between the two possible structures $SF_5N(CF_3)CF_2CFClCF_3$ and $SF_5N(CF_3)CF(CF_2Cl)CF_3$.

Anal. Calcd. for C_4ClF_4NS: Cl, 8.95; F, 67.2. Found: Cl, 8.73; F, 66.6.

Reactions of $SF_5N{=}CF_2$. A. Preparation of $SF_5N{=}CFN(CF_3)SF_5$.—Potassium fluoride (50 g., 0.86 mole) and $SF_5N{=}CF_2$ containing about 15% $SF_4{=}NCF_3$ (40 g., 0.21 mole total) were heated for 3 hr. at 225° with agitation in a 500-ml., Hastelloy C pressure reactor. The gaseous product (32 g.) was shown by infrared analysis to contain, on a molar basis, 70% $SF_5N{=}CF_2$, 20% $SF_4{=}NCF_3$, and 10% SF_5NCO. The 4.5 g. of liquid product was purified by preparative gas chromatography.

Anal. Calcd. for $C_2F_{14}N_2S_2$: F, 69.6; S, 16.8. Found: F, 69.5; S, 17.3.

The infrared spectrum (liquid) showed C=N absorption at 1725 cm.$^{-1}$. The F^{19} n.m.r. spectrum revealed the presence of two SF_5 groups, a CF_3 group, and CF in about the proper 5:5:3:1 intensity ratio. The spectrum was a composite of an AB_4X_3 and an AB_4X pattern with the CF multiplet at −66.3 p.p.m., the CF_3 multiplet at −11.5 p.p.m., the AB_4X_3 pattern centered around −142 p.p.m., and the AB_4X pattern around −131 p.p.m.

Potassium fluoride (70 g., 1.21 moles) and SF_5NHCF_3 (49 g., 0.23 mole) were heated with agitation for 1 hr. at 100° and for 2 hr. at 225° in a 300-ml. Hastelloy C pressure reactor. The crude gaseous and liquid product (38 g.) yielded 23 g. of volatiles which infrared analysis showed was 40% $SF_5N{=}CF_2$, 20% $SF_4{=}NCF_3$, 15% SF_5NHCF_3, and 10% SF_5NCO, as well as 6.8 g., b.p. 88–92°, of $SF_5N{=}CFN(CF_3)SF_5$.

B. **Preparation of $Hg[N(CF_3)SF_5]_2$.**—The liquid products (212 g.) from two experiments, each involving the reaction of mercuric fluoride (53.3 g., 0.22 mole) and $SF_5N{=}CF_2$ (68.5 g., 0.36 mole) at 100° for 3 hr. and at 125° for 3 hr. in a 300-ml. Hastelloy C reactor, were combined. Distillation yielded 169 g. (76% conversion) of the colorless mercurial, b.p. 43–44° (3 mm.).

Anal. Calcd. for $C_2F_{16}HgN_2S_2$: F, 49.0; Hg, 32.3. Found: F, 49.0; Hg, 31.9.

The F^{19} n.m.r. spectrum was an AB_4X_3 pattern with the CF_3 multiplet at −20.4 p.p.m. and the AB_4 pattern centered around −148 p.p.m. The liquid mercurial was rapidly hyrolyzed by moist air with the formation of yellow mercuric oxide.

Benzoyl chloride (10 g., 0.07 mole) was added with stirring to $Hg[N(CF_3)SF_5]_2$ (20 g., 0.03 mole) over a period of 0.30 hr. during which the temperature rose from 25 to 35° and large amounts of a white solid formed. Reaction was completed by warming gradually to 88° over a period of 0.80 hr. The liquid product (16 g.) was decanted from the solid mercuric chloride and distilled at 46–47° (2.2 mm.). Since the product contained unreacted benzoyl chloride, the sample was stirred with 50 ml. of 10% aqueous sodium hydroxide for 5 hr. Redistillation yielded 5.8 g. of colorless $C_6H_5C({=}O)N(CF_3)SF_5$, b.p. 56–57° (4.35 mm.).

Anal. Calcd. for $C_8H_5F_8NOS$: C, 30.4; H, 1.59; F, 48.2; S, 10.2. Found: C, 31.3; H, 1.89; F, 48.0; S, 9.9.

