Nitrogen *versus* Metal Protonation in Pyrazolylborate Complexes of Rhodium(I) and Iridium(I). Unexpected Reactions of a Cationic Iridium(III) Hydride

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Protonation of $[M(HBPz^*_3)(CO)_2]$ (Pz* = 3,5-dimethylpyrazol-1-yl) occurs at the nitrogen for M = Rh forming $[Rh\{\eta^2\text{-}HBPz^*_2(Pz^*H)\}(CO)_2][BF_4]$, of which the *X*-ray crystal structure has been determined; for M = Ir a cationic Ir^{III} hydride is formed which is attacked by strong nucleophiles at a carbonyl carbon.

Pyrazolylborate complexes of rhodium and iridium have been little studied.[1] To support our work in carbon–hydrogen activation by some of these complexes,[2] we have been investigating other reactions and the general co-ordination chemistry of $[Rh(HBPz^*_3)(CO)_2]$[3] (**1**) and $[Ir(HBPz^*_3)(CO)_2]$ (**2**) (Pz* = 3,5-dimethylpyrazol-1-yl). The results on protonation we describe here emphasise the differences between (**1**) and (**2**) and the η-C_5H_5 or η-C_5Me_5 derivatives with which they have traditionally been compared.†

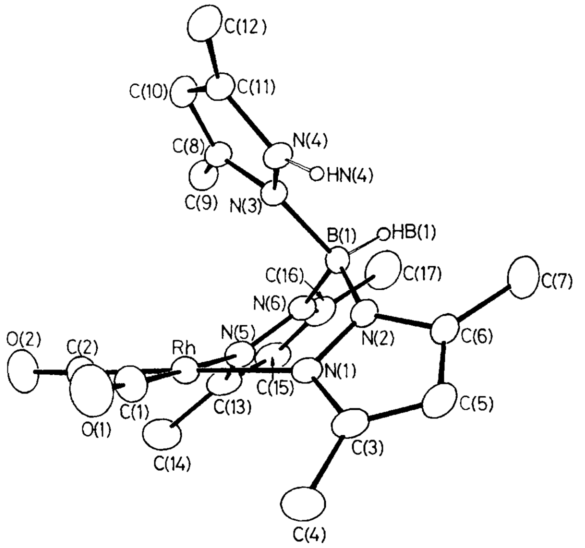

Figure 1. Structure of the cation of (**3**). Selected interatomic distances are: Rh–C(1) 1.848(5), Rh–C(2) 1.867(6), Rh–N(1) 2.070(4), Rh–N(5) 2.093(4) Å. Selected angles are: C(1)–Rh–C(2) 86.0(3), C(1)–Rh–N(1) 92.7(2), N(1)–Rh–N(5) 86.5(1), C(2)–Rh–N(5) 94.8(2)°. The dihedral angles between the plane N(1)–N(5)–N(6)–N(2) and the planes N(1)–Rh–N(5) and N(2)–N(6)–B(1) are 145.3 and 134.7° respectively.

Addition of one equivalent of $HBF_4{\cdot}OEt_2$ to a stirred solution of (**1**) in CH_2Cl_2 [ν_{CO} of (**1**) in this solvent: 2058, 1982 cm^{-1}]‡ afforded, after recrystallisation from CH_2Cl_2–hexane, a 96% yield of the pale yellow crystalline salt $[Rh\{\eta^2\text{-}HBPz^*_2(Pz^*H)\}(CO)_2][BF_4]$ (**3**).† The shift of ν_{CO} by only *ca.* 30 cm^{-1} to higher frequency was not consistent with protonation at rhodium. A ^1H n.m.r. signal at δ 11.56 and the lack of any resonance at high field indicated that a pyrazole nitrogen had been protonated. The *X*-ray structure of (**3**) (Figure 1) was consistent with this, showing square planar co-ordination of rhodium(I) in the cation.§ Triethylamine quantitatively converted (**3**) to (**1**).

Protonation of (**2**) in the same fashion afforded $[Ir(\eta^3\text{-}HBPz^*_3)(H)(CO)_2][BF_4]$ (**4**) as colourless crystals. Spectroscopic data,† the high field ^1H n.m.r. signal in particular, leave no doubt that (**4**) is an iridium(III) hydride with octahedral co-ordination. The differing behaviour of (**1**) and (**2**) can be attributed to the greater basicity of iridium as compared with rhodium, which would accord with a well-recognized trend among the middle and late transition metals.

Further chemical reactions of (**4**) (Scheme 1) are noteworthy. While (**4**) does not react with Et_3N, the strong, non-nucleophilic base DBU (1,8-diazabicyclo[5.4.0.]undec-7-ene) removes the proton to regenerate (**2**). Surprisingly, strong nucleophiles such as NaOMe or Bu^nLi attack a carbonyl carbon forming methoxycarboxyl or acyl hydrides (**5**) or (**6**),† providing synthetic access to novel complexes which are quite robust.

