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Pyrazolato-iridium(III) complexes

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Abstract

The preparation of new mononuclear and dinuclear compounds is reported. The complex $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**1**) reacts with several donors, yielding the mononuclear complexes $[IrH_2(Hpz)(L)(PPh_3)_2]BF_4$ (L = CO (**2**), $P(OMe)_3$ (**3**), CH_3CN (**4**) or Hpz (**9**)). Treatment of **9** with a methanol solution of KOH affords $[IrH_2(pz)(Hpz)(PPh_3)_2]$ (**10**) from which the pyrazolate ligand can be displaced by chlorine (**14**) or acetate (**19**) groups. Treatment of **3**, **10**, **14** or **19** with the dimers $[M_2(\mu\text{-OMe})_2(\eta^4\text{-diolefin})_2]$ (M = Rh or Ir; diolefin = cycloocta-1,5-diene or tetrafluorobenzobarrelene) leads to the heterodinuclear compounds containing the moiety "Ir(μ-X)(μ-pz)M" M = Rh or Ir; X = H, pz, Cl or $OCOCH_3$). The reaction of **1** with KOH affords the homodinuclear complex $[\{IrH_2(\mu\text{-pz})(PPh_3)_2\}_2]$ (**7**), which upon treatment with a stoichiometric amount of HBF_4 in diethyl ether gives $[IrH_2(Hpz)(PPh_3)_2]BF_4$ (**8**).

Key words: Iridium; Pyrazolate; Rhodium

1. Introduction

Pyrazole-type heterocycles are important groups in organometallic chemistry; they can behave as neutral monodentate, anionic monodentate or exo-bidentate anionic ligands [1]. It has been shown recently that heteronuclear complexes which have the azolate anion bridges and involve rhodium, ruthenium and iridium [2–5] can be synthesized.

Much of the interest in heterodinuclear complexes arises from their role in catalytic reactions. The heterodinuclear compounds $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})M(\eta^4\text{-COD})]$ (bim = 2,2′-bimidazolate; COD = cycloocta-1,5-diene; M = Rh or Ir) and $[H(CO)(PPh_3)_2Ru(\mu\text{-pz})_2Ir(\eta^4\text{-TFB})]$ (pz = pyrazolate; TFB = tetrafluorobenzobarrelene) are more active catalysts than their mononuclear parent compounds in the hydrogenation of cyclohexene [6,7] and hydrogen transfer from 2-propanol to cyclohexanone, styrene or benzylideneacetophenone [6,8]. This is caused by electronic communication between the metal atoms through the bridging ligands. The catalytic reactions mainly proceed on one metal atom with the other metal atom acting as the core of a complex of variable electron density [7,8].

We describe here the reaction of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ [9] with Lewis bases and KOH, as well as with some mononuclear azole complexes which contain other groups capable of acting as bridging ligands; we also report the reactions of the mononuclear compounds with methoxy-bridged rhodium or iridium dimers to form several homo- and hetero-bridged bimetallic complexes.

2. Results and discussion

2.1. Reaction of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (1) with Lewis bases

The acetone molecule of **1** can be replaced by neutral donors such as CO, $P(OMe)_3$ or acetonitrile. When carbon monoxide is bubbled through a dichloromethane solution of **1**, $P(OMe)_3$ is added to a tetrahydrofuran solution of **1**, or this compound is dissolved in acetonitrile and stirred at room temperature for 1 h, the complexes $[IrH_2L(Hpz)(PPh_3)_2]BF_4$ (L = CO (**2**), $P(OMe)_3$ (**3**) or CH_3CN (**4**)) are formed.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of compounds **2** and **3** (Table 1) are consistent with the proposed structures (Scheme 1). The ^1H NMR spectrum of **2** in

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TABLE 1. ^1H and ^{31}P NMR spectra of the new complexes

