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Alcohol activation by [Ir(COD)(tris(pyrazol-1-yl)methane)]$^+$ and [Ir(COD)(tris(pyrazol-1-yl)ethane]$^+$ cations: formation of alkoxycarbonyl derivatives [(tpzm)IrH(CO_2R')(CO)]$^+$ and [(tpze)IrH(CO_2R')(CO)]$^+$ (R' = Me, Et, i-Pr)

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Abstract

The reactions of iridium and rhodium complexes derived from tris(pyrazolyl)-methane (tpzm) and tris(pyrazolyl)ethane (tpze) have been examined. One of the most interesting reactions involves the formation of alkoxycarbonyl derivatives of iridium tris(pyrazolyl)alkanes from carbon monoxide and alcohols. In the case of rhodium derivatives, a dimer of formula $[(tpzm)_2Rh_2(CO)_3](ClO_4)_2$ has been obtained. A careful ^1H and ^{13}C NMR study has allowed assignment of all the signals of the compound $[(tpzm)IrH(CO_2Me)(CO)]BF_4$.

Introduction

We recently described the preparation of the cationic diolefin complexes of formulae $[Rh(bpzm)(diolefin)]^+$ [1], and $[M(tpzm)(diolefin)]^+$ (M = Rh or Ir) [2], where bpzm and tpzm are bis(pyrazol-1-yl)methane and tris(pyrazol-1-yl)methane, respectively. The cations $[Rh(bpzm)(diolefin)]^+$ react with CO to form the di-carbonyl complex $[Rh(CO)_2(bpzm)]^+$, which is inert towards methanol [1]. In continuation of this work, we now report an unusual activation of methanol by the cations $[Ir(COD)(tpzm)]^+$ and $[Ir(COD)(tpze)]^+$ (tpze = tris(pyrazol-1-yl)ethane, $MeCpz_3$), which leads to the formation of new methoxycarbonyl compounds. A similar activation has been reported for the complex $[(C_5Me_5)RhCl_2]_2$, which reacts with CO and methanol in the presence of triethylamine to give $[(C_5Me_5)Rh(CO_2Me)_2(CO)]$ [3].

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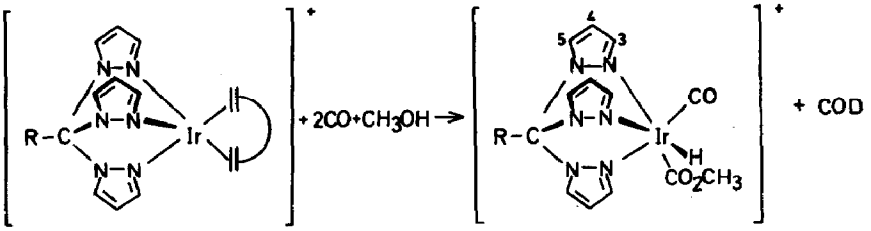


R=H (3), Me (4)

In this context, it is noteworthy that the neutral tridentate ligand tpzm is isosteric with the anions $[HBpz_3]^-$ and $[MeGapz_3]^-$, which react similarly. Thus, the related complexes $[Pt(CH_3)(HBpz_3)L]$ [4,5] and $[Pt(CH_3)(tpzm)L]^+$ [6] (L = CO, olefin, or acetylene) have been reported. Furthermore, the anionic ligands $[HBpz_3]^-$ and $[MeGapz_3]^-$ are 6-electron donors, like the cyclopentadienyl ligand, and much of the chemistry developed with these anions involves compounds whose Cp analogues are well established; for example, $[CpRu(HBpz_3)]$ [7] and $[RuCp_2]$ [8] or $[(HBpz_3)_2Rh_2(CO)_3]$ [9] and $[(MeGapz_3)_2Rh_2(CO)_3]$ [14] and $[Cp_2Rh_2(CO)_3]$ [15].

Results and discussion

Iridium complexes

Recently, we reported that the complex $[IrCl(COD)]_2$ reacts with tpzm in 1/1 molar to form the ion-pair complex $[Ir(COD)(tpzm)][IrCl(COD)]_2$ (**1**) [2]. Similarly, addition of tpze to a dichloromethane solution of $[IrCl(COD)]_2$ gives $[Ir(COD)(tpze)][IrCl_2(COD)]$ (**2**), according to eq. 1. Thus, the presence of a methyl group on

$$[IrCl(COD)]_2 + L \xrightarrow{CH_2Cl_2} [Ir(COD)L]^+ + [IrCl_2(COD)]^- \quad (1)$$

the sp^3 carbon does not affect the mode of reaction of the ligand.

