position leading to a shorter Cr–PPh_3 bond. Thus a significant component of π bonding to the full bond between chromium and triphenylphosphine is indicated.

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Registry No. *trans*-$Cr(CO)_4PPh_3(PBu_3)$, 17652-69-6; *trans*-$Cr(CO)_4PPh_3(P(OMe)_3)$, 95341-15-4; *trans*-$Cr(CO)_4PPh_3(P(OPh)_3)$, 82613-90-9; $Et_4N[(PBu_3)Cr(CO)_4Cl]$, 95218-76-1; $Et_4N[(P(OMe)_3Cr(CO)_4Cl]$, 95341-14-3; $Et_4N[(P(OPh)_3Cr(CO)_4Cl]$, 95218-78-3; $Et_4N[Cr(CO)_5Cl]$, 14780-95-1; $Cr(CO)_6$, 13007-92-6; Cr, 7440-47-3; P, 7723-14-0.

Supplementary Material Available: Tables of thermal parameters, bond distances and angles, and observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

Nucleophilic Addition to Coordinated Cycloheptatriene: A Mechanistic and Structural Study

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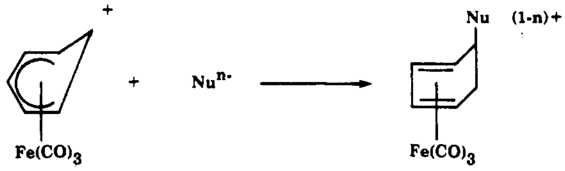
The addition of phosphorus and nitrogen donor nucleohiles (Nu) to the cycloheptatriene ring in $(C_7H_8)Mn(CO)_2L^+$ (1; L = CO, PPh_3) yields (*exo*-$NuC_7H_8)Mn(CO)_2L^+$. *N,N*-Dimethylaniline undergoes an electrophilic aromatic substitution reaction with 1 (L = CO) to give (*exo*-$Me_2NC_6H_4C_7H_8)Mn(CO)_3$, in which the carbon para to the NMe_2 substituent is bonded to the C_7H_8 ring. Kinetic studies of the addition reactions show that 1 (L = CO) is an extremely reactive electrophile and that the relative nucleophilic reactivities are the same as found for other, less reactive, organometallic substrates as well as for free carbonium ions. A single-crystal X-ray analysis of [(*exo*-$PPh_3C_7H_8)Mn(CO)_3]BF_4$ showed that it crystallizes in the monoclinic space group $P2_1/c$ with a = 9.595 (3) Å, b = 14.580 (4) Å, c = 19.574 (6) Å, β = 107.23 (8)°, and R_w = 0.0448. The structure shows that the dienyl carbons (C4–C5–C6–C7–C8) are planar and form a dihedral angle of 45.8° with the nonbonded plane (C10–C9–C8–C4). The carbon skeleton defining the cycloheptadienyl ring possesses approximate C_s symmetry.

Introduction

The electrophilic activation of normally unreactive π-hydrocarbons as well as the stabilization of certain highly reactive carbonium ions (e.g., $C_6H_7^+$, $C_7H_7^+$) can frequently be accomplished by coordination to a transition-metal center.[2] This chemistry has attracted considerable attention due to its applications in organic synthesis. The best known reactions involving *cyclic* π-hydrocarbons are the addition of nucleophiles to the ring in (cyclohexadienyl)$Fe(CO)_3^+$ (eq 1)[3-6] and (arene)$Cr(CO)_3$[7] to give



(1)

(diene)$Fe(CO)_3$ and (dienyl)$Cr(CO)_3$ complexes. The functionalized diene or dienyl ligands can then be removed from the metal by a variety of oxidizing procedures. While (cyclohexadienyl)$Fe(CO)_3^+$ complexes are reactive toward even mild nucleophiles, only the most powerful carbanions react successfully with (arene)$Cr(CO)_3$. However, due in part to the positive charge, cationic (arene)$Mn(CO)_3^+$ complexes react smoothly with relatively mild carbon donors,[8] and in some cases the addition of two nucleophiles to the arene is possible[9,10] starting with (arene)$Mn(CO)_3^+$.

Nucleophilic addition to the π-hydrocarbon ring in (ring)ML_n^{m+} is closely related to additions to free carbonium ions. The latter reaction involves simple electrophile–nucleophile (E–N) combination, whereas the organometallic reactions also involve cleavage of a metal–metal bond, i.e., are really S_N2 reactions in which the leaving group (ML_n) remains bonded to the periphery of the molecule. Ritchie[11] has found that oxygen and nitrogen donor nucleophiles add to free carbonium ions (trityl, tropylium, pyronin, etc.) such that the relative nucleophilic reactivity is electrophile independent. Furthermore, this may also be true for atack on esters and activated arenes, providing the leaving group departure is not rate deter-

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Table I. ^{1}H NMR[a] and IR[b] Data for Cycloheptatriene Complexes $[(C_7H_8)Mn(CO)_2L]BF_4$

L	ν_{CO}, cm^{-1}	H(3,4)	H(2,5)	H(1,6)	H(7-endo)	H(7-exo)	L
CO	2078, 2022	6.96 (t, J = 4 Hz)[c]	5.82 (m)	4.61 (td, J = 9, 4 Hz)	3.34 (dt, J = 14, 9 Hz)	1.70 (dt, J = 14, 4 Hz)	
PPh_3	2007, 1961	6.26[d]	4.97	4.13	3.21	1.58	7.47[e]

[a] δ scale; see text for numbering scheme. [b] In CH_3NO_2. [c] In CD_3NO_2 with internal reference CHD_2NO_2 at δ 4.28. [d] In CD_2Cl_2 with ingernal reference $CHDCl_2$ at δ 5.32. [e] Average of aryl protons.