The F^{19} n.m.r. spectrum was an AB_4X_3 pattern with the CF_3 multiplet at −13.3 p.p.m. and the AB_4 pattern centered around −143 p.p.m. Mass spectrometric analysis was satisfactory with peaks present which corresponded to the parent, and lower mass fragments which supported the structure, including large SF_5, CF_3, and $C_6H_5C{=}O$ peaks. The infrared carbonyl stretching frequency was 1740 cm.$^{-1}$.

NOTE ADDED IN PROOF.—R. Tunder and B. Siegel, *J. Inorg. Nucl. Chem.*, **25**, 1097 (1963), report the synthesis of $(CH_3)_4N^+SF_5^-$ from SF_4 and $(CH_3)_4NF$.

[CONTRIBUTION NO. 921 FROM THE CENTRAL RESEARCH DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON, DELAWARE]

Borane Complexes of Transition Metals

BY G. W. PARSHALL

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Crystalline complexes containing BH_3 as an electron-accepting ligand have been obtained by reaction of diborane with group VII metal carbonyl anions. Salts of $[Re(CO)_5]^-$, $[Mn(CO)_5]^-$, and $[(C_6H_5)_3PMn(CO)_4]^-$ give monoborane complexes in which the BH_3 is coordinated to the metal. Salts of a bis(borane) complex, $[(H_3B)_2Re(CO)_5]^-$, have also been isolated.

One of the dominating aspects of boron hydride chemistry is the electron deficiency of the lower boranes. Borane (BH_3), the simplest boron hydride, seems incapable of independent existence. Many stable derivatives of borane have been obtained by complex formation with molecules or ions which can supply an electron pair to the boron. Neutral ligands, such as amines, phosphines, and ethers, and anions ranging from hydride to fluoride have given isolable borane complexes. Recently Shriver[1] has reported the isolation of complexes in which BF_3 and BH_3 are coordinated to the cyanides of dicyanobis(1,10-phenanthroline)iron. To date, however, no compounds in which borane is coordinated to a transition metal have been described.

In the present work, such borane complexes have been obtained by treating borane etherates with relatively basic transition metal anions. Crystalline complexes containing BH_3 as a ligand have been isolated by reaction with salts of $[Re(CO)_5]^-$, $[Mn(CO)_5]^-$, and $[(C_6H_5)_3PMn(CO)_4]^-$. In addition, some reaction has been noted with $[Co(CO)_4]^-$.

Rhenium Complexes.—The reaction of $NaRe(CO)_5$[2] with an equivalent amount of a borane etherate gave the simple complex I. Treatment with an excess of borane etherate gave II which contains two borane moieties per rhenium atom. The course of complex formation was followed by the change of diborane pressure over a solution of $NaRe(CO)_5$ in bis(2-methoxyethyl) ether. No further absorption beyond two boranes per rhenium was noted.

$$[Re(CO)_5]^- + R_2O{\cdot}BH_3 \longrightarrow \underset{\text{I}}{[H_3B{\cdot}Re(CO)_5]^-} + R_2O$$

$$\text{I} + R_2O{\cdot}BH_3 \longrightarrow \underset{\text{II}}{[(H_3B)_2Re(CO)_5]^-} + R_2O$$

The sodium salts of the complexes crystallize as solvates containing several molecules of the ether, but crystalline, nonsolvated tetraethylammonium and tetrabutylphosphonium salts of both borane complexes have been isolated by metathetical reactions in tetrahydrofuran. Both of the borane complexes hydrolyze readily in water or dilute acid to give boric acid and $HRe(CO)_5$. They are very mild reducing agents in tetrahydrofuran solution. At room temperature, they readily reduce quinones but do not reduce acetone or benzaldehyde.

The spectral properties of the two borane complexes of the pentacarbonylrhenate anion are somewhat similar. The infrared spectra (Table I) in tetrahydrofuran solution show three similar, strong metal carbonyl stretching frequencies. The additional bands noted in the mull spectra may be due to coupling with crystal lattice vibrations. Both spectra show B–H stretching absorption at 2400–2408 cm.$^{-1}$. The mull spectrum of the bis(borane) complex (II) also shows an equally strong absorption at 2453 cm.$^{-1}$. If the two bands are assigned to nonequivalent BH_3 groups,

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[1] D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963). Shriver recently has reported that BF_3 and $(C_5H_5)_2WH_2$ give a complex which is believed to contain a W–B coordinate bond [*ibid.*, **85**, 3509 (1963)].