Treatment of a dichloromethane solution of the cations **1** or **2** as the tetrafluoroborate salt * with bubbling CO and an excess of methanol at room temperature produces, after 2 h, a colourless solution. Evaporation of the solvent in vacuo and addition of diethyl ether gives white solids. The C, H, N analysis, IR and ^1H NMR spectra are consistent with formulation of the products as methoxycarbonyl complexes, produced according to eq. 2.

The analogous $[(tpzm)IrH(CO_2R')(CO)]^+$ (R' = Et, **5**, i-Pr, **6**) and $[(tpze)IrH(CO_2R')(CO)]^+$ (R' = Et, **7**, i-Pr, **8**) compounds can be made by reaction of CO with **1** or **2** in ethanol (R' = Et) or isopropanol (R' = i-Pr).

The IR and ^1H NMR data for compounds **3–8** are listed in Tables 1 and 2. The IR spectra (Nujol) show the absorptions due to the BF_4^- anion with T_d symmetry, along with bands characteristic of coordinated ligands tpzm or tpze and three

* The $[Ir(COD)L]BF_4$ complexes were prepared "in situ" by reaction of $[IrCl(COD)]_2$ with the ligand (tpzm or tpze) in the presence of $AgBF_4$ (see Experimental).

Table 1

IR (Nujol) data for complexes 3–8 (in cm^{-1})

Compounds	ν(Ir–H)	ν(CO)	
		Ir–CO	Ir–CO_2R'
[(tpzm)IrH(CO_2Me)(CO)]BF_4 (3)	2191	2086 2061	1650,1642
[(tpze)IrH(CO_2Me)(CO)]BF_4 (4)	2191	2066	1655
[(tpzm)IrH(CO_2Et)(CO)]BF_4 (5)	2186(2205) [a]	2081(2072) [a] 2051	1642(1663) [a] 1630
[(tpze)IrH(CO_2Et)(CO)]BF_4 (6)	2186	2081	1655
[(tpzm)IrH(CO_2iPr)(CO)]BF_4 (7)	2200	2075	1648
[(tpze)IrH(CO_2iPr)(CO)]BF_4 (8)	2190	2070	1642

[a] In CH_2Cl_2.

absorption bands between 2200 and 1642 cm^{-1}: 2200–2186 cm^{-1} [ν(Ir–H)], 2086–2051 and 1655–1642 cm^{-1} [ν(CO)]. The bands between 1655 and 1642 cm^{-1} are characteristic of alkoxycarbonyl ligands [16]. The ^1H NMR ($CDCl_3$-Me_4Si) of 3–8 contains the signals of non-equivalent protons of the ligands tpzm or tpze along those coming from the CO_2R' groups, and a high-field signal (−16.70 and −16.43 ppm) that confirms the presence of a metal-hydride bond in the compounds.

In order to assign the various signals in the proton and ^{13}C NMR spectra, compound 3 was carefully studied. A Newman projection of this compound (only one enantiomer is shown) illustrates the origin of the anisochrony of pyrazolyl

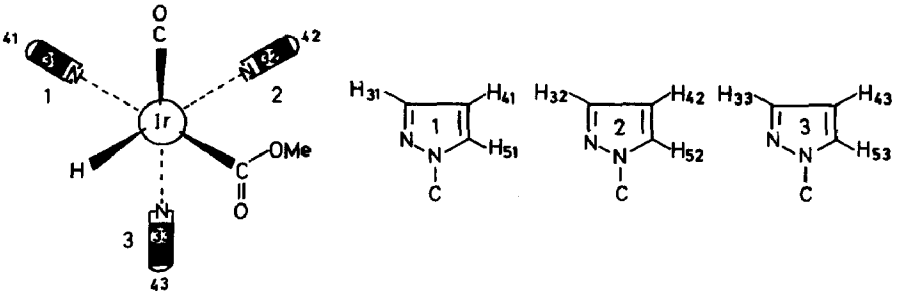
Table 2

^1H NMR chemical shifts (ppm) and coupling constants (Hz) for complexes 3–8 (in $CDCl_3$)

Compounds	H(3) [a]	H(4)	H(5)	R	R′	Ir–H
[(tpzm)IrH(CO_2Me)(CO)]BF_4 (3)	8.41 8.11 7.82	6.60–6.55	8.61–8.53	9.74(CH)	3.72(OMe)	−16.76
[(tpze)IrH(CO_2Me)(CO)]BF_4 (4)	8.34 8.05	6.64–6.36	8.67–8.41	3.64(CMe)	3.65(OMe)	−16.45
[(tpzm)IrH(CO_2Et)(CO)]BF_4 (5)	8.40 8.10 7.84	6.61–6.52	8.60–8.52	9.79(CH)	1.20(OCH$_2$*Me*) 4.20(O*CH*$_2$Me) *J* 7.0 Hz	−16.72
[(tpze)IrH(CO_2Et)(CO)]BF_4 (6)	8.40 8.09 7.80	6.65–6.45	8.63–8.50	3.64(CMe)	1.25(OCH$_2$*Me*) 4.19(O*CH*$_2$Me) *J* 7.3 Hz	−16.43
[(tpzm)IrH(CO_2iPr)(CO)]BF_4 (7)	8.41 8.08 7.82	6.60–6.51	8.59–8.50	9.73(CH)	1.27 and 1.23 (OCH*Me*$_2$) 5.12 (O*CH*Me$_2$) *J* 6.3 Hz	−16.79
[(tpze)IrH(CO_2iPr)(CO)]BF_4 (8)	8.45 8.10 7.80	6.62–6.55	8.59–8.52	3.61(CMe)	1.27 and 1.23 (OCH*Me*$_2$) 5.12 (O*CH*Me$_2$) *J* 6.4Hz	−16.44

