Journal of Organometallic Chemistry, 396 (1990) C31–C34
Elsevier Sequoia S.A., Lausanne
JOM 21288PC

Preliminary communication

Bis(benzotriazol-1-yl)borato complexes of ruthenium and rhodium

Jonathan Cartwright, Alan Harman and Anthony F. Hill *

Department of Chemistry, University of Warwick, Coventry CV4 7AL (U.K.)

(Received July 20th, 1990)

Abstract

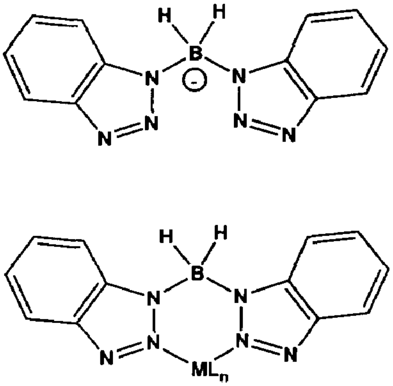
The reactions of $K[H_2B(bta)_2]$ (bta = benzotriazol-1-yl) with the coordinatively unsaturated complexes $[RuRCl(CO)(PPh_3)_2]$ {R = C_6H_4Me-4, C(C≡CPh)=CHPh} proceed with loss of a chloride ligand to give the compounds $[RuR(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ in high yield. Similar treatment of the complexes $[RuHCl(CO)(PPh_3)_3]$ or $[RuH(CO)(NCMe)_2(PPh_3)_2]^+$ leads to the related hydride derivative $[RuH(CO)(PPh_3)_2\{HB_2(bta)_2\}]$. The reaction of $K[H_2B(bta)_2]$ with $[RhCl(CA)(PPh_3)_2]$ (A = O, S) gives $[Rh\{H_2B(bta)_2\}(CA)(PPh_3)_2]$, the carbonyl ligand of $[Rh\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ being labile and readily replaced by xylyl isonitrile to give the complex $[Rh\{H_2B(bta)_2\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$. Intermediates involving monodentate coordination of the dihydrobis(benzotriazolyl) borate ligand are implicated in some of these reactions.

Lalor [1] and Shiu [2] have reported the convenient synthesis of poly(benzotriazolyl)borate salts and described preliminary results regarding their application to coordination chemistry. We report herein the use of the dihydrobis(benzotriazolyl) borato chelate (Scheme 1) as a co-ligand for organo-ruthenium and rhodium chemistry, specifically complexes bearing carbonyl thiocarbonyl, isonitrile, aryl vinyl and hydrido ligands.

The red coordinatively unsaturated σ-*p*-tolyl complex $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ [3] reacts readily with the salt $K[H_2B(bta)_2]$ (bta = benzotriazol-1-yl) in dichloromethane at room temperature to produce the 18-electron colourless complex $[Ru(C_6H_4Me\text{-}4)\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ (**1**) (Scheme 2) [4*]. A similar reaction ensues with the unusual α-phenylethynyl-β-styryl complex [Ru{C(C≡CPh)=CHPh}Cl(CO)$(PPh_3)_2$] [5] producing the yellow complex [Ru{C(C≡CPh)=CHPh}$\{H_2B(bta)_2\}(CO)(PPh_3)_2$] (**2**) [4*]. The syntheses of **1** and **2**

