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FULL PAPER

Synthesis and characterisation of bis- and tris-(pyrazol-1-yl)borate acetyl complexes of Fe^{II} and Ru^{II} and isolation of an intermediate of B–N bond hydrolysis

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Complexes *cis*,*trans*-[MI(Me)$(CO)_2(PMe_3)_2$] (M = Fe **1a** or Ru **1b**), in CH_2Cl_2, reacted with K[$(pz)_2BH_2$] and Na[$(pz)_3BH$] affording the acetyl complexes *trans*-[M(COMe){$(pz)_2BH_2$}$(CO)(PMe_3)_2$] **2a** and **2b** and *trans*-[M(COMe){κ^2-$(pz)_3BH$}$(CO)(PMe_3)_2$] **3a** and **3b**, respectively. If the reactions are carried out in polar solvents decomposition of both starting materials occurs. Upon standing in *n*-hexane solution, the free pyrazol-1-yl arm in complex **3a** displaces a co-ordinated PMe_3 forming [Fe(COMe){κ^3-$(pz)_3BH$}$(CO)(PMe_3)$] **4a**. The analogous ruthenium complex was formed directly from the tricarbonyl complex *fac*-[RuI(Me)$(CO)_3(PMe_3)$] **5** with Na[$(pz)_3BH$]. One of the intermediates of the decomposition of a pyrazolyl donor, *trans*-[Fe(COMe){κ^2-(mpz)-$OB(C_8H_{14})$}$(CO)(PMe_3)_2$] **6** (mpz = 3-methylpyrazolyl), was isolated from the reaction of **1a** with K[$(mpz)_2$-$B(C_8H_{14})$]. This complex was fully characterised both in solution (IR, multinuclear and multidimensional NMR spectroscopy) and in the solid state (X-ray single-crystal diffraction).

There has been an increasing number of reports describing organometallic complexes containing bis- and tris-(pyrazol-1-yl)borate ligands in recent years.[1] However, few are carbonyl complexes containing these ligands, particularly of ruthenium[2] and iron.[3] Furthermore, it has been pointed out that decomposition of these nitrogen donors can occur because of an electrophilic attack on the B–H groups or cleavage of the B–N bonds.[4]

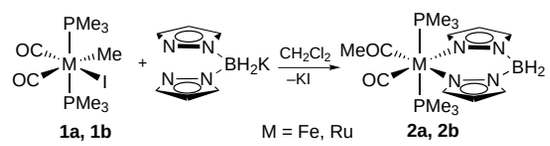
Previous studies have shown that the M–I bonds in complexes *cis*,*trans*-[MI(Me)$(CO)_2(PMe_3)_2$] (M = Fe[5] **1a** or Ru[6] **1b**) are easily ionised[7,8] and, consequently, migration of the methyl group onto the CO ligands in *cis* positions could generate two 'free' co-ordination positions. Furthermore, the reactions of **1a** and **1b** with bis- and tris-(pyrazol-1-yl)methane give the corresponding cationic acetyl complexes *trans*-[M(COMe)(CO)-$(PMe_3)_2L]^+$ [L = $(pz)_2CH_2$ or $(pz)_3CH$] the interionic structures of which were investigated by NOESY and heteronuclear Overhauser spectroscopy (HOESY) spectroscopy.[9,10] Therefore, it was thought worthwhile investigating the reactivity of **1a** and **1b** with isosteric bis- and tris-pyrazolylborate anions.

This paper reports (a) the synthesis of acetyl complexes *trans*-[M(COMe){$(pz)_2BH_2$}$(CO)(PMe_3)_2$] **2a** and **2b**, *trans*-[M(COMe){κ^2-$(pz)_3BH$}$(CO)(PMe_3)_2$] **3a** and **3b** and [M-(COMe){κ^3-$(pz)_3BH$}$(CO)(PMe_3)$] **4a** and **4b** and (b) the full characterisation of an intermediate of the hydrolytic process occurring during the reaction of **1a** with bis(3-methylpyrazol-1-yl)borate, *trans*-[Fe(COMe){κ^2-(mpz)$OB(C_8H_{14})$}$(CO)(PMe_3)_2$] **6**.