Complex	^1H NMR ($CDCl_3$): δ (ppm)			^{31}P NMR ($CDCl_3$): δ (ppm)
	Hpz (H^3, H^5, H^4)	L	Ir–H	
2	11.2 (br, NH), —, 6.79, 5.45 (both br)		−7.5 (td, 1, J_{PH} = 17.2 Hz, J_{HH} = 4.3 Hz) −18.19 (td, 1, J_{PH} = 18.3 Hz, J_{HH} = 4.3 Hz)	13.9 (s)
3	11.4 (br, NH), 7.67, 6.79, 5.45 (all br)	3.22 (d, 3, J_{PH} = 10.8 Hz, $POCH_3$)	−9.23 (dtt, 1, J_{PH} = 202 Hz, J_{PH} = 19 Hz, J_{HH} = 4.5 Hz) −20.28 (dvc, 1, J_{PH} = 14.3 Hz, J_{HH} = 4.5 Hz)	98 (t, J_{PP} = 21 Hz) 22 (d, J_{PP} = 21 Hz)
4a	11.1 (br, NH), —, 6.33, 5.43 (both br)	1.70 (s, 3, $NCCH_3$)	−20.18 (td, 1, J_{PH} = 16.2 Hz, J_{HH} = 6.5 Hz) −20.76 (td, 1, J_{PH} = 16.2 Hz, J_{HH} = 6.5 Hz)	20.8 (s)
4b	9.7 (br, NH), —, 6.88, 6.10 (both br)	1.64 (s, 3, $NCCH_3$)	−20.5 (t, 2, J_{PH} = 15.6 Hz)	19.6 (s)
5	6.90, 5.84, 5.53 (all br)	3.19 (d, 3, J_{PH} = 11.4 Hz, $POCH_3$) 3.73, 2.7 (both br, each 2, -HC=CH- of C_8H_{12}) 1.89, 1.56 (both br, each 2, $-CH_2-$ of C_8H_{12}) 1.36 (br, 4, $-CH_2-$ of C_8H_{12})	−16.31 (dvc, 1, J_{PH} = 120 Hz, J_{RhH} = 17) −18.02 (vc, 1, J_{PH} = 15.4 Hz)	70 (t, J_{PP} = 24 Hz) 4.2 (d, J_{PP} = 24 Hz)
6	7.13, 5.70, 5.52 (all br)	4.83 (br, 2, -CH of TFB) 3.18, 2.75 (both br, each 2, -HC=CH- of TFB) 3.29 (d, 3, J_{PH} = 11.1 Hz)	−16.38 (dvc, 1, J_{PH} = 115 Hz, J_{RhH} = 20 Hz) −18.20 (vc, 1, J_{PH} = 15.4 Hz)	72 (t, J_{PP} = 25 Hz) 3.3 (d, J_{PP} = 25 Hz)
7 [a]	7.06 (d, 4; J_{HH} = 1.8 Hz), 5.75 (t, 2, J_{HH} = 1.8 Hz)		−19.33 (t, 2, J_{PH} = 17.3 Hz)	20.1 (s)
8	9.9 (s, NH), 6.81, 5.73 (both br, each 1)		−20.99 (t, 2, J_{PH} = 16.9 Hz)	20.8 (s)
11	—, 6.80, 5.37 (both br, each 2)	3.41 (br, 4, -HC=CH- of C_8H_{12}) 2.06, 1.46 (br, each 4, $-CH_2-$ of C_8H_{12})	−20.32 (t, 2, J_{PH} = 19.9 Hz)	16.6 (s)
12	6.66, 6.35, 5.42 (all br, each 2)	5.2 (br, 2, -CH of TFB) 3.1 (br, 4, -HC=CH- of TFB)	−20.0 (t, 2; J_{PH} = 18.8 Hz)	17.9 (s)
13 [a]	7.20, 6.90, 5.79 (all br, each 2)	5.19 (br, 2, -CH of TFB) 2.48 (br, 4, -HC=CH- of TFB)	−19.32 (t, 2, J_{PH} = 17.2 Hz)	20.4 (s)

14	11.8 (br, 1, NH), 7.20, 6.90, 5.79 (all br, each 2)		-20.37 (td, 1, $J_{PH} = 17$ Hz, $J_{HH} = 7$ Hz) -23.48 (td, 1, $J_{PH} = 16.4$, $J_{HH} = 7$ Hz)	20.7 (s)
16 [a]	7.27, 6.09, 5.66 (all br, each 1)	4.93 (br, 2, -CH of TFB) 3.00, 2.81 (both br, each 2, -HC=CH- of TFB)	-19.21 (td, 1, $J_{PH} = 17.7$ Hz, $J_{HH} = 7.2$ Hz) -22.19 (td, 1, $J_{PH} = 16.2$ Hz, $J_{HH} = 7.2$ Hz)	20.0 (s)
17	6.87, 6.82 (both d, each 1, $J_{HH} = 1.9$ Hz) 5.41 (t, 1; $J_{HH} = 1.9$ Hz)	3.54, 3.29 (both br, each 2, -HC=CH- of C_8H_{12}) 2.0, 1.82 (both br, each 2, -CH_2- of C_8H_{12}) 1.28, 0.82 (both br, each 2, -CH_2- of C_8H_{12})	-19.88 (td, 1, $J_{PH} = 17.8$ Hz, $J_{HH} = 6.8$ Hz) -22.46 (td, 1, $J_{PH} = 17.0$ Hz, $J_{HH} = 6.8$ Hz)	20.3 (s)
18 [a]	—, 6.20, 5.52 (both br, each 1)	4.96 (br, 2, -CH of TFB) 2.33, 1.96 (both br, each 2; -HC=CH- of TFB)	-19.14 (td, 1, $J_{PH} = 17.3$ Hz, $J_{HH} = 7.4$ Hz) -22.19 (td, 1, $J_{PH} = 16.8$ Hz, $J_{HH} = 7.4$ Hz)	20.4 (s)
19	15.9 (br, 1; NH), 6.91, 6.36, 5.41 (all br, each 1)	1.42 (s, 3; $OCOCH_3$)	-20.02 (td, 1, $J_{PH} = 17.1$ Hz, $J_{HH} = 6.9$ Hz) -27.03 (td, 1, $J_{PH} = 16.6$ Hz, $J_{HH} = 6.9$ Hz)	23.2 (s)
20 [a]	7.35 (br, 2), 6.11 (br, 1)	4.28, 3.99 (both br, each 2, -HC=CH- of C_8H_{12}) 2.51, 2.42 (both br, each 2, -CH_2- of C_8H_{12}) 1.84, 1.76 (both br, each 2, -CH_2- of C_8H_{12}) 1.09 (s, 3, $OCOCH_3$)	-28.41 (t, 2, $J_{PH} = 16.6$ Hz)	23.8 (s)
21 [a]	7.22 (br, 2), 6.12 (br, 1)	5.50 (br, 2, -CH of TFB) 3.20 (br, 4, -HC=CH- of TFB) 1.20 (s, 3, $OCOCH_3$)	-28.93 (t, 2, $J_{PH} = 16.2$ Hz)	23.8 (s)
22	7.46 (br, 2), 6.16 (br, 1)	4.09, 3.61 (both br, each 2, -HC=CH- of C_8H_{12}) 2.43, 1.79 (both br, each 4, -CH_2- of C_8H_{12}) 1.13 (s, 3, $OCOCH_3$)	-28.36 (t, 2, $J_{PH} = 16.5$ Hz)	24.1 (s)
23 [a]	6.91 (d, 2, $J_{HH} = 2$ Hz), 6.11 (t, 1, $J_{HH} = 2$ Hz)	5.21 (br, 2, -CH of TFB) 2.47 (br, 4, -HC=CH- of TFB) 1.45 (s, 3, $OCOCH_3$)	-28.36 (t, 2, $J_{PH} = 16.5$ Hz)	24.1 (s)

