Iridium(III) *cis*-Dihydrido Complexes with 3,6-Bis(2′-pyridyl)pyridazine. Crystal Structure of the Pyridazinyl Complex $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]PF_6$ *

Anna Maria Manotti Lanfredi, Antonio Tiripicchio, and Franco Ugozzoli
Istituti di Chimica Generale ed Inorganica e di Strutturistica Chimica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, I 43100 Parma, Italy
Mauro Ghedini and Francesco Neve
Dipartimento di Chimica, Università della Calabria, I 87030 Arcavacata (CS), Italy

The complexes $[IrH_2(Me_2CO)_2(PPh_3)_2]X$ (X = PF_6 or SbF_6) react with 3,6-bis(2′-pyridyl)pyridazine, dppn, in dichloromethane at 20 or 0 °C. At 20 °C the resulting products are the mononuclear species $[IrH_2(dppn)(PPh_3)_2]X$ only, while at 0 °C, in addition the salts dppn·HX (X = PF_6 or SbF_6) and the homobinuclear complexes $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]X$ form. The structure of the dichloromethane solvate of the latter (X = PF_6) has been determined by *X*-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, with a = 14.014(4), b = 22.781(8), c = 14.328(3) Å, α = 108.58(4), β = 68.79(5), γ = 99.04(5)°, and Z = 2. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.052 for 6 725 observed reflections. The structure consists of binuclear cationic complexes, of PF_6^- anions, and of dichloromethane molecules of solvation. The cation has imposed C_i symmetry, so that the organic ligand, chelating on its opposite sides both metals through three nitrogen and one carbon atoms, must be disordered and statistically distributed in two positions with the carbon atom bonded to both metals. The distorted octahedral co-ordination around each Ir atom is completed by two P atoms from PPh_3 ligands in *trans* positions and by two terminal hydrides in *cis* positions.

3,6-Bis(2′-pyridyl)pyridazine, dppn, is a binucleating ligand useful for studies of the binding modes of small molecules with metal centres in a side-by-side arrangement. We have previously shown that, in heterobinuclear nitrosyl complexes, NO symmetrically bridges the metals in the dppn plane.[1,2] Extending our investigation to hydrido compounds, we now report the reactivity of $[IrH_2(Me_2CO)_2(PPh_3)_2]X$, X = PF_6 or SbF_6, with dppn, and the *X*-ray structure of the homobinuclear complex $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]PF_6$, the first structurally characterized example of metallation occurring at a pyridazine ring.

Results and Discussion

The synthesis of the above mentioned dppn binuclear nitrosyl compounds was carried out in two steps: (*i*) formation of the dppn mononuclear nitrosyl species and (*ii*) reaction with a second metal centre. Both steps are replacement reactions, therefore starting complexes containing weakly bonded ligands were used. As a source of hydrido species, we selected the acetone complexes $[IrH_2(Me_2CO)_2(PPh_3)_2]X$ [X = PF_6 (**1a**) or SbF_6 (**1b**)].

The reactions between (**1a**) or (**1b**) and dppn in a 1:1 molar ratio in dichloromethane, at 20 or 0 °C, lead to different products depending on the temperature.

Reaction at 20 °C.—When the reactions are carried out at 20 °C yellow products which analyse for the mononuclear species $[IrH_2(dppn)(PPh_3)_2]X$ [X = PF_6 (**2a**) or SbF_6 (**2b**)] are formed in high yields.

Such salts, 1:1 electrolytes in nitromethane solutions,[3] were characterized by spectral methods (data in Table 1 and Experimental section). In particular, i.r. and ^1H n.m.r. data† indicate terminal *cis* dihydrides and the single resonance in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra [at 19.02 p.p.m. for (**2a**) and 19.08 p.p.m. for (**2b**)] indicates equivalence of the two phosphines. The structure of the cation of complex (**2a**) or (**2b**), deduced from these data as well as by comparison with the known parent complex (**1a**),[5] and from the *X*-ray structure determination of the homologous rhodium compound $[RhH_2(dppn)(PPh_3)_2]PF_6$,[6] appears in Scheme 1.

Reaction at 0 °C.—At this temperature the reactions between dppn and complex (**1a**) or (**1b**) afford three products, (**A**)—(**C**). The only difference between (**1a**) and (**1b**) was in the relative yields (Experimental section). These products were characterized by microanalytical, conductivity, and spectral methods.

Compounds (**A**), the main products, were identified as the mononuclear dihydrido complexes (**2a**) or (**2b**) by comparison with the compounds formed at 20 °C.

The products (**B**) are white solids that do not contain iridium. Their i.r. spectra display absorptions characteristic of the anion (PF_6 or SbF_6) together with NH stretches, at about 3 250 cm^{-1}. Moreover, upon reaction with $NaHCO_3$ they give dppn quantitatively. Such compounds are therefore formulated as dppn·HX, where X is PF_6 or SbF_6.

