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Chemistry of Metalloborane Derivatives Containing the $B_{10}H_{12}$ Ligand

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Ligand displacement reactions of $(B_{10}H_{12})Pd(PPh_3)_2$ were used to prepare $[(B_{10}H_{12})Pd(CN)_2]^{2-}$, $\{(B_{10}H_{12})Pd[C_2S_2(CN)_2]\}^{2-}$, and $(B_{10}H_{12})Pd(1,10\text{-}C_{10}H_8N_2)$. The reaction of the latter phenanthroline complex with butyllithium produced $\{[(B_{10}H_{11})Pd]_2C_{10}H_8N_2\}^{2-}$. The reaction of $C_2S_2(CN)_2^{2-}$ with $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ led to $\{(B_{10}H_{12})Ir(CO)[C_2S_2(CN)_2](PPh_3)\}^-$ and $\{(B_{10}H_{12})Ir[C_2S_2(CN)_2](PPh_3)_2\}^-$. The reaction of $[(C_2H_5)_4N][(B_{10}H_{12})Ir(CO)(PPh_3)_2]$ in 1,2-$C_2H_4Cl_2$ with D_2 led to a regiospecific H–D exchange at the B(5,10) positions and the isolation of a $(B_{10}D_2H_{10})$ analogue. In CH_3CN solvent, exchange also took place at the bridge hydrogen positions. A mechanism for this reaction was proposed. Exchange of the carbonyl group in the iridaborane with ^{13}CO was observed.

Introduction

Transition metal ions react with the $B_{10}H_{13}^-$ [1] or $B_{10}H_{14}^{2-}$ [2] ions to form metalloboranes which formally contain the $B_{10}H_{12}^{2-}$ ligand. The structure of $[(CH_3)_4N]_2[(B_{10}H_{12})_2Ni]$ has been determined by x-ray crystallographic techniques[3] and it is presumably the structural archetype for metalloboranes of this class, although other possibilities may exist. In contrast to the more robust *closo*-metallocarboranes whose chemistry has been delineated by Hawthorne and co-workers,[4] less is known about the chemistry of the *nido*-metalloboranes of the $(B_{10}H_{12})M$ class. This paper presents some initial results of experiments with such materials.

Results and Discussion

Treatment of $[(B_{10}H_{12})_2Ni]^{2-}$ salts and $(B_{10}H_{12})Pd(PPh_3)_2$ (**1**) with elemental bromine or chlorine under a wide variety of conditions led to extensive decomposition and no new products were isolated. Cyclic voltammetry revealed that $[(B_{10}H_{12})_2Ni]^{2-}$ in acetonitrile underwent irreversible oxidation at +1.03 V vs. SCE. Recent x-ray photoelectron spectroscopic studies of $[(B_9C_2H_{11})_2Ni]^{n-}$ have indicated the presence of formal Ni(III) ($n = 1$) and Ni(IV) ($n = 0$) in these dicarbollide complexes.[5] Thus, while the 7,8- and 7,9-$B_9C_2H_{11}^{2-}$ ions can stabilize high oxidation states in transition metal complexes,[6-9] $B_{10}H_{12}^{2-}$ complexes of Ni(III) appear not to be stable. However, treatment of **1** with 1 equiv of *N*-bromosuccinimide afforded a yellow product whose elemental analysis corresponded to $(B_{10}H_{11}Br)Pd(PPh_3)_2$ (**2**). Solutions of this compound were unstable and decomposed on standing to form insoluble black solids.

The 70.6 MHz ^{11}B NMR of solutions of $(B_{10}H_{12})Pd(PPh_3)_2$ contained broad, structureless peaks, typical of phosphinometalloboranes.[10,11] It was thought that the lack of resolution might be due to dissociation of the triphenylphosphine ligands, which suggested that these phosphines could be displaced by other ligands to form new compounds. This was the case, and the reaction of $(B_{10}H_{12})Pd(PPh_3)_2$ with disodium maleonitriledithiolate produced $\{(B_{10}H_{12})Pd[C_2S_2(CN)_2]\}^{2-}$ (**3**) isolated as the yellow, crystalline tetraphenylarsonium salt. The infrared spectrum of **3** disclosed a sharp band at 2180 cm^{-1} due to ν_{CN} in the MNT ligand. This band appears to be only slightly shifted by coordination to sulfur, cf. 2210 cm^{-1} in Na_2MNT and $[Pd(MNT)_2]^{2-}$.[12] A similar reaction with sodium cyanide led to pale yellow $[(CH_3)_4N]_2[(B_{10}H_{12})Pd(CN)_2]$ (**4**). The infrared spectrum of **4** exhibited ν_{CN} at 2105 cm^{-1}. The $B_{10}H_{12}^{2-}$ ligand is presumably a poorer π acceptor than CN^- and stabilizes the dipolar $Pd^+{=}C{=}N^-$ structure, resulting in a lower ν_{CN} than that in $K_2Pd(CN)_4{\cdot}H_2O$, 2143 cm^{-1}.[13] The ^{11}B NMR spectra of these metalloboranes, Figure 1, are well defined and are similar to the spectrum of $[(B_{10}H_{12})_2Ni]^{2-}$, suggesting the presence of similar $(B_{10}H_{12})$–metal bonding in all three compounds. Ligand exchange with 1,10-phenanthroline produced $(B_{10}H_{12})Pd$(phenanthroline) (**5**) in good yield. This complex had a low solubility in common organic solvents and a meaningful ^{11}B NMR spectrum could not be obtained.