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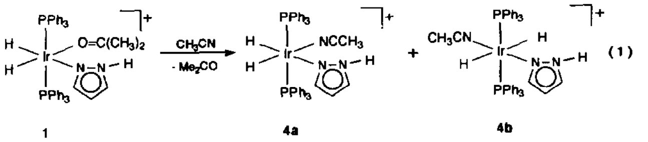
[a] In acetone-d_6.

chloroform-d_1 contains two triplets of doublets in the hydride region at -7.5 (J(PH) = 17.2 Hz, J(HH) = 4.3 Hz) and at -18.19 (J(PH) = 18.3 Hz, J(HH) = 4.3 Hz) ppm, whereas the spectrum of **3** shows a doublet of triplets of doublets at -9.23 (J(PH) = 19.1 Hz, J(PH) = 202.3 Hz, J(HH) = 4.5 Hz) ppm and a double virtual quartet at -20.28 (J(PH) = J(PH) = 14.3 Hz, J(HH) = 4.5 Hz) ppm. The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a singlet at 13.9 ppm, while the spectrum of **3** shows a characteristic AB_2 splitting pattern with a P–P coupling constant of 21.7 Hz.

The replacement of the acetone by CO or $P(OMe)_3$ takes place without isomerization, but CH_3CN gives a mixture of two isomers **4a** and **4b** (eqn. (1)).



The composition of the mixture as determined by NMR spectroscopy was 95% **4a** and 5% **4b**. In the hydride region of the ^1H NMR spectrum of **4** in chloroform-d_1 at room temperature (Table 1), the isomer **4a** is characterized by two triplets of doublets at -20.18 ppm and -20.76 ppm with P–H and H–H coupling constants of 16.2 Hz and 6.5 Hz respectively; the resonance of the isomer **4b** appears as a triplet at -20.5 ppm with a P–H coupling constant of 15.6 Hz.

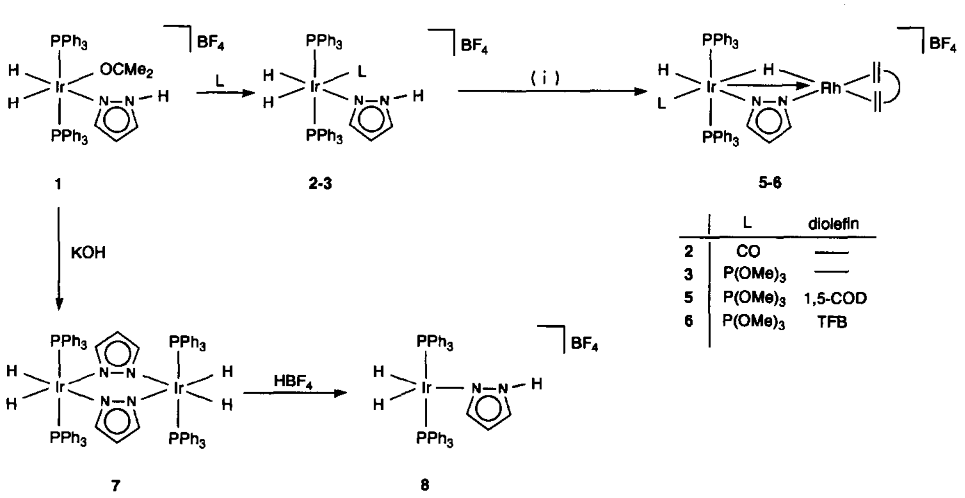
2.2. *Dinuclear Ir^{III}–Rh^{I} hydride- and pyrazolate-bridged complexes*

The acidic NH group of the pyrazole ligand in compounds **2–4** is capable of reacting with the methoxy-bridged rhodium dimers $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-diolefin})_2]$ to give heterodinuclear compounds. Thus the complexes $[H(P(OMe)_3)(PPh_3)_2Ir(\mu\text{-}H)(\mu\text{-}pz)Rh(\eta^4\text{-diolefin})]BF_4$ (diolefin = COD (**5**) or TFB (**6**)) are formed by addition of the stoichiometric amount of **3** to suspensions of the rhodium dimers in acetone or dichloromethane (Scheme 1).

The bridging hydride ligand in these compounds is shown by their ^1H NMR spectra, which show two sets of metal hydride resonances. One of them, due to Ir–H–Rh, is coupled to the following nuclei: two chemically equivalent *cis*-phosphorus atoms, one *trans*-phosphorus atom, one rhodium atom and one *cis*-hydrogen atom. The other resonance, due to H–Ir, is coupled to three *cis*-phosphorus atoms and one *cis*-hydrogen atom (Table 1). Furthermore, as the rhodium in these heterobimetallic compounds is coordinatively unsaturated, a dative Ir → Rh bond is possible. Analogous Os–Rh and Os–Ir dinuclear complexes $[(CO)_2(P^iPr_3)_2Os(\mu\text{-}H)(\mu\text{-}pz)M(\eta^4\text{-diolefin})]BF_4$ (M = Rh; diolefin = COD, TFB) (M = Ir; diolefin = COD) have recently been prepared in our laboratory [10]. Previously, Cowie and coworkers [11] had reported the synthesis of related compounds containing bridging bis(diphenylphosphino)methane.

