π-Arene Complexes. 7.[1] Heterobimetallic Complexes of Chromium and Manganese with Bridging σ,π-Benzene and -Benzoyl Ligands

Simon Lotz,* Minet Schindehutte, and Petrus H. van Rooyen

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Received July 24, 1991

The complexes $[Cr\{\eta^6\text{-}C_6H_4XLi\}(CO)_3]$ (X = H (**a**), F (**b**)) react with $[Mn(CO)_5Br]$ to produce novel heterobimetallic compounds with bridging σ,π-benzoyl ligands, $(\eta^6\text{-}\{(CO)_5Mn\}C(O)C_6H_4X)Cr(CO)_3$ (**1**). When the reaction was executed in the presence of $P(OMe)_3$, complexes with a bridging benzoyl, $(\eta^6\text{-}\{(CO)_4(P(OMe)_3)Mn\}C(O)C_6H_5)Cr(CO)_3$ (**1c** (higher yield)), as well as a bridging phenyl ligand, $(\eta^6\text{-}\{(CO)_4(P(OMe)_3)Mn\}C_6H_5)Cr(CO)_3$ (**3c**), were obtained. By the refluxing of **1c** in hexane, it was converted quantitatively into **3c**. Using PPh_3 instead, the only product from the reaction was the unique complex $(\eta^6\text{-}\{(CO)_4(PPh_3)Mn\}C_6H_4X)Cr(CO)_3$ (**3a,b**). Bridging benzoyl complexes $(\eta^6\text{-}\{(CO)_3(L\frown L)Mn\}C(O)C_6H_5\}Cr(CO)_3$ were obtained with $L\frown L$ = dppe $(Ph_2PCH_2CH_2PPh_2)$ (**4a**) or $L\frown L$ = tmeda $(Me_2NCH_2CH_2NMe_2)$ (**4b**). The formation of $[(\eta^6{:}\eta^6\text{-}XC_6H_4C(O)C_6H_4X)\{Cr(CO)_3\}_2]$ (**2**) as a minor byproduct from the reactions which generated benzoyl dimers represents an interesting carbonyl-transfer reaction. Upon isolation of **1a** from a dichloromethane–hexane solution, the complex crystallizes in the orthorhombic space group $Pna2_1$, with a = 13.084 (2) Å, b = 6.089 (2) Å, c = 40.036 (5) Å, and Z = 8 with two molecules in the asymmetric unit. The structure of **1a** was determined from 5306 unique data ($0 \le h \le 18$, $0 \le k \le 8$, $0 \le l \le 56$), and refinement of 469 variables against 3521 observed ($>\sigma(I)$) data yielded R_w = 0.059. Recrystallization of the manganese–phosphorous complex **3a** from a dichloromethane–hexane solution yielded crystals that were orthorhombic, $Pbca$, with a = 17.217 (2) Å, b = 16.407 (5) Å, c = 20.530 (10) Å, and Z = 8. The structure of **3a** was determined from 8996 unique data ($0 \le h \le 24$, $0 \le k \le 22$, $0 \le l \le 28$), and refinement of 371 variables against 3465 observed ($>3\sigma(I)$) data yielded R_w = 0.035.

Introduction

The synthesis of heterobimetallic compounds constitutes a research area that is currently very active.[2] Because of the wide application of π-arene complexes of chromium in stereoselective[3] and regiocontrolled[4] syntheses, we became interested in the additional activation of π-bonded arene rings by its attachment to a second organometallic fragment.

Recently the preparation of heterobimetallic compounds utilizing $(\eta^6\text{-haloarene})Cr(CO)_3$ and anionic metal substrates, such as $Na_2[Fe(CO)_4]$,[5,6] $K_2[M(CO)_5]$[6] (M = W, Cr), $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$,[7,8] and $Na[Co(CO)_4]$,[9] was reported. However, the majority of monoanionic metal carbonyls failed to react, seriously limiting this approach as a general synthetic route to heterobimetallic complexes with bridging benzene and benzoyl ligands. This was ascribed to the weakness of the nucleophile[10] and is demonstrated by the failure of $Na[Mn(CO)_5]$, $Na[Ni(\eta^5\text{-}C_5H_5)CO]$, $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$, etc. to react with $(\eta^6\text{-}RC_6H_4Cl)Cr(CO)_3$.[7] Conversion of the η^6-arene ligand of $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ upon addition of pentacarbonylrhenate into a fluxional cyclohexadienyl-bridging ligand in the dimer $(\eta^5\text{-}\{(CO)_5Re\}C_6H_6)Mn(CO)_3$ was recently observed.[11]

The possibility of using $(\eta^6\text{-}C_6H_5Li)Cr(CO)_3$ in the reverse reaction with transition-metal halides seems a more attractive alternative route to neutral heterobimetallic complexes with bridging phenyl ligands. This aspect has apparently been neglected, presumably because of the expected weaker nucleophilicity of the arene[12] due to the electron-withdrawing effects of the chromium tricarbonyl fragment. The strong nucleophilic character of lithiated arenes of chromium is long known and was demonstrated by Fischer and co-workers[13] in their synthesis of the bimetallic carbene complex $(\eta^6\text{-}\{(CO)_5Cr\}C(OMe)C_6H_5)Cr(CO)_3$ and by Heppert and co-workers[5] in their preparation of the bimetallic lithium acyllate $Li[Cr(\eta^6\text{-}\{(CO)_4Fe\}C(O)C_6H_5)(CO)_3]$. The latter reacted with a variety of electrophiles, R^+, to produce mononuclear complexes, $(\eta^6\text{-}o\text{-}C_6H_4ClC(O)R)Cr(CO)_3$, with modified arene ligands. Many examples[14] of strong nucleophilic interaction of lithiated cyclopentadienyl complexes of iron and manganese have also been reported.

We selected, for this study, the reaction of $(\eta^6\text{-}C_6H_4XLi)Cr(CO)_3$ (X = H, F) with $[Mn(CO)_5Br]$ under

---

[1] Part 6: Schindehutte, M.; Van Rooyen, P. H.; Lotz, S. *Organometallics* **1990**, *9*, 293.

[2] Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41 and references therein.

[3] (a) Besancon, J.; Tiroflet, J.; Card, A.; Dusausoy, Y. *J. Organomet. Chem.* **1973**, *59*, 267. (b) Caro, B.; Jaouen, G. *J. Organomet. Chem.* **1982**, *228*, 87. (c) Solladie-Cavallo, A.; Sufferth, J. *Tetrahedron Lett.* **1984**, *25*, 1897. (d) Davies, S. G.; Bashiardes, G.; Beckett, R. P.; Coote, S. J.; Dordor-Hedgecock, I. M.; Goodfellow, C. L.; Gravatt, G. L.; McNally, J. P.; Whittaker, M. *Phil. Trans. R. Soc. London A* **1988**, *326*, 619 and references therein. (e) Rose-Munch, F.; Bellot, O.; Laurent, M.; Semra, A.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1991**, *402*, 1.

[4] (a) Semmelhack, M. F.; Bisaha, J.; Czarney, M. *J. Am. Chem. Soc.* **1979**, *101*, 768. (b) Widdowson, D. A. *Phil. Trans. R. Soc. London A* **1988**, *326*, 595 and references therein. (c) Ghavshou, M.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans.* **1983**, *1*, 3065.

[5] Heppert, J. A.; Thomas-Miller, M. E.; Swepston, P. N.; Extine, M. W. *J. Chem. Soc., Chem. Commun.* **1988**, 280.

[6] Heppert, J. A.; Thomas-Miller, M. E.; Scherubel, D. M.; Takusagawa, F.; Morgenstern, M. A.; Shaker, M. R. *Organometallics* **1989**, *8*, 1199.

[7] Heppert, J. A.; Morgenstern, M. A.; Scherubel, D. M.; Takusagawa, F.; Shaker, M. R. *Organometallics* **1988**, *7*, 1715.

[8] Richter-Addo, G.; Hunter, A. D.; Wichrowska, N. *Can. J. Chem.* **1990**, *68*, 41.

[9] (a) Galamb, V.; Palyi, G. *J. Chem. Soc., Chem. Commun.* **1982**, 487. (b) Galamb, V.; Palyi, G.; Ungvary, F.; Marko, L.; Boese, R.; Schmid, G. *J. Am. Chem. Soc.* **1986**, *108*, 3344.

[10] Dessey, R. E.; Pohl, R. C.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121.

[11] Niemer, B.; Steinmann, M.; Beck, W. *Chem. Ber.* **1988**, *121*, 1767.

[12] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 20.

[13] Fischer, E. O.; Gammel, F. J.; Neugebauer, D. *Chem. Ber.* **1980**, *113*, 1010.

[14] (a) Fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261. (b) Connor, J. A.; Lloyd, J. P. *J. Chem. Soc., Dalton Trans.* **1972**, 1740. (c) Härter, P.; Boguth, G.; Hertdweck, E.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1008. (d) Nesmeyanov, A. N.; Makarova, L. G.; Vinogradova, V. N. *Izv. Akad. SSSR* **1973**, *22*, 2796; *Engl. Transl.* 2731. (e) Fischer, E. O.; Postnov, V. N.; Kreissl, F. R. *J. Organomet. Chem.* **1982**, *231*, C73.

0276-7333/92/2311-0629$03.00/0

varied reaction conditions. The reaction was also executed in the presence of different monodentate and bidentate ligands, leading to the synthesis and structural analysis of the first examples of manganese σ-bonded to a π-coordinated benzene of (η^6-arene)$Cr(CO)_3$. In addition, these reactions gave evidence of the relative stabilities of bridging σ,π-coordinated benzene and benzoyl ligands in heterobimetallic complexes of chromium. Whenever a benzoyl heterobimetallic intermediate was eminent, the formation of the known complex,[15] (η^6:η^6-benzophenone)bis(tricarbonylchromium), as a minor product from the reaction was noted. Therefore, a carbonyl originating from the manganese precursor now links two (arene)chromium tricarbonyl fragments in the final product. Crystal structure determinations of the first examples of Cr–Mn dimers with bridging benzene and benzoyl ligands were undertaken and are reported.

We are presently extending the use of lithiated arenes of chromium to other transition-metal complexes containing halogen ligands but without carbonyls. Preliminary results[16] show that this approach provides an effective and more general route to synthesize heterobimetallic compounds of chromium with bridging arenes.

Experimental Section

Materials. All manipulations were performed under a dry, oxygen-free nitrogen atmosphere. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl prior to use, and other solvents were purified, degassed, and dried according to standard procedures. Reagent grade chemicals were used without further purification. Bromopentacarbonylmanganese(I) and bromobis(triphenylphosphine)tricarbonylmanganese(I) were prepared according to the methods by Angelici[17] and Abel and Wilkinson,[18] respectively. The arene complexes {η^6-benzene}tricarbonylchromium(0), (η^6-1,4-dibromobenzene)tricarbonylchromium(0), and the fluorobenzene derivative were synthesized according to published procedures.[19] NMR solvents were degassed by several freeze–pump–thaw cycles, and NMR tubes were sealed under nitrogen atmosphere. Elemental analyses were performed by the Analytical Division (PCMT) of the Council for Scientific and Industrial Research, Pretoria.