Reactions between $(B_{10}H_{12})Pd(PPh_3)_2$ and bases such as butyllithium or pyridine led only to decomposition. However, treatment of a suspension of **5** in tetrahydrofuran with butyllithium at −78 °C led to the formation of a red, air-sensitive anion which could be precipitated from water solution with large cations. Cesium and tetraphenylarsonium salts were obtained as microcrystals; the tetraethylammonium salt was isolated as fine red needles from acetonitrile–butanone. Analytical data indicated the formulation $[(C_2H_5)_4N]_2\{[(B_{10}H_{11})Pd]_2$phenanthroline)$\}$ (**6**). The conductivity of this salt in acetonitrile was 371 Ω^{-1} cm^2 mol^{-1}, indicative of a 2:1 electrolyte.[14] The ^1H NMR spectrum showed the presence of only one B–H–B bridge proton environment (broad singlet at +2.3 ppm) and of one phenanthroline and two tetraethylammonium moieties. The ^{11}B NMR spectrum, Figure 1, differed significantly from those of other $(B_{10}H_{12})M$ metalloboranes studied and contained at least six separate resonances and two sharp doublets of unit area at high field. Specific labeling studies[15] have shown that the sharp high-field doublet ($\delta_{acetone} = 21.6$ ppm) in $[(B_{10}H_{12})_2Ni]^{2-}$ is due to the B(2,4) set. The NMR spectral data suggest that deprotonation of $(B_{10}H_{12})Pd$(phenanthroline) has generated a complex of the $B_{10}H_{11}^{3-}$ ion; this new boron hydride ion appears to have no mirror planes of symmetry and B(2) and B(4) are nonequivalent. It presumably serves as a six-electron donor so as to maintain a 16-electron configuration about palladium. A $B_{10}H_{11}^{3-}$ ion of the requisite low symmetry could be produced by simple removal of one of the bridge protons from the $B_{10}H_{12}^{2-}$ ligand. An alternative possibility might contain a $Pd_2B_{10}H_{10}$ cage with $B_{10}H_{12}$ and phenanthroline ligands, analogous to $B_{10}H_{10}(NiC_5H_5)_2$.[16] The *closo*-nickelaborane, however, contains a low field signal in the ^{11}B NMR spectrum at −54.3 ppm which is attributable to boron atoms bonded to two nickel centers; no such signal was observed in the spectrum of **6**. Additional commentary on the structure of this palladium complex must await an x-ray structure determination.

Solutions of $[(C_2H_5)_4N][(B_{10}H_{12})Ir(CO)(PPh_3)_2]$ (**7**) in dimethyl sulfoxide also displayed broad, featureless ^{11}B NMR spectra. To confirm that dissociation of the triphenylphosphine ligand was occurring, the analogous tri(*p*-tolyl)phosphine complex was studied. Examination of the 220-MHz ^1H NMR spectrum of this compound in dimethyl sulfoxide-d_6 revealed signals at −2.34 and −2.27 ppm, due to the methyl groups of free and complexed phosphine, respectively, in a ratio of 1:4.8.

Displacement of triphenylphosphine from **6** was attempted using $Na_2[C_2S_2(CN)_2]$. Thin layer chromatography of the reaction mixture led to the separation of two products, isolated as the methyltriphenylphosphonium salts. The formulation

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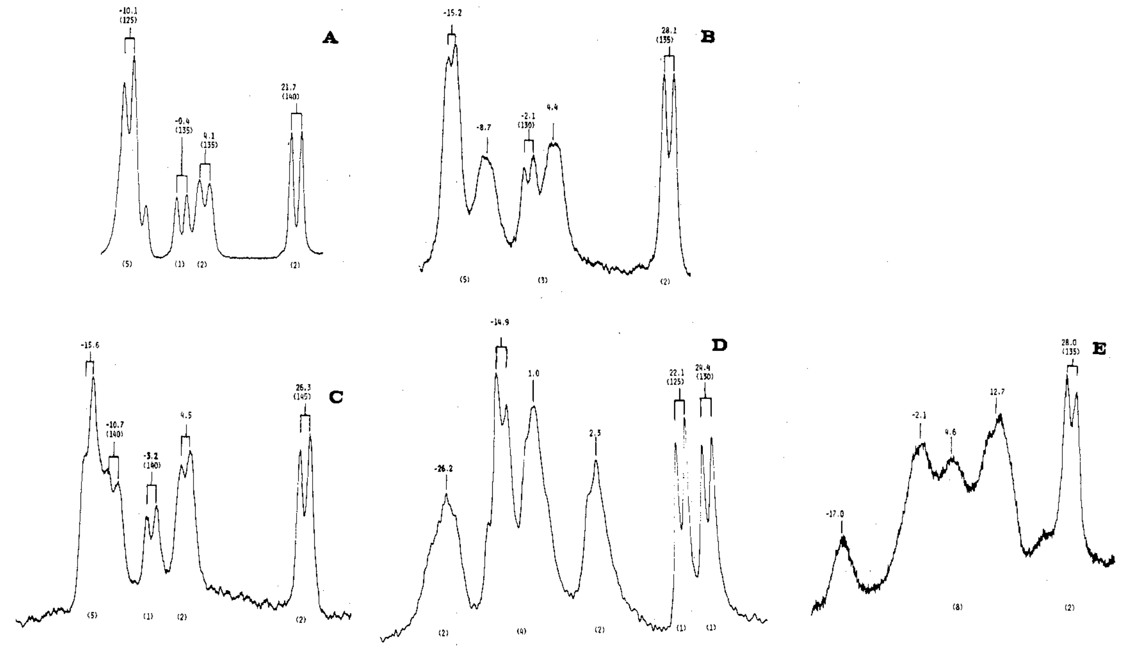