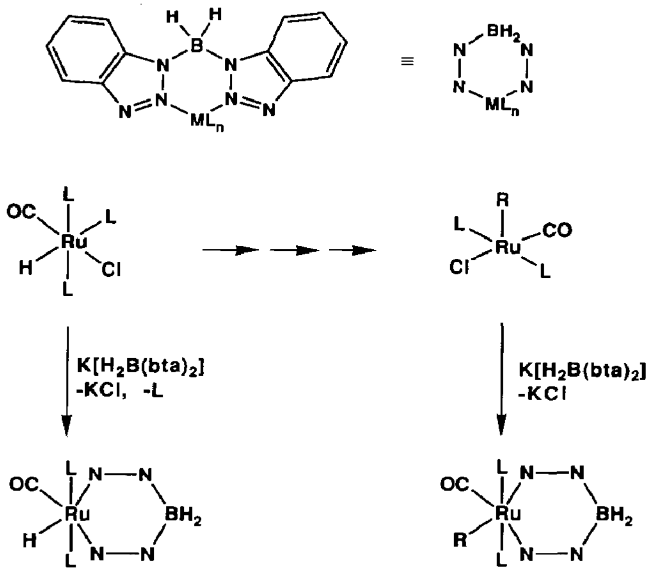
---

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

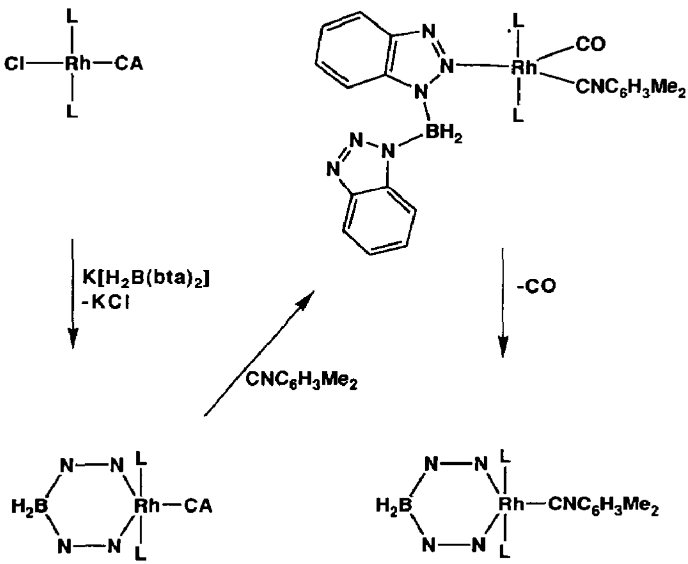


Scheme 1. Free and bidentate-coordinated dihydrobis(benzotriazol-1-yl)borate anions.

proceed in a manner similar to those of the hydrotris(pyrazol-1-yl)borate analogues, with no evidence for intermediate complexes. If a similar reaction is attempted with the complex $[RuClH(CO)(PPh_3)_3]$ [6] [a synthetic equivalent for the 16-electron species "$RuClH(CO)(PPh_3)_2$"], the desired complex $[RuH\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ (3) [4*] is obtained when the reaction is carried out under comparatively high dilution. However, under more concentrated conditions, a sparingly soluble intermediate precipitates from dichloromethane solution. This species redissolves under ultrasonic trituration to provide **3** consistent with it being an intermediate and we tentatively formulate it as an anionic complex of a monodentate coordinated bis(benzotriazolyl)borate ligand, viz $[RuHCl\{\eta^1\text{-}H_2B(bta)_2\}(CO)(PPh_3)_2]K$ (**4**). A complex of benzotriazole $[RuClH(CO)(PPh_3)_2(C_6H_5N_3)]$ [7] has been recently described indicating that the steric requirements of **4** are not excessive.



Scheme 2. Synthesis of ruthenium dihydrobis(benzotriazol-1-yl)borate complexes. R = $C_6H_4Me\text{-}4$, $C(C\equiv CPh)=CHPh$; L = PPh_3



Scheme 3. Synthesis of rhodium dihydrobis(benzotriazol-1-yl)borate complexes. L = PPh_3; A = O, S.

For larger scale preparations of **3** it is more convenient to use the cationic hydrido complex $[RuH(NCMe)_2(CO)(PPh_3)_2]^+$ to avoid the precipitation of **4**.

Dihydrobis(benzotriazolyl)borate complexes of monovalent rhodium are also readily accessible via anion metathesis of suitable precursors: The complexes $[RhCl(CA)(PPh_3)_2]$ (A = O [8], S[9]) react with $K[H_2B(bta)_2]$ to provide the 18-electron bis(phosphine) complexes $[Rh\{H_2B(bta)_2\}(CA)(PPh_3)_2]$ {A = O (**5**) S (**6**) [4*]} (Scheme 3). The analogous iridium complex $[Ir\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ results from the reaction of Vaska's complex $[IrCl(CO)(PPh_3)_2]$ and $K[H_2B(bta)_2]$. The corresponding isonitrile derivative $[Rh\{H_2B(bta)_2\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ (**7**) [4*] may be prepared in high yield conveniently via the substitution of the labile carbonyl ligand of **5** with xylyl isonitrile in dichloromethane solution. Somewhat surprisingly this reaction appears to proceed via an associative pathway: If the reaction is carried out in diethyl ether suspension, a blue intermediate of apparent composition $[Rh\{\eta^1\text{-}H_2B(bta)_2\}(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ may be isolated which instantaneously converts to yellow **6** upon dissolution in dichloromethane. Thus once gain monodentate coordination of the bis(benzotriazolyl)borate ligand must be considered and we suspect that this feature may further prove important in the chemistry of these ligands.

Acknowledgments. We thank Johnson-Matthey Chemicals for a generous loan of ruthenium salts and the University of Warwick Research and Innovations Fund for financial support.

References and notes

1 F.J. Lalor, S. Miller and N. Garvey, J. Organomet. Chem., 356 (1988) C57; F.J. Lalor, S. Miller and N. Garvey, Polyhedron, 9 (1990) 63.
2 K.-B. Shiu, F.-M. Shen, S.-L. Wang and S.-C. Wei, J. Organomet. Chem., 372 (1989) 251.
3 W.R. Roper and L.J. Wright, J. Organomet. Chem., 142 (1977) C1.