[2] W. Beck, W. Hieber, and G. Braun, *Z. anorg. allgem. Chem.*, **308**, 23 (1961).

TABLE I

INFRARED SPECTRA OF GROUP VII METAL CARBONYL ANIONS

Metal complex	State	B–H stretch, cm.⁻¹	C=O, stretch, cm.⁻¹
$NaRe(CO)_5$	THF solution		2085 w, 2070 w, 2058 w, 2036 w, 2014 s, 1972 s, 1922 s, 1887 m
$Na[H_3B \cdot Re(CO)_5]$	THF solution	2404	2060 w, 2002 s, 1974 vs, 1916 s
$(C_2H_5)_4N[H_3B \cdot Re(CO)_5]$	KBr wafer	2400	1998 s, 1953 s, 1886 s
$(C_2H_5)_4N[H_3B \cdot Re(CO)_5]$	Nujol mull	2405 m	2000 s, 1954 s, 1936 sh, 1907 m, 1850 s
$(C_2H_5)_4N[(H_3B)_2Re(CO)_5]$	Nujol mull	2453 m, 2404 m	2000 s, 1950 s, 1901 s, 1863 s
$(C_4H_9)_4P[(H_3B)_2Re(CO)_5]$	THF solution	2408	2086 w, 2074 w, 2058 w, 2032 w, 2000 m, 1968 vs, 1920 s
$Na[(C_6H_5)_3PMn(CO)_4]$	THF solution		2068 w, 1946 s, 1900 w, 1863 s, 1828 s, 1780 s
$Na[H_3B \cdot Mn(CO)_4 \cdot P(C_6H_5)_3]$	THF solution	2387	2068 s, 1968 vs, 1905 m, 1846 m, 1830 m, 1779 w
$(C_2H_5)_4N[Mn(CO)_5]$	THF solution		1902 s, 1878 s
$(C_2H_5)_4N[H_3B \cdot Mn(CO)_5]$	Nujol mull	2470, 2410	Broad, featureless

the absence of the second band in the solution spectrum of II suggests that one BH_3 group dissociates or that the two become equivalent in solution. The similarity of the carbonyl stretching frequencies also suggests that the two complexes have similar effective symmetries (no higher than C_{4v}) in solution.

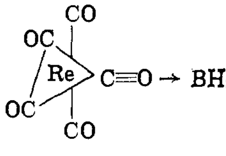
The electronic spectra of the two borane complexes (Table II) are similar. Both show strong, featureless absorption in the ultraviolet with weak "tails" extending into the visible region. The nuclear magnetic resonance spectra were not definitive. The B^{11} spectra showed only broad, featureless peaks at *ca.* 20 p.p.m. to the high-field side of methyl borate. Since the borane etherates also absorb in the same region, no conclusion can be drawn as to the degree of dissociation of II. The proton resonance signal of the BH_3 group of I appeared as a quadruplet (J = 83 c.p.s.) centered at 0.59 p.p.m. to the high field side of tetramethylsilane (external reference). Neither I nor II gave a paramagnetic resonance signal.

TABLE II

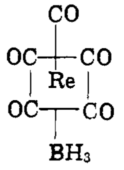
ELECTRONIC SPECTRA OF GROUP VII METAL CARBONYL COMPLEXES

Complex	Solvent	Maxima, Å.	Molecular extinction coefficient
$Re_2(CO)_{10}$	CH_2Cl_2	3100	16,000
		2760	13,000
		2280	23,000
$NaRe(CO)_6$	THF	3170	720
		2860 sh	920
		2160 sh	4,400
$(C_2H_5)_4N[H_3B \cdot Re(CO)_5]$	THF	3100 sh	2,000
		2220 sh	7,500
$(C_2H_5)_4N[(H_3B)_2Re(CO)_5]$	THF	2500 sh	14,000
$[(C_6H_5)_3PRe(CO)_4]_2$	CH_2Cl_2	3000	28,800
		2270	58,000
$(C_6H_5)_3PMn(CO)_4$	$C_6H_5CH_3$	4350 sh	1,360
		3700	8,800
$(C_6H_5)_3PMn(CO)_4$	THF	4380	1,560
		3730	9,240
		2600	6,780
$Na[(C_6H_5)_3PMn(CO)_4]$	THF	3720	160
		2600 sh	8,000
		2250 sh	27,000
$(C_2H_5)_4N[H_3B \cdot Mn(CO)_4P(C_6H_5)_3]$	THF	2560	10,600
		2250	24,400