Compounds (**C**) analyse for binuclear complexes of stoicheiometry $[\{IrH_2(PPh_3)_2\}_2(C_{14}H_9N_4)]X$, X = PF_6 or SbF_6, denoted as (**3a**) or (**3b**) respectively in Table 1, and in nitromethane solutions they behave as 1:1 electrolytes. Their i.r. spectra show bands of medium intensity due to terminal ν(Ir–H) (Experimental section). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra

* μ-[3,6-Bis(2′-pyridyl)pyridazin-4-yl-N^1N':C^4N'']-bis[dihydridobis(triphenylphosphine)iridium] hexafluorophosphate–dichloromethane (1/1).

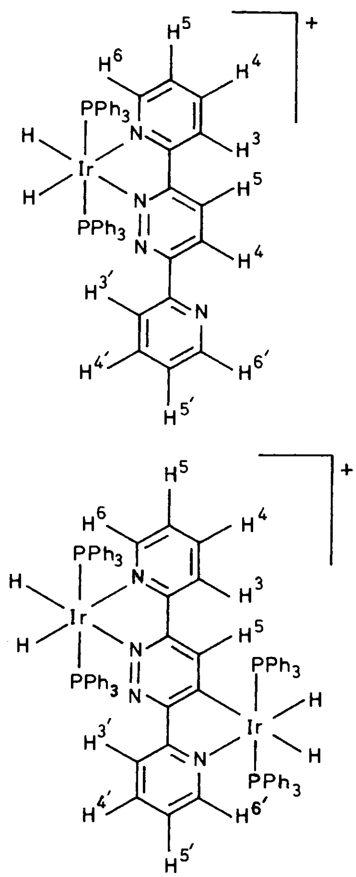
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

† The assignment of the ligand's signals was performed as previously described.[4]

Table 1. Proton and $^{31}P-\{^{1}H\}$ n.m.r. data[a]

	Ir-H[b]			
Complex	δ(H)	^{2}J(PH)	^{2}J(HH)	δ(P)[c]
$[IrH_2(MeCN)_2(PPh_3)_2]BF_4$[d]	−20.63	15.0		21.49
(**2a**)	−19.38	17.0	7.0	19.02
	−18.74	17.0	7.0	
(**2b**)	−19.37	16.7	7.4	19.08
	−18.72	16.7	7.4	
(**3a**)	−20.30	18.3	6.6	20.32
	−18.72	16.3	6.6	18.34
	−19.51	17.2	3—4	
	−10.98	20.5	3—4	
(**3b**)	−20.30	18.0	6.7	20.40
	−18.71	17.0	6.9	18.50
	−19.50	17.5	3—4	
	−10.99	20.0	3—4	

[a] In CD_2Cl_2 solution at room temperature. [b] Chemical shifts (δ) in p.p.m. (relative to $SiMe_4$); coupling constant (J) in Hz. [c] Chemical shifts (δ) in p.p.m. to high frequency of 85% H_3PO_4. [d] From ref. 5.



Scheme 1. Proposed co-ordination geometry for the complex cation (**2a**) or (**2b**) and that found for the complex cation (**3a**) or (**3b**) with the numbering scheme for the hydrogens

show two resonances [20.32 and 18.34 p.p.m. for (**3a**), 20.40 and 18.50 p.p.m. for (**3b**)] each attributable to a *trans*-$Ir(PPh_3)_2$ moiety. The ^{1}H n.m.r. spectra in the dppn region show only a singlet due to one pyridazinic proton, while in the hydridic region two set of resonances, fingerprints of two *cis*-IrH_2 arrangements, are observed.

Interestingly, only an IrH_2 moiety [−20.30 and −18.72 for (**3a**), −20.30 and −18.71 for (**3b**)] results in an environment, as in the mononuclear complex (**2a**) or (**2b**), with both IrH *trans* to N. The second IrH_2 moiety exhibits signals at −19.51 and −10.98 for (**3a**) [−19.50 and −10.99 for (**3b**)] where the former can be attributed to Ir–H *trans* to N, while the latter simply indicates a stronger *trans* effect on the Ir–H bond.[7]

Table 2. Selected bond distances (Å) and angles (°) in complex (**3a**) (two independent cations)*

