Heterobinuclear Complexes formed from [3,6-Bis(2'-Pyridyl)pyridazine]-nitrosylbis(triphenylphosphine)iridium(2+) and Palladium(II) or Platinum(II)

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The reaction of the iridium nitrosyl complexes $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ or $[Ir(NO)(dppn)(PPh_3)_2X][PF_6]$ [dppn = 3,6-bis(2'-pyridyl)pyridazine; X = Cl, Br, or I) with $[PdCl_2(PhCN)_2]$ or $[PtI_2(1,5\text{-cod})]$ (1,5-cod = cyclo-octa-1,5-diene) yields mixed-metal binuclear species. In such compounds the presence of a bridging NO group is suggested on the basis of spectroscopic data.

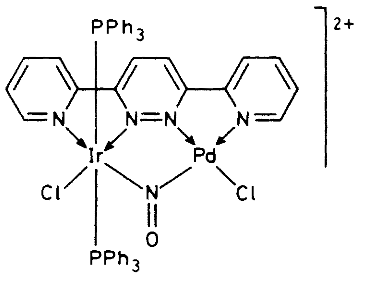
Binuclear transition-metal complexes are currently receiving considerable attention in connection with their potential catalytic activity [1-3] as well as their role as models of surface catalysis processes.[4] Among these complexes those containing small molecules (*e.g.* CO, CO_2, SO_2, NO, and acetylenes) bonded to both the metal centres are therefore of particular interest.

To synthesise these compounds, a suitable method may be the preparation of mononuclear complexes, containing both the substrate and a connecting ligand, followed by reaction with a second metal atom. In an early experiment designed to test this hypothesis the cation $[Ir(NO)(dppn)(PPh_3)_2]^{2+}$ (1), prepared from $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ and 3,6-bis-(2'-pyridyl)pyridazine (dppn), was treated with $CuCl_2$ and a new NO-bridged mixed iridium–copper complex was formed.[5] As part of our continuing investigation on heterobimetallic compounds, we now report the syntheses and spectroscopic characterization of mixed iridium–palladium and -platinum nitrosyl complexes.

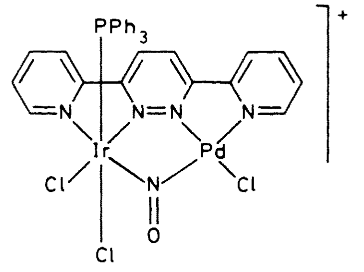
Results and Discussion

Iridium–Palladium Nitrosyl Complexes.—The cationic complex (1) and $[PdCl_2(PhCN)_2]$ immediately react in dichloromethane to give a dark red solution from which a product analysing for $[Ir(NO)(dppn)(PPh_3)_2(PdCl_2)][PF_6]_2$ [(2) in Table] can be isolated. The i.r. spectrum of this compound displays a low-frequency NO stretch at 1 522 cm^{-1} (KBr), and two absorptions in the M–Cl region at 368 and 335 cm^{-1} (Nujol). Conductivity measurements carried out on a freshly prepared nitromethane solution show the presence of a 1 : 2 electrolyte.[6] The ^{31}P n.m.r. spectrum in dichloromethane shows a single resonance at -16.85 p.p.m. indicating equivalence of the two phosphines in an environment attributable to an octahedral iridium complex.[7,8] This compound, although air-stable as a solid, slowly decomposes in solution.

Previously we reported [5] the *X*-ray crystal structure determination of $[(Ph_3P)_2ClIr(\mu\text{-dppn})(\mu\text{-NO})CuCl][PF_6]_2$ (3), a heterobinuclear complex having the same stoicheiometry as found for (2). In compound (3) the iridium atom has octahedral co-ordination, with two PPh_3 ligands in the apical positions, and migration of a chlorine atom formerly bound to copper. The square-planar configuration around the copper atom is achieved with the contribution of the NO group, which changes its co-ordination mode from terminal to bridged. Bearing this in mind, while no definite assignment of structure can be made on the basis of spectral data alone, the very close parallel between the physical properties of compounds (2) and (3) (see Table) leads us to suggest for dication (2) an overall geometry analogous to that possessed by (3).



(2)



(7)

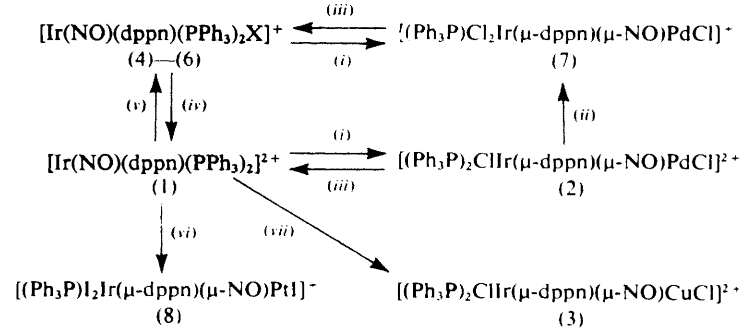
Complex (1) dissolved in dichloromethane reacts with anions X^- yielding the monocationic species $[Ir(NO)(dppn)(PPh_3)_2X][PF_6]$ [X = Cl (4), Br (5), or I (6)]. These mononuclear six-co-ordinated iridium complexes exhibit NO stretches at very low frequencies (nearly 1 500 cm^{-1}), consistent with the presence of a nitrosyl bonded in a bent fashion.[9] Moreover addition of X^- is reversible, the parent complex (1) being recovered in quantitative yield by reaction with $AgPF_6$.