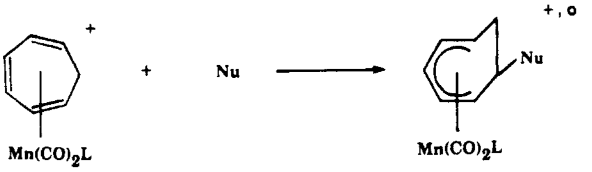
Table II. IR[a] Data for Cycloheptadienyl Complexes 2

L	Nu	ν_{CO}, cm^{-1}
CO	PPh_3	2029, 1949
CO	$P(4\text{-}ClC_6H_4)_3$	2027, 1950
CO	$P(OCH_2)_3CCH_3$	2031, 1955
CO	PBu_3	2028, 1950
CO	$P(OPh)_3$	2034, 1952
CO	$P(2\text{-}MeOC_6H_4)_3$	2020, 1945
CO	$P(C_2H_4CN)_3$	2034, 1955
CO	pyridine	2038, 1955[b]
CO	imidazole	2022, 1945
CO	$C_6H_5NMe_2$	2026, 1950, 1940[c]
CO	H^-	2026, 1951, 1941[c]
CO	CN^-	2026, 1945
CO	OH^-	2030, 1960, 1950[c]
CO	Ph^-	2016, 1944, 1934[d]
PPh_3	PPh_3	1945, 1887
PPh_3	$P(OBu)_3$	1944, 1883
PPh_3	$P(C_2H_4CN)_3$	1949, 1890
PPh_3	pyridine	1946, 1885
PPh_3	3-picoline	1946, 1887
PPh_3	imidazole	1940, 1879
PPh_3	H^-	1943, 1885

[a] In CH_3NO_2 unless otherwise noted. [b] In CH_2Cl_2. [c] In hexane. [d] In Et_2O.

mining. We have found[2] that phosphorus and nitrogen donor nucleophiles also follow an electrophile independent reactivity order for attack on coordinated cyclic π-hydrocarbons in a wide variety of organometallic electrophiles (vide infra). Moreover, the relative reactivities of P and N donors toward free carbonium ions seem to be the same as that observed with organometallic electrophiles,[12] meaning that nucleophilic attack on both free and complexed π-hydrocarbons follows a simple unified reactivity law that is independent of the electrophile. If this surprising result holds for carbon donors as well, the synthetic chemist will have a powerful predictive tool in synthetic procedures.

While nucleophilic addition to coordinated arene and cyclohexadienyl complexes has received considerable attention, comparatively few mechanistic, synthetic, or structural investigations have dealt with the coordinated seven-membered ring analogues, cycloheptatriene[13-15] and cycloheptadienyl[16-21] complexes. Herein we report a mechanistic study of P and N donor nucleophile addition to (cycloheptatreine)$Mn(CO)_2L^+$ (L = CO, PPh_3) according to eq 2. For most of the nucleophiles used (tertiary phosphines and phosphites and pyridines) the product 2 is cationic. With imidazole and *N,N*-dimethylaniline, however, the adduct 2 is neutral because a proton is lost from the nucleophile. Also presented herein is the X-ray structural characterization of 2 (Nu = PPh_3; L = CO; anion = BF_4^-).



1 2 (2)

Experimental Section

General Remarks. All solvents were distilled and dried prior to use. Nucleophiles were recrystallized or distilled. $P(OCH_2)_3CCH_3$ was synthesized as previously described[22] and was sublimed prior to use. Infrared and 250-MHz proton NMR spectra were obtained on Perkin-Elmer 681 and Bruker WM 250 instruments. The cycloheptatriene complexes $[(C_7H_8)Mn(CO)_2L]BF_4$ (L = CO, PPh_3) were prepared by procedures similar to published ones.[13] Some of the cationic cycloheptadienyl adducts 2 were prepared in situ while others were isolated by addition of diethyl ether to a CH_2Cl_2 solution of 1 containing excess nucleophile. IR and NMR data are given in Tables I–III. Elemental analysis was performed on 1 (L = CO, PPh_3) and 2 (L = CO; Nu = PPh_3, $P(4\text{-}ClC_6H_4)_3$, pyridine, $C_6H_4N(CH_3)_2$). In each case the analysis was satisfactory. The adducts 2 that were not isolated or analyzed gave clean IR and NMR spectra that clearly established their purity and structure.

Synthesis of $(Me_2NC_6H_4C_7H_8)Mn(CO)_3$. *N,N*-Dimethylaniline (0.075 g) and $[(C_7H_8)Mn(CO)_3]BF_4$ (0.15 g) were combined in 4 mL of freshly distilled nitromethane. The reaction mixture was kept at room temperature under N_2 and in the dark for ca. 30 min. An IR spectrum showed that the reaction had gone to completion. After the addition of 8 mL of diethyl ether, the reaction mixture was put through an acidic alumina column using diethyl ether as eluant. The solvent was evaporated and the residue dissolved in pentane and cooled to −10 °C. Filtration yielded 0.090 g of pure product. The IR and NMR data are listed in Tables II and III.

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Table III. ^{1}H NMR[a] Data for Cycloheptadienyl Complexes 2

L	Nu	H(3)	H(2)	H(4)	H(1)	H(5)	H(6)	H(7-endo)	H(7-exo)	Nu
CO	PPh_3	5.58 (t, J = 6 Hz)[b]	5.25[c]	4.93 (td, J = 8, 2 Hz)	4.80 (dt, J = 9, 2 Hz)	3.64 (m)	3.92 (t, J = 7 Hz)	2.65 (m)	1.39 (m)	7.77[d]
CO	$P(4\text{-ClC}_6H_4)_3$	5.59 (t, J = 6 Hz)[b]	5.24[c]	4.90 (m)	4.90 (m)	3.56 (m)	3.94 (t, J = 8 Hz)	2.73 (m)	1.38 (m)	7.67[d]
CO	$P(OCH_2)_3CCH_3$	6.05 (t, J = 6 Hz)[b]	5.38 (m)	5.38 (m)	4.02 (bt, J = 10 Hz)	3.42 (m)	3.66 (m)	2.69 (m)	1.98 (btd, J = 16, 6 Hz)	CH_2 4.81 (d) CH_3 1.06 (s)
CO	$C_6H_4NMe_2^-$	5.87 (t, J = 5 Hz)[e]	5.41 (dd, J = 8, 5 Hz)	4.94 (dd, J = 8, 5 Hz)	3.59 (bt, J = 9 Hz)	3.95 (bd)	4.20 (td, J = 10, 3 Hz)	2.07 (dt, J = 13, 10 Hz)	0.89 (m, J = 13, 10 Hz)	6.75[d] CH_3 2.9 (s)
CO	H^-	4.92 (tt, J = 6, 1 Hz)[f]	4.41 (dd, J = 10, 6 Hz)	4.41	3.32 (m)	3.32	1.86 (m)	1.86	1.1 (m)	1.1
CO	pyridine	6.09 (t, J = 6 Hz)[b]	5.68 (m)	5.50 (dd, J = 9, 7 Hz)	3.56 (m)	3.77 (d, J = 9 Hz)	5.68 (m)	2.65 (dt, J = 13, 9 Hz)	0.96 (m, J = 13, 10, 4 Hz)	8.42[d]
PPh_3	PPh_3	5.37[b,c]	4.94	4.35	4.61	2.90	3.24	2.37	1.09	7.76[d]

[a] δ scale; see text for numbering scheme. [b] In CD_2Cl_2 with internal reference $CHDCl_2$ at δ 5.32. [c] Partially obscured by solvent. [d] Average of aryl protons. [e] In CD_3Cl with Me_4Si reference at δ 0. [f] In C_6D_6 with internal reference C_6D_5H at δ 7.15.

