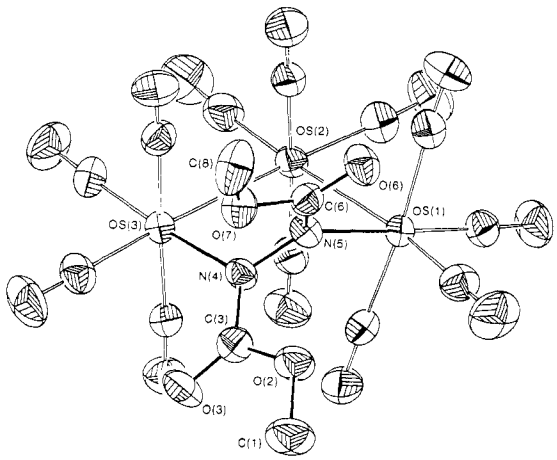

Figure 2. The structure of $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ (**5**). Selected bond lengths (Å) and angles (deg) are Os(1)–Os(2) = 2.967 (1), Os(2)–Os(3) = 3.008 (1), Os(1)···Os(3) = 4.198 (1), Os(1)–N(5) = 2.095 (5), N(4)–N(5) = 1.411 (7), N(4)–C(3) = 1.351 (8), C(3)–O(3) = 1.220 (8), Os(3)–N(4) = 2.092 (5), N(5)–C(6) = 1.336 (8), C(6)–O(6) = 1.226 (8), Os(1)–Os(2)–Os(3) = 89.27 (2).

Compound **4** reacted quantitatively with CO (1500 psi, room temperature, 12 h) to form **5**, formulated as $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ on the basis of its mass (m/z 1058, based on ^{192}Os, fast atom bombardment), IR (2123 (s), 2075 (s), 2062 (s), 2026 (m), 1995 (mw) cm^{-1} (hexane), 1633 (m), 1433 (mw) cm^{-1} (C_2Cl_4)), and NMR (δ 3.64 in $CDCl_3$). It crystallized from CH_2Cl_2–hexane as yellow air-stable crystals, mp 126 °C, the structure of which 2).[2] (Figure 2).[2] In relation to compound **4** compound **5** is derived by the replacement of the two ligating methoxycarbonyl groups by carbon monoxide. The organic ligand thus is now a two-electron donor bridging hydrazido group, consistent with retention of the long N–N bond (1.41 Å) and the nonbonding Os···Os distance of 4.198 Å. Compound **5** is therefore a unique example of a 50-electron $Os_3(CO)_{12}X_2$ type of cluster that retains a triangular disposition of Os atoms.

The intermediate **3** formulated as $Os_3(CO)_{11}(CH_3OCONNCOOCH_3)$ could be isolated by stopping the reaction of **1** with **2** at 10 °C after 1.5 h, followed by flash chromatography on cellulose with hexane–benzene (1:1) as eluent. Due to a tendency to transform to **4** on attempted crystallization, no X-ray structure is available, but it is assigned the structure illustrated from spectroscopic evidence. The ^1H NMR exhibits two sharp singlets of equal intensity at δ 3.64 and 3.82, readily assigned to the methyls of the free and coordinated methoxycarbonyl groups respectively by comparison with **4** and **5**. The IR also shows the absorptions of the free and complexed carbonyls of these groups, again by comparison with **4** and **5**: IR 2134 (mw), 2095 (s), 2060 (s, br), 2040 (sh), 2020 (m), 2007 (s, br) cm^{-1} (benzene), 1658 (mw), 1530 (mw), 1472 (mw) cm^{-1} (C_2Cl_4). Furthermore **3** takes up CO under very mild conditions (1 atm, 0 °C, CH_2Cl_2) to give **5** quantitatively. The course of the reaction of **1** with excess **2** could be followed conveniently by ^1H NMR in $CDCl_3$ at 10 °C. The signal at 2.76 ppm due to the CH_3CN ligand in **1** decreased, with a corresponding smooth increase in the signals at 3.64 and 3.82 ppm due to formation of **3** alone and at 1.98 ppm (free CH_3CN). After the disappearance of **1** the temperature was raised to 35 °C, and this produced a smooth decrease in the signals of **3** and an increase in a new signal at 3.87 ppm due to **4**. At 60 °C a small amount of **5** was detected, probably due to uptake by **3** of CO released from decomposition.

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Registry No. **1**, 65702-94-5; **2**, 2446-84-6; **3**, 86409-58-7; **4**, 86409-59-8; **5**, 86409-60-1; Os, 7440-04-2.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles and structure factors for **4** and **5** (59 pages). Ordering information is given on any current masthead page.