	Cation 1	Cation 2
Ir–P(1)	2.290(4)	2.294(4)
Ir–P(2)	2.272(4)	2.291(4)
Ir–N(1)	2.133(11)	2.148(9)
Ir–N(2),C(8)	2.117(15)	2.078(12)
N(1)–C(1)	1.35(2)	1.31(2)
C(1)–C(2)	1.42(2)	1.42(2)
C(2)–C(3)	1.40(4)	1.45(3)
C(3)–C(4)	1.36(4)	1.39(3)
C(4)–C(5)	1.39(3)	1.43(2)
N(1)–C(5)	1.36(3)	1.35(2)
C(1)–C(6)	1.46(3)	1.47(2)
C(6)–N(2),C(8)	1.31(2)	1.36(2)
C(6)–N(3),C(7)	1.38(2)	1.40(2)
N(2),C(8)–N(3′),C(7′)	1.37(2)	1.34(2)
P(1)–Ir–N(1)	95.7(3)	93.6(3)
P(1)–Ir–N(2),C(8)	95.5(4)	97.4(4)
P(2)–Ir–N(1)	93.8(3)	94.3(3)
P(2)–Ir–N(2),C(8)	98.7(3)	94.1(4)
P(1)–Ir–P(2)	164.5(2)	167.3(2)
N(1)–Ir–N(2),C(8)	75.6(5)	76.6(5)
Ir–N(1)–C(5)	123(1)	122(1)
Ir–N(1)–C(1)	117(1)	116(1)
C(1)–N(1)–C(5)	120(1)	122(1)
N(1)–C(1)–C(6)	114(1)	115(1)
N(1)–C(1)–C(2)	122(1)	123(2)
C(2)–C(1)–C(6)	124(1)	122(2)
C(1)–C(2)–C(3)	115(1)	117(2)
C(2)–C(3)–C(4)	124(2)	120(2)
C(3)–C(4)–C(5)	118(2)	118(2)
N(1)–C(5)–C(4)	121(2)	121(2)
C(1)–C(6)–N(2),C(8)	117(1)	116(1)
C(1)–C(6)–N(3),C(7)	119(1)	120(1)
N(3),C(7)–C(6)–N(2),C(8)	124(1)	125(1)
C(6)–N(2),C(8)–N(3′),C(7′)	118(1)	116(1)
Ir–N(2),C(8)–C(6)	117(1)	116(1)
Ir–N(2),C(8)–N(3′),C(7′)	125(1)	128(1)
C(6)–N(3),C(7)–N(2′),C(8′)	118(1)	120(1)

* The primed atoms are related to the unprimed by an inversion centre.

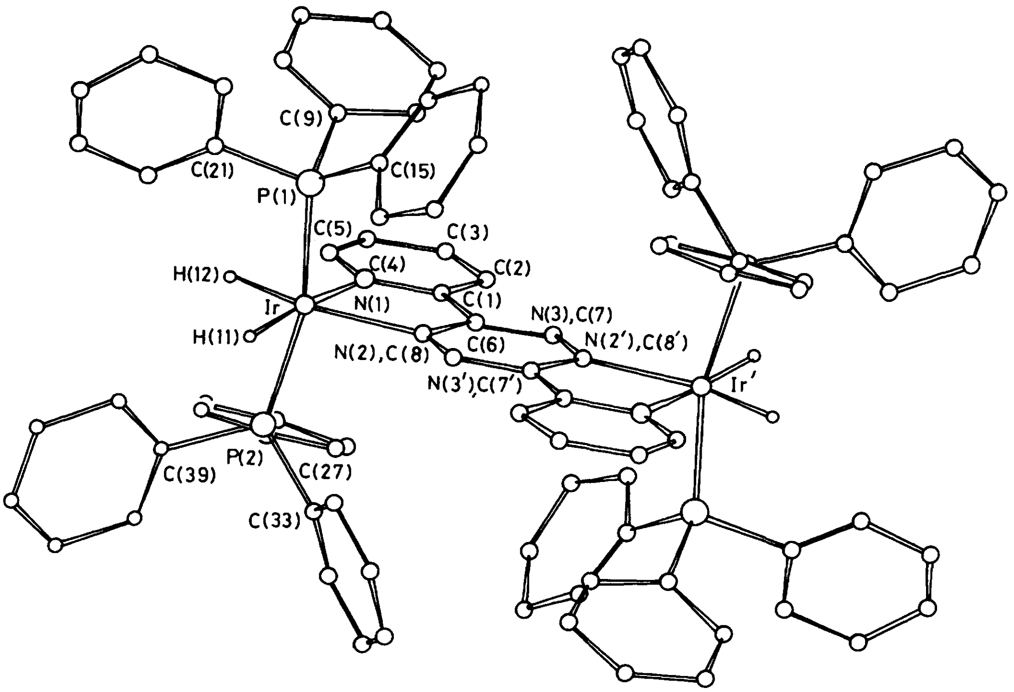


Figure. View of the cationic complex $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]^+$ with the atomic numbering system. Because of the disordered organic ligand, atoms N(2) and N(3) of the central ring can be replaced by C(7) and C(8). The primed atoms are related to the unprimed ones by an inversion centre

Crystal Structure of $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]PF_6$ (**3a**).—The crystal structure of complex (**3a**) consists of di-iridium cations, PF_6^- anions, and dichloromethane molecules of solvation. In the unit cell there are two crystallographically independent, but practically equivalent, cations, of imposed C_i symmetry. The deprotonated dppn acts as a quadridentate ligand chelating, on opposite sides, the two metal atoms, one through one pyridyl and one pyridazinyl nitrogen atom, the other through one pyridyl nitrogen and one pyridazinyl carbon atom. Since this ligand is not centrosymmetric, it must be disordered and distributed in two positions of equal occupancy with the pyridazinyl carbon statistically bonded to both metals. The structure of one of the two independent cations is depicted in the Figure together with the atomic numbering system; selected bond distances and angles are given in Table 2. Half of the ligand is bonded to one Ir atom through two N atoms and half through one N and one C atom in such a way that in the central ring the N(2) and N(3) atoms are statistically replaced by the C(7) and C(8) atoms.