Figure 1. ^{11}B NMR spectra (70.6 MHz), relative to $BF_3 \cdot O(C_2H_5)_2$, of (a) $[(CH_3)_4N]_2[(B_{10}H_{12})_2Ni]$ (acetone); (b) $[(Ph_4As)_2]\{(B_{10}H_{12})Pd[C_2S_2(CN)_2]\}$ (**3**) (acetone); (c) $[(CH_3)_4N]_2[(B_{10}H_{12})Pd(CN)_2]$ (**4**) (CH_3CN); (d) $[(C_2H_5)_4N]_2\{[(B_{10}H_{11})Pd]_2C_{10}H_8N_2\}$ (**6**) (CH_3CN); (e) $(Ph_3PCH_3)\{(B_{10}H_{12})Ir(CO)[C_2S_2(CN)_2](PPh_3)_2\}$ (**9**) (acetone).

of the slower component as $(Ph_3PCH_3)\{(B_{10}H_{12})Ir[C_2S_2(CN)_2](PPh_3)_2\}$ (**8**) was straightforward and followed from the elemental analysis, the integrated ^1H NMR spectrum, which showed a 15:1 ratio of aromatic to P–CH_3 protons, and the infrared spectrum, which contained a sharp CN stretching band at 2190 cm^{-1} but no bands due to a carbonyl group. The infrared spectrum of the faster moving product demonstrated ν_{CO} 1980 cm^{-1} and ν_{CN} 2145 cm^{-1} and the ^1H NMR spectrum contained resonances due to aromatic and P–CH_3 protons in a 15:1 ratio. These data, taken with the elemental analyses, suggest the formulation $(Ph_3PCH_3)\{(B_{10}H_{12})Ir(CO)[C_2S_2(CN)_2](PPh_3)_2\}$ (**9**). Although meaningful assignment of oxidation states of metals in complexes in which ligands participate in delocalized bonding is difficult, both of these compounds may be considered to contain *formal* Ir(III) in order to preserve electroneutrality and it is likely that oxidation of the iridium occurred on workup in air.

Plausible structures for **9** are not obvious because of the difficulty in accommodating all the ligands around the central metal atom. If the $B_{10}H_{12}$ and $C_2S_2(CN)_2$ ligands were both bidentate, the iridium would have a coordination number of seven, which seems unrealistic in this case. Transition metal complexes containing monodentate dialkyldithiocarbamate ligands are known[17,18] but a recent review of metal 1,2-dithiolene complexes[19] does not disclose any monodentate complexes containing these ligands. Two ν_{CN} bands would be expected in a monodentate $C_2S_2(CN)_2$ complex whereas only one was observed. Therefore, it is probable that $\{(B_{10}H_{12})Ir(CO)[C_2S_2(CN)_2](PPh_3)_2\}^-$ contains a chelating, bidentate maleonitriledithiolate moiety. The 70.6 MHz ^{11}B NMR spectrum of this anion in acetone solution contained four broad resonances at −17.0, −2.1, 4.6, and 12.6 ppm of total relative area eight and a sharp doublet of relative area two at 28.0 ppm (J_{BH} = 135 Hz) attributed to B(2,4) by analogy to $[(B_{10}H_{12})_2Ni]^{2-}$. The ^1H NMR spectrum revealed a single, broad resonance at +5.5 ppm which is attributed to the bridge protons in the $B_{10}H_{12}$ ligands (vide infra). The NMR spectral data indicate that the borane fragment is symmetrically bonded to iridium so as to maintain a mirror plane of symmetry passing through B(1,3). Bonding in a monodentate fashion would lead to six coordinate iridium and could arise if $B_{10}H_{12}$ in this compound acted as a two-electron donor involving the metal atom and the B(5,10) borons rather than a four-electron donor employing the B(5,6,9,10) set as in $[(B_{10}H_{12})_2Ni]^{2-}$.

Oxidative addition reactions are involved in the activation of small covalent molecules by transition metals.[20] Intramolecular activation of ortho C–H bonds in coordinated triphenylphosphine and triphenyl phosphite[21,22] ligands also appear to proceed by such a mechanism. Accordingly, it was anticipated that the iridium(I) center in $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ should participate in analogous reactions. Irreversible addition of Ir(I) to the B–H bond in pentaborane[23] and in carboranes[11,24] has been reported and Hawthorne et al. have recently prepared *closo*-rhodacarboranes[25] and found that these compounds, as well as materials such as $(Ph_3P)_3RuHCl$ and palladium on charcoal, catalyze exchange reactions between dideuterium and boranes and carboranes.[26] Indeed, it was found that dideuterium is activated by this iridaborane.[27] Before discussing these results, however, commentary on the structure and some spectroscopic properties of **6** is warranted.

The ^1H NMR resonances of bridge protons in metalloboranes and metallocarboranes usually appear <5 ppm upfield of tetramethylsilane and higher field shifts are usually considered to be indicative of the presence of a hydrogen bridge between boron and a metal atom.[28-31]

The bridge protons in dimethyl sulfoxide-d_6 solutions of $[(C_2H_5)_4N][(B_{10}H_{12})Ir(CO)(PPh_3)_2]$ appear as a broad singlet at δ = 5.6_1 ppm. The chemical shifts are not appreciably solvent dependent ($\delta_{acetone} = 5.6_3$, $\delta_{1,2\text{-}C_2H_4Cl_2} = 5.4_1$) or affected by the addition of triphenylphosphine. For comparison, the bridge proton shifts in the related molecules[1] $(Ph_3PCH_3)_2[(B_{10}H_{12})_2Pt]$ and $[(CH_3)_4N][(B_{10}H_{12})Rh(CO)(PPh_3)_2]$ are $\delta_{acetone}$ = 2.1 and δ_{DMSO} = 4.5 ppm, respectively. The bridge proton shift in the carefully characterized $[(C_6H_5)_2PC_2H_5]_2PtB_3H_7$ is 4.9 ppm.[32] The absence of an observed shift in the bridge resonance upon addition of triphenylphosphine suggests that dissociation of triphenylphosphine does not generate a vacant coordination site which is filled by the creation of B–H–Ir bridges. A possible explanation for the unusually high field bridge proton