Instrumentation. Infrared spectra were recorded with a Bomem Michelson-100 FT spectrometer, mass spectra on a Perkin-Elmer RMU-6H instrument operating at 70 eV, and ^{1}H and ^{13}C NMR spectra with a Bruker 300 AC NMR spectrometer. Column chromatography on SiO_2 (0.063–0.200 mm) was performed on columns cooled by recycling cold (−20 °C) methanol through column jackets.

Synthesis. A. Reaction of (η^6-LiC_6H_4X)$Cr(CO)_3$ (X = H, F) with [$Mn(CO)_5Br$]. To a well-stirred THF solution of [(η^6-C_6H_6)$Cr(CO)_3$] (0.64 g, 3 mmol) maintained at −78 °C with a dry ice/acetone bath was added *n*-butyllithium (1.6 M in hexane, 1.87 mL, 3 mmol). Following the dropwise addition, the solution was allowed to warm slowly to −30 °C and stirring was continued for 20 min. The reaction mixture was again cooled (−78 °C) and added to a THF solution (−50 °C) of [$Mn(CO)_5Br$] (0.825 g, 3 mmol). The resulting solution was allowed to warm slowly to room temperature and was stirred for a further 30 min. The solvent was removed in vacuo and the deep red residue chromatographed on a silica gel column with hexane–dichloromethane (3:1) as eluent. The first yellow fraction was (η^6-C_6H_6)$Cr(CO)_3$. The subsequent orange band was collected, the solvent removed, and the product crystallized from dichloromethane–hexane to give (η^6-{$(CO)_5Mn$}$C(O)C_6H_5$)$Cr(CO)_3$ (**1a**): mp = 117 °C dec; 0.41 g, 0.94 mmol, 31%. Anal. Calc for $CrMnC_{15}H_5O_9$: C, 41.3; H, 1.15. Found: C, 41.7; H, 1.03. Further elution yielded a red band, which, after recrystallization from dichloromethane–hexane, was identified as (η^6:η^6-$C_6H_5C(O)C_6H_5$){$Cr(CO)_3$}$_2$ (**2**): mp = 164–168 °C; 0.28 g, 0.6 mmol, 20%. The same procedure was followed for the fluorobenzene derivative. Chromatography was executed with a 1:1 dichloromethane–hexane mixture, and products were collected as above. (η^6-{$(CO)_5Mn$}$C(O)C_6H_4F$)$Cr(CO)_3$ (**1b**): mp = 75–77 °C; 0.71 g, 1.5 mmol, 52%. Anal. Calc for $CrMnC_{15}H_4O_9F$: C, 39.7; H, 0.88. Found: C, 40.0; H, 0.81.

B. Reaction in the Presence of Other Ligands. (i) PPh_3. To a stirred solution of $Mn(CO)_5Br$ (1.38 g, 5 mmol) in THF (20 mL) at −30 °C was added a 5-mmol solution of (η^6-LiC_6H_4X)$Cr(CO)_3$ (see above for preparation). After 15 min, PPh_3 (1.31 g, 5 mmol) was added in small portions to the cooled solution with vigorous stirring. The reaction mixture was removed from the cold bath after 10 min and stirred at ambient temperature for 30 min before the solvent was removed under reduced pressure. The red brown crude product was subjected to chromatography on a silica gel column with dichloromethane–hexane (1:1) as eluent. The first yellow product eluted was identified as $Mn_2(CO)_{10}$, and the second fraction was found to be (η^6-C_6H_6)$Cr(CO)_3$. The next band, an orange fraction, was collected and the solvent removed to afford (η^6-{$(CO)_4(PPh_3)Mn$}C_6H_4X)$Cr(CO)_3$, X = H (**3a**): mp = 177–178 °C; 1.5 g, 2.3 mmol, 47%. Anal. Calc for $CrMnC_{31}H_{20}O_7P$: C, 57.9; H, 3.12. Found: C, 57.7; H, 3.01. *For X = F (**3b**), the same method was employed.* $CrMnC_{31}H_{19}O_7PF$: mp = 162–164 °C; 0.9 g, 1.3 mmol, 28%. Anal. Calc: C, 56.3; H, 2.87. Found: C, 55.9; H, 2.63. In addition a yellow compound, [$Mn(CO)_4${PPh_3}Br], formed in low yield and was identified spectroscopically.

(ii) $P(OMe)_3$. The same procedure as above for PPh_3 was used. The first yellow fraction was found to be (η^6-C_6H_6)$Cr(CO)_3$, and the next fraction afforded the orange product (η^6-{$(CO)_4${$P(OMe)_3$}Mn}C_6H_5)$Cr(CO)_3$ (**3c**), which was characterized by ^{1}H NMR and IR spectroscopy. The third fraction was the main product and, after recrystallization from dichloromethane–hexane mixtures, yielded (η^6-{$(CO)_4${$P(OMe)_3$}Mn}$C(O)C_6H_5$)$Cr(CO)_3$ (**1c**): mp = 94–95 °C; 1.1 g, 2.1 mmol, 69%. Anal. Calc for $CrMnC_{17}H_{14}PO_{11}$: C, 38.3; H, 2.63. Found: C, 39.1; H, 2.72.

(iii) To a stirred solution of $Mn(CO)_3(PPh_3)_2Br$ (2.23 g, 3 mmol) in THF (30 mL) at −30 °C was added dropwise a 3-mmol solution of (η^6-LiC_6H_5)$Cr(CO)_3$ (see part A for preparation). After the reaction mixture had been stirred for 40 min, it was removed from the cold and stirred at room temperature for another 1 h. The solvent was removed, and the orange-brown product was chromatographed on a silica gel column with dichloromethane–hexane (1:1) as eluent. The first yellow band yielded unreacted chromium starting material, while the next yellow fraction afforded (η^6-{$(CO)_3(PPh_3)_2Mn$}(C_6H_5)$Cr(CO)_3$ (**3d**): 0.95 g, 1.08 mmol, 36%.

C. Reactions in the Presence of Bidentate Ligands. (i) dppe. To a stirred solution of [$Mn(CO)_5Br$] (0.83 g, 3 mmol) in THF (30 mL) at −30 °C was added a 3-mmol solution of (η^6-LiC_6H_5)$Cr(CO)_3$ (see above for preparation). After 10 min, $Ph_2PCH_2CH_2PPh_2$ (1.2 g, 3 mmol) was added to the cooled solution in small portions with vigorous stirring. The reaction mixture was removed from the cold after 15 min and stirred at room temperature for a further 30 min whereafter the solvent was removed in vacuo. The crude product was chromatographed on a silica gel column with dichloromethane–hexane (1:1) as eluent. Again the first yellow fraction yielded unreacted (η^6-C_6H_6)$Cr(CO)_3$. The next orange band was collected and the solvent removed to give (η^6-{$(CO)_3(Ph_2\overline{PCH_2CH_2PPh_2)Mn}$}$C(O)C_6H_5$)$Cr(CO)_3$ (**4a**): mp = 90–91 °C; 1.22 g, 1.6 mmol, 52%. Anal. Calc for $CrMnC_{39}H_{29}P_2O_7$: C, 60.2; H, 3.73. Found: C, 60.7; H, 4.01. The last red band afforded the known compound **2**.

(ii) tmeda. To a stirred solution of $Me_2NCH_2CH_2NMe_2$ (0.76 mL, 5 mmol in 5 mL of THF) at −78 °C was added *n*-butyllithium (1.6 M in hexane, 1.87 mL, 3 mmol). Following the addition, the solution was allowed to slowly warm to ca. −30 °C and stirring was continued for 10 min. This solution was added to a well-stirred THF solution of (η^6-C_6H_6)$Cr(CO)_3$ (0.64 g, 3 mmol) at −78 °C *and stirred for 20 min while the temperature was raised to* −40 °C. The reaction mixture was again cooled (−78 °C) and added to a THF solution of [$Mn(CO)_5Br$] (1.38 g, 3 mmol). The products

---

(15) Also prepared by three different methods: (a) Seyferth, D.; Merola, J. S.; Eschbach, C. S. *J. Am. Chem. Soc.* **1978**, *100*, 4124. (b) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1979**, *182*, 381. (c) Yang, X.; Huang, J.; Huang, J. *Jiegou Huaxue* (J. Struct. Chem.) **1985**, *4*, 60.

(16) Reaction of (η^6-C_6H_4XLi)$Cr(CO)_3$ with $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $Au(PPh_3)Cl$ afforded binuclear π-arene complexes of chromium.

(17) Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 160.

(18) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501.

(19) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 1a and 3a

	1a	**3a**
empirical formula	$CrMnC_{15}H_5O_9$	$CrMnC_{31}H_{20}O_7P$
mol wt	439.08	642.41
cryst dimens, mm	0.13 × 0.20 × 0.60	0.21 × 0.27 × 0.36
space group	$Pna2_1$	*Pbca*
cell dimens		
a, Å	13.084 (2)	17.217 (2)
b, Å	6.089 (2)	16.407 (5)
c, Å	40.036 (5)	20.530 (10)
V, Å^3	3189 (1)	5672 (1)
Z	8	8
D_{calc}, g·cm^{-3}	1.829	1.504
μ(Mo Kα), cm^{-1}	14.35	8.73
F(000)	1727.9	2607.9
zones collcd		
h	0, 18	0, 24
k	0, 8	0, 22
l	0, 56	0, 28
scan type (ω:2θ ratio)	1:1	3:1
scan angle ω, deg	0.57 + 0.34 tan θ	0.44 + 0.34 tan θ
no. of measd reflcns	5306	8996
no. of unique reflcns used	3521, $>\sigma(I)$	3465, $>3\sigma(I)$
no. of params refined	469	371
Δs/esd(max)	0.67	0.02
R_w [2σ(*F*) weights)]	0.059	0.035
R	0.091	0.055

were separated chromatographically as above to yield $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (**2**) and $[(\eta^6\text{-}\{(CO)_3(Me_2\overline{NCH_2CH_2NMe_2)Mn}\}C(O)C_6H_5)Cr(CO)_3]$ (**4b**): mp = 146–148 °C; 0.9 g, 1.9 mmol, 37%. Anal. Calc for $CrMnC_{19}H_{21}N_2O_7$: C, 45.9; H, 4.23. Found: C, 46.5; H, 4.51.

D. Reaction of $(\eta^6\text{-}(1,4\text{-}Li_2C_6H_4))Cr(CO)_3$ with $[Mn(CO)_5Br]$. To a THF (50 mL) solution of $(\eta^6\text{-}(1,4\text{-}C_6H_4Br_2))Cr(CO)_3$ (0.74 g, 2 mmol) at −78 °C was added 2.2 equiv of *n*-BuLi (3.1 mL, 4.4 mmol). After the mixture had been stirred for 10 min at low temperature, the temperature was raised to −20 °C and stirring was continued for 20 min. The resulting orange-yellow solution was added dropwise to a stirred solution of 2 equiv $MnBr(CO)_5$ (1.1 g, 4 mmol) in THF at −78 °C. The dark brown mixture was stirred for 0.5 h at −50 °C, removed from the cold, and allowed to reach room temperature, while being stirred vigorously. After 1 h the solvent was removed at low pressure and the red-brown oil was extracted with cold (0 °C) hexane (3 × 20 mL). The combined hexane extracts were filtered through Celite, and the hexane was evaporated in vacuo. The yellow oily product was identified as $(\eta^6\text{-}\{(CO)_5MnC(O)\}_2C_6H_4)Cr(CO)_3$ (**1d**). The remaining yellow-orange solid was extracted with ether (at 25 °C) and filtered, and the solvent was evaporated in vacuo, to leave an orange oil which could not be crystallized and decomposed extensively in solution, leading to it being discarded.