Two structures, Ia and Ib, have been considered for the monoborane complex. The structure (Ia) in which the BH_3 group is coordinated to the oxygen of a carbonyl would be expected to show a substantial shift in the C=O stretching frequency in the infrared. The borane adduct of dicyanobis(phenanthroline)iron in which the BH_3 is coordinated to a CN shows a shift of nearly 100 cm.⁻¹ in the CN stretching frequency.[1] On the other hand, a structure such as Ib in which the BH_3 group is coordinated to the metal should show only a slight increase in the CO stretching frequency compared to $[Re(CO)_5]^-$. The great similarity in the spectra of $[H_3BRe(CO)_5]^-$ and $[Re(CO)_5]^-$ (Table I) strongly supports structure Ib.



Ia



Ib

The bis(borane) complex poses a similar structural problem. If we assume that one BH_3 group is coordinated to the rhenium as in Ib, the second may also be bound to the rhenium in a seven-coordinate structure. However, it could also be bound to a carbonyl or to the first BH_3 group. A hydrogen bridge structure (IIa) analogous to that proposed for the $B_2H_7^-$ ion[3] seems quite plausible but the spectral evidence is inconclusive.

$$[H_3B\text{–}H\text{–}BH_2 \cdot Re(CO)_5]^-$$

IIa

Manganese Complexes The $[Mn(CO)_5]^-$ ion appears to be considerably less basic toward BH_3 than is $[Re(CO)_5]^-$. When a solution of $NaMn(CO)_5$ in tetrahydrofuran was treated with diborane, one half mole of diborane was absorbed per mole of $NaMn(CO)_5$ (by comparison with the diborane absorption of an equivalent quantity of pure solvent). However, when the solution was evaporated to dryness, only $NaMn(CO)_5$ was recovered. Seemingly, an equilbrium existed between $[Mn(CO)_5]^-$ and its borane complex (III). A borane adduct was isolated by precipitation of its tetraethylammonium salt at −78°. However, the complex lost diborane on standing for several days at −25°.

$$[Mn(CO)_5]^- + R_2O \cdot BH_3 \rightleftharpoons [H_3B \cdot Mn(CO)_5]^- + R_2O$$

III

The anion derived from triphenylphosphinemanganese tetracarbonyl[4] gave a much more stable borane complex (IV) than did $[Mn(CO)_5]^-$. No dissociation of this complex was noted in tetrahydrofuran at room temperature. The complex CO stretching absorption (Table I) of IV indicates a relatively low degree of symmetry in its structure. An octahedral structure with the phosphorus and boron atoms *cis* to one another on the metal atom would have suitably low symmetry

$$[Mn(CO)_4 \cdot P(C_6H_5)_3]^- + C_4H_8O \cdot BH_3 \longrightarrow [H_3B \cdot Mn(CO)_4 \cdot P(C_6H_5)_3]^- + C_4H_8O$$

IV

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[3] H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).

[4] W. Hieber, G. Faulhaber, and F. Theubert, *Z. anorg. allgem. Chem.*, **314**, 125 (1962).

but even a *trans* structure might have low symmetry based on the arrangement of the three phenyl groups on the phosphorus.

Cobalt Carbonyl Anion.—The $[Co(CO)_4]$ ion appears to react reversibly with ethereal diborane solutions. In several experiments, a solution of $NaCo(CO)_4$ in tetrahydrofuran absorbed 0.5 mole of diborane (in excess of that absorbed by tetrahydrofuran alone) per mole of the salt. However, attempts to isolate the borane complex were unsuccessful. Evaporation of solutions gave only solvated $NaCo(CO)_4$.

Discussion

The results cited above are particularly interesting in two respects. One is that the BH_3 moiety apparently coordinates to the transition metal atom rather than to a carbonyl group in these complexes. The other is that an unexpected order of basicities toward BH_3 as a Lewis acid is encountered.