Results and Discussion

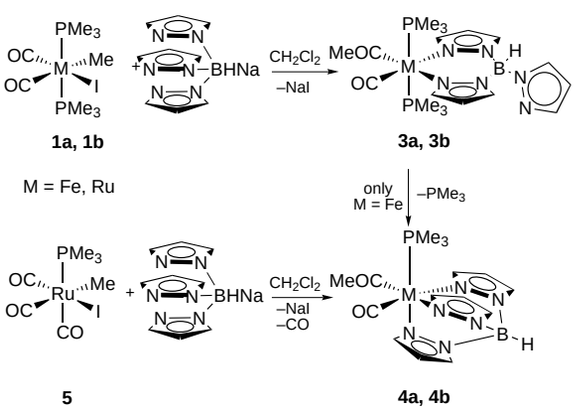
Synthesis

The reactions of complexes **1a** and **1b** with bis- and tris-(pyrazol-1-yl)borates K[$(pz)_2BH_2$] and Na[$(pz)_3BH$], respectively, in CH_2Cl_2 afford acetyl complexes *trans*-[M(COMe)-{$(pz)_2BH_2$}$(CO)(PMe_3)_2$] **2a** and **2b** and *trans*-[M(COMe)-{κ^2-$(pz)_3BH$}$(CO)(PMe_3)_2$] **3a** and **3b** as shown in Schemes 1 and 2. As K[$(pz)_2BH_2$] and Na[$(pz)_3BH$] are apparently insoluble in CH_2Cl_2, the reactions are likely to take place at the interface between the solid ligands and the solution of complexes **1a** and **1b** and go to completion in under 2 h. Upon refluxing complex **3a** in *n*-hexane for 1 h also the third pyrazolyl group co-ordinates to the metal replacing one of the phosphine ligands and producing complex **4a** (see Scheme 2). Complex **3b** does not undergo an analogous reaction. This difference is probably of kinetic origin as the rates of substitution reactions at ruthenium(II) complexes are generally slower by several



1a, 1b **2a, 2b**

Scheme 1



1a, 1b **3a, 3b**

5 **4a, 4b**

Scheme 2

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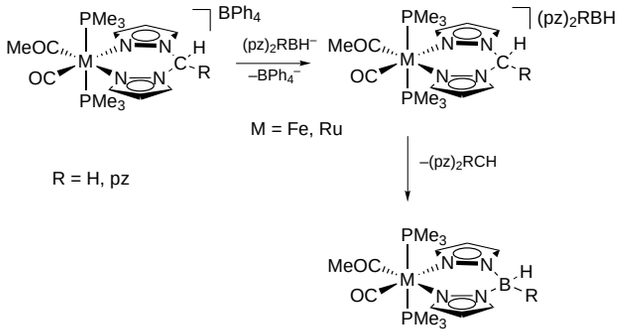
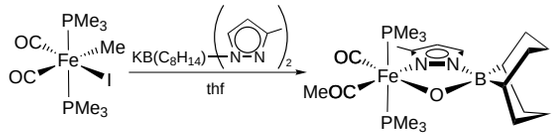


Scheme 3



1a **6**

Scheme 4

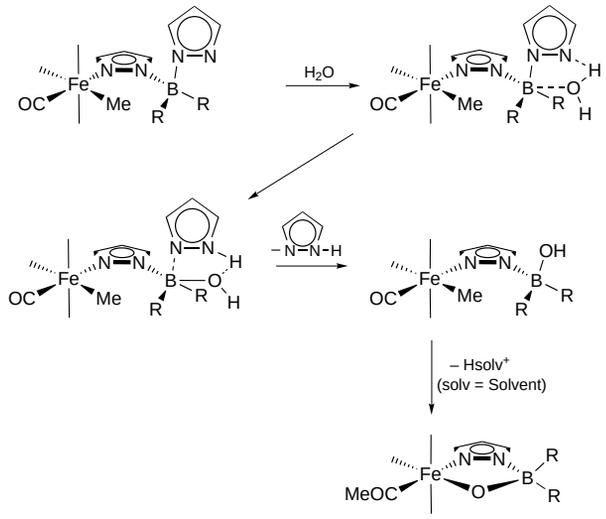
orders of magnitude than those of the corresponding iron(II) low-spin species.[11] Complex **4b** can be synthesized by treating the tricarbonyl complex *fac*-[RuI(Me)(CO)$_3$(PMe$_3$)] **5**[6] with Na[(pz)$_3$BH] owing to the ionisation of the Ru–I bond, migration of the methyl group onto a CO in *cis* position and dissociation of a Ru–CO bond (see Scheme 2).

Complexes **2**–**4** can also be obtained by replacing the co-ordinated isosteric poly(pyrazol-1-yl)methanes with the borates as shown in Scheme 3. The initial reaction consists of the formation of the pyrazolylborate salts of the positively charged pyrazolylmethane complexes. Successively, the former ligands replace the latter, the driving force for the reaction presumably being charge compensation between the positively charged fragment 'M(COMe)(CO)(PMe$_3$)$_2^{+}$' and the negatively charged ligand [(pz)$_{4-x}$BH$_x$]$^-$ (x = 1 or 2).

Slow decomposition of the reagents occurs when the complexes **1a** and **1b** and K[(pz)$_2$BH$_2$] and Na[(pz)$_3$BH] are treated in solvents which dissolve the borates, *e.g.* thf, EtOH and MeCN. Decomposition occurs also when (a) solvent mixtures such as thf–*n*-hexane (1 : 1) are used, where neither NaI nor KI is soluble, (b) the corresponding thallium salts of the ligands are employed, (c) the complexes *cis*,*trans*-[MMe(CO)$_2$(MeCN)-(PMe$_3$)$_2$][BPh$_4$] **7a** and **7b** are used as starting materials and (d) when sodium dihydro-3,5-bis(trifluoromethyl)borate is used.