[a] $J_{34} = 2.2 \pm 0.2$.

signals, and shows why those coming from H(3) and C(3) are the most sensitive.



Initially we carried out a COSY experiment, which allowed us to connect the three protons of each pyrazole ring:

	A	B	C	
H(3)	8.41	8.11	7.86	J_{34} 2.1 Hz
H(4)	6.55	6.60	6.56	J_{45} 2.8 Hz
H(5)	8.53	8.60	8.61	

Then we performed NOESY experiment in order to determine the configuration around the metal. A correlation between the hydride hydrogen and H(31) and H(33) protons and between the methoxycarbonyl hydrogens and H(32) and H(33) protons was expected. The reality was somewhat more complex. Some obvious correlations were observed [H(4) ↔ H(3),H(5); HC(sp)^3 ↔ H(5); H(hydride) ↔ Me(ester)], but the more significant were:

H(−16.76) ↔ H(3)(8.41) and H(3)(7.86)

$$MeO_2C(3.72) \leftrightarrow \begin{cases} H(4)(6.56) \text{ and } H(4)(6.60) \\ H(5)(8.60) \text{ and } H(5)(8.61) \\ H(3)(8.11) \end{cases}$$

It appears that the three pyrazolyl residues labelled A, B, C correspond to 1, 2 and 3, respectively, since the only signals unaffected by irradiation of the methoxycarbonyl protons are those of the A ring H(31), H(41), H(51)).

It is now possible to account for the chemical shifts of the protons at position 3 or, at least, the order in which they appear. Taking into account the anisotropic effects of double and triple C–O bonds (the C≡O bond was assumed to be similar to the C≡N bond) [17,18] we can present the picture shown in fig. 1 With this conformation of the ester group, protons H(31) and H(32) would be deshielded by the C≡O bond anisotropy, whereas protons H(32) and H(33) would be shielded by the C=O bond.

The ^{13}C NMR spectrum of compound **3** is very similar to that of compound **5** (See Experimental): HC, 76.8 ppm (^1J 167.1 Hz); CO, 161.4 ppm (^2J(OC–Ir–H) 8.1 Hz); CO_2Me, 155.8 (CO) and 51.8 ppm (Me, ^1J 146.0 Hz); C(3), 147.3 (^1J 197.4 Hz), 146.9 (^1J 193.9 Hz), 145.4 ppm (^1J 195.0 Hz); C(4), 109.4 (^1J 185.8 Hz), 109.2 (^1J 185.8 Hz), and 108.7 ppm (^1J 185.2 Hz); C(5), 134.9 and 134.6 ppm (2C)(^1J ~ 200 Hz).

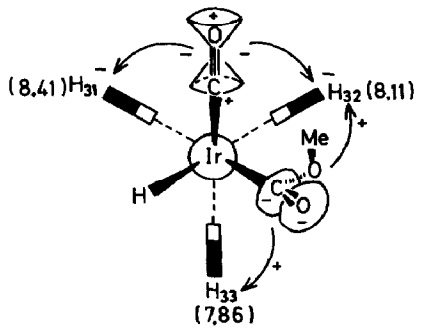


Fig. 1.

A 2D (^{1}H–^{13}C) correlated spectrum established the following relationships (Fig. 2):

	Position 3	Position 4	Position 5
Ring no 1	8.41 ↔ 147.3	6.55 ↔ 108.7	8.53 ↔ 134.6
Ring no 2	8.11 ↔ 145.4	6.60 ↔ 109.2	8.60 ↔ 134.9
Ring no 3	7.86 ↔ 146.9	6.56 ↔ 109.4	8.61 ↔ 134.6