E. Decarbonylation of $(\eta^6\text{-}\{(CO)_4(P(OMe)_3)Mn\}C(O)C_6H_5)Cr(CO)_3$. A hexane (50 mL) suspension of $(\eta^6\text{-}\{(CO)_4(P(OMe)_3)Mn\}C(O)C_6H_5)Cr(CO)_3$ (**1c**) (1.06 g, 2 mmol) was refluxed at 60 °C. The reaction was monitored by the disappearance of the band at 1584 cm^{-1} in the infrared, and the conversion was quantitative after 4 h. The yellow powder obtained after removal of the solvent was characterized as $(\eta^6\text{-}\{(CO)_4(P(OMe)_3)Mn\}C_6H_5)Cr(CO)_3$ (**3c**).

X-ray Structural Determinations. The unit cell dimensions were obtained by the refinement of the setting angles of 25 reflections, with $12 \le \theta \le 22°$ for **1a** and 17 of the 25 reflections with $14 \le \theta \le 17°$ for **3a**. Applying ω–2θ scan techniques and Mo Kα radiation (λ = 0.7107 Å) on an Enraf Nonius CAD4 diffractometer with an aperture of 1.3 × 4.0 mm, the intensity data for **1a** and **3a** were collected at 22 °C in the range $3 \le \theta \le 30°$. The crystal data and refinement parameters are listed in Table I.

A variable but maximum scan speed of 5.49° min^{-1} and a maximum scan time of 60 s per reflection were employed for both crystals. The positions of three control reflections were remeasured every 200 intensity measurements (reorientation limit 0.1°), and the hourly intensity controls indicated a decay of 2.8% for **1a** and 1% for **3a** (uncorrected). Azimuthal scans were recorded at the end of the data collection for nine reflections of **1a** near χ 90° in 10° increments of rotation of the crystal along the diffraction vector. The EAC factors used for **1a** were 0.999 maximum, 0.923 minimum, and 0.970 average. The data for **3a** were not corrected for absorption.

The data were corrected for Lorentz and polarization effects. The structures were solved by conventional Patterson and Fourier techniques using SHELX86.[20a] All the non-hydrogen atoms in both structures were refined anisotropically,[20b] and the hydrogen atoms were placed in calculated positions and refined with a common isotropic thermal parameter for each structure that converged to U_{iso} = 0.073 (3) Å^2 for **1a** and U_{iso} = 0.082 (4) Å^2 for **3a**. The hydrogen atoms were constrained to ride upon their associated non-hydrogen atoms. The final difference maps were essentially featureless, with all the peaks >1 e Å^{-3} approximately 1 Å from the metal atoms.

Results and Discussion

Although a number of heterobimetallic complexes have been reported with σ,π-arene ligands, no examples for Cr and Mn bridged in a σ,π-fashion by benzene or benzoyl ligands are known. As far as we are aware, the only other known examples containing bridging benzene ligands π-bonded to chromium and σ-bonded to another metal, $[Et_4N][(\eta^6\text{-}\{(CO)_5M\}C_6H_5Cr(CO)_3]$[6] (M = W, Cr) and $[(\eta^6\text{-}\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}RC_6H_4)Cr(CO)_3]$,[7,8] were synthesized from anionic transition-metal precursors by Heppert and Hunter and their co-workers. To overcome the restrictions encountered by Heppert[9] with respect to the strength of the nucleophile, we utilized the strong nucleophilic properties of lithiated arene chromium compounds in reactions with electrophilic complexes. By using transition-metal substrates with both carbonyl and halide ligands, such as $[Mn(CO)_5Br]$, two potential sites of nucleophilic attack by the lithiated arene reagents exist. Attack on the metal and subsequent exclusion of the bromide leads directly to the formation of an intermediate with a bridging σ,π-benzene ligand. Alternatively, the reaction on a carbonyl, followed by the release of the bromide and arene migration onto the manganese, also generates a σ,π-benzene ligand. Nucleophilic attack on a carbonyl ligand or the migration of the σ-coordinated phenyl to an adjacent carbonyl in the presence of an available ligand could lead to the formation of a bimetallic intermediate which contains a bridging σ,π-benzoyl ligand. Discrimination between these pathways was not attempted. On the grounds of the high yields obtained and the relatively few other reaction products from the reactions, a free-radical mechanism is unlikely.

The reactions of $(\eta^6\text{-}LiC_6H_4X)Cr(CO)_3$ and $[Mn(CO)_5Br]$ in THF (Scheme I) yielded the heterobimetallic compounds $[(\eta^6\text{-}\{(CO)_5Mn\}C(O)C_6H_4X)Cr(CO)_3]$ (X = H (**1a**), F (**1b**)). The orange crystalline compounds are stable under inert atmosphere and were purified by column chromatography and recrystallized from dichloromethane–hexane mixtures. Spectroscopic data of these and the other new complexes depicted in Scheme I are listed in Tables II and III. In addition to **1**, a second product, the known bis(tricarbonylchromium) dimer, **2**[15] (vide infra), was formed. Several attempts to isolate and unambiguously show spectroscopically that an anionic intermediate, $[\{Br(CO)_4MnC(O)C_6H_5\}Cr(CO)_3]^-$, with a bridging, σ,π-benzoyl ligand or any other anionic intermediate, was formed initially were unsuccessful. The reaction of PhLi with $[Mn(CO)_5Br]$ yielded the colorless complex $[Mn(Ph)(CO)_5]$,[21] which was previously isolated

---

(20) (a) Sheldrick, G. M. SHELX86. A program for the solution of crystal structures. University of Göttingen, Federal Republic of Germany, 1986. (b) Sheldrick, G. M. SHELX76 Program for crystal structure determination. University of Cambridge, England, 1976.

(21) Hieber, W.; Lindner, E. *Chem. Ber.* **1962**, *95*, 273.

Table II. Infrared and Mass Spectral Data of the Bimetallic Complexes

	infrared ν(CO),[a] cm^{-1}							
	Cr(CO)$_3$		Mn(CO)$_n$			M–C(O)		
complex	A	E	A	B	E	A		obsd mass peaks,[b] m/e values
1a	1977 (m)	1909 (s)	2122 (w)	2064 (vw)	2027 (s), 2021 (s)	2021[e] (s)	1593 (m)	436 (m$^+$, 8), 408 (7), 352 (8), 324 (8), 268 (24), 240 (16), 212 (28), 184 (54), 130 (23), 129 (42)
1b[c]	1980 (s), 1963 (m)	1892 (vs, br)	2129 (w)	2052 (s)	2036 (vs)	2011 (m)	1607 (w)	454 (m$^+$, 1), 426 (3), 370 (36), 342 (30), 314 (10), 286 (71), 258 (22), 230 (67), 203 (18), 202 (100)
	1962 (s)	1886 (vs)	2128 (m)	2072 (vw)	2040 (vs)	2010 (s)	1611 (m)	
			A	A	B	B		
1c[d]	1976 (s)	1888 (vs), 1872 (vs)	2085 (m)	2012 (s)	1988 (s)	1949 (s)	1584 (m)	532 (m$^+$, 2), 504 (70), 448 (20), 420 (68), 392 (64), 364 (75), 336 (7), 308 (100), 278 (76), 253 (84), 246 (41), 256 (23), 253 (84), 246 (41), 221 (14), 191 (18), 184 (33), 154 (20), 129 (63)
1d	1974 (s)	1918 (vs, br)	2117 (w)	2100 (vw)	2049 (s), 2020 (s)	2012 (s)	1583 (w), 1579	
2	1992 (m), 1979 (m)	1913 (s, br)					1647 (w)	454 (m$^+$, 1), 426 (1), 398 (22), 342 (27), 314 (61), 286 (67), 234 (69), 182 (2), 121 (4)
			A	A	B	B		
3a	1983 (s), 1970 (s)	1877 (vs, br)	2090 (w), 2075 (w)	2027 (s)	2006 (s)	1953 (s)		642 (m$^+$, 2), 586 (1), 558 (1), 530 (3), 484 (4), 454 (3), 446 (30), 428 (28), 422 (32), 394 (84), 372 (26), 352 (12), 316 (8), 262 (100), 214 (18), 184 (32), 183 (87), 130 (27)
3b	1956[e] (bs, br)	1877 (vs)	2080 (s)	2011 (s)	1991 (s)	1956[e] (vs, br),		
3c	1973 (s)	1868 (vs)	2098 (w), 2084 (w)	2014 (s)	1989 (s)	1951 (s)		504 (m$^+$, 25), 448 (s), 420 (23), 392 (19), 364 (27), 336 (3), 308 (100), 278 (25), 256 (10), 253 (38), 246 (12), 184 (10), 129 (22)
			A	E				
3d	1967 (vs)	1887 (vs)	2075 (w)	2004 (w)	1950 (s)			
4a	1960 (s)	1897 (vs, br)	2023 (s)	2002 (s)	1972 (s)		1572 (w)	778 (m$^+$, 1), 694 (1), 666 (1), 638 (2), 582 (3), 530 (9), 453 (10), 398 (46), 370 (16), 289 (32), 184 (10), 183 (67), 130 (36)
4b	1973 (s), 1957 (vw)	1879 (vs), 1825 (w)	2052 (s)	2028 (s)	2007 (s)		1588 (w)	

[a] Spectra recorded as solutions in CH_2Cl_2. Bands were sometimes split, and both values were recorded and are given next to each other. Abbreviations: v = very, w = weak, m = medium, s = strong, and br = broad. [b] For fragmentation pattern and peak assignments, see text. Intensities relative to principle ion peak are in given parentheses. [c] Second set of values were recorded in hexane. [d] Values were recorded in Nujol. [e] Uncertainty in value due to overlapping of bands.

from the thermal decarbonylation of [Mn{C(O)Ph}(CO)$_5$].[22]

We had expected the fluorine-substituted derivative (η^6-LiC$_6$H$_4$F)Cr(CO)$_3$ to be less reactive than the unsubstituted lithiated arene reagent, due to the presence of the very electronegative fluorine, but surprisingly, with the same reaction conditions, better yields of **1b** were obtained. This result was ascribed to the more efficient generation of the lithiated fluoro arene. When *t*-BuLi, instead of *n*-BuLi, was used to effect metalation,[23] extremely low yields of the anticipated product were obtained under the same reaction conditions.