Also the reaction of complex **1a** with the potassium salt of the 5-substituted pyrazolyl ligand (mpz)$_2$B(C$_8$H$_{14}$), where the carbocyclic group is known to protect the B–N function against electrophilic attack, does not give the expected product. However, in this case, the complex *trans*-[Fe(COMe){κ^2-(mpz)OB-(C$_8$H$_{14}$)}(CO)(PMe$_3$)$_2$] **6** (see Scheme 4) can be isolated in low yield. Complex **6** is particularly interesting because it can be considered as an intermediate of hydrolysis of the B–N bonds. This process appears to occur more rapidly when at least one arm of the ligand is not co-ordinated which makes possible the interaction of water with the B and N atoms of an unco-ordinated ring. A likely reaction pathway for this type of hydrolytic B–N bond cleavage is shown in Scheme 5. The first pyrazolyl ring substitutes I$^-$ while the second one should take the place of the methyl group that migrates onto a *cis* CO. This process is slow enough to allow hydrolytic cleavage of the unco-ordinated B–N bond as the partially hydrolysed borate is rapidly stabilised by Fe–O bond formation.

Once complexes **2a** and **2b** and **3a** and **3b** are formed they are stable and the borate ligands do not undergo hydrolytic attack as tested by dissolving them in non-purified solvents (even polar) and even adding small quantities of water. This confirms that the hydrolytic process not only requires a protic solvent but



Scheme 5

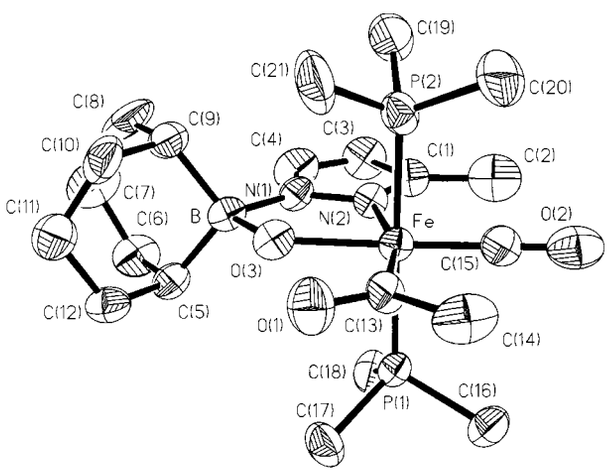


Fig. 1 An ORTEP view of complex **6**

also that one nitrogen should be unco-ordinated. The cleavage of boron–nitrogen bonds in co-ordinated (pyrazolyl)borates was previously reported,[4] but this is the first time that an intermediate formed during partial hydrolysis of the borate ligands has been intercepted and characterised by single-crystal X-ray diffraction.

Structural characterisation of complexes

(a) Solid state. X-Ray crystallographic studies of complex **6** were carried out. The crystals contain individual molecules separated by normal van der Waals contacts. An ORTEP[12] view is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The geometry at iron in complex **6** is approximately octahedral. The five-membered ring Fe–N(2)–N(1)–B–O(3) induces constraints in the N(2)–Fe–O(3) angle which becomes substantially smaller than 90° (77.9°) and, consequently, affects all the other equatorial angles. The nitrogen co-ordinated to iron is *trans* to the acetyl group and O(3) is *trans* to CO. It is difficult to compare the length of the Fe–O(3) [1.995(4) Å] bond as there are few related structures. However, it is close to those found in some iron complexes containing the fragment B–O–Fe.[13] The angle Fe–O(3)–B (125.9°) is wider than that expected for the standard sp^3 hybridisation and this, again, is due to the formation of the above-mentioned five-membered ring. Other bond distances and angles fall in the expected ranges for compounds of this type.

(b) Solutions. The complexes were characterised by IR and ^{1}H, ^{13}C, ^{31}P and ^{11}B NMR spectroscopy. The IR spectra of **2**