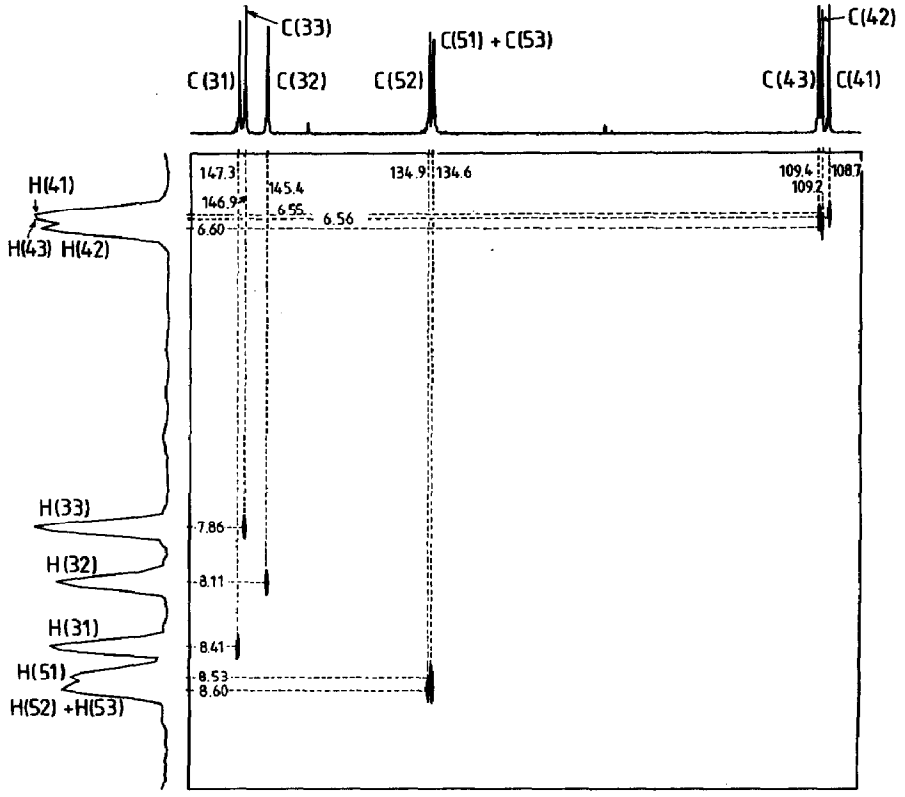
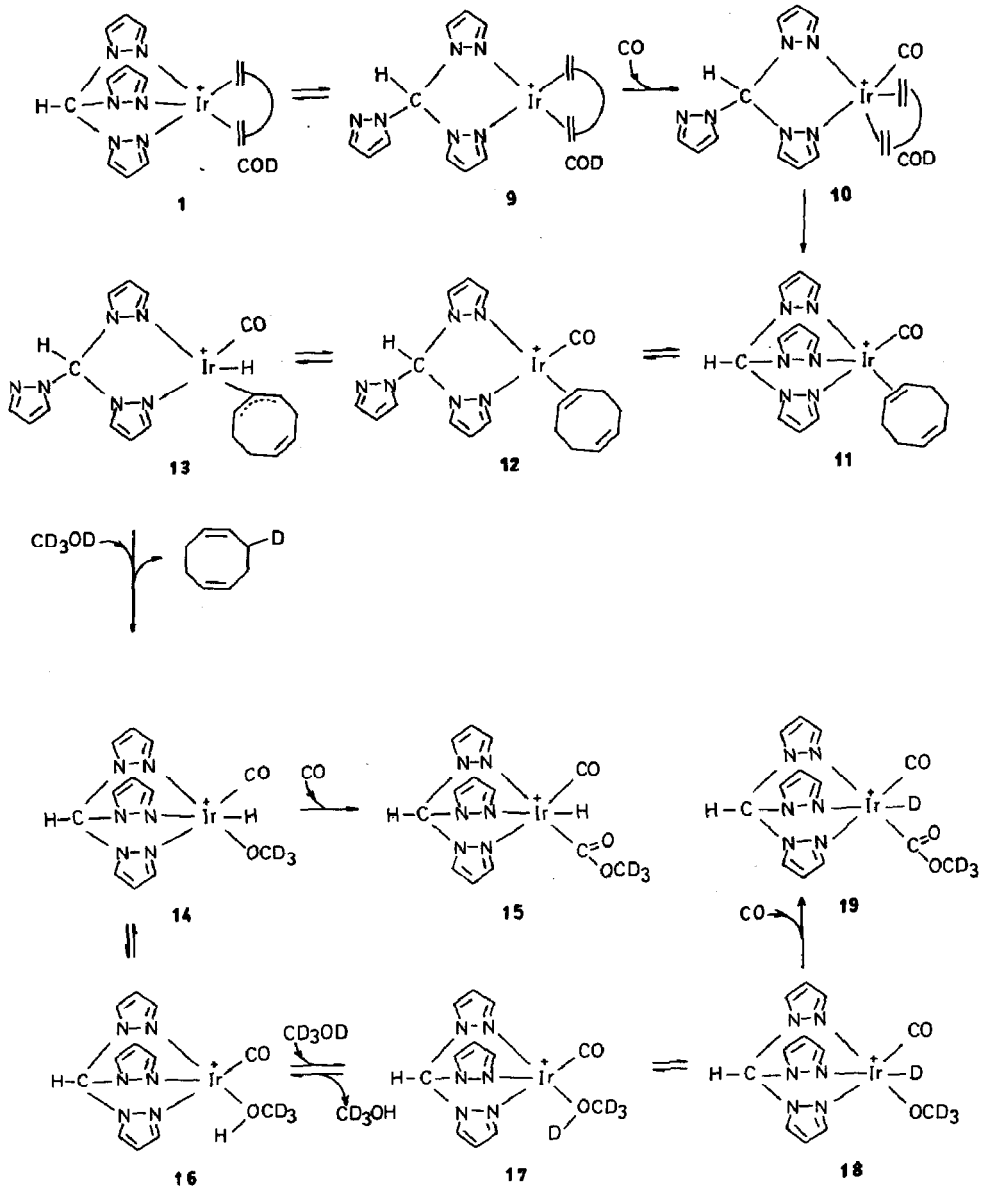


