

Preparation and characterisation of rhenium(I) and platinum(IV) complexes of 2,6-bis(pyrazol-1-ylmethyl)pyridine and 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine. Crystal structure of *fac*-[ReI(CO)₃(BMPz)]

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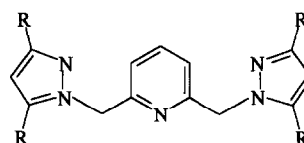
Abstract—Under mild conditions [ReX(CO)₃(THF)₂] reacts with pyrazolylmethylpyridines to form the complexes *fac*-[ReX(CO)₃(BPz)] and *fac*-[ReX(CO)₃(BMPz)] (X = Cl, Br, or I; BPz = 2,6-bis(pyrazol-1-ylmethyl)pyridine; BMPz = 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine) that involve BPz and BMPz acting as non-fluxional bidentate chelate ligands. Under more severe reaction conditions *fac*-[ReX(CO)₃(BPz)] is converted to *fac*-[Re(CO)₃(BPz)]X (X = Cl, Br, or I). Trimethylplatinum(IV)iodide reacts with BPz to form *fac*-[PtMe₃(BPz)]I. The crystal structure of *fac*-[ReI(CO)₃(BMPz)] confirms the bidentate chelate bonding of BMPz with a N—Re—N angle of 85.8°. © 1997 Elsevier Science Ltd

Keywords: rhenium; platinum; pyridine; pyrazol-1-yl.

Planar NNN ligands such as 2,2':6':2''-terpyridine [1] (terpy), 2,6-bis(pyrazol-1-yl)pyridine [2] (bppy), and 2,6-bis[(1-phenylimino)ethyl]pyridine [3] (BIP) predominantly act as terdentate chelate ligands involving essentially planar five-membered chelate rings. Around octahedral metal centres these ligands are always disposed in a *meridional* arrangement. Complexes are also known in which these ligands act in a bidentate chelate mode [2,3(g),4,5]. In the bidentate complexes a fluxional motion involving a 1,4-metallotropic shift has been observed and the mechanism elucidated [2,4,6].

In order to investigate the generality of the 1,4 metallotropic shift in potentially terdentate pyridine-based ligands it was decided to extend the study to non-planar NNN ligands. In this context the compounds 2,6-bis(pyrazol-1-ylmethyl)pyridine (BPz) and 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine

(BMPz), (Scheme 1), are both potentially terdentate ligands, involving the donor set N₃, which form six-membered chelate rings and are well suited for the study. BPz and BMPz usually bond to a metal as terdentate ligands [7-11], and in octahedral complexes adopt a *mer* configuration around the metal. In this work we explore the reactions of BPz and BMPz with the metal species [ReX(CO)₃(THF)₂], [ReX(CO)₅] (X = Cl, Br, or I) and [Pt(IME)₃]₄.



BPz : R = H

BMPz : R = Me

Scheme 1.

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EXPERIMENTAL

Materials

The rhenium carbonyl halides were prepared from decacarbonyl dirhenium [12]. Trimethylplatinum iodide was prepared from potassium hexachloroplatinate(IV) [13]. The ligands, 2,6-bis(pyrazol-1-ylmethyl)pyridine (BPz) and 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (BMPz) were prepared by a method previously described [7].

Physical measurements

Elemental analyses were carried out by Butterworth Laboratories (Teddington, Middlesex, London). Melting points were recorded open to air on a Galenkamp melting point apparatus and are uncorrected. Mass spectra were recorded on a Kratos Profile HV-3 spectrometer. Conductivity measurements were carried out on a PTI-20 conductivity meter utilising 10^{-3} M acetonitrile solutions. Infrared spectra were recorded as CHCl_3 solutions using matched CaF_2 solution cells on a Perkin-Elmer 881 spectrometer. Both instruments were calibrated from the 1602 cm^{-1} signal of polystyrene. ^1H NMR spectra were recorded either on a Bruker AM250 or a Bruker AC300 spectrometer operating at 250.13 MHz or 300.13 MHz respectively. A standard B-VT 100 variable temperature unit was used to control the probe temperature, the calibration of this unit being checked periodically against a Comark digital thermometer.

Single-crystal X-ray studies of $\text{fac-}[\text{ReI}(\text{CO})_3(\text{BMPz})]$

$\text{C}_{20}\text{H}_{21}\text{IN}_5\text{O}_3\text{Re} \cdot \text{C}_4\text{H}_8\text{O}$, $M_r = 1529.24$, monoclinic, $a = 9.434(7)$, $b = 15.894(2)$, $c = 18.007(5)$ Å, $\beta = 101.36(2)^\circ$ (by least-squares analysis of 50 reflections), $U = 2647(2)$ Å³, space group $P2_1/c$ (No. 14), $Z = 4$, $D_c = 1.919\text{ g cm}^{-3}$, $F(000) = 1472$, $\mu = 5.795\text{ mm}^{-1}$, $T = 120\text{ K}$, crystal size $0.215 \times 0.215 \times 0.007\text{ mm}$ (approx).

Data were collected on a Delft Instruments FAST TV area detector at the window of a rotating anode generator, with a molybdenum target (Mo-K_α , $\lambda = 0.71069$ Å), following previously described procedures [14]. 4376 reflections were collected ($2.31 < \theta < 25.06^\circ$), index ranges $-10 < h < 10$; $-17 < k < 13$; $-19 < l < 20$, producing 2609 unique data ($R_{\text{int}} = 0.0608$ after absorption correction, DIFABS [15]).