Table 1 Selected bond lengths (Å) and angles (°) for complex **6**

Fe–P(1)	2.272(2)	B–C(9)	1.609(8)
Fe–P(2)	2.256(3)	N(1)–N(2)	1.363(6)
Fe–O(3)	1.995(4)	N(2)–C(1)	1.335(7)
Fe–C(15)	1.702(6)	N(1)–C(4)	1.335(7)
Fe–N(2)	2.044(4)	O(1)–C(13)	1.571(8)
Fe–C(13)	1.966(5)	O(2)–C(15)	1.183(8)
B–N(1)	1.595(7)	C(1)–C(3)	1.376(8)
B–C(5)	1.628(9)	C(1)–C(2)	1.509(9)
B–O(3)	1.498(7)	C(3)–C(4)	1.362(9)
P(1)–Fe–P(2)	177.9(1)	N(2)–Fe–O(3)	77.9(2)
P(2)–Fe–N(2)	91.3(1)	P(2)–Fe–C(13)	88.9(2)
P(2)–Fe–O(3)	89.5(1)	O(3)–Fe–C(13)	84.4(2)
P(1)–Fe–C(13)	89.5(2)	P(2)–Fe–C(15)	89.1(2)
P(1)–Fe–C(15)	89.7(2)	O(3)–Fe–C(15)	178.5(2)
N(2)–Fe–C(15)	102.6(2)	Fe–P(1)–C(16)	115.9(2)
C(13)–Fe–C(15)	95.1(3)	Fe–P(2)–C(19)	115.4(2)
Fe–N(2)–N(1)	116.8(3)	N(1)–B–O(3)	99.3(4)
Fe–C(13)–C(14)	120.6(4)	B–N(1)–N(2)	120.2(4)
Fe–C(15)–O(2)	178.6(5)	Fe–N(2)–C(1)	135.9(4)
P(1)–Fe–N(2)	90.5(1)	Fe–O(3)–B	125.9(3)
P(1)–Fe–O(3)	91.6(1)	Fe–C(13)–O(1)	122.4(5)

and **3** show two bands in the carbonyl stretching region: that due to the COMe ligands which is metal-insensitive and falls close to 1600 cm^{-1} and the other, ν(CO), are at 1934 and 1914 cm^{-1} for the ruthenium and iron complexes, respectively, and show the typical difference of 20 cm^{-1}.[14] These values, although low, are reasonable for complexes of Fe^{II} and Ru^{II} having high electron density on the metal due to the presence of four good donor ligands (two phosphines and two nitrogens) causing considerable π-back donation to the CO, strengthening the M–C and, consequently, weakening the C–O bond. Interestingly, the CO stretches of complexes **4a** and **4b** fall at higher wavenumbers than those of **3a** and **3b** (Δ = 37 and 7 cm^{-1} for Fe and Ru, respectively) indicating that the pyrazolyl ring is a better π acceptor than PMe_3. Furthermore, the substantial enhancement in the case of Fe suggests that a structural modification, in the angles involving the Fe–CO moiety may have occurred. The CO stretches in complex **6** [ν(CO) 1907 and ν(COMe) 1578 cm^{-1}] fall at lower wavenumbers relative to those of **2** and **3** indicating that the oxygen atom is a better electron donor compared with nitrogen. This is particularly evident in the wavenumber of the COMe group *trans* to the oxygen in complex **6**.

The ^{31}P-{^1H} NMR spectra of complexes containing the bis(pyrazol-1-yl)borate and the κ^3-bonded tris(pyrazol-1-yl)borate ligands appear as singlets. Those of complexes with a κ^2-tris(pyrazol-1-yl)borate ligand show the typical pattern of an AB system due to the non-equivalence of the two phosphorus caused by the position of the free pyrazolyl group. The values of the $^2J_{PP}$ coupling constants are large, as expected for complexes with high electron density on the metal, and increase from iron (162 Hz) to ruthenium (292 Hz).[15]

The ^1H and ^{13}C-{^1H} NMR spectra of the complexes do not show particular features. All the pyrazolyl hydrogen and carbon atoms are magnetically inequivalent. The phase-sensitive ^1H NOESY spectrum of **6** does not show any contact between the Me group in 5 position and COMe, indicating that the stereochemistry in solution is the same as that in the solid state, *i.e.* with the oxygen atom *trans* to COMe.

Conclusion

Acetyl complexes of Fe^{II} and Ru^{II} containing κ^2-bonded bis- and either κ^2- or κ^3-tris-(pyrazol-1-yl)borate ligands were synthesized either by migratory insertion of a methyl group onto a *cis* CO and ionisation of the M–I bond or by ligand exchange with bis- and tris-(pyrazol-1-yl)methane in the isosteric, positively charged complexes. In polar solvents decomposition of the reagents occurred before the reaction. One of the intermediates of the decomposition process was intercepted and characterised by X-ray single-crystal studies. This represents the first fully characterised example of a pyrazolylborate compound formed by a hydrolytic process.