The octahedral co-ordination of the Ir atoms involves the two N or one N and one C atom from the chelating ligand, two hydrides in *cis* positions, and two P atoms from PPh_3 ligands in *trans* positions. The hydrides have been located clearly in the Fourier difference map in the expected positions, although at a slightly short distance from the metal in one cation [Ir–H 1.41 and 1.48 Å, H–Ir–H 75.2° in cation 1, Ir–H 1.82 and 1.87 Å, H–Ir–H 76.3° in cation 2].

The conformation of the deprotonated dppn ligand is the same as that of neutral dppn in the mononuclear iridium [(**2a**) and (**2b**)] and rhodium complexes,[6] *i.e.* with the pyridyl nitrogen atoms *trans* to each other with respect to the central ring, but differs from that found in the mixed-metal cation $[IrCl(PPh_3)_2(\mu\text{-dppn})(\mu\text{-NO})CuCl]^{2+}$ where the pyridyl nitrogen atoms are on the same side in order to allow chelation of the two metals through the four nitrogen atoms.[1] As in this mixed-metal complex, in the present di-iridium complex all the atoms are nearly coplanar, except those of the PPh_3 ligand.

It is noteworthy that the Ir–N distances in complex (**3a**) [2.133(11) and 2.148(9) Å involving N(1); 2.117(15) and 2.078(12) Å involving N(2), overlapped by Ir–C(8)] are longer than the corresponding bond distances in the Ir–Cu mixed-metal complex [1.98(2) *trans* to Cl, 2.03(2) Å *trans* to nitrogen from the nitrosyl group] confirming the pronounced *trans* effect exerted by the H ligand, already noted in the complex $[RhH(NH_3)_5][ClO_4]_2$.[8]

The Ir ··· Ir separation [6.975(3) Å in both cations] in (**3a**) is much greater than the Ir ··· Cu one in the mixed-metal complex [3.416(5) Å], where the metals are chelated on the same side of the dppn ligand.

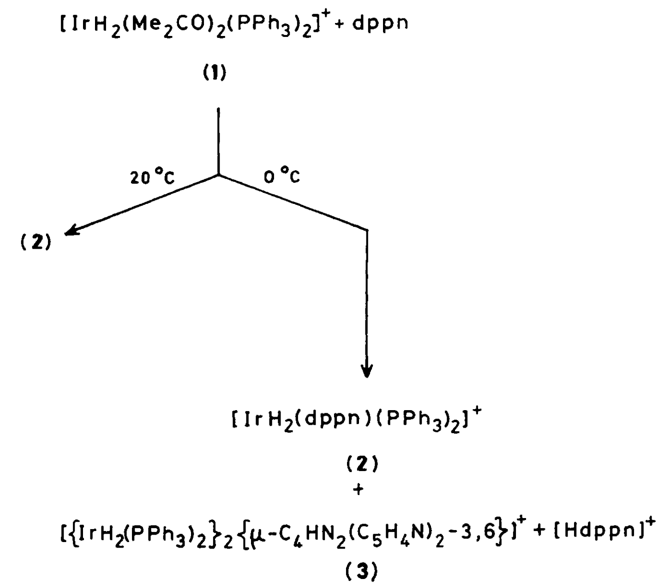
The PF_6^- anion is quite regular with P–F bonds in the range 1.50(2)—1.60(2) Å and F–P–F angles, involving *cis*-F atoms, in the range 85.7(1)—94.7(1)°.

Conclusions

The reactivity of the cation $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$ with dppn is illustrated in Scheme 2.

Remarkably, at 20 °C the reaction affords the straightforward product (**2**), while at 0 °C both (**2**) and the binuclear complex (**3**) are formed. Moreover, further attempts to synthesize (**3**) by reaction between (**2**) and (**1**) were unsuccessful.