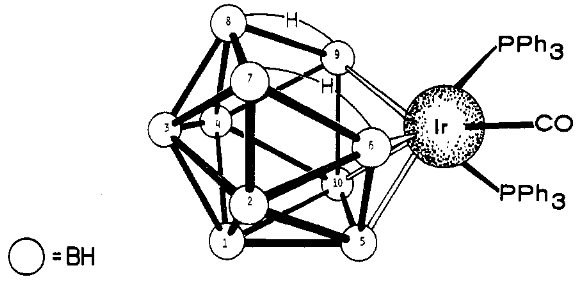

Figure 2. Proposed structure of $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$.

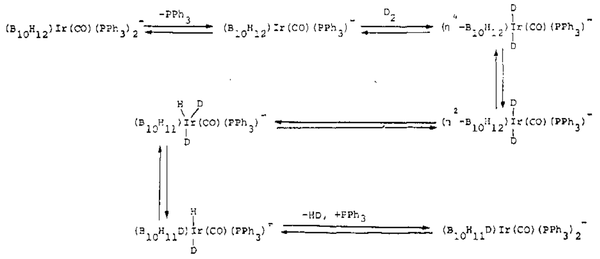

Figure 3. Possible mechanism for H–D Exchange in $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$.

shifts observed is a bending of the bridge hydrogens away from B(7,8) and toward the iridium atom, as suggested by Guggenberger et al.[32] for the platinum borallyl complexes. Nevertheless, the gross arrangement of heavy atoms (boron and iridium) is presumably similar to that in the nickelaborane $[(B_{10}H_{12})_2Ni]^{2-}$ as shown in Figure 2. In a potassium bromide matrix 7 exhibits ν_{CO} at 1975 cm^{-1} compared with 1953 cm^{-1} for $(Ph_3P)_2Ir(CO)Cl$, which strongly suggests that the iridaborane is a complex containing formal Ir(I).

When deuterium gas at atmospheric pressure was passed through a 1,2-dichloroethane solution of $[(C_2H_5)_4N][(B_{10}H_{12})Ir(CO)(PPh_3)_2]$ at room temperature, exchange with some of the BH groups in the $B_{10}H_{12}$ ligand occurred. The exchange was monitored by infrared spectroscopy by noting an increase in absorption at 1850 cm^{-1} due to ν_{BD}. The exchange was complete in about 12 h, when the relative intensities of the B–H and B–D stretching bands indicated that the product contained 1.8 deuteriums, corresponding to $[(C_2H_5)_4N][(B_{10}H_{12}D_2)Ir(CO)(PPh_3)_2]$. Falling drop deuterium analysis revealed the presence of 1.9_7 deuteriums, in agreement with the infrared analysis. Additional deuterium was not incorporated by extending the reaction time up to 100 h. The exchange was reversible and treatment of the deuterated iridaborane with hydrogen regenerated the starting material.

Examination of the infrared spectrum of the reaction mixture failed to disclose the presence of any new iridium hydride species or any new iridium carbonyl derivative; thus, the intermediate(s) present under steady state conditions must have been present in low concentrations. The ^1H NMR spectrum of the exchanged product still showed a signal due to the borane bridge protons, indicating that large amounts of deuterium had not entered those positions. Infrared analysis did not show the presence of any bands due to C–D stretching, therefore, the protons of the triphenylphosphine ligand do not participate in the exchange. This was confirmed by the synthesis of the $(C_6D_5)_3P$ analogue of the iridaborane and the finding that no deuterium transfer from the aromatic ring to the borane ligand occurred.

Salts of $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ did not catalyze H–D exchange between D_2 and other substrates such as $[(7,8\text{-}B_9C_2H_{11})_2Fe]^-$ and the closely related $[(B_{10}H_{12})_2Ni]^{2-}$. This information indicates that the H–D exchange is intramolecular, for if a highly reactive iridium hydride intermediate were formed, it would be expected to attack other boron hydride containing substrates as well.

Exchange experiments with hydrogen and $[(1,2,3,4\text{-}B_{10}D_4H_8)Ir(CO)(PPh_3)_2]^-$, prepared from $1,2,3,4\text{-}B_{10}D_4H_{10}$,[33] showed that no deuterium was lost from the B(1,2,3,4) positions, indicating that these are not involved in the exchange.

Boron environments in $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ may be divided by mirror planes into the unique sets B(1), (3), (2,4), (5,10), (6,9), and (7,8), Figure 2. The retroexchange experiments just discussed indicate that the B(1,2,3,4) positions are not involved. The remaining potentially reactive boron sites all occur in pairs and because the exchange introduces only two terminal deuteriums, a regiospecific reaction is strongly implied, in contrast with exchange reactions of $1,2\text{-}B_{10}C_2H_{12}$ in which attack occurs at more than one position, although probably at different rates.[26] If the H–D exchange reaction is intramolecular, as indicated above, examination of models of $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ and reference to Figure 2 disclose that the B(7,8) positions are too distant from the iridium center to participate by such a mechanism. This leaves the B(6,9) and B(5,10) positions as realistic choices for the reactive sites. $[(C_2H_5)_4N][6\text{-}PhCH_2B_{10}H_{11})Ir(CO)(PPh_3)_2]$ was synthesized from $6\text{-}PhCH_2B_{10}H_{13}$[35,36] and allowed to react with D_2. If the reactive sites were at B(6,9), this compound should incorporate only one deuterium, since half of these sites are blocked by the benzyl group. If, on the other hand, the reactive sites were at B(5,10), then introduction of two deuteriums would be expected. In fact, the deuterated benzyl derivative contained 1.8 D by infrared analysis and 1.7_6 D by falling drop determination, indicating that the exchange takes place at B(5,10). Control experiments showed that the benzyl group was not cleaved by hydrogen under the reaction conditions employed for deuteration.