Mechanism of Hydroboration of Alkenes by Dibromoborane–Methyl Sulfide. Remarkable Catalysis of the Reaction by Small Quantities of Boron Tribromide

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Summary: The hydroboration of alkenes with $BHBr_2 \cdot SMe_2$ proceeds by a prior dissociation of the reagent followed by the reaction of $BHBr_2$ with the alkene to give $RBBr_2$, which then forms a complex with Me_2S formed in the dissociation step. In conformity with this mechanism, the reaction is remarkably catalyzed by small quantities of BBr_3.

Since their discovery,[2] the haloborane–methyl sulfide complexes have found extensive use in organic synthesis,[3-5] but the mechanism of their reaction with alkenes is not yet well understood.

In the past, we have established that 9-BBN·Lewis base complexes hydroborate alkenes by the dissociation mechanism.[6] For example, excess Me_3N represses the rate of hydroboration of 2-methyl-1-pentene by 9-BBN·NMe_3 complex significantly, indicating that the complex dissociates into 9-BBN and Me_3N prior to hydroboration. It is also known that the ease of hydroboration by BH_3·Lewis base complexes increases with decreasing stability of the complex.[7,8] Consequently, we were led to think that haloborane–methyl sulfide complexes also will hydroborate alkenes by a prior dissociation of the complex into the free borane. In fact, addition of 1 equiv of methyl sulfide significantly retards the rate of hydroboration of alkenes and alkynes by $BHBr_2 \cdot SMe_2$[9] and thexylchloroborane–methyl sulfide.[5b]

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(2) Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938–2939.
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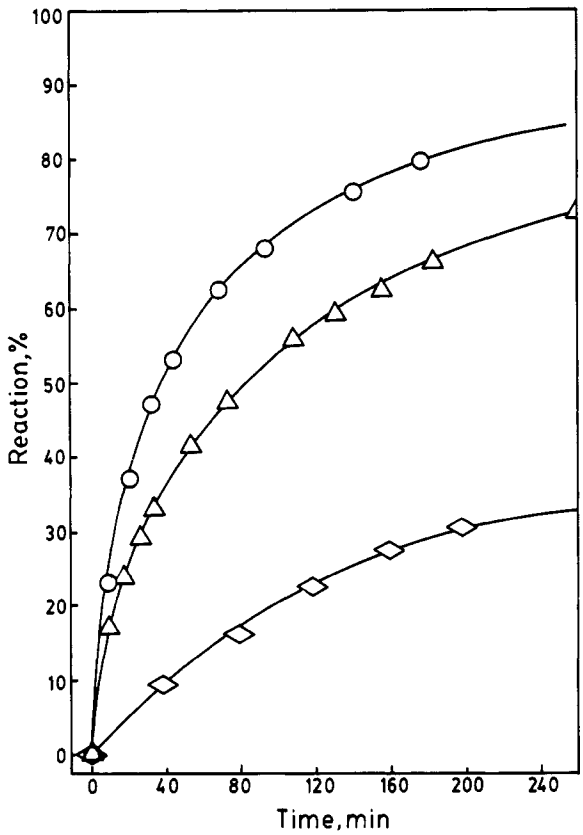

Figure 1. Rate data for the hydroboration of 1-hexene (0.1 M) with $BHBr_2{\cdot}SMe_2$ (0.1 M) in CH_2Cl_2 at 25 °C and the effects of (*n*-hexyl)$BBr_2{\cdot}SMe_2$ and Me_2S (○, without the addition of Me_2S or (*n*-hexyl)$BBr_2{\cdot}SMe_2$, $t_{1/2}$ = 39 min; △, in the presence of (*n*-hexyl)$BBr_2{\cdot}SMe_2$ (0.1 M), $t_{1/2}$ = 78 min; ◇, in the presence of Me_2S (0.1 M), $t_{1/2}$ = 490 min).