The structure was solved by heavy atom methods (SHELX-S) [16] and then subjected to full-matrix least squares refinement based on F^2 (SHELXL-93) [17]. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. Final wR_2 and R_1 values are 0.1402 and 0.0554 respectively for all data and 325 parameters ($\rho_{\text{max}}, \rho_{\text{min}} 0.899, -0.847\text{ e \AA}^{-3}$). Corresponding wR_2 and R_1 values for

1880 data with $F_o > 4\sigma(F_o)$ are 0.0902 and 0.0387 respectively.

Diagrams were drawn with SNOOPI [18]. The source of scattering factor data was [17]. Full tables of bond lengths and angles, atomic coordinates, anisotropic displacement parameters of non-hydrogen atoms, hydrogen atom parameters and tables of structure factors have been deposited as supplementary data.

Preparations

fac-}[\text{ReX}(\text{CO})_3(\text{BPz})] and *fac-}[\text{ReX}(\text{CO})_3(\text{BMPz})]* ($X = \text{Cl, Br, or I}$). These complexes were all prepared by the same general method, the only variable being the length of reaction. The rheniumpentacarbonyl halide (0.10 g) was dissolved in THF (10 cm³) and heated under reflux for several hours to form the complex $[\text{ReX}(\text{CO})_3(\text{THF})_2]$ [19]. This solution was cooled to 40°C, a slight excess over an equimolar amount of ligand was added, and stirring was continued for a further period of time (Table 1). Hexane (10 cm³) was added and the mixture was allowed to stand overnight at -20°C. The crystals that precipitated were washed with hexane (2 × 2 cm³) and subsequently dried *in vacuo*.

fac-}[\text{Re}(\text{CO})_3(\text{BPz})]\text{Cl} \cdot \text{THF}. Rheniumpentacarbonyl chloride (0.3 g, 0.83 mmol) was heated under reflux in THF (30 cm³) for 16 h. The solution was cooled to 45°C, BPz (0.198 g, 0.84 mmol) added and stirred for 68 h at approximately the same temperature. The white precipitate produced was then washed with THF (2 × 10 cm³) and dried *in vacuo* at 79°C for 36 h. Yield 0.476 g, 93.0%.

fac-}[\text{Re}(\text{CO})_3(\text{BPz})]\text{Br}. Rheniumpentacarbonyl bromide (0.1 g, 0.25 mmol) and BPz (0.07, 0.29 mmol) were heated under reflux in benzene (10 cm³) for 6 h. The white precipitate obtained was washed with benzene (2 × 30 cm³) and dried *in vacuo* at 53°C for 24 h. Yield 0.12 g, 87%.

*fac-}[\text{Re}(\text{CO})_3(\text{BPz})]\text{I} \cdot 0.5(\text{C}_6\text{H}_6). Rheniumpentacarbonyl iodide (0.10 g, 0.22 mmol) and BPz (0.06 g, 0.25 mmol) were heated under reflux in benzene (10 cm³) for 20 h. The white precipitate produced was washed with diethylether (2 × 35 cm³) and dried *in vacuo* at 79°C for 36 h. Yield 0.13 g, 87.2%.*

*fac-}[\text{Re}(\text{CO})_3(\text{BPz})]\text{PF}_6. The complex *fac-}[\text{Re}(\text{CO})_3(\text{BPz})]\text{Cl} \cdot \text{THF} (0.08 g, 0.13 mmol) was dissolved in ethanol at 40°C. An ethanolic solution of NH_4PF_6 (20 cm³, 5%) was slowly added until no more precipitate was seen to form. This precipitate was washed with ethanol (2 × 10 cm³) and dried at 50°C *in vacuo* for 20 h. Yield 0.084 g, 99.0%.**

fac-}[\text{PtMe}_3(\text{BPz})]\text{I}. Trimethylplatinum iodide (0.100 g, 0.27 mmol based on monomeric unit) and BPz (0.065 g, 0.27 mmol) were heated under reflux in benzene (20 cm³) for 3.5 h. The solvent was reduced to approximately 6 cm³ and hexane was added to precipitate a white flocculent material. It was washed

Table 1. Analytical data for the complexes *fac*-[ReX(CO)₃(BPz)] and *fac*-[ReX(CO)₃(BMPz)] (X = Cl, Br or I)

Complex	Reaction time (min)	Yield (%)	M.p. (°C)	Elemental Analysis ^a (%)			νCO ^b (cm ⁻¹)	Λ _M ^c (Ω ⁻¹ cm ² mol ⁻¹)
				C	H	N		
[ReCl(CO) ₃ (BPz)]	10	56	292/4 (dec)	35.2 (35.9)	2.4 (2.2)	12.2 (12.5)	2035vs 1936s 1898s	5.9
[ReBr(CO) ₃ (BPz)]	20	99	298/300 (dec)	32.6 (30.5)	2.2 (2.0)	11.0 (11.6)	2036vs 1937vs 1900s	9.3
[ReI(CO) ₃ (BPz)]	30	86	269/71 (dec)	30.2 (30.5)	2.0 (2.0)	11.0 (10.5)	2034vs 1938s 1902s	12.3
[ReCl(CO) ₃ (BMPz)]	10	72	222/4	40.0 (40.2)	3.5 (3.4)	11.7 (11.3)	2031vs 1928s 1897s	1.5
[ReBr(CO) ₃ (BMPz)]	25	75	225/7	37.2 (37.6)	3.2 (3.2)	10.8 (10.7)	2032vs 1931s 1898s	3.2
[ReI(CO) ₃ (BMPz)]	30	72	195/7	34.7 (34.5)	3.0 (2.7)	10.1 (10.1)	2030vs 1930s 1903s	7.0

^a Calculated values in parentheses.