Fig. 2. 2D(^{1}H–^{13}C) correlated spectrum of cation 3.



Scheme 1.

As the chemical shifts in ^{13}C NMR are less sensitive to the anisotropy of the neighbouring groups than to other effects, such as electron density, the interpretation is more complex. However, it can be that C(3) of ring 1 is still the most deshielded signal for this position.

Cation 1 reacts with CO in CD_3OD to give a mixture of $[(tpzm)IrH(CO_2CD_3)(CO)]^+$ (**15**) and $[(tpzm)IrD(CO_2CD_3)(CO)]^+$ (**19**), plus $C_8H_{11}D$ and CD_3OH, detected by ^1H NMR. Scheme 1 shows a possible mechanism for this reaction.

We have previously shown that in solution **1** is in equilibrium with **9** [2]. The attack of CO upon the four-coordinated 16-electron intermediate would lead to **11**,

probably through **10**, as suggested by other authors in similar cases [9]. The formation of $C_8H_{11}D$ involves an intramolecular oxidative addition of a C–H sp^3 bond of the coordinate 1,5-cyclooctadiene followed by electrophilic attack by CD_3OD on the olefinic ligand, leading to formation of **14**. This intermediate then undergoes competing intramolecular reductive elimination to give **16** and CO-insertion to give **15**. The formation of **19** probably involves the insertion of a CO ligand into the Ir–OCD_3 bond in **18**, which could be formed by intramolecular oxidative addition of CD_3OD present in the reaction medium.

The attack of CO upon the thermally accessible four-coordinated 16-electron form of [$(HBpz_3)$Rh(COD)], followed by a sequence of displacement and associative steps in which the tris(pyrazol-1-yl)borate is alternately bidentate and tridentate has been proposed by Cocivera et al. for the formation of [$(HBpz_3)$Rh(CO)(η^2-COD)], which leads ultimately to [$(HBpz_3)_2Rh_2(CO)_3$] [9].

There are in the literature some other examples of methoxycarbonyl complexes of type [$IrClH(CO_2CH_3)(PMe_3)_3$] [10,11] and [$RhClH(CO_2CH_3)(PMe_3)_3$] [12,13], but in none of them did the preparation involve an insertion of a CO molecule into an Ir–OR bond, as in our case.

Rhodium complexes

The dimeric complex $[RhCl(COD)]_2$ reacts with the ligand tpzm in the presence of silver perchlorate to give the species $[Rh(COD)(tpzm)]^+$ (eq. 3) [2].

$$\tfrac{1}{2}[RhCl(COD)]_2 + AgClO_4 + tpzm \rightarrow \underset{\textbf{(20)}}{[Rh(COD)(tpzm)]ClO_4} + AgCl \qquad (3)$$

Bubbling carbon monoxide through a methanol solution of **20** leads to displacement of the coordinate olefin and formation of a mixture of $[Rh(CO)_2(tpzm)]ClO_4$ (**21**) and $[(tpzm)_2Rh_2(CO)_3](ClO_4)_2$ (**22**). Although we have not isolated **21** in a pure state, its IR (Nujol) spectrum (ν(CO) at 2095 and 2028 cm^{-1}) points to the proposed formulation when comparison is made with the spectrum of the ion-pair complex $[Rh(CO)_2(tpzm)][RhCl_2(CO)_2]$ (**23**), which was prepared by reaction of $[RhCl(CO)_2]_2$ with tpzm in acetone. In refluxing, two molecules of **21** condense to form **22**, with extrusion of CO (eq. 4).

$$2\underset{\textbf{(21)}}{[Rh(CO)_2(tpzm)]ClO_4} \rightarrow \underset{\textbf{(22)}}{[(tpzm)_2Rh_2(CO)_3](ClO_4)_2} + CO \qquad (4)$$