4 Selected data for the new complexes: **1**: IR (Nujol/cm^{-1}) 2417 ν(VBH), 1957 ν(CO): ^{1}H NMR(CDCl$_3$) δ 2.31 [s, 3 H, $C_6H_4CH_3$], 3.66 [s(br), 2 H, BH_2], 6.5–7.95 [m, 42 H, C_6H_4, and C_6H_5] ppm. ^{31}P-{^{1}H} NMR (CDCl$_3$), δ 28.5 ppm. FAB-MS (nitrobenzyl alcohol) 994 $[M]^+$, 902 $[M-C_7H_8]^+$, 745 $[M-H_2B(bta)_2]^+$, 716 $[M-H_2B(bta)_2-CO]^+$, 625 $[Ru(PPh_3)_2]^+$, 455 $[Ru(PPh_3)(C_7H_7)]^+$, 363 $[RuPPh_3]^+$, 263 $[HPPh_3]^+$], **2**: IR (Nujol/cm^{-1}) 2448 ν(BH) 2168w ν(C≡C), 1976 ν(CO). ^{1}H NMR (CDCl$_3$) 3.63 [s(br), 2 H, BH_2], 6.7–7.6 [m×7, 49 H, C_6H_4, and C_6H_5]. ^{31}P-{^{1}H} NMR (CDCl$_3$), δ 28.1 ppm. FAB-MS (nitrobenzyl alcohol) 1106 $[M]^+$, 919, 857 $[M-H_2B(bta)_2]^+$, 716, 627, 363 $[RuPPh_3]^+$, 263 $[HPPh_3]^+$. **3**: IR (Nujol/cm^{-1}) 2423 ν(BH), 2019 ν(RuH) 1938 ν(CO). ^{1}H NMR (CDCl$_3$) δ −11.5 (t, 1 H, RuH, J(HP) 20.8 Hz], 3.62 [s(br), 2 H, BH_2], 6.95–7.84 [m, 38 H, C_6H_4, and C_6H_5] ppm. ^{31}P-{^{1}H} NMR (CDCl$_3$), δ 45.0 ppm. FAB-MS (nitrobenzyl alcohol) 903 $[M]^+$, 655 $[M-H_2B(bta)_2]^+$, 627 $[M-H_2B(bta)_2-CO]^+$, 363 $[RuPPh_3]^+$, 263 $[HPPh_3]^+$. **5**: IR (Nujol/cm^{-1}) 2403 ν(BH) 1995 ν(CO). ^{1}H NMR (CDCl$_3$) δ 4.16 [s(br), 2 H, BH_2], 6.9–7.7 [m×7, 38H, C_6H_4, and C_6H_5] ppm (the molecule undergoes a dynamic process involving the phosphine ligands at 300 K). ^{31}P-{^{1}H} NMR (CDCl$_3$) δ 30.1 ppm. FAB-MS (nitrobenzyl alcohol) 905 $[M]^+$, 655 $[M-H_2B(bta)_2]^+$, 627 $[Rh(PPh_3)_2]^+$, 393 $[Rh(PPh_3)(CO)]^+$. **6**: IR (Nujol/cm^{-1}) 2413 ν(BH) 1327 ν(CS). ^{1}H NMR (CDCl$_3$) δ 4.18 [s(br), 2 H, BH_2], 6.9–7.85 [m×7, 38 H, C_6H_4, and C_6H_5] ppm. ^{31}P-{^{1}H} NMR (CDCl$_3$) δ 31.3 ppm. FAB-MS (nitrobenzyl alcohol) 920 $[M]^+$, 670 $[M-H_2B(bta)_2]^+$, 409 $[Rh(PPh_3)(CS)]^+$. **7**: IR (Nujol/cm^{-1}) 2412 ν(BH) 2115 ν(CN). ^{1}H NMR (CDCl$_3$) δ 1.59 [s, 6H, CH_3], 6.6–7.90 [m×9, 41 H, C_6H_3, C_6H_4, and C_6H_5] ppm. ^{31}P -{^{1}H} NMR (CDCl$_3$) δ 30.3 ppm. FAB-MS (nitrobenzyl alcohol) 1008 $[M]^+$, 889 $[M-C_6H_5N_3]$, 758 $[M-H_2B(bta)_2]^+$, 627 $[Rh(PPh_3)_2]^+$, 496 $[Rh(PPh_3)(CNC_6H_3Me_2)]^+$.

5 A.F. Hill and R.P. Melling, J. Organomet. Chem., 396 (1990) C22.

6 K.R. Laing and W.R. Roper, J. Chem. Soc. (A), (1970), 2149.

7 B.G. Olby, S.D. Robinson, M.B. Hursthouse and R.L. Short, J. Chem. Soc., Dalton Trans., (1990) 621.

8 D. Evans, J.A. Osborn and G. Wilkinson, Inorg. Chem., 11 (1968) 99.

9 M.C. Baird and G. Wilkinson, Chem. Commun., (1966) 267.