Iridium Nitrosyl and Carbonyl Complexes with 2-Pyridinecarbaldehyde Azines

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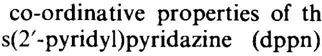
The reactions of the cationic iridium complexes $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ and $[Ir(CO)(MeCN)(PPh_3)_2][PF_6]$ with the binucleating ligands 2-pyridinecarbaldehyde azine (paa), 6-methyl-2-pyridinecarbaldehyde azine (mpaa), and 3,6-bis(2′-pyridyl)pyridazine (dppn) are reported. The newly synthesized compounds were characterized by elemental analysis, conductivity measurements, i.r. and n.m.r. spectroscopy. The formation of mononuclear and binuclear species and the inability to obtain mixed binuclear complexes are discussed.

In previous studies devoted to the synthesis of bimetallic homo- and hetero-nuclear complexes of Group 8 transition metals we investigated the co-ordinative properties of the bis-chelating molecule 3,6-bis(2′-pyridyl)pyridazine (dppn). Our results showed the good reactivity of such a ligand and a wide series of bimetallic species, containing the two metals mutually *cis*, was described.[1–3]

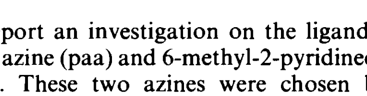
Now we report an investigation on the ligands 2-pyridinecarbaldehyde azine (paa) and 6-methyl-2-pyridinecarbaldehyde azine (mpaa). These two azines were chosen because they are quite similar to dppn as regards their co-ordination behaviour, but, in addition, they can give rise to compounds having different geometries.[4] All the above cited ligands were reacted in a two-step synthesis with two cationic species, namely $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ and $[Ir(CO)(MeCN)(PPh_3)_2][PF_6]$, in order to prepare mixed binuclear complexes to be studied in reactions involving the activation of both CO and NO groups.

Results and Discussion

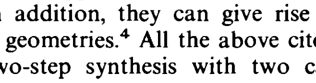
Ligands.—The quadridentate ligands (L) studied are shown below. They were synthesized as described previously,[5–7] and characterized by n.m.r. spectroscopy. The ${}^{1}H$ and ${}^{13}C$ chemical shifts are reported in Tables 1 and 2 respectively.



paa



mpaa



dppn

Mononuclear Nitrosyl Complexes.—The binucleating ligands paa and mpaa react with the starting iridium nitrosyl compound $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ (**1**) [1:1 in tetrahydrofuran (thf)], affording the mononuclear species (**2**) and (**3**) (Table 3). The synthesis and physical properties of (**4**) have been reported previously.[1]

The i.r. spectra of the new complexes, which analyse for $[Ir(NO)(L)(PPh_3)_2][PF_6]_2$, display a high-frequency NO stretch at *ca.* 1 800 cm^{-1} (KBr).[8] Conductivity measurements, carried out in nitromethane, are in agreement with 1:2 electrolytes.[9] The ${}^{31}P-\{{}^{1}H\}$ n.m.r. spectra show a single resonance at *ca.* 10 p.p.m. (Table 3) indicating equivalence of the phosphines in the Ir^I environment.[10,11]

The ${}^{1}H$ n.m.r. spectra of complexes (**2**)—(**4**) were run in CD_2Cl_2. The assignments of the ligand signals and their shifts upon co-ordination are reported in Tables 4 and 5 respectively. As examples the spectra of complexes (**2**) and (**4**), in the range 7—10 p.p.m., are shown in Figures 1 and 2.

From the analysis of the spectral multiplicity and by homonuclear decoupling experiments it was possible both to separate and assign the signals of the pyridyl protons in two sets, one set being much broader than the other. Furthermore the different shapes of the two signal sets (the pyridyl ring showing the sharpest signal was attributed to an unco-ordinated ring, see below) helped to distinguish them. Nuclear Overhauser enhancement experiments allowed the two methyl signals in the spectra of (**3**) to be assigned to each pyridyl ring, as well as assignment of the two pyridazine signals of (**4**). For both (**2**) and (**3**), two signals are observed for the N=CH protons, one being a triplet. All these observations are consistent with monochelating behaviour of the ligands L, co-ordinated to the metal through two adjacent nitrogen atoms [one pyridyl in every case; N=CH in complexes (**2**) and (**3**) and from the pyridazine moiety in (**4**)].

