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Synthesis and nuclear magnetic resonance studies of some ethylene and ethyltris(pyrazolyl)boratoiridium complexes

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Abstract

The synthesis of $[Ir\{HB(pz)_3\}(C_2H_4)(CO)]$ (**2**), $[Ir\{HB(pz)_3\}(C_2H_5)(\eta^2\text{-}C_2H_4)][BF_4]$ (**3**), and $[Ir\{HB(pz)_3\}(C_2H_5)(CO)][BF_4]$ (**4**) is described. Compound **2** is prepared by reaction of $[Ir\{HB(pz)_3\}(C_2H_4)_2]$ (**1**) with carbon monoxide followed by treatment with ethylene under atmospheric pressure. Treatment of **1** and **2** with HBF_4 affords compounds **3** and **4**, respectively. Complex **2** is fluxional and its frozen structure is trigonal bipyramidal with the ethylene in the equatorial plane and the carbonyl group in one axial position; no rotation of the olefin is detected. Complexes **3** and **4** are square-pyramidal and are rigid on the nuclear magnetic resonance (NMR) time scale. These structural inferences are based on ^1H and ^{13}C NMR spectra for the complexes and nuclear Overhauser effect (NOE) measurements for **2**.

1. Introduction

During the past decade interest in the chemistry of transition metal complexes containing poly(1-pyrazolyl)borato ($H_nB(pz)_{4-n}$) ligands has grown steadily [1,2]. Part of this interest stems from the supposed structural and electronic similarity between complexes with cyclopentadienyl (or pentamethylcyclopentadienyl) and those with $H_nB(pz)_{4-n}$ [3,4]. We have previously reported [5,6] the preparation of alkenyl and carbonyl iridium complexes with $H_nB(pz)_{4-n}$ ligands. We wish to report here the preparation and structural aspects of some ethylene- and ethyl-tris(pyrazolyl)boratoiridium complexes. Detailed nuclear magnetic resonance (NMR) studies on the complexes reveal interesting structural features and the slow rotation of ethylene on the NMR timescale in a pentacoordinate iridium(I) complex.

2. Results and discussion

Treatment of $[Ir\{HB(pz)_3\}(CO)_2]$, prepared *in situ* by reaction of $[Ir\{HB(pz)_3\}(C_2H_4)_2]$ (**1**) with carbon monoxide in cyclohexane [7], with ethylene under atmospheric pressure gives $[Ir\{HB(pz)_3\}(C_2H_4)(CO)]$ (**2**) as the only product. Replacement of carbon monoxide by ethylene in $[Ir\{HB(pz)_3\}(CO)_2]$ is slow, whilst the two ethylene groups in complex **1** are completely replaced by carbon monoxide in a few minutes. Compound **1** is isolated as white, air-stable crystals in reasonable yield. Its formulation is supported by microanalysis, and ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopy. Variable temperature ^1H NMR studies and nuclear Overhauser effect (NOE) measurements on complex **2** revealed interesting structural features.

2.1. NMR studies on complex 2

The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **2** at room and at higher temperatures show that the three pyrazolyl rings became equivalent. Both NMR spectra display the typical pattern of an *N*-substituted pyrazolyl group; incidentally, the resonances of the H3 and H5 protons of the three rings are coincident in $CDCl_3$ and in CD_2Cl_2 but not in deuterotoluene. On the other hand, rotation of the ethylene ligand is not detected since its proton resonances appear invariant as a simple AA′XX′ system in the range 373–200 K. Furthermore, the carbon nuclei of the ethylene ligand are equivalent, giving rise to a single resonance shifted

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noticeably to high field ($\delta = 6.4$ ppm) at all temperatures. The equivalence of the three pyrazolyl rings can be explained in terms of the rotation of the tris(pyrazolyl)borate ligand around the Ir ··· B–H axis. Similar behaviour has been described for other complexes with this type of ligand [8] and in particular for pentacoordinate rhodium and platinum compounds [9,10], but in contrast with all these compounds the fluxional movement in **2** is easily slowed.

Below the temperature of coalescence (near 0°C) the pyrazolyl proton resonances merge as sharp doublets and triplets in the ^1H NMR spectrum, assigned to two kinds of pyrazolyl ring in relative proportions 1:2 (see Fig. 1, trace a). The $^{13}C\{^1H\}$ NMR spectrum (see experimental details) is consistent with this. This equivalence of two pyrazolyl rings in the slow-exchange region is compatible only with a trigonal bipyramidal rigid structure (C_s symmetry) in which the three pyrazolyl rings are coordinated. As observed for pentacoordinate and octahedral tris(pyrazolyl)borate complexes [10–12], the nitrogen atoms should occupy *fac* positions, *i.e.* one axial and two equatorial coordination sites. Structures A and B (Fig. 2) can exist within this geometry, but the equivalence of the ethylene carbon atoms and NOE measurements show that complex **2** has structure A. Figure 2A shows clearly that the resonances due to the H31 protons will be most affected by the ethylene protons in NOE experiments.