The ^{1}H NMR spectrum for **1a** is consistent with the adoption of a substituted η^6-arene bonding mode displaying a characteristic AA′BB′X pattern at room temperature with the ortho, para, and meta resonances appearing at 5.94, 5.80 and 5.70 ppm in acetone-d_6, respectively. Notable is the relative position of the chemical shifts for the bridging benzoyl ligand in **1a** of the order $o > p > m$, which corresponds with the sequence found for monosubstituted (benzene)tricarbonylchromium derivatives with electron-withdrawing substituents.[24] The chemical shifts, their splitting patterns, and $^nJ_{FC}$ coupling constants suggest an ortho-substituted benzoyl dimer for **1b**. This is expected, as lithiation under these reaction conditions occurs ortho to the electronegative fluorine atom.[4,23] The influence of the fluorine substituent on the resonances of free or π-coordinated fluorobenzene is of the order $m > o > p$.[25] In **1b** the combined effect of the fluorine and the manganese substituent is demonstrated by a change in the ordering of chemical shifts for **1b**: m_F ($p_{C(O)Mn}$) > o_F > m_F ($o_{C(O)Mn}$) > p_F. The positions most affected are o_F and o_{Mn}, which became deshielded and shielded, respectively. The ^{13}C NMR spectra for **1a** and **1b** show two distinct resonances for the carbonyl ligands, with the resonance near 235 ppm representing the Cr(CO)$_3$ fragment and the resonance near 210 ppm arising from the Mn(CO)$_5$ unit. The benzoyl carbonyl resonates near 270 ppm for **1a**, and the position of the chemical shift of the *ipso*-carbon (manganese) is near 130 ppm for **1b** and 110 for **1a**. The difference of ca. 20 ppm illustrates the pronounced affect of the fluorine atom of the arene ligand on the *ipso*-carbon. Thus, not only the chemical shifts but the magnitude of the coupling constants, $^nJ_{FC}$, is determined by the fluorine substituent and compares with

---

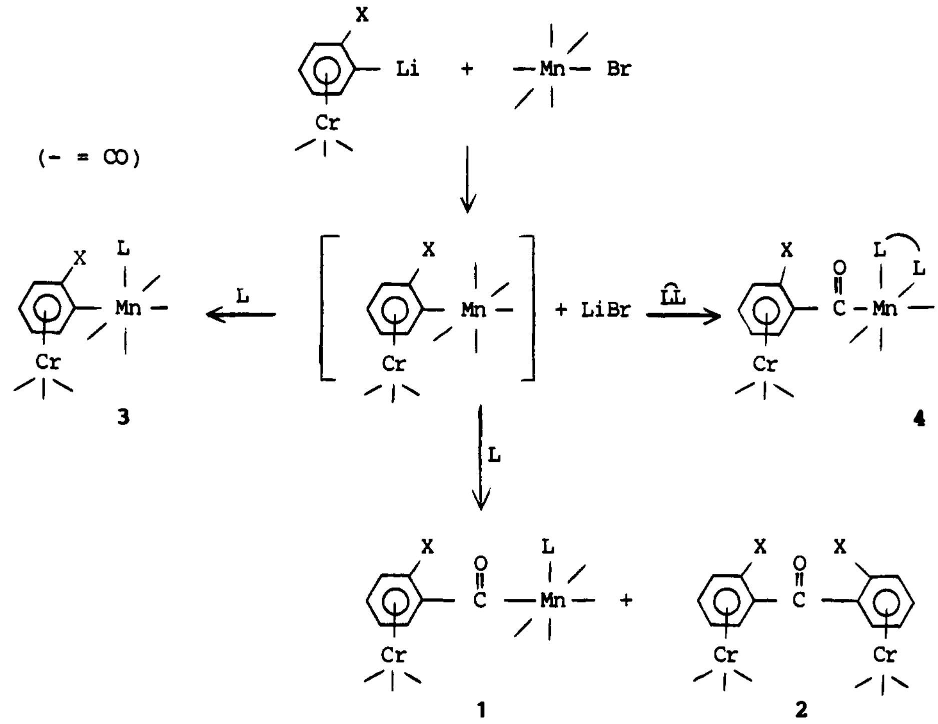
(22) Coffield, T. H.; Kozikowski, J.; Closson, R. D. *J. Org. Chem.* **1957**, *22*, 598.

(23) (a) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2560. (b) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2555. (c) Heppert, J. A.; Thomas-Miller, M. E.; Milligan, M. L.; Van der Velde, D.; Aube, J. *Organometallics* **1988**, *7*, 2581.

(24) Mangini, A.; Taddei, F. *Inorg. Chim. Acta* **1968**, *2*, 8.

(25) (a) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, Germany, 1979; p 256. (b) ^{1}H NMR (CDCl$_3$, 25 °C) of (η^6-C$_6$H$_5$F)Cr(CO)$_3$: δ 5.48 (*m*, m, H), 5.29 (*o*, m, 2 H), 4.36 (*p*, m, 1 H).

Scheme I



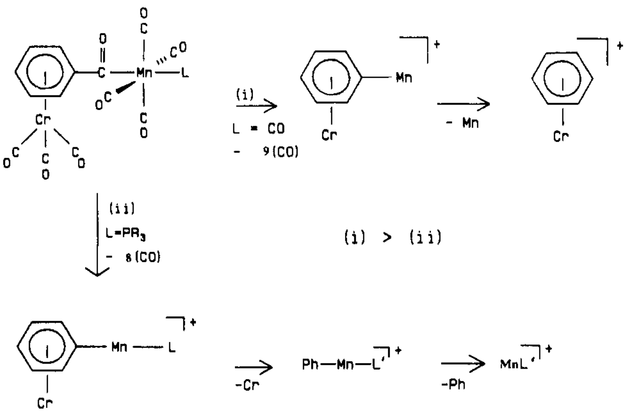
	X	L		X	L
1a	H	CO	3b	F	PPh$_3$
1b	F	CO	3c	H	P(OMe)$_3$
1c	H	P(OMe)$_3$	4a	H	Ph$_2$PCH$_2$CH$_2$PPh$_2$
2	H	-	4b	H	Me$_2$NCH$_2$CH$_2$NMe$_2$
3a	H	PPh$_3$			

values reported for C$_6$H$_5$F,[26] (η^6-C$_6$H$_5$F)Cr(CO)$_3$,[27] and (η^6-C$_6$H$_4$MeF)Cr(CO)$_3$.[28]

The IR spectra of **1a** and **1b** display the anticipated CO stretching bands of virtual A and E symmetry for the Cr(CO)$_3$ moiety and A, B, and E symmetry for the Mn(CO)$_5$ moiety. The band at 1593 cm^{-1} was assigned to the carbonyl of the benzoyl ligand and compares with the values of 1595 and 1613 cm^{-1} recorded for the anionic complex NEt$_4$[(η^6-{(OC)$_4$Fe}C(O)C$_6$H$_4$Cl)Cr(CO)$_3$][5] and (η^6-1,3-C$_6$H$_4${C(O)Mn(CO)$_5$}$_2$),[29] respectively.

The pattern which emerges from the mass spectra of **1a** and **1b** has interesting aspects associated with the fragmentation of the bridging arene ligand and is represented by pathway i in Scheme II. Initially all the carbonyls from both metals were lost successively from the parent ions (m/e = 436 (**1a**), 454 (**1b**)). The mass peak for **1a** at m/e = 184, which corresponds to the fragment ion {Cr(η^6-C$_6$H$_5$)Mn}$^+$, indicates that the carbonyl of the bridging benzoyl ligand was lost simultaneously. This also applies for **1b**. In a systematic investigation of the mass spectral measurements of π-bonded organometallic compounds of chromium, iron, and manganese, similar results were recorded for the fragmentation of the π-arene and -cyclopentadienyl complexes containing a carbonyl in the α-position to the π-ligand.[30] The σ-bond between the manganese and the π-arene was cleaved next as was deduced from the absence of a peak at m/e 132 corresponding to the fragment ion {MnC$_6$H$_5$}$^+$, while the peak at m/e 129 was assigned to {Cr(η^6-C$_6$H$_5$)}$^+$.

Scheme II



Final confirmation of the structure of **1a** was found in a single-crystal X-ray diffraction study. The structure solution for **1a** could only be accomplished in the noncentered space group *Pna*2$_1$. Attempts using SHELX86[20a] (heavy-atom and direct methods) as well as MULTAN80[31]

---

(26) Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C-NMR Spektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1984; p 524.

(27) ^{13}C NMR ((CD$_3$)$_2$CO, 25 °C) of (η^6-C$_6$H$_5$F)Cr(CO)$_3$: δ 148 (*i*, d, $^1J_{FC}$ = 264.0 Hz), 95.7 (*m*, d, $^3J_{FC}$ = 7.4 Hz), 89.0 (*p*, s), 81.4 (*o*, d, $^2J_{FC}$ = 19.6 Hz).

(28) Sandilands, L. M.; Lock, C. J. L.; Faggiani, R.; Hao, N.; Sayer, B. G.; Quilliam, M. A.; McCarry, B. E.; McGlinchey, M. J. *J. Organomet. Chem.* **1982**, *224*, 267.

(29) Hunter, A. D.; Szigety, A. B. *Organometallics* **1989**, *8*, 2670.

(30) (a) Mandelbaum, A.; Cais, M. *Tetrahedron Lett.* **1964**, *51*, 3847. (b) Maoz, N.; Mandelbaum, A.; Cais, M. *Tetrahedron Lett.* **1965**, *52*, 2087.

(31) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Universities of York, England, and Louvain, Belgium, 1980.

Table III. ^1H NMR and Selected ^{13}C NMR Data[a] of the Bimetallic Complexes 1–4

		^1H chem shifts, δ (ppm)				
complex	solvent	π-arene[b]				others
		m	o	p		
1a	CD_3SOCD_3	5.74 (t, 2 H)	6.29 (d, 2 H)	6.12 (t, H)		
	CD_3COCD_3	5.70 (t, 2 H)	5.94 (d, 2 H)	5.80 (t, H)		
		p (Mn)	o (F)	o (Mn)	(F)	
1b	$CDCl_3$	5.45 (m, H)	5.37 (m, H)	5.29 (m, H)	4.86 (m, H)	
	CD_3COCD_3	5.89 (m, H)	5.76 (m, H)	5.68 (m, H)	5.18 (m, H)	
		m	o	p		$\underline{P(OMe)_3}$
1c	$CDCl_3$	5.25 (m, 2 H)	5.72 (d, 2 H)	5.41 (m, H)		3.76 (d, 9 H, J_{PH} = 11.4)
	CD_3COCD_3	5.59 (t, 2 H)	5.83 (d, 2 H)	5.71 (t, H)		3.84 (d, 9 H, $^3J_{PH}$ = 10.6)
1d	C_6D_6		4.34 (s, 4 H)			
2	CD_3SOCD_3	5.76 (t, 2 H)	6.20 (d, 2 H)	6.09 (t, H)		
	C_6D_6	4.16 (t, 2 H)	5.49 (d, 2 H)	4.42 (t, H)		
	CD_3COCD_3	5.68 (t, 2 H)	6.31 (d, 2 H)	5.98 (t, H)		
						$\underline{PPh_3}$
3a	CD_3COCD_3	5.16 (t, 2 H)	5.38 (d, 2 H)	5.30 (t, H)		7.58–7.41 (m, 15 H)
	$CDCl_3$	4.91 (t, 2 H)	5.19 (d, 2 H)	5.09 (t, H)		7.47–7.26 (m, 15 H)
		p (Mn)	o (F)	o (Mn)	p (F)	
3b	CD_3COCD_3	5.53 (m, H)	5.39 (m, H)	5.33 (m, H)	4.72 (m, H)	7.56–7.39 (m, 15 H)
		m	o	p		$\underline{P(OMe)_3}$
3c	CD_3COCD_3	5.40 (t, 2 H)	5.65 (d, 2 H)	5.60 (m, H)		3.92 (d, 9 H, $^3J_{PH}$ = 11.1)
						$\underline{2PPh_3}$
3d	CD_3COCD_3	5.67 (t, 2 H)	5.78 (d, 2 H)	5.57 (t, H)		7.39–7.26 (m, 30 H)
						$\underline{Ph_2PCH_2CH_2PPh_2}$
4a	$CDCl_3$	4.97 (t, 2 H)	5.41 (d, 2 H)	5.28 (t, H)		7.65–7.26 (m, 20 H), 3.44 (m, H), 3.12 (m, H), 2.74 (m, 2 H)
						$\underline{Me_2NCH_2CH_2NMe_2}$
4b	$CDCl_3$	5.34 (m, 2 H)	5.65 (m, 2 H)	5.46 (m, H)		2.77 (s, 12 H), 2.54 (s, 4 H)