Moreover, by comparison of the $\Delta\delta$ values reported in Table 5, some interesting trends can be seen. In (**2**) and (**4**) the H^6 resonances are significantly shifted downfield. The same behaviour is observed also in (**3**) for the 6-methyl protons.

Such deshieldings, previously described for the similar complex $[Ir(NO)(bipy)(PPh_3)_2][PF_6]_2$ (bipy = 2,2′-bipyridyl, Table 5), are related to the effect of the co-ordinated metal centres and constitute a useful tool for recognizing the co-ordinated pyridine ring. The same trend (to a smaller extent) is observed also for H^5, while the H^4 protons appear to be nearly insensitive to the co-ordination of the $Ir(NO)(PPh_3)_2$ moiety. By contrast the H^3 signals exhibit marked upfield shifts ($\Delta\delta$ *ca.* 1 p.p.m.), which may be explained only in terms of anisotropic shielding exerted by the phenyl rings of the two PPh_3 molecules above and below the co-ordination plane of the N_4 ligands.[12,13] Therefore the general trend observed on going from H^6 to H^3 suggests that the chemical shifts of H^5 and H^4 are probably the result of two combined effects: the deshielding by metal co-ordination and the shielding by the PPh_3 aromatic rings. Remarkably the imino protons on the chelate ring of the paa and mpaa complexes, (**2**) and (**3**) respectively, show a P–H

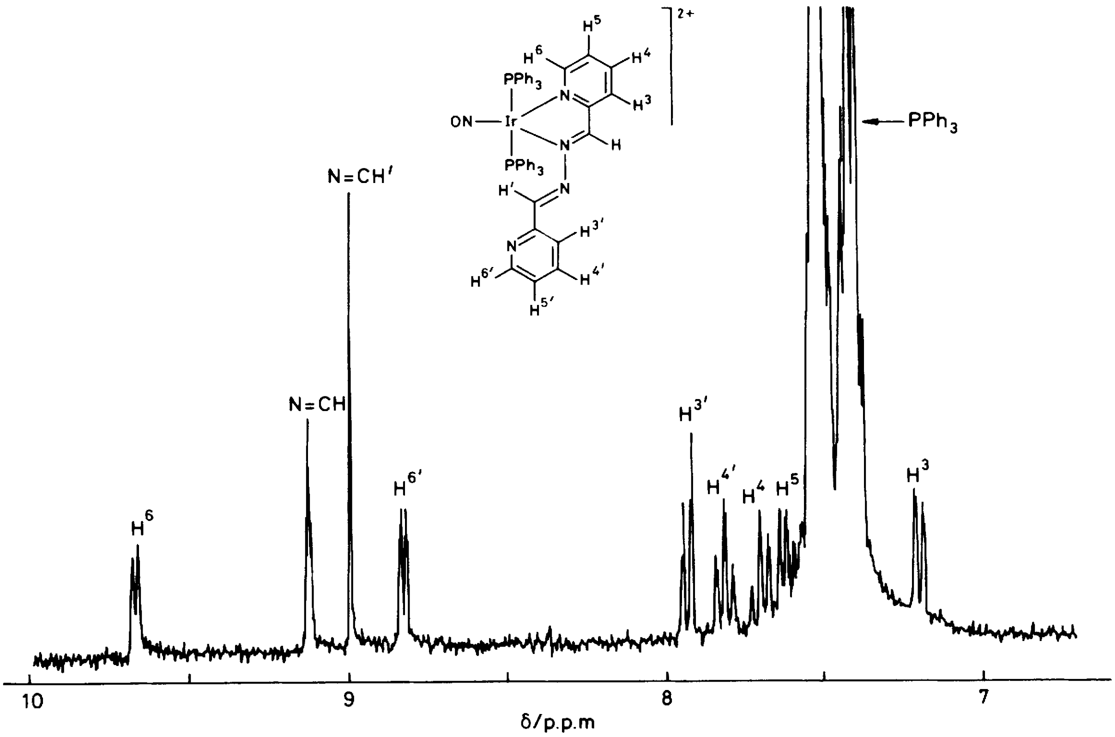


Figure 1. ^{1}H N.m.r. spectrum (300 MHz) at 20 °C of $[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$ (**2**) in the range 7—10 p.p.m.

