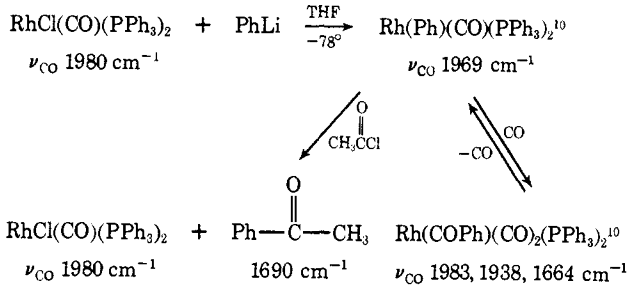
this method, has recently been isolated and characterized.[6] The oxidative addition of acid chlorides to coordinatively unsaturated metal(I) complexes to produce acylmetal(III) complexes (**2** → **3**) is also well known.[7] The enhanced reactivity toward oxidative addition of acid halides displayed by **2** (hours at $-78°$) compared with **1** (inert)[8] is likely a result of the increase of electron density at the central metal caused by replacement of halogen with alkyl.[9] The reductive elimination step (**3** → **1** + ketone) (reverse of oxidative addition) is likewise a well-known reaction.[7,9]

In an attempt to characterize some of the intermediates proposed in Scheme I, the reaction mixture was periodically examined by infrared spectroscopy (AgBr sealed cells) as the reaction ensued. Bis(triphenylphosphine)carbonylchlororhodium(I) (ν_{CO} (THF) 1980 cm^{-1}) was treated with methyllithium at $-78°$. After 1 hr, all the starting complex had dissolved producing $Rh(CH_3)(CO)(PPh_3)_2$. The infrared spectrum showed a shift of the CO absorption to 1962 cm^{-1}, as expected ($CH_3 > Cl$ in electron-donating abilities). Benzoyl chloride was added. The resulting solution had absorptions at 1980 (ν_{CO} $RhCl(CO)(PPh_3)_2$), 1962 (ν_{CO} $Rh(CH_3)(CO)(PPh_3)_2$), 1794 and 1734 (ν_{CO} $PhC(=O)Cl$), and 1690 cm^{-1} (ν_{CO} $PhC(=O)CH_3$). There were *no* absorptions in the 2100–2000-cm^{-1} region, indicating the absence of any rhodium(III) carbonyl species, and none in the 1650-cm^{-1} region, indicating the absence of acylrhodium species. Thus, the Rh^{III}(alkyl)(acyl) complex **3** must be very unstable, and immediately collapse to ketone and $RhCl(CO)(PPh_3)_2$. As the reaction progressed, the band at 1962 cm^{-1} decreased and the band at 1980 cm^{-1} increased, as $Rh(CH_3)(CO)(PPh_3)_2$ was converted to $RhCl(CO)(PPh_3)_2$.

A portion of the $Rh(CH_3)(CO)(PPh_3)_2$ solution was stirred for 1 hr under an atmosphere of CO. The color of the solution went from red to pale yellow and developed bands at 1983 and 1955 cm^{-1} (RhCO) as well as a band at 1679 cm^{-1} ($RhC(=O)CH_3$). The complex is likely to be $Rh(COCH_3)(CO)_2(PPh_3)_2$ resulting from carbonylation and insertion of CO by $Rh(CH_3)(CO)(PPh_3)_2$. This complex readily lost CO.

A similar series of reactions was carried out using phenyllithium and acetyl chloride at $-78°$ in THF. The infrared spectral results are summarized in Scheme II. Again no Rh^{III}(acyl)(alkyl) complex could be detected.

Scheme II



We have also initiated investigations directed toward producing alkylrhodium(I) complexes from hydridorhodium(I) complexes and unsaturated carbon compounds.[10,11] An initial result is reported in eq 1.[12] The full details of these studies, as well as further

$$Rh(H)(CO)L_3 + PhC{\equiv}CPh + CH_3COCl \xrightarrow[\substack{25° \\ 40\%}]{THF} PhCH{=}C(Ph)COCH_3 + Rh(Cl)(CO)L_2 \quad (1)$$

reactions of alkylrhodium(I) complexes with reactive organic substrates, will be forthcoming.

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New Metalloboranes. $[Mn(CO)_3(B_9H_{13})]^-$ and $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$

Sir:

In studying the chemistry of the $B_9H_{14}^-$ anion we have found that reaction with $Mn(CO)_5Br$ in refluxing tetrahydrofuran (THF) produces several metalloboranes. To date we have isolated salts of the metalloborane anion $[Mn(CO)_3(B_9H_{13})]^-$ (I) and the neutral $Mn(CO)_3[B_9H_{12}(THF)]$ (II).

The tetramethylammonium salt of I, obtained in about 40% yield, is an air-stable reddish orange crystalline material exhibiting 1:1 electrolyte behavior in acetonitrile. *Anal.* Calcd for $[(CH_3)_4N][Mn(CO)_3(B_9H_{13})]$: C, 25.97; H, 7.79; N, 4.33; B, 30.08; Mn, 16.99. Found: C, 23.21; H, 7.93; N, 4.37; B, 30.65; Mn, 17.18; mp 200° (dec). The neutral II is also an air-stable reddish orange crystalline material that will sublime in high vacuum at 50–70°, mp 189° (dec). High-resolution mass spectral data confirmed the composition: calcd for $^{55}Mn(^{12}C^{16}O)_3(^{11}B_9{}^1H_{12}\cdot{}^{16}O^{12}C_4{}^1H_8)$, 322.1580; found, 322.1604. The electronic spectra of I and II were virtually identical, consisting of two broad, well defined peaks at 4570 and 3080 Å.