2.3. *Dinuclear Ir^{III}–Ir^{III} bis(pyrazolate)-bridged complex*

Pyrazole in **1** is also capable of reacting with potassium hydroxide to give $[\{IrH_2(\mu\text{-}pz)(PPh_3)_2\}_2]$ (**7**). The dinuclear character of this compound is inferred on the basis of its ^1H NMR spectrum (Table 1), which contains two CH signals due to the pyrazolate ligands at 7.06 (d, J(HH) = 1.8 Hz) and 5.75 (t, J(HH) = 1.8 Hz) ppm; the signal at 7.06 ppm is assigned to the four chemically equivalent CH groups bonded directly to

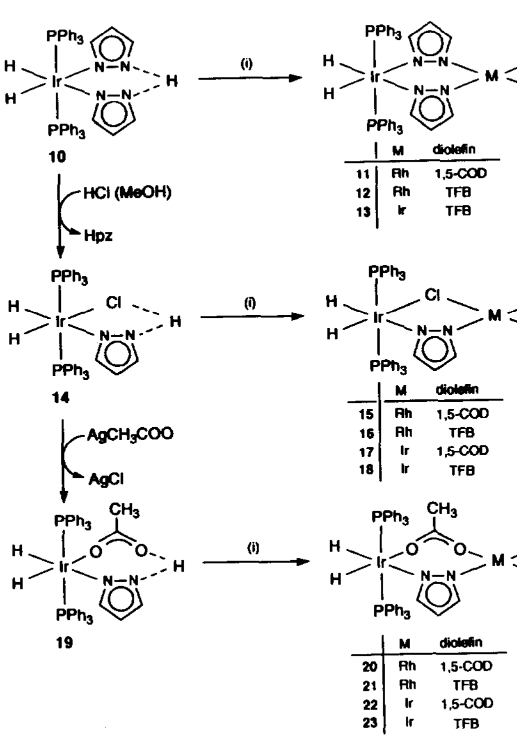


	L	diolefin
2	CO	—
3	P(OMe)3	—
5	P(OMe)3	1,5-COD
6	P(OMe)3	TFB

Scheme 1. (i) $\frac{1}{2}[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-diolefin})_2]$.

the four chemically equivalent nitrogen atoms, while the signal at 5.75 ppm corresponds to the two chemically equivalent CH groups bonded to the other CH groups. Integration of these signals gives an intensity ratio of 2 : 1, which supports the proposed assignment. Furthermore, in the hydride region, the spectrum displays a triplet at −19.33 ppm with a P–H coupling constant of 17.3 Hz. The presence of two hydride ligands coordinated to each iridium atom is inferred from the ^{31}P NMR spectrum, which shows a singlet at 20.1 ppm that, under the off-resonance conditions, splits into a triplet owing to P–H coupling. On the basis of kinetic studies the related compound $[IrH_2(\mu\text{-}pz)(\eta^4\text{-}TFB)]_2$ has been suggested to be the active catalytic intermediate, in the hydrogenation of cyclohexene catalysed by $[\{Ir(\mu\text{-}pz)(\eta^4\text{-}TFB)\}_2]$ [7].

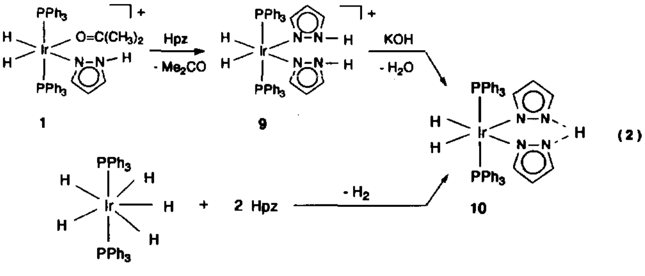
The pyrazolate bridges in the dimeric compound **7** are readily cleaved by H^+. Treatment of a diethyl ether solution of **7** with a stoichiometric amount of HBF_4 leads to the five-coordinated mononuclear complex **8**. In accordance with the proposed structure (Scheme 1) the $^{31}P\{^1H\}$ NMR spectrum of **8** exhibits a singlet at 20.8 ppm, the ^1H NMR spectrum in the hydride region shows a triplet at −20.99 ($J(PH) = 16.9$ Hz) ppm and the IR spectrum contains two $\nu(IrH)$ bands at 2150 and 2180 cm^{-1}.



Scheme 2. (i) $[M_2(\mu\text{-}OMe)_2(\eta^4\text{-}diolefin)_2]$.

2.4. *Dinuclear Ir^{III}–Ir^{I} and Ir^{III}–Rh^{I} bis(pyrazolate)-bridged complexes*

The acetone molecule of **1** can also be displaced without isomerization by pyrazole, giving the mononuclear complex $[IrH_2(Hpz)_2(PPh_3)_2]BF_4$ (**9**) in which the pyrazole groups are *cis*. Proton abstraction by KOH from complex **9** (1 : 1 molar ratio) leads to the neutral pyrazole–pyrazolate complex $[IrH_2(pz)(Hpz)(PPh_3)_2]$ (**10**), which can also be obtained by reaction of $[IrH_5(PPh_3)_2]$ with pyrazole in refluxing toluene [12] (eqn. (2)):



Reaction of **10** with the methoxy-bridged dimers $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}diolefin)_2]$ in refluxing tetrahydrofuran or acetone affords the neutral dimetal bis(pyrazolate)-bridged complexes $[H_2(PPh_3)_2Ir(\mu\text{-}pz)_2M(\eta^4\text{-}diolefin)]$ (M = Rh; diolefin = COD (**11**) or TFB (**12**)) (M = Ir; diolefin = TFB (**13**)) with a good yield (Scheme 2). They were characterized by the elemental analysis and spectroscopic data. The IR spectra of the solids in Nujol mulls confirm the presence of two terminal hydride ligands. The high field ^1H NMR spectra in $CDCl_3$ solutions show a triplet for the hydride ligands. These spectra also exhibit signals due to the protons of the pyrazolate and the diolefin groups. As expected, the $^{31}P\{^1H\}$ NMR spectra each contain only one peak (Table 1).

