(d, J_{CP} = 20.6 Hz); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 552 (M, 25), 387 (M − fluorenyl, 20).

[η^1-2,3-Diphenyl-1-(9-fluorenyl)phosphirene-*P*]pentacarbonyltungsten (28). The 9-fluorenylphosphanorbornadiene **26** (0.74 g, 1 mmol) and 0.71 g (4 mmol) of tolan in 7 mL of mesitylene were heated 5 h at 125 °C. The solid obtained at room temperature was suction-filtered and then recrystallized from dichloromethane by slow evaporation of the solvent: yield 0.5 g (70%); mp 228 °C; ^{31}P NMR (CH_2Cl_2) δ −140.8 ($^1J_{PW}$ = 268 Hz); ^{1}H NMR ($CDCl_3$) δ 4.25 (d, $^2J_{HP}$ = 7.2 Hz, 1 H, CH), 7.2–7.9 (m, 18 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 60.2 (d, $^1J_{CP}$ = 9.3 Hz, CH), 125.4 (d, $^1J_{CP}$ = 3.7 Hz, =CP), 195.0 (d, $^2J_{CP}$ = 4.2 Hz, cis CO), aromatic carbons 127.5, 128.1, 129.1, 129.8 (d, J_{CP} = 3.1 Hz), 130.4, 140.9, 141.8; mass spectrum (46 eV, ^{184}W), *m/z* (relative intensity) 698 (M, 3), 533 (M − fluorenyl, 30). Anal. Calcd for $C_{32}H_{19}O_5PW$: C, 55.02; H, 2.74; P, 4.43; W, 26.33. Found: C, 54.95; H, 2.69; P, 4.41; W, 26.42.

Registry No. **1**, 105857-15-6; **2**, 115076-19-2; **3**, 115076-20-5; **5**, 115076-21-6; **6**, 115076-22-7; **7**, 115076-23-8; **10**, 105812-22-4; **11**, 115076-24-9; **12**, 115076-25-0; **13**, 115076-26-1; **14**, 115076-27-2; **15**, 115076-28-3; **16**, 115076-29-4; **17**, 115076-30-7; **18**, 108504-07-0; **19**, 115076-31-8; **20**, 115076-32-9; **21**, 115076-33-0; **22**, 115076-34-1; **23**, 115076-35-2; **24**, 115076-36-3; **25**, 115076-37-4; **26**, 115076-38-5; **27**, 115076-39-6; **28**, 115076-40-9; $ClCO_2Et$, 541-41-3; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; BrCN, 506-68-3; $W(CO)_5CH_3CN$, 15096-68-1; $LiC{\equiv}CH$, 1111-64-4; $PhC{\equiv}CMgBr$, 6738-06-3; tolan, 501-65-5; 9-fluorenyllithium, 881-04-9.

Synthesis and X-ray Crystal Structures of the Mono- and Binuclear Arylmanganate Complexes $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$, $[Li(THF)_4]_2[Mn_2Ph_6]$, and $[Li(THF)_4][MnMes_3]$

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The synthesis and X-ray crystal structures of the arylmanganate complexes $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ (1), $[Li(THF)_4]_2[Mn_2Ph_6]$ (2), and $[Li(THF)_4][MnMes_3]$ (3) are reported. They are the first X-ray structural characterizations of compounds of the type $LiMnR_3$ which are, in conjunction with neutral organomanganous species, of growing importance in organic synthesis. The complex "$LiMnPh_3$", derived from a manganese dihalide and 3 equiv of PhLi, crystallizes as a centrosymmetric dimer in the case of both 1 and 2. The structure of 1 may be described as a linear array of the four metals LiMnMnLi. Each metal is located at the centers of four edge-sharing distorted tetrahedra. Thus, both manganese atoms are surrounded by four bridging phenyls, and the two outer lithiums are coordinated to two bridging phenyls and two ethers. The ionic complex 2 has a similar structure except that the more strongly coordinating THF's effect separation of the lithium ions as $[Li(THF)_4]^+$ leaving the free dimeric $[Mn_2Ph_6]^{2-}$ ion with a core structure similar to that seen in 1. Use of the bulkier mesityl group affords the mononuclear ionic species $[Li(THF)_4][MnMes_3]$ (Mes = 2,4,6-$Me_3C_6H_2$) featuring a trigonal-planar structure for the $[MnMes_3]^-$ ion. Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K are as follows: 1, a = 14.764 (6) Å, b = 15.496 (6) Å, c = 21.889 (8) Å, Z = 4, orthorhombic, space group *Pbca*, R = 0.059; 2, a = 10.494 (5) Å, b = 15.746 (8) Å, c = 19.659 (9) Å, β = 97.17 (4)°, Z = 2, monoclinic, space group $P2_1/n$, R = 0.081; 3, a = 15.089 (5) Å, b = 16.288 (5) Å, c = 17.249 (6) Å, Z = 4, orthorhombic, space group $P2_12_12_1$, R = 0.073.

Introduction

σ-Bonded organomanganese complexes were first reported by Gilman, who used the reagents "$MnPh_2$" and "MnPhI" in situ.[1,2] Unfortunately, no structures were reported and definitive characterizations could not be claimed. In a more recent paper Andersen, Wilkinson, and co-workers described the syntheses and characterization of several neutral and ionic manganese(II) alkyls.[3] In addition, the first X-ray structures of σ-bonded, homoleptic, Mn(II) alkyls $[\{Mn(CMe_2Ph)_3\}_2]$ (4) and $[\{Mn(CH_2SiMe_3)_2\}_\infty]$ (5) were reported. Subsequent work by a number of groups has involved the synthesis of several new complexes. Examples include $[LiMnMes_3{\cdot}2dioxane{\cdot}2THF]$,[4] $[\{Mn(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}_2]$,[5] $[\{MnMes_2\}_3]$,[6] $[Li(THF)_4][\{(Me_3Si)_3C\}_3Mn_3Cl_4(THF)]$,[7] $[Mn\{C(SiMe_3)_3\}_2]$,[8] $[Mn(CH_2\text{-}t\text{-}Bu)_2]$,[9] and $[MnPh_2\{P(C_6H_{11})_3\}]$[10] as well as the dimeric tertiary phosphine adducts of the manganese(II) alkyls $[Mn_2R_4(PMe_3)_2]$ (R = CH_2SiMe_3, CH_2CMe_3, and CH_2Ph) and $[Mn_2(CH_2SiMe_3)_2(PR_3)_2]$ (R = Et_3, Me_2Ph, $MePh_2$, and $(C_6H_{11})_3$).[11] Some were structurally characterized, and those of $[Mn\{C(SiMe_3)_3\}_2]$[8] and $[Mn(CH_2\text{-}t\text{-}Bu)_2]$[9] are particularly interesting since their structures were the first authenticated examples of two-coordination in a transition metal which did not have a d^{10} electron configuration. In spite of this activity there is, at present, little structural information available for ionic "ate" complexes. In a recent review,[12] Normant and Cahiez have shown that organomanganous reagents, both neutral and ionic, i.e. RMnX, MnR_2, or $LiMnR_3$ (R = alkyl, aryl; X = halide), have considerable synthetic utility in organic chemistry. Their advantages compared with organo-