Table IV. Rate Constants[a] for the Addition of Nucleophiles to $(C_7H_8)Mn(CO)_2L^+$

L	nucleophile	k_1, M^{-1} s^{-1}	k_{-1},[d] s^{-1}	K_{eq},[b] M^{-1}
CO	$P(4\text{-ClC}_6H_4)_3$	62000[c]		
CO	$P(CH_2CH_2CN)_3$	8300		
CO	$P(OBu)_3$	7050		
CO	$P(2\text{-MeC}_6H_4)_3$	370[c]	0.24 ± 0.05	1500
CO	$P(OCH_2)_3CCH_3$	28		
CO	$P(OC_6H_5)_3$	2.8	0.010 ± 0.002	280
PPh_3	3-picoline	40000		
PPh_3	$P(C_6H_5)_3$	21000		
PPh_3	imidazole	5500		
PPh_3	$P(OBu)_3$	120		
PPh_3	$P(CH_2CH_2CN)_3$	94	0.40 ± 0.10	230

[a] Data collected at 25 °C in nitromethane. Errors in k_1 estimated as ≤10%. [b] Calculated as k_1/k_{-1}. [c] From ref 14. [d] k_{-1} values are zero unless otherwise indicated.

Kinetic Studies. The kinetics of reaction 2 were studied in nitromethane with a Dionex stopped-flow spectrophotometer thermostated at 25 °C. Most reactions were followed at 395 or 402 nm with the metal complex at ca. 5 × 10^{-4} M and the nucleophile in at least tenfold excess. Pseudo-first-order rate constants were obtained two or more times at five or more nucleophile concentrations. Plots of the observed rate constant, k_{obsd}, vs. nucleophile concentration gave excellent fits to eq 3 from which the equilibrium constant could be calculated as k_1/k_{-1}. Table IV gives the results.

$$k_{obsd} = k_1[\text{Nu}] + k_{-1} \tag{3}$$

Collection and Refinement of X-ray Data. Crystals of $[(PPh_3C_7H_8)Mn(CO)_3]BF_4$ suitable for diffraction studies were obtained by slow diffusion of pentane into a CH_2Cl_2 solution at 0 °C. Reflection data was collected with a Nicolet R3m/E crystallographic system using the θ:2θ scan collection technique within the ranges 3.5° < 2θ < 45° and using Mo Kα radiation from a graphite monochromator (λ = 0.71069 Å). After Lorentz and polarization corrections a total of 2338 unique reflections were used for the calculations. An absorbance correction was made by defining a pseudoellipsoid based upon the psi scan data for seven reflections equally distributed throughout the range of 2θ. Crystal decomposition during data collection was not significant, as shown by a less than 2% decay of the intensity of three standard reflections that were monitored. The structure was solved by direct methods using the SHELXTL programs (Nicolet XRD Corporation, Madison, WI). Block-diagonal least-squares refinement was applied to all non-hydrogen atoms, which were ultimately refined anisotropically to minimize $\sum w(|F_c - F_o|^2)/F_o^2$, where $w = 1/[\sigma(F_o)^2 + 0.002(F_o)^2]$. Hydrogen atoms were located in a subsequent Fourier difference map and in the final stages of refinement were placed in calculated positions (r_{C-H} = 0.97 Å) from the phenyl carbons and constrained to r_{C-H} = 0.97 ± 0.03 Å from the cycloheptadienyl carbons to give R_w = 0.0448 based on F^2. A summary of X-ray diffraction data is given in Table V. Final positional parameters and selected bond distances and angles are presented in Tables VI–VIII. The atom numbering scheme in given in Figure 1.

Results and Discussion

Kinetic Studies. The rate law (eq 3) and the lack of any spectral evidence for intermediate species suggest that reaction 2 follows a simple bimolecular mechanism, without any initial interaction between the nucleophile and the metal. In support of this conclusion, the PPh_3 nucleophile is situated exo to the metal in $[(PPh_3C_7H_8)Mn(CO)_3]BF_4$ (vide infra). X-ray studies[23–25] have similarly shown that

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Table V. Summary of X-ray Diffraction Data

complex	$[(PPh_3C_7H_8)Mn(CO)_3]BF_4$
formula	$C_{28}H_{23}O_3F_4BPMn$
fw	580.199
a, Å	9.595 (3)
b, Å	14.580 (4)
c, Å	19.574 (6)
β, deg	107.23 (8)
V, Å³	2615.42
ρ(calcd), g cm⁻³	1.473
space group	$P2_1/c$—C_{2h}^5 (No. 14)
temp, °C	21 ± 1
radiatn	Mo K*α*, 0.710 69 Å
μ, cm⁻¹	6.00
2*θ* limits, deg	3.5-45
unique data $F_o^2 > 2.5\sigma(F_o^2)$	2338
final no. of variables	367
R_w	4.48
R	6.82