But we encountered an unexpected theoretical problem. $BHBr_2{\cdot}SMe_2$ hydroborates alkenes much faster than does $BHCl_2{\cdot}SMe_2$.[3b] Since BBr_3 is a stronger Lewis acid than BCl_3,[10] $BHBr_2$ should be a stronger acid than $BHCl_2$. This would make $BHBr_2{\cdot}SMe_2$ a tighter complex than $BHCl_2{\cdot}SMe_2$. Consequently, according to the dissociation mechanism, one would expect $BHCl_2{\cdot}SMe_2$ to hydroborate alkenes faster than $BHBr_2{\cdot}SMe_2$. In practice, the hydroboration of alkenes by $BHCl_2{\cdot}SMe_2$ is much slower and 1 molar equiv of BCl_3 is needed to effect a satisfactory hydroboration.[3b] Moreover, the hydroboration of 2-methyl-2-butene with $BHBr_2{\cdot}SMe_2$ leads to 7% of boron on the tertiary carbon, much higher than that observed for either $BHCl_2{\cdot}SMe_2$ or $BH_2Br{\cdot}SMe_2$ (3%). These observations refrained us from ruling out the possibility of a direct attack of alkenes on the $BHBr_2{\cdot}SMe_2$ complex. However, we deferred a final conclusion pending a more detailed study.[3b] In this communication we report our results on the kinetics and mechanism of hydroboration of a representative alkene, 1-hexene, by $BHBr_2{\cdot}SMe_2$ in CH_2Cl_2 at 25 °C and an unexpected explanation of the apparent anomaly.

The reaction of alkenes with $BHBr_2{\cdot}SMe_2$ may either proceed by a direct reaction of the alkene with the complex (eq 1) or by a prior dissociation of the complex into $BHBr_2$

$$\rangle C{=}C\langle + BHBr_2{\cdot}SMe_2 \longrightarrow RBBr_2{\cdot}SMe_2 \quad (1)$$

and Me_2S followed by the reaction of the free $BHBr_2$ with

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Table I. Effect of BBr_3 on the Hydroboration of Alkenes by $BHBr_2{\cdot}SMe_2$[a]

alkene	catalyst	temp, °C	time for completn
1-hexene[b]		25	8 h
1-hexene[c]	BBr_3, 5 mol %	25	15 min
cyclohexene[d]		40	> several days
cyclohexene[c]	BBr_3, 10 mol %	40	6 h

[a] 1.0 M in the reactants in CH_2Cl_2. [b] Data for 1-octene taken from ref 3b. [c] To the rest of the materials, BBr_3 in CH_2Cl_2 was added dropwise at 0 °C and the reaction mixture was then raised to the mentioned temperature. [d] The reaction becomes very slow at later stages.

the alkene to give $RBBr_2$, which will then form a complex with Me_2S formed in the dissociation step (eq 2–4). The

$$BHBr_2{\cdot}SMe_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BHBr_2 + SMe_2 \quad (2)$$

$$BHBr_2 + \text{alkene} \xrightarrow{k_2} RBBr_2 \quad (3)$$

$$RBBr_2 + Me_2S \overset{K'}{\rightleftharpoons} RBBr_2{\cdot}SMe_2 \quad (4)$$

direct attack mechanism is kinetically simple and will lead to second-order kinetics, first-order in the alkene and first-order in the reagent, while the dissociation mechanism predicts complex kinetics. The rate equation for the dissociation mechanism can be derived by using the steady-state hypothesis (eq 5).[11]

$$\frac{d[RBBr_2{\cdot}SMe_2]}{dt} = \frac{k_1k_2[BHBr_2{\cdot}SMe_2][\text{alkene}]}{k_{-1}(K')^{1/2}[RBBr_2{\cdot}SMe_2]^{1/2} + k_2[\text{alkene}]} \quad (5)$$

Our kinetic study of the hydroboration of 1-hexene with $BHBr_2{\cdot}SMe_2$ in CH_2Cl_2 at 25 °C, followed by monitoring the disappearance of the B–H absorption peak of the reagent at 4.0 μm using a quantitative IR spectrometer,[12] revealed a typical downward drifting of the second-order rate constants.[13] Considering that this is indicative of the dissociation mechanism (eq 2–4), wherein the product inhibits the reaction, we studied the effect of (*n*-hexyl)$BBr_2{\cdot}SMe_2$ (1 molar equiv) on the rate of hydroboration of 1-hexene (0.1 M) by $BHBr_2{\cdot}SMe_2$ (0.1 M). We found a significant rate retardation (Figure 1). This retardation can be readily accounted for by the dissociation mechanism. Since $RBBr_2{\cdot}SMe_2$ is a weaker complex than $BHBr_2{\cdot}SMe_2$, it can act as a source of small concentrations of Me_2S, which will compete with the alkene for the intermediate, $BHBr_2$. If this is so, addition of Me_2S should decrease the rate of hydroboration even more severely than (*n*-hexyl)$BBr_2{\cdot}SMe_2$. Indeed, addition of 1 molar equiv of Me_2S represses the rate of hydroboration by $BHBr_2{\cdot}SMe_2$ very severely (Figure 1). If the reaction proceeds by the direct attack mechanism (eq 1), the rate of the reaction will be unaffected by the addition of Me_2S or the product.