[a] Deuterated solvents were used as internal references, and chemical shifts are relative to TMS. Coupling constants in Hertz. Abbreviations: s = singlet, d= doublet, t = triplet, m = multiplet, o = ortho, m = meta, p = para, i = ipso, br = broad. [b] Positions relative to substituents in parentheses. [c] Not discernible as a result of poor S/N. [d] Not observed.

Table IV. Selected Bond Distances (Å) and Valence Angles (deg) for 1a (Averaged for Both Molecules in the Asymmetric Unit)

Bond Distances			
Cr–C(carbonyl)	1.845	(Cr)C–O(carbonyl)	1.150
Cr–C(arene)	2.217	C(arene)–C(arene)	1.400
C(9)–C(10)	1.519	C(10)–O(4)	1.241
C(10)–Mn	2.076	Mn–C(carbonyl)	1.874
(Mn)C–O(carbonyl)	1.119	Cr–CNTR	1.721
Bond Angles			
C(9)–C(10)–Mn	126.0	Mn–C–O	175.9
C–Mn–C(cis)	90.0	Cr–CNTR–C(arene)	90.0
C–Mn–C(trans)	176.0	CNTR–C(9)–C(10)	177.3
C(carbonyl)–Cr–C(carbonyl)	88.0		

(also including the complete molecule in NORMAL as a fragment) failed to produce any solution in the centered space group *Pnma*. The value for $|E^2 - 1|$ was 0.784 for all data, and the calculated theoretical values for acentric and centric sets were 0.736 and 0.968, respectively. The solution in the space group $Pna2_1$ was thus accepted as the correct solution. The asymmetric unit of **1a** contains two molecules that are mirror images, but essentially similar, although some significant differences are noticeable. The crystallographic data were influenced by the relative poor quality of the crystals and the presence of the long *c* axis but were adequate to allow analysis of the averaged molecular parameters. An ORTEP representation of the structure of **1a** is shown in Figure 1, and selected bond lengths and angles are given in Table IV. The final atomic coordinates of the non-hydrogen atoms of **1a** are given in Table VI.

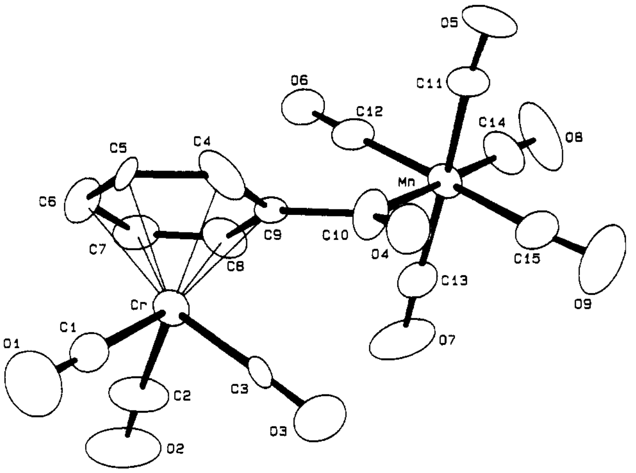


Figure 1. Perspective drawing of the molecular structure of $(\eta^6\text{-}\{(CO)_4Mn\}C(O)C_6H_5)Cr(CO)_3$ (**1a**, molecule A).

The mean Cr–C(arene), Cr-C(carbonyl), and CrC–O distances of 2.217, 1.845, and 1.150 Å respectively, are

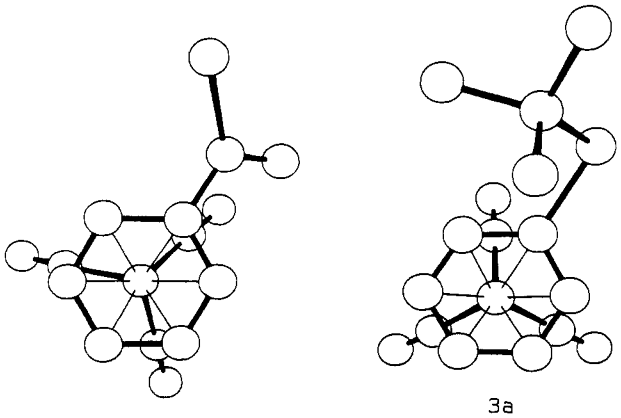
^{13}C chem shifts, δ (ppm)								
$Cr(CO)_3$	$Mn(CO)_n$	M–C(O)	π-arene[b]					others
			i	m	o	p		
237.7	206.4	268.1	109.6	95.6	94.0	87.9		
				p (Mn)	o (F)	o (Mn)	p (F)	
233.6	207.6	x[c]	150.8 (F) (d, $^1J_{CF}$ = 263), 129.3 (Mn)	93.7 (d, $^3J_{CF}$ = 8.3)	80.9 (d, $^2J_{CF}$ = 30.9)	107.2 (d, $^3J_{CF}$ = 10.9)	89.5	
				m	o	p		
231.8	211.7 (br)	260.4 (d, $^2J_{PC}$ = 36)	115.3	89.7	93.0	93.9		53.4 (d, $^2J_{PC}$ = 7.2)
233.6	213.0 (br)	262.4 (d, $^1J_{PC}$ = 36.1)	119.0	92.2	94.0	95.8		54.2 (d, $^2J_{PC}$ = 7.4)
		263.0 262.8	108.5		92.4			
232.2		186.8	98.9	91.6	97.2	97.3		
234.9	211.8		128.6 (d, $^2J_{PC}$ = 3.7)	93.5	109.0 (d, $^3J_{PC}$ = 4.2)	92.3		132.0 ($^1J_{PC}$ = 37), 133.4, 129.7, 131.9
				p (Mn)	o (F)	o (Mn)	p (F)	
235.8	214.8 (br)		152.6 (F) (d, $^1J_{CF}$ = 264), 129.3 (Mn) (dd, $^2J_{CF}$ = 39.3) ($^2J_{PC}$ = 5.3)	95.8 (d, $^3J_{CF}$ = 10)	82.5 (d, $^2J_{CF}$ = 30.9)	110.0 (dd, $^3J_{CF}$ = 15.2) ($^3J_{PC}$ = 4.8)	90.7	130.1 ($^1J_{PC}$ = 45), 134.2, 129.7, 131.9
				m	o	p		
236.5	213.9 (br)		110.3 (d, $^3J_{PC}$ = 5.2)	95.7	93.8	96.7		54.1 (d, $^2J_{PC}$ = 7.5)
234.7	216.3 (br)		128.8 (d, $^2J_{PC}$ = 10.9)	95.2	91.5 (d, $^3J_{PC}$ = 8.1)	93.4		134.4 ($^2J_{PC}$ = 19.9), 129.4 ($^3J_{PC}$ = 7.5), 129.7
232.2	219.0	279.3	108.4	87.9	95.6	96.0		130.4 ($^1J_{PC}$ = 96), 131.7, 128.9, 130.1, 27.1 (t, $^1J_{PC}$ = 20.5), 26.1 (t, $^1J_{PC}$ = 20.4)
235.8	209.9	x[d]	109.5	91.4	96.5	96.9		60.9 (NCH_2–), 56.4 (NCH_3)

Table V. Selected Bond Distances (Å) and Valence Angles (deg) for 3a

Bond Distances			
Cr–C(carbonyl)	1.830	(Cr)C–O(carbonyl)	1.154
Cr–C(arene)	2.228	C(arene)–C(arene)	1.409
C(9)–Mn	2.103	(Mn)C–O(carbonyl)	1.143
Mn–C(carbonyl)	1.828	Cr–CNTR	1.727
Bond Angles			
C(carbonyl)–Cr–C(carbonyl)	89.2	Cr–CNTR–C(arene)	90.0
CNTR–C(9)–Mn	175.4	C–Mn–C(cis)	89.5
C–Mn–C(trans)	177.2	Mn–C–O	176.9

typical for simple mononuclear η^6-coordinated arene complexes (values for (η^6-$C_6H_5CO_2Me$)$Cr(CO)_3$: 2.217 (3), 1.842 (3), 1.155 (4) Å, respectively).[32] The Cr–CNTR (the calculated centroid of the aromatic ring) distance of 1.721 Å, as well as the averaged Cr–CNTR–C(arene) angle of 90.0°, confirms the planar η^6-coordination of the arene ligand.

The carbonyl of the benzoyl deviates by more than 34° from the arene plane, probably as a result of the steric interaction between C(15) and O(4) (nonbonded distance = 2.721 Å; C(15)–Mn–C(10)–O(4) torsion angles = 23 (1)°). Figure 2 shows a veiw along the Cr–CNTR vector, displaying the slight deviation from the syn-eclipsed conformation, expected for an electron-donating ring substituent.[33] The C(9)–CNTR–Cr–C(3) torsion angle is 13.8°. Similar bond distances of 1.124 (2) Å for MnC–O-(acyl) and 1.52 (2) Å for C(arene)–CO were found for 1a when compared with the corresponding distances in [(η^6:η^6-$C_6H_5C(O)C_6H_5$){$Cr(CO)_3$}$_2$] (1.215 (6), 1.496 (6) Å).[15c]



1a

3a

Figure 2. Perspective views of 1a and 3a along the Cr–arene bond.

---

(32) Saillard, J.-Y.; Grandjean, D. *Acta Crystallogr.* **1976**, *B32*, 2285.

(33) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* **1982**, *82*, 499.