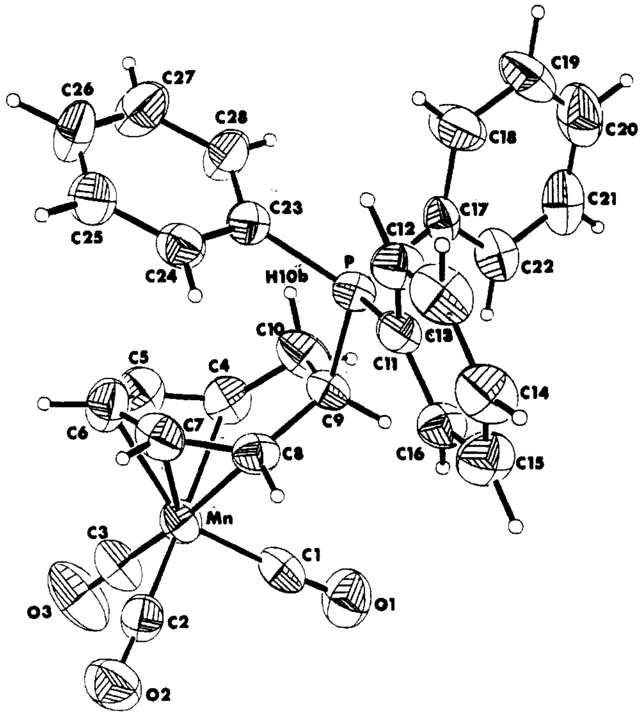

Figure 1. Structure and atom numbering scheme for the cation in $[(PH_3C_7H_8)Mn(CO)_3]BF_4$.

tertiary phosphines attack exo in $(C_4H_4)Fe(CO)_2NO^+$, $(C_6H_7)Fe(CO)_3^+$, and $(PhC_6H_6)Mn(CO)_2NO^+$.

Table VI. Fractional Coordinates (×10⁴) and Temperature Factors (Å × 10³) for $[(PPh_3C_7H_8)Mn(CO)_3]BF_4$

atom	*x*	*y*	*z*	*U*, Å²
Mn(1)	7470 (1)	114 (1)	1206 (1)	44 (1)[a]
P(1)	6013 (2)	1071 (1)	3193 (1)	37 (1)[a]
B(1)	7979 (10)	3503 (6)	1472 (4)	61 (4)[a]
F(1)	9123 (4)	2943 (3)	1544 (3)	129 (3)[a]
F(2)	8264 (5)	4162 (3)	1995 (2)	113 (2)[a]
F(3)	7573 (4)	3931 (2)	814 (2)	89 (2)[a]
F(4)	6820 (4)	2975 (3)	1541 (2)	78 (2)[a]
O(1)	5642 (4)	1587 (3)	350 (2)	71 (2)[a]
O(2)	10337 (4)	805 (3)	1145 (2)	69 (2)[a]
O(3)	7561 (4)	−997 (3)	−43 (2)	95 (2)[a]
C(1)	6373 (5)	1011 (4)	675 (3)	49 (2)[a]
C(2)	9210 (6)	553 (4)	1180 (3)	49 (2)[a]
C(3)	7487 (6)	−573 (4)	446 (3)	60 (3)[a]
C(4)	5428 (6)	−388 (4)	1373 (3)	52 (3)[a]
C(5)	6562 (7)	−1019 (4)	1606 (3)	59 (3)[a]
C(6)	7916 (7)	−819 (4)	2090 (4)	57 (3)[a]
C(7)	8359 (6)	67 (4)	2341 (3)	49 (2)[a]
C(8)	7467 (6)	855 (4)	2181 (3)	42 (2)[a]
C(9)	5944 (6)	977 (4)	2240 (3)	39 (2)[a]
C(10)	4876 (6)	230 (4)	1863 (3)	57 (3)[a]
C(11)	7123 (5)	2020 (3)	3619 (3)	40 (2)[a]
C(12)	7650 (5)	2040 (4)	4361 (3)	47 (2)[a]
C(13)	8434 (6)	2794 (4)	4706 (3)	55 (2)[a]
C(14)	8696 (6)	3518 (4)	4311 (4)	56 (3)[a]
C(15)	8186 (6)	3508 (4)	3577 (3)	56 (3)[a]
C(16)	7388 (6)	2762 (4)	3226 (3)	42 (2)[a]
C(17)	4206 (5)	1257 (3)	3268 (3)	38 (2)[a]
C(18)	3947 (7)	1125 (4)	3925 (3)	67 (3)[a]
C(19)	2592 (8)	1323 (5)	3996 (4)	84 (4)[a]
C(20)	1487 (7)	1666 (4)	3438 (5)	76 (4)[a]
C(21)	1740 (7)	1796 (4)	2790 (4)	62 (3)[a]
C(22)	3081 (6)	1595 (4)	2697 (3)	52 (3)[a]
C(23)	6764 (6)	33 (4)	3646 (3)	39 (2)[a]
C(24)	8279 (6)	−66 (4)	3935 (3)	46 (2)[a]
C(25)	8856 (7)	−896 (5)	4205 (3)	58 (3)[a]
C(26)	7968 (8)	−1623 (5)	4206 (3)	70 (3)[a]
C(27)	6482 (7)	−1538 (4)	3945 (3)	69 (3)[a]
C(28)	5879 (7)	−707 (4)	3660 (3)	56 (3)[a]
H(4)	4666 (39)	−580 (28)	943 (17)	64
H(5)	6375 (57)	−1565 (24)	1320 (23)	68
H(6)	8710 (38)	−1236 (25)	2228 (23)	69
H(7)	9383 (30)	109 (34)	2562 (22)	59
H(8)	8048 (39)	1401 (20)	2263 (21)	53
H(9)	5643 (50)	1584 (20)	2086 (24)	50
H(10a)	3958 (33)	470 (28)	1585 (21)	68
H(10b)	4579 (46)	−182 (25)	2177 (19)	68
H(12)	7472	1533	4636	60
H(13)	8794	2809	5219	66
H(14)	9243	4036	4551	68
H(15)	8378	4017	3307	68
H(16)	7022	2757	2714	51
H(18)	4707	895	4326	83
H(19)	2417	1220	4448	101
H(20)	554	1812	3498	87
H(21)	974	2031	2394	73
H(22)	3239	1688	2240	67
H(24)	8911	447	3941	58
H(25)	9894	−964	4397	66
H(26)	8387	−2203	4390	83
H(27)	5862	−2050	3960	81
H(28)	4839	−647	3471	66

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U'_{ij} tensor.