The IR (Nujol) spectrum of **22** shows one very strong ν(CO) band at 1865 cm^{-1}. The appearance of only a single peak, and its low frequency, suggest that the three CO ligands are doubly bridging. On the other hand, the 18-electron rule requires that the complex contains a metal–metal single bond (Fig. 3). The structure represented in Fig. 3 is very similar to that of the dimeric methyl tris(pyrazol-1-yl)gallato $[(MeGapz_3)_2Rh_2(CO)_3]$ [14], determined by X-ray crystallography, and that of the corresponding borato derivative $[(HBpz_3)_2Rh_2(CO)_3]$ [9]. Also related to these compounds are the η^5-cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)_2M_2(CO)_3]$ (M = Rh [15], Co [19]). The insolubility of the borato derivative has led some authors [14] to conclude that it could be a polymer.

Compound **22** insolubility likewise prevented recording of its NMR spectrum. However, a polymeric structure can be ruled out, since its ^{13}C NMR spectrum in the solid state (CP/MAS technique, see experimental part) shows only one kind of

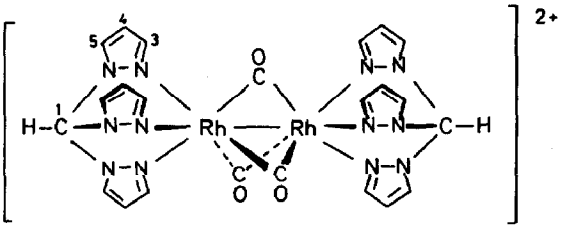


Fig. 3. Structure of the dinuclear cation **22**.

pyrazole, which is consistent only with a highly symmetric structure, such as that shown in **22**.

In conclusion, the cation $[M(COD)L]^+$ (M = Ir, L = tpzm, tpze; M = Rh, L = tpzm) reacts with carbon monoxide in methanol to give rather unusual products. The formation of the unexpected methoxycarbonyliridium(III) complexes is observed for this metal, whilst the binuclear dirhodium $[(tpzm)_2Rh_2(CO)_3]^{2+}$ cation is the final product for M = Rh.

Experimental

All reactions were carried out under nitrogen by Schlenk techniques. Starting materials tpzm [21], $[IrCl(COD)]_2$ [22], $[Rh(COD)(tpzm)]ClO_4$ [2], and $[RhCl(CO)_2]_2$ [23] were prepared by published methods. Tris(pyrazol-1-yl)ethane was prepared by methylation of tris(pyrazol-1-yl)methane, as described by Katritzky [24] for other derivatives; m.p. 92–93°C (hexane/ether), ^1H NMR ($CDCl_3$, ppm) 2.98 (s, CH_3), 6.33 (q, H_4), 6.85 (q, H_5), 7.69 (q, H_3), J_{34} 1.8, J_{45} 2.6, J_{35} 0.8 Hz. The complexes $[Ir(cod)(tpzm)]BF_4$ and $[Ir(COD)(tpze)]BF_4$ were prepared in situ by reaction of $[IrCl(COD)]_2$ with tpzm or tpze ligands in the presence of $AgBF_4$. The cation $[Ir(COD)(tpze)]^+$ (**2**) was isolated as the $[IrCl_2(COD)]$ salt. The other iridium cations were isolated as their BF_4 salts.

C, H, N, analyses were determined with a Perkin–Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin–Elmer 783 spectrometer. ^1H NMR spectra were recorded on a Bruker AC200 spectrometer working at 200 MHz, spectral width SW: 2000–6000 Hz, memory size SI: 16 K, relaxation delay RD: 0 s, pulse width PW: 7.5 μs (90° flip angle). The ^{13}C NMR spectra at 50 MHz were recorded on the same spectrometer, SW: 10000 Hz, SI: 32 K, acquisition time AQ: 1.6 s, PW: 3.2 μs, RD: 1s. Chemical shifts are given in ppm from TMS (δ) and coupling constants (J) in Hz for $CDCl_3$ solutions of 10% concentration (w/v). The data acquisition parameters for the heteronuclear (^1H–^{13}C) 2D-correlation experiment were: F_1 domain (SI1: 128 W, SW1: 500 Hz, relaxation delay D1: 3 s), F_2 domain (SI2: 4 K, SW2: 2800 Hz), number of transients per FID, NS: 128, number of preparatory dummy transients per FID, *DS*: 0. For the 2D-COSY experiment: F_1 domain (SI1: 2 K, SW1: 234 Hz, D1: 2 s), F_2 domain (SI2: 4 K, SW2: 468 Hz), NS: 16, *DS*: 2, and, finally, for the 2D-NOESY experiment: F_1 domain (SI1: 1 K, SW1: 2800 Hz, *D1*: 2 s), F_2 domain (SI2: 2 K SW2: 5600 Hz), NS: 64, *DS*: 2. All the 2D experiments were processed with a sine bell window (WDW1 = WDW2 = *S*, SSB1 = SSB2 = 0) [20].

