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Preliminary communication

Addition of electrophiles to metalladiborane anions $[M(CO)_4(\eta^2\text{-}B_2H_5)]^-$ (Fe, Ru, Os) *

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Abstract

Addition of the electrophiles $[CH_3]^+$, H^+, $[(PPh_3)Au]^+$ to the metalladiborane anions $[M(CO)_4(\eta^2\text{-}B_2H_5)]^-$ (M = Fe, Ru, Os) has been investigated. Addition occurs at the metal center. The complexes $CH_3Os(CO)_4(\eta^2\text{-}B_2H_5)$, $HM(CO)_4(\eta^2\text{-}B_2H_5)$ (M = Ru, Os), and $(PPh_3)AuM(CO)_4(\eta^2\text{-}B_2H_5)$ (M = Fe, Ru, Os) have been formed. NMR spectra of $HM(CO)_4(\eta^2\text{-}B_2H_5)$ indicate that the H atom on the metal is *cis* to the B_2H_5 ligand. Relative stabilities of the complexes $LM(CO)_4(\eta^2\text{-}B_2H_5)$ are in the order M = Os > Ru > Fe for a given electrophile and the order L = $(Ph_3P)Au$ > H for a given metal.

We recently reported on metalladiborane anions of the type $[M(CO)_4(\eta^2\text{-}B_2H_5)]^-$ (M = Fe, Ru, Os) [1]. Their structures are considered to be like that of diborane(6), with a bridge proton replaced by an $M(CO)_4$ unit. They are analogues of metal–olefin complexes in which $[B_2H_5]^-$ is isolobal with C_2H_4 [2]. Bonding can be viewed in the Dewar Duncanson Chatt [3] sense as a mixing of a π bonding orbital of $[B_2H_5]^-$ with a vacant metal orbital of $M(CO)_4$, accompanied by possible back-bonding from a filled metal orbital to the π^* orbital of $[B_2H_5]^-$. The Mössbauer spectrum of $[Fe(CO)_4(\eta^2\text{-}B_2H_5)]^-$ is consistent with this type of bonding in that it suggests the presence of Fe(0) in the complex [1]. Metal–boron bonding in the related complex $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2\text{-}B_2H_5)$, analyzed by photoelectron spectroscopy and Fenske–Hall analysis, indicates that the primary mode of bonding appears to be donation of electron density from the boron–boron bond to the vacant iron orbital, with little indication of back electron donation [4].

In a continuing study of metalladiboranes, reactions of $[M(CO)_4(\eta^2\text{-}B_2H_5)]^-$ with electrophilic reagents have been examined. It was of interest to determine if the metal center is sufficiently basic to add the reagents $[CH_3]^+$, H^+, and $[(Ph_3P)Au]^+$ or if the electrophile would displace $M(CO)_4$ by adding to $[B_2H_5]^-$

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* This work is dedicated to Professor F.G.A. Stone, a distinguished boron chemist as well as organometallic chemist.

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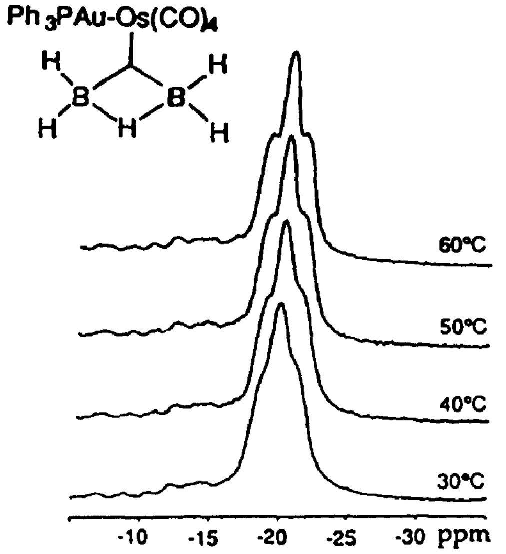

Fig. 1. Boron-11 NMR spectra of $(PPh_3)AuOs(CO)_4(\eta^2\text{-}B_2H_5)$.