Attempts to prepare a labeled iridaborane from $\mu_4\text{-}5,6,7,8,9,10\text{-}B_{10}D_{10}H_4$ were unsuccessful; the product always contained four rather than the expected six terminal deuteriums, and the two deuteriums were lost from the positions involved in the H–D exchange, for subsequent treatment with D_2 formed $[(B_{10}D_8H_4)Ir(CO)(PPh_3)_2]^-$. The source of the unexpected protons was found to be the water used during workup and if D_2O was used instead of H_2O, no loss of deuterium occurred and a $B_{10}D_8H_4$ derivative was produced. This exchange with solvent presumably involves the conjugate base $[(B_{10}H_{11})Ir(CO)(PPh_3)_2]^{2-}$; base catalyzed bridge terminal hydrogen exchanges are well documented in decaborane chemistry[34] and the synthesis of a $B_{10}H_{11}^{3-}$ derivative has been previously mentioned. In agreement with this suggestion, it was found that when the reaction with deuterium gas was carried out in Lewis bases such as acetonitrile, the product, $[(C_2H_5)_4N][(B_{10}D_4H_8)Ir(CO)(PPh_3)_2]$, contained two terminal deuteriums by infrared analysis and four deuteriums by falling drop determination. The signal due to the bridge protons had disappeared in this compound, indicating that in basic solvents exchange at both bridge and terminal positions takes place.

A plausible mechanism by which the H–D exchange could proceed is shown in Figure 3. The first step, dissociation of the arylphosphine, had already been demonstrated by ^1H NMR studies of the analogous tri-*p*-tolylphosphine derivative. This dissociation is of kinetic significance, for, in the presence of excess triphenylphosphine, no reaction with deuterium was observed.

Logically, the exchange reaction requires the development of two coordination sites on iridium, one for the addition of D_2 and one for the addition of a B–H bond, but the sequence of these two steps is indeterminate. Oxidative addition of D_2 to coordinatively unsaturated $[(B_{10}H_{12})Ir(CO)(PPh_3)]^-$ to form an intermediate $[(B_{10}H_{12})Ir(CO)(D_2)(PPh_3)]^-$ has ample precedent in the reactions of hydrogen with Ir(I) compounds.[20] It is proposed that this step is followed by a rearrangement which converts η^4-$B_{10}H_{12}^{2-}$ to a monodentate η^2-$B_{10}H_{12}^{2-}$ complex in which the borane now acts as a two-electron donor. Precedent for such a bonding arrangement may be derived from the previously reported $\{(B_{10}H_{12})Ir(CO)[C_2S_2(CN)_2](PPh_3)_2\}^-$. The metal center in such an intermediate is coordinatively unsaturated and intramolecular addition of B(5,10)–H to iridium would then be anticipated on the basis of earlier work with boranes and carboranes. Loss of HD and the reverse of the steps noted above would then lead to the site specific exchange observed.

An exchange process which requires fewer vacant metal sites and which occurred even in the presence of excess triphenylphosphine took place with carbon monoxide. Treatment of **6** in acetonitrile with ^{13}CO produced $[(B_{10}H_{12})Ir(^{13}CO)(PPh_3)_2]^-$ in which $\nu_{^{13}CO}$ at 2030 cm^{-1} was observed. The calculated frequency in the ^{13}C derivative is 2055 cm^{-1}.

Experimental Section[37]

Decaborane was purified by vacuum sublimation. Tetrahydrofuran was distilled from lithium aluminum hydride and acetonitrile from phosphorus pentoxide. Reagent grade 1,2-dichloroethane was purified by passage through a column of Woelm neutral alumina and deoxygenated with a brisk stream of nitrogen. Silica gel 100–200 mesh was obtained from Fisher Scientific Co. Unless otherwise noted, all reactions were carried out under nitrogen.

^{11}B and ^1H NMR spectra were obtained at 70.6 and 220 MHz, respectively, on a Varian HR-220 spectrometer. Shifts are with reference to external $BF_3{\cdot}O(C_2H_5)_2$ and internal $(CH_3)_4Si$; positive shifts refer to higher field. Infrared spectra were recorded in KBr disks on a Perkin-Elmer 21 or 457 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Bromination of $(B_{10}H_{12})Pd(PPh_3)_2$. *N*-Bromosuccinimide (0.125 g; 0.7 mmol) and a tiny crystal of dibenzoyl peroxide were added to 0.7 mmol of **1** suspended in 10 ml of acetonitrile. The mixture was stirred for 12 h then filtered. The filtrate was evaporated and chromatographed on a 14 × 1 in. silica gel column. Chloroform–acetone, 5:1, eluted 0.1 g of **1**; this was followed by a yellow-brown band which was rechromatographed on a 3 × 0.5 in. silica gel column. Acetonitrile–chloroform, 1:1, eluted 0.12 g (26%) of product as yellow microcrystals. Anal. Calcd for $C_{36}H_{41}B_{10}BrPdP_2$: C, 52.11; H, 4.94; Br, 9.65; Pd, 12.79. Found: C, 53.01; H, 5.04; Br, 10.54; Pd, 12.17. The infrared spectrum contained strong bands at 2470, 1420, 1000, 740, and 690 cm^{-1}.