^b Infrared spectra run in CHCl₃: s = strong, vs = very strong.

^c Recorded in acetonitrile.

with hexane (2 × 20 cm³) and dried *in vacuo*. Yield 0.165 g, 90.8%.

fac-[PtMe₃(BPz)]PF₆. The complex *fac*-[PtMe₃(BPz)]I (0.10 g) was dissolved in the minimum volume of methanol. A methanolic solution of NH₄PF₆ (1 g in 20 cm³) was slowly added until no more precipitate was seen to form. The white precipitate was then washed with ethanol (2 × 10 cm³) and dried at room temperature *in vacuo* for 20 h. Yield 0.10 g, 97.1%.

RESULTS AND DISCUSSION

Bidentate complexes

Rhenium carbonyl halides were reacted with THF to produce the complexes [ReX(CO)₃(THF)₂] (X = Cl, Br, I) in solution. BPz or BMPz was added and allowed to react in strictly monitored conditions (the IR spectrum of the reaction mixture was recorded every 3 to 4 minutes), to produce the complexes *fac*-

[ReX(CO)₃(L-L)] (X = Cl, Br or I; L-L = BPz or BMPz) in which the BPz or BMPz is acting as a bidentate chelate ligand.

Mass spectral analysis reflected the monomeric nature of these complexes (Table 2). For the BPz complexes the highest *m/z* value represents an ion corresponding to the loss of halide, [M—X]⁺. However for the BMPz complexes the highest *m/z* value corresponds to the molecular ion [M]⁺. For both BPz and BMPz complexes the most abundant fragment corresponds to a loss of halide. For all cases the observed and calculated isotope patterns are in agreement. In the carbonyl stretching region (2200 to 1700 cm⁻¹) of the infrared spectra the complexes show the usual pattern of three almost equally intense absorptions (Table 1) associated with a *facial* arrangement of the three carbonyl groups. Most absorptions for the BMPz complexes are at lower wavenumbers than those for the BPz analogues. This can be explained by the inductive effect of the methyl groups on the pyrazoles.

In order to firmly establish the structure of these

Table 2. Mass spectral data^a for BPz and BMPz complexes

Complex	<i>m/z</i>
[ReCl(CO) ₃ (BPz)]	510* [M—Cl] ⁺ , 482 [M—Cl(CO)] ⁺ , 426 [M—Cl(CO) ₃] ⁺
[ReBr(CO) ₃ (BPz)]	510* [M—Br] ⁺ , 482 [M—Br(CO)] ⁺ , 426 [M—Br(CO) ₃] ⁺
[ReI(CO) ₃ (BPz)]	510* [M—I] ⁺ , 482 [M—I(CO)] ⁺ , 426 [M—I(CO) ₃] ⁺
[ReCl(CO) ₃ (BMPz)]	601 [M] ⁺ , 566* [M—Cl] ⁺ , 482 [M—Cl(CO) ₃] ⁺
[ReBr(CO) ₃ (BMPz)]	646 [M] ⁺ , 566* [M—Br] ⁺ , 482 [M—Br(CO) ₃] ⁺
[ReI(CO) ₃ (BMPz)]	694 [M] ⁺ , 566* [M—I] ⁺ , 482 [M—I(CO) ₃] ⁺
[Re(CO) ₃ (BPz)]I	510* [M—I] ⁺ , 426 [M—I(CO) ₃] ⁺
[Re(CO) ₃ (BPz)]PF ₆	510* [M—PF ₆] ⁺ , 482 [M—PF ₆ (CO)] ⁺ , 426 [M—PF ₆ (CO) ₃] ⁺
[PtMe ₃ (BPz)]I	479* [M—I] ⁺ , 448 [M—IME ₂] ⁺ , 433 [M—IME ₃] ⁺

^a Acquired using the LSIMS technique.

* Most abundant fragment.

complexes an X-ray crystallographic study of a representative sample, *fac*-[ReI(CO)₃(BMPz)], was carried out. This is the first X-ray structure of a compound involving BMPz in a bidentate chelate mode. A view of the molecule indicating the numbering scheme adopted is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 3.

The crystal structure confirms the carbonyls in a *facial* arrangement and BMPz as a bidentate chelate ligand. The compound crystallises with a molecule of

tetrahydrofuran. The rhenium atom is hexacoordinated with distorted octahedral geometry. The BMPz "bite angle", N(1)—Re—N(2), is 85.8(3)° and the bond distance to the central pyridyl, Re—N(1), 2.296 Å, is somewhat longer than the bond distance to the pyrazole, Re—N(2), 2.215 Å. This is consistent with findings for metal complexes in which BPz or BMPz is acting as a terdentate ligand [7,20]. The six-membered chelate ring is not expected to be planar, and is arranged in a boat conformation with the car-