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(1) Gilman, H.; Bailie, J. C. *J. Org. Chem.* **1937**, *2*, 84.

(2) Gilman, H.; Kirby, R. H. *J. Am. Chem. Soc.* **1941**, *63*, 2046.

(3) Andersen, R. A.; Carmona-Guzman, E.; Gibson, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2204.

(4) Seidel, W.; Bürger, I. *Z. Chem.* **1977**, *17*, 31.

(5) Manzer, L. E.; Guggenberger, L. J. *J. Organomet. Chem.* **1977**, *139*, C34–C39.

(6) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1128.

(7) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1985**, 534.

(8) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1985**, *1380*.

(9) Andersen, R. A.; Haaland, A.; Rypdal, K.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1807.

(10) Maruyama, K.; Ito, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 849.

(11) Howard, G.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2025.

(12) Normant, J. F.; Cahiez, G. In *Modern Synthetic Methods*; Schefford, R., Ed.; Salle and Savenlander: Frankfurt, 1983; Vol. 3.

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copper/cuprate reagents include better thermal stability, a tolerance of "unusual solvents", and no requirement for expensive additives. In addition, the authors drew attention to the lack of structural data on organomanganates of formula $LiMnR_3$. Indeed such species have never been structurally characterized, although in the case of [$LiMnMes_3$·2dioxane·2THF], an elemental analysis and magnetic moment was reported.[4] Some attempts to isolate trialkylmanganates, i.e. $[MnR_3]^-$, have apparently given tetraalkylmanganates instead.[3] In this paper, we report the first structures of organomanganates of formula $LiMnR_3$. These are the title compounds $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ (1), $[\{Li(THF)_4\}_2[Mn_2Ph_6]$ (2), and $[Li(THF)_4][MnMes_3]$ (3), which were synthesized from 3 equiv of the aryllithium reagent and $MnBr_2$ or MnI_2.

Experimental Section

All manipulations were carried out under an N_2 atmosphere by using standard Schlenk techniques. All solvents were distilled from drying agents and degassed three times prior to use. Anhydrous $MnBr_2$ was purchased from Aldrich and used as received. MnI_2 was synthesized by a literature procedure.[12] Halide-free PhLi and MesLi were freshly synthesized from PhI and *n*-BuLi.[13] Mesityllithium was synthesized from MesBr and *n*-BuLi.[14] NMR data were recorded on an NT-200 spectrometer.

$[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ (1). Phenyllithium (1.76 g, 21 mmol) was dissolved in diethyl ether (60 mL) and cooled in a dry ice/acetone bath. Anhydrous $MnBr_2$ (1.5 g, 7.0 mmol) was added slowly by a solid addition tube. A gray-green precipitate formed slowly when the solution gradually warmed to room temperature. Stirring was continued overnight giving a pale orange solution. Filtration through Celite followed by reduction of the volume to 30 mL under reduced pressure gave further amounts of off-white precipitate that were removed by filtration. Cooling in a −20 °C freezer over 3–4 days gave the product 1 as amber crystals. Yield: 1.25 g, 40%. Addition of more than 3 equiv of PhLi to $MnBr_2$ under identical conditions also gave crystals of 1 and unreacted $[(PhLiEt_2O)_4]$.

$[Li(THF)_4]_2[Mn_2Ph_6]$ (2). Phenyllithium (2.35 g, 28.0 mmol) in Et_2O (25 mL) was added dropwise to a slurry of $MnBr_2$ (4.0 g, 19.0 mmol) in Et_2O (40 mL) and THF (10 mL). The solution was allowed to come to room temperature, and stirring was continued for 12 h. Reduction of the volume of the solution under reduced pressure to ca. 15 mL and addition of 25 mL of Et_2O gave a pale amber, cloudy solution. Filtration and reduction in volume to 10 mL followed by the addition of *n*-hexane/toluene to incipient crystallization and cooling gave the product as pale amber plates. Yield: 2.1 g, 38%.

$[Li(THF)_4][MnMes_3]$ (3). Mesityllithium (1.31 g, 10.5 mmol) in THF (5 mL) and Et_2O (10 mL) was added dropwise to a slurry of MnI_2 (1.08 g, 3.50 mmol) in THF (10 mL) and dioxane (1 mL) and cooled in an ice bath. The solution became a pale brown color and was allowed to come to room temperature with stirring overnight. The volatiles were removed almost to dryness under reduced pressure to give a brown residue. THF (5 mL) and Et_2O (10 mL) were added, and the solution was filtered. Addition of hexane (3–5 mL) to incipient crystallization and filtration followed by cooling in a refrigerator gave pale brown crystals of the product 3. Yield: 1.1 g, 31%. The crystals slowly decompose at temperatures >100 °C.

