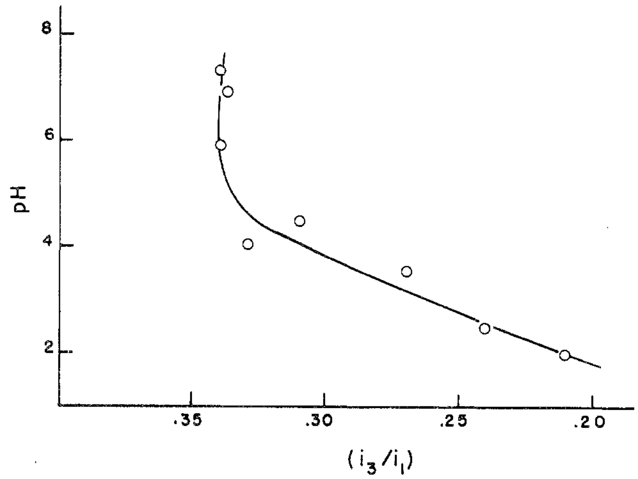

Figure 2. Ratio of anodic current of wave 3 to cathodic current of wave 1 for a solution of $[Cr(phen)_2Cl_2]^+$ as a function of pH. Scan rate was 0.1 V/sec.

behavior for a system in which the initial electron-transfer reaction process (reduction) is followed by a fast chemical reaction producing a new species capable of being oxidized in the potential range under study. In the $[Cr(bipy)_2Cl_2]^+$ study it was concluded[3] that the new species being produced after the reduction was $[Cr(bipy)_3]^{2+}$. Since the positions of cyclic voltammetric waves 3 and 4 are similar to those of waves observed in a cyclic voltammetric study of $[Cr(phen)_3]^{3+}$, which have been shown to be associated with the $[Cr(phen)_3]^{3+}$–$[Cr(phen)_3]^{2+}$ couple,[1] it is reasonable to conclude that the mechanism parallels that found for the $[Cr(bipy)_2Cl_2]^+$ system.[3] The mechanism, then, is as given in eq 1–4. The symbol ↔ represents a polarographically reversible reaction at the potential indicated.

$$[Cr(phen)_2Cl_2]^+ + e^- \longleftrightarrow [Cr(phen)_2Cl_2]^0 \quad E_{1/2} = -0.73\ V \qquad (1)$$

$$[Cr(phen)_2Cl_2]^0 + 2H_2O \overset{fast}{\rightleftharpoons} [Cr(phen)(H_2O)_2Cl_2]^0 + phen \qquad (2)$$

$$[Cr(phen)_2Cl_2]^0 + phen \overset{fast}{\rightleftharpoons} [Cr(phen)_3]^{2+} + 2Cl^- \qquad (3)$$

$$[Cr(phen)_3]^{2+} \longleftrightarrow [Cr(phen)_3]^{3+} + e^- \quad E_{1/2} = -0.49\ V \qquad (4)$$

This mechanism satisfactorily accounts for the polarographic and cyclic voltammetric data obtained. As in the $[Cr(bipy)_2Cl_2]^+$ study, a number of experiments were performed to test the validity of the mechanism, namely, measurement of the amount of phenanthroline liberated on reduction, controlled-potential reduction in the presence of excess phenanthroline, and slow and rapid oxidations of chromium(II) solutions. These experiments have been described in a study of the corresponding chromium–bipyridine system and the results for this study were in all cases exactly parallel to those previously reported for that system.[3]

It should be emphasized that slow oxidation of a reduced solution, even in the presence of excess phenanthroline, where the oxidized and unoxidized portions are intimately mixed (*e.g.*, bubbling air through the solution) results in formation of $[Cr(phen)_2(H_2O)_2]^{3+}$ almost exclusively. This is the result of a fast electron-transfer reaction between the oxidized (tris) species and the reduced (bis) species. Reaction 5 occurs even in the presence of excess 1,10-phenanthroline where only a small equilibrium amount of the bis(diaquo)chromium(II) complex exists. This phenomenon has important connotations in attempting to synthesize the tris complex.[6]

$$[Cr(phen)_2(H_2O)_2]^{2+} + [Cr(phen)_3]^{3+} \rightarrow [Cr(phen)_2(H_2O)_2]^{3+} + [Cr(phen)_3]^{2+} \qquad (5)$$

Two further successive one-electron reductions were performed at −1.06 and −1.30 V but no further unusual behavior was noted. Polarograms of the solutions after each reduction are shown in Figure 1. The reduction at −1.06 V produced a black precipitate suspended in a clear liquid. Very little electroactive material was dissolved as evidenced by the small polarographic response (Figure 1C). Addition of the third electron at −1.30 V took nearly six times as long as that of either of the first two electrons, probably because of the insolubility of the two-electron-reduced species. The result of the final reduction was again a black suspension showing very little polarographic activity (Figure 1D). The final reduced solution could be rapidly oxidized to produce the tris complex in the same manner as the one-electron reduced solution.