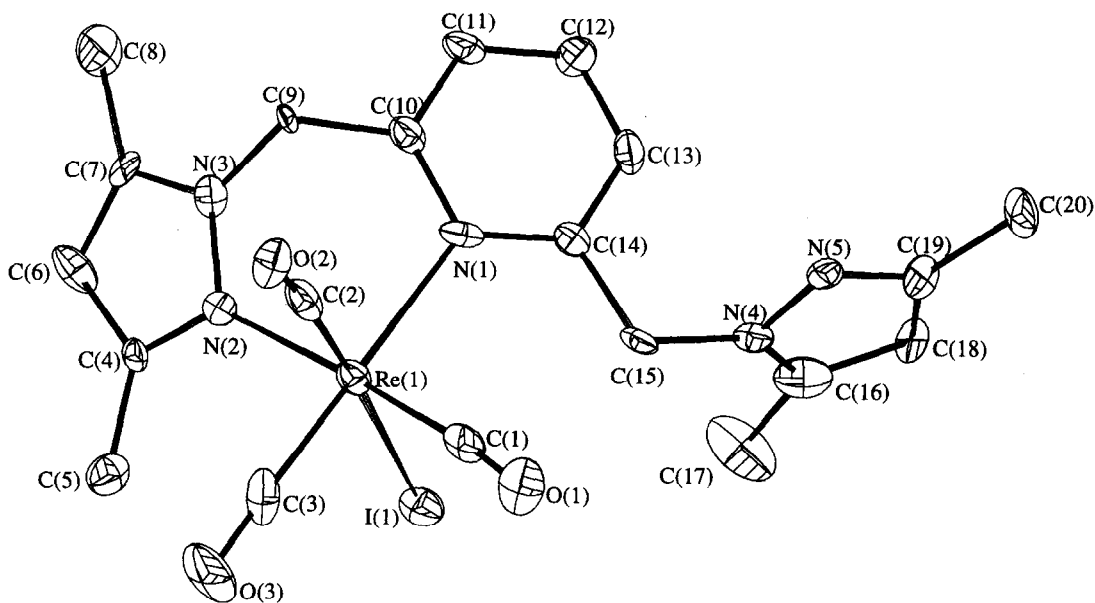
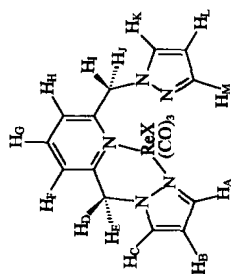


Fig. 1. The crystal structure of *fac*-[ReI(CO)₃(BMPz)] showing the atomic numbering, with hydrogen atoms and solvent molecule (THF) omitted for clarity.

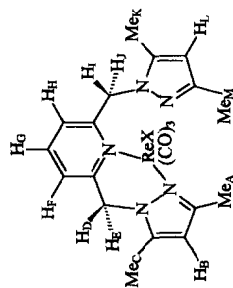
Table 3. Selected bond lengths (Å) and angles (°) for *fac*-[ReI(CO)₃(BMPz)]

Re(1)—C(1)	1.922(11)	Re(1)—C(2)	1.88(2)
Re(1)—C(3)	1.888(12)	Re(1)—N(1)	2.296(8)
Re(1)—N(2)	2.215(7)	Re(1)—I(1)	2.823(2)
N(1)—C(10)	1.383(12)	N(1)—C(14)	1.349(14)
N(2)—N(3)	1.360(10)	N(2)—C(4)	1.346(11)
N(3)—C(7)	1.321(12)	N(3)—C(9)	1.471(11)
N(4)—N(5)	1.373(10)	N(4)—C(15)	1.430(14)
N(4)—C(16)	1.33(2)	N(5)—C(19)	1.33(2)
C(1)—Re(1)—C(2)	86.2(5)	C(1)—Re(1)—C(3)	84.6(4)
C(2)—Re(1)—C(3)	86.5(5)	C(1)—Re(1)—N(1)	97.2(4)
C(2)—Re(1)—N(1)	96.0(4)	C(3)—Re(1)—N(1)	177.0(4)
C(1)—Re(1)—N(2)	177.0(3)	C(2)—Re(1)—N(2)	94.1(4)
C(3)—Re(1)—N(2)	92.4(4)	C(1)—Re(1)—I(1)	92.5(4)
C(2)—Re(1)—I(1)	175.8(3)	C(3)—Re(1)—I(1)	89.4(4)
N(1)—Re(1)—I(1)	88.2(2)	N(2)—Re(1)—I(1)	87.0(2)
Re(1)—N(1)—C(10)	117.5(7)	Re(1)—N(1)—C(14)	125.8(6)
C(10)—N(1)—C(14)	116.6(9)	C(4)—N(2)—N(3)	105.8(7)
Re(1)—N(2)—C(4)	134.0(6)	Re(1)—N(2)—N(3)	120.2(5)
N(2)—N(3)—C(7)	112.8(7)	C(7)—N(3)—C(9)	127.5(8)
N(2)—N(3)—C(9)	119.6(7)	C(16)—N(4)—N(5)	112.2(10)
C(16)—N(4)—C(15)	129.9(9)	N(5)—N(4)—C(15)	117.5(10)
N(4)—N(5)—C(19)	103.3(9)		

Table 4. ¹H NMR data^a for *rac*-[ReX(CO)₃(BPz)] (X = Cl, Br or I) in CDCl₃ at 30 °C