The rate constants for reaction 2 can be examined via eq 4, which is the expression used by Ritchie.[11] In this

$$\log k_1/k_0 = N_M \qquad (4)$$

equation k_1 is the second-order rate constant for nucleophile addition and k_0 refers to a reference nucleophile ($P(OBu)_3$ in our case). If relative nucleophilic reactivity is electrophile independent, the parameter N_M should be invariant, i.e., depend only on the nucleophile. Stated another way, plots of log k_1 vs. N_M should be linear with unit slope for *all* electrophiles. Table IX collects the N_M values for the nucleophiles used in this study. The N_M numbers given are averaged over a wide variety of organometallic substrates containing various π-hydrocarbon and metal fragments, although in fact nearly the same set of N_M values are found for each complex.[2] Preliminary evidence suggests that the same N_M numbers apply also to nonsterically crowded free carbonium ions.[12] Plots of log k_1 vs. N_M for reaction 2 are given in Figure 2. For 1 (L = CO) the slope is 1.02 ± 0.01 and for 1 (L = PPh_3) the slope is also 1.02 ± 0.10. These plots demonstrate that the reactions of 1 adhere closely to eq 4.

Particularly interesting is the reaction of 1 (L = CO) with $P(OBu)_3$ and the caged phosphite $P(OCH_2)_3CCH_3$, which is much less basic and has a smaller cone angle than

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Table VII. Bond Lengths (Å) for $[(PPh_3C_7H_8)Mn(CO)_3]BF_4$

Mn(1)-C(1)	1.803 (5)	Mn(1)-C(2)	1.802 (6)
Mn(1)-C(3)	1.796 (6)	Mn(1)-C(4)	2.205 (7)
Mn(1)-C(5)	2.123 (7)	Mn(1)-C(6)	2.142 (7)
Mn(1)-C(7)	2.133 (5)	Mn(1)-C(8)	2.195 (6)
P(1)-C(9)	1.853 (6)	P(1)-C(11)	1.793 (5)
P(1)-C(17)	1.802 (6)	P(1)-C(23)	1.794 (5)
B(1)-F(1)	1.342 (10)	B(1)-F(2)	1.371 (10)
B(1)-F(3)	1.379 (9)	B(1)-F(4)	1.392 (10)
O(1)-C(1)	1.157 (6)	O(2)-C(2)	1.163 (7)
O(3)-C(3)	1.159 (8)	C(4)-C(5)	1.394 (8)
C(4)-C(10)	1.522 (9)	C(5)-C(6)	1.393 (8)
C(6)-C(7)	1.403 (9)	C(7)-C(8)	1.411 (8)
C(8)-C(9)	1.509 (8)	C(9)-C(10)	1.528 (7)
C(11)-C(12)	1.391 (7)	C(11)-C(16)	1.393 (8)
C(12)-C(13)	1.388 (7)	C(13)-C(14)	1.376 (9)
C(14)-C(15)	1.373 (9)	C(15)-C(16)	1.389 (7)
C(17)-C(18)	1.394 (9)	C(17)-C(22)	1.394 (7)
C(18)-C(19)	1.378 (11)	C(19)-C(20)	1.373 (10)
C(20)-C(21)	1.373 (13)	C(21)-C(22)	1.383 (10)
C(23)-C(24)	1.402 (8)	C(23)-C(28)	1.379 (8)
C(24)-C(25)	1.370 (9)	C(25)-C(26)	1.360 (10)
C(26)-C(27)	1.371 (10)	C(27)-C(28)	1.386 (8)

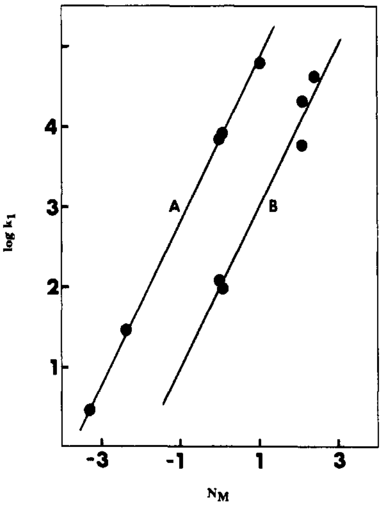
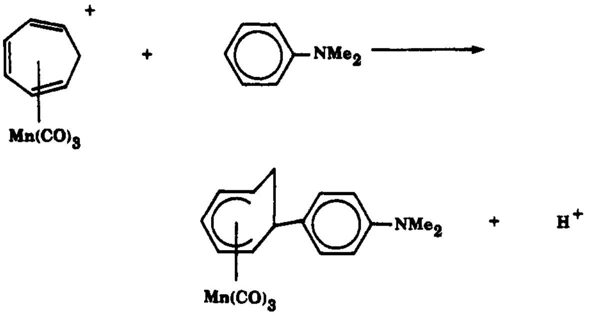


Figure 2. Plot of reactivity vs. N_M according to eq 4: (A) $(C_7H_8)Mn(CO)_3^+$; (B) $(C_7H_8)Mn(CO)_2L^+$.

$P(OBu)_3$. The rate constants show that $P(OBu)_3$ is 250 times more reactive, clearly establishing the importance of basicity while suggesting that steric interactions are not large for cone angles at least up to that for $P(OBu)_3$ (ca. 110°). In fact, the adherence to eq 4 suggests that substantially larger cone angles can be tolerated without steric congestions.[26]

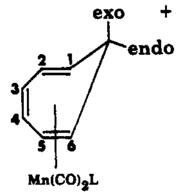
The effect of changing the ligand L in 1 from CO to PPh_3 is to cause a rate reduction, as would be expected. The rate constants k_1 decrease by a factor of ca. 75, which is nearly the same reduction found for addition to $(C_6H_7)Fe(CO)_3^+$, $(C_4H_4)Fe(CO)_2NO^+$, and $(RC_6H_6)Mn(CO)_2NO^+$,[2,27] It seems, therefore, that relative electrophilic activation is affected by an appoximately constant amount as CO ligands are replaced by phosphines. This, of course, has predictive value. Although replacing a CO ligand by PPh_3 reduces reactivity, such a modification can have a beneficial effect by decreasing the probability of single electron transfer from the nucleophile. It can also influence the reaction regiochemistry.[20]

Of the $(ring)ML_n^{m+}$ complexes that we have studied, 1 (L = CO) is the most electrophilic. **Table X** gives the relative reactivities for coordianted *triene* complexes. The data show that upon coordination to $Mn(CO)_3^+$, C_7H_8 is ca. 10^4 times more electrophilic than C_6H_6. This must be due to the resonance energy of the arene ring that is disrupted when a nucleophile adds. The large influence of the metal fragment is highlighted by the ca. 10^4 difference in reactivity of $(C_7H_8)Mn(CO)_3^+$ and $(C_7H_8)Fe(Cp)^+$. Another indication of the remarkable reactivity of 1 (L = CO) is the ease of reaction 5. This electrophilic aromatic substitution reaction goes cleanly as shown within a few minutes at room temperature in nitromethane. The NMe_2 substituent directs the electrophile exclusively para (vide infra). The reactivity of 1 (L = CO) is in fact so great that polar solvents with any nucleophilic properties (acetone, acetonitrile, etc.) rapidly attack the ring or the metal. Only carefully purified nitromethane was found to be a suitable solvent for 1 (L = CO). For many synthetic purposes it would probably be desirable to reduce the reactivity by using 1 (L = PPh_3), which is still quite electrophilic but not as sensitive to impurities as 1 (L = CO).