2.5. *Dinuclear Ir^{III}–Ir^{I} and Ir^{III}–Rh^{I} (chloro)(pyrazolate)-bridged complexes*

The starting material used to prepared hetero-bridged dinuclear compounds is the (chloro)pyrazole compound $[IrH_2Cl(Hpz)(PPh_3)_2]$ (**14**); this complex is formed by treatment of a dichloromethane solution of **10** with a methanolic solution of HCl; its IR spectrum shows two $\nu(IrH)$ bands at 2220 and 2190 cm^{-1}, as well as a strong band at 3260 cm^{-1} for $\nu(NH)$ of the coordinated Hpz; the lower wavenumber compared with that of compounds **2**–**4** may be attributed to the presence of a hydrogen bond N–H ··· Cl [13].

The ^1H NMR spectrum of **14** is consistent with the presence of two non-equivalent hydride groups and shows two triplets of doublets at −20.35 ($J(PH) = 17$

Hz, $J(HH) = 7$ Hz) and at -23.48 ($J(PH) = 16.4$ Hz, $J(HH) = 7$ Hz) ppm and a singlet at 11.8 ppm for the NH proton. The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 20.7 ppm (Table 1).

As expected, **14** reacts in acetone or tetrahydrofuran with the methoxy-bridged rhodium or iridium dimers $[M_2(\mu\text{-OMe})_2(\eta^4\text{-diolefin})_2]$ to give the heterobridged dinuclear complexes $[H_2(PPh_3)_2Ir(\mu\text{-Cl})(\mu\text{-pz})M(\eta^4\text{-diolefin})]$ (M = Rh; diolefin = COD (**15**) a TFB (**16**)) (M = Ir; diolefin = COD (**17**) or TFB (**18**)). The IR spectra show no absorption assignable to ν(NH) but do show two ν(IrH) absorptions in the 2100–2300 cm^{-1} region. The ^1H NMR data (Table 1) confirm the structure proposed in Scheme 2. Resonances due to the phosphine and the diolefin groups and two triplets of doublets, in the hydride region, are observed.

2.6. *Dinuclear Ir^{III}–Ir^{I} and Ir^{III}–Rh^{I} acetate–pyrazolate-bridged complexes*

The procedure used for the synthesis of these complexes involves the initial preparation of the mononuclear acetate complex $[IrH_2(\eta^1\text{-OCOCH}_3)(Hpz)(PPh_3)_2]$ (**19**) which is obtained as a white microcrystalline solid from a dichloromethane–acetone solution of **14** and silver acetate (Scheme 2). Its IR spectrum exhibits two bands for the ν(IrH) absorptions, at 2200 and 2170 cm^{-1}, but no absorption assignable to ν(NH) was found in the 3500–3000 cm^{-1} region. The acetate gives rise to ν_{asym}(OCO) and ν_{sym}(OCO) at 1530 cm^{-1} and 1380 cm^{-1} respectively: the difference $\Delta\nu$ between the values is less than those reported for unidentate acetate ligands and closer to the values observed for chelating acetate ligands [14]. All these data suggest the presence of a hydrogen bond N–H ··· O, as in compound **10**.

The reaction of **19** with the dimers $[M_2(\mu\text{-OMe})_2(\eta^4\text{-diolefin})_2]$ in refluxing acetone or tetrahydrofuran produces the dinuclear heterobridged compounds $[H_2(PPh_3)_2Ir(\mu\text{-}\eta^2\text{-O}_2CCH_3)(\mu\text{-pz})M(\eta^4\text{-diolefin})]$ (M = Rh; diolefin = COD (**20**) or TFB (**21**) (M = Ir; diolefin = COD (**22**) or TFB (**23**)). The analytical data, and IR and NMR spectra of these complexes (Table 1 and Experimental section) are in good agreement with the proposed structures; the acetate ligand shows bands in the IR spectra for ν_{asym}(OCO) and ν_{sym}(OCO) at around 1530 cm^{-1} and 1375 cm^{-1} respectively. The values of $\Delta\nu$ coincide with those established for bidentate coordination of the acetate group [14]. The ^1H NMR spectra contain the signals of the diolefin, phosphine, pyrazolate and acetate groups together with a triplet in the high field region for the hydride ligands *cis* to phosphorus. The $^{31}P\{^1H\}$NMR spectra consist of a singlet.

3. Experimental details

3.1. *General considerations*

All reactions were carried out under argon by using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting materials $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ [9], $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ [15], $[Ir_2(\mu\text{-OMe})_2(\eta^4\text{-diolefin})_2]$ (diolefin = COD [16] or TFB [17]) and $(Rh_2(\mu\text{-OMe})_2(\eta^4\text{-diolefin})_2]$ (diolefin = COD or TFB) [16] were prepared by published methods.

3.2. *Physical measurements*

IR spectra were recorded on a Perkin–Elmer 783 IR spectrophotometer and NMR spectra on Varian XL 200 and UNITY 300 spectrophotometers. Chemical shifts are expressed in parts per million upfield from Me_4Si (^1H) and 85% H_3PO_4 (^{31}P) as external references. C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyser.

3.3. *Preparation of $[IrH_2(CO)(Hpz)(PPh_3)_2]BF_4$ (2)*

The complex $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**1**) (93.1 mg, 0.10 mmol) was dissolved in dichloromethane (7 ml) and CO bubbled into the solution for 1 h. After concentration to about 1 ml, the microcrystalline white solid was precipitated by addition of diethyl ether, filtered off and washed with diethyl ether (yield, 63 mg (70%)). Anal. Found: C, 52.96; H, 4.12; N, 3.09. $C_{40}H_{36}BF_4IrN_2OP_2$ calc.: C, 53.29; H, 4.02; N, 3.12%. IR (CH_2Cl_2): ν(CO) 2010 cm^{-1}. IR (Nujol): ν(NH) 3380, ν(IrH) 2220, 2100, ν(CO) 2000 cm^{-1}.