Registry No. *cis*-$[Cr(phen)_2Cl_2]^+$, 27803-06-1.

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Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007

Action of Lewis Acids upon Base–Pentaborane(9) Adducts

Anton B. Burg* and Leon Maya

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A recent doctoral dissertation, exploring the behavior of HCl, B_2H_6, BF_3, and CH_3OH toward the adducts $B_5H_9{\cdot}2(CH_3)_3N$, $B_5H_9{\cdot}2(CH_3)_3P$, and $B_5H_9{\cdot}(CH_3)_2NC_2H_4N(CH_3)_2$ (the basic ligands of which are hereinafter designated as TMA, TMP, and TMED, respectively) showed a variety of chemical consequences which would correlate with different structures for these adducts.[1]

For example, only the action of HCl upon the adduct $B_5H_9{\cdot}2TMA$ led to appreciable yields of B_6H_{10}, and a more thorough study of this reaction finally led to better than 25% yields of this hexaborane. Thus it could be argued that either a different adduct structure or a Lewis acid very different from HCl would fail to produce an intermediate required for the formation of B_6H_{10}. A more general result was the persistent formation of useful yields of HBF_2 from the BF_3 reactions; also $TMA{\cdot}B_3H_7$ and $TMED{\cdot}B_4H_8$ with BF_3 gave as much as 0.2 HBF_2/mol.

In general, it seems that the formation of a base adduct of a polyborane leads to enhanced boron–base character. Thus either HCl or BF_3 may insert at an electron-dense B–B bond, presumably forming BHB or BBB three-center bonds, with interesting consequences. No doubt diborane can attack in the same manner; indeed, Onak, *et al.*, indicated that its absorption by $B_5H_9{\cdot}2TMA$ is the first step toward the liberation of B_5H_9.[2] Accordingly, it is interesting that their $^{10}B_2H_6$ reaction led to B_5H_9 having a ^{10}B content (43.5%) only 6.3% less than expected (49.8%) for its formation from $^{10}B_2H_6$ and a B_3H_x fragment. The difference may relate to some more direct action of $^{10}BH_3$ to remove TMA.

Exploratory Experiments. A summary of typical results is given by Table I. For such experiments, each of the three

Table I. Reactions of B_5H_9 Adducts

Millimoles of Reactants	Millimoles of Products
6.0 $B_5H_9\cdot 2TMA$, 10.0 HCl	3.0 H_2, 0.72 B_2H_6, 0.36 B_4H_{10}, 0.36 B_5H_9, 0.2 B_6H_{10}; $TMA\cdot BH_2Cl$, $TMA\cdot BHCl_2$, $TMA\cdot B_3H_7$ in ratio 9:1:3
5.0 B_5H_9, 10 HCl; 10 TMA put into gas-phase mixture	5.3 H_2, 1.67 B_5H_9; $TMA\cdot BH_3$, $TMA\cdot BH_2Cl$, $TMA\cdot BHCl_2$, $TMA\cdot B_3H_7$, in ratio 1:2:2:1.
5.0 $B_5H_9\cdot 2TMA$, 10.0 HCl (in xylene)	1.15 H_2, 0.42 B_2H_6, trace B_4H_{10}, amine complexes etc.
5 $B_5H_9\cdot 2TMA$, 10.0 HCl + 1.4 B_2H_6	2.2 H_2, 0.45 B_2H_6, 0.25 B_4H_{10}, 0.54 B_5H_9; rising to 0.73 B_2H_6, 0.35 B_4H_{10}, 0.92 B_5H_9, 0.18 B_6H_{10}; solids
1.4 $B_5H_9\cdot 2TMA$, 1.4 B_2H_6	Nil H_2, 0.45 B_2H_6, 0.70 B_5H_9; much $TMA\cdot BH_3$[a]
1.3 $B_5H_9\cdot 2TMA$, 2.6 BF_3	Nil H_2, 0.15 B_5H_9, 0.2 HBF_2, 0.2 B_2H_6; TMA complexes
2.2 $B_5H_9\cdot 2TMP$, 4.3 HCl	1.7 H_2, 0.07 B_2H_6, 0.65 B_5H_9, complexes
2.0 $B_5H_9\cdot 2TMP$, 2.36 B_2H_6	0.5 H_2, 1.1 B_2H_6, 0.41 B_5H_9, complexes including $TMP\cdot BH_3$, ($TMP\cdot B_3H_7$)
1.58 $B_5H_9\cdot 2TMP$, 2.56 BF_3	0.30 B_2H_6, 0.30 HBF_2, 0.10 B_5H_9, complexes
5.1 $B_5H_9\cdot TMED$, 11.0 HCl	3.4 H_2, 0.22 B_2H_6, 0.75 B_4H_{10}, 0.65 B_5H_9, complexes
3.0 $B_5H_9\cdot TMED$, 2.7 B_2H_6	1.4 H_2, 0.79 B_2H_6, 0.09 B_5H_9, complexes
2.38 $B_5H_9\cdot TMED$, 4.72 BF_3	0.60 B_2H_6, 0.6 HBF_2, 0.60 BF_3, 0.30 B_5H_9, complexes
3.0 $B_5H_9\cdot 2TMA$, CH_3OH excess	4.1 H_2, 3.38 $B(OCH_3)_3$; obsd $TMA\cdot BH_3$, $(CH_3)_3NH^+B_3H_8^- \rightarrow TMA\cdot B_3H_7 + H_2$
2.42 $B_5H_9\cdot 2TMP$, CH_3OH excess	0.7 H_2, 0.66 $B(OCH_3)_3$, slow, incomplete
9.5 $B_5H_9\cdot TMED$, CH_3OH excess	12 H_2, much $B(OCH_3)_3$; synthesis of $TMED\cdot B_4H_8$[b]