The main feature of complex (**3**) is the new Ir–C bond with the pyridazine ring. The formation of such a bond may tentatively be explained by kinetic considerations. The rate of formation of (**2**) at 0 °C is slower than at 20 °C, so that other reactions can compete [equation (1)]. In particular, as previously suggested by Schrock and Osborn[9] in a similar case concerning a rhodium complex, deprotonation of the cationic dihydrido species (**1**) can occur [equation (2)]. Thereafter, in the present case, free dppn traps the proton giving rise to the dppn salt [equation (3)], while the reactive monohydrido intermediate could react with the free pyridinic ring of (**2**) and restore the IrH_2 moiety by



Scheme 2. Reactivity of $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$ with dppn

insertion of the metal in the neighbouring C–H pyridazine bond [equation (4)].

$$[IrH_2(Me_2CO)_2(PPh_3)_2]^+ + dppn \longrightarrow [IrH_2(dppn)(PPh_3)_2]^+ + 2Me_2CO \quad (1)$$

$$[IrH_2(Me_2CO)_2(PPh_3)_2]^+ \rightleftharpoons [IrH(Me_2CO)_2(PPh_3)_2] + H^+ \quad (2)$$

$$dppn + H^+ \longrightarrow [Hdppn]^+ \quad (3)$$

$$[IrH_2(dppn)(PPh_3)_2]^+ + [IrH(Me_2CO)_2(PPh_3)_2] \longrightarrow [\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]^+ \quad (4)$$

Finally, noteworthy is the inertness of complexes (**2**), since in reactions with acid, alkali, olefin, or CO, as well as with a second metal centre such as Cu^{II} or Pt^{II}, they were recovered unchanged.

Experimental

All reactions were carried out under nitrogen, although the complexes were not air-sensitive. Anhydrous methylene chloride was obtained by distillation from calcium hydride. Other solvents were reagent grade. The ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra were recorded on a Bruker WH 300 spectrometer, i.r. spectra on a Perkin-Elmer 1330 spectrophotometer. Conductivity measurements were performed using a LKB 5300 B conductolyser conductivity bridge. The melting points are uncorrected. Elemental analyses were carried out by the Microanalyses Laboratory of the Istituto di Farmacia dell' Università di Pisa, Pisa. The ligand 3,6-bis(2'-pyridyl)pyridazine (dppn)[10] and the complexes $[IrH_2(Me_2CO)_2(PPh_3)_2]X$ (X = PF_6 or SbF_6)[11] were prepared by the literature methods.

Preparations.—$[IrH_2(dppn)(PPh_3)_2]PF_6$ (**2a**). The complex $[IrH_2(Me_2CO)_2(PPh_3)_2]PF_6$ (0.1 g, 0.1 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of dppn (0.024 g, 0.1 mmol) in CH_2Cl_2 (2 cm^3). The resulting yellow solution was stirred at room temperature for 1 h. A light yellow solid was formed by addition of diethyl ether (20 cm^3) and recrystallized from CH_2Cl_2–Et_2O (0.1 g, 89%), m.p. 240—242 °C (Found: C, 51.95; H, 3.85; N, 4.85. $C_{50}H_{42}F_6IrN_4P_3{\cdot}CH_2Cl_2$ requires C, 51.8; H, 3.75; N, 4.75%), Λ = 73.75 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): ν 2 210 and 2 170 cm^{-1} (Ir–H). N.m.r. data of complexed dppn (300 MHz, CD_2Cl_2, standard $SiMe_4$, py = pyridine): δ_H 6.84 [1 H, ddd, $J(H^5H^4)$ = 7.5, $J(H^5H^3)$ = 1.5, H^5 of py], 7.55 [ddd, 1 H, $J(H^{5'}H^{4'})$ = 7.8, $H^{5'}$ of py], 7.79 [1 H, br vt (virtual triplet), $J(H^4H^3)$ = 7.8, H^4 of py], 7.84 (1 H, br d, H^3 of py), 8.00 (1 H, d, H^5 of pyridazine], 8.06 [1 H, vt, $J(H^{4'}H^{3'})$ = 8.0, $H^{4'}$ of py], 8.14 [1 H, br d, $J(H^6H^5)$ = 5.5, H^6 of py], 8.57 [1 H, d, $J(H^5H^4)$ = 9.0, H^4 of pyridazine], 8.58 (1 H, ddd, $H^{3'}$ of py), and 8.76 [1 H, ddd, $J(H^{6'}H^{5'})$ = 4.8, $J(H^{6'}H^{4'})$ = 1.8, $J(H^{6'}H^{3'})$ = 1.0 Hz, $H^{6'}$ of py].

$[IrH_2(dppn)(PPh_3)_2]SbF_6$ (**2b**). The SbF_6^- salt was obtained in a similar way from $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (0.1 g, 0.094 mmol) and dppn (0.022 g, 0.094 mmol) as a light yellow crystalline solid (0.1 g, 90%), m.p. 233—235 °C (Found: C, 49.05; H, 3.55; N, 4.20. $C_{50}H_{42}F_6IrN_4P_2Sb{\cdot}0.5CH_2Cl_2$ requires C, 49.25; H, 3.50; N, 4.55%), Λ = 74.10 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): ν 2 210 and 2 170 cm^{-1} (Ir–H). This complex was spectroscopically analogous to (**2a**) and corresponding data are not extensively reported.