Three types of reactions were studied:

$$K[Os(CO)_4(\eta^2\text{-}B_2H_5)] + [(CH_3)_3O][BF_4] \rightarrow CH_3Os(CO)_4(\eta^2\text{-}B_2H_5) + K[BF_4] + (CH_3)_2O \quad (1)$$

$$K[Os(CO)_4(\eta^2\text{-}B_2H_5)] + HCl \rightarrow HOs(CO)_4(\eta^2\text{-}B_2H_5) + KCl \quad (2)$$

$$K[Os(CO)_4(\eta^2\text{-}B_2H_5)] + (Ph_3P)AuCl \rightarrow (Ph_3P)AuOs(CO)_4(\eta^2\text{-}B_2H_5) + KCl \quad (3)$$

Based upon NMR spectra, the electrophile adds to the metal and the B_2H_5 unit remains intact in these reaction. Proton NMR spectra [5*-7*] of these complexes reveal the presence of a bridging hydrogen, terminal hydrogens on boron, and for $CH_3Os(CO)_4(\eta^2\text{-}B_2H_5)$ and $HOs(CO)_4(\eta^2\text{-}B_2H_5)$ the CH_3 hydrogens and the OsH hydrogen are also revealed. Boron-11 NMR spectra of $CH_3Os(CO)_4(\eta^2\text{-}B_2H_5)$ [5*] and $HOs(CO)_4(\eta^2\text{-}B_2H_5)$ [6*] display the characteristic triplet of doublets arising from coupling of terminal and bridge hydrogens with boron. Temperature-dependent ^{11}B NMR spectra of $(Ph_3P)AuOs(CO)_4(\eta^2\text{-}B_2H_5)$ [7*] (Fig. 1) at 60 °C reveal a well-resolved triplet due to terminal hydrogen–boron coupling. Rapid decomposition of the sample at higher temperatures prevented observation of bridge hydrogen–boron coupling which is expected to be resolved at higher temperatures. The ^{13}C NMR spectrum of $HOs(CO)_4(\eta^2\text{-}B_2H_5)$ [6*] consists of three signals in the ratio 1(doublet) : 2 : 1, which indicate that the hydrogen bound to the metal is *cis* to the B_2H_5 ligand. A proposed structure is shown in Fig. 2.

Stabilities of these complexes, $LOs(CO)_4(\eta^2\text{-}B_2H_5)$, at room temperature in vacuum are in the order $L = (PPh_3)Au > H > CH_3$. The gold complex decomposes very slowly at room temperature to give off PPh_3BH_3. The protonation product is

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* Reference number with asterisk indicates a note in the list of references.

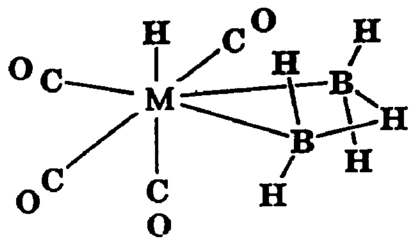

Fig. 2. Proposed structure of $HM(CO)_4(\eta^2\text{-}B_2H_5)$ (M = Os, Ru).

less stable, giving off B_2H_6 and H_2, but it can be handled at room temperature for several hours without significant decomposition. The methylation derivative is completely decomposed in about an hour at room temperature, evolving B_2H_6 and CH_4.

For the preparation of $CH_3Os(CO)_4(\eta^2\text{-}B_2H_5)$, 102 mg (0.277 mmol) of $K[Os(CO)_4(\eta^2\text{-}B_2H_5)]$ and 43 mg of $[(CH_3)_3O][BF_4]$ (0.290 mmol) in 2 mL of dry $(CH_3)_2O$ were allowed to react for 4 h at −78 °C. After pumping away $(CH_3)_2O$ at −78 °C, $CH_3Os(CO)_4(\eta^2\text{-}B_2H_5)$ was extracted with CH_2Cl_2, which was then pumped away at −65 °C, leaving behind the product $CH_3Os(CO)_4(\eta^2\text{-}B_2H_5)$ as a yellow oil.

For the preparation of $HOs(CO)_4(\eta^2\text{-}B_2H_5)$, 17 mg (0.291 mmol) of $K[Os(CO)_4(\eta^2\text{-}B_2H_5)]$ and 0.538 mmol of HCl reacted rapidly (less than 1 min) in 1 mL of dry CH_2Cl_2 at −78 °C. Excess HCl was pumped away at −78 °C, the reaction mixture was filtered and then the product, $HOs(CO)_4(\eta^2\text{-}B_2H_5)$, was isolated as a yellow oil by pumping away the CH_2Cl_2 at −65 °C.

In the preparation of $(Ph_3P)AuOs(CO)_4(\eta^2\text{-}B_2H_5)$, 5 mL of dry THF was condensed onto a mixture of 110 mg (0.298 mmol) of $K[Os(CO)_4(\eta^2\text{-}B_2H_5)]$ and 134 mmol (0.274 mmol) of $(Ph_3P)AuCl$ at −78 °C. The mixture was warmed to 0 °C and stirred for 15 min. Solvent was then pumped away and the product was extracted with CH_2Cl_2. Removal of solvent from the precipitate gave solid yellow-brown $(Ph_3P)AuOs(CO)_4(\eta^2\text{-}B_2H_5)$, 162 mg (75% yield based on $(Ph_3P)AuCl$). Anal. Calcd for $C_{22}H_2AuB_2O_4OsP$: C, 33.53; H, 2.56. Found: C, 33.43; H, 2.39.