Compound	δ_A J_{AB}	δ_M J_{ML}	δ_B J_{BC}	δ_L J_{LM}	δ_C J_{CB}	δ_K J_{KL}	δ_D J_{DE}	δ_I J_{ID}	δ_E J_{ED}	δ_J J_{JI}	δ_F J_{FG}	δ_H J_{HG}	δ_G J_{GH}
BPz	d7.48 1.5	d7.48 1.5	t6.28 2.2	t6.28 1.5	d7.54 2.2	d7.54 2.2	s5.43 —	s5.43 —	s5.43 —	s5.43 —	d6.81 7.8	d6.81 7.8	t7.51 7.8
[ReCl(CO) ₃ (BPz)]	d8.11 2.5	d7.68 2.0	t6.50 2.4	t6.35 2.0	d7.67 2.4	d7.64 1.8	d7.24 17.1	d5.93 15.5	d5.84 17.1	d5.38 15.5	d7.39 7.7	d6.81 7.8	t7.75 7.8
$\Delta\delta$	0.63	0.20	0.22	0.07	0.13	0.10	—	—	—	—	0.58	0	0.24
[ReBr(CO) ₃ (BPz)]	d8.19 2.5	d7.71 1.9	t6.50 2.2	t6.38 1.9	d7.68 2.2	d7.65 1.8	d7.32 17.1	d5.86 15.4	d5.77 17.1	d5.40 15.4	d7.41 7.1	d6.76 7.8	t7.75 7.8
$\Delta\delta$	0.71	0.23	0.22	0.10	0.14	0.11	—	—	—	—	0.60	-0.05	0.24
[ReI(CO) ₃ (BPz)]	d8.34 2.5	d7.76 2.2	t6.48 2.4	t6.38 2.2	d7.67 2.4	d7.65 1.8	d7.33 17.0	d5.76 15.2	d5.69 17.0	d5.42 15.2	d7.42 6.8	d6.66 7.8	t7.75 7.8
$\Delta\delta$	0.86	0.28	0.20	0.10	0.13	0.11	—	—	—	—	0.61	-0.15	0.24

^a Chemical shifts (δ) relative to TMS ($\delta = 0$); $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$; scalar coupling constants in Hz.

Table 5. ¹H NMR data^a for complexes *fac*-[ReX(CO)₃(BMPz)] (X = Cl, Br, or I) in CD₂Cl₂ at -50°C

Ligand X	δ_A	δ_B	δ_M	δ_L	δ_C	δ_K	δ_D	δ_J	δ_E	δ_I	δ_F	δ_H	δ_G
							J_{DE}	J_{JI}	J_{ED}	J_{IU}	J_{FG}	J_{HG}	J_{GH}
BMPz	s2.5	s5.86	s2.15	s5.86	s2.15	s2.15	s5.23	s5.23	s5.23	s5.23	d6.54	d6.54	t7.53
Cl	s2.58	s6.07	s2.20	s5.93	s2.39	s2.13	d7.01	d5.56	d5.60	d5.27	d7.41	d6.18	t7.76
$\Delta\delta$	0.43	0.21	0.05	0.07	0.24	-0.02	17.7	15.7	17.7	15.7	7.4	7.8	7.8
Br	s2.61	s6.08	s2.20	s5.94	s2.41	s2.17	d7.01	d5.49	d5.57	d5.28	d7.43	d6.15	t7.76
$\Delta\delta$	0.46	0.22	0.05	0.08	0.26	0.02	17.5	15.8	17.5	15.8	7.1	7.8	7.8
I	s2.61	s6.14	s2.22	s5.95	s2.43	s2.20	d6.94	d5.38	d5.51	5.26	d7.42	d6.11	t7.77
$\Delta\delta$	0.46	0.26	0.07	0.09	0.28	0.05	17.4	15.2	17.4	15.2	6.3	7.8	7.8
							—	—	—	—	0.88	-0.43	0.24

^aChemical shifts (δ) are relative to TMS ($\delta = 0$); $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$; scalar coupling constants in Hz.