Table 1. ^{1}H N.m.r. data (δ/p.p.m.)[a] for the ligands L

L	Pyridyl				Pyrid-		
	H^6	H^5	H^4	H^3	azine	N=CH	Methyl
paa[b]	8.73	7.37	7.80	8.13		8.70	
mpaa[c]		7.26	7.73	8.00		8.66	2.60
dppn[d]	8.73	7.43	7.93	8.72	8.67		

[a] In CD_2Cl_2. [b] $J_{65} = 4.9$, $J_{64} = 1.7$, $J_{63} = 1.0$, $J_{54} = 7.8$, $J_{53} = 1.2$, $J_{43} = 7.8$ Hz. [c] $J_{54} = 8.0$, $J_{53} = 1.0$, $J_{43} = 8.0$ Hz. [d] $J_{65} = 5.0$, $J_{64} = 1.7$, $J_{54} = 7.8$, $J_{53} = 1.2$, $J_{43} = 7.8$ Hz.

coupling with $^4J_{PH}$ = *ca.* 2 Hz, as found for other complexes.[14] Regarding their spectral positions, an opposite trend is observed. In (**2**) the signal is shifted upfield 0.40 p.p.m., while in (**3**) it is shifted downfield 0.05 p.p.m., behaviour which we are unable to explain at present. The corresponding protons on the unco-ordinated part of the azine ligands follow the same trend and appear as singlets with $\Delta\delta$ +0.27 p.p.m. in (**2**) and −0.59 p.p.m. in (**3**). The two protons on the pyridazine ring of complex (**4**), having $\Delta\delta$ +0.10 p.p.m. and −0.72 p.p.m., were assigned to H^5 and H^4 respectively. Their chemical shifts can be rationalized as due to opposite effects: that for H^5 is determined by co-ordination deshielding, while for H^4 the anisotropic shielding induced by the PPh_3 is dominant.

Complexes (**2**)—(**4**) form a series of isoelectronic five-co-ordinate compounds. For (**2**) and (**3**), on the basis of their spectroscopic data (Table 3) and by analogy with similar complexes of known structures,[12,15] the suggested geometry is trigonal bipyramidal, as previously proposed also for complex (**4**).[1] The two equivalent triphenylphosphine molecules occupy the apical positions, and the NO group is linearly bound to the metal in the plane of the ligand which forms a five-membered chelate ring (Figure 3).

Mononuclear Carbonyl Complexes.—The cationic carbonyl complex $[Ir(CO)(MeCN)(PPh_3)_2][PF_6]$ (**5**) reacts with the ligands L (1:1 molecular ratio) giving the mononuclear complexes (**6**)—(**8**) (Table 3). In order to aid the assignment of the ^{1}H n.m.r. spectra of (**6**)—(**8**) we synthesized the related complex (**9**) containing bipy ligand. Compounds (**6**), (**7**), and (**9**) are air stable as solids and in solution, while compound (**8**) is stable as a solid only.

Conductivity measurements on nitromethane solutions of (**6**), (**7**), and (**9**) are in agreement with 1:1 electrolytes.[9] The ^{31}P-{^{1}H} n.m.r. spectra consist of single resonances at *ca.* 20 p.p.m. demonstrating the equivalence of the two phosphines. The i.r. spectrum shows a strong CO stretch at *ca.* 1 900 cm^{-1} (KBr).

The ^{1}H n.m.r. spectra of (**6**) and (**7**) appear similar to those observed for the mononuclear nitrosyl complexes (**2**)—(**4**) (Table 4). The signals of the ligands, as previously discussed, are split into two sets attributable to their co-ordinated and unco-ordinated parts. With respect to the free ligands, the resonances of the protons of the co-ordinated pyridyl ring in (**2**)—(**4**) are deshielded significantly more than those of complexes (**6**)—(**7**), consistent both with the lower effective charge on the carbonyl cations and with the stronger π-acid character of NO^+.[16]

On the basis of the physical properties reported in Tables 3—5 the five-co-ordinate complexes (**6**) and (**7**) are isostructural with the nitrosyl species in Figure 3. Complex (**8**) is not stable in solution and was characterized only as a solid; however, it seems reasonable to assume that it is isostructural with (**6**) and (**7**).

Binuclear Carbonyl Complexes.—The reaction between the mononuclear complexes (**6**) or (**7**) and one equivalent of (**5**) gives good yields of bimetallic compounds of stoicheiometry $[Ir_2(CO)_2(PPh_3)_4(L)][PF_6]_2$ (**10**) and (**11**). For dppn the binuclear species was not obtained.