Table 2 Experimental data for X-ray diffraction study of complex **6**

Formula	$C_{21}H_{40}BFeN_2O_3P_2$
M	497.1
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
a/Å	14.410(12)
b/Å	10.228(7)
c/Å	18.202(14)
β/°	98.35(7)
Z	4
U/Å^3	2654(4)
D_c/g cm^{-3}	1.244
λ(Mo-Kα)/Å	0.710 73
μ/mm^{-1}	0.711
Reflections collected	2657
Independent reflections	2467
Observed reflections [$I > 2\sigma(I)$]	2375
R	0.0671
R'	0.0976

Experimental

Materials

Infrared spectra were taken on a 1725 X FTIR Perkin-Elmer spectrophotometer, one- and two-dimensional ^1H, ^{13}C, ^{31}P and ^{11}B NMR spectra on Bruker AC 200, DRX 500 and Varian UNITY 400WB spectrometers. Referencing was relative to $SiMe_4$ for ^1H and ^{13}C, external $NaBPh_4$ for ^{11}B and external 85% H_3PO_4 for ^{31}P. Two-dimensional NOESY spectra, with a mixing time of 500 ms, were measured as previously described.[16] Reactions were carried out in dried apparatus under a dry inert atmosphere of nitrogen using standard Schlenk techniques. Complexes **1a**,[5] **1b**,[6] *fac*-[RuI(Me)(CO)$_3$(PMe$_3$)] **5**,[6] *cis*,*trans*-[FeMe(CO)$_2$(MeCN)(PMe$_3$)$_2$][BPh$_4$] **7**[7] and *trans*-[Ru(COMe){κ^2-(pz)$_3$CH}(CO)(PMe$_3$)$_2$] **8**[10] were prepared according to the literature. Solvents were dried prior to use by conventional methods.[17] The salts K[(mpz)$_2$B(C$_8$H$_{14}$)][18] and sodium dihydrobis(3,5-trifluoromethylpyrazolyl)borate[19] were prepared according to the literature; K[(pz)$_2$BH$_2$] and Na[(pz)$_3$BH] (Fluka) were utilised without further purification.

X-Ray crystallography

Crystals of complex **6** suitable for the X-ray single-crystal analysis were obtained from *n*-hexane. Diffraction intensities were collected at 20 °C by the ω-scan method on a graphite-monochromatised Syntex P21 diffractometer and reduced to F_o^2 values. The structure was solved by Patterson methods and refined by full-matrix least-squares calculations. For all computations the SHELXTL package of crystallographic programs was used.[20] Thermal vibrations were treated anisotropically for all non-H atoms. All H atoms were positioned geometrically (C–H 0.96 Å) and refined with adequate constraints. The highest Fourier-difference peaks were lower than 1.3 e Å^{-3} and occurred in the proximity of the Fe atom. Experimental data are given in Table 2.

CCDC reference number 186/849.

Synthesis of complexes

***trans*-[Fe(COMe){(pz)$_2$BH$_2$}(CO)(PMe$_3$)$_2$] 2a.** Complex **1a** (100 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (8 cm^3) and solid K[(pz)$_2$BH$_2$] (65 mg, 0.40 mmol) added. The resulting suspension was stirred for 30 min. The solid (KI) was filtered out. The

solution was dried and the residue extracted with *n*-hexane. The extract was concentrated until incipient precipitation and put in a refrigerator at −18 °C. Red microcrystals of complex **2a** were obtained (yield 80%) (Found: C, 41.9; H, 6.8; N, 12.9. $C_{15}H_{29}BFeN_4O_2P_2$ requires C, 42.3; H, 6.9; N, 13.2%). IR (*n*-hexane): $\tilde{\nu}_{max}/cm^{-1}$ 1914 (CO) and 1597 ($COCH_3$). ^1H NMR (CD_2Cl_2, 294 K): δ_H 7.91 (1 H, d, $^3J_{HH}$ = 1.8, H^3), 7.85 (1 H, s, H^5), 7.63 (1 H, s, $H^{5'}$), 7.55 (1 H, d, $^3J_{HH}$ = 2.1, $H^{3'}$), 6.25 (1 H, t, $^3J_{HH}$ = 2.2, H^4), 6.24 (1 H, t, $^3J_{HH}$ = 2.3, $H^{4'}$), 2.48 (3 H, s, COMe) and 0.91 (18 H, t,[21] $|^2J_{PH} + {}^4J_{PH}|$ = 7.7 Hz, PMe_3). ^{31}P-{^1H} NMR (CD_2Cl_2, 294 K): δ_P 23.2 (s, PMe_3). ^{13}C-{^1H} NMR (CD_2Cl_2, 263 K): δ 147.4 (s, C^3), 143.5 (s, $C^{3'}$), 138.2 (s, C^5), 136.9 (s, $C^{5'}$), 106.2 (s, C^4), 105.2 (s, $C^{4'}$), 50.1 (s, CO*Me*) and 15.2 (t,[21] $|^1J_{CP} + {}^3J_{CP}|$ = 24.5 Hz, PMe_3).