[a] *Cf.* ref 2. [b] *Cf.* ref 3.

adducts was formed during slow warming of the components, which had been condensed into an appropriate reaction tube from a Stock-type high-vacuum manifold. The mixture was recooled whenever the process seemed too vigorous, and a magnetic stirring bar was used to develop a large surface and to minimize occlusion. In most cases the base ligand was in excess and was removed afterward. The indicated attacking reagents were condensed upon the adducts and allowed to react during slow warming to 25°, again with magnetic stirring for maximum contact. The volatile products were separated by high-vacuum fractional condensation methods, identified by volatility, infrared spectra, and ^{11}B nmr when feasible, and weighed or measured. Nonvolatiles or slightly volatile sublimates were studied by ^{11}B nmr, which gave the relative but not absolute quantities.

The original dissertation[1] presents further factual details and numerous inferences based upon such results, well correlated with recent suggestions concerning adduct structures. For example, the chelation of one boron by TMED in $B_5H_9\cdot TMED$, indicated by a high yield of $TMED\cdot B_4H_8$ by methanolysis,[3] gains further support from the major formation of $TMEDBH_2^+B_3H_8^-$ by action of diborane, whereas the formation of $(CH_3)_3NH^+B_3H_8^-$ (converting to $TMA\cdot B_3H_7$) by the methanolysis of $B_5H_9(TMA)_2$ would correlate with either 2,3 or 2,4 attachment of TMA.[4] The failure of the acid–$B_5H_9\cdot 2TMP$ reactions to form any B_6H_{10} suggests that the B_3H_x group always includes the 1-B atom and here appears only as $TMP\cdot B_3H_7$ because 1-B holds TMP.[5]

The general scrambling process indicated especially in the HCl–$B_5H_9\cdot 2TMA$ reaction may have some analogy to the base-catalyzed disproportionation of B_5H_{11},[6] such as structures analogous to the $B_5H_{11}^{2-}$ anion might imply. However, the conditions for the formation of B_6H_{10} seem to be fairly specific, as indicated by its absence when the HCl–$B_5H_9\cdot 2TMA$ reaction was performed in xylene. It seemed that the formation of B_6H_{10} might require solid-phase contact between structures offering B_3H_x units. However, an attack by HCl upon solid $TMA\cdot B_3H_7$ gave no B_6H_{10}; apparently this adduct is a product of the HCl–$B_5H_9\cdot 2TMA$ reaction, but rather a competitor than a precursor of B_6H_{10}. Similarly, $(CH_3)_4NB_3H_8$, in tetrahydrofuran with HCl, gave no B_6H_{10}; along with equimolar H_2 there was a 10% yield of B_4H_{10} and nmr evidence of a B_3H_7 complex other than $THF\cdot B_3H_7$. With BF_3, this $B_3H_8^-$ salt gave a 7.6% yield of B_2H_6 and a 43% yield of B_4H_{10} (but very little HBF_2), demonstrating a new and more convenient method for getting B_4H_{10} from this commercially available reagent than the phosphoric acid process.