Compounds (**10**) and (**11**) are air stable both as solids and in solution; in nitromethane they behave as 1:2 electrolytes.[9] The i.r. spectra of solid samples (KBr), or as CH_2Cl_2 solutions, show

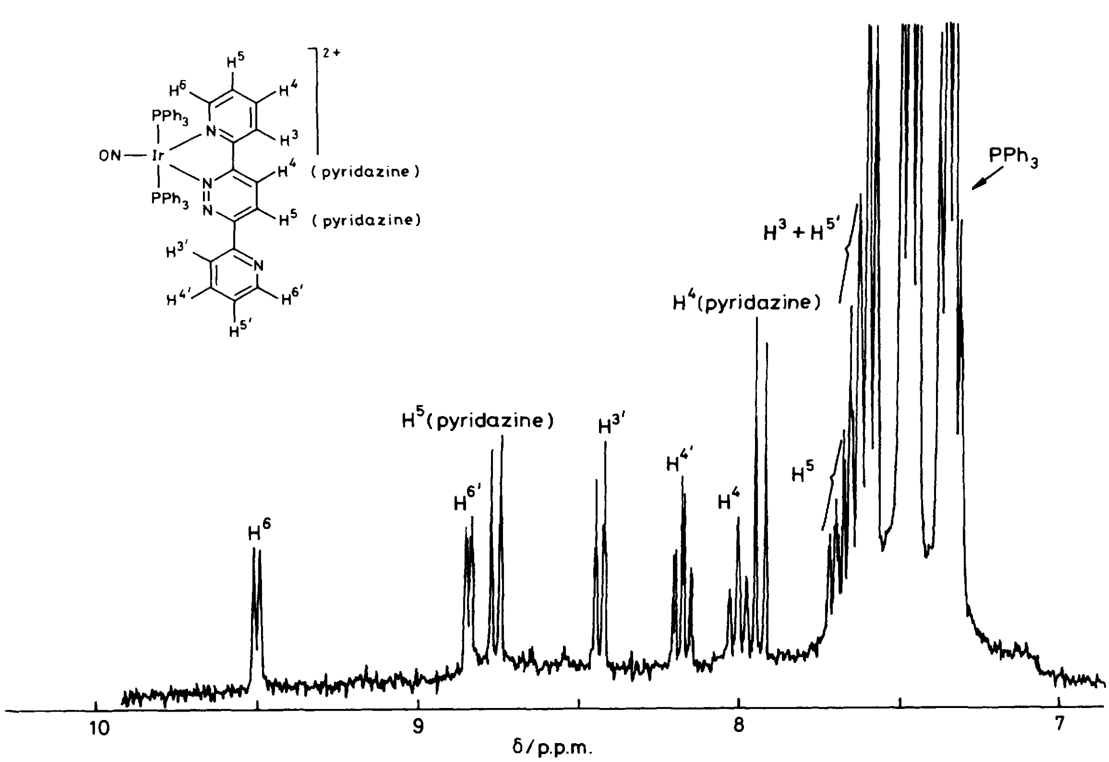


Figure 2. ^{1}H N.m.r. spectrum (300 MHz) at 20 °C of $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ (4) in the range 7—10 p.p.m.

Table 2. ^{13}C N.m.r. data (δ/p.p.m.)[a] for the ligands L

L	Pyridyl C^6	Pyridyl C^5	Pyridyl C^4	Pyridyl C^3	Pyridyl C^2	Pyridazine $C^{3,6}$	Pyridazine $C^{4,5}$	N=CH	Me
paa[b]	150.0	122.5	136.6	125.1	152.9			162.1	
mpaa[c]	158.8	119.6	136.7	124.7	152.4			162.0	24.4
dppn[c]	150.4	122.1	138.0	125.6	154.4	159.1	125.7		

[a] All values are relative to $SiMe_4$. [b] In CD_3NO_2. [c] In $CDCl_3$.