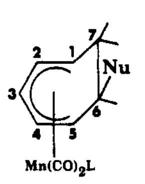


(5)

NMR Studies. NMR spectra for complexes 1 and 2 are reported in Tables I and III. Assignments were generally made by a combination of decoupling experiments, deuterium labeling experiments, comparisons with other spectra, and a consideration of coupling constants and dihedral angles obtained from X-ray structures of related systems. For example, the number and areas of the peaks and the splitting patterns in the spectrum of 1 (L = CO) indicates that a plane of symmetry exists which bisects the C3–C4 bond and passes through C7.



1



2

The NMR assignments of the exo and endo hydrogens in 1 and 2 were made by using a variety of criteria. Published spectra[28-31] of cycloheptatriene and cycloheptadienyl complexes suggest that the exo hydrogens generally are found at higher field. For $(C_7H_8)Mn(CO)_3^+$, the coupling constants definitely show that the high field band (δ 1.70) is exo-H^7. Thus, $J(\text{exo-}H^7, H^{1,6}) = 4$ Hz while $J(\text{endo-}H^7, H^{1,6}) = 9$ Hz. This is to be expected from models, which show a small dihedral angle between $H^{1,6}$ and endo-H^7 but a large one between $H^{1,6}$ and exo-H^7. X-ray structures of $(C_7H_8)Mo(CO)_3$[32] and (*exo*-PhC_7H_7)-

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[26] Steric effects can be large for some systems, e.g., $(PhC_6H_6)Mn(CO)_2NO^+$: Chung, Y. K.; Sweigart, D. A., unpublished results.

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Table VIII. Bond Angles (deg) for [(PPh$_3$C$_7$H$_8$)Mn(CO)$_3$]BF$_4$

C(1)-Mn(1)-C(2)	96.5 (2)	Mn(1)-C(8)-C(0)	122.1 (3)	C(7)-Mn(1)-C(8)	38.0 (2)
C(2)-Mn(1)-C(3)	86.6 (3)	P(1)-C(9)-C(8)	109.8 (3)	C(9)-P(1)-C(17)	110.2 (2)
C(2)-Mn(1)-C(4)	173.3 (2)	C(8)-C(9)-C(10)	133.9 (5)	C(9)-P(1)-C(23)	108.9 (3)
C(1)-Mn(1)-C(5)	122.9 (2)	P(1)-C(11)-C(12)	118.9 (4)	C(17)-P(1)-C(23)	110.1 (3)
C(3)-Mn(1)-C(5)	88.7 (3)	C(12)-C(11)-C(16)	119.3 (5)	F(1)-B(1)-F(3)	111.6 (8)
C(1)-Mn(1)-C(6)	150.3 (3)	C(12)-C(13)-C(14)	119.7 (5)	F(1)-B(1)-F(4)	107.8 (6)
C(3)-Mn(1)-C(6)	105.4 (3)	C(14)-C(15)-C(16)	119.9 (6)	F(3)-B(1)-F(4)	109.1 (6)
C(5)-Mn(1)-C(6)	38.1 (2)	P(1)-C(17)-C(18)	199.5 (4)	Mn(1)-C(2)-O(2)	177.1 (5)
C(2)-Mn(1)-C(7)	87.3 (2)	C(18)-C(17)-C(22)	118.8 (5)	Mn(1)-C(4)-C(5)	68.0 (4)
C(4)-Mn(1)-C(7)	86.2 (2)	C(18)-C(19)-C(20)	121.7 (8)	C(5)-C(4)-C(10)	124.6 (5)
C(6)-Mn(1)-C(7)	38.3 (2)	C(20)-C(21)-C(22)	121.3 (6)	Mn(1)-C(5)-C(6)	71.7 (4)
C(2)-Mn(1)-C(8)	95.1 (2)	P(1)-C(23)-C(24)	120.2 (4)	Mn(1)-C(6)-C(5)	70.2 (4)
C(4)-Mn(1)-C(8)	78.7 (2)	C(24)-C(23)-C(28)	118.9 (5)	C(5)-C(6)-C(7)	123.8 (6)
C(6)-Mn(1)-C(8)	70.2 (2)	C(24)-C(25)-C(26)	120.5 (6)	Mn(1)-C(7)-C(8)	73.4 (3)
C(9)-P(1)-C(11)	111.3 (3)	C(26)-C(27)-C(28)	119.6 (6)	Mn(1)-C(8)-C(7)	68.6 (3)
C(11)-P(1)-C(17)	107.4 (2)	C(1)-Mn(1)-C(3)	94.3 (2)	C(7)-C(8)-C(9)	128.1 (5)
C(11)-P(1)-C(23)	109.0 (2)	C(1)-Mn(1)-C(4)	86.2 (2)	P(1)-C(9)-C(10)	111.0 (4)
F(1)-B(1)-F(2)	111.9 (6)	C(3)-Mn(1)-C(4)	99.4 (2)	C(4)-C(10)-C(9)	114.7 (5)
F(2)-B(1)-F(3)	108.6 (6)	C(2)-Mn(1)-C(5)	140.5 (2)	P(1)-C(11)-C(16)	121.6 (4)
F(2)-B(1)-F(4)	107.7 (7)	C(4)-Mn(1)-C(5)	37.5 (2)	C(11)-C(12)-C(13)	120.2 (5)
Mn(1)-C(1)-O(1)	177.8 (5)	C(2)-Mn(1)-C(6)	106.5 (2)	C(13)-C(14)-C(15)	120.9 (5)
Mn(1)-C(3)-O(3)	176.7 (5)	C(4)-Mn(1)-C(6)	69.1 (2)	C(11)-C(16)-C(15)	120.0 (5)
Mn(1)-C(4)-C(10)	122.8 (4)	C(1)-Mn(1)-C(7)	127.4 (2)	P(1)-C(17)-C(22)	121.6 (5)
Mn(1)-C(5)-C(4)	74.5 (4)	C(3)-Mn(1)-C(7)	138.2 (2)	C(17)-C(18)-C(19)	119.7 (5)
C(4)-C(5)-C(6)	124.4 (6)	C(5)-Mn(1)-C(7)	70.8 (2)	C(19)-C(20)-C(21)	118.7 (7)
Mn(1)-C(6)-C(7)	70.5 (3)	C(1)-Mn(1)-C(8)	89.6 (2)	C(17)-C(22)-C(21)	119.9 (6)
Mn(1)-C(7)-C(6)	71.2 (3)	C(3)-Mn(1)-C(8)	175.6 (2)	P(1)-C(23)-C(28)	120.7 (4)
C(6)-C(7)-C(8)	124.8 (5)	C(5)-Mn(1)-C(8)	87.4 (2)	C(23)-C(24)-C(25)	119.9 (6)
				C(25)-C(26)-C(27)	120.8 (6)
				C(23)-C(28)-C(17)	120.4 (6)