Table VI. Fractional Coordinates ($\times 10^4$) and Equivalent Thermal Factors ($Å^2 \times 10^3$) for Compound 1a

	x/a	y/b	z/c	U_{eq}[a]
CrA	1553 (2)	1483 (3)	10000	26 (1)
CA(1)	2065 (11)	3232 (19)	10342 (4)	35 (1)
OA(1)	2401 (11)	4305 (17)	10553 (3)	72 (1)
CA(2)	2655 (10)	−370 (17)	10077 (5)	51 (1)
OA(2)	3366 (8)	−1467 (16)	10113 (4)	77 (1)
CA(3)	2312 (10)	3090 (21)	9717 (4)	39 (1)
OA(3)	2825 (8)	4219 (17)	9540 (3)	64 (1)
CA(4)	10 (13)	2584 (20)	9845 (5)	48 (1)
CA(5)	−6 (10)	2173 (18)	10188 (3)	26 (1)
CA(6)	247 (11)	92 (18)	10308 (4)	39 (1)
CA(7)	598 (9)	−1431 (18)	10065 (4)	36 (1)
CA(8)	666 (10)	−1024 (17)	9719 (4)	36 (1)
CA(9)	368 (8)	1146 (16)	9608 (3)	19 (1)
CA(10)	421 (12)	1707 (18)	9243 (4)	36 (1)
OA(4)	644 (8)	3676 (13)	9191 (3)	40 (1)
MnA	−69 (2)	−224 (3)	8845 (1)	27 (1)
CA(11)	−1224 (9)	1544 (18)	8846 (4)	31 (1)
OA(5)	−1876 (8)	2682 (15)	8827 (4)	48 (1)
CA(12)	−747 (11)	−2129 (19)	9144 (5)	38 (1)
OA(6)	−1167 (8)	−3314 (15)	9308 (3)	42 (1)
CA(13)	1184 (11)	−1756 (18)	8883 (5)	36 (1)
OA(7)	1977 (10)	−2553 (15)	8909 (5)	77 (1)
CA(14)	−523 (13)	−1978 (21)	8492 (5)	50 (1)
OA(8)	−794 (11)	−2814 (16)	8276 (3)	83 (1)
CA(15)	598 (11)	1743 (20)	8578 (4)	38 (1)
OA(9)	975 (11)	3016 (15)	8397 (4)	72 (1)
CrB	1016 (2)	−1453 (3)	1381 (1)	26 (1)
CB(1)	506 (11)	−3228 (19)	1056 (4)	40 (1)
OB(1)	128 (10)	−4333 (16)	858 (3)	59 (1)
CB(2)	−122 (9)	330 (23)	1329 (6)	76 (1)
OB(2)	−788 (7)	1421 (16)	1277 (4)	78 (1)
CB(3)	244 (12)	−3131 (19)	1687 (5)	45 (1)
OB(3)	−263 (9)	−4044 (18)	1867 (4)	78 (1)
CB(4)	2512 (10)	−2574 (18)	1555 (4)	24 (1)
CB(5)	2622 (12)	−2128 (20)	1223 (5)	52 (1)
CB(6)	2303 (10)	−206 (24)	1086 (4)	68 (1)
CB(7)	1986 (10)	1503 (17)	1311 (3)	31 (1)
CB(8)	1915 (10)	1082 (17)	1661 (3)	29 (1)
CB(9)	2168 (11)	−1029 (17)	1777 (4)	30 (1)
CB(10)	2171 (8)	−1608 (17)	2151 (3)	20 (1)
OB(4)	1975 (9)	−3540 (14)	2214 (3)	42 (1)
MnB	2627 (2)	473 (3)	2528 (1)	27 (1)
CB(11)	3786 (11)	−1437 (18)	2558 (4)	41 (1)
OB(5)	4487 (10)	−2523 (16)	2588 (5)	82 (1)
CB(12)	3329 (10)	2328 (18)	2227 (4)	27 (1)
OB(6)	3789 (8)	3411 (15)	2059 (3)	51 (1)
CB(13)	1380 (10)	1929 (18)	2480 (4)	33 (1)
OB(7)	626 (7)	2676 (15)	2477 (4)	45 (1)
CB(14)	3040 (12)	2188 (21)	2871 (5)	48 (1)
OB(8)	3315 (10)	3404 (17)	3086 (4)	73 (1)
CB(15)	1911 (12)	−1423 (20)	2836 (4)	46 (1)
OB(9)	1531 (10)	−2459 (15)	3006 (4)	58 (1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_ia_j)$.

The long Mn–C(acyl) distance of 2.07 (2) Å shows little carbene character and is significantly longer than the Mn–C(carbene) distance of 1.96 (1) Å recorded for *cis*-$[Mn(CO)_4\{COCH_2CH_2O\}Cl]$.[34] Although this bond length is shorter than the 2.207 (6) Å found for the acyl of the five-membered chelate ring in $[Mn\{C(O)CH_2CH_2PPh_2\}(dppm)(CO)_2$,[35] it is identical to the 2.062 (7) Å reported for the σ-coordinated acyl ligand in $[Mn\{P(OPh)_3\}_3(CO)_2\{C(O)H\}]$.[36]

The reaction was also carried out in the presence of mono- and bidentate ligands to create conditions suitable for the promotion of phenyl migration. When the reaction was performed in the presence of $P(OMe)_3$, the main product was the corresponding heterobimetallic benzoyl complex, **1c**. In addition, the less stable complex $[(\eta^6\text{-}\{(CO)_4\{P(OMe)_3\}Mn\}C_6H_5)Cr(CO)_3]$ (**3c**) was isolated in very low yield. Thermal decarbonylation of the benzoyl dimer **1c** in hexane produced the benzene dimer **3c** in quantitative yields. It is well documented that acylmanganese complexes are effective sources of alkylmanganese compounds through stereospecific decarbonylation.[37] The possible photochemical decarbonylation of **1** or carbonylation of **3** under positive CO pressure was not attempted and is a matter of further investigations.

Contrary to expectations, the addition of PPh_3 gave the target complexes **3a** and **3b** with bridging benzene ligands in improved yields. Neither the corresponding benzoyl analogue nor significant amounts of **2** formed, and the only other product was $Mn_2(CO)_{10}$. From these results, we inferred that CO substitution on the manganese by PPh_3 before or after the attack of $(\eta^6\text{-}C_6H_4XLi)Cr(CO)_3$ to give **3a** and **3b** are not only favored but also stabilizes the bridging σ,π-benzene ligand. Haszeldine and co-workers[38] showed that the acyl $[Mn\{C(O)Ph\}(CO)_4PPh_3]$ was very unstable at room temperature and decarbonylated to the stable *cis*-$[Mn(Ph)(CO)_4PPh_3]$. Further support for the fact that the phosphine ligand inhibits phenyl migration followed from the results of the reaction of $[Mn(PPh_3)_2(CO)_3Br]$ with $(\eta^6\text{-}C_6H_5Li)Cr(CO)_3$, which again only yielded a benzene-bridged dimer. The complex **3d** was far less stable than **3a** or **3b** and could only be characterized spectroscopically. A carbonyl ligand was displaced without C_5H_5 migration in a similar reaction when $[(\eta^5\text{-}\{(CO)_5Mn\}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ was treated with excess triphenylphosphine.[39] The IR spectra of complexes **3a** and **3b** exhibit four bands, with relative intensities characteristic for compounds of the type *cis*-$LL'M(CO)_4$ with the arene ring and substituting ligand in mutually cis positions. This geometry is in accordance with results obtained by Dobson that CO is lost preferentially from this cis position in $[Mn(CO)_5Br]$.[40] The lower wavenumbers recorded for the carbonyl stretching vibrations of the $Mn(CO)_4$ fragment in the IR spectra of **3a** and **3b** compared to **1a** and **1b** are expected on account of an increase in back-bonding to the remaining carbonyls on the manganese unit after substitution of a carbonyl by PPh_3. Lower frequencies are also registered for the $Cr(CO)_3$ fragment, indicating a greater flow of electron density from the metal-substituted arene to the chromium fragment in these complexes. The absence of the acyl stretching band in the IR spectrum of **3c**, obtained from the reaction which also afforded **1c** or from the decarbonylation of **1c**, as well as the observed shift of the terminal CO bands to lower wavenumber compared to corresponding bands for **3c**, confirms the loss of carbon monoxide from **3c**. The IR spectrum for the decarbonylated product is identical to that for the product obtained in low yield in the general reaction, and both indicate that the cis product is formed exclusively, with the bridging benzene and phosphite ligand mutually cis. Since it is known that proton chemical shifts reflect the π-electron densities[41] on the carbon atoms to which the

---

[34] Green, M.; Moss, J. R.; Nowell, I. W.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1339.

[35] Carriedo, G. A.; Parra Sotta, J. B.; Riera, V.; Solans, X.; Miravitlles, C. *J. Organomet. Chem.* **1985**, *297*, 193.

[36] Berke, H.; Huttner, G.; Scheidsteger, O.; Weiler, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 735.

[37] (a) Drew, D.; Darensbourg, M. V.; Darensbourg, D. J. *J. Organomet. Chem.* **1975**, *85*, 73. (b) Calderazzo, F.; Noack, K. *Coord. Chem. Rev.* **1966**, *1*, 118. (c) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (d) Johnson, R. W.; Pearson, R. G. *J. Chem. Soc., Chem. Commun.* **1970**, 986. (e) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87.

[38] Booth, B. L.; Green, M.; Haszeldine, R. N.; Woffenden, N. P. *J. Chem. Soc. A* **1969**, 920.

[39] Herberhold, M.; Kniesel, H. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1988; Vol. 4, p 169.

[40] Dobson, G. R.; Brown, R. A. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2785.

protons are attached, it can be deduced that the manganese group lowers the amount of charge on the substituted benzene ring in **3a** to a lesser extent than the acylmanganese group (**1**). The protons on the arene ligand of **3** are shielded to a greater extend compared to the corresponding arene precursor. This correlates with electronegativity differences and results from the replacement of a proton of the arene ligand by the manganese moiety. Whereas an order of $o > m, p$ was recorded for Na[(η^6-{(CO)$_4$Fe}C$_6$H$_5$)Cr(CO)$_3$][7] and [(η^6-C$_6$H$_5$Fp)Cr(CO)$_3$][8] (Fp = (η^5-C$_5$H$_5$)Fe(CO)$_2$), the relative positions of the chemical shifts for the bridging arene protons in **3a** are $o > p > m$.

Assignment of the signals in the ^{1}H and ^{13}C spectra of **3b** was frustrated because of insufficient information concerning the relative substituent effects of the fluorine and Mn(CO)$_4$(PPh$_3$) unit. Allocation of the resonances on the basis of coupling constants was not unambiguous, as some uncertainty exists in the literature concerning the carbon-13 chemical shift assignments in related compounds.[7] However, a two-dimensional ^{1}H–^{13}C shift correlation experiment for **3b** allows a complete unambiguous assignment of the ^{1}H and ^{13}C resonances. The complete assignments are indicated in Table II. Further distinction among the ortho and meta signals is made possible by ^{31}P–^{13}C coupling considerations, since only the carbon atoms directly bonded or ortho to the manganese experience a resolvable ^{31}P–^{13}C coupling. Using the estimated chemical shift values and ^{31}P–^{13}C and ^{19}F–^{13}C coupling considerations as criteria,[26] the assignment of the carbon resonances is accomplished. These assignments correspond to those reported by Hunter[8] for (η^6-C$_6$H$_5$Fp)Cr(CO)$_3$. The δ values of the chemical shifts in the ^{13}C NMR spectra of the Mn–C(ipso) resonances for **3a–c** (ca. 129 ppm) fall within the range of values recorded for Fe–C(ipso) (118–132 ppm) in the compounds 1,4-C$_6$H$_4$Fp$_2$, 1,3-C$_6$H$_4$Fp$_2$, and 1,3,5-C$_6$H$_3$Fp$_3$ (Fp = (η^5-C$_5$H$_4$R)Fe(CO)$_2$).[42] Discrepancies are possible in the C_i(Mn) resonances of compounds with phosphorus-containing ligands on manganese because of the low intensities of signals for the nonprotonated carbons attached to the metal.