Table 3. Physical properties of iridium nitrosyl and carbonyl complexes

Compound[a]	Λ^{b}/Ω^{-1} cm^{-2} mol^{-1}	$\tilde{\nu}(NO)^{c}$/cm^{-1}	$\tilde{\nu}(CO)^{c}$/cm^{-1}	^{31}P N.m.r.[d] (δ/p.p.m.)
(1) $[Ir(NO)(MeCN)_3(PPh_3)_2]^{2+}$	178.00	1 540[e]		−13.27[e]
(2) $[Ir(NO)(paa)(PPh_3)_2]^{2+}$	172.70	1 800		9.07[f]
(3) $[Ir(NO)(mpaa)(PPh_3)_2]^{2+}$	177.80	1 805		9.00[f]
(4) $[Ir(NO)(dppn)(PPh_3)_2]^{2+}$	182.00	1 795		10.84[f]
(5) $[Ir(CO)(MeCN)(PPh_3)_2]^{+}$	76.02		1 975	23.20[g]
(6) $[Ir(CO)(paa)(PPh_3)_2]^{+}$	81.90		1 915	22.30[f]
(7) $[Ir(CO)(mpaa)(PPh_3)_2]^{+}$	87.70		1 925	21.67[f]
(8) $[Ir(CO)(dppn)(PPh_3)_2]^{+}$			1 910	
(9) $[Ir(CO)(bipy)(PPh_3)_2]^{+}$	92.20		1 890	23.53[f]
(10) $[\{Ir(CO)(PPh_3)_2\}_2(\mu\text{-paa})]^{2+}$	193.50		1 970	26.12[f]
(11) $[\{Ir(CO)(PPh_3)_2\}_2(\mu\text{-mpaa})]^{2+}$	174.00		1 990	24.50[f]

[a] The anion is PF_6^-. [b] In $MeNO_2$(10^{-3} mol dm^{-3} solution) at 25 °C. [c] KBr pellets. [d] Chemical shifts relative to external 85% H_3PO_4, downfield being positive. [e] In MeCN. [f] In CH_2Cl_2. [g] A. F. Williams, S. Bhaduri, and A. G. Maddock, *J. Chem. Soc., Dalton Trans.*, 1975, 1958.

one band attributable to a CO stretch (Table 3), indicating in both complexes the presence of two carbonyls in equivalent electronic environments. Remarkably, the ν(CO) values are shifted some 20 cm^{-1} to higher frequencies with respect to the mononuclear parent complexes (**6**) and (**7**), in agreement with the reduced electronic back-donation from the metals due to the bis-chelation of the ligands. The equivalence of the two metals bonded to the same ligand is, in both cases, confirmed by the presence of single resonances in the ^{31}P-$\{^{1}H\}$ n.m.r. spectra at 26.12 p.p.m. for (**10**) and 24.50 p.p.m. for (**11**).

The ^{1}H n.m.r. spectrum of (**11**) [poor solubility prevented an accurate spectrum of (**10**)] (Tables 4 and 5) shows signals