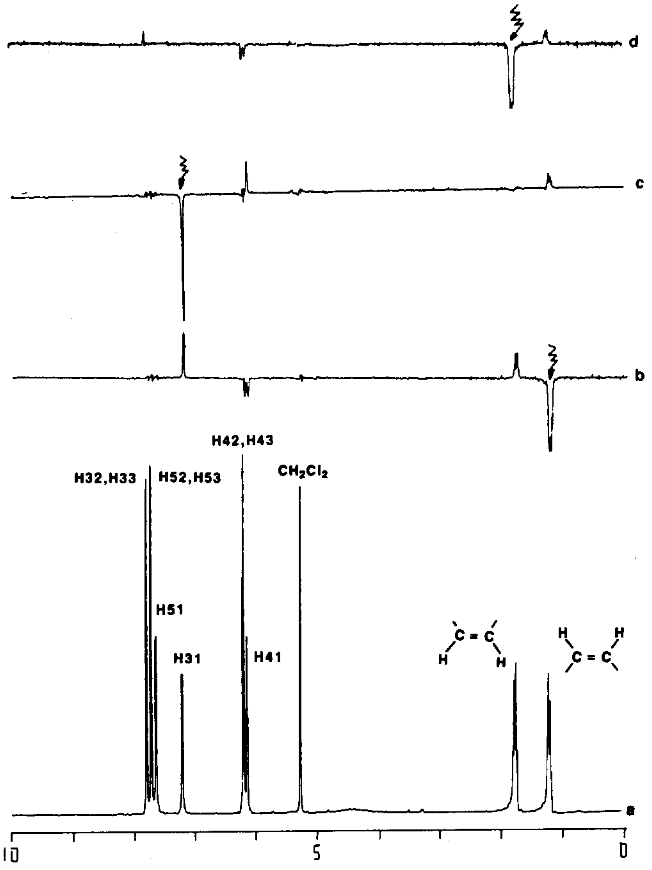

Fig. 1. (a) Reference spectrum of complex **2** in CD_2Cl_2 at −80°C; (b), (c) and (d) difference spectra on irradiation at δ 1.24, 7.27 and 1.79 ppm respectively.

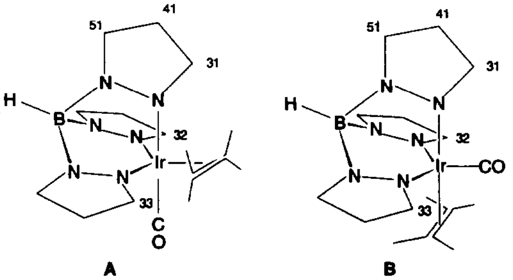

Fig. 2. Possible structures for complex **2**.

The ^1H NMR spectrum of **2** shows two doublets at δ 7.81 and 7.22 ppm which are assigned to the H32, H33 and H31 protons of the pyrazolyl groups, respectively, consistent with their coupling constants [J(H41H51) > (H31H41)] [13]. If structure A (Fig. 2) is adopted, proton H31 of the pyrazolyl group (at δ 7.22 ppm) and two of the ethylene protons should be related by NOE, according to proximity arguments; in addition, the other two ethylene protons and the H32 and H33 pyrazolyl protons (at δ 7.81 ppm) should be also related in NOE experiments. On the contrary, if structure B (Fig. 2) is adopted, the ethylene protons and only the H32 and H33 pyrazolyl protons should show NOE enhancements.

Difference NOE spectra were run at −80°C to avoid chemical exchange. As shown in Fig. 1 (trace b), a strong positive NOE for the doublet due to H31 (at δ 7.22 ppm) occurs on saturation of the ethylene multiplet at δ 1.24 ppm. Conversely, irradiation at δ 7.22 ppm gives a positive NOE for the proton at δ 1.24 and obviously on the apparent triplet due to H41 (trace c). Moreover, the resonances of the pyrazolyl protons H32 and H33 and ethylene (at δ 7.81 and δ 1.79) are weakly related (trace d). This corroborates the predictions of structure A for complex **2**.