It occurred to us that if the dissociation mechanism is

(11) The steady-state condition was imposed on $BHBr_2$ and the rate equation was derived for the first two steps (eq 2 and 3) as

$$\text{rate} = \frac{k_1k_2[BHBr_2{\cdot}SMe_2][\text{alkene}]}{k_{-1}[Me_2S] + k_2[\text{alkene}]}$$

$[Me_2S]$ was then replaced by $(K')^{1/2}[RBBr_2{\cdot}SMe_2]^{1/2}$ assuming that eq 4 represents a rapid equilibrium.

(12) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303–5306.

(13) For the reaction of 1-hexene with $BHBr_2{\cdot}SMe_2$ (0.1 M in each), the second-order rate constants varied from (6.2–3.7) × 10^{-3} M^{-1} s^{-1} for the range 20–80% of the reaction. Changing the initial concentration to 0.2 M in both the reactants did not alter the magnitude or the drift of the rate constants appreciably.

correct, small quantities of an added Lewis acid, say BBr_3, should catalyze the reaction by trapping the free Me_2S. In fact, 5 mol % of BBr_3 catalyzes the hydroboration of 1-hexene with $BHBr_2{\cdot}SMe_2$ remarkably (Table I).

The dissociation mechanism (eq 2–4) clearly explains why $BHBr_2{\cdot}SMe_2$ is able to hydroborate alkenes much faster than $BHCl_2{\cdot}SMe_2$. $RBCl_2{\cdot}SMe_2$ is a weaker complex than $RBBr_2{\cdot}SMe_2$ since $RBCl_2$ is a weaker Lewis acid than $RBBr_2$. As a result, $RBCl_2{\cdot}SMe_2$ dissociates into $RBCl_2$ and Me_2S to a greater extent than does $RBBr_2{\cdot}SMe_2$ and thus has a larger rate-retarding effect on the reaction with the alkene.

We now have a general understanding on the mechanism of hydroboration of alkenes by borane·Lewis base adducts. The evidence presented in this paper on the behavior of $BHBr_2{\cdot}SMe_2$ reinforces superbly our conclusions on 9-BBN·Lewis base adducts. Pasto and co-workers examined the reaction of 2,3-dimethyl-2-butene with $H_2BCl{\cdot}THF$ in THF[14] as well as the reaction of the same alkene with $BH_3{\cdot}THF$.[15] Both reactions displayed second-order kinetics, first-order in 2,3-dimethyl-2-butene and first-order in borane complex. From the observed entropies of activation, they deduced that the reactions must proceed through a direct reaction of the alkene with the borane complex. Our observations on the 9-BBN·Lewis base adducts and $BHBr_2{\cdot}SMe_2$ argue strongly for the dissociation mechanism.

The catalysis of the hydroboration of alkenes by small quantities of BBr_3 is of immediate use in organic synthesis. Even though $BHBr_2{\cdot}SMe_2$ is capable of hydroborating many alkenes at satisfactory rates even in the absence of added Lewis acid, with less reactive alkenes such as cyclohexene, the reaction is very slow and it is practically impossible to complete the reaction.[16] With 10 mol % of BBr_3 as the catalyst, we are able to effect the hydroboration of cyclohexene to completion in 6 h in CH_2Cl_2 at reflux temperature (Table I).

In conclusion, the identification of the correct mechanism of hydroboration by $BHBr_2{\cdot}SMe_2$ has resulted in the discovery of a remarkable catalysis by small quantities of BBr_3.

Acknowledgment. We gratefully acknowledge the financial support (Grant CHE 79-18881) from the National Science Foundation. We thank Professor Kung K. Wang for helpful discussions.

Registry No. (*n*-hexyl)$BBr_2{\cdot}SMe_2$, 64770-04-3; $BHBr_2{\cdot}SMe_2$, 55671-55-1; BBr_3, 10294-33-4; cyclohexene, 110-83-8; 1-hexene, 592-41-6.

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(15) Pasto, D. J.; Lepeska, B.; Cheng, T.-C. *J. Am. Chem. Soc.* **1972**, *94*, 6083–6090.
(16) We circumvented this problem earlier by doing the hydroboration of cyclohexene with $BHBr_2{\cdot}SMe_2$ in the presence of 1 molar equiv of BBr_3. Recently, (cyclohexyl)BBr_2 has been made conveniently by a redistribution of tricyclohexylborane with BBr_3 in the presence of BMS as the catalyst (Brown, H. C.; Basavaiah, D.; Bhat, N. G. *Organometallics*, in press).