Table 4. ^{1}H N.m.r. assignments (δ/p.p.m.)[a] for the complexes

Compound[b]	Chemical shifts[c]	Coupling constants
$[Ir(NO)(bipy)(PPh_3)_2]^{2+}$[d]	H^{6}, 9.29; H^{5}, n.a. H^{4}, 7.91; H^{3}, n.a.	$J_{65} = 5.1$; $J_{43} = J_{54} = 7.3$
(2)	H^{6}, 9.64; H^{5}, 7.61 H^{4}, 7.70; H^{3}, 7.20	$J_{65} = 5.0$; $J_{54} = J_{43} = 7.7$ $J_{53} = 1.5$
	H$^{6'}$, 8.80; H$^{5'}$, n.a. H$^{4'}$, 7.81; H$^{3'}$, 7.93	$J_{6'5'} = 4.8$; $J_{5'4'} = J_{4'3'} = 7.8$ $J_{5'3'} = 1.0$; $J_{6'3'} = 0.9$ $J_{6'4'} = 1.7$
	N=CH, 9.10 N=CH′, 8.97	$^{4}J_{PH} = 1.8$—2.0
(3)	CH$_3$, 3.10; H^{5}, 7.30 H^{4}, 7.73; H^{3}, 7.27	$J_{54} = J_{43} = 7.8$
	CH′$_3$, 2.73, H$^{5'}$, n.a. H$^{4'}$, 7.74; H$^{3'}$, n.a.	$J_{5'4'} = J_{4'3'} = 7.7$
	N=CH, 8.61 N=CH′, 8.07	$^{4}J_{PH} = 1.9$—2.1
(4)	H^{6}, 9.51; H^{5}, 7.72 H^{4}, 8.02; H^{3}, 7.66	$J_{65} = 5.1$; $J_{54} = J_{43} = 7.8$ $J_{53} = 1.5$
	H$^{6'}$, 8.86; H$^{5'}$, 7.65 H$^{4'}$, 8.19; H$^{3'}$, 8.45	$J_{6'5'} = 4.8$; $J_{5'4'} = J_{4'3'} = 7.8$ $J_{5'3'} = J_{6'3'} = 0.9$; $J_{6'4'} = 1.7$
	pyridazine H^{4}, 7.95 pyridazine H^{5}, 8.77	$J_{45} = 9.0$
(6)	H^{6}, 8.69; H^{5}, 7.13 H^{4}, 7.63; H^{3}, 7.01	$J_{65} = 5.2$; $J_{54} = 7.3$ $J_{43} = 7.8$; $J_{53} = 1.2$
	H$^{6'}$, 8.87; H$^{5'}$, n.a. H$^{4'}$, 7.82; H$^{3'}$, 7.92	$J_{6'5'} = 4.8$; $J_{5'4'} = 7.5$ $J_{4'3'} = 7.8$; $J_{6'4'} = 1.5$
	N=CH, 8.34 N=CH′, 10.10	
(7)	CH$_3$, 2.84; H^{5}, 7.05 H^{4}, 7.55; H^{3}, 6.90	$J_{54} = J_{43} = 7.8$ $J_{53} = 1.0$
	CH′$_3$, 2.73; H$^{5'}$, n.a. H$^{4'}$, n.a.; H$^{3'}$, n.a.	
	N=CH, 8.42 N=CH′, 9.77	$^{4}J_{PH} = 1.1$
(9)	H^{6}, 8.83; H^{5}, 7.16 H^{4}, 7.66, H^{3}, n.a.	$J_{65} = 5.3$; $J_{54} = 7.7$ $J_{43} = 8.0$, $J_{64} = 1.7$ $J_{53} = 1.2$
(11)	CH$_3$, 2.53; H^{5}, 6.97 H^{4}, 7.85; H^{3}, 7.64	$J_{54} = J_{43} = 7.8$ $J_{53} = 1.0$
	N=CH, 10.26	

[a] Values are relative to SiMe$_4$; in CD$_2$Cl$_2$. All *J* values are in Hz. [b] The anion is PF$_6^-$. [c] n.a. = Not assigned because superimposed on PPh$_3$ protons. [d] Ref. 12.

corresponding to a symmetrically co-ordinated mpaa ligand, bis-chelating to two Ir(CO)(PPh$_3$)$_2$ moieties. The n.m.r. chemical shifts are not discussed because of the effect of the strong magnetic fields of the four close PPh$_3$ groups.

For each iridium atom in (**10**) and (**11**) a trigonal-bipyramidal co-ordination (Figure 4), as in the mononuclear complexes, is proposed. Therefore the overall geometry can be visualised as a combination of two regular bipyramids, one for each metal, which are joined by the N–N bond of the azine ligands and which are also probably tilted to some extent around the N–N axis.[4]

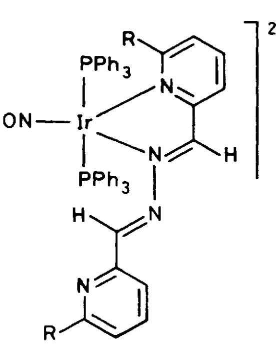


Figure 3. Proposed co-ordination geometry for the complex cations (**2**) (R = H) and (**3**) (R = Me)

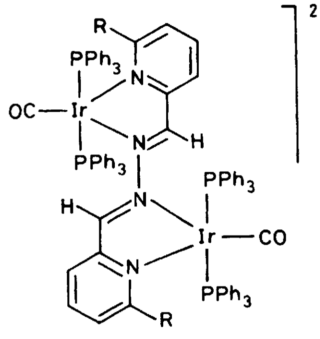


Figure 4. Proposed geometry for the binuclear complex cations (**10**) (R = H) and (**11**) (R = Me)

Conclusions

All the new complexes in Table 3 have been synthesized in good yields; none of the mixed binuclear complexes has been obtained. However, we can draw the following conclusions.

The parent complexes (**1**) and (**5**) form, by reaction with the ligand dppn, only mononuclear species, (**4**) and (**8**). In bimetallic compounds, dppn should impose a *cis* geometry, therefore the formation of binuclear species is probably forbidden due to the high steric demands of the bulky PPh$_3$ ligands above and below the dppn plane.

This view is supported by the results from the reaction of the mononuclear carbonyl complexes (**6**) or (**7**) with (**5**). The binuclear species (**10**) and (**11**) which form are obtained because paa and mpaa can arrange the two bulky Ir(CO)(PPh$_3$)$_2$ moieties in a transoid conformation.