Further, the ethylene, more precisely the C=C bond, is in the equatorial plane because the carbon nuclei are equivalent. The multiplets at δ 1.24 and δ 1.79 in the ^1H NMR spectrum are due to the two sets of chemically equivalent ethylene protons above and below the equatorial plane. The three pyrazolyl groups are coordinated to the metal, which brings H31 of the group in the axial position close to two protons of the olefin above the equatorial plane. Slow rotation of the olefin occurs; otherwise an enhancement of both multiplets due to the ethylene protons would occur on irradiation at the pyrazolyl resonance due to H31 by chemical exchange.

A clue to the fluxion of the tris(pyrazolyl)borate at room temperature becomes clear when NOE measurements are carried out in the slow-exchange region (at $-40°C$). Saturation of any of the H3 doublets of the pyrazolyl groups gives positive NOEs on the ethylene signal at δ 1.24 and on both triplets due to the H4 protons, and saturates also the other resonance for H3. These effects are clearly caused by spin-saturation-transfer [14] in the exchange of the axial and equatorial pyrazolyl groups. To explain this exchange, Berry pseudorotation and the rotation of the $HB(pz)_3$ around the $H{-}B \cdots Ir$ axis proposed in previous studies [8–10,12c,15] should be considered. The difficulty of spanning *trans* positions with the $HB(pz)_3$ ligand acting as a tripod required for the pseudorotation, makes a turnstile movement the most likely. Rotation of the $HBpz_3$ ligand through 60° would give the isomer B as intermediate in the 120° rotation for the exchange of coordination positions by the pyrazolyl groups. Molecular orbital calculations at extended Hückel Theory (EHT) [16–18] level show an activation energy of 0.7 eV (67 KJ mol^{-1}) for this movement in complex **2**.

The slow rotation of the ethylene ligand in complex **2** is even more striking when compared with **1** in which the rotation of the olefins and $HB(pz)_3$ ligands occur easily. The ^1H NMR spectrum of **1** at room temperature shows equivalent pyrazolyl groups and a singlet for the olefinic protons. At the slow-exchange limit ($-80°C$), the fluxional movement of the $HB(pz)_3$ group is still too fast. A value of 0.3 eV (29 KJ mol^{-1}) is obtained by EHT calculation for the rotation of the $HB(pz)_3$ ligand in **1**. At $-80°C$, the rotation of the olefins in **1** is slow, so that the ^1H NMR spectrum shows equivalent pyrazolyl groups and ethylene ligands. The latter gives rise to an apparent AB spin system similar to that found in $[Rh(C_5H_5)(C_2H_4)_2]$ [19]. A rough estimate of the barrier for the rotation of the olefins in **1** gives 50 kJ mol^{-1}, calculated from the coalescence temperature ($-23°C$) and the separation of the resonances (152 Hz). Similar values have been reported for other ethylene complexes [7,20].

It is not clear why there is slow rotation of ethylene in **2**. Theoretical studies on pentacoordination [21] for d^8 complexes predict a strong metal–ligand π-interaction in the equatorial position, where the ethylene lies. Strong back-donation to the empty π^* orbitals of ethylene would lead to a formulation of the iridium–ethylene bond near to a metallacyclopropane. This is a plausible explanation for both the high barrier for the rotation of the olefin in **2** and the anomalous chemical shift for the olefinic carbons, which appear in the aliphatic region in the ^{13}C NMR spectrum.

2.2. *Protonation reactions*

Reactions of the ethylene complex **1** and **2** with tetrafluoroboric acid lead to the ethyl complexes $[Ir\{HB(pz)_3\}(C_2H_5)(\eta^2\text{-}C_2H_4)]$ $[BF_4]$ (**3**), and $[Ir\{HB(pz)_3\}(C_2H_5)(CO)][BF_4]$ (**4**) respectively. Microanalysis and ^1H and ^{13}C NMR data are consistent with the formulations. Probably the ethyl ligand is formed by protonation of the metal to give a cationic monohydrido species; the hydrido ligand rapidly migrates to the coordinated ethylene to yield the ethyliridium species [22]. The decrease of electron density on the metal on protonation is reflected by the shift to higher frequency of $\nu(CO)$ for complex (**4**) relative to (**2**). Although complexes (**3**) and (**4**) might be protonated again because they still have a vacant coordination position, the decrease of metal basicity prevents a further reaction with tetrafluoroboric acid.

The structures of the pentacoordinate iridium(III) species (**3**) and (**4**) are easily deduced from their NMR spectra. As the compounds are non-fluxional on the NMR time scale, the inequivalence of the three pyrazolyl groups in their ^1H and ^{13}C NMR spectra is indicative of the lack of elements of symmetry in the molecules and hence their structure is square pyramidal as depicted in Fig. 3.