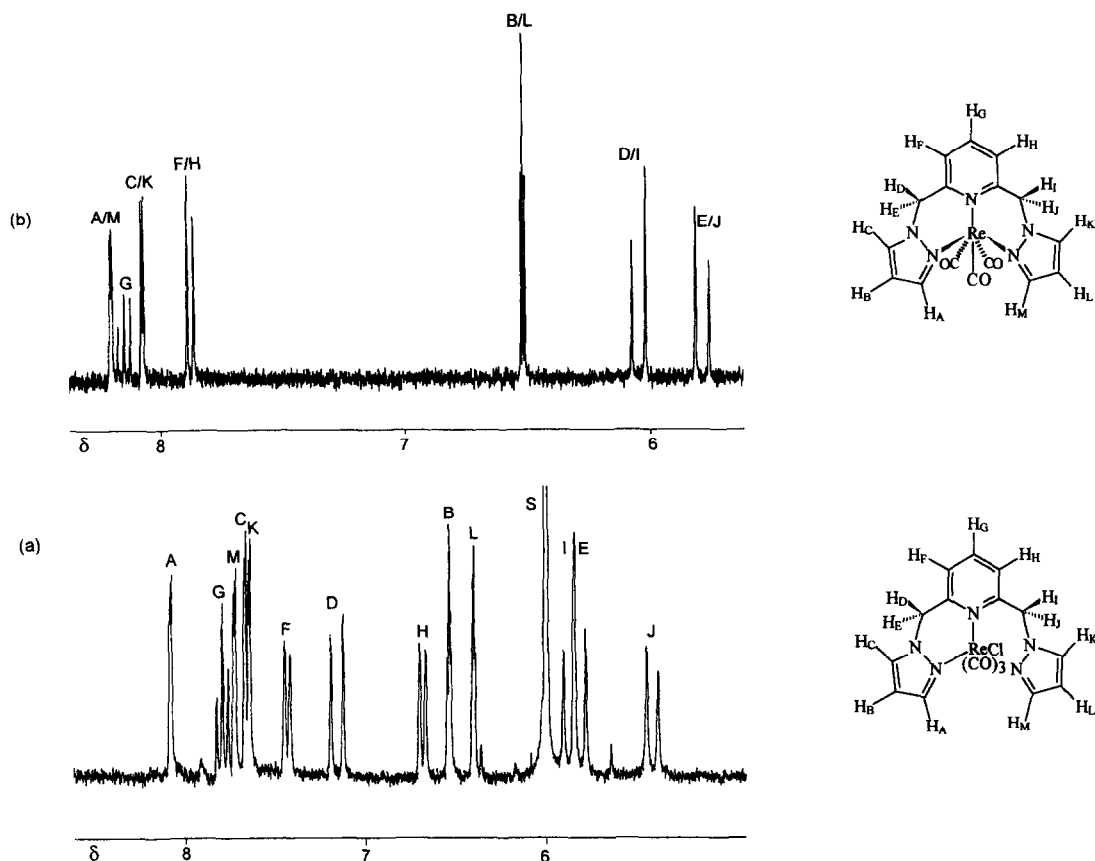


Fig. 2. ¹H NMR spectra of (a) *fac*-[ReCl(CO)₃(BPz)] in (CDCl₂)₂ and (b) *fac*-[Re(CO)₃(BPz)]Cl in CD₃CN both recorded at room temperature. Note that the scale expansions are different for the two cases. S = solvent.

bon atom C(9) pointing towards the halide. None of the heterocycles is co-planar.

¹H NMR chemical shifts (δ) and coordination shifts ($\Delta\delta$) for bidentate complexes of BPz and BMPz are listed in Tables 4 and 5, respectively. Inspection of these data allows a number of observations to be made. For the free ligands BPz and BMPz the preferred conformations probably will involve the structure shown in Scheme 1. Note that in the case of BPz the assignments of signals due to H_A and H_C are rather tentative and could be reversed in Table 4. The *meta* protons of the pyridyl ring experience a significant high frequency coordination shift on complexation arising from the change of orientation of the pyrazole ring from that shown in Scheme 1 to a *cisoidal* orientation with respect to the pyridyl nitrogen (see head of Table 4).

For the BPz complexes (Table 4) signal H_F shows a trend in which $\Delta\delta$ decreases with the increase of electrophilicity of the metal centre. This is consistent with the characteristic distribution of partial charge in aromatic six-membered heterocycles. Signal H_A shows a significant high frequency coordination shift. The trend in $\Delta\delta$ is explained by a reduction in the electronic density in the C=N double bond of the metal-bound nitrogen as a result of the increase in metal electrophilicity. This consequently reduces the

strength of the anisotropic magnetic field caused by this C=N bond, and thus reduces the deshielding field that affects signals H_A. The trend in H_M shifts can also be attributed to the anisotropic magnetic field decreasing with the increase in electrophilicity of the metal. Other coordination shifts do not show any trends of major significance. It is noteworthy that both methylene groups form AB spin systems. This shows that the pairs of protons are diastereotopic. The assignments are only tentative and are based primarily on the differing internal chemical shifts of the geminal pairs. The methylene hydrogens of the chelate ring are assumed to differ more in their chemical shifts than the geminal hydrogens of the pendant part of the ligand. Assignments of individual geminal hydrogens are uncertain. Considering the chelate side, since the chemical shift of H_E shows a strong halogen influence (Table 4), H_E is assumed to be *cis* to the axial halide ligand. Distinction between the hydrogens H_I and H_J on the pendant side is less clear because of the effects of C—C bond rotation of this part of the ligand.

In the BMPz complexes (Table 5) there are also notable high frequency shifts for signals H_A and H_F. Both pairs of methylene protons are diastereotopic and appear as AB spin systems. As for BPz their assignment is based primarily on the differing internal chemical shifts and halogen dependencies of shifts.

Table 6. Analytical data for the complexes *fac*-[Re(CO)₃(BPz)]X (X = Cl, Br, I, or PF₆) and *fac*-[PtMe₃(BPz)]X (X = I or PF₆)

Complex	M.p. (°C)	Yield ^a	νCO ^b (cm ⁻¹)	ν(PF ₆) ^c (cm ⁻¹)	Analysis ^d (%)			Λ _M ^e (Ω ⁻¹ cm ² mol ⁻¹)
					C	H	N	
[Re(CO) ₃ (BPz)]Cl	278/81 (dec)	93	2037s 1934vs,br	—	36.6 (38.9) ^f	2.9 (3.4) ^f	10.8 (11.3) ^f	112.0
[Re(CO) ₃ (BPz)]Br	321/4 (dec)	87	2038s 1938s,br	—	32.6 (32.5)	2.2 (2.2)	11.9 (11.5)	127.3
[Re(CO) ₃ (BPz)]I	303/6 (dec)	87	2039s 1940vs,br	—	33.7 (33.5) ^g	2.4 (2.4) ^g	10.4 (10.4) ^g	133.0
[Re(CO) ₃ (BPz)]PF ₆	302/4 (dec)	99	2037s 1936s 1907m	949s,br	29.4 (29.2)	2.0 (1.9)	10.7 (10.4)	—
[PtMe ₃ (BPz)]I	225/7	91	—	—	31.7 (31.5)	3.7 (3.5)	11.5 (11.4)	142.2
[PtMe ₃ (BPz)]PF ₆	306/9	97	—	850s,br	30.8 (30.5)	3.5 (3.3)	11.2 (10.7)	—

^a Yield quoted relative to metal containing reactant.

^b Recorded as chloroform solution; s = strong, vs = very strong, br = broad, m = medium, sh = shoulder.

^c Recorded as KBr disc.

^d Calculated values in parentheses.

^e Recorded in acetonitrile.

^f Figures allow for solvent of crystallisation; [Re(CO)₃(BPz)]Cl · THF.

^g Figures allow for solvent of crystallisation; [Re(CO)₃(BPz)]I · 0.5C₆H₆.