The syntheses of binuclear species by reaction of paa or mpaa with two equivalents of the dicationic nitrosyl complex (**1**), or by reaction of the mononuclear nitrosyl complexes (**2**) and (**3**) with one additional equivalent of the carbonyl parent compound (**5**), were unsuccessful; kinetic and/or thermodynamic considerations may help to explain this. Taking into account that the formation of the binuclear species must take place in two steps, in the latter reaction the kinetics of the process would be severely affected by repulsion between the charge of the mononuclear cationic intermediate and the charge of the other approaching cation. Moreover, from the thermodynamic point of view, the total charge that would result for the bimetallic systems (*e.g.* 4+ or 3+) would reduce the stability of the products. The crucial value of the positive charge in determining both the formation and the stability of such a family of binuclear complexes seems to be 2+, as it is demonstrated by the preparation of the dicarbonyl complexes (**10**) and (**11**).

Table 5. ^{1}H Co-ordination shifts ($\Delta\delta$/p.p.m.)[a]

Compound[b]	H^6	H^5	H^4	H^3	$H^{6'}$	$H^{5'}$	$H^{4'}$	$H^{3'}$	N=CH	N=CH′
$[Ir(NO)(bipy)(PPh_3)_2]^{2+}$	+0.64	n.c.	+0.12	n.c.						
(2)	+0.91	+0.24	−0.10	−0.93	+0.07	n.c	+0.01	−0.20	+0.40	+0.27
(3)	+0.50[c]	+0.04	0.00	−0.73	+0.13[d]	n.c.	+0.01	n.c.	−0.05	−0.59
(4)	+0.78	+0.29	+0.09	−1.06	+0.13	+0.22	+0.26	−0.27	−0.72[e]	+0.10[f]
(6)	−0.04	−0.24	−0.17	−1.12	+0.14	n.c.	+0.02	−0.21	−0.36	+1.40
(7)	+0.24[c]	—0.21	−0.18	−1.10	+0.13[d]	n.c.	n.c.	n.c.	−0.24	+1.11
(9)	+0.15	−0.12	−0.14	n.c.					+1.60	
(11)	−0.07[c]	−0.29	+0.12	−0.36						

[a] $\Delta\delta$ = δ(complex) − δ(free ligand). Positive values are downfield from $SiMe_4$. n.c. = Not calculated because the relative signal was not assigned. [b] The anion is PF_6^-. [c] CH_3. [d] CH'_3. [e] Pyridazine H^4. [f] Pyridazine H^5.

Experimental

Apparatus and Techniques.—All experiments were performed in an oxygen-free nitrogen atmosphere. Proton, ^{13}C-{^1H}, and ^{31}P-{^1H} n.m.r. spectra were recorded on a Bruker WH 300 spectrometer. Infrared spectra were recorded for KBr pellets on a Perkin-Elmer 1330 spectrometer. Conductivity measurements were performed using a LKB 5300 B Conductolyser conductivity bridge. The melting points are uncorrected. Elemental analyses were carried out at the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Italy.

Tetrahydrofuran (thf) and diethyl ether were distilled from sodium diphenylketyl under a nitrogen atmosphere. Anhydrous CH_2Cl_2 was obtained by distillation from calcium hydride. Other solvents were reagent grade.

Preparation of Complexes.—Complexes **(1)**[17] and **(5)**[18] were prepared by standard routes; complex **(4)** was prepared by a published procedure.[1]

$[Ir(NO)(paa)(PPh_3)_2][PF_6]_2$ **(2)**. A solution of paa (0.055 g, 0.26 mmol) in thf (5 cm^3) was added to a stirred suspension of **(1)** (0.300 g, 0.26 mmol) in thf (15 cm^3). The resultant red solution was stirred at room temperature for 1.5 h. The pale yellow precipitate was filtered off, washed with thf and diethyl ether, and vacuum dried. Yield 68%, m.p. 200—201 °C (Found: C, 46.35; H, 3.25; N, 5.20. Calc for $C_{48}H_{40}F_{12}IrN_5OP_4$: C, 46.25; H, 3.25; N, 5.60%).