$[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]PF_6$ (**3a**). A cold solution of dppn (0.054 g, 0.23 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of $[IrH_2(Me_2CO)_2(PPh_3)_2]PF_6$ (0.225 g, 0.23 mmol) in CH_2Cl_2 (3 cm^3) cooled at 0 °C. The resulting pale yellow solution was stirred at this temperature for 30 min. After this time a small amount of white precipitate (0.02 g, 25%) was formed. This precipitate, identified as dppn·HPF_6, was removed by filtration and characterized by i.r. spectroscopy [ν(N–H) 3 270—3 200, ν(P–F) 850—830 cm^{-1}]. Addition of diethyl ether (25 cm^3) to the yellow filtrate followed by cooling at 20 °C for several hours resulted in the formation of a yellow precipitate of (**3a**) and a yellow solution. By addition of diethyl ether, a light yellow solid (0.075 g, 30%) identical to complex (**2a**) was recovered from the solution. Complex (**3a**) was recrystallized from CH_2Cl_2–EtOH (0.056 g, 25%), m.p. 270 °C (Found: C, 55.0; H, 4.00; N, 2.90. $C_{86}H_{73}F_6Ir_2N_4P_5{\cdot}CH_2Cl_2$ requires C, 55.0; H, 4.05; N, 2.95%), Λ = 83.45 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): ν 2 180, 2 100, and 1 950 cm^{-1} (Ir–H). N.m.r. data of complexed dppn (300 MHz, CD_2Cl_2, standard $SiMe_4$): 6.27 [1 H, ddd, $J(H^6H^5)$ = 5.0, $J(H^5H^4)$ = 7.0, $J(H^5H^3)$ = 1.4, H^5 of py], 6.34 [1 H, ddd, $J(H^{6'}H^{5'})$ 5.5, $J(H^{5'}H^{4'})$ = 7.4, $J(H^{5'}H^{3'})$ = 1.2, $H^{5'}$ of py], 7.60 (1 H, br d, H^3 of py), 7.65 [1 H, br vt, $J(H^4H^3)$ = 7.8, H^4 of py], 7.78 [1 H, br vt, $J(H^{4'}H^{3'})$ = 7.9 Hz, $H^{4'}$ of py], 8.08 (1 H, s, H^5 of pyridazine), and 8.51 (1 H, br, d, $H^{3'}$ of py).

$[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]SbF_6$. Starting from $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (0.2 g, 0.19 mmol) and dppn (0.044 g, 0.19 mmol), at 0 °C three products were obtained: (**2b**) (0.12 g, 54%), dppn·$HSbF_6$ (0.02 g, 23%) [ν(N–H) 3 250, 3 200, ν(Sb–F) 658 cm^{-1}], and (**3b**). The latter was recrystallized from CH_2Cl_2–EtOH (0.04 g, 23%), m.p. 253 °C (Found: C, 51.85; H, 3.65; N, 3.30. $C_{86}H_{73}F_6Ir_2N_4P_4Sb{\cdot}CH_2Cl_2$ requires C, 52.45; H, 3.80; N, 2.80%), Λ = 79.08 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane. I.r. (KBr disc): ν 2 220, 2 160, and 1 960—1 935 cm^{-1} (Ir–H). As for (**2b**), the spectroscopic data for (**3b**) are not extensively reported.

Crystal Structure Determination of the Dichloromethane Solvate of Complex (**3a**).—An irregularly shaped yellow crystal of approximate dimensions 0.25 × 0.34 × 0.40 mm was used. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 carefully centred reflections (with θ in the range 10—15°), chosen from diverse regions of the reciprocal space.

Crystal data. $C_{86}H_{73}F_6Ir_2N_4P_5{\cdot}CH_2Cl_2$, M = 1 900.78, triclinic, a = 14.014(4), b = 22.781(8), c = 14.328(3) Å, α = 108.58(4), β = 68.79(5), γ = 99.04(5)°, U = 4 038(3) Å^3, space

Table 3. Fractional atomic co-ordinates (× 10⁴) with estimated standard deviations in parentheses for the non-hydrogen atoms except the hydridic ones