The coordination of BH_3 to the metal of a metal carbonyl anion is in contrast to its coordination to a CN in dicyanobis(phenanthroline)iron.[1] However, these results parallel those found in protonation of carbonyl and cyanide complexes. While several types of metal carbonyl complexes react with protonic acids to give metal hydrides,[5] dicyanobis(phenanthroline)-iron is protonated on the cyanide nitrogens.[6] Similarly alkylations of metal carbonyl anions give alkyl metal carbonyls while metal cyanides give metal isonitrile complexes.[6] A further parallel is found in the fact that the compound $H_3B\text{-}CO$, prepared from B_2H_6 and CO, does not react further with diborane to give $H_3B\text{-}CO\text{-}BH_3$.[7]

The selectivity of BH_3 in forming complexes with transition metal compounds provides some useful information about the basicity of these compounds. While it is reasonable that an anionic complex should be more basic than a neutral compound, it is less obvious that $[Re(CO)_5]^-$ should be more basic than $[Co(CO)_4]^-$ or $[Mn(CO)_5]^-$. The fact that all the anions that give stable complexes with BH_3 are pentacoordinate suggests that there may be a thermodynamic advantage in going from the trigonal bipyramid to the octahedral configuration compared to the transition from a tetrahedral to a five-coordinate configuration.

Perhaps the most significant result is that $[Mn(CO)_4 \cdot P(C_6H_5)_3]^-$ gives a more stable complex with borane than does $[Mn(CO)_5]^-$. This finding suggests that triphenylphosphine behaves primarily as a σ-donor in this anion and, hence, tends to increase the electron density on the metal atom. The proton n.m.r. spectrum of the paramagnetic neutral compound, $(C_6H_5)_3PMn(CO)_4$, from which the anion is prepared, indicates that triphenylphosphine also behaves as a σ-donor in this complex and that little back-bonding occurs between the metal and the phosphorus. If substantial $d\pi\text{-}d\pi$ interaction took place, some electron spin density would be expected to be distributed on the phenyl rings and significant shifts would appear in the proton resonance spectrum.[8] Instead it was found (Table III) that the proton resonance lines are distributed over a span of only 0.5 p.p.m., the same separation as in the diamagnetic rhenium complex, $[(C_6H_5)_3PRe(CO)_4]_2$.

TABLE III

PROTON MAGNETIC RESONANCE SPECTRA

Compound	Solvent	Chemical shift (τ)[a] of three major peaks	Total signal width, c.p.s.
$(C_6H_5)_3P$	THF	2.68, 2.70, 2.76	8
$(C_6H_5)_3PMn(CO)_4$	THF	2.47, 2.52, 2.80	40
$(C_6H_5)_3PMn(CO)_4$	CH_2Cl_2	2.46, 2.52, 2.78	30
$[(C_6H_5)_3PRe(CO)_4]_2$	CH_2Cl_2	2.38, 2.58, 2.79	35

[a] τ (p.p.m.) = [10–10^6(frequency of $(CH_3)_4Si$ − frequency of sample)/oscillator frequency; G. V. D. Tiers, *J. Phys. Chem.*, **62,** 1151 (1958).

Experimental

Preparation of $(C_4H_9)_4P[Re(CO)_5]$.—Sodium pentacarbonylrhenate[2] was prepared by stirring a mixture of 2.17 g. (3.33 mmoles) of rhenium carbonyl, 23 g. of 1.4% sodium amalgam, and 13 ml. of tetrahydrofuran at room temperature overnight in a nitrogen-filled vacuum train flask. The $NaRe(CO)_5$ solution was decanted from the mercury by means of a hypodermic needle inserted through a serum vial stopper on a side arm of the flask. The solution was mixed with a solution of 2.25 g. (6.66 mmoles) of tetra-*n*-butylphosphonium bromide in 4 ml. of tetrahydrofuran. The sodium bromide which formed was filtered and the filtrate was concentrated to a volume of 5 ml. under reduced pressure. Ether (4 ml.) was added and the mixture was cooled to −78°. A red-orange solid precipitated and was separated by decantation. The tetrabutylphosphonium pentacarbonylrhenate liquefied on warming to room temperature. The infrared spectrum (tetrahydrofuran solution) showed strong metal carbonyl stretching absorption at 1895 (s), 1925 (s), 1980 (s), 2025 (s), and 2085 (w) $cm.^{-1}$.

Anal. Calcd. for $C_{21}H_{36}O_5PRe$: C, 43.06; H, 6.20; P, 5.29. Found: C, 44.18; H, 6.84; P, 5.75.