All attempts to prepare complexes of the type [PtI-Me₃(L-L)] (L-L = BPz or BMPz) by reaction of L-L with [PtI-Me₃]₄ or with [PtI-Me₃(Et₂S)₂] led to ionic materials (see later) or to mixtures of products that could not be satisfactorily characterised.

Solutions of the complexes [ReX(CO)₃(BPz)] were investigated by ¹H NMR at above-ambient temperatures in an attempt to identify any 1,4-metallotropic shifts analogous to those previously seen in similar complexes of terpy [1], bpy [2], and BIP [3]. None were detected, however, presumably as a result of the methylene linkage between the pyridyl and pyrazolyl rings introducing many more degrees of freedom into the pendant arm of the ligand, making it less likely that the pyrazolyl nitrogen donor will be suitably placed to attach to the rhenium atom during any fluxional twisting process [6]. The NMR spectra did, however, provide evidence for these present BPz complexes undergoing irreversible change, and this was further investigated (see below).

Terdentate complexes

By prolonged reaction under the same moderate conditions used for the synthesis of the bidentate complexes, ligand BPz forms the ionic complexes, *fac*-[Re(CO)₃(BPz)]X (X = Cl, Br, or I). These terdentate ligand complexes differ significantly from their bidentate counterparts on account of their higher symmetry and stereochemical rigidity. Whereas all thirteen hydrogens of the bidentate complex are non-equivalent, there are only seven NMR-distinct hydrogen environments in the terdentate species. The difference

is illustrated by the ¹H spectra of the pair of complexes, *fac*-[ReCl(CO)₃(BPz)] and *fac*-[Re(CO)₃(BPz)]Cl in Fig. 2. (It should be noted that these spectra were, of necessity, recorded in different solvents and the chemical shift scales are not precisely the same.) The ionic compounds can also be prepared in high yields by the direct reaction of a rhenium pentacarbonyl halide with an equimolar amount of ligand. The direct reaction of BPz with trimethylplatinum iodide also produced an ionic complex (Table 6). The ionic nature of these complexes was inferred from conductivity measurements and by adding ammonium hexafluorophosphate to an ethanolic solution of *fac*-[Re(CO)₃(BPz)]Cl to instantaneously form *fac*-[Re(CO)₃(BPz)]PF₆, or by performing the same procedure with *fac*-[PtMe₃(BPz)]I to produce *fac*-[PtMe₃(BPz)]PF₆. Measurements of conductivity confirmed that these complexes are all 1:1 electrolytes [21] in acetonitrile solutions (Table 6). In these ionic complexes BPz is again acting as a terdentate chelate ligand.

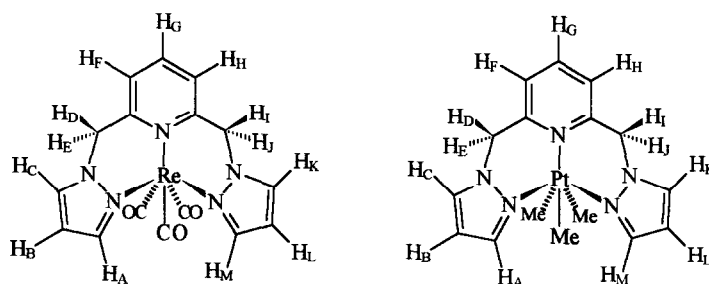
Mass spectra were recorded for [Re(CO)₃(BPz)]I, [Re(CO)₃(BPz)]PF₆ and [PtMe₃(BPz)]I (Table 2). For all three complexes the highest *m/z* represents a loss of the anion as expected, [M-X]⁺ (X = I or PF₆). This is also the most abundant fragment. For all cases the observed and calculated isotope patterns are in agreement. In the infrared spectrum the carbonyl stretching vibrations for the rhenium complexes show a strong absorption band at high wavenumber and a broad absorption at lower value. It is apparent that this broad band is in fact composed of two unresolved absorptions. In [Re(CO)₃(BPz)]PF₆ these absorptions

are sufficiently separated to occur as separate bands (Table 6). For all point groups possible for this tricarbonyl octahedral rhenium centre there are three infra-red-active absorptions expected in the carbonyl region. However in view of the high *trans* effect of the carbonyl groups and the tripodal nature of BPz, the most likely structure is one in which the carbonyls and BPz are in a *facial* conformation. The preparation of *fac*-[PtMe₃(BPz)]X (X = I or PF₆) supports this conclusion.

¹H NMR spectra of these complexes were recorded in deuterated acetonitrile at 30°C. Chemical shifts (δ) and coordination shifts ($\Delta\delta$) are listed in Table 7. In the ionic complexes, with the BPz ligand bonded in a terdentate fashion, a plane of symmetry bisects the pyridyl and passes through an axial ancillary ligand (CO or Me). This provides a symmetrical environment and results in much simplified ¹H NMR spectra compared with the neutral bidentate compounds. The coordination shifts are all positive, and for most signals are of greater magnitude than in the neutral com-

plexes. The pyridyl *meta* signals H_F/H_H experience the relative deshielding due to coordination to the metal as for H_F in the neutral complexes. The notable high frequency shifts for signals H_A/H_M, H_C/H_K and H_G indicate the dramatic changes affecting the molecule compared to the neutral complexes. There is no apparent trend of $\Delta\delta$ with the counter ion X (X = Cl, Br, I, or PF₆). The methylene protons give rise to an AB quartet. Assignments of H_D/H_J and H_E/H_I are tentative, and are based on the assumption that H_D/H_I experience the deshielding of the anisotropic magnetic field of the C=C double bond of the pyrazolyl rings and that H_E/H_I experience the shielding effects of the anisotropic fields of the equatorial carbonyls. The notable coordination shift, $\Delta\delta$, in H_G may be a consequence of the electrophilicity of the metal centre. The magnitudes of $\Delta\delta$ in signals H_A/H_M are probably due to the fact that these nuclei fall in the deshielding fields of the C=N bond of the opposing pyrazolyl ring. The effect of metal coordination is also evident. Similarly, the $\Delta\delta$ values of signals H_C/H_K are probably due to

