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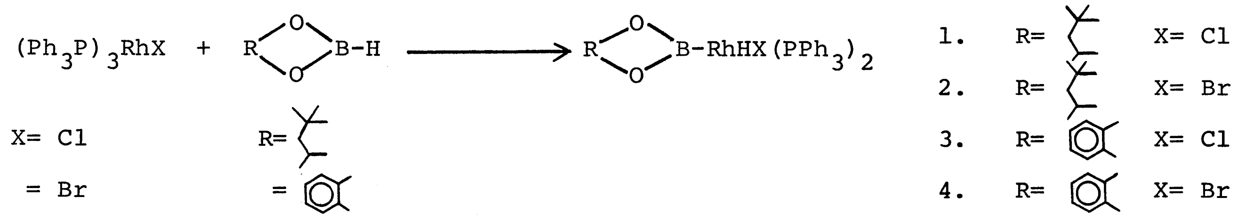
OXIDATIVE ADDITION OF 4,4,6-TRIMETHYL-1,3,2-DIOXABORINANE AND BENZO[1,3,2]DIOXABOROLE TO TRIS(TRIPHENYLPHOSPHINE)HALOGENORHODIUM

Hiromichi KONO*, Kazushi ITO
Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara Kanagawa 229
and Yoichiro NAGAI
Department of Chemistry, Gunma University, Kiryu, Gunma 376

Oxidative addition of 4,4,6-trimethyl-1,3,2-dioxaborinane and benzo[1,3,2]dioxaborole to $(Ph_3P)_3RhX$, where X= Cl or Br, gives σ-metalloborne which reacts with triethylsilane to afford quantitatively $Et_3SiRhHX(PPh_3)_2$.

σ-Metal-boron bond has been reported to be formed by the reaction of boronhalide^{1,2,3} or boron hydride^{3,4} with transition metal complexes including Ti, Mn, Re, Co, Ir, and Pt. Although $(Ph_3P)_3RhCl^5$, $(Ph_3P)_2Rh(CO)Cl^{6,7,8}$, $(C_2H_4)_2Rh(acac)^9$ and $[(C_2H_4)_2RhCl]_2{}^9$ as well as other transition metals^{10} were found to react with $B_9C_2H_{11}{}^{2-}$, $B_{10}H_{13}{}^{-}$, and $n\text{-}B_{18}H_{20}{}^{2-}$ ions and B_6H_{10} to give a variety of rhodium-boron complexes, no formation of σ-rhodium-boron bond has been reported so far. We now report addition of 4,4,6-trimethyl-1,3,2-dioxaborinane and benzo[1,3,2]dioxaborole to $(Ph_3P)_3RhX$ [X= Cl or Br], and the first isolation of σ-rhodium-boron compounds.

Treatment of $(Ph_3P)_3RhCl$ with excess of 4,4,6-trimethyl-1,3,2-dioxaborinane (at room temperature) followed by addition of ether, and filtration afforded colorless powder of (1), mp 115-116°C(decomp.), Anal. Calcd. for $C_{42}H_{43}P_2O_2ClBRh$: C, 63.78; H, 5.48; Cl, 4.48%. Found: C, 63.53; H, 5.52; Cl, 4.19%. The ir spectrum of (1) contained absorptions characteristic of triphenylphosphine and the 4,4,6-trimethyl-1,3,2-dioxaborinane moiety, and additional bands at 2080 cm^{-1} assigned to ν(Rh-H) and at 286 cm^{-1} assigned to ν(Rh-Cl). ^1H nmr spectrum(100 MHz,in $CDCl_3$) indicated a multiplet at τ 2.15-3.30(phenyl protons), a multiplet at τ 5.60-5.99(methine proton), a multiplet at τ 8.18-8.63(methylene protons), and a complex mutliplet involving a singlet at τ 8.75 and a doublet at τ 8.79(J= 3cps)(methyl protons) with an area ratio 32: 1: 2.1: 8.9. High field resonance measurement (from τ 10 to 40) did not indicate any signal which is usually assignable to Rh-H^{5,11}. The hydride resonance of $2\text{-}[IrClH(CO)(PMe_3)_2]B_5H_8$ including σ-Ir-B bond was reported^3 to be observed at τ 3.1. Therefore we assumed that the Rh-H resonance could be masked by that of protons of triphenylphosphine.

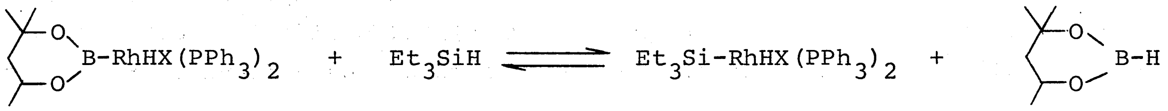


With benzo[1,3,2]dioxaborole in benzene the corresponding rhodium-boron complex (3) was obtained. Bromo derivatives, (2) and (4), were analogously prepared from (Ph$_3$P)$_3$RhBr, and indicated less stability to air and light than (1) and (3), respectively. Physical properties of the rhodium-boron complexes were summarized in Table.

Table. Rhodium-boron Complexes

Complex	M.P.	IR (cm^{-1})	
	°C	ν(Rh-H)	ν(Rh-X)
1	115-116(dec.)	2080	286
2	103-104(dec.)	2080	284
3	131-132(dec.)	2120	298
4	134-135(dec.)	2125	298

Treatment of (1) and (2) with excess of Et$_3$SiH gave quantitatively Et$_3$SiRhHX-(PPh$_3$)$_2$[12] which was reversely converted to (1) and (2) in the presence of excess of the dioxaborinane.



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