The infrared spectrum of I contains BH stretching frequencies at 2630 (m), 2560 (s), and 2480 (s) cm^{-1} and CO stretching frequencies at 2060 (s), 2005 (vs), and 2025 (vs) cm^{-1}. The infrared spectrum of II is somewhat different, having BH stretching frequencies at 2610 (s), 2580 (s), and 2520 (s) cm^{-1} and CO stretching frequencies at 2055 (vs), 1950 (vs sh), and 1930 (vs) cm^{-1}.

The ^{11}B nmr spectra of I and II are reminiscent of those of decaborane(14) derivatives. The spectrum (32.1 MHz, $BF_3 \cdot OEt_2$ as reference) of I consists of a multiplet of two overlapping doublets (determined by decoupling ^1H) at -11.8 and -9.2 ppm (relative intensity of approximately 2:2), a doublet at 0.9 ppm (intensity 3), and two small doublets (both intensity 1) at 27.4 and 34.3 ppm. The spectrum of II was similar at low field with less well resolved doublets at -9.0, -6.9, and 2.9 ppm (overall intensity 8) and a single high-field doublet at 36.5 ppm (intensity 1). Coupling constants, where resolved, were similar to those of decaborane(14) derivatives. The ^1H nmr spectra of I and II were quite similar, containing five overlapping sets of quartets at $\tau \sim 6$ to 12 (BH terminal, determined by decoupling ^{11}B), a single broad peak at $\tau \sim 13.5$ (B–H–B), and a similar broad peak at $\tau \sim 21.4$ (Mn–H–B). The complexed THF in II was readily identified.

The crystal and molecular structure of II has been determined by single-crystal X-ray techniques. The compound crystallizes in space group $P\bar{1}$ with lattice constants $a = 12.866$ (23), $b = 9.792$ (21), $c = 7.183$ (13) Å; α 90.21 (6), $\beta = 108.12$ (6), $\gamma = 104.48$ (6)°. There are two molecules in the unit cell. The intensity data were collected by using a FACS-I diffractometer, at room temperature, using Mo Kα radiation. A complete sphere of data bounded by $2\theta = 45°$ was collected. All the atomic positions were located by Patterson and Fourier techniques, and full-matrix refinement of 1363 observed reflections provided conventional and weighted R values of 3.4 and 4.1%, respectively. The structure is shown in Figure 1.

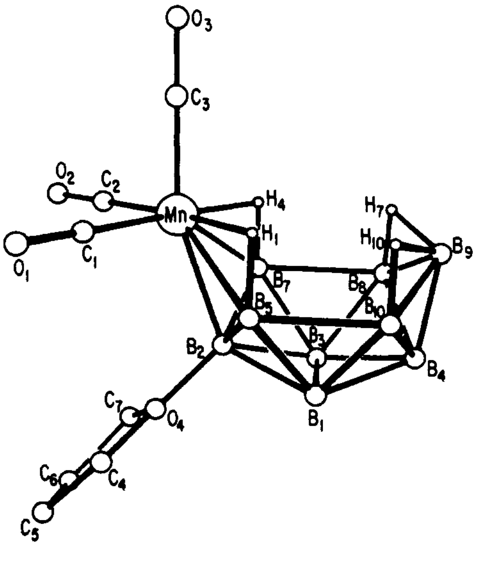

Figure 1. The structure of $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$. Terminal hydrogens on C_4–C_7, B_1, and B_3–B_{10} have been omitted for clarity.

Representative angles and distances around the manganese atom in II are listed in Table I. The angles and distances in the remainder of the B_9 cage are very similar to those in $B_{10}H_{14}$.[1] The spectroscopic similarities of I and II suggest that they possess identical metalloborane cage arrangements. This similarity has been further verified by a preliminary crystallographic investigation of the potassium salt of I.

Table I. Selected Interatomic Distances and Angles in $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$ (II)

Angles, deg		Distances, Å	
H_1–Mn–H_4	93.45 (2.30)[a]	Mn–C_3	1.793 (5)
H_1–Mn–C_3	91.32 (1.46)	Mn–H_1	1.75 (4)
H_1–Mn–C_2	175.70 (1.48)	B_5–H_1	1.24
C_1–Mn–C_2	90.10 (18)	Mn–B_5	2.237 (5)
C_1–Mn–C_3	91.11 (23)	Mn–B_2	2.196 (6)
B_2–Mn–C_3	161.38 (07)	B_2–O_4	1.526
B_2–Mn–H_1	77.52 (1.45)		

[a] Standard deviations.

A unique feature of these new metalloboranes is their high thermal, hydrolytic, and oxidative stability compared to that of other metalloboranes.[2] This stability is undoubtedly related to unusual bonding of the metal to the borane cage. The B_9 moiety can be considered to be tridentate and is formally a five-electron donor bound to the Mn by two three-center two-electron hydrogen bridge bonds (that contribute a total of three electrons to the metal) and a single boron–metal bond [Mn–B(2)] (that contributes two electrons to the metal). It has been suggested that the B_9 moiety in *trans*-$[(C_2H_5)_3P]_2PtB_9H_{11}L$[3] is effectively a bidentate ligand. The evidence at hand indicates that these latter compounds are most likely not related, in a bonding sense, to the compounds reported here.

Under selected photolytic conditions it has been possible to exchange triphenylphosphine ligands for several of the CO ligands on I and II and also for the complexed tetrahydrofuran on the covalent species II. Attempts to displace THF using amines results in a more complex reaction that is described elsewhere.[4]

The chemistry of these compounds and other transition metal derivatives of $B_9H_{14}^-$ is under investigation and will be more fully reported later.

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Diaminocyclopropenones and Diaminocyclopropenethiones. Quasi-urea and Quasi-thiourea

Sir:

The highly strained, smallest ring systems having heterosubstituents are of considerable interest from organic and theoretical viewpoints. As has been re-