Protonation of $[Rh(\eta\text{-}C_5Me_5)(CO)_2]$ by $HBF_4{\cdot}OEt_2$ leads, presumably by CO labilization following metal protonation, to binuclear species.[4] Similar protonation of $[Ir(\eta\text{-}C_5Me_5)(CO)_2]$ affords the hydride $[Ir(\eta\text{-}C_5Me_5)(H)$-

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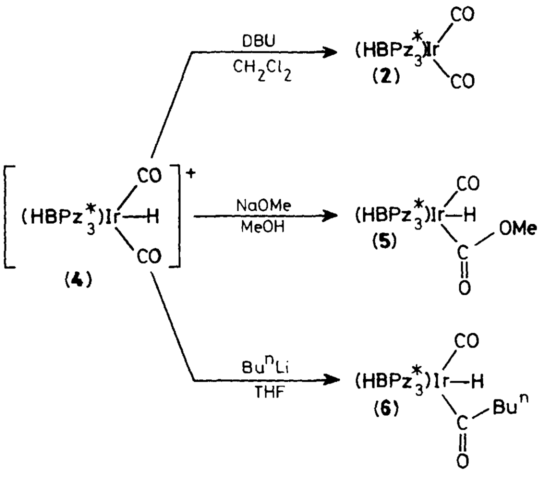
† Satisfactory elemental analyses were obtained for all new compounds. *Selected spectroscopic data*: (**2**), i.r. (ν_{CO}, n-hexane) 2039, 1960 cm^{-1}. ^1H N.m.r. δ (CD_2Cl_2, ambient) 5.50 (s, 3H), 2.29 (s, 9H), 2.12 (s, 9H). (**3**) i.r. (ν_{CO}, CH_2Cl_2) 2091, 2026 cm^{-1}; ^1H n.m.r. δ(CD_2Cl_2) 11.56 (s, 1H), 6.19 (s, 1H), 6.04 (s, 2H), 2.44 (s, 3H) 2.40 (s, 12H), 1.69 (s, 3H). (**4**) i.r. (CH_2Cl_2) ν_{IrH} 2181 (w, br), ν_{CO} 2144(s), 2101(s) cm^{-1} with prominent shoulders at 2153, 2113 cm^{-1} which are not present in MeCN solvent and are attributed to contact ion pairing; ^1H n.m.r. δ(CD_2Cl_2) 6.14 (s, 1H), 6.05 (s, 2H), 2.48 (s, 3H), 2.41 (s, 9H), 2.34 (s, 6H), −13.18 (s, 1H). (**5**) i.r. (hexane) 2173 (w, br, ν_{IrH}), 2043 (s, $\nu_{C\equiv O}$), 1671 (m, $\nu_{C=O}$) cm^{-1}; ^1H n.m.r. δ (CD_2Cl_2) 5.92 (s, 1H), 5.86 (s, 1H), 5.83 (s, 1H), 3.55 (s, 3H), 2.42 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.24 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H), −15.88 (s, 1H). (**6**) i.r. (hexane) 2154 (w, br, ν_{IrH}), 2021 (s, $\nu_{C\equiv O}$), 1648 (m, $\nu_{C=O}$) cm^{-1}; ^1H n.m.r. δ (CD_2Cl_2) 5.89 (s, 1H), 5.85 (s, 1H), 5.76 (s, 1H), 2.40 (s, 6H), 2.38 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H), 2.12 (s, 3H), 1.95—2.10 (m, 4H), 1.20—1.35 (m, 5H), −16.50 (s, 1H).

‡ In CH_2Cl_2 the i.r. spectrum of (**1**) exhibits in addition very weak bands (shoulders) at 2080 and 2012 cm^{-1}. We attribute these to a small amount of $[Rh(\eta^2\text{-}HBPz^*_3)(CO)_2]$ in equilibrium with the major five-co-ordinate form. The fact that only the five-co-ordinate form of (**2**) can be observed in its solutions does not account for its differing reactivity upon protonation; the analogue of (**2**) using unsubstituted pyrazole, $[Ir(HBPz_3)(CO)_2]$, exhibits in solution nearly equal amounts of four- and five-co-ordinate forms, yet behaves as does (**2**) upon protonation.

§ *Crystal data for compound* (**3**): $C_{17}H_{23}B_2F_4N_6O_2Rh$, $M = 543.93$, monoclinic, space group $P2_1/n$, $a = 10.028(4)$, $b = 9.768(1)$, $c = 3.482(6)$ Å, $\beta = 90.36(3)°$, $U = 2300$ Å^3, $Z = 4$, $D_c = 1.571$ g cm^{-3}, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.71073$ Å, μ(Mo-K_α) = 7.86 cm^{-1}. Data were collected at 296 K using an ω–2θ scan to a 2θ limit of 55°. The structure was solved by direct and Fourier methods and refined by least squares to give agreement factors *R* 7.6% (R_w 10.6%) for 3449 unique observations having $I > 3\sigma(I)$. All hydrogen atoms were placed in calculated positions in the final refined model. Extensive disordering of the fluoride atoms of the anion was not successfully modelled. The resulting poor agreement to the low angle data is thought to be responsible for residual peaks above and below the rhodium atom in the final difference Fourier. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

$(CO)_2][BF_4]$ (**7**) which is rapidly and completely deprotonated by NaOMe/MeOH.[4] We find that (**7**) is also deprotonated by Et_3N in acetonitrile solution, while (**4**) is not. Thus, as far as the conjugate bases are concerned, $[Ir(\eta\text{-}C_5Me_5)(CO)_2]$ is weaker than (**2**). Methoxide and n-butyl-lithium are clearly capable of deprotonating (**4**). The fact that carbonyl attack takes priority implies a low kinetic acidity[5] for (**4**); that in turn might result from the secluded position of the proton among the 3-methyl groups of the bulky $HBPz_3^*$ ligand.

The kinetic acidities of (**4**) and (**7**) and the synthetic opportunities provided by (**4**) are being investigated.

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