***trans*-[Fe(COMe){κ²-(pz)₃BH}(CO)(PMe₃)₂] 3a.** Complex **1a** (150 mg, 0.37 mmol) was dissolved in CH_2Cl_2 (11 cm^3) and solid Na[$(pz)_3$BH] (140 mg, 0.60 mmol) added. The resulting suspension was stirred for 120 min. The solid (NaI) was filtered out. The solution was dried and the residue was extracted with *n*-hexane. The extract was concentrated until incipient precipitation and put in a refrigerator at −18 °C. Orange microcrystals of complex **3a** were obtained (yield 80%). IR (*n*-hexane): $\tilde{\nu}_{max}/cm^{-1}$ 1915 (CO) and 1598 ($COCH_3$). ^1H NMR (CD_2Cl_2, 294 K): δ_H 8.00 (1 H, s, H^3), 7.96 (1 H, s, $H^{3'}$), 7.72 (2 H, s, $H^{3''}$ and H^5), 6.90 (1 H, d, $^3J_{HH}$ = 1.8, $H^{5'}$), 6.79 (1 H, s, $H^{5''}$), 6.33 (1 H, t, $^3J_{HH}$ = 1.7, H^4), 6.26 (1 H, t, $^3J_{HH}$ = 2.1, $H^{4'}$), 6.24 (1 H, t, $^3J_{HH}$ = 2.2, $H^{4''}$), 2.52 (3 H, s, COMe), 1.11 (9 H, dd, $^2J_{HP}$ = 9.5, $^4J_{HP}$ = 0.7, PMe_3^1) and 0.85 (9 H, d, $^2J_{HP}$ = 8.4 Hz, PMe_3^2). ^{31}P-{^1H} NMR (CD_2Cl_2, 263 K): δ_P 23.4 (d, $^2J_{PP}$ = 162, PMe_3^1) and 11.6 (d, $^2J_{PP}$ = 162 Hz, PMe_3^2). ^{13}C-{^1H} NMR (CD_2Cl_2, 263 K): δ_C 283.0 (t, $^2J_{CP}$ = 23.2, *C*OMe), 221.8 (t, $^2J_{CP}$ = 30.5, CO), 147.3 (s, C^3), 144.6 (s, $C^{3'}$), 143.6 (s, $C^{3''}$), 137.1 (s, C^5), 136.2 (s, $C^{5'}$), 136.1 (s, $C^{5''}$), 106.6 (s, C^4), 106.0 (s, $C^{4'}$), 105.0 (s, $C^{4''}$), 50.1 (s, CO*Me*), 15.0 (d, $^1J_{CP}$ = 25.1, PMe_3^1) and 14.1 (d, $^1J_{CP}$ = 22.9 Hz, PMe_3^2).

[Fe(COMe){κ³-(pz)₃BH}(CO)(PMe₃)] 4a. Complex **3a** was dissolved in *n*-hexane and refluxed for 1 h. The solution was put in a refrigerator at −18 °C and microcrystals of **4a** were obtained (Found: C, 41.2; H, 5.01; N, 19.2. $C_{15}H_{22}BFeN_6O_2P$ requires C, 43.31; H, 5.32; N, 20.20%). IR (*n*-hexane): $\tilde{\nu}_{max}/cm^{-1}$ 1952 (CO) and 1598 ($COCH_3$). ^1H NMR (CD_2Cl_2, 294 K): δ_H 7.87 (1 H, d, $^3J_{HH}$ = 2.1, H^3), 7.82 (1 H, d, $^3J_{HH}$ = 1.5, $H^{3'}$), 7.69 (1 H, s, $^3J_{HH}$ = 2.1, $H^{3''}$), 7.66 (2 H, s, H^5 and $H^{5'}$), 7.59 (1 H, s, $H^{5''}$), 6.35 (1 H, t, $^3J_{HH}$ = 2.1, H^4), 6.19 (1 H, t, $^3J_{HH}$ = 2.0, $H^{4'}$), 6.14 (1 H, t, $^3J_{HH}$ = 2.0, $H^{4''}$), 2.08 (3 H, s, COMe) and 1.19 (9 H, d, $^2J_{HP}$ = 8.9 Hz, PMe_3). ^{31}P-{^1H} NMR (CD_2Cl_2, 263 K): δ_P 29.0 (s, PMe_3). ^{13}C-{^1H} NMR (CD_2Cl_2, 263 K): δ_C 289.4 (d, $^2J_{CP}$ = 25.6, *C*OMe), 220.0 (d, $^2J_{CP}$ = 34.2, CO), 144.4 (s, C^3), 143.6 (s, $C^{3'}$), 142.3 (s, $C^{3''}$), 136.9 (s, C^5), 135.8 (s, $C^{5'}$), 135.6 (s, $C^{5''}$), 105.5 (s, C^4, $C^{4'}$ and $C^{4''}$), 44.5 (s, CO*Me*) and 16.4 (d, $^1J_{CP}$ = 25.6 Hz, PMe_3).