3.4. *Preparation of $[IrH_2(Hpz)(P(OMe)_3)(PPh_3)_2]BF_4$ (3)*

A suspension of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**1**) (93.1 mg, 0.10 mmol) in 12 ml of tetrahydrofuran was treated with a slight excess of trimethyl phosphite (13 μl, 0.11 mmol) and stirred for 5 h at room temperature. The resulting suspension was concentrated and then hexane was added to complete the precipitation. The white solid was filtered off, washed with hexane and vacuum dried (yield, 90 mg (90%)). Anal. Found: C, 50.70; H, 5.25; N, 3.01. $C_{42}H_{45}BF_4IrN_2O_3P_3$ calc.: C, 50.56; H, 4.55; N, 2.81%. IR (Nujol): ν(NH) 3330, ν(IrH) 2240, 2070 cm^{-1}.

3.5. *Preparation of $[IrH_2(CH_3CN)(Hpz)(PPh_3)_2]BF_4$ (4a and 4b)*

A solution of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**1**) (93.1 mg, 0.10 mmol) in 6 ml of acetonitrile was stirred for 1 h at room temperature. The solution was concentrated to about 0.5 ml *in vacuo*, and then 6 ml of diethyl ether were added. A white solid precipitated, which was filtered off, repeatedly washed with diethyl ether and dried *in vacuo* (yield, 80 mg (88%)). Anal. Found: C, 53.81; H, 4.47; N, 4.40. $C_{41}H_{39}BF_4IrN_3P_2$: C, 53.84; H, 4.30; N, 4.59%. IR (Nujol): ν(NH) 3360, ν(CN) and ν(IrH) 2245, 2230 and 2210 cm^{-1}.

3.6. Preparation of [H(P(OMe)$_3$)(PPh$_3$)$_2$Ir(μ-H)(μ-pz)Rh(η^4-COD)]BF$_4$ (5)

A stoichiometric amount of **3** (99.7 mg, 0.10 mmol) was added to a suspension of $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}COD)_2]$ (24.2 mg, 0.05 mmol) in 10 ml of acetone, and the reaction mixture was then stirred for 13 h under reflux. After being cooled to room temperature, the solution was filtered through kieselguhr and concentrated to about 1 ml. Addition of 6 ml of diethyl ether led to a yellow precipitate, which was repeatedly washed with diethyl ether and dried *in vacuo* (yield, 37.4 mg (31%)). Anal. Found: C, 49.65; H, 4.97; N, 2.10. $C_{50}H_{56}BF_4IrN_2O_3P_3Rh$ calc.: C, 49.72; H, 4.67; N, 2.32%. IR (Nujol): ν(IrH) 2240 cm^{-1}.

3.7. Preparation of [H(P(OMe)$_3$)(PPh$_3$)$_2$Ir(μ-H)(μ-pz)Rh(η^4-TFB)]BF$_4$ (6)

A stoichiometric amount of **3** (99.7 mg, 0.10 mmol) was added to a suspension of $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}TFB)_2]$ (36.1 mg, 0.05 mmol) in 10 ml of dichloromethane, and the reaction mixture was then stirred for 2 h under reflux. The solution obtained was filtered through kieselguhr and concentrated to about 1 ml. Addition of 6 ml of diethyl ether led to the formation of a yellow precipitate, which was repeatedly washed with diethyl ether and dried *in vacuo* (yield, 75.6 mg (57%)). Anal. Found: C, 48.31; H, 3.61; N, 2.07. $C_{54}H_{50}BF_4IrN_2O_3P_3Rh$ calc.: C, 48.92; H, 3.80; N, 2.11%. IR (Nujol): ν(IrH) 2130 cm^{-1}.

3.8. Preparation of [{IrH$_2$(μ-pz)(PPh$_3$)$_2$}$_2$] (7)

A solution of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**1**) (93.1 mg, 0.10 mmol) in 10 ml of methanol was treated with a methanol solution of KOH (2 ml, 0.077 N). After being stirred for 40 min at room temperature the resulting suspension was concentrated and the precipitate obtained washed with methanol. The solid was recrystallized from toluene–methanol (yield, 36.9 mg (47%)). Anal. Found: C, 59.78; H, 4.51; N, 3.73. $C_{78}H_{70}Ir_2N_4P_4$ calc.: C, 59.60; H, 4.49; N, 3.56%. IR (Nujol): ν(IrH) 2160 cm^{-1}.

3.9. Preparation of [IrH$_2$(Hpz)(PPh$_3$)$_2$]BF$_4$ (8)

A solution of **7** (39.3 mg, 0.05 mmol) in 10 ml of diethyl ether was treated with an ether solution of HBF_4 (15 μl, 0.11 mmol). After the mixture had been stirred for 15 min at room temperature, a yellow solid precipitated which was repeatedly washed with diethyl ether and dried *in vacuo* (yield, 74 mg (85%)). Anal. Found: C, 53.28; H, 4.41; N, 3.58. $C_{39}H_{36}BF_4IrN_2P_2$ calc.: C, 53.62; H, 4.12; N, 3.21%. IR (Nujol): ν(NH) 3600, ν(IrH) 2180, 2150 cm^{-1}.