$(C_4H_9)_4P[H_3B \cdot Re(CO)_5]$.—A 1.45-g. (2.48-mmole) sample of $Bu_4P[Re(CO)_5]$ was placed in a vacuum train flask and diborane (1.6 mmoles) was condensed in the apparatus. When the mixture warmed to room temperature, the pressure rose to 90 mm. in the system. The pressure slowly fell to 86 mm. over a period of 30 min. and fine, orange, acicular crystals formed on the surface of the $(C_4H_9)_4P[Re(CO)_5]$. Absorption of diborane ceased due to failure to penetrate the solid layer. The flask was cooled to −196° and 5.0 ml. of xylene was distilled into the system. On warming to room temperature, two liquid phases appeared in the flask. Rapid diborane absorption occurred and the mixture became warm (*ca.* 35°). The colorless top layer was decanted and was evaporated under reduced pressure (no residue). The red lower layer was filtered and evaporated. It partially crystallized when allowed to stand at room temperature (under nitrogen) for 3 days. The red-orange acicular crystals were collected by filtration and were washed with methylcyclohexane. The infrared spectrum (Nujol mull) contained B-H stretching absorption at 2405 $cm.^{-1}$ and strong, broad metal carbonyl stretching absorption at 1850–2020 $cm.^{-1}$.

Anal. Calcd. for $C_{21}H_{39}BO_5PRe$: C, 42.07; H, 6.56; B, 1.80; P, 5.17. Found: C, 41.10; H, 6.76; B, 2.13; P, 5.60.

$(C_4H_9)_4P[(H_3B)_2Re(CO)_5]$.—Diborane (7.0 mmoles) was condensed in a flask containing a solution of 6.6 mmoles of $(C_4H_9)_4P[Re(CO)_5]$ in 20 ml. of tetrahydrofuran. The diborane dissolved exothermally when the system was allowed to warm to room temperature. The solvents and diborane were evaporated under reduced pressure and the red residue was washed with ether. The semicrystalline residue was dissolved in tetrahydrofuran. Addition of ether and chilling gave red-orange crystals which were collected by filtration. The crystalline $(C_4H_9)_4P[(H_3B)_2Re(CO)_5]$ was dried at 10^{-4} mm. at room temperature.

Anal. Calcd. for $C_{21}H_{42}B_2O_5PRe$: C, 41.1; H, 6.92; B, 3.54; P, 5.05. Found: C, 40.08; H, 6.84; B, 4.33; P, 4.97.

$(C_2H_5)_4N[H_3B \cdot Re(CO)_5]$.—A pentacarbonylrhenate salt free of the colored dimeric anion $[Re_2(CO)_9]^{-2}$ was prepared by the following procedure for spectroscopic purposes. The reaction of sodium amalgam with $HRe(CO)_5$ seemed to give much less of the dimer than did the preparation from $Re_2(CO)_{10}$.

Rhenium pentacarbonyl hydride (3.3 g.) and tetrahydrofuran (20 ml.) were condensed in a flask with 13 g. of 1.4% sodium amalgam and the mixture was stirred at room temperature for 72 hr. The faintly yellow solution was decanted and metathesis was carried out with 9.0 ml. of a 1.0 *M* solution of tetraethylammonium chloride in acetonitrile. The filtered solution was evaporated to dryness, and the residue was treated with 5.0 mmoles of diborane in 20 ml. of tetrahydrofuran. The solution was evaporated to a volume of 10 ml. and ether was added to induce crystallization. Pale yellow crystals of $(C_2H_5)_4N[H_3B \cdot Re(CO)_5]$ separated and were dried under reduced pressure. Hydrolysis of a sample in 10% sulfuric acid gave 118 ml. of hydrogen per gram or 2.49 moles of hydrogen per mole of complex.

(5) (a) M. L. H. Green, *Angew. Chem.*, **72,** 719 (1960); (b) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(6) N. K. Hamer and L. E. Orgel, *Nature*, **190,** 439 (1961).

(7) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59,** 780 (1937).

(8) (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37,** 347 (1962); (b) E. A. LaLancette and D. R. Eaton, unpublished results; extensive spin delocalization from the metal atom onto the phenyl rings is found in $[(C_6H_5)_3P]_2NiX_2$ complexes.