Preparation of [Ir(COD)(tpzm)][IrCl$_2$(COD)]. A solution of [IrCl(COD)]$_2$ (100 mg, 0.15 mmol) in 20 ml of dichloromethane was treated with tpzm (34.0 mg, 0.15 mmol) and the mixture was stirred for 30 min at room temperature. The yellow precipitate was filtered off, repeatedly washed with hexane, and dried in vacuo; yield 111 mg (76%). The crystals contain one mol of CH_2Cl_2 per mol of complex. Anal. Found: C, 33.59; H, 3.94; N, 8.40. $C_{28}H_{38}N_6Cl_4Ir$ calcd.: C, 34.16; H, 3.89; N, 8.53%. ^{1}H NMR ($CDCl_3$, ppm) 8.67 (d, 3H, H(5)), 7.94 (d, 3H, H(3)), 6.53 (q, 3H, H(4), J_{34} 2.1, J_{45} 2.4 Hz), 5.30 (s, 2H, CH_2Cl_2), 3.90 (m, 4H, =CH, COD_{anion}), 3.76 (s, 3H, CH_3–Cpz_3), 3.58 (m, 4H, =CH, COD_{cation}), 2.41 (m, 4H, CH_2, COD_{cation}), 2.28 (m, 4H, CH_2, COD_{anion}), 1.75 (m, 4H, COD_{cation}), 1.42 (m, 4H, CH_2, COD_{anion}).

Preparation of [(tpzm)IrH(CO$_2$Me)(CO)]BF$_4$. A solution of [IrCl (COD)]$_2$ (100.0 mg, 0.15 mmol) in 20 ml of dichloromethane was treated with tpzm (65.0 mg, 0.30 mmol) and $AgBF_4$ (60.0 mg, 0.30 mmol) and the mixture then stirred for 1 h. The AgCl was removed by filtration through kieselguhr. The yellow filtrate was treated with 3 ml of methanol and carbon monoxide was bubbled through the solution for 2 h at room temperature. The resulting colourless solution was concentrated in vacuo. Addition of diethyl ether gave a white precipitate, which was filtrated off, and recrystallized from dichloromethane/ether; yield 109.5 mg (64%). Anal. Found: C, 26.85; H,2.56; N, 13.96. $C_{13}H_{14}N_6O_3BF_4Ir$ calcd.: C, 26.86; H, 2.43; N, 14.46%.

Preparation of [(tpze)IrH(CO$_2$Me)(CO)]BF$_4$. The complex was prepared by the procedure described for [(tpzm)IrH(CO_2Me)(CO)]BF_4 from [IrCl(COD)]$_2$ (100.0 mg, 0.15 mmol), tpze (68.0 mg, 0.30 mmol), $AgBF_4$ (60.0 mg, 0.30 mmol) and methanol (3 ml). 94.0 mg (53%) of the white complex were obtained. Anal. Found: C, 28.61; H, 2.77; N, 13.93. $C_{14}H_{16}N_6O_3BF_4Ir$ calcd.: C, 28.24; H, 2.71; N, 14.12%.

Preparation of [(tpzm)IrH(CO$_2$Et)(CO)]BF$_4$. The complex was prepared by the procedure described for [(tpzm)IrH(CO_2Me)(CO)]BF_4 from [IrCl(COD)]$_2$ (200.0 mg, 0.30 mmol), tpzm (128.0 mg, 0.60 mmol), $AgBF_4$ (120.0 mg, 0.60 mmol) and ethanol (3 ml). 304.2 mg (86%) of the white complex were obtained. Anal. Found: C, 28.45; H, 2.73; N, 14.00%. $C_{14}H_{16}N_6O_3BF_4Ir$ calcd.: C, 28.24; H, 2.71; N, 14.12%.

Preparation of [(tpze)IrH(CO$_2$Et)(CO)]BF$_4$. The complex was prepared by the procedure described for [(tpzm)IrH(CO_2Me)(CO)]BF_4 from [IrCl(COD)]$_2$ (150.0 mg, 0.22 mmol), tpze (100.0 mg, 0.44 mmol), $AgBF_4$ (86.9 mg, 0.45 mmol) and ethanol (3 ml). 200.0 mg (74%) of the white complex were obtained. Anal. Found: C, 29.39; H, 3.09; N, 13.71. $C_{15}H_{18}N_6O_3BF_4Ir$ calcd.: C, 29.58; H, 2.98; N, 13.79%. The ^{13}C NMR spectrum shows the presence of the ligands CO (161.6), ethoxycarbonyl (155.3, 60.4 and 14.7) and the non-equivalent pyrazolyl signals (C(3): 147.2, 146.8 and 145.2; C(4): 109.4, 109.2 and 108.4; C(5): 134.9, 134.8 and 134.6).

