Journal of Organometallic Chemistry, 425 (1992) C8–C10
Elsevier Sequoia S.A., Lausanne
JOM 22454PC

Preliminary communication

Synthesis and reactivity of hydrido, halogeno, and σ-organyl ruthenatetraboranes: Crystal structure of $[RuH(B_3H_8)(CO)(PPh_3)_2]$

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(Received October 10, 1991)

Abstract

The reactions of $[RuClR(CO)(PPh_3)_n]$ ($n = 2$, R = σ-vinyl, σ-aryl; $n = 3$, R = H) with $NMe_4[B_3H_8]$ provide the ruthenatetraboranes $[RuR(B_3H_8)(CO)(PPh_3)_2]$. The crystal structure was determined for the compound with R = H. The latter reacts with *N*-halogeno succinimides to give the halogeno derivatives $[RuR(B_3H_8)(CO)(PPh_3)_2]$ (R = Cl, Br, I) and with ${}^tBuNC$ in dichloromethane to give $[RuClH(CN{}^tBu)_2(PPh_3)_2]$. Sodium dialkyldithiocarbamate displaces the B_3H_8 moiety from the halogeno derivatives, with formation of $[Ru(S_2CNMe_2)_2(CO)(PPh_3)]$.

Metalla-octahydrotetraboranes ($L_nMB_3H_8$) bearing halide or σ-organyl ligands are unknown [1], but the former are assumed to be intermediates in the formation of the unusual boraallyl complexes of Group 10 metals [2]. We report below initial investigations of the σ-organometallic and halide chemistry of the $L_nMB_3H_{8/7}$ metallaboranes.

We initially thought that a possible entry into σ-organyl/B_3H_8 chemistry might be opened by the synthesis of a hydrido/B_3H_8 complex followed by hydrometallation of suitable alkynes or alkenes. The reaction of $[RuClH(CO)(PPh_3)_3]$ or $[RuH(CO)(NCMe)_2(PPh_3)_2]ClO_4$ with $NMe_4[B_3H_8]$ in dichloromethane gives a high yield of the colourless complex $[RuH(B_3H_8)(CO)(PPh_3)_2]$ [3*], which we have structurally characterised [4*] (Fig. 1). The retention of the solid-state structure in solution is suggested by ${}^{31}P$, ${}^{11}B$ and ${}^{1}H$ NMR spectroscopy [3*]. This complex has been described previously [5], but as with most metallatetraborane

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

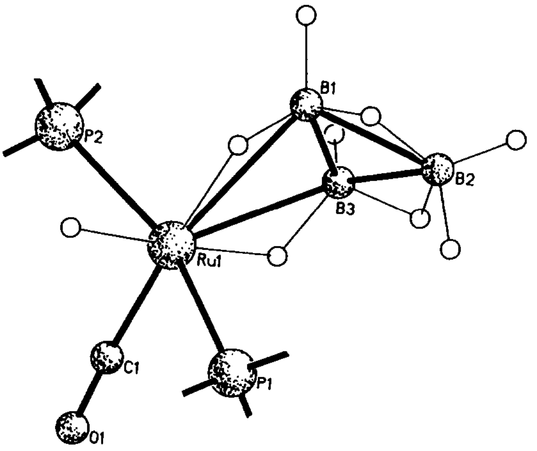
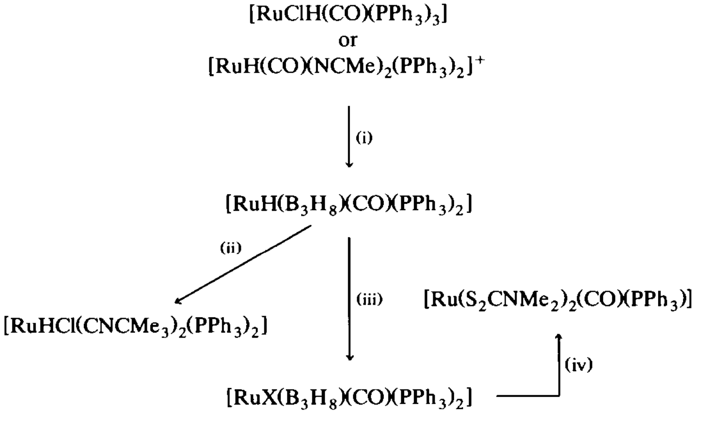