$(Ph_4As)_2\{(B_{10}H_{12})Pd[C_2S_2(CN)_2]\}$. A mixture of 0.75 g of **1**, 0.19 g of $Na_2C_2S_2(CN)_2$,[38] and 30 ml of 1:1 acetone–acetonitrile was stirred at room temperature for 20 h. The solution was filtered and the filtrate taken to dryness under reduced pressure. Water, 25 ml, and dichloromethane, 35 ml, were added. The aqueous layer was separated and treated with excess $Ph_4AsCl{\cdot}H_2O$ whereupon a yellow oil separated. Recrystallization from ethanol yielded 0.5 g (55%) of yellow needles, mp 205–207 °C. Anal. Calcd for $C_{52}H_{52}As_2B_{10}N_2PdS_2$: C, 55.12; H, 4.59; B, 9.54; S, 5.65. Found: C, 54.88; H, 4.74; B, 9.00; S, 5.93. Ir: 3130 (w), 2500 (s), 2180 (m), 1460 (w), 1425 (s), 1175 (w), 1150 (w), 1100 (w), 1075 (w), 995 (m), 740 (s), 690 (s) cm^{-1}. Electronic spectrum (CH_3CN) (λ_{max}, log ϵ): 305 (4.46), 408 (4.72) nm.

$[(CH_3)_4N]_2[(B_{10}H_{12})Pd(CN)_2]$. A mixture of 0.35 g (0.5 mmol) of **1**, 0.2 g of vacuum-dried sodium cyanide (4 mmol), and 15 ml of acetonitrile was stirred for 24 h then filtered. The filtrate was evaporated in vacuo and water and dichloromethane were added. Treatment of the aqueous layer with excess tetramethylammonium chloride caused the product to separate as pale yellow-orange plates. These were collected on a filter, washed with ice water, and vacuum dried. The yield was 0.09 g (45%). Anal. Calcd for $C_{10}H_{36}B_{10}N_2Pd$: C, 28.17; H, 8.45; B, 25.35; N, 13.15. Found: C, 28.34; H, 8.60; B, 25.59; N, 13.36. Ir: 3000 (w), 2500 (s), 2100 (m), 1490 (m), 1400 (w), 1070 (w), 1020 (m), 990 (m), 950 (s), 875 (2), 800 (w), 750 (br, w) cm^{-1}.

$(B_{10}H_{12})Pd(C_{10}H_8N_2)$. Vacuum dried 1,10-phenanthroline (0.13 g; 0.7 mmol), 0.5 g of **1** (0.7 mmol), and 35 ml of 1,2-dichloroethane were stirred at room temperature for 8 h. The solid phase was collected on a filter then stirred with 25 ml of hot acetonitrile. Filtration afforded 0.2 g (75%) of product as yellow microcrystals which decomposed on heating but did not melt up to 300 °C. Anal. Calcd for $C_{10}H_{20}B_{10}N_2Pd$: C, 31.41; H, 5.24; N, 7.33. Found: C, 31.69; H, 5.48; N, 7.30. Ir: 3030 (w), 2500 (s), 1590 (w), 1500 (m), 1410 (m), 1350 (w), 1225 (w), 1150 (w), 1100 (w), 1065 (w), 1010 (m), 880 (w), 850 (s), 795 (w), 770 (w), 760 (w), 725 (s), 700 (sh) cm^{-1}.

Deprotonation of $(B_{10}H_{12})Pd$(phenanthroline). A suspension of 0.39 g (1 mmol) of $(B_{10}H_{12})Pd(C_{10}H_8N_2)$ in 30 ml of tetrahydrofuran was cooled in a dry ice bath. *n*-Butyllithium, 2 mmol, in hexane was added dropwise with stirring. After 30 min, the reaction mixture was warmed to room temperature and poured into 60 ml of water. The mixture was repeatedly extracted with toluene. Addition of excess tetraethylammonium chloride to the aqueous phase gave a maroon precipitate which was collected on a filter. Recrystallization from acetonitrile–2-butanone gave 0.07 g (18%) of product as frail red needles. A thin-layer chromatogram (silica, acetone) showed only one component. Anal. Calcd for $C_{26}H_{70}B_{20}N_4Pd_2$: C, 36.03; H, 8.08; B, 24.94; N, 6.42; Pd, 24.48. Found: C, 36.30; H, 8.22; B, 24.75; N, 6.15; Pd, 24.06. The infrared spectrum contained bands at 2980 (w), 2460 (s), 1450 (m), 1415 (m), 1160 (w), 1170 (w), 1060 (m), 990 (s), 835 (m), 770 (m), and 715 (s) cm^{-1}. Electronic spectrum (CH_3CN): 275 (4.56), 374 (4.20). ^1H NMR (CD_3CN): −9.35, −8.38 (d), −7.77 (m, 8 H); −3.1 (q, 16 H); −1.14 (t, 24 H); a broad resonance at +2.3 ppm was assigned to the bridge protons. This compares with −9.15 (d), −8.45 (d), −7.93 (s), −7.75 (q) ppm for 1,10-phenanthroline in CD_3CN. Λ_M (5.1×10^{-4} M in CH_3CN): 371 Ω^{-1} cm^{-2} mol^{-1}.