***trans*-[Ru(COMe){$(pz)_2BH_2$}(CO)$(PMe_3)_2$] 2b.** The procedure was the same as that for complex **2a**. Yield 65% (Found: C, 37.8; H, 6.2; N, 11.4. $C_{15}H_{29}BN_4O_2P_2Ru$ requires C, 38.2; H, 6.2; N, 11.9%). IR (*n*-hexane): $\tilde{\nu}_{max}/cm^{-1}$ 1934 (CO) and 1602 ($COCH_3$). ^1H NMR (CD_2Cl_2, 294 K): δ_H 8.00 (1 H, dt, $^3J_{HH}$ = 2.1, $^4J_{PH}$ = 0.7, H^3), 7.67 (1 H, d, $^3J_{HH}$ = 2.0, H^5), 7.60 (1 H, dt, $^3J_{HH}$ = 2.1, $^4J_{PH}$ = 0.8, $H^{3'}$), 7.57 (1 H, d, $^3J_{HH}$ = 2.1, $H^{5'}$), 6.23 (1 H, t, $^3J_{HH}$ = 2.1, H^4), 6.21 (1 H, t, $^3J_{HH}$ = 2.3, $H^{4'}$), 2.45 (3 H, s, COMe) and 0.97 (18 H, t,[21] $|^2J_{PH} + {}^4J_{PH}|$ = 6.8 Hz, PMe_3). ^{31}P-{^1H} NMR (CD_2Cl_2, 294 K): δ_P 2.2 (s, PMe_3). ^{13}C-{^1H} NMR (CD_2Cl_2, 294 K): δ_C 146.3 (s, C^3), 143.3 (s, C^5), 138.0 (s, $C^{3'}$), 136.6 (s, $C^{5'}$), 105.8 (s, C^4), 104.9 (s, $C^{4'}$), 51.4 (s, CO*Me*) and 15.5 (t,[21] $|^1J_{CP} + {}^3J_{CP}|$ = 28.6 Hz, PMe_3).

***trans*-[Ru(COMe){κ²-(pz)₃BH}(CO)$(PMe_3)_2$] 3b.** The procedure was the same as that for complex **3a**. Yield 70% (Found: C, 39.5; H, 5.8; N, 15.0. $C_{18}H_{31}BN_6O_2P_2Ru$ requires C, 40.2; H, 5.8; N, 15.6%). IR (*n*-hexane): $\tilde{\nu}_{max}/cm^{-1}$ 1935 (CO) and 1601 ($COCH_3$). ^1H NMR (CD_2Cl_2, 294 K): δ_H 8.19 (1 H, d, $^3J_{HH}$ = 2.0, H^3), 7.77 (1 H, d, $^3J_{HH}$ = 1.8, $H^{3'}$), 7.72 (1 H, d, $^3J_{HH}$ = 1.5, $H^{3''}$), 7.61 (1 H, d, $^3J_{HH}$ = 2.1, H^5), 7.05 (1 H, d, $^3J_{HH}$ = 2.4, $H^{5'}$), 6.93 (1 H, d, $^3J_{HH}$ = 2.4, $H^{5''}$), 6.31 (1 H, t, $^3J_{HH}$ = 1.9, H^4), 6.24 (1 H, t, $^3J_{HH}$ = 2.2, $H^{4'}$), 6.21 (1 H, t, $^3J_{HH}$ = 2.3, $H^{4''}$), 2.48 (3 H, s, COMe), 1.18 (9 H, dd, $^2J_{HP}$ = 9.1, $^4J_{HP}$ = 2.0, PMe_3^1) and 0.85 (9 H, dd, $^2J_{HP}$ = 8.4, $^4J_{HP}$ = 1.8 Hz, PMe_3^2). ^{31}P-{^1H} NMR (CD_2Cl_2, 294 K): δ_P −1.3 (d, $^2J_{PP}$ = -296.2, PMe_3^1) and −7.9 (d, $^2J_{PP}$ = 296.4 Hz, PMe_3^2). ^{13}C-{^1H} NMR (CD_2Cl_2, 294 K): δ_C 263.8 (t, *C*OMe), 206.6 (t, CO), 146.5 (s, C^3), 143.6 (s, $C^{3'}$), 142.0 (s, $C^{3''}$), 137.1 (s, C^5), 136.5 (s, $C^{5'}$), 136.1 (s, $C^{5''}$), 106.1 (s, C^4), 105.2 (s, $C^{4'}$), 104.9 (s, $C^{4''}$), 51.1 (s, CO*Me*), 15.5 (d, $^1J_{CP}$ = 27.3, PMe_3^1) and 14.5 (d, $^1J_{CP}$ = 25.2 Hz, PMe_3^2).

Alternatively, complex **8** (20 mg, 0.023 mmol) was dissolved in CH_2Cl_2 (8 cm^3) and solid Na[$(pz)_3$BH] (8 mg, 0.034 mmol) added. The resulting suspension was stirred for 120 min. The solid ($NaBPh_4$) was filtered out. The solution was dried and the residue extracted with *n*-hexane. The extract was concentrated until incipient precipitation and put in a refrigerator at −18 °C. Yield 68%.