X-ray Crystallographic Studies

Structure Determination and Refinement. Crystals of the title compounds were coated with hydrocarbon oil to retard decomposition, attached to a glass fiber with silicone grease, and mounted in the cold stream of Syntex $P2_1$ diffractometer equipped with a locally modified LT-1 low-temperature device. No decay in the intensity of standard reflections was observed during data collection. Solution of the structures was accomplished by using the Patterson technique. All computing was carried out by using SHELXTL version 5 programs installed on a Data General Eclipse computer. Atomic scattering factors and anomalous dispersion corrections were from common sources.[15] An absorption correction[16] was applied, and structural refinement proceeded smoothly in the case of all compounds. All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were refined by using a riding model in which an idealized C–H vector, 0.96 Å in length, was recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded atom. The correct handedness for 3 was confirmed by SHELXTL ndf variable refinement. Further details are in Table I. Atom coordinates for 1, 2, and 3 are given in Table II. Selected bond distances and angles are given in Table III. Computer-

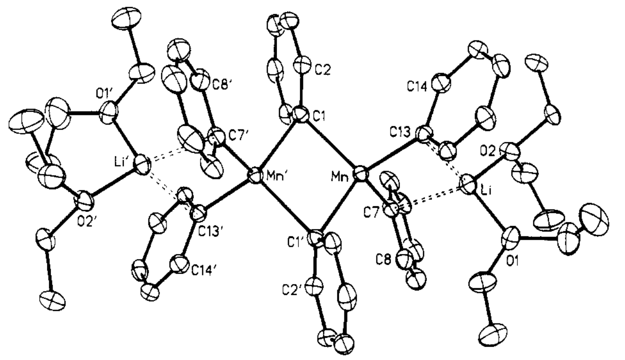

Figure 1. Thermal ellipsoid plot (30% probability) of 1. H atoms and disordered ether carbons omitted for clarity.

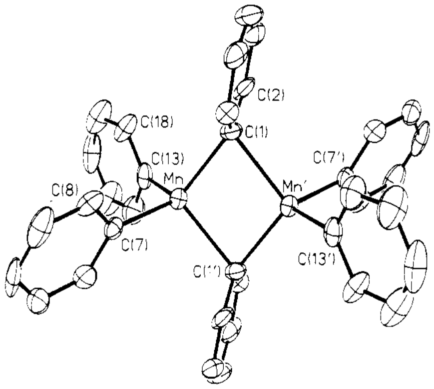

Figure 2. Thermal ellipsoid plot (30% probability) of the anion of 2. H atoms omitted for clarity.

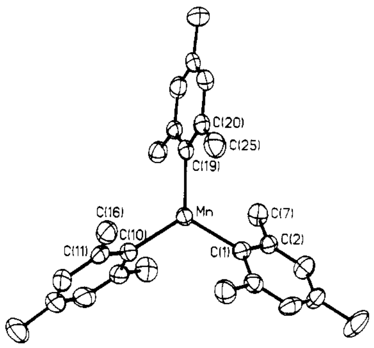

Figure 3. Thermal ellipsoid plot (30% probability) of the anion of 3. H atoms omitted for clarity.

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(13) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193.

(14) Goldwhite, H.; Millhauser, G., unpublished results. Fraenkel, G.; Dayagi, S.; Kobayashi, S. *J. Phys. Chem.* **1968**, *72*, 953. See also: Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117.

(15) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1976; Vol. IV.

(16) Program XABS was written by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences. Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

Table I. Crystallographic Data for $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ (1), $[Li(THF)_4]_2[Mn_2Ph_6]$ (2), and $[Li(THF)_4][MnMes_3]$ (3)

	1	2	3
formula	$Mn_2O_4C_{52}Li_2H_{70}$	$Mn_2O_8C_{68}Li_2H_{94}$	$MnO_4C_{43}LiH_{65}$
mol wt	882.89	1163.26	707.87
color and habit	amber parallelepipeds	amber needles	amber plates
cryst system	orthorhombic	monoclinic	orthorhombic
space group	*Pbca*	$P2_1/n$	$P2_12_12_1$
a, Å	14.764 (6)	10.494 (5)	15.089 (5)
b, Å	15.496 (6)	15.746 (8)	16.288 (5)
c, Å	21.889 (8)	19.659 (9)	17.249 (6)
β, deg		97.14 (4)	
V, Å^3	5008 (3)	3223 (3)	4239 (2)
T, K	130	130	130
Z	4	2	4
cryst dimens, mm	1.0 × 0.87 × 0.63	0.62 × 0.20 × 0.15	0.43 × 0.43 × 0.95
d(calcd), g cm^{-3}	1.17	1.20	1.11
μ(Mo Kα), cm^{-1}	5.2	4.2	3.3
range of abs fctrs	1.31–1.60	1.06–1.09	1.13–1.18
scan speed, deg min^{-1}	30	8	30
scan width, deg	1.5	1	1.7
ω offset for bkgd, deg	2.0	1	1.5
2θ range, deg	0–55	0–55	0–55
octants collcd	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,+l$
no. of data collcd	6427	4659	5400
no. of unique data	6357	4208	5366
R(merge)		0.025	
no. of data used in rfnmt	3288, $I > 2.5\sigma(I)$	2868, $I > 2.5\sigma(I)$	3665, $I > 2.5\sigma(I)$
no. of parameters rfnd	297	361	381
data/variable ratio	11.1	7.9	9.6
R(*F*)	0.059	0.081	0.073
$R_w(F)$	0.063	0.077	0.081
weighting scheme	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$
largest Δ/σ	0.002 for U$_{22}$O(2)	0.029	0.10
largest feature on final diff map, e Å^{-3}	0.515	0.44	0.67

[a] $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}$ with *w* as listed above in weighing scheme. [b] Compound 1 has disorder in both ether molecules at C(21) and C(24). In both cases, occupancy was allowed to refine freely. The final occupancies for C(21A) and C(21B) were 0.4768 and 0.05, respectively, and for C(24A) and C(24B) were 0.5761 and 0.4239, respectively. All disordered positions were refined anisotropically. Hydrogen atoms were not included on either the disordered carbons or the carbons bonded directly to them. [c] Disorder was observed in three THF groups of the $[Li(THF)_4]$ cation of 3. The occupancies for the disordered positions of C35, C39, C41, C42, A, and B were set at one-half. As a result of this disorder the $[Li(THF)_4]$ cation was not refined anisotropically. Hydrogens were included only on the one THF which did not exhibit disorder.

generated thermal ellipsoidal plots of 1, 2, and 3 are given in Figures 1, 2, and 3, respectively.