Anal. Calcd. for $C_{13}H_{23}BNO_5Re$: C, 33.19; H, 4.93; B, 2.30; Re, 39.6. Found: C, 31.65; H, 5.50; B, 2.51; Re, 38.7.

$(C_2H_5)_4N[(H_3B)_2Re(CO)_5]$.—This compound was prepared by dissolving *ca.* 2.5 g. (5 mmoles) of $(C_2H_5)_4N[H_3B{\cdot}Re(CO)_5]$ prepared as described in 10 ml. of tetrahydrofuran. The solution was treated with 10 mmoles of diborane for 1 hr. at room temperature. The solution was partially evaporated and ether was added to give yellow-orange crystals of $(C_2H_5)_4N[(H_3B)_2Re(CO)_5]$. This complex was distinguished from the monoborane complex by appearance of a doublet in the BH stretching region of the infrared spectrum. The X-ray powder pattern also displayed a slight displacement of one line and minor intensity differences.

Anal. Calcd. for $C_{13}H_{26}B_2NO_5Re$: B, 4.46; Re, 38.5. Found: B, 5.00; Re, 39.6.

$(C_2H_5)_4N[H_3B{\cdot}Mn(CO)_4P(C_6H_5)_3]$.—A solution of 2.2 g. (5.1 mmoles) of triphenylphosphinemanganese tetracarbonyl in 40 ml. of tetrahydrofuran was treated with 12 g. of 1.4% sodium amalgam at room temperature under nitrogen. The red solution soon became yellow-orange and some yellow solid separated. The suspension was treated with 5.0 ml. of a 1.0 *M* solution of tetraethylammonium chloride in acetonitrile. The solution was partially evaporated, was filtered to remove NaCl, and was evaporated to dryness under reduced pressure. The residue was dissolved in 10 ml. of tetrahydrofuran and was treated with 5 mmoles of diborane. The solution was partially evaporated (to *ca.* 5 ml.) until yellow crystals separated. The crystals were collected by filtration and were dried under reduced pressure.

Anal. Calcd. for $C_{30}H_{38}BMnNO_4P$: C, 62.8; H, 6.68; B, 1.89. Found: C, 61.80; H, 6.52; B, 1.59.

$(C_2H_5)_4N[Mn(CO)_5]$.—A mixture of 3.9 g. (10 mmoles) of manganese carbonyl, 70 g. of 1.4% sodium amalgam, and 40 ml. of tetrahydrofuran was stirred at room temperature in a nitrogen atmosphere overnight. The solution was decanted with a hypodermic syringe and was evaporated to 20 ml. under reduced pressure. Tetraethylammonium chloride (20 ml. of 1.0 *M* solution in CH_3CN) was added and the NaCl which formed was collected by filtration. The clear, pale green filtrate was evaporated to give a faintly yellow, solid residue. The $(C_2H_5)_4N[Mn(CO)_5]$ was dried at 25° (0.1 μ) for 2 hr. and was sealed in a glass ampoule. After brief storage, a thin layer of the material on the side of the ampoule toward the light turned green but most of the solid was unaffected.

Anal. Calcd. for $C_{13}H_{20}MnNO_5$: C, 48.01; H, 6.20; Mn, 16.89; N, 4.31. Found: C, 46.27; H, 6.19; Mn, 13.87; N, 4.21.

$(C_2H_5)_4N[H_3B{\cdot}Mn(CO)_5]$.—A solution of 7.0 mmoles of $(C_2H_5)_4N[Mn(CO)_5]$ in 3 ml. of tetrahydrofuran was allowed to equilibrate with 7 mmoles of diborane and 7 ml. of ether was added. On cooling to −78°, fine yellow crystals separated from the solution. The crystals were collected by filtration and were dried under reduced pressure (25° (0.1 μ) for 5 hr.). The sample was stored in glass ampoules at −25° for 5 days until it could be analyzed but some discoloration occurred. Diminution of the B–H stretching absorption in the infrared suggests that loss of diborane occurred.

Anal. Calcd. for $C_{13}H_{23}BMnNO_5$: C, 46.05; H, 6.84; Mn, 16.20. Found: C, 46.78; H, 6.74; Mn, 14.04.