Table IX. Relative Nucleophilic Reactivities[a]

nucleophile	N_M[a]	nucleophile	N_M[a]
3-picoline	2.4 (4)	P(CH$_2$CH$_2$CN)$_3$	0.1 (4)
imidazole	2.1 (5)	P(OBu)$_3$	(0) (11)
P(C$_6$H$_5$)$_3$	2.1 (12)	P(OCH$_2$)$_3$CCH$_3$	−2.4[b]
P(4-ClC$_6$H$_4$)$_3$	1.0 (3)	P(OC$_6$H$_5$)$_3$	−3.3 (4)

[a] The N_M values were calculated from eq 4 and are averaged from data for a variety of organometallic electrophiles, the number of which is given in parentheses. The maximum standard deviation in N_M is ±0.2 units. [b] N_M only available for (C$_7$H$_8$)Mn(CO)$_3^+$.

Table X. Relative Reactivity of Organometallic Electrophiles Containing Coordinated Trienes

complex	rel reactivity	complex	rel reactivity
Mn(CO)$_3$(C$_7$H$_8$)$^+$	45000	Os(C$_6$H$_6$)$_2^{2+}$	150
Fe(C$_6$H$_6$)$_2^{2+}$	18000	Fe(Cp)(C$_7$H$_8$)$^+$	4.0
Mn(CO)$_2$(PPh$_3$)(C$_7$H$_8$)$^+$	700	Mn(CO)$_3$(C$_6$H$_6$)$^+$	1.1
Ru(C$_6$H$_6$)$_2^{2+}$	600	Re(CO)$_3$(C$_6$H$_6$)$^+$	1.0

Cr(CO)$_3$[33] show the exo-H^7 dihedral angle to be 110–120° and the endo-H^7 to be 1–3°. For (C$_7$H$_8$)Mo(CO)$_3$ the exo- and endo-H^7 coupling to the olefinic protons is 2.6 and 8.7 Hz, respectively.[31]

The exo,endo assignments for the cycloheptadienyl complexes also comply with anticipated or known dihedral angles (vide infra). The addition and removal of H$^-$ or D$^-$ to 1 (L = CO) allows a self-consistent interpretation of reaction stereochemistry and NMR exo, endo assignments. Thus, the addition of NaBD$_4$ to 1 (L = CO) gives (C$_7$H$_8$-D)Mn(CO)$_3$. When compared to (C$_7$H$_9$)Mn(CO)$_3$, the highest field band is reduced in intensity by 50%. This shows that the addition is stereospecific and probably exo, as expected. Trityl fluoroborate reacts with (C$_7$H$_8$D)Mn(CO)$_3$ to give 60% (C$_7$H$_7$D)Mn(CO)$_3^+$ and 40% (C$_7$H$_8$)Mn(CO)$_3^+$. With the usual assumption that trityl cation only abstracts from the exo positions, the isotope effect is then 1.5. The fact that (C$_7$H$_8$)Mn(CO)$_3^+$ is formed in this reaction shows that the initial deuteride addition was exo, and hence the NMR assignements are verified.

As previously suggested,[29] the NMR spectrum of (C$_7$H$_9$)Mn(CO)$_3$ shows that the molecule has a plane of symmetry bisecting C6–C7. It is claimed[29] that in (exo-RC$_7$H$_8$)Mn(CO)$_3$ (R = Me, OMe) the ring skeleton is twisted about the C6–C7 bond such that the exo group on C6 eclipses the endo hydrogen on C7, with associated changes in dihedral angles and coupling constants. However, as discussed below, such a deformation from a pseudosymmetrical ring skeleton is not found in [(*exo*-PPh$_3$C$_7$H$_8$)Mn(CO)$_3$]BF$_4$. Since PPh$_3$ is quite bulky, we suggest that sterically induced skeletal deformations probably do not exist as claimed in (*exo*-RC$_7$H$_8$)Mn(CO)$_3$.

The NMR spectrum of the product of reaction 5 shows from the arene ring proton pattern that the substitution occurred para to the NMe$_2$ group.

Description of the Structure of [(PPh$_3$C$_7$H$_8$)Mn(CO)$_3$]BF$_4$. The observed structure confirms that PPh$_3$ adds to 1 (L = CO) in the exo position, as inferred from NMR data. The bond lengths and angles in [(PPh$_3$C$_7$H$_8$)Mn(CO)$_3$]BF$_4$ are all fairly typical. The dienyl carbon atoms C4–C5–C6–C7–C8 are planar (maximum deviation = 0.031 Å). The attached hydrogen atoms are displaced slightly toward the metal. The carbon atoms C10–C9–C8–C4 are roughly planar (maximum deviation = 0.060 Å). The dihedral angle between these two planes is 45.8 (0.5)°, which is typical for six- and seven-membered diene, dienyl, and triene rings.[34] The average dihedral angle defined by the ring sp^3 carbons and the next three sp^2 carbon atoms (C6–C7–C8–C9; C6–C5–C4–C10) is 49.5 (0.5)°, which is about the same as that found in coordinated cyclohexadiene rings.[34] The approximate symmetrical arrangement of the seven-membered ring is further shown by the small dihedral angles defined by P1–C9–

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C10–H10b (15 (2)°) and H9–C9–C10–H10a (11 (3)°). There is no evidence for substantial skeletal twisting as proposed[29] for (*exo*-RC_7H_8)$Mn(CO)_3$ (vide supra).