Structural Description

$[\{Li(Et_2O_2\}_2Mn_2Ph_6]$ (1). Compound 1 exists as discrete $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ dimers with a crystallographically imposed center of symmetry. The four metals LiMnMnLi form an essentially linear array with a Li–Mn–Mn angle of 172.6 (2)°. In addition, each metal is located at the center of a distorted tetrahedral arrangement of ligands so that the structure is derived from four edge-bridged tetrahedra. Four bridging phenyl groups surround each manganese center, and two bridging phenyls and two terminally bound ethers are coordinated to each lithium. The average Mn–C distance for the phenyls bridging the two Mn atoms is 2.255 (4) Å whereas for the phenyls bridging to Li the Mn–C distance averages a somewhat shorter 2.178 (4) Å. There is a small, but apparently significant, asymmetry of about 0.05 Å (see Table III) in the MnC(1) and MnC(1)′ bridge bonds. There are no unusually short Mn···C (closest is C(2)′ at 3.083 Å) or Mn···H approaches (the shortest is H(14) at 3.113 Å). In addition the angles between the C(1)···C(6) vector and the MnMn′C(1)C(1)′ plane is 91.1° and the angle between the normal to the C1 ring and the Mn···Mn′ line is 6.2°, indicating only minor structural distortions. The Li–C bonds are much longer, averaging 2.429 (8) Å, while the Li–O bonds average 1.946 (8) Å. The internal C–Mn–C and Mn–C–Mn angles are 105.4 (1)° and 74.6 (2)°, respectively, resulting in an Mn···Mn′ distance of 2.733 (1) Å. Not surprisingly, the angles at lithium display much more variation from tetrahedral values than those of manganese, ranging from 95.8 (3)° to 123.0 (4)°. Distances and angles within the phenyl ligands are all within the normal range, although the C–C bonds involving a bridging carbon atom, are on average, longer than other C–C bonds, i.e., 1.406 (6) Å vs 1.382 (6) Å.

$[Li(THF)_4]_2[Mn_2Ph_6]$ (2). Compound 2 crystallizes as separate $[Li(THF)_4]^+$ cations and $[Mn_2Ph_6]^{2-}$ dianions. The cation $[Li(THF)_4]^+$ has been observed previously[17] and has four THF's, roughly tetrahedrally disposed with the angles at Li$^+$ varying from 106.6 (6)° to 113.5 (7)°. The Li–O bonds average 1.924 (13) Å. The centrosymmetric $[Mn_2Ph_6]^{2-}$ ion has a structure very similar to same moiety in 1. The average bridging Mn–C bond length is 2.285 (7) Å, and the terminal Mn–C distances average 2.146 (7) Å. There are some distortions from idealized tetrahedral values in the angles surrounding Mn as evident from the deviations which range from 105.6 (3)° to 114.2 (3)°. The Mn···Mn′ distance is 2.763 (2) Å, and the Mn–C(1)–Mn′ angle is 74.4 (1)°. Both bridging and nonbridging phenyl rings exhibit a pattern of longer C–C bonds where one carbon is bonded to Mn. Like 1, compound 2 displays unequal MnC(1) and MnC(1)′ distances. In this case the asymmetry is somewhat larger being 0.08 Å (see Table III). There are no other close contacts to the Mn centers; the closest involve C(2)···Mn′ at 3.136 Å and H(12)···Mn at 3.06 Å. The angle between the vector C(1)···C(6) and the

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[17] Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* 1977, *99*, 1765. See also: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* 1985, *24*, 354 for further examples.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 1, 2, and 3