The infrared spectrum (Nujol mull) showed B–H absorption at 2410 and 2470 cm.$^{-1}$ and strong, broad metal carbonyl absorption at 1850 cm.$^{-1}$. However, when the crystals were dissolved in diglyme, no B–H stretching absorption could be detected and the metal carbonyl stretching reverted to a doublet at 1902 and 1876 cm.$^{-1}$ as in $[Mn(CO)_5]^-$.

Analytical.—Considerable difficulty was encountered in obtaining useful carbon analyses on compounds containing both boron and rhenium. Some of the difficulty may have been due to the great hydrolytic sensitivity of the borane complexes. However, the fact that the carbon analyses were always low suggests that some of the carbon may have been converted to an oxidation-resistant carbide during combustion. This supposition is supported by the fact that combustions carried out at high temperatures gave higher carbon values than those carried out at conventional temperatures.

Rhenium analyses were done by X-ray fluorescense measurement on pellets of the complex in an inert solid. Infrared spectra were determined on Perkin-Elmer Models 21 and 237 instruments with NaCl and grating optics, respectively. Proton magnetic resonance measurements were made with a Varian A-60 spectrometer with tetramethylsilane as an internal reference in the specimen.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

The Formation of Copper(I) Chloride by the Action of Copper(I) Ion on Carbon Tetrachloride in 2-Butanol

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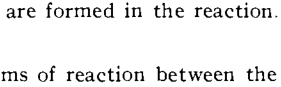
A remarkable reaction between copper(I) perchlorate and carbon tetrachloride in 2-butanol solutions containing small amounts of water has been uncovered and investigated. Copper(I) chloride, two acidic species, one weak and one strong, and an ether of the apparent formula  $CH_3CH_2\underset{\underset{\displaystyle OCCl_3}{|}}{C}HCH_3$ are formed in the reaction. The production of the acidic species and the ether is reasonably explained in terms of reaction between the bases water and 2-butanol with the trichloromethyl cation, $(CCl_3)^+$.

During the course of an investigation of the preparation of copper(I) perchlorate in 2-butanol, an unexpected and novel reaction was encountered. Reduction of hydrated copper(II) perchlorate in 2-butanol solution by means of metallic copper yields colorless solutions of copper(I). Attempts to precipitate the corresponding perchlorate at room temperature by addition of carbon tetrachloride gave a white solid, shown by analysis to be copper(I) chloride. Preliminary experiments soon showed that there were formed no organic products which could arise as a result of a free radical mechanism. The nature of the various products can be accounted for in a reasonable manner in terms of an initial ionic attack of copper(I) on carbon tetrachloride.

Experimental

Chemicals.—Matheson Coleman and Bell Spectroquality carbon tetrachloride and Eastman White Label 2-butanol were used without further purification. Copper(II) perchlorate 6-hydrate (G. F. Smith Chemical Company) was dried under vacuum at 60° for 48 hr. Analysis of the "dried" product for water content by the Karl Fischer method gave the value 19.55%; theoretical for $Cu(ClO_4)_2{\cdot}3.5H_2O$, 19.36%. Commercially available "Chore Girl" pot cleaner was employed as the source of copper metal. Silver nitrate, sodium hydroxide, hydrochloric acid, and perchloric acid solutions were prepared and standardized in the usual manner.

Apparatus.—The reaction vessel was a three-necked round-bottomed flask to which was connected a reflux condenser, a nitrogen gas inlet tube, and a thermometer. A gas outlet tube was placed at the top of the condenser and led into a 100-ml. round-bottomed flask containing standardized sodium hydroxide solution.

General Procedure.—2-Butanol solutions of copper(I) perchlorate were prepared by the addition of an excess of copper metal to a weighed quantity of $Cu(ClO_4)_2{\cdot}3.5H_2O$ (*ca.* 0.34 or 0.04 g.) in 50 ml. of the alcohol, followed by refluxing in a nitrogen atmosphere at 80° for 6 hr. The copper(I) perchlorate solution was permitted to cool to room temperature and unreacted copper metal was removed. Deaerated carbon tetrachloride (25 ml./50 ml. of butanol) was then added to the copper(I) solution. After a period of 2–3 min., a white precipitate appeared. The mixture was allowed to stand for varying periods of time and then the white precipitate, which was shown to be copper(I) chloride, was filtered, washed with a 1:1 solution of carbon tetrachloride in 2-butanol, and dried at 110°.