Compound (4) reacts with $[PdCl_2(PhCN)_2]$ to form the new bimetallic species $[Ir(NO)(dppn)(PPh_3)(PdCl_3)][PF_6]$ (7). The ^{31}P n.m.r. spectrum in nitromethane solution consists of a single resonance at -17.64 p.p.m., while the i.r. spectrum shows ν(NO) at 1 560 cm^{-1} (KBr) and three absorptions in the M–Cl region at 345, 302, and 280 cm^{-1} (Nujol). The far-i.r. results are consistent with two chlorine atoms bonded mutually *cis* to the same metal with the remaining chloro-ligand bonded to the second metal atom. Furthermore, compound (7) can be isolated even from the decomposition products of (2) in acetonitrile solution. Therefore, the most reasonable geometry for (7) would seem to be that containing square-planar palladium(II), and octahedral iridium(III) having a phosphine molecule and a chlorine atom in apical positions.

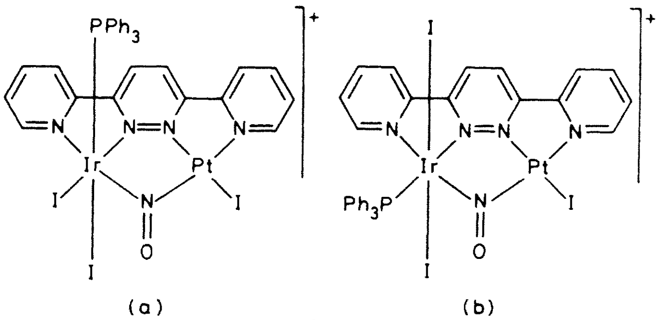
Table. Physical properties of iridium nitrosyl complexes

Compound [a]	$\tilde{\nu}$(NO) [b]/cm^{-1}	$\tilde{\nu}$(M–X) [c]/cm^{-1}	Λ [d]/Ω^{-1} cm^2 mol^{-1}	^{31}P N.m.r. (δ/p.p.m.)
(1) $[Ir(NO)(dppn)(PPh_3)_2]^{2+}$	1 795		182.00	10.84 [e]
(2) $[(Ph_3P)_2ClIr(\mu\text{-}dppn)(\mu\text{-}NO)PdCl]^{2+}$	1 522	368, 335	175.00	−16.85 [f]
(3) $[(Ph_3P)_2ClIr(\mu\text{-}dppn)(\mu\text{-}NO)CuCl]^{2+}$	1 525	356, 325	177.50	
(4) $[Ir(NO)(dppn)(PPh_3)_2Cl]^{+}$	1 502	298	79.25	−10.42 [g]
(5) $[Ir(NO)(dppn)(PPh_3)_2Br]^{+}$	1 501	219	77.05	
(6) $[Ir(NO)(dppn)(PPh_3)_2I]^{+}$	1 502		83.65	
(7) $[(Ph_3P)Cl_2Ir(\mu\text{-}dppn)(\mu\text{-}NO)PdCl]^{+}$	1 560	345, 302, 280	71.50	−17.64 [g]
(8) $[(Ph_3P)I_2Ir(\mu\text{-}dppn)(\mu\text{-}NO)PtI]^{+}$	1 480		81.20	−16.41, −22.29 [g]

[a] The anion is PF_6^-. [b] KBr pellets. [c] Nujol mull. [d] In $MeNO_2$ (10^{-3} mol dm^{-3} solution) at 20 °C. [e] In CD_3CN. [f] In CD_2Cl_2. [g] In CD_3NO_2.



Scheme. Anion PF_6^- is not shown. (*i*) $[PdCl_2(PhCN)_2]$; (*ii*) in MeCN; (*iii*) $2PPh_3$; (*iv*) $AgPF_6$; (*v*) LiX (excess); (*vi*) $[PtI_2(1,5\text{-cod})]$; (*vii*) see ref. 5



(a) (b)

(8)

For the heteronuclear iridium–palladium nitrosyl complexes (2) and (7) the reactivity with PPh_3 is of particular significance. From these reactions $[PdCl_2(PPh_3)_2]$ and complex (1) or (4) are recovered in quantitative yield, indicating that the two metal centres react independently even if bridged by dppn and NO ligands. The synthesis and behaviour of compound (1) is summarized in the Scheme.