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ir(1)	714	702	2 994	C(401)	1 821(13)	2 192(8)	2 617(13)
Ir(2)	2 264	5 747	363	C(411)	2 444(15)	2 727(10)	2 290(15)
P(11)	1 539(3)	−135(2)	1 726(3)	C(421)	2 055(15)	3 313(9)	2 825(15)
P(21)	171(3)	1 671(2)	3 940(3)	C(431)	1 129(14)	3 420(8)	3 646(14)
P(12)	2 726(3)	6 259(2(	−890(3)	C(441)	554(13)	2 898(8)	3 997(13)
P(22)	2 030(3)	5 402(2)	1 772(3)	C(92)	1 683(10)	6 496(6)	−1 141(11)
P(3)	3 994(4(	1 982(3)	7 276(5)	C(102)	1 722(11)	6 450(7)	−2 157(12)
N(11)	−797(8)	308(5)	3 123(9)	C(112)	939(13)	6 678(8)	−2 321(13)
N(21)	313(11)	298(6)	4 235(10)	C(122)	135(13)	6 987(8)	−1 416(14)
N(31)	−950(10)	−289(6)	5 234(10)	C(132)	93(12)	7 020(8)	−429(13)
N(12)	2 677(9)	4 861(5)	−757(8)	C(142)	871(11)	6 772(7)	−275(11)
N(22)	879(9)	5 349(6)	180(9)	C(152)	3 490(11)	6 990(7)	−693(12)
N(32)	46(10)	4 412(6)	−659(10)	C(162)	3 556(14)	7 371(9)	−1 320(15)
C(11)	−1 245(11)	23(7)	3 877(11)	C(172)	4 263(17)	7 923(10)	−1 233(17)
C(21)	−2 260(12)	−237(7)	4 071(14)	C(182)	4 752(14)	8 082(9)	−504(15)
C(31)	−2 742(13)	−191(8)	3 399(20)	C(192)	4 615(12)	7 713(8)	122(13)
C(41)	−2 309(16)	99(10)	2 642(17)	C(202)	4 007(13)	7 153(8)	22(13)
C(51)	−1 310(13)	344(7)	2 502(13)	C(212)	3 522(10)	5 790(6)	−2 137(11)
C(61)	−591(11)	11(6)	4 469(10)	C(222)	3 076(11)	5 289(7)	−2 699(12)
C(12)	1 924(12)	4 505(6)	−1 006(12)	C(232)	3 710(13)	4 864(8)	−3 580(13)
C(22)	2 086(16)	3 922(7)	−1 782(12)	C(242)	4 756(14)	4 925(8)	−3 857(14)
C(32)	3 126(21)	3 715(10)	−2 242(15)	C(252)	5 194(14)	5 444(9)	−3 306(15)
C(42)	3 910(17)	4 087(8)	−1 934(14)	C(262)	4 618(13)	5 877(8)	−2 456(14)
C(52)	3 649(12)	4 673(7)	−1 169(11)	C(272)	2 565(10)	4 653(6)	1 363(10)
C(62)	907(10)	4 768(7)	−485(11)	C(282)	2 060(10)	4 115(6)	900(11)
C(91)	681(12)	−675(7)	1 144(12)	C(292)	2 553(11)	3 565(7)	365(11)
C(101)	−86(11)	−1 034(7)	1 738(11)	C(302)	3 620(12)	3 554(7)	240(12)
C(111)	−833(12)	−1 363(7)	1 394(12)	C(312)	4 118(11)	4 075(7)	708(12)
C(121)	−868(15)	−1 391(9)	415(15)	C(322)	3 621(10)	4 619(6)	1 245(11)
C(131)	−114(16)	−1 070(10)	−215(16)	C(332)	2 583(9)	5 885(6)	2 761(10)
C(141)	681(14)	−712(9)	142(15)	C(342)	2 538(12)	5 643(7)	3 562(12)
C(151)	2 142(11)	−624(7)	2 105(12)	C(352)	2 919(12)	6 022(8)	4 383(13)
C(161)	2 065(15)	−1 253(9)	1 814(15)	C(362)	3 326(15)	6 600(9)	4 330(15)
C(171)	2 615(18)	−1 638(11)	2 086(17)	C(372)	3 356(12)	6 822(8)	3 540(13)
C(181)	3 163(17)	−1 288(11)	2 690(17)	C(382)	2 991(12)	6 464(7)	2 725(12)
C(191)	3 352(18)	−629(11)	3 077(18)	C(392)	725(9)	5 320(6)	2 624(10)
C(201)	2 753(13)	−285(8)	2 715(14)	C(402)	89(11)	5 808(7)	2 911(11)
C(211)	2 601(11)	51(7)	622(11)	C(412)	−900(13)	5 797(8)	3 658(13)
C(221)	3 335(17)	−386(10)	81(17)	C(422)	−1 225(12)	5 327(7)	4 114(12)
C(231)	4 150(21)	−230(13)	−853(22)	C(432)	−603(12)	4 833(8)	3 847(13)
C(241)	4 174(17)	315(11)	−1 032(17)	C(442)	398(11)	4 837(7)	3 099(12)
C(251)	3 452(15)	715(9)	−500(15)	F(1)	4 728(15)	2 371(9)	7 871(15)
C(261)	2 611(14)	597(8)	379(14)	F(2)	3 063(17)	2 402(10)	8 027(17)
C(271)	−1 110(10)	1 755(6)	4 008(11)	F(3)	3 236(12)	1 603(7)	6 714(12)
C(281)	−1 242(13)	1 958(8)	3 209(13)	F(4)	4 793(15)	1 550(9)	6 471(15)
C(291)	−2 243(18)	1 591(11)	3 169(18)	F(5)	3 647(13)	1 540(9)	7 978(15)
C(301)	−3 063(15)	1 735(9)	3 857(15)	F(6)	4 334(10)	2 411(7)	6 510(11)
C(311)	−2 960(16)	1 547(10)	4 681(16)	Cl(1)	3 913(14)	1 739(9)	3 747(15)
C(321)	−1 953(12)	1 545(7)	4 700(13)	Cl(2)	4 821(17)	3 006(10)	4 128(19)
C(331)	165(11)	1 957(6)	5 303(11)	Cl(3)	2 997(19)	3 007(12)	4 777(24)
C(341)	−557(12)	2 339(7)	6 096(13)	C(45)	3 910(25)	2 539(13)	4 507(29)
C(351)	−432(15)	2 556(9)	7 136(15)	H(11)	1 636(82)	1 130(51)	2 933(85)
C(361)	406(13)	2 385(8)	7 269(13)	H(12)	944(83)	852(51)	2 050(87)
C(371)	1 135(14)	2 017(8)	6 444(14)	H(21)	1 778(80)	6 459(49)	1 374(84)
C(381)	1 034(12)	1 775(7)	5 420(13)	H(22)	3 453(80)	6 234(50)	456(83)
C(391)	916(11)	2 311(7)	3 453(11)				