A different fragmentation pattern is observed in the mass spectra for **1c**, **3a**, and **3c**. Similar fragmentation patterns were observed for **1c** and **3c** in their mass spectra with the only difference being the higher molecular ion peak for **1c**. In addition to the fragmentation pathway i, a second pathway ii of lesser significance (peaks are of lower intensities than those for pathway i was found and is also represented in Scheme II. According to this route, fragmentation of the π-arene bond to chromium takes preference over the σ-arene–manganese bond, as shown by peaks at m/e 394 and 317, which correspond to the fragment ions {Mn(C$_6$H$_5$)(PPh$_3$)}$^+$ and {Mn(PPh$_3$)}$^+$, respectively. Whereas the PPh$_3$ ligand was cleaved as an entity, the P(OMe)$_3$ fragmented in smaller units while remaining coordinated to the metal.

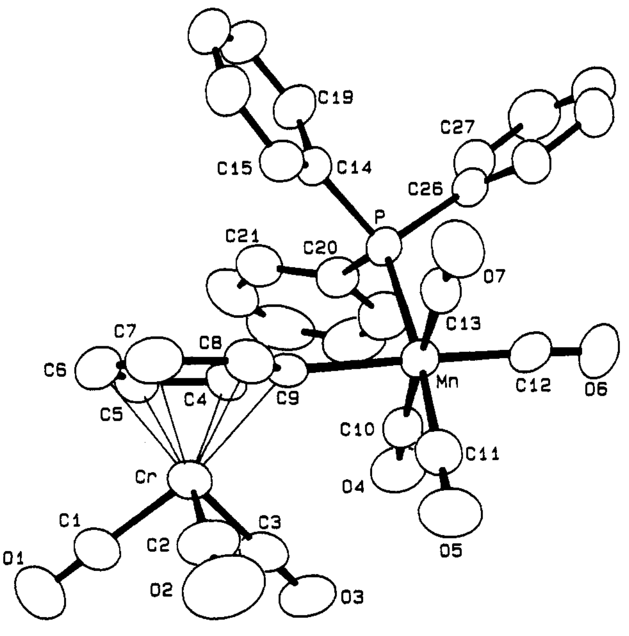


Figure 3. Perspective drawing of the molecular structure of (η^6-{(CO)$_4$(Ph$_3$P)Mn}C$_6$H$_5$)Cr(CO)$_3$ (**3a**).

Table VII. Fractional Coordinates (×10^4) and Equivalent Thermal Factors (Å^2 × 10^3) for Compound 3a

	x/a	y/b	z/c	U_{eq}[a]
Cr	1803 (1)	10756 (1)	3336 (1)	50 (1)
C(1)	2142 (3)	11773 (4)	3616 (3)	64 (2)
O(1)	2354 (3)	12422 (3)	3773 (2)	95 (1)
C(2)	1403 (4)	10539 (4)	4143 (3)	68 (2)
O(2)	1128 (3)	10400 (3)	4649 (2)	101 (2)
C(3)	870 (3)	11235 (3)	3120 (3)	52 (2)
O(3)	289 (2)	11543 (2)	2983 (2)	70 (1)
C(4)	2001 (3)	10412 (3)	2304 (2)	46 (1)
C(5)	2689 (3)	10746 (4)	2566 (3)	65 (2)
C(6)	3020 (3)	10379 (4)	3122 (3)	79 (2)
C(7)	2640 (4)	9722 (4)	3432 (3)	75 (2)
C(8)	1952 (3)	9402 (3)	3158 (3)	52 (1)
C(9)	1613 (3)	9713 (3)	2579 (2)	40 (1)
Mn	651 (1)	9146 (1)	2128 (1)	38 (1)
C(10)	360 (3)	10171 (3)	1802 (3)	50 (1)
O(4)	125 (2)	10786 (3)	1614 (2)	71 (1)
C(11)	107 (3)	9399 (3)	2859 (3)	53 (1)
O(5)	−228 (3)	9554 (3)	3323 (2)	85 (1)
C(12)	−191 (3)	8694 (3)	1730 (3)	45 (1)
O(6)	−739 (2)	8436 (3)	1481 (2)	67 (1)
C(13)	896 (3)	8136 (3)	2493 (3)	45 (1)
O(7)	1014 (2)	7507 (2)	2744 (2)	62 (1)
P	1461 (1)	8871 (1)	1216 (1)	38 (1)
C(14)	2433 (3)	8432 (3)	1333 (2)	42 (1)
C(15)	2694 (3)	8187 (3)	1944 (3)	49 (1)
C(16)	3426 (3)	7807 (3)	2010 (3)	61 (2)
C(17)	3886 (3)	7695 (4)	1469 (3)	71 (2)
C(18)	3625 (3)	7942 (4)	872 (3)	73 (2)
C(19)	2900 (3)	8302 (4)	792 (3)	61 (2)
C(20)	1634 (3)	9801 (3)	723 (2)	47 (1)
C(21)	2342 (4)	10201 (4)	696 (3)	64 (2)
C(22)	2414 (5)	10936 (4)	335 (3)	82 (2)
C(23)	1795 (5)	11242 (4)	−2 (3)	95 (3)
C(24)	1084 (4)	10858 (5)	31 (3)	86 (2)
C(25)	1012 (4)	10143 (4)	391 (3)	65 (2)
C(26)	1072 (3)	8120 (3)	630 (2)	44 (1)
C(27)	1135 (3)	8220 (4)	−40 (3)	62 (2)
C(28)	887 (3)	7599 (5)	−457 (3)	76 (2)
C(29)	579 (3)	6877 (5)	−224 (3)	79 (2)
C(30)	513 (3)	6772 (4)	440 (3)	70 (2)
C(31)	759 (3)	7382 (3)	858 (3)	57 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_ia_j)$.

The structure of **3a** is depicted in the ORTEP drawing in Figure 3, and selected bond distances and bond angles are given in Table V. The final atomic coordinates of the non-hydrogen atoms of **3a** are given in Table VII. The average Cr–C(arene) distance is 2.228 Å and compares with the average Cr–C(arene) distance of 2.217 Å in **1a**.[43a] Within the Cr–arene ring the average C–C distances is 1.409 Å with no systematic trend that could be ascribed to localized olefinic bonding properties. The C(3)–Cr–

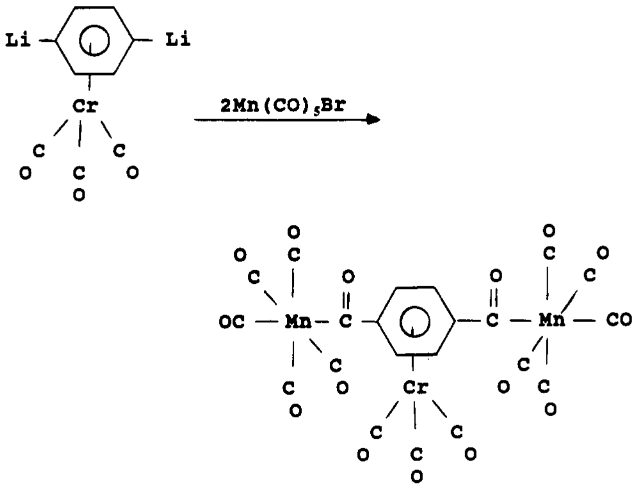
---

(41) Wu, A.; Biehl, E. R.; Reeves, P. C. *J. Chem. Soc., Perkin Trans.* **1972**, *2*, 449.

(42) Hunter, A. D.; McLernon, J. L. *Organometallics* **1989**, *8*, 2679.

(43) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146. A systematic search of the Cambridge Data Base yielded the following: (a) the average Cr–C(arene) distance of 2.227 Å for 139 entries of (arene)tricarbonylchromium complexes; (b) 140 entries; (c) from 428 P–Mn fragment entries.

Scheme III



CNTR–C(4) and C(3)–Cr–CNTR–C(9) torsion angles of 28.7 (3) and −34.2 (3)°, respectively, are indicative of a staggered conformation of the chromium tricarbonyl fragment relative to the arene ring, which is usually found for $(\eta^6\text{-}C_6R_6)Cr(CO)_3$ (R = H, Me) complexes.[44] This conformation is also displayed in Figure 2. By contrast, a much smaller deviation was recorded for $NEt_4[(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3$.[5]

A noteworthy structural feature of **3a** ascribed mainly to the close proximity of the arene and phosphine ligands is the exceptionally long Mn–C(9) bond distance of 2.103 (5) Å relative to the average Mn–C(sp^2) distance of 1.985 Å.[43b] This bond is comparable to the Mn–C(acyl) distance of **1a** and the distances of 2.097 (9) and 2.040 (9) Å recorded for σ-bonded phenyl ligands in the metallacyclic complexes $[Mn\{C_6H_3(Me)P(C_6H_4Me)_2\}(CO)_4]$[45] and $[Ph_2P\{C_6H_3(CO)Mn(CO)_3PPh_3\}Mn(CO)_4]$,[46] respectively. The Mn–C(carbonyl) trans to the phosphine and σ-bonded arene ligands are the shortest of the manganese–carbon(carbonyl) bonds—both are 1.816 (5) Å. The average of the other two Mn–C(carbonyl) distances of 1.840 (6) Å is similar to the corresponding distance of 1.84 (2) Å recorded for $[Mn(CO)_4(PPh_3)Cl]$.[47] The Mn–P bond distance of 2.375 (1) Å is typical of P–Mn(CO)$_n$ complexes when compared to the reported average distance of 2.313 Å.[43c]

Reactions performed in the presence of chelating diphosphines (dppe) or diamines (tmeda) induced phenyl migration and afforded complexes with bridging benzoyl ligands, **4a**,**b**, respectively. Spectroscopic data of **4** were very similar to those of the mono-substituted derivatives **1**, the largest deviation occurring in the positions of the resonances recorded in the IR and ^{13}C NMR spectra for the Mn(CO)$_3$ fragment. Metalation of $(\eta^6\text{-}1,4\text{-}C_6H_4Br_2)Cr(CO)_3$ with *n*-BuLi and its subsequent reaction with 2 molar equiv of Mn(CO)$_5$Br afforded $[\{Mn(CO)_5\}_2(\mu\text{-}\eta^1{:}\eta^1{:}\eta^6\text{-}p\text{-}\{C(O)\}_2C_6H_4)Cr(CO)_3]$ (**1d**) in low yield according to Scheme III. The yellow-orange compound is extremely air- and light-sensitive and soluble in most organic solvents but only sparingly soluble in pentane. The trimetallic complex **1d** is the first example of a symmetrically substituted arene complex of chromium containing two manganese acyl groups analogous to the (arene)chromium complex with two dicarbonylcyclopentadienyliron (Fp) groups, $(1,4\text{-}C_6H_4Fp_2)Cr(CO)_3$,[42,48] and the uncomplexed manganese acyl species, $1,4\text{-}C_6H_4\{C(O)Mn(CO)_5\}_2$,[29] reported by Hunter and co-workers.