Reactions like (2) and (3) were also studied employing $K[Fe(CO)_4(\eta^2\text{-}B_2H_5)]$ and $K[Ru(CO)_4(\eta^2\text{-}B_2H_5)]$. Protonation of $[Fe(CO)_4(\eta^2\text{-}B_2H_5)]^-$ gave an adduct which decomposed above −120 °C to give B_2H_6 and $Fe(CO)_5$. Because of its instability the site of protonation could not be determined. However, NMR evidence was obtained for the formation of $HRu(CO)_4(\eta^2\text{-}B_2H_5)$ [8*], $(Ph_3P)AuFe(CO)_4(\eta^2\text{-}B_2H_5)$ [9*], and $(Ph_3P)AuRu(CO)_4(\eta^2\text{-}B_2H_5)$ [10*]. The ^{13}C NMR spectrum of $HRu(CO)_4(\eta^2\text{-}B_2H_5)$ indicates a structure like that assigned to $HOs(CO)_4(\eta^2\text{-}B_2H_5)$ (Fig. 2). The complex $HRu(CO)_4(\eta^2\text{-}B_2H_5)$ decomposes slowly at −80 °C. Complexes $(Ph_3P)AuFe(CO)_4(\eta^2\text{-}B_2H_5)$ and $(Ph_3P)AuRu(CO)_4(\eta^2\text{-}B_2H_5)$ are completely decomposed at room temperature in 15 min and 2 h, respectively. The relative stabilites of electrophile adducts $LM(CO)_4(\eta^2\text{-}B_2H_5)$ are in the order M = Os > Ru > Fe for a given electrophile and the order L = $(Ph_3P)Au$ > H for a given metal.

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5 NMR spectra $CH_3Os(CO)_4(\eta^2\text{-}B_2H_5)$ (CD_2Cl_2): δ ^1H (δ $Si(CH_3)_4 = 0.00$ ppm) 2.80 (4BH, quartet $J(BH) = 105$ Hz), 0.324 (3CH), -5.51 (1BHB) ppm. δ ^{11}B(δ $Et_2OBF_3 = 0.00$ ppm) -8.0 (triplet of doublets, $J(BH) = 105$ Hz, $J(BHB) = 26$ Hz) ppm.

6 NMR spectra $HOs(CO)_4(\eta^2\text{-}B_2H_5)$ (CD_2Cl_2): δ ^1H 2.50 (4BH, quartet $J(BH) = 104$ Hz), -6.09 (1BHB), -8.56 (1OsH) ppm. ^{11}B -14.4 (triplet of doublets, $J(BH) = 101$ Hz, $J(BHB) = 32$ Hz) ppm. δ ^{13}C (δ $Si(^{13}CH_3)_4 = 0.00$ ppm) 171.6 (doublet 1CH), $J(CH) = 9.0$ Hz), 169.0 (2C), 167.5 (1C) ppm.

7 NMR spectra $(Ph_3P)AuOs(CO)_4(\eta^2\text{-}B_2H_5)$ $(CDCl_3$, 60 °C): δ ^1H 7.5–7.3 (multiplet PPh_3), 2.31 (4BH, quartet $J(BH) = 106$ Hz), -3.99 (1BHB) ppm. ^{11}B -20.0 (triplet $J(BH) = 104$ Hz) ppm.

8 NMR spectra $HRu(CO)_4(\eta^2\text{-}B_2H_5)$ (CD_2Cl_2): δ ^1H (-70 °C) 2.22 (4BH, $J(BH) = 104$ Hz), -5.12 (1BHB), -7.51 (1RuH). δ ^{11}B (-10 °C) -14.4 (triplet of doublets, $J(BH) = 104$ Hz, $J(BHB) = 32$ Hz). δ ^{13}C (-80 °C) 189.9 (doublet, $J(CH) = 17.7$ Hz), 188.1 (2C), 186.1 (1C) ppm.

9 NMR spectra $(Ph_3P)AuFe(CO)_4(\eta^2\text{-}B_2H_5)$ $(CDCl_3$, 25 °C): δ ^{11}B -12.1 (poorly resolved triplet) ppm.

10 NMR spectra $(Ph_3P)AuRu(CO)_4(\eta^2\text{-}B_2H_5)$ $(CDCl_3$, 25 °C): δ ^1H 7.7–7.5 (multiplet PPh_3), 2.49 (poorly resolved quartet 2BH), -3.99 (1BHB) ppm. ^{11}B -14.9 (poorly resolved triplet) ppm.