[Ru(COMe){κ³-(pz)₃BH}(CO)(PMe₃)] 4b. Complex **5** (132 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (11 cm^3) and solid Na[$(pz)_3$BH] (86 mg, 0.36 mmol) added. The resulting suspension was stirred for 120 min. The solid (NaI) was filtered out. The solution was dried and the residue extracted with *n*-hexane. The extract was concentrated until incipient precipitation and put in a refrigerator at −18 °C. Orange microcrystals of complex **4b** were obtained (yield 50%) (Found: C, 39.1; H, 4.81; N, 18.2. $C_{15}H_{22}BN_6O_2PRu$ requires C, 39.1; H, 4.81; N, 18.2%). IR (*n*-hexane): $\tilde{\nu}_{max}/cm^{-1}$ 1942 (CO) and 1602 ($COCH_3$). ^1H NMR (CD_2Cl_2, 298 K): δ_H 7.95 (1 H, d, $^3J_{HH}$ = 2.2, H^3), 7.48 (1 H, dd, $^3J_{HH}$ = 2.1, $^4J_{PH}$ = 0.5, $H^{3'}$), 7.70 (1 H, dd, $^3J_{HH}$ = 2.2, $^4J_{PH}$ = 0.5, $H^{3'}$), 7.67 (1 H, d, $^3J_{HH}$ = 2.2, $H^{5'}$ or $H^{5''}$), 7.66 (1 H, d, $^3J_{HH}$ = 2.3, $H^{5''}$ or $H^{5'}$), 7.46 (1 H, d, $^3J_{HH}$ = 1.7, $H^{5'}$), 6.29 (1 H, t, $^3J_{HH}$ = 2.3, H^4), 6.20 (2 H, m, $H^{4'}$ and $H^{4''}$), 2.30 (3 H, s, COMe) and 1.38 (9 H, d, $^2J_{PH}$ = 9.3 Hz, PMe_3). ^{31}P-{^1H} NMR (CD_2Cl_2, 298 K): δ_P 13.4 (s).

***trans*-[Fe(COMe){κ²-(mpz)OB(C_8H_{14})}(CO)$(PMe_3)_2$] 6.** Complex **1a** (100 mg, 0.25 mmol) was dissolved in thf (5 cm^3) and K[$(mpz)_2B(C_8H_{14})$] (120 mg, 0.37 mmol), dissolved in thf (3 cm^3), slowly added. The resulting solution was stirred for 120 min. The precipitated solid (KI) was filtered out. The solution was dried and the residue extracted with *n*-hexane. The extract was concentrated until incipient precipitation and put in a refrigerator at −18 °C. Yellow crystals of complex **6** were obtained (yield 15%) (Found: C, 50.6; H, 8.0; N, 5.7; O, 9.4. $C_{21}H_{40}BFeN_2O_3P_2$ requires C, 50.7; H, 8.1; N, 5.6; O, 9.4%). IR (*n*-hexane): $\tilde{\nu}_{max}/cm^{-1}$ 1907 (CO) and 1578 ($COCH_3$). ^1H NMR [$(CD_3)_2CO$, 294 K]: δ_H 7.70 (1 H, d, $^3J_{HH}$ = 2.1, H^5), 6.07 (1 H, d, $^3J_{HH}$ = 2.1, H^4), 2.87 (1 H, br), 2.84 (2 H, br), 2.45 (3 H, s, 3-Me), 2.43 (3 H, s, COMe), 2.01 (2 H, m), 1.75 (2 H, m), 1.65 (2 H, m), 1.63 (2 H, m), 1.41 (1 H, d), 1.07 (18 H, t,[21] $|^2J_{PH} + {}^4J_{PH}|$ = 8.0 Hz, PMe_3) and 0.31 (2 H, br). ^{31}P-{^1H} NMR [$(CD_3)_2CO$, 294 K]: δ_P 16.6 (s, PMe_3). ^{13}C-{^1H} NMR [$(CD_3)_2CO$, 294 K]: δ_C 290.1 (t, $^2J_{CP}$ = 24, *C*OMe), 221.3 (t, $^2J_{CP}$ = 34, CO), 149.3 (s, C^3), 135.8 (s, C^5), 106.7 (s, C^4), 48.4 (s, CO*Me*), 34.0 (s, $C^{2'}$ or $C^{3'}$), 32.4 (s, $C^{3'}$ or $C^{2'}$), 29.5 (br, $C^{1'}$), 26.1 (s, $C^{4'}$ or $C^{5'}$), 25.4 (s, $C^{5'}$ or $C^{4'}$), 16.2 (s, 3-Me) and 14.0 (t,[21] $|^1J_{CP} + {}^3J_{CP}|$ = 23.9 Hz, PMe_3). ^{11}B-{^1H} NMR [$(CD_3)_2CO$, 294 K]: δ_B 7.40 (s).

Reactions

The reactions of complexes **1a** and **1b** in polar solvents with different ligands were carried out by dissolving them (100 mg) in *ca.* 10 cm^3 of solvent and adding an equimolar quantity of the ligand.

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