3.10. Preparation of [H$_2$(PPh$_3$)$_2$Ir(μ-pz)$_2$Rh(η^4-COD)] (11)

A stoichiometric amount of $[IrH_2(pz)(Hpz)(PPh_3)_2]$ (**10**) (128.1 mg, 0.15 mmol) was added to a suspension of $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}COD)_2]$ (36.3 mg, 0.075 mmol) in 10 ml of tetrahydrofuran and the reaction mixture was then stirred for 12 h under reflux. The yellow solution obtained was filtered through kieselguhr and concentrated to about 1 ml. The addition of methanol led to a yellow precipitate, which was filtered off, repeatedly washed with methanol and dried *in vacuo* (yield, 130.8 mg (82%)). Anal. Found: C, 56.65; H, 4.95; N, 5.18. $C_{50}H_{50}IrN_4P_2Rh$ calc.: C, 56.44, H, 4.74; N, 5.27%. IR (Nujol): ν(IrH) 2165, 2150 cm^{-1}.

3.11. Preparation of [H$_2$(PPh$_3$)$_2$Ir(μ-pz)$_2$Rh(η^4-TFB)] (12)

This compound was prepared analogously to **11**, starting from $[IrH_2(pz)(Hpz)(PPh_3)_2]$ (**10**) (128.1 mg, 0.15 mmol) and $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}TFB)_2]$ (54.0 mg, 0.075 mmol) in 10 ml of acetone. A light-yellow solid was formed (yield, 141.8 mg (80%)). Anal. Found: C, 54.59; H, 3.98; N, 4.66. $C_{54}H_{44}F_4IrN_4P_2Rh$ calc.: C, 54.87; H, 3.75; N, 4.74%. IR (Nujol): ν(IrH) 2160, 2138 cm^{-1}.

3.12. Preparation of [H$_2$(PPh$_3$)$_2$Ir(μ-pz)$_2$Ir(η^4-TFB)] (13)

This compound was prepared analogously to **11**, starting from $[IrH_2(pz)(Hpz)(PPh_3)_2]$ (**10**) (128.1 mg, 0.15 mmol) and $[Ir_2(\mu\text{-}OMe)_2(\eta^4\text{-}TFB)_2]$ (67.4 mg, 0.075 mmol) in 10 ml of tetrahydrofuran. A light-yellow solid was formed, which was filtered and washed with hexane (yield, 99 mg (52%)). Anal. Found: C, 50.57; H, 3.69; N, 4.56. $C_{54}H_{44}F_4Ir_2N_4P_2$ calc.: C, 51.02; H, 3.49; N, 4.41%. IR (Nujol): ν(IrH) 2150 cm^{-1}.

3.13. Preparation of [IrH$_2$Cl(Hpz)(PPh$_3$)$_2$] (14)

A solution of $[IrH_2(pz)(Hpz)(PPh_3)_2]$ (**10**) (128.1 mg, 0.15 mmol) in 10 ml of dichloromethane was treated with a methanol solution of HCl (0.45 N; 0.66 ml, 0.3 mmol) and stirred for 2 h at room temperature. The resulting solution was filtered through kieselguhr and concentrated to about 1 ml. Addition of methanol led to the formation of a white solid, which was washed with methanol and dried *in vacuo* (yield, 96.2 mg (78%)). Anal. Found: C, 57.08; H, 4.54; N, 3.48. $C_{39}H_{36}ClIrN_2P_2$ calc.: C, 56.96; H, 4.41; N, 3.41%. IR (Nujol): ν(NH) 3260, ν(IrH) 2220, 2190 cm^{-1}.

3.14. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}Cl)(\mu\text{-}pz)Rh(\eta^4\text{-}COD)]$ *(15)*

A stoichiometric amount of **14** (123.3 mg, 0.15 mmol) was added to a suspension of $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}COD)_2]$ (36.3 mg, 0.075 mmol) in 10 ml of acetone and the reaction mixture was then stirred for 14 h under reflux. The resulting suspension was concentrated and then methanol was added to complete the precipitation. The yellow solid obtained was washed with methanol and dried in vacuo (yield, 117.7 mg (76%)). Anal. Found: C, 54.81; H, 4.82; N, 2.76. $C_{47}H_{47}ClIrN_2P_2Rh$ calc.: C, 54.68; H, 4.59; N, 2.71%. IR (Nujol): ν(IrH) 2235, 2140 cm^{-1}.

3.15. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}Cl)(\mu\text{-}pz)Rh(\eta^4\text{-}TFB)]$ *(16)*

A stoichiometric amount of **14** (123.3 mg, 0.15 mmol) was added to a suspension of $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}TFB)_2]$ (54.0 mg, 0.075 mmol) in 12 ml of acetone and the reaction mixture was then stirred for 8 h under reflux. The resulting solution was filtered through kieselguhr and concentrated to about 1 ml. The addition of methanol led to a yellow solid, which was washed with methanol and dried *in vacuo* (yield, 136.3 mg (79%)). Anal. Found: C, 53.07; H, 3.60; N, 2.26. $C_{51}H_{41}ClF_4IrN_2P_2Rh$ calc.: C, 53.25; H, 3.59; N, 2.43%. IR (Nujol): ν(IrH) 2270, 2170 cm^{-1}.

3.16. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}Cl)(\mu\text{-}pz)Ir(\eta^4\text{-}COD)]$ *(17)*

This compound was prepared analogously to **15**, starting from **14** (123.3 mg, 0.15 mmol) and $[Ir_2(\mu\text{-}OMe)_2(\eta^4\text{-}COD)_2]$ (49.7 mg, 0.075 mmol) in 12 ml of acetone. A yellow solid was formed, which was washed with acetone (yield, 50.5 mg (30%)). Anal. Found: C, 50.69; H, 4.28; N, 2.12. $C_{47}H_{47}ClIr_2N_2P_2$ calc.: C, 50.33; H, 4.22; N, 2.50%. IR (Nujol): ν(IrH) 2240, 2140 cm^{-1}.