The binuclear complex ($\eta^6{:}\eta^6$-benzophenone)bis(tricarbonylchromium) (**2**), also prepared previously according to three alternative methods,[15] was formed in varying quantities from all reactions involving $(\eta^6\text{-}C_6H_5Li)Cr(CO)_3$ and intermediates which resulted in benzoyl dimers. A single-crystal X-ray analysis of **2** was reported on crystals obtained by refluxing Cr(CO)$_6$ and benzophenone in decane.[15c] Additional spectroscopic data of **2** are listed in Tables II and III. Although our particular interest is not in the bis(chromium) compound as such, the mechanism whereby this compound was formed was intriging enough to warrant some attention. A plausible route is the attack of a second lithiated chromium reagent on the activated (via metal coordination) electrophilic carbon of the carbonyl of the bridging benzoyl ligand, followed by the release of the manganese fragment, which finally leads to the formation of **2**. According to this proposed pathway for the reaction, a carbonyl from [Mn(CO)$_5$Br] is transferred and ultimately acts as a link between two (benzene)tricarbonylchromium fragments. When the order was reversed during preparation by adding [Mn(CO)$_5$Br] to a solution of the lithiated chromium substrate, the yield of **2** was greatly increased. In a control experiment to determine the origin of the carbonyl, *n*-butyllithium was reacted with $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ without addition of any other reagent. The dimeric benzophenone did not form, thereby excluding the chromium tricarbonyl as a possible source of transfering a carbonyl to the arene ligand via a intermolecular mechanism.[49] The only product isolated from this reaction in low yield was the known complex $\{\eta^6{:}\eta^6\text{-}(C_6H_5\text{–}C_6H_5)\}\{Cr(CO)_3\}_2$.[50] In the formation of the analogous $(\eta^6{:}\eta^6\text{-}\{(C_6H_3RF)_2C(O)\}\{Cr(CO)_3\}_2$ (R = H, Me) from the reaction of $(\eta^6\text{-}LiC_6H_3RF)Cr(CO)_3$ and MeOC(O)Cl, Lock, McGlinchey, and co-workers[28] postulated the existence of a dianionic intermediate with a carbene functionality, which, after intramolecular rearrangement, gave the final product. A simpler pathway would involve the formation of a neutral intermediate $(\eta^6\text{-}C_6H_3RFC(O)OMe)Cr(CO)_3$ followed by the attack of a second lithiated arene and the sequential liberation of the methoxy group to afford the corresponding dimer. These steps represent a similar route to that proposed above. The fact that **2** is absent from the reaction in which the intermediate $Et_4N[(\eta^6\text{-}\{(CO)_4Fe\}C(O)C_6H_5)Cr(CO)_3]$ was formed[5] is obvious, as attack from the lithiated η^6-arene on an anionic intermediate is unlikely. We found further proof of this phenomenon from the reaction of $(\eta^6\text{-}LiC_6H_5)Cr(CO)_3$ with the cationic substrate $[(\eta^5\text{-}C_5H_5)Mn(CO)_2NO]^+BF_4^-$, where product **2** again formed.[49] These observations suggest that product **2** could always be expected to form as a byproduct when a neutral intermediate with a π-coordinated, activated benzoyl ligand is simultaneously present in a solution with unreacted $(\eta^6\text{-}LiC_6H_5)Cr(CO)_3$. This was certainly true for all the reactions described in our studies. The carbonyl linking the two (arene)chromium fragments in **2** displayed higher CO bond order than that of the acyl carbonyl in **1**, as is deduced from the IR data of the C=O vibrations. In addition greater shielding for the acyl carbon and less

---

(44) (a) Rees, B.; Coppens, P. *Acta Crystallogr.* **1973**, *B29*, 2516. (b) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1298.

(45) McKinney, R. J.; Knobler, C. B.; Huie, B. T.; Kaesz, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 2988.

(46) Huie, B. T.; Knobler, C. B.; McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 7862.

(47) Vahrenkamp, H. *Chem. Ber.* **1971**, *104*, 449.

(48) Hunter, A. D. *Organometallics* **1989**, *8*, 1118.

(49) Lotz, S.; Schindehutte, M. Unpublished results.

(50) Rieke, R. D.; Daruwala, K. P. *J. Org. Chem.* **1988**, *53*, 2073.

shielding for the adjacent carbon of the phenyl substituent in the ^{13}C NMR spectra of 2 are recorded compared to the corresponding values of the acyl carbonyl of the bridging benzoyl complexes 1.

Conclusion. The reaction conditions described provide heterobimetallic complexes of chromium and manganese with σ,π-bridging benzene and benzoyl ligands in reasonable yields. The advantage of using lithiated arenes above those where anionic transition-metal precursors were employed is found in the stronger nucleophilicity of these reagents. The negative charge is highly localized on the arene ring and on the metalated carbon, instead of being delocalized over the whole complex, resulting in a very reactive reagent and a more general method for the preparation of bridged benzene or benzoyl dimers of chromium.

Whereas the formation of bridged benzoyl dimers is promoted by the smaller, stronger π-acceptor ligands (CO, $P(OMe)_3$), bridged benzene dimers are found with the larger and more basic PPh_3 ligand on the manganese. Furthermore, phenyl migration for the reaction with dppe is promoted during the chelation step of the bidentate ligand. Close correlation with these results were obtained by Herberhold,[51] who showed that PPh_3 inhibits cyclopentadienyl migration in $Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4Mn(CO)_4(PPh_3)\}$ and promotes it in $Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4C(O)\}Mn(CO)_3(dppe)$.

Acknowledgment. S.L. and P.H.v.R. wish to acknowledge financial support from the Foundation for Research Development.

Registry No. **1a**, 138090-85-4; **1b**, 138128-53-7; **1c**, 138090-86-5; **1d**, 138090-87-6; **2**, 57347-34-9; **3a**, 138090-88-7; **3b**, 138128-54-8; **3c**, 138090-89-8; **3d**, 138090-90-1; **4a**, 138090-91-2; **4b**, 138090-92-3; $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, 12082-08-5; $(\eta^6\text{-}C_6H_5F)Cr(CO)_3$, 12082-05-2; $[Mn(CO)_5Br]$, 14516-54-2; $Mn(CO)_3(PPh_3)_2Br$, 14244-44-1; $(\eta^6\text{-}(1,4\text{-}C_6H_4Br_2))Cr(CO)_3$, 117939-67-0.

Supplementary Material Available: For **1a** and **3c**, tables of bond distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates (11 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

---

(51) Herberhold, M.; Kniesel, H. *J. Organomet. Chem.* 1987, *334*, 347.

Alkanediyl and Related Derivatives of Permethylhafnocene

John E. Bercaw and John R. Moss*[,1]

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received July 31, 1991

The reactions of $Cp^*_2HfH_2$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$) with α,ω-dienes (1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene and 1,6-heptadiene) in a 2:1 molar ratio yield the new binuclear alkanediyl derivatives $Cp^*_2(H)Hf(CH_2)_nHf(H)Cp^*_2$ (n = 4–7). The reactions of $Cp^*_2HfH_2$ with the same dienes in a 1:1 molar ratio lead to the mononuclear compounds $Cp^*_2(H)Hf(\eta^3\text{-}CH_2CHCHCH_3)$, $Cp^*_2\overline{HfCH_2(CH_2)_2C}H(CH_3)$, $Cp^*_2\overline{HfCH_2(CH_2)_3C}H(CH_3)$, and the α-hafna-ω-alkene $Cp^*_2(H)HfCH_2(CH_2)_4CH{=}CH_2$, respectively. Allene reacts with $Cp^*_2HfH_2$ (1:1) to cleanly afford the allyl hydride derivative, $Cp^*_2(H)Hf(\eta^3\text{-}CH_2CHCH_2)$; reaction with a 1:2 ratio yields a mixture of products, one of which appears to be $Cp^*_2(H)Hf(CH_2)_3Hf(H)Cp^*_2$. Reaction of $Cp^*_2HfH_2$ with acetylene yields $Cp^*_2(H)HfCH{=}CH_2$, which does not react with excess $Cp^*_2HfH_2$ to yield the ethanediyl derivative. 1,3-Pentadiene and $Cp^*_2HfH_2$ cleanly yield $Cp^*_2(H)Hf(\eta^3\text{-}CH_2CHCHCH_2CH_3)$. The thermal stabilities and reactions of some of these derivatives with excess diene, ethylene, CO, H_2, and H_2O have been investigated. The possibility of extending this chemistry to the permethyltitanocene and permethylzirconocene systems has also been explored.

Introduction

Binuclear alkanediyl complexes may be useful models for hydrocarbons bound to metal catalyst surfaces in important reactions such as olefin polymerization and the Fischer–Tropsch reaction. They may also serve as precursors for the synthesis of bifunctional organic compounds. In recent years, the number of known transition-metal alkanediyl compounds has increased dramatically.[2,3] Apart from the ethanediyl complexes of zirconium, $[Cp_2ZrCl]_2(\mu\text{-}CH_2CH_2)$ and $[Cp_2ZrCl(AlEt_3)]_2(\mu\text{-}CH_2CH_2)$,[4a,b] and the novel complexes $M_2X_6(PEt_3)_4(CH_2CH_2)$ (M = Zr, Hf; X = Cl, Br) prepared by Cotton and Kibala,[4c] there are few such complexes known for the early transition metals. It was the object of this study to investigate the synthesis of alkanediyl complexes of some of the early transition metals and to compare their chemistry with that of the known mononuclear alkyl complexes.

Results and Discussion

Alkyl hydride complexes of hafnium have been previously prepared in our laboratories using the following route:[5]

$$Cp^*_2HfH_2 + CH_2{=}CHR \rightarrow Cp^*_2Hf(H)(CH_2CH_2R) \quad (1)$$

This reaction, formally 1,2 insertion of an olefin into a Hf–H bond, proceeds quantitatively and cleanly to yield the thermally stable mononuclear alkyl hydride complexes.

---

(1) Present address: Department of Chemistry, University of Cape Town, Private Bag, Rondesbosch 7700, South Africa

(2) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* 1984, *60*, 171.

(3) Casey, C. P.; Audett, J. L. *Chem. Rev.* 1986, *86*, 329.

(4) (a) Kaminsky, W.; Sinn, H. *Liebigs Ann. Chem.* 1975, 424 and 438. (b) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H. J. *Angew. Chem., Int. Ed. Engl.* 1976, *15*, 629. (c) Cotton, F. A.; Kibala, P. A. *Inorg. Chem.* 1990, *29*, 3192.

(5) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* 1985, *4*, 97.

0276-7333/92/2311-0639$03.00/0