Iridium–Platinum Nitrosyl Complex.—Upon reaction of $[PtI_2(1,5\text{-cod})]$ (1,5-cod = cyclo-octa-1,5-diene) and complex (1) in dichloromethane the dark brown solid $[Ir(NO)(dppn)(PPh_3)(PtI_3)][PF_6]$ (8) is obtained. Compound (8) is air-stable as the solid and in nitromethane solution behaves as a 1 : 1 electrolyte [6] (see the Table). It shows a nitrosyl stretching frequency at 1 480 cm^{-1}. The ^{31}P n.m.r. spectrum consists of two resonances of different intensities (about 1 : 2) at −16.41 and −22.29 p.p.m., without satellites due to ^{195}Pt. The lack of ^1J(Pt–P) coupling suggests that the phosphine molecule is solely bonded to the six-co-ordinate iridium atom as in compound (7). Therefore, the two signals found for complex (8) can be attributed to two isomeric forms, which differ in the position occupied by the phosphine ligand. Recalling that isomer (8a) is isostructural with compound (7) (PPh_3 at −17.64 p.p.m.), of the two ^{31}P n.m.r. resonances the one at −22.29 p.p.m. is most likely due to the PPh_3 *trans* to I. Similar shifts of ^{31}P resonances to high frequencies are observed with octahedral complexes when, in a *trans* position with respect to the PPh_3 ligand, chlorine is replaced by iodine.[10]

Conclusions

Since the compounds investigated are not very stable in solution, our attempts to obtain single crystals suitable for *X*-ray analysis have been unsuccessful. However, spectroscopic data indicate quite clearly that where the mononuclear iridium nitrosyl cation $[Ir(NO)(dppn)(PPh_3)_2]^{2+}$ reacts with Pd^{II} or Pt^{II} the NO co-ordination mode changes from terminal to bridged as in the case of the previously reported copper(II) complex.[5] This seems to be a general trend followed by the nitrosyl group when two metallic centres are constrained in a close arrangement (*ca.* 3.5 Å) by a ligand such as dppn.

Experimental

Apparatus and Techniques.—All experiments were performed in an oxygen-free nitrogen atmosphere. The solvents were deoxygenated prior to use and transfers were carried out with the flexible needle technique. ^{31}P-{^{1}H} N.m.r. spectra were recorded on a Varian Associates XL-100 Fourier-transform spectrometer; chemical shifts, δ (p.p.m.), are relative to 85% phosphoric acid (external) and the high-frequency-positive convention is used. Infrared spectra were recorded for KBr pellets or Nujol mulls on a Perkin-Elmer 180 i.r. spectrometer. Conductivity measurements were performed using a LKB 5300 B Conductolyser conductivity bridge. Elemental analyses were carried out at the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

Preparation of Compounds.—The ligand 3,6-bis(2′-pyridyl)-pyridazine (dppn) was prepared as reported previously,[11] as were the complexes $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$, $[PdCl_2(PhCN)_2]$, $[PtI_2(1,5\text{-cod})]$, and $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ (1).[5,12–14]

$[(Ph_3P)_2ClIr(\mu\text{-dppn})(\mu\text{-NO})PdCl][PF_6]_2$ (2). To a solution of complex (1) (0.200 g, 0.15 mmol) in dichloromethane (10 cm^3) was added a solution containing $[PdCl_2(PhCN)_2]$ (0.060 g, 0.15 mmol) in dichloromethane (5 cm^3). The resulting dark red solution was stirred at room temperature for 30 min. The dark brown air-stable microcrystals obtained on adding drop-wise ethanol (10 cm^3) were collected by filtration, washed with ethanol then diethyl ether, and dried under vacuum; yield 92% (Found: C, 41.9; H, 3.15; N, 4.90. Calc. for $C_{50}H_{40}Cl_2F_{12}IrN_5OP_4Pd$: C, 41.45; H, 2.80; N, 4.85%).

$[Ir(NO)(dppn)(PPh_3)_2X][PF_6]$ [X = Cl (4), Br (5), *or* I (6)]. In a typical preparation, to a dichloromethane solution (5 cm^3) of complex (1) (0.200 g, 0.15 mmol) was added a five-fold excess of the appropriate LiX dissolved in ethanol (10 cm^3). The reaction mixture was stirred at room temperature for 2 h. The microcrystalline solid formed was collected by filtration, washed with ethanol then diethyl ether, and dried under vacuum. Compound (4; X = Cl), pale green, yield 90% (Found: C, 50.25; H, 3.55; N, 6.30. Calc. for $C_{50}H_{40}ClF_6IrN_5OP_3$: C, 51.7; H, 3.45; N, 6.05%). Compound (5; X = Br), green, yield 92% (Found: C, 49.35; H, 2.95; N, 5.70. Calc. for $C_{50}H_{40}BrF_6IrN_5OP_3$: C, 49.8; H, 3.35; N, 5.80%). Compound (6; X = I), yellow-brown, yield 90% (Found: C, 47.85; H, 3.20; N, 6.05. Calc. for $C_{