7(1)
O14	0.1695(5)	0.0142(6)	−0.0215(4)	6.1(1)
HY	0.283(5)	0.140(5)	0.24(1)	4.0

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}$.

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Supplementary Material Available: Tables of H atom atomic coordinates, all bond angles, thermal parameters for non-H atoms, and deviations from least-squares planes and an additional ORTEP drawing for **2** and a table of atomic coordinates of non-H atoms and figures giving the numbering system and a ball and stick drawing for **5a** (12 pages). Ordering information is given on any current masthead page.

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[48] Although all other hydrogens were fixed in position, the hydride was refined by the least-squares program to a position closer to manganese than that normally expected. Placement of the hydride at a more normal distance and angular position did not lead to a significant increase in the R value.

[49] Frenz, B. A. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: College Station, TX, 1981.