Fuller Study of HCl Action on the TMA Adduct. On the basis that $B_5H_9\cdot 2TMA$ is an analog of the $B_5H_{11}^{2-}$ anion and would behave as a boron base, a more thorough study of the HCl reaction began with the formation of high-surface samples of the adduct from solid B_5H_9 (spread thinly upon the lower walls of a vertical reaction tube) by slow introduction of TMA vapor during warming from −78 to −20°. The product always contained some occluded B_5H_9, so that the usual ratio of TMA to B_5H_9 (after removal of excess TMA at 0°) was 1.95. Now HCl was introduced slowly at −78°, with absorption of as much as 5 HCl per $B_5H_9\cdot 2TMA$ at HCl pressures as low as 30 mm at −78°. At this stage the evolution of H_2 amounted to 0.18 per $B_5H_9\cdot 2TMA$. The excess HCl (much of which may have been reversibly bound to the polyborane base) was pumped off (with more H_2 passing the −196° trap) during warming to −50°, leaving a solid almost described by the formula $B_5H_9\cdot 2TMA\cdot 2HCl$; for example, 7.02 B_5H_9, 13.79 TMA, and 14.01 HCl (minus 2.26 H_2), all in millimoles, was a typical composition.

Since no B_5H_9 was liberated, it seemed best to interpret the main product as an analog of the unknown B_5H_{13}, wherein the replacement of 2 H^- by 2 TMA would give the cation $(TMA)_2B_5H_{11}^{2+}$, balanced by 2 Cl^-. Obviously, any such analog of B_5H_{13} should be very unstable, and indeed its decomposition began to be perceptible at −50°.

The cleanest decompositions of $B_5H_9\cdot 2TMA\cdot 2HCl$ occurred by slow warming from −50 to +25°, with steady removal of the H_2 through a −196° trap by means of an automatic Sprengel pump;[7] then small further yields of volatiles came from heating to 80–100°, with delivery of sublimates not volatile at 25°.

In the experiment corresponding to the above-mentioned stoichiometry (7.02 B_5H_9 etc.), the volatiles were (in mmol)

0.55 B_5H_9, 4.33 H_2, 0.87 B_2H_6, 0.002 B_4H_{10}, 1.544 B_6H_x, and 0.7 TMA·BH_3. The B_6H_x fraction included a very unstable component which could have been B_6H_{12}, the decomposition of which left 1.383 mmol of purified B_6H_{10}—representing 25.5% of the unrecovered B_5H_9. In a similar experiment, the possible 12% B_6H_{12} impurity was sought by low-temperature ^{11}B nmr but could not be recognized clearly. The actual presence of B_6H_{12} could have been far less than 12% if its decomposition included an attack upon the main component, B_6H_{10}. The decomposition products included 0.067 mmol of B_2H_6, 0.025 mmol each of B_5H_9 and B_5H_{11}, and 7 mg of nonvolatile solids.

Two further experiments of similar scale and character showed a B_6H_{10} yield of only 9% when the B_5H_9·2TMA·2HCl was allowed to decompose in the presence of much diborane, or only 4% when HCl was present in large excess.

The sublimates from all such experiments consisted chiefly of TMA·BH_2Cl and TMA·B_3H_7, whose ^{11}B nmr spectra (in toluene) indicated molar ratios approximating 6:1. The experiment with excess HCl showed also a moderate amount of TMA·$BHCl_2$, as might be expected. The glassy yellow-brown residues proved to be toluene soluble, with ^{11}B nmr spectra showing only that some TMA·BH_2Cl and TMA·B_3H_7 had been held back from sublimation. In sum, these TMA complexes probably represented about half of the boron material not volatile at 25°.

Discussion. It is interesting that the yields of B_6H_{10} represent almost half of the B_3H_7 units which would be available if the decomposition of B_5H_9·2TMA·2HCl occurred primarily by removal of 2 TMA·BH_2Cl. Also, the conversion of 2 B_3H_7 to B_6H_{10} and 2 H_2 would account for two-thirds of the observed H_2. A major loss of B_6H_{10} yield might be ascribed to the very strong Lewis-acid character of B_3H_7, such that it would compete with BH_2Cl for attachment to TMA. Quite probably, it is just that effect which is minimized by keeping the temperature as low as possible during the decomposition. Competitive also would be the formation of B_6H_{12}, which seems to decompose mostly to B_2H_6, B_5H_9, and B_5H_{11}. More speculative would be the idea that BH_2Cl, liberated by action of B_3H_7 to remove TMA, would attack the precursors of B_6H_{10}, just as B_2H_6 or HCl probably do.