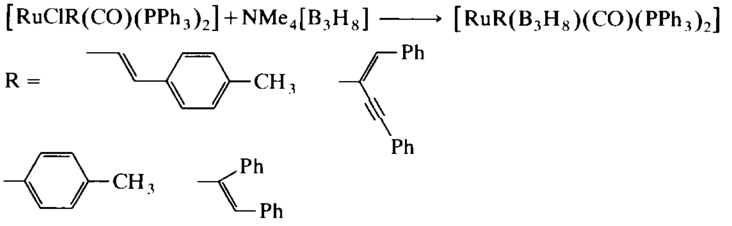
Fig. 1. Molecular geometry of the complex $[RuH(B_3H_8)(CO)(PPh_3)_2]$. Bond lengths (Å): Ru1–B1 2.439(6), Ru1–B3 2.484(6), B1–B3 1.738(9), B1–B2 1.80(1), B2–B3 1.808(9) Å. Angle between the planes defined by Ru1–B1–B3 and B1–B2–B3 = 124.4°. Phenyl groups are omitted for clarity.

chemistry, nothing is known about its reactivity. We find that the B_3H_8 unit is readily cleaved from this complex by an excess of tert-butylisonitrile in dichloromethane, giving $[RuHCl(CN^tBu)_2(PPh_3)_2]$. Treatment of $[RuH(B_3H_8)(CO)(PPh_3)_2]$ with *N*-halogenosuccinimides, however, leads to selective cleavage of the Ru–H bond and formation of the first transition metal-halide derivatives of B_3H_8, *viz.* $[RuX(B_3H_8)(CO)(PPh_3)_2]$ [6], despite the stability of the hydrido complex towards simple acids ($HClO_4$, HPF_6, *etc.*). Electrophilic halogenation of $[Mn(B_3H_8)(CO)_4]$ leads exclusively to *exo*-bromination of the unique BH_2 group [7], but in the present case it is the Ru–H bond which is cleaved. Both the halide and B_3H_8 ligands are cleaved from the halide complexes upon treatment with sodium dimethyldithiocarbamate, to give the complex $[Ru(S_2CNMe_2)_2(CO)(PPh_3)]$.

The complex $[RuH(B_3H_8)(CO)(PPh_3)_2]$ is suprisingly unreactive towards alkynes or alkenes under ambient conditions. The required σ-organyl complexes $[Ru(R)(B_3H_8)(CO)(PPh_3)_2]$ [R = C_6H_4Me-4, CH=CHC_6H_4Me-4, CPh=CHPh,



Scheme 1. (i) $NMe_4[B_3H_8]$; (ii) $CNCMe_3$; (iii) X-$NC_4H_4O_2$, X = Cl, Br, I; (iv) NaS_2CNMe_2.



Scheme 2. Synthesis of organometallic ruthenatetraboranes.

C(C≡CPh)=CHPh] [8*] are, however, accessible *via* the reactions of the coordinatively unsaturated complexes [RuClR(CO)(PPh$_3$)$_2$] with NMe$_4$[B$_3$H$_8$] in dichloromethane solution or methanolic suspension under ultrasonic irradiation. The complexes are remarkably robust, and show no tendancy to undego reductive elimination of arene or olefin, or intramolecular hydroboration under ambient conditions.

Acknowledgements. We are grateful to Johnson Matthey Ltd for a generous loan of ruthenium salts.