A tetraphenylarsonium salt was prepared and recrystallized from acetone–toluene. Anal. Calcd for $C_{58}H_{70}As_2B_{20}N_2Pd$: C, 50.73; H, 5.10. Found: C, 50.58; H, 5.26. The infrared spectrum showed absorptions at 3125 (w), 2450 (s), 1425 (s), 1075 (m), 995 (s), 845 (w), 740 (s), 725 (m), 685 (s) cm^{-1}. The ^{11}B NMR spectrum in CH_3CN was identical with that of the tetraethylammonium salt.

The cesium salt was prepared as described above, using cesium fluoride instead of tetraethylammonium chloride, and recrystallized from acetonitrile–water. Anal. Calcd for $C_{10}H_{30}B_{20}Cs_2N_2Pd_2$: C, 13.76; H, 3.44. Found: C, 13,12; H, 3.75. The infrared spectrum showed bands at 2900 (w), 2470 (vs), 1510 (w), 1420 (s), 1060 (m), 1010 (m), 995 (m), 840 (m), and 720 (w) cm^{-1}.

These materials decomposed on exposure to air and were stored under nitrogen. The cesium salt degraded over several days to a black powder even when kept in an inert atmosphere.

Reaction of $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ with Maleonitriledithiolate. A mixture of $[(C_2H_5)_4N][(B_{10}H_{12})Ir(CO)(PPh_3)_2]$, 0.33 g, and 0.062 g of freshly recrystallized $Na_2C_2S_2(CN)_2$[37] and 12 ml of acetonitrile were stirred overnight under reflux. The resulting orange solution was filtered and passed through a column of Na^+ ion exchange resin. The solution obtained by this procedure was evaporated and taken up in aqueous methanol. Addition of excess methyltriphenylphosphonium bromide gave a precipitate which was collected and dried in vacuo.

Preparative thin layer chromatography (silica gel, 1:1 acetone–dichloromethane) separated two yellow components. Each was eluted with acetone and rechromatographed using pure dichloromethane as the developing solvent.

The faster component was twice recrystallized from boiling ethanol containing a small amount of acetone to afford 0.075 g of $(Ph_3PCH_3)\{(B_{10}H_{12})Ir(CO)[C_2S_2(CN)_2](Ph_3P)_2\}$, mp 149–151 °C dec, as yellow microcrystals. Several recrystallizations are usually required to remove small amounts of a more soluble impurity which exhibited ν_{CO} at 2000 cm^{-1}. Anal. Calcd for $C_{60}H_{60}B_{10}IrN_2OP_3S_2$: C, 56.21; H, 4.68; S, 5.00. Found: C, 56.17; H, 4.63; S, 4.84. Ir: 3055 (w), 2910 (w), 2485 (s), 2195 (m), 1980 (s), 1580 (w), 1475 (m), 1430 (s), 1110 (m), 1095 (m), 1020 (w), 990 (w), 890 (m), 740 (s), 685 (s) cm^{-1}. Electronic spectrum (CH_3CN): 338 (3.07), 425 (2.68). ^1H NMR (acetone-*d*): −7.5 (m, 15 H), ~3.11 (d, $^2J_{P-C-H}$ = 15 Hz, 1 H).

The slower component was also eluted with acetone and recrystallized from acetone–ethanol to yield 0.09 g of (Ph_3PCH_3)-$\{(B_{10}H_{12})Ir[C_2S_2(CN)_2](Ph_3Pl_2\}$ as yellow orange microcrystals, mp 131–133 °C dec. Anal. Calcd for $C_{59}H_{60}B_{10}IrN_2P_3S_2$: C, 56.50; H, 4.79; S, 5.11. Found: C, 56.46; H, 4.63; S, 5.32. Ir: 3050 (w), 2890 (w), 290 (w), 2480 (s), 2190 (s), 1580 (w), 1465 (s), 1430 (s), 1115 (m), 1090 (m), 1010 (m), 900 (m), 745 (s), 690 (s) cm^{-1}. Electronic spectrum (CH_3CN): 330 (3.27), 426 (2.64). ^1H NMR (CD_3CN): −7.5 (complex multiplet, 15 H); −3.11 (d, 14 Hz, 1 H).

Reaction of $(C_2H_5)_4N[(B_{10}H_{12})Ir(CO)(PPh_3)_2]$ with Dideuterium. The literature method[1] was used to prepare $Na[(B_{10}H_{12})Ir(CO)(PPh_3)_2]$. It was converted to the tetraethylammonium salt by metathesis with $(C_2H_5)_4NCl$ and recrystallized from acetone–ethanol. Anal. Calcd for $C_{45}H_{62}B_{10}IrNOP_2$: C, 54.33; H, 6.24. Found: C, 54.62; H, 6.39. A 0.1-g sample of this salt was dissolved in 10 ml of 1,2-dichloroethane. Deuterium, which had previously been passed through a bubbler containing the same solvent, was introduced, after first flushing the apparatus with deuterium, at a rate of approximately 20 bubbles/min. The deuterated product was isolated by evaporation of the solvent.

Under these conditions, no reaction was observed between D_2 and $[(C_2H_5)_4N]_2[(B_{10}H_{12})_2Ni]$, $(Ph_3PCH_3)_2[(B_{10}H_{12})_2Pt]$, or $[(C_2H_5)_4N]_2[(B_{10}H_{12})Rh(CO)(PPh_3)_2]$ although solutions of the latter material appeared to darken and decompose on standing in solution.

$[(C_2H_5)_4N][(6\text{-}PhCH_2B_{10}H_{11})Ir(CO)(Ph_3P)_2]$ was prepared[1] using $6\text{-}PhCH_2B_{10}H_{13}$[35] in place of decaborane. Anal. Calcd for $C_{52}H_{68}B_{10}IrNOP_2$: C, 57.57; H, 6.27. Found: C, 57.31; H, 6.07. ^{1}H NMR (acetone-d_6): −7.25 (m, 35 H); −3.25 (q, 8 H), −1.22 (t, 12 H); a broad singlet at −1.7 is attributed to the benzylic CH_2 group.