	x	*y*	*z*	*U*^{a}		*x*	*y*	*z*	*U*^{a}
				[{Li(Et$_2$O)$_2$}Mn$_2$Ph$_6$] (1)					
Mn	4784 (1)	703 (1)	348 (1)	29 (1)*	C(14)	3050 (3)	846 (3)	1150 (2)	42 (1)*
O(1)	5316 (2)	2156 (2)	1877 (1)	49 (1)*	C(15)	2453 (3)	720 (3)	1634 (2)	44 (1)*
O(2)	3752 (2)	3115 (2)	115 (2)	48 (1)*	C(16)	2760 (3)	355 (3)	2169 (2)	45 (2)*
C(1)	3975 (3)	166 (3)	−424 (2)	35 (1)*	C(17)	3662 (3)	124 (3)	2218 (2)	44 (2)*
C(2)	3179 (3)	−279 (3)	−272 (2)	43 (1)*	C(18)	4241 (3)	272 (3)	1735 (2)	38 (1)*
C(3)	2407 (3)	−260 (4)	−636 (2)	56 (2)*	C(19)	6146 (3)	1663 (4)	1858 (2)	57 (2)*
C(4)	2407 (4)	209 (4)	−1160 (3)	68 (2)*	C(20)	5134 (5)	2508 (7)	2476 (4)	114 (4)*
C(5)	3165 (4)	674 (4)	−1332 (2)	57 (2)*	C(21A)	4784 (10)	2092 (13)	2926 (5)	104 (7)*
C(6)	3938 (3)	652 (3)	−970 (2)	41 (1)*	C(21B)	4233 (9)	2472 (12)	2573 (7)	112 (7)*
C(7)	5192 (3)	2026 (3)	142 (2)	38 (1)*	C(22)	6974 (4)	2244 (4)	1862 (3)	77 (2)*
C(8)	6023 (3)	2395 (3)	308 (2)	45 (1)*	C(23)	4003 (4)	3978 (3)	1024 (3)	69 (2)*
C(9)	6321 (4)	3199 (3)	112 (2)	57 (2)*	C(24A)	2879 (5)	2994 (5)	792 (4)	44 (3)*
C(10)	5788 (4)	3667 (3)	−276 (3)	64 (2)*	C(24B)	3005 (7)	3130 (7)	1647 (4)	42 (3)*
C(11)	4977 (3)	3348 (3)	−465 (3)	59 (2)*	C(25)	2086 (3)	3188 (4)	1248 (2)	57 (2)*
C(12)	4675 (3)	2540 (3)	−255 (2)	48 (2)*	C(26)	4761 (4)	4276 (4)	1376 (4)	84 (3)*
C(13)	3973 (3)	636 (3)	1173 (2)	34 (1)*	Li	4542 (5)	2112 (4)	1156 (3)	39 (2)*
				[Li(THF)$_4$]$_2$Mn$_2$Ph$_6$ (2)					
Mn	4686 (1)	4186 (1)	4775 (1)	24 (1)*	C(16)	5582 (11)	2630 (6)	2672 (5)	65 (4)*
O(1)	−724 (4)	749 (3)	2816 (2)	37 (2)*	C(17)	4440 (9)	3046 (6)	2685 (4)	63 (4)*
O(2)	1933 (4)	933 (3)	3783 (2)	37 (2)*	C(18)	4243 (8)	3530 (5)	3265 (4)	44 (3)*
O(3)	197 (5)	2482 (3)	3395 (3)	40 (2)*	C(19)	−1039 (8)	−138 (5)	2842 (4)	50 (3)*
O(4)	−768 (4)	1046 (4)	4374 (2)	43 (2)*	C(20)	−2357 (8)	−202 (5)	2479 (4)	55 (3)*
C(1)	3443 (6)	5341 (4)	4576 (3)	28 (2)*	C(21)	−2367 (10)	450 (6)	1924 (5)	81 (4)*
C(2)	3313 (7)	5697 (5)	3903 (3)	37 (3)*	C(22)	−1432 (7)	1107 (4)	2207 (3)	32 (3)*
C(3)	2204 (8)	6124 (5)	3620 (4)	53 (3)*	C(23)	2584 (7)	422 (6)	3321 (4)	49 (3)*
C(4)	1159 (8)	6182 (5)	3970 (4)	58 (3)*	C(24)	3949 (7)	696 (6)	3393 (4)	59 (3)*
C(5)	1227 (7)	5851 (5)	4620 (4)	45 (3)*	C(25)	4175 (7)	1098 (5)	4088 (4)	49 (3)*
C(6)	2340 (7)	5444 (4)	4912 (4)	33 (3)*	C(26)	2891 (7)	1433 (6)	4208 (4)	50 (3)*
C(7)	3905 (6)	3237 (4)	5380 (3)	25 (2)*	C(27)	824 (9)	2777 (5)	2831 (4)	56 (3)*
C(8)	2638 (7)	3163 (5)	5537 (3)	35 (3)*	C(28)	661 (9)	3729 (5)	2822 (4)	57 (3)*
C(9)	2227 (9)	2497 (5)	5922 (4)	54 (3)*	C(29)	596 (10)	3934 (5)	3556 (5)	75 (4)*
C(10)	3035 (9)	1848 (5)	6151 (4)	58 (3)*	C(30)	117 (10)	3168 (5)	3867 (5)	69 (4)*
C(11)	4288 (9)	1892 (5)	6005 (4)	53 (3)*	C(31)	−2121 (7)	877 (6)	4379 (4)	52 (3)*
C(12)	4698 (8)	2558 (5)	5632 (3)	38 (3)*	C(32)	−2412 (9)	1148 (8)	5064 (5)	87 (5)*
C(13)	5133 (7)	3609 (4)	3840 (3)	32 (3)*	C(33)	−1233 (8)	1318 (8)	5474 (5)	84 (5)*
C(14)	6274 (9)	3148 (5)	3778 (4)	51 (3)*	C(34)	−192 (9)	1238 (7)	5064 (4)	74 (4)*
C(15)	6519 (9)	2682 (6)	3212 (5)	60 (4)*	Li	160 (11)	1305 (8)	3603 (6)	36 (4)*
				[Li(THF)$_4$][MnMes$_3$] (3)					
Mn	9350 (1)	5085 (1)	4728 (1)	33 (1)*	C(27)	7536 (5)	4888 (5)	3682 (4)	52 (2)*
C(1)	9818 (4)	6217 (4)	5209 (3)	36 (2)*	O(1)	2717 (4)	6361 (3)	3045 (3)	61 (1)
C(2)	9364 (4)	6970 (4)	5105 (3)	38 (2)*	O(2)	2254 (4)	7017 (3)	1410 (3)	59 (1)
C(3)	9705 (5)	7716 (4)	5407 (4)	51 (2)*	O(3)	3819 (3)	7828 (3)	2302 (3)	57 (1)
C(4)	10494 (5)	7721 (4)	5819 (4)	51 (2)*	O(4)	1834 (3)	8098 (3)	2859 (3)	53 (1)
C(5)	10938 (4)	6988 (4)	5930 (4)	46 (2)*	Li	2673 (8)	7332 (8)	2417 (7)	50 (3)
C(6)	10630 (4)	6262 (4)	5641 (3)	39 (2)*	C(28)	2310 (6)	6284 (6)	3790 (5)	70 (2)
C(7)	8522 (5)	6983 (5)	4634 (4)	52 (2)*	C(29)	2576 (6)	5501 (5)	4119 (5)	64 (2)
C(8)	10862 (7)	8526 (5)	6175 (7)	87 (4)*	C(30)	3355 (6)	5211 (6)	3626 (5)	71 (2)
C(9)	11113 (5)	5487 (5)	5808 (4)	52 (2)*	C(31)	3228 (9)	5637 (7)	2941 (7)	106 (4)
C(10)	10206 (4)	4463 (4)	3930 (3)	39 (2)*	C(32)	2174 (5)	6248 (5)	1066 (5)	58 (2)
C(11)	10587 (4)	3717 (4)	4127 (4)	40 (2)*	C(33)	2061 (5)	6385 (5)	188 (5)	60 (2)
C(12)	11188 (5)	3316 (5)	3615 (4)	54 (2)*	C(34)	1975 (6)	7352 (6)	123 (5)	70 (2)
C(13)	11405 (5)	3668 (5)	2889 (4)	58 (3)*	C(35A)	1687 (8)	7624 (8)	927 (7)	40 (3)
C(14)	11010 (5)	4386 (5)	2698 (4)	59 (3)*	C(35B)	2240 (11)	7683 (11)	830 (10)	68 (4)
C(15)	10428 (4)	4798 (4)	3193 (4)	49 (2)*	C(36)	4149 (5)	8531 (5)	2705 (4)	55 (2)
C(16)	10438 (4)	3327 (4)	4882 (4)	50 (2)*	C(37)	4971 (5)	8816 (5)	2272 (4)	58 (2)
C(17)	12069 (6)	3263 (6)	2340 (6)	82 (4)*	C(38)	5234 (8)	8062 (7)	1806 (7)	98 (3)
C(18)	9975 (6)	5597 (5)	2938 (4)	63 (3)*	C(39A)	4399 (11)	7642 (9)	1666 (9)	57 (4)
C(19)	8072 (4)	4364 (4)	5051 (4)	38 (2)*	C(39B)	4639 (12)	7333 (11)	2055 (10)	73 (5)
C(20)	7856 (4)	4376 (4)	5809 (4)	40 (2)*	C(40)	2012 (7)	8656 (6)	3476 (6)	84 (3)
C(21)	6988 (5)	4147 (4)	6017 (4)	52 (2)*	C(41A)	1336 (10)	8562 (10)	4092 (9)	55 (4)
C(22)	6313 (5)	4168 (4)	5482 (4)	54 (2)*	C(41B)	838 (10)	8785 (10)	3665 (9)	56 (4)
C(23)	6508 (4)	4412 (4)	4744 (5)	52 (2)*	C(42A)	574 (17)	8413 (14)	3578 (14)	104 (7)
C(24)	7377 (4)	4644 (4)	4520 (4)	40 (2)*	C(42B)	404 (10)	8011 (10)	3434 (9)	57 (4)
C(25)	8581 (5)	4305 (5)	6416 (4)	54 (2)*	C(43)	897 (7)	7986 (7)	2744 (6)	86 (3)
C(26)	5376 (5)	3960 (6)	5704 (6)	76 (3)*					