References

1 J.D. Kennedy, Prog. Inorg. Chem., 32 (1984) 519.

2 L.J. Guggenberger, A.R. Kane and E.L. Muetterties, J. Am. Chem. Soc., 94 (1972) 5665.

3 Data for [RuH(B$_3$H$_8$)(CO)(PPh$_3$)$_2$]: IR (CH$_2$Cl$_2$) 2513, 2455 (ν(BH)), 1977 (ν(CO)); (Nujol) 2520, 2491, 2464 (ν(BH)) 2162, 2098 (ν(B$_2$H/RuH)), 1978, 1933 (ν(CO)). ^{1}H NMR (CDCl$_3$, −50°C) 2.61, 1.91, −0.51, −1.35 (B*H*), −7.22, −9.41 (B$_2$*H*), −9.14 [t, *J*(PH) 20.7 Hz]. ^{11}B NMR (CDCl$_3$, 25°C) 0.21, −36.6, −38.62. ^{31}P NMR (CDCl$_3$, −25°C) 49.3, 44.0 ppm [AB quartet, J_{AB} 248.8 Hz]. NMR data indicate that the phosphine ligands in complexes [RuR(B$_3$H$_8$)(CO)(PPh$_3$)$_2$] are mutually *trans*.

4 X-ray structure analysis of [RuH(B$_3$H$_8$)(CO)(PPh$_3$)$_2$]: colourless crystals (0.2×0.2×0.2 mm), M_r = 695.19, space group $P2_1/c$ (No. 14), $a = 14.424(5)$, $b = 10.628(4)$, $c = 22.987(9)$ Å, $V = 3491(2)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.32$ g cm^{-3}, μ(Mo-K_α) = 0.56 mm^{-1}, Nicolet P3m, T = ambient, 6794 symmetry independent reflections ($2\theta_{max.} = 50°$), 4592 with $|F| > 4\sigma(F)$ used for the structure determination (Patterson methods) and refinement (424 parameters), non-H atoms anisotropically refined, metallaborane hydrogens isotropically refined, aryl-H atoms in calculated positions, analytical absorption correction; $R = 0.047$ ($R_w = 0.052$, $w^{-1} = \sigma^2(F) + 0.004564F^2$) [9].

5 N.N. Greenwood, J.D. Kennedy, M. Thornton-Pett and J.D. Woollins, J. Chem. Soc., Dalton Trans., (1985) 2397.

6 Data for [RuCl(B$_3$H$_8$)(CO)(PPh$_3$)$_2$]: IR (CH$_2$Cl$_2$) 2538, 2471 (ν(BH)), 2002 (ν(CO)); (Nujol) 2539, 2519, 2476, (ν(BH)) 2167 (ν(B$_2$H), 2007 (ν(CO)). ^{1}H NMR (CDCl$_3$, 25°C) 2.48, 2.16, −0.44, −1.08 (B*H*), −6.03, −17.08 (B$_2$*H*). ^{11}B NMR (CDCl$_3$, 25°C) 2.04 [integ. 1 B], −35.9 [integ. 2 B, (sh)]. ^{31}P NMR (CDCl$_3$, −25°C) 33.6, 31.4 ppm [AB quartet, J_{AB} 301.3 Hz].

7 M.W. Chem, S.J. Calabrese, D.F. Gaines and D.F. Hildebrand, J. Am. Chem. Soc., 102 (1980) 4928.

8 Data for [Ru{C(C≡CPh)=CHPh}(B$_3$H$_8$)(CO)(PPh$_3$)$_2$]: IR (CH$_2$Cl$_2$) 2527, 2462 (ν(BH)), 1977 (ν(CO)); (Nujol) 2532, 2503sh, 2458, (ν(BH)) 2154 (ν(C≡C)), 2118 (ν(B$_2$H)), 1970 (ν(CO)). ^{1}H NMR (CDCl$_3$, 25°C) δ 2.40, 2.0 vbr (B*H*), −0.43, −1.08 (B$_2$*H*), −6.27, −9.26 (Ru*H*B). ^{11}B NMR (CDCl$_3$, 25°C) −1.11 (1 B), −36.15 (2 B). ^{31}P NMR (CDCl$_3$, −25°C) 37.3, 39.1 ppm [AB quartet, J_{AB} 271.6 Hz].

9 Further details of the crystal structure investigation are available from AFH.