$[Ir(NO)(mpaa)(PPh_3)_2][PF_6]_2$ **(3)**. Complex **(1)** (0.500 g, 0.43 mmol) and mpaa (0.103 g, 0.43 mmol) were suspended in thf (20 cm^3) and the mixture was stirred for 12 h. The resultant beige precipitate was filtered off and dissolved in CH_2Cl_2 (10 cm^3). Ethanol (10 cm^3) was then slowly added to the soluble portion of crude product; by removal of half of the mixed solvents under reduced pressure a pale yellow solid was obtained which was filtered off, washed with diethyl ether, and dried under vacuum. Yield 34%, m.p. 158—159 °C (Found: C, 46.15; H, 3.65; N, 4.90. Calc. for $C_{50}H_{44}F_{12}IrN_5OP_4$: C, 47.10; H, 3.50; N, 5.50%).

$[Ir(CO)(paa)(PPh_3)_2][PF_6]$ **(6)**. A solution of paa (0.082 g, 0.39 mmol) in diethyl ether (20 cm^3) was added to a stirred solution of **(5)** (0.300 g, 0.32 mmol) in dichloromethane (10 cm^3) giving a red-brown solution. After 1 h the resultant microcrystalline yellow-brown precipitate was filtered off, washed with diethyl ether, and vacuum dried. Yield 91%, m.p. 152—153 °C (Found: C, 53.65; H, 3.65; N, 5.00. Calc. for $C_{49}H_{40}F_6IrN_4OP_3$: C, 53.50; H, 3.65; N, 5.10%).

$[Ir(CO)(mpaa)(PPh_3)_2][PF_6]$ **(7)**. The complex was prepared in a similar way (but using mpaa and a reaction time of 30 min) as a microcrystalline yellow brown solid. Yield 80%, m.p. 190—191 °C (Found: C, 53.70; H, 3.85; N, 4.75. Calc. for $C_{51}H_{44}F_6IrN_4OP_3$: C, 54.30; H, 3.95; N, 4.95%).

$[Ir(CO)(dppn)(PPh_3)_2][PF_6]$ **(8)**. A solution of dppn (0.116 g, 0.5 mmol) in EtOH (50 cm^3) was added to a suspension of **(5)** (0.463 g, 0.5 mmol) in EtOH (15 cm^3) and the mixture was stirred for 24 h at room temperature. The resultant beige precipitate was filtered off, washed with ethanol and diethyl ether, and vacuum dried. Yield 93%, m.p. 192—193 °C (Found: C, 54.25; H, 3.60; N, 4.85. Calc. for $C_{51}H_{40}F_6IrN_4OP_3$: C, 54.50; H, 3.60; N, 5.00%).

$[Ir(CO)(bipy)(PPh_3)_2][PF_6]$ **(9)**. The complex was prepared in a similar way as a pale yellow solid, reaction time 1 h. Yield 86%, m.p. 209—210 °C (Found: C, 53.70; H, 3.65; N, 2.45. Calc. for $C_{47}H_{38}F_6IrN_2OP_3$: C, 54.00; H, 3.65; N, 2.70%).

$[\{Ir(CO)(PPh_3)_2\}_2(\mu\text{-paa})][PF_6]_2$ **(10)**. A solution of **(5)** (0.232 g, 0.25 mmol) in dichloromethane (10 cm^3) was added to a stirred suspension of **(6)** (0.275 g, 0.25 mmol) in dichloromethane (5 cm^3) and the mixture was allowed to stand overnight at room temperature. The resultant yellow ochre solid was filtered off, washed with diethyl ether, and vacuum dried. Yield 81%, m.p. 219 °C (Found: C, 51.60; H, 3.35; N, 2.85. Calc. for $C_{86}H_{70}F_{12}Ir_2N_4O_2P_6$: C, 51.90; H, 3.55; N, 2.80%).

$[\{Ir(CO)(PPh_3)_2\}_2(\mu\text{-mpaa})][PF_6]_2$ **(11)**. Complex **(5)** (0.205 g, 0.22 mmol) and **(7)** (0.248 g, 0.22 mmol) were suspended in thf (15 cm^3). The mixture was refluxed for 5 h then cooled at room temperature. The orange product formed was filtered off, washed with thf and diethyl ether, and dried under vacuum. Recrystallization from dichloromethane–ethanol afforded bright orange crystals. Yield 72%, m.p. 227 °C (Found: C, 52.05; H, 3.40; N, 2.70. Calc. for $C_{88}H_{74}F_{12}Ir_2N_4O_2P_6$: C, 52.40; H, 3.70; N, 2.75%).

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