[a] Parameters with an asterisk are equivalent isotropic *U* defined as one-third of the trace of the orthogonalised $\mathbf{U}_{ij}$ tensor.

MnMn′C(1)C(1)′ plane is 90.5°, and the angle between the normal to the C(1) ring and the Mn···Mn′ line is 8.4°.

[Li(THF)$_4$][MnMes$_3$] (3). This compound crystallizes as separate [Li(THF)$_4$]$^+$ cations and [MnMes$_3$]$^-$ anions. The cation needs no further comment because of its similarity to those previously reported except to note that three of the THF ligands are slightly disordered. The [MnMes$_3$]$^-$ anion involves a central planar MnC(1), C(10), C(19) array with slightly irregular angles at Mn of 117.2 (2)°, 119.5 (2)°, and 123.3 (2)°. The MnC bonds average 2.141 (6) Å in length, and the mesityl groups have dihedral angles of 59.1°, 67.3°, and 68.5° with respect to the MnC$_3$

Table III. Selected Bond Distances (Å) and Angles (deg) for 1, 2, and 3

	$[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ (1)		
Mn···Mn′	2.733 (1)	Mn···Li	2.833 (7)
Mn–C(1)	2.230 (4)	Li–C(7)	2.422 (8)
Mn–C(1′)	2.280 (4)	Li–C(13)	2.437 (8)
Mn–C(7)	2.185 (4)	Li–O(1)	1.950 (8)
Mn–C(13)	2.170 (4)	Li–O(2)	1.942 (8)
C(1)–Mn–C(1′)	105.4 (1)	Mn–C(1)–Mn′	74.6 (1)
C(1)–Mn–C(7)	110.0 (2)	Mn–C(7)–Li	75.7 (2)
C(1)–Mn–C(13)	108.5 (1)	Mn–C(13)–Li	75.6 (2)
C(7)–Mn–C(13)	111.6 (2)	C(7)–Li–C(13)	95.7 (3)
	$[Li(THF)_4]_2[Mn_2Ph_6]$ (2)		
Mn···Mn′	2.763 (2)	Li–O(1)	1.914 (12)
Mn–C(1)	2.243 (7)	Li–O(2)	1.940 (12)
Mn–C(1′)	2.326 (7)	Li–O(3)	1.898 (14)
Mn–C(7)	2.137 (7)	Li–O(4)	1.944 (13)
Mn–C(13)	2.155 (7)		
C(1)–Mn–C(1′)	105.6 (3)	O(1–)–Li–O(2)	111.5 (7)
C(1)–Mn–C(7)	114.2 (3)	O(1)–Li–O(3)	107.1 (6)
C(1)–Mn–C(13)	112.1 (2)	O(1)–Li–O(4)	107.1 (6)
C(1′)–Mn–C(7)	105.9 (3)	O(2)–Li–O(3)	106.8 (6)
C(1′)–Mn–C(13)	110.1 (2)	O(2)–Li–O(4)	110.9 (6)
C(7)–Mn–C(13)	108.6 (3)	O(3)–Li–O(4)	113.5 (7)
Mn–C(1)–Mn′	74.4 (1)		
	$[Li(THF)_4][MnMes_3]$ (3)		
Mn–C(1)	2.142 (6)	Li–O(1)	1.917 (13)
Mn–C(10)	2.144 (6)	Li–O(2)	1.919 (13)
Mn–C(19)	2.137 (6)	Li–O(3)	1.919 (13)
		Li–O(4)	1.934 (13)
C(1)–Mn–C(10)	117.2 (2)	O(1)–Li–O(2)	107.6 (6)
C(1)–Mn–C(19)	119.5 (2)	O(1)–Li–O(3)	112.0 (6)
C(10)–Mn–C(19)	123.3 (2)	O(1)–Li–O(4)	109.4 (6)
		O(2)–Li–O(3)	108.4 (6)
		O(2)–Li–O(4)	108.2 (6)
		O(3)–Li–O(4)	111.1 (6)

plane. There are no other short Mn···H or Mn···C contacts.