Manganese-Centered Coupling of Pentadienyl Ligands. Isolation of a Metal Complex of the Coupled Product

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Summary: Reaction of $MnBr_2$ with potassium 2,4-dimethylpentadienide and $P(CH_3)_3$ results in the formation of (η^8-2,4,7,9-tetramethyl-1,3,7,9-decatetraene)(trimethylphosphine)manganese (**1**). The decatetraene ligand is derived from the manganese-centered coupling of two 2,4-dimethylpentadienyl ligands. The crystal structure of **1**, as determined by a single-crystal X-ray diffraction study, is reported. A mechanism for the pentadienyl coupling reaction is proposed.

Although cyclopentadienylmetal complexes are ubiquitous in organotransition-metal chemistry, the synthesis and reactivity of metal complexes possessing *acyclic* pentadienyl ligands remains largely unexplored.[1,2] Because the acyclic pentadienyl ligand can adopt a variety of bonding modes (η^5,[1,2] η^3,[3] and probably η^1), we anticipate that pentadienylmetal complexes will, in general, possess a rich reaction chemistry. We now report the phosphine-induced, manganese-centered coupling of two acyclic pentadienyl ligands and the isolation of a manganese–phosphine complex of the coupled product. The stereochemistry of the coupled product has led us to postulate a coupling mechanism involving bis(η^3-pentadienyl)manganese intermediates.

The reaction of $MnBr_2$ with potassium 2,4-dimethylpentadienide[4] and $P(CH_3)_3$ in tetrahydrofuran at −78 °C, followed by warming to room temperature with vigorous stirring, produced in high yield a green, paramagnetic, pentane-soluble complex, (η^8-2,4,7,9-tetramethyl-1,3,7,9-decatetraene)(trimethylphosphine)manganese (**1**).[5,6] A single-crystal X-ray diffraction study of **1** was carried out.[7] An ORTEP drawing of the molecular structure is shown in Figure 1, and selected bond lengths and angles are given in Table I. The molecular geometry is square pyramidal with the four C–C double bonds of the decatetraene ligand occupying basal sites and the phosphorus atom of the $P(CH_3)_3$ ligand occupying the axial site.[8] The two butadiene moieties of the decatetraene ligand are planar and are fully eclipsed. The two internal double bonds of the decatetraene ligand have trans configurations (vide infra). The methyl groups bonded to C4 and C7 are displaced substantially out of the plane of their respective butadiene fragments away from the manganese atom (C4′ is 1.217 Å from the plane containing C1, C2, C3, and C4, while C7′ is 1.234 Å from the plane containing C7, C8, C9, C10).[9] In

(1) An important contribution to this area has recently been made by Ernst, who has synthesized a series of "open metallocenes", i.e., metallocene analogues possessing two η^5-acyclic pentadienyl ligands: Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5930. Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. Ibid. **1982**, *104*, 1120. Liu, J.-Z.; Ernst, R. D. Ibid. **1982**, *104*, 3737.
(2) Other reports of pentadienylmetal complexes include the following: (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 1511. (b) Giannini, U.; Pellino, E.; Lachi, M. P. *J. Organomet. Chem.* **1968**, *12*, 551. (c) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189. (d) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708.
(3) We have recently synthesized and carried out a single-crystal X-ray diffraction study on (η^3-2,4-dimethylpentadienyl)tris(trimethylphosphine)cobalt. The η^3-2,4-dimethylpentadienyl ligand in this complex adopts an anti (U-shaped) configuration: Bleeke, J. R.; Peng, W.-J., submitted for publication.
(4) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.
(5) In a typical reaction, 0.152 g (7.08×10^{-4} mol) of $MnBr_2$ was refluxed in tetrahydrofuran for 0.5 h. The solution was cooled to −78 °C, and 1.08 g (1.42×10^{-2} mol) of $P(CH_3)_3$ and 0.220 g (1.07×10^{-3} mol) of potassium 2,4-dimethylpentadienide–tetrahydrofuran ($KC_7H_{11}{\cdot}C_4H_8O$) in tetrahydrofuran were added slowly with stirring, producing an orange solution. This solution was allowed to warm to room temperature and stirred for 12 h. The resulting green solution was filtered through Celite and evaporated to dryness. The green product **1** was extracted with pentane and crystallized from pentane at −30 °C: yield (based on limiting reagent, $KC_7H_{11}{\cdot}C_4H_8O$) 0.15 g (87.2%). All manipulations were carried out under N_2.
(6) MS (chemical ionization, CH_4, 120 eV) M^+. Anal. Calcd for $MnPC_{17}H_{31}$: C, 63.53; H, 9.74. Found: C, 63.01; H, 9.52.

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