The protonation of the ethylene ligand in the Ir^I compounds implies an oxidative-addition reaction leading to a remarkable change in structure, probably for electronic reasons.

3. Experimental details

The reactions were carried out at room temperature under a nitrogen armosphere using standard Schlenk techniques. The compound $[Ir\{HB(pz)_3\}(C_2H_4)_2]$ (**1**) was prepared as previously reported [7]. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL200 spectrometer; chemical shifts are given relative to tetramethylsilane as an external reference. IR spectra were recorded on a Perkin–Elmer 783 spectrophotometer. Elemental analyses were performed with a Perkin–Elmer 240c elemental analyzer. NOE measurements were carried out on dilute CD_2Cl_2 solutions of com-

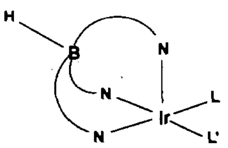

Fig. 3. Structure of the complexes **3** and **4** ($L = C_2H_5$; $L' = C_2H_4$ or CO).

plex (**2**) at −80°C. A particular resonance was presaturated for 6 s and the FID was acquired with the decoupler off. The NOE was observed by substracting each irradiated spectrum from a reference spectrum. Typically, 32 acquisitions per spectrum were used. Temperatures were calibrated with methanol and ethylene glycol.

3.1. Synthesis of $[Ir\{HB(pz)_3\}(C_2H_4)(CO)]$ *(2)*

Carbon monoxide was bubbled through a suspension of complex **1** (208 mg, 0.45 mmol) in cyclohexane (20 ml) for 15 min to give a yellow solution. Then ethylene was bubbled for 3 h. After concentration of the solution under vacuum, addition of pentane (15 ml) gave a white precipitate which was filtered off, washed with pentane and dried under vacuum (100 mg, 48%). Anal. Found: C, 30.7; H, 3.0; N, 18.2. $C_{12}H_{14}BIrN_6O$ calc.: C, 31.2; H, 3.0; N, 18.2%. IR: ν(B–H) 2520 cm^{-1} (Nujol); ν(CO) 2000 cm^{-1} (cyclohexane). ^1H NMR (CD_2Cl_2, −80°C): δ 7.80 (d, 2H, pz), 7.73 (d, 2H, pz), 7.65 (d, 1H, pz), 7.22 (d, 1H, pz), 6.22 (t, 2H, pz), 6.16 (t, 1H, pz), 1.80 (m, 2H, C_2H_4), 1.23 (m, 2H, C_2H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ 168.6 (CO), 143.8 (2C, pz), 136.8 (1C, pz), 135.2 (2C, pz), 134.8 (1C, pz), 106.4 (2C, pz), 105.8 (1C, pz) and 6.45 (2C, C_2H_4).

3.2. Synthesis of $[Ir\{HB(pz)_3\}(C_2H_5)(\eta^2\text{-}C_2H_4)]\ [BF_4]$ *(3)*

Tetrafluoroboric acid in diethyl ether (30 μl, 0.22 mmol) was added to a solution of complex (**1**) (100 mg, 0.22 mmol) in diethyl ether (20 ml). Rapid precipitation of a white solid was observed. The mixture was allowed to react for 30 min and then the white solid was filtered off, washed with diethyl ether and dried under vacuum (96 mg, 74%). Anal. Found: C, 28.2; H, 3.5; N, 15.2. $C_{13}H_{19}B_2F_4IrN_6$ calc.: C, 28.4; H, 3.5; N, 15.3%. IR: ν(B–H) 2520 cm^{-1} (Nujol). ^1H NMR (acetone-d_6, 20°C): δ 8.12 (d, 1H, pz), 8.06 (d, 1H, pz), 8.01 (d, 1H, pz), 8.00 (d, 1H, pz), 7.91 (d, 1H, pz), 7.51 (d, 1H, pz), 6.54 (t, 1H, pz), 6.48 (t, 1H, pz), 6.32 (t, 1H, pz), 4.65 (m, 2H, C_2H_4), 4.13 (m, 2H, C_2H_4), 2.79 (m, 1H, $\mathit{CH_2}\mathrm{CH_3}$), 2.35 (m, 1H, $\mathit{CH_2}\mathrm{CH_3}$), 0.84 (t, 3H, $\mathrm{CH_2}\mathit{CH_3}$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 20°C): δ 143.3 (1C, pz), 140.1 (1C, pz), 139.7 (1C, pz), 138.1 (1C, pz), 137.1 (1C, pz), 137.0 (1C, pz), 108.0 (1C, pz), 107.8 (1C, pz), 107.6 (1C, pz), 67.9 (2C, C_2H_4), 14.9 (1C, $\mathit{CH_2}\mathrm{CH_3}$), and 0.6 (1C, $\mathrm{CH_2}\mathit{CH_3}$).