Reaction of $[(C_2H_5)_4N][(B_{10}H_{12})Ir(CO)(PPh_3)_2$ with Carbon Monoxide. Acetonitrile, 4 ml, was condensed onto 0.02 g of the iridaborane which was contained in a small flask attached to the vacuum line. The resulting solution was stirred for 24 h under a 35-mm pressure of 90% enriched ^{13}CO. The exchanged product was isolated by evaporation of the solvent and contained equal amounts of ^{13}C and ^{12}C in the carbonyl group by infrared analysis.

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Registry No. **1**, 60282-43-1; **2**, 60305-63-7; **3** (tetraphenylarsonium salt), 60282-42-0; **4**, 60282-40-8; **5**, 60282-38-4; **6** (tetraethylammonium salt), 60349-64-6; **6** (tetraphenylarsonium salt), 60349-63-5; **6** (cesium salt), 60305-64-8; **7**, 57373-31-6; **8**, 60282-45-3; **9**, 60282-47-5; $[(C_2H_5)_4N][(6\text{-}Ph\text{-}CH_2B_{10}H_{11})Ir(CO)(Ph_3P)_2]$, 60282-49-7; *N*-bromosuccinimide, 128-08-5; ^{11}B, 14798-13-1.

References and Notes

(1) F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 7, 2072 (1968).
(2) A. R. Siedle and T. A. Hill, *J. Inorg. Nucl. Chem.*, **31**, 3874 (1969).
(3) L. J. Guggenberger, *J. Am. Chem., Soc.*, **94**, 114 (1972).
(4) M. F. Hawthorne, *Rev. Pure Appl. Chem.*, **29**, 547 (1972).
(5) L. O. Pont, A. R. Siedle, M. S. Lazarus, and W. L. Jolly, *Inorg. Chem.*, **13**, 483 (1974).
(6) C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973).
(7) R. J. Wilson, L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **91**, 758 (1969).
(8) L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 4823 (1968).
(9) L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **92**, 1157 (1970).
(10) E. L. Muetterties, *Rev. Pure Appl. Chem.*, **29**, 585 (1972).
(11) E. L. Hoel and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 6770 (1974).
(12) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 633 (1964).
(13) M. F. El Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).
(14) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(15) A. R. Siedle, G. M. Bodner, W. F. Wright, and L. J. Todd, to be submitted for publication.
(16) B. P. Sullivan, R. N. Leyden, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 455 (1975).
(17) C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc. A*, 84 (1969).
(18) A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966).
(19) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(20) M. Deeming, *MTP Int. Rev. Sci.; Inorg. Chem., Ser. One*, **9**, 117 (1972).
(21) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970).
(22) G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).
(23) M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, and S. S. Wreford, *J. Am. Chem. Soc.*, **96**, 4041 (1974).
(24) E. L. Hoel and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 2712 (1973).
(25) T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 4674 (1974).
(26) E. L. Hoel and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 4676 (1974).
(27) A. R. Siedle, *J. Organomet. Chem.*, **9**, C4 (1975).
(28) L. G. Sneddon and R. N. Grimes, *J. Am. Chem. Soc.*, **94**, 7161 (1972).
(29) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 7633 (1973).
(30) J. W. Lott and D. F. Gaines, *Inorg. Chem.*, **13**, 2261 (1974).
(31) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 6623 (1973).
(32) L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 5665 (1972).
(33) J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 1804 (1962).
(34) M. F. Hawthorne, "The Chemistry of Boron and Its Compounds", E. L. Muetterties, Ed., Wiley, New York, N.Y., 1967, p 265.
(35) R. J. F. Palchak, J. H. Norman, and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 3380 (1961).
(36) A. R. Siedle, D. McDowell, and L. J. Todd, *Inorg. Chem.*, **13**, 2735 (1974).
(37) Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.
(38) A. Davison and R. H. Holm, *Inorg. Synth.*, **10**, 11 (1967).

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Preparation and Characterization of 1,2,3,4,5,6-Hexakis(dimethylamino)-*closo*-hexaborane(6)–Hexakis(dimethylaminodimethylaluminum), a Novel Boron Cluster Compound[1a]

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Treatment of tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, with aluminum trimethyl, $[Al(CH_3)_3]_2$, under specific reaction conditions, results in the generation of $B_6[N(CH_3)_2]_{12}\cdot Al_6(CH_3)_{12}$ (I). Formation of I is a result of the induced disproportionation of $B_2[N(CH_3)_2]_4$ and most likely represents a cluster species with an octahedral boron core. A molecular orbital description of core bonding is presented assuming T_h symmetry. Finally, the reactions of I with H_2O, $N(CH_3)_3$, $P(CH_3)_3$, $HN(CH_3)_2$, NH_3, and acetylacetone are presented.

The chemistry of closo polyhedral borane derivatives has been extensively investigated; however, relatively few examples are known in which B–H bonds are totally absent. Several exceptions are B_4Cl_4, B_8Cl_8, B_9Cl_9, $B_{11}Cl_{11}$, $B_{12}Cl_{11}$, $B_{10}Cl_{10}^{2-}$, and $B_{12}Cl_{12}^{2-}$.[2-12] The methods employed for the synthesis of molecular boron chlorides have usually involved electric discharge reactions utilizing BCl_3 or the thermal decomposition of B_2Cl_4. Anionic haloborane species have resulted from halogenation of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ salts taking advantage of the relative inertness of these cage systems