Discussion

Compounds 1, 2, and 3 are the first organomanganates, whose formulae correspond to "$LiMnR_3$", to be structurally characterized. Since 1 and 2 involve phenyl groups, it is interesting to note that manganese phenyls were the first organomanganese compounds to be reported.[1,2] However, they were never well-characterized. A later report by Yamamoto and co-workers has shown that $MnPh_2$ is obtainable as the adduct $[MnPh_2P(C_6H_{11})_3]$ from $AlPh_3{\cdot}Et_2O$, $Mn(acac)_3$, and $P(C_6H_{11})_3$ in diethyl ether.[10] More recent work by Andersen and Wilkinson et al. indicated that no pure Ph/Mn products could be readily isolated from reaction mixtures of $MgPh_2$ and $MnCl_2$ or $MnBr_2$.[3] That paper also gave details of several thermally stable manganese dialkyls and showed that manganates of formula $LiMnR_3$ (R = Me or CH_2SiMe_3) are not found except, possibly, as intermediates, in solution. Instead, Li_2MnR_4·solvate complexes are obtained. Shortly afterwards, Seidel and Bürger reported the synthesis of the complex $[LiMnMes_3{\cdot}2THF{\cdot}2dioxane]$ which is very close to the formula for 3. (It is interesting to note that dioxane was also used in the synthesis of 3 but none was apparent in the product.) This complex was characterized by elemental analysis and magnetic data (magnetic moment = 5.9 μ_B).[4] Almost simultaneously, the complex $[Li_2(THF)_2MnI_2\{C_6H_4\text{-}2\text{-}CH_2NMe_2\}_2]$ and the related neutral species $Mn\{C_6H_4\text{-}2\text{-}CH_2NMe_2\}_2$ were reported and characterized.[5] Oddly, only the isomeric neutral alkyl complex $Mn(CH_2C_6H_4\text{-}2\text{-}NMe_2)_2$ was isolated under the same conditions.[5] These results suggested to us that $LiMnR_3$ compounds might be more readily obtainable if R was an aromatic group. A related neutral arylmanganese(II) compound was in fact reported and structurally characterized in 1983.[6] This was the linear trimer $[\{MnMes_2\}_3]$ featuring bridging mesityl groups and two three-coordinate outer Mn atoms with the central Mn having a distorted tetrahedral coordination. However, no anionic species of the type $MnMes_3^-$ was mentioned.

The synthesis of compounds 1, 2, and 3 proceeded smoothly and in good yield. Crystals of 2 and 3, however, are less easy to obtain, and frequently the product appears as an amber oil that crystallizes with difficulty. It is evident from the X-ray structures that there are only minor differences between the $Mn_2Ph_6^{2-}$ moieties in compounds 1 and 2. However, the interaction of two solvated $Li(Et_2O)_2$ ions with the $Mn_2Ph_6^{2-}$ core in 1 has the effect of lengthening the external Mn–C bonds from 2.146 to 2.178 Å and the internal Mn–C distance from 2.255 to 2.285 Å. These small changes suggest that the interaction of the phenyl groups with the $Li(Et_2O)_2^+$ ions is quite weak. This is borne out by the very long LiC(9)–C(13) bonds of 2.429 Å. These distances are much longer than those normally seen in organometallic compounds involving four-coordinate Li^+. For example, the average Li–C distance in $[(PhLi{\cdot}Et_2O)_4]$ is 2.33 Å and the Li–C bond lengths in $[(LiEt_2O)_4VPh_6]$ are almost 2.28 Å.[20] Due to the weakness of the Li–C bonds in 1, use of the more strongly coordinating THF readily effects separation of the Li^+ ions resulting in the ionic structure seen in 2. The Mn–C bond lengths are in the expected range and are consistent with those seen in $[\{MnMes_2\}_3]$, $[\{Mn(CMe_2Ph)_2\}_2]$, $[\{Mn(CH_2SiMe_3)_2\}]$, $[Mn_3\{C(SiMe_3)_3\}_3Cl_4(THF)]^-$, or $[Mn\{CH_2C_6H_4\text{-}2\text{-}NMe_2\}_2]$ with allowances for variation in coordination number. Comparisons of structural parameters in 1 and 2 with the dimeric structures[11] of $[Mn_2(CH_2CMe_3)_4(PMe_3)_2]$, $[Mn_2(CH_2Ph)_4(PMe_3)_2]$, and $[Mn_2(CH_2SiMe_3)_4(PR_3)_2]$ (R_3 = Me_3 or Me_2Ph) show that the bonds and angles surrounding the manganese centers are very similar. It is also notable that the asymmetric bridging in 1 and 2 is similar to, but significantly less than, the asymmetry (ca. 0.16–0.2 Å) observed in the manganese–alkyl–phosphine complexes above.[11] In the latter species it was proposed that the observed distortion might be due to an interaction between one hydrogen atom on each of the bridging methylenes with the manganese. The absence of such an interaction in 1 and 2 and the much smaller asymmetry observed supports this explanation. The structures of both compounds 1 and 2 also bear a close resemblance to that of $[(LiTMEDA)_2Mg_2Ph_6]$.[18] The Mn–C distances in 1 are almost identical with the corresponding Mg–C bond lengths which display an almost identical asymmetry (0.04 Å) in the case of the bridging Mg–C bonds. Even the Li–C bonds in the magnesium compound, 2.45 Å, closely match the long 2.43 Å distance seen in 1. It is therefore surprising that the excellent donor TMEDA is not sufficient to separate the Li^+ cation from the $[Mg_2Ph_6]^{2-}$ moiety.

The coordination number of manganese in 1 and 2 also merits comment. Prior work from this laboratory and elsewhere has shown that some first-row transition metals are capable of binding five or six phenyl groups to give negatively charged compounds. Structurally characterized examples are $[\{Na(solvate)_2\}_2CrPh_5]$,[19] $[(LiEt_2O)_3CrPh_6]$,[20] and $[(LiEt_2O)_4VPh_6]$.[20] It is quite probable that Ti, Zr, Mo, and W are capable of forming similar compounds. In

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[18] Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726.