Preparation of [(tpzm)IrH(CO$_2$iPr)(CO)]BF$_4$. The complex was prepared by the procedure described for [(tpzm)IrH(CO_2Me)(CO)]BF_4 from [IrCl(COD)]$_2$ (100.0 mg, 0.15 mmol), tpzm (64.0 mg, 0.30 mmol), $AgBF_4$ (60.0 mg, 0.30 mmol) and propan-2-ol (3 ml). 120.3 mg (66%) of the white complex were obtained. Anal. Found: C, 29.79; H, 3.29; N, 14.01. $C_{15}H_{18}N_6O_3BF_4Ir$ calcd.: C, 29.58; H, 2.98; N, 13.79%.

Preparation of [(tpze)IrH(CO$_2$iPr)(CO)]BF$_4$. The complex was prepared by the procedure described for [(tpzm)IrH(CO_2Me)(CO)]BF_4 from [IrCl(COD)]$_2$ (150.0 mg, 0.22 mmol), tpze (100.0 mg, 0.44 mmol), $AgBF_4$ (86.9 mg, 0.45 mmol) and

propan-2-ol (3 ml). 123.4 mg (44%) of the white complex were obtained. Anal. Found: C, 30.70; H, 3.88; N, 13.79. $C_{16}H_{20}N_6O_3BF_4Ir$ calcd.: C, 30.83; H, 3.23; N, 13.48.

Preparation of [(tpzm)IrH(CO_2CD_3)(CO)]BF_4 and [(tpzm)IrD(CO_2CD_3)(CO)]BF_4. A solution of [Ir(tpzm)(COD)]BF_4 (200.0 mg, 0.34 mmol) in 3 ml of deuteromethanol was stirred at room temperature under CO, for 2 h. The ^1H NMR spectrum of the colourless solution formed showed the presence of CD_3OH (4.78, s), $C_8H_{11}D$ (5.67, br, 4H, =CH; 2.45, br, 7H, CH_2) and signals of the mixture of [(tpzm)IrD(CO_2CD_3)(CO)]BF_4 and [(tpzm)IrH(CO_2CD_3)(CO)]BF_4. The solution was concentrated under reduced pressure, and diethyl ether was added to give a white precipitate, which was filtered off and dried in vacuo: 145.6 mg of solid were obtained. IR (Nujol): ν(Ir–H) 2195 (w) cm^{-1}; ν(CO) 2080(s), 2060(s), 1657(s), 1650(s), 1637(s) cm^{-1}; ν(Ir–D) 1572(m) cm^{-1}.

Preparation of [$(tpzm)_2Rh_2(CO)_3$]$(ClO_4)_2$. A solution of [Rh(COD)(tpzm)]ClO_4 (100 mg, 0.19 mmol) in 20 ml of dichloromethane and 3 ml of methanol was stirred at room temperature under CO for 2 h. The solution was concentrated under reduced pressure and diethyl ether added to give a yellow precipitate, which was filtered off and dried in vacuo: 85.1 mg of solid were obtained. IR (nujol): ν(CO) 2095(s), 2028(s), 1865(m) cm^{-1}. 80.3 mg of this solid was treated with 10 ml of THF and the solution was refluxed for 30 min. The resulting yellow precipitate was filtered off, washed with diethyl ether, and dried in vacuo, yield 72 mg. Anal. Found: C, 29.72; H, 2.43; N, 17.93. $C_{23}H_{20}N_{12}O_{11}Cl_2Rh_2$ calcd.: C, 30.12; H, 2.20; N, 18.3. IR (Nujol): ν(CO) 1865 (vs) cm^{-1}. ^{13}C (solid, ppm): 144.6 (C(3)), 134.8 (C(5)), 109.7 (C(4)), 74.6 (C sp^3); the signal of the CO ligands was not observed.

Preparation of [$Rh(CO)_2$(tpzm)][$RhCl_2(CO)_2$]. A suspension of $[RhCl(CO)_2]_2$ (77.7 mg, 0.2 mmol) in 10 ml of acetone was treated with tpzm (21.4 mg, 0.1 mmol) and the mixture was stirred for 30 min at room temperature. The yellow precipitate was filtered off, repeatedly washed with hexane, and dried in vacuo: yield 80.6 mg (81%). Anal. Found: C, 27.85; H, 1.64; N, 14.02. $C_{14}H_{10}N_6O_4Cl_2Rh_2$ calcd.: C, 27.89; H, 1.67; N, 13.94%. IR (Nujol): ν(CO) 2095, 2080, 2028 and 2000 cm^{-1}.

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