Table 7. ¹H NMR data^a for complexes *fac*-[Re(CO)₃(BPz)]X (X = Cl, Br, I, or PF₆) and *fac*-[PtMe₃(BPz)]X (X = I or PF₆) in CD₃CN at 30°C



Compound	$\delta_{A,M}$ J_{AB}/J_{ML}	$\delta_{B,L}$ J_{BC}/J_{LK}	$\delta_{C,K}$ J_{CB}/J_{KL}	$\delta_{D,I}$ J_{DE}/J_{JI}	$\delta_{E,J}$ J_{ED}/J_{JI}	$\delta_{F,H}$ J_{FG}/J_{HG}	δ_G J_{GF}/J_{GH}	$\delta_{Me,eq}$ J_{Pt-H}	$\delta_{Me,ax}$ J_{Pt-H}
BPz	d7.51 1.5	t6.33 2.2	d7.68 2.2	s5.41 —	s5.41 —	d6.91 7.8	t7.67 7.8	—	—
[Re(CO) ₃ (BPz)]Cl	d8.20 2.6	t6.52 2.6	d8.07 2.6	d6.05 16.5	d5.78 16.5	d7.88 7.7	t8.15 7.7	—	—
$\Delta\delta$	0.69	0.19	0.39	—	—	0.97	0.48	—	—
[Re(CO) ₃ (BPz)]Br	d8.21 2.5	t6.51 2.5	d8.08 2.5	d6.04 16.5	d5.78 16.5	d7.90 7.8	t8.16 7.8	—	—
$\Delta\delta$	0.70	0.18	0.40	—	—	0.99	0.49	—	—
[Re(CO) ₃ (BPz)]I	d8.20 2.6	t6.52 2.6	d8.06 2.6	d6.00 16.5	d5.79 16.5	d7.89 7.9	t8.17 7.9	—	—
$\Delta\delta$	0.69	0.19	0.38	—	—	0.98	0.50	—	—
[Re(CO) ₃ (BPz)]PF ₆	d7.93 2.5	t6.50 2.5	d8.17 2.5	d5.80 16.8	d5.80 16.8	d7.78 7.9	t8.13 7.9	—	—
$\Delta\delta$	0.42	0.17	0.49	—	—	0.87	0.46	—	—
[PtMe ₃ (BPz)]I	d7.98 2.5	t6.48 2.5	d7.90 2.5	d5.52 16.2	d5.83 16.2	d7.74 7.8	t8.08 7.8	1.07 71.8	1.41 71.3
$\Delta\delta$	0.47	0.15	0.22	—	—	0.83	0.41	—	—
[PtMe ₃ (BPz)]PF ₆	d8.17 2.5	t6.50 2.5	d7.93 2.5	d5.47 16.2	d5.82 16.2	d7.78 7.8	t8.13 7.8	1.06 71.8	1.41 71.3
$\Delta\delta$	0.66	0.17	0.25	—	—	0.87	0.46	—	—

^aChemical shifts (δ) relative to TMS ($\delta = 0$); scalar coupling constants in Hz; $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$.

these nuclei falling in the deshielding fields of the C=C bond of the opposing ring. Both these suggestions are supported by a study of a model of the complex.

All Pt—Me signals have associated ^{195}Pt satellites. It will be seen from Table 7 that the magnitudes of the couplings $^2J_{\text{Pt-H}}$ are greater for the equatorial methyl groups than for the axial methyl group, implying that for this complex the pyrazolyl rings exert a stronger *trans* influence than the pyridyl. It is also notable that the equatorial signals appear at lower frequencies than the axial. This is probably due to the deshielding field of the C=N bonds of the pyrazolyl rings. The fact that the Pt—Me signals appear at positive chemical shifts is also an indication of the *facial* arrangement of the methyl groups. For complexes of Pt^{IV} in which there are methyl groups *trans* to each other, the chemical shifts appear at negative chemical shifts. This is the case for complexes $\text{Li}_2[\text{PtMe}_6]$ ($\delta = -0.55$ in deuterated ether), $[(\text{Me}_3\text{P})_2\text{PtMe}_4]$ ($\delta = -0.35$ in CDCl_3) and $[(\text{Me}_2\text{PhP})_2\text{PtMe}_4]$ ($\delta = -0.23$ in CDCl_3) [22].

Attempts to prepare ionic complexes of rhenium for BMPz, either by heating *fac*- $[\text{ReX}(\text{CO})_3(\text{BMPz})]$ or by direct reaction of the ligand with $\text{ReX}(\text{CO})_5$, lead to decomposition. A similar result was obtained by direct reaction of $[\text{Pt}(\text{Ime}_3)_4]$ with the ligand. These findings can be rationalised on the basis that the iso-electronic $\text{Re}(\text{CO})_3$ and PtMe_3 moieties strongly favour a *facial* configuration whereas the BMPz ligand in a terdentate bonding mode in an octahedral environment is unlikely to adopt a *facial* configuration because of steric interactions.

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