[19] Müller, E.; Krausse, J.; Schmiedeknecht, K. *J. Organomet. Chem.* **1972**, *44*, 127.

[20] Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Organometallics* **1988**, *7*, 1380.

such complexes there is a considerable crystal field stabilization incentive for octahedral over tetrahedral coordination. In the case of a d^5 Mn(II) compound there is no stabilization of this type for the high-spin octahedral configuration. This is consistent with the finding that reaction mixtures involving 7:1 PhLi:Mn ratios did not give any new compound suitable for an X-ray crystal structure. Magnetic measurements[21] at ambient temperature indicate that the magnetic moment of **1** is 2.9 μ_B. This low value is consistent with two high-spin tetrahedral Mn(II) centers with considerable antiferromagnetic metal–metal interaction. The Mn···Mn′ distance in both compounds is about 2.73 Å. This length is near to those seen in $[\{Mn(CMe_2Ph)_2\}]_2$,[3] $[Mn\{CH_2C_6H_4\text{-}2\text{-}NMe_2\}]_2$,[5] and the dialkylmanganese–phosphine dimers of Wilkinson and coworkers[11] and slightly shorter than the 2.851 Å seen in $[\{MnMes_2\}_3]$ which also possess low magnetic moments. These distances are indeed probably too long for any significant metal–metal bonding. Similarly, the Li···Mn vector, 2.831 (7) Å, is merely a consequence of the association of the $Li(Et_2O)_2^+$ moieties with the negatively charged manganese dianion.

When mesityl groups are used instead of phenyls, the mononuclear anion $[MnMes_3]^-$ is obtained. The lowered nuclearity is undoubtedly a result of the steric effects of the larger mesityl group. The magnetic moment of 5.9 μ_B indicates that the manganese has the high-spin, d^5, configuration. The three-coordinate environment at the manganese is also notable since this is a rare,[6,22] but by no means unknown, coordination number for the metal. The average Mn–C distance, 2.142 Å, is within the expected range for a three-coordinate high-spin Mn^{2+} complex. Thus, it is slightly longer than the 2.10 Å found in the two-coordinate $Mn\{C(SiMe_3)_3\}_2$ and $Mn(CH_2\text{-}t\text{-}Bu)_2$ and very close to the terminal Mn–C bond lengths in **2**. The structural differences between **2** and **3** may be compared to the recently reported structures of the magnesiate ions $[Mg_2Et_6]^{2-}$ and $[Mg(CH_2\text{-}t\text{-}Bu)_3]^-$.[23] Both pairs of compounds exhibit many similarities in the M–C bond distances and angles that underlines the close correspondence between many classes of magnesium and manganese compounds. Structural and reactivity studies on these and related species are continuing.

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Supplementary Material Available: Full tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (12 pages); listings of structure factor amplitudes (59 pages). Ordering information is given on any current masthead page.

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[21] Evans, D. F. *J. Chem. Soc.* 1959, 2005.

[22] Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* 1977, *24*, 1–95. Murray, B. D.; Power, P. P. *Inorg. Chem.* 1984, *23*, 4586.

[23] Squiller, E. P.; Whittle, R. H.; Rickey, H. G. *J. Am. Chem. Soc.* 1985, *107*, 437.

Gas-Phase Ligand Substitution Reactions with $(OC)Fe(NO)_2^{\bullet-}$, $(OC)_2Co(NO)^{\bullet-}$, $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$, $(C_3H_5)Co(CO)_3^{\bullet-}$, and $CpCo(CO)_2^{\bullet-}$[†]

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Three 17-electron transition-metal complex negative ions $LM(CO)_{x-1}^{\bullet-}$ ($(OC)Fe(NO)_2^{\bullet-}$, $(OC)_2Co(NO)^{\bullet-}$, and $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$) and two parent molecular anion radicals $LM(CO)_x^{\bullet-}$ ($(C_3H_5)Co(CO)_3^{\bullet-}$ and $CpCo(CO)_2^{\bullet-}$) were generated by electron impact on the corresponding $LM(CO)_x$ complexes in the gas phase. The ion–molecule reactions of these five metal complex negative ions were studied with the neutral molecules PF_3, PMe_3, NO, SO_2, olefins with electron-donating and -withdrawing vinyl substituents, acetone and certain fluorinated derivatives, biacetyl, O_2, CO, and CS_2. In general, the $LM(CO)_{x-1}^{\bullet-}$ complexes and $CpCo(CO)_2^{\bullet-}$ reacted by ligand substitution involving the associative mechanism. In many cases, the product ions of adduct formation and ligand substitution were directly observed in the same reaction. These ligand substitution reactions appear to take advantage of the abbility of the NO, $\eta^3\text{-}C_3H_5$, and Cp ligands to reduce their hapticities as the neutral ligand bonds to the metal. The reaction of $(C_3H_5)Co(CO)_3^{\bullet-}$ with PF_3 occurred by fragmentation of the allyl radical. This latter result was considered to occur by radical β-fragmentation of the excited acyl complex $[C_3H_5C({=}O)Co(CO)_2(PF_3)^{\bullet-}]^*$ formed by CO insertion into the Co–allyl bond. Both parent molecular anion radicals were observed to undergo electron transfer with several of the neutral substrates yielding $EA((\eta^3\text{-}C_3H_5)Co(CO)_3) = EA(CpCo(CO)_2) = 0.62 \pm 0.1$ eV; $EA((\eta^3\text{-}C_3H_5)Co(CO)_2) = 0.9 \pm 0.2$ eV was also measured. The results of the reactions of the parent $LM(CO)_x^{\bullet-}$ species with the neutral ligands were consistent with their structures having a 17-electron configuration about the metal with η^3-Cp and $\eta^1\text{-}C_3H_5$ ligands.

Introduction

Ligand substitution reactions with transition-metal complexes represent a well-studied and reasonably well-understood chemical conversion.[1-3] In general, condensed-phase ligand substitution reactions are described

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[†] Dedicated to Professor Arthur G. Anderson on his 70th birthday and retirement from the University of Washington.

[1] For a recent review of ligand substitution reactions, see: Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* 1983, *83*, 557.

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