group $P\bar{1}$, $Z = 2$, $D_c = 1.563$ g cm^{-3}, $F(000) = 1\,884$, μ(Mo-K_α) = 35.03 cm^{-1}.

Data collection and processing. Data were collected at room temperature on a Siemens AED diffractometer using niobium-filtered Mo-K_α radiation ($\lambda = 0.710\,69$ Å) and the θ—2θ scan mode, the individual reflections profiles having been analysed according to Lehmann and Larsen.[12] All reflections in the range $3 \leqslant \theta \leqslant 25°$ were measured; of 15 418 independent reflections, 6 725 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis. A correction for the absorption effects was applied[13] using the program ABSORB[14] (maximum and minimum values for the absorption corrections in the polar angles φ and μ are 1.156 and 0.908 respectively).

Structure solution and refinement. The structure was solved by direct and Fourier methods, and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms except the carbon atoms of the phenyl rings and the atoms of the solvent molecule. The hydridic atoms were clearly localized in the final ΔF map and refined isotropically. No attempts were made to localize the other hydrogen atoms because of the atom-number limits of the programs used (SHELX system[15]). The unit cell does not contain one crystallographically independent cation as expected, but two half-independent cations, as they have crystallographically imposed C_i symmetry. As the ligand is not centrosymmetric, it must be disordered with the atom C(8) statistically bonded to both metals, so that in the pyridazinyl ring the atoms N(2) and N(3) can be replaced by C(7) and C(8). Also the dichloromethane molecule of solvation has been found disordered with one Cl atom statistically distributed in two positions of equal occupancy, labelled Cl(2) and Cl(3).

The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.6635$ and $g = 0.005\,37$. Final R and R' values were 0.052 and 0.067 respectively. Final atomic co-ordinates are given in Table 3. Atomic scattering factors, corrected for the anomalous dispersion of Ir, P, and Cl, were taken from ref. 16. All calculations were performed on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturisticà Diffrattometrica del C.N.R., Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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References

1 A. Tiripicchio, A. M. Manotti Lanfredi, M. Ghedini, and F. Neve, *J. Chem. Soc., Chem. Commun.*, 1983, 97.
2 M. Ghedini and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1984, 1417.
3 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
4 M. Ghedini, M. Longeri, and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1986, 2669.
5 R. H. Crabtree, G. G. Hlatky, C. P. Parnell, B. E. Segmuller, and R. J. Uriarte, *Inorg. Chem.*, 1984, **23**, 354.
6 M. Ghedini, F. Neve, A. M. Manotti Lanfredi, and F. Ugozzoli, unpublished work.
7 R. H. Crabtree and M. Lavin, *J. Chem. Soc., Chem. Commun.*, 1985, 794.
8 B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1105.
9 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1976, **98**, 2134.
10 W. Butte and F. H. Case, *J. Org. Chem.*, 1961, **26**, 4690.
11 R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.*, 1982, **104**, 107; R. H. Crabtree and C. P. Parnell, *Organometallics*, 1984, **3**, 1727.
12 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
13 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
14 F. Ugozzoli, ABSORB, A computer program for correcting observed structure factors from absorption effects in crystal structure analysis, *Comput. Chem.*, 1987, **11**, 109.
15 G. M. Sheldrick, SHELX, Program for crystal structure determination, University of Cambridge, 1976.
16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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