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Registry No. 1 (L = CO), 95345-58-7; 1 (L = PPh_3), 95345-59-8; **2** (L = CO, Nu = PPh_3)·BF_4, 95345-61-2; **2** (L = CO, Nu = $P(4–ClC_6H_4)_3$)·BF_4, 95405-35-9; **2** (L = CO, Nu = $P(OCH_2)_3CCH_3$)·BF_4, 95363-22-7; **2** (L = CO, Nu = PBu_3)·BF_4, 95345-63-4; **2** (L = CO, Nu = $P(OPh)_3$)·BF_4, 95345-65-6; **2** (L = CO, Nu = $P(2–MeOC_6H_4)_3$)·BF_4, 95345-67-8; **2** (L = CO, Nu = $P(C_2H_4CN)_3$)·BF_4, 95363-24-9; **2** (L = CO, Nu = pyridine)·BF_4, 95345-69-0; **2** (L = Co, Nu = imidazole), 95345-70-3; **2** (L = Co, Nu = $C_6H_5NMe_2$)·BF_4, 95345-72-5; **2** (L = CO, Nu = H^-), 32798-86-0; **2** (L = CO, Nu = D^-), 95345-87-2; **2** (L = CO, Nu = CN^-), 65878-76-4; **2** (L = CO, Nu = OH^-), 95345-73-6; **2** (L = CO, Nu = Ph^-), 95405-36-0; **2** (L = CO, Nu = $P(oBu)_3$), 95345-86-1; **2** (L = PPh_3, Nu = PPh_3)·BF, 95345-75-8; **2** (L = PPh_3, Nu = $P(oBu)_3$)·BF, 95345-77-0; **2** (L = PPh_3, Nu = $P(C_2H_4CN)_3$)·BF_4, 95345-79-2; **2** (L = PPh_3, Nu = pyridine)·BF_4, 95345-81-6; **2** (L = PPh_3, Nu = 3–picoline), 95345-83-8; **2** (L = PPh_3, Nu = imidazole), 95345-84-9; **2** (L = PPh_3, Nu = H^-), 32798-88-2; $(C_7H_7D)Mn(CO)_3{}^+BF_4{}^-$, 95345-89-4; $Mn(CO)_3(C_7H_8)^+$, 46238-50-0; $Fe(C_6H_6)2^{2+}$, 51263-22-0; $Mn(CO)_2(PPh_3)(C_7H_8)^+$, 95345-90-7; $Ru(C_6H_6)_2{}^{2+}$, 71825-67-7; $Os(C_6H_6)_2{}^{2+}$, 76680-98-3; $Fe(Cp)(C_7H_8)^+$, 79105-23-0; $Mn(CO)_3(C_6H_6)^+$, 41656-02-4; $Re(CO)_3(C_6H_6)^+$, 68927-89-9; PPh_3, 603-35-0; $P(4–ClC_6H_4)_3$, 1159-54-2; $P(OCH_2)_3CCH_3$, 1449-91-8; PBu_3, 998-40-3; $P(OPh)_3$, 101-02-0; $P(2-MeOC_6H4)_3$, 4731-65-1; $P(C_2H_4CN)_3$, 4023-53-4; $C_6H_5NMe_2$, 121-69-7; $P(OBu)_3$, 102-85-2; pyridine, 110-86-1; imidazole, 288-32-4; 3-picoline, 108-99-6.

Supplementary Material Available: Tables of anisotropic thermal factors and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

Preparation of Binuclear Copper–Cobalt Compounds. Crystal Structure of (tmed)$CuCo(CO)_4$

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The reaction of L_2CuCl with $Co(CO)_4{}^-$ or $Co(CO)_3PR_3{}^-$ leads to the formation of binuclear Cu–Co complexes. Solution infrared data indicates that these complexes contain a single Cu–Co bond with no CO–Cu interaction. The solid-state spectra were similar except for that of (tmed)$CuCo(CO)_4$ which exhibits a low-frequency band at 1820 cm^{-1}. A single-crystal structural analysis of this material was undertaken. The molecule $[(CH_3)_2NCH_2CH_2N(CH_3)_2]CuCo(CO)_4$ crystallizes in the orthorhombic space group $Pna2_1$ with a = 16.681 (3) Å, b = 8.797 (1) Å, and c = 9.994 (1) Å. Full-matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms and fixed, isotropic thermal parameters for the hydrogens have converged to R = 0.051 and R_ω = 0.053 for the 862 observed reflections. The Cu and Co are bonded at a distance of 2.38 Å. One of the carbonyl groups asymmetrically bridges the Cu–Co bond; the three remaining carbonyls are terminally bonded to the Co atom. The tmed molecule functions as a bidentate ligand on the Cu, which exhibits nearly planar coordination.

Introduction

Motivated by the use of copper oxide in the commercial low-pressure methanol synthesis catalysts,[1] there has been a renewed interest in the chemistry of copper(I) carbonyl species. Although the function of the copper in the Cu/Zn methanol catalysts is not known for certain, it has been postulated that CO is activated by forming a Cu(I) complex.[2] This type of activation by Cu(I) complexes has yet to be demonstrated in homogeneous systems although a variety of different types of copper(I) carbonyl complexes are known.

One of the more interesting classes of compounds in the binuclear copper complexes with a bridging carbonyl group first discovered by Floriani and his co-workers.[3,4] It has been suggested that these complexes with bridging carbonyls contain CO in an environment with facilitates its metal-promoted reduction, but this has not been substantiated. In addition to our work on homobinuclear copper complexes,[5] we wished to also investigate some heterobinuclear complexes containing copper and another transition metal. A small number of these complexes had previously been prepared and characterized[6] but little was known of their catalytic properties. The structure of one complex, (*o*-triars)$CuMn(CO)_5$, has been determined and was found to have a Cu–Mn bond but little interaction between the copper atom and the carbonyl groups.[7] It

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(1) The production of methanol under relatively mild conditions is described in a number of patents. Among the most pertinent are the following assigned to either BASF or ICI, Ltd.: Ger. Apt. 2 056 612, Ger. Pat. 2 302 658, Fr. Pat. 1 489 682, Fr. Pat. 2 037 567, Ger. Pat. 2 116 949, and U.S. Pat. 3 326 956.

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