3.17. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}Cl)(\mu\text{-}pz)Ir(\eta^4\text{-}TFB)]$ *(18)*

This compound was prepared analogously to **16**, starting from **14** (123.3 mg, 0.15 mmol) and $[Ir_2(\mu\text{-}OMe)_2(\eta^4\text{-}TFB)_2]$ (67.4 mg, 0.075 mmol) in 12 ml of tetrahydrofuran. Addition of hexane led to a yellow solid, which was washed with hexane (yield, 117 mg (63%)). Anal. Found: C, 49.62; H, 3.50; N, 2.09. $C_{51}H_{41}ClF_4Ir_2N_2P_2$ calc.: C, 49.41; H, 3.33; N, 2.26%. IR (Nujol): ν(IrH) 2270, 2170 cm^{-1}.

3.18. *Preparation of* $[IrH_2(\eta^1\text{-}OCOCH_3)(Hpz)(PPh_3)_2]$ *(19)*

Complex **14** (82.2 mg, 0.10 mmol) was dissolved in acetone (3 ml)–dichloromethane (5 ml) and a stoichiometric amount of $AgOOCCH_3$ (16.7 mg, 0.10 mmol) was added. After stirring for 1 h under dinitrogen in the dark, the resulting solution was filtered through kieselguhr and concentrated to about 1 ml. The addition of methanol led to a white solid, which was washed with methanol and dried *in vacuo* (yield, 64.3 mg (76%)). Anal. Found: C, 58.03; H, 4.70; N, 3.32. $C_{41}H_{39}IrN_2O_2P_2$ calc.: C, 58.21; H, 4.65; N, 3.31%. IR (Nujol): ν(IrH) 2200, 2170, ν_{asym}(OCO) 1530, ν_{sym}(OCO) 1380 cm^{-1}.

3.19. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}\eta^2\text{-}O_2CCH_3)(\mu\text{-}pz)Rh(\eta^4\text{-}COD)]$ *(20)*

A stoichiometric amount of $[IrH_2(\eta^1\text{-}OCOCH_3)(Hpz)(PPh_3)_2]$ (**19**) (84.5 mg, 0.10 mmol) was added to a suspension of $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}COD)_2]$ (24.2 mg, 0.05 mmol) in 10 ml of tetrahydrofuran and the reaction mixture was then stirred for 7 h under reflux. The resulting suspension was concentrated and then hexane was added to complete the precipitation. The light-yellow solid obtained was washed with hexane and dried *in vacuo* (yield, 73.9 mg (70%)). Anal. Found: C, 55.51; H, 4.96; N, 2.51. $C_{49}H_{50}IrN_2O_2P_2Rh$ calc.: C, 55.73; H, 4.77; N, 2.65%. IR (Nujol): ν(IrH) 2230, 2210, ν_{asym}(OCO) 1530, ν_{sym}(OCO) 1375 cm^{-1}.

3.20. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}\eta^2\text{-}O_2CCH_3)(\mu\text{-}pz)Rh(\eta^4\text{-}TFB)]$ *(21)*

This compound was prepared analogously to **15**, starting from $[IrH_2(\eta^1\text{-}OCOCH_3)(Hpz)(PPh_3)_2]$ (**19**) (84.5 mg, 0.10 mmol) and $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-}TFB)_2]$ (36.0 mg, 0.05 mmol), with precipitation by hexane. A yellow solid was formed (yield, 70 mg (60%)). Anal. Found: C, 53.73; H, 3.97; N, 2.18. $C_{53}H_{44}F_4IrN_2O_2P_2Rh$ calc.: C, 54.22; H, 3.78; N, 2.39%. IR (Nujol): ν(IrH) 2210, ν_{asym}(OCO) 1530, ν_{sym}(OCO) 1380 cm^{-1}.

3.21. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}\eta^2\text{-}O_2CCH_3)(\mu\text{-}pz)Ir(\eta^4\text{-}COD)]$ *(22)*

This compound was prepared analogously to **15**, starting from $[IrH_2(\eta^1\text{-}OCOCH_3)(Hpz)(PPh_3)_2]$ (**19**) (84.5 mg, 0.10 mmol) and $[Ir_2(\mu\text{-}OMe)_2(\eta^4\text{-}COD)_2]$ (49.7 mg, 0.075 mmol) in 12 ml of acetone. A red solid was formed (yield, 139 mg (81%)). Anal. Found: C, 51.89; H, 4.40; N, 2.12. $C_{49}H_{50}Ir_2N_2O_2P_2$ calc.: C, 51.39; H, 4.40; N, 2.45%. IR (Nujol): ν(IrH) 2230, 2210, ν_{asym}(OCO) 1530, ν_{sym}(OCO) 1375 cm^{-1}.

3.22. *Preparation of* $[H_2(PPh_3)_2Ir(\mu\text{-}\eta^2\text{-}O_2CCH_3)(\mu\text{-}pz)Ir(\eta^4\text{-}TFB)]$ *(23)*

A stoichiometric amount of $[IrH_2(\eta^1\text{-}OCOCH_3)(Hpz)(PPh_3)_2]$ (**19**) (123.3 mg, 0.15 mmol) was added to a suspension of $[Ir_2(\mu\text{-}OMe)_2(\eta^4\text{-}TFB)_2]$ (67.4 mg, 0.075 mmol) in 12 ml of acetone and the reaction mixture was then stirred for 15 h under reflux. The resulting solution was filtered through kieselguhr and concentrated to about 1 ml. The addition of methanol led to an orange solid, which was washed with methanol and dried *in vacuo* (yield, 130.7 mg (69%)). Anal. Found: C, 50.17; H, 3.63; N, 2.13. $C_{53}H_{44}F_4Ir_2N_2O_2P_2$ calc.: C, 50.39; H, 3.51; N, 2.22%. IR (Nujol): ν(IrH) 2220, ν_{asym}(OCO) 1530, ν_{sym}(OCO) 1375 cm^{-1}.

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