It is interesting that HCl attacks the solid product of the B_2H_6–B_5H_9·TMED reaction, to form (per mole of B_5H_9) 1.05 H_2, 0.03 B_2H_6, 0.115 B_4H_{10}, and 0.11 B_6H_{10}. Here the mechanism of formation of B_6H_{10} may be very different, possibly involving a B_6H_x anion formed from B_2H_6 and a B_4H_y fragment.

The reasons for three different structures for the three base–B_5H_9 adducts might be surmised. The TMED complex would gain stability from the chelation of one boron to make a five-atom ring. A 2,3 attachment would be less favorable, and 1,2 or 2,4 seems quite unlikely. The mono-N base TMA would be free to attach to those boron atoms which bond best to its lone-pair electrons. A 2,4 attachment would make the two TMA molecules least competitive. It is unfortunate that the ^{11}B nmr spectrum cannot decide between 2,3 and 2,4 attachment. In our spectra (done in dichloroethane) the two kinds of boron appeared only as a broad singlet at 16.8 ppm and an even broader singlet (N-quadrupole effect?) at 39 ppm, measured from methyl borate. The 1-B atom was shown by a poorly resolved doublet at 71.8 ppm.

The 1-B attachment of one TMP would be favored by the adjacent skeletal electrons, the π attitude of which would permit some interaction with the phosphorus π-acceptor orbitals. More important might be the width of the sp hybrid on 1-B favoring bonding to P more than to N.

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Registry No. B_5H_9·2TMA, 12115-95-6; B_5H_9·2TMP, 39661-74-0; B_5H_9·TMED, 53965-74-5; B_2H_6, 19287-45-7; BF_3, 7637-07-2; HCl, 7647-01-0; CH_3OH, 67-56-1; B_5H_9·2TMA·2HCl, 54036-71-4.

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Contribution from the Istituto di
Chimica Generale ed Inorganica and
the Instituto di Chimica Organica, University of Venezia,
Venice, Italy

Reactivity of Halogenotetrakis(diethyl phenylphosphonite)cobalt(II) Complexes with Carbon Monoxide

Gabriele Albertin, Emilio Bordignon, Angelo A. Orio,*[1] and Giuseppe Rizzardi

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In a previous paper[2] we have reported the synthesis and characterization of some phosphine–carbon monoxide and phosphine–isocyanide mixed-ligand low-spin cobalt(I) complexes obtained *via* reduction of halogenotetrakis(diethyl phenylphosphonite)cobalt(II) derivatives with CO and isocyanides, respectively.

Although the reduction of cobalt(II) complexes by carbon monoxide has been observed previously,[3] the mechanism and the nature of intermediates still remain to be clarified.

We now report on a study of the reduction of complexes of the type $[CoXL_4]^+$ (X = Cl, Br, or I; L = $PPh(OEt)_2$) by carbon monoxide with regard to stoichiometry and the nature of carbonyl intermediates.

Experimental Section

Materials. Reagent grade anhydrous cobalt(II) halides were obtained from Alfa and used without further purification. The solvents were purified by standard methods and distilled under a current of nitrogen. The diethyl phenylphosphonite, $PhP(OEt)_2$, was prepared by a method reported previously.[4]

Apparatus. The volume of CO taken up at constant pressure was measured by the gas-buret apparatus and procedure described previously.[5] Conductivities of 10^{-3} *M* solutions of complexes in nitrobenzene were measured at 25° with an LKB bridge. Infrared spectra of solids as KBr pellets and/or as dichloromethane solutions were recorded on a Perkin-Elmer 621 spectrophotometer. A Bruker HFX-10 instrument equipped with a variable-temperature probe and using TMS as internal reference was used for pmr measurements. Gas chromatographic results were carried out with an Aerograph A-700 instrument.

Syntheses of Complexes. The preparation and characterization of the complexes $[Co(CO)_2(PhP(OEt)_2)_3]BPh_4$ and $[CoI(CO)_2(PhP(OEt)_2)_2]$ have been reported elsewhere.[2]

Carbonyltetrakis(diethyl phenylphosphonite)cobalt(I) Iodide. In a two-necked round-bottomed flask, equipped with magnetic stirrer and inlet and outlet tube, was placed anhydrous cobalt(II) iodide (3.12