3.3. $[Ir\{HB(pz)_3\}(C_2H_5)(CO)][BF_4]$ *(4)*

The complex was prepared using the procedure described for **3**, but with **2** (101 mg, 0.22 mmol) and HBF_4 in diethyl ether (25 μl, 0.22 mmol). The white complex was obtained in 46% yield (55 mg). Anal. Found: C, 26.3; H, 3.0; N, 15.2. $C_{12}H_{15}B_2F_4IrN_6O$ calc.: C, 26.2; H, 2.7; N, 15.3%. IR: ν(B–H) 2520 cm^{-1} (Nujol); ν(CO) 2065 cm^{-1} (CH_2Cl_2). ^1H NMR (acetone-d_6, 20°C): δ 8.1 (m, 6H, pz), 6.57 (t, 1H, pz), 6.5 (m, 2H, pz), 2.50 (q, 2H, $\mathit{CH_2}\mathrm{CH_3}$), and 1.44 (t, 3H, $\mathrm{CH_2}\mathit{CH_3}$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 20°C): δ 162.2 (1C, CO), 144.5 (1C, pz), 143.7 (1C, pz), 140.3 (1C, pz), 138.7 (1C, pz), 137.2 (1C, pz), 108.9 (1C, pz), 108.0 (1C, pz), 107.9 (1C, pz), 18.8 ($\mathit{CH_2}\mathrm{CH_3}$), and −0.6 ($\mathrm{CH_2}\mathit{CH_3}$).

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References

1 S. Trofimenko, *Prog. Inorg. Chem.*, *34* (1986) 115.

2 S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, *26* (1987) 1507.

3 P. M. Maitlis, *Chem. Soc. Rev.*, (1981) 1.

4 S. May, P. Reinsalv and J. Powell, *Inorg. Chem.*, *19* (1980) 1582.

5 M. J. Fernández, M. J. Rodriguez, L. A. Oro and F. J. Lahoz, *J. Chem. Soc., Dalton Trans.*, (1989) 2073.

6 M. J. Fernández, M. J. Rodriguez and L. A. Oro, *Polyhedron, 14* (1991) 1595.

7 R. S. Tanke and R. H. Crabtree, *Inorg. Chem.*, *28* (1989) 3444.

8 A. Shaver, in *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford, 1987, p. 245.

9 M. Cociveira, G. Ferguson, F. J. Lalor and P. Szczecinski, *Organometallics, 1* (1982) 1139.

10 L. E. Manzer and P. Z. Meakin, *Inorg. Chem.*, *15* (1976) 3117.

11 M. Cociveira, G. Ferguson, B. Kaitner, F. J. Lalor, D. O'Sullivan, M. Parvez, and B. Ruhl, *Organometallics, 1* (1982) 1132.

12 (a) C. K. Ghos and W. A. G. Graham, *J. Am. Chem. Soc.*, *111* (1989) 375;
(b) M. Angaroni, G. A. Ardizzoia, G. D'Alfonso, G. La Monica, N. Masciocchi and M. Moret, *J. Chem. Soc., Dalton Trans.*, (1990) 1895;
(c) M. M. de V. Steyn, E. Singleton, S. Hietkamp and D. C. Liles, *J. Chem. Soc. Dalton Trans.*, (1990) 2991.

13 C. López, R. M. Claramunt, D. Sanz, C. Foces-Foces, F. H. Cano, R. Faure, E. Cayón and J. Elguero, *Inorg. Chim. Acta, 176* (1990) 195.

14 R. Freeman, in *A Handbook of Nuclear Magnetic Resonance*, Longman, Harlow (1988) p. 198.

15 D. L. Reger and M. E. Tarquini, *Inorg. Chem.*, *22* (1983) 1064.

16 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, *36* (1962) 2179.

17 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, *36* (1962) 3489.

18 R. Hoffmann, *J. Chem. Phys.*, *37* (1962) 1397.

19 R. Cramer, J. B. Kline and J. Roberts, *J. Am. Chem. Soc.*, *91* (1969) 2519.

20 B. E. Mann, in *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, 1982, Chapter 20.

21 A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, *14* (1975) 365.

22 H. Werner and R. Feser, *Ang. Chem. Int. Ed. Engl.*, *18* (1979) 157.