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Preliminary communication

ACTIVATION OF MOLECULAR HYDROGEN BY A *nido*-METALLOBORANE

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Summary

Reaction of quaternary ammonium salts of $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ in dichloroethane with dideuterium at ambient temperature and pressure leads to reversible H—D exchange at two terminal B—H sites in the $B_{10}H_{12}$ ligand. Exchange is thought to occur at the 5-10 boron atoms.

Oxidative addition reactions are involved in the activation of small covalent molecules by transition metals [1] and intramolecular oxidative addition reactions of C—H bonds in coordinated triphenylphosphine and triphenylphosphite are well documented [2,3]. Recent reports of the irreversible addition of iridium(I) to the B—H bond in carboranes [4,5] and pentaborane [6] presage an extensive chemistry of metalloboranes derived from low valent metals. Indeed, Hawthorne and co-workers have recently synthesized *closo*-rhodacarboranes [7] and found that these compounds, as well as other materials such as Ph_3P_3RuHCl and palladium on charcoal, catalyze the exchange between dideuterium and boranes and carboranes [8]. This report concerns a reaction of molecular hydrogen (deuterium) under mild conditions with an iridium-containing *nido*-metalloborane leading to regiospecific exchange of two hydrogen atoms in the coordinated boron hydride ligand.

When deuterium gas at atmospheric pressure is passed through ethylene chloride solutions of $(C_2H_5)_4N[(B_{10}H_{12})Ir(CO)(PPh_3)_2]$ [9] at room temperature some of the B—H groups in the $B_{10}H_{12}$ ligand are converted to B—D groups. The exchange can be followed by infrared spectroscopy, noting an increase in absorption at 5.4 μ due to ν(B—D). The exchange is complete in about 12 hours and, after this time, the relative intensities of the B—H and B—D stretching bands indicate that the product contains 1.8 terminal

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*NRC-NBS Postdoctoral Research Associate, 1973-1975 deuteriums. Falling drop deuterium analysis revealed the presence of 1.97 deuteriums, in agreement with the infrared analysis. Additional deuterium is not incorporated by extending the reaction time up to 100 hours. The exchange is reversible and treatment with H_2 of the deuterated material regenerates the starting compound.

The 70.6 MHz ^{11}B NMR spectrum of salts of the iridaborane consists of four broad, overlapping resonances between —14 and 28 ppm (from $BF_3 \cdot O(C_2H_5)_2$). The lack of resolution, also observed in the ^{11}B NMR spectra of other metalloboranes [5], frustrated efforts to follow the exchange reaction by ^{11}B NMR spectroscopy. Examination of the infrared spectrum of the reaction mixture failed to disclose the presence of an iridium hydride species or any C—D stretching absorptions due to exchange involving the triphenylphosphine ligands or, indeed, any other species than the starting material and its B-deuterated analogue.

Exchange experiments employing $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ analogues, prepared from specifically deuterated decaboranes [10], and hydrogen show that the exchange sites are on the open face of the $B_{10}H_{12}$ moiety, *i.e.*, at the B(5) to B(10) positions. The iridaborane and the nickelaborane $[(CH_3)_4N]_2[(B_{10}H_{12})_2Ni]$ presumably have the same gross arrangement of boron and metal atoms (Fig. 1) [11]. Because the BH sites in the B(5)-B(10) set may be divided by mirror planes of symmetry into three sets B(7), B(8); B(6), B(9) and B(5), B(10) containing two BH units each, the observation that only two BH sites participate in the exchange process implies that the reaction is regiospecific. This is in contrast to exchange reactions of 1,2-$B_{10}C_2H_{12}$ [8], in which reaction occurs at more than one position, although probably at different rates.

The reaction is evidently intramolecular (*vide infra*); reference to Fig. 1 indicates that the B(7), B(8) hydrogens are too distant from the metal center to be involved in the H—D exchange. The realistic choices remaining are B(6), B(9) and B(5), B(10). When one of the hydrogens at the former position is replaced by a benzyl group in $[(6\text{-}PhCH_2B_{10}H_{11})Ir(CO)(PPh_3)_2]^-$, the anion still incorporates 1.8 D by infrared analyses and 1.7 D by falling drop determination. This evidence indicates that the exchange sites are located at B(5), B(10).

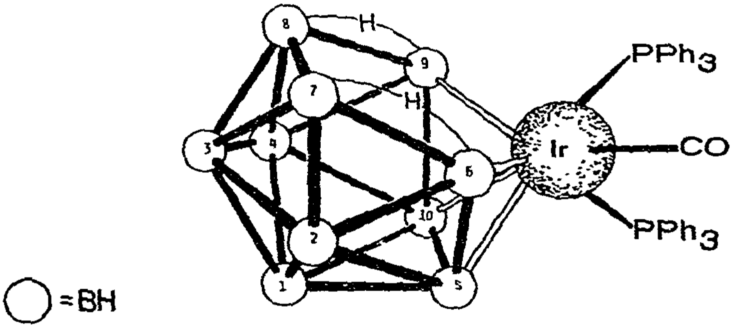
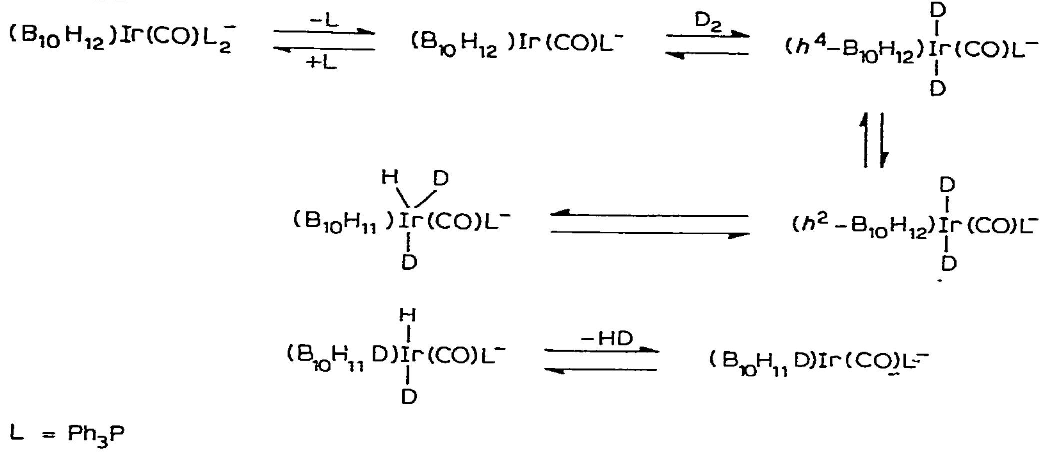


Fig. 1. Proposed structure of $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$.

SCHEME 1



The tetraalkylammonium salts of the $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ anion in a KBr matrix exhibit ν(CO) at 1975 cm^{-1} compared with 1953 cm^{-1} for $(Ph_3P)_2Ir(CO)Cl$, so it is reasonable to regard the iridaborane as containing *formal* Ir^I. It is suggested that the hydrogen—deuterium exchange reaction involves oxidative addition of a B—H bond in the $B_{10}H_{12}$ ligand to Ir^I. Selectivity and an intramolecular mechanism are implied by the inability of $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ to catalyze H—D exchange in other boron hydride substrates such as the closely related $[(B_{10}H_{12})_2Ni]^{2-}$ ion. A possible pathway by which the exchange could proceed is shown in Scheme 1, most of which follows by analogy with more conventional organometallic systems and with recent results with boron hydrides [4-8]. Studies of the ^1H NMR spectra of solutions of $(C_2H_5)_4N\{(B_{10}H_{12})Ir(CO)[(p\text{-}CH_3C_6H_4)_3P]_2\}$ indicate extensive dissociation of the $(p\text{-}CH_3C_6H_4)_3P$ ligand. Arylphosphine dissociation is presumably kinetically important in the observed H—D exchange, for no reaction with dideuterium occurs in the presence of excess triphenylphosphine.

Further labeling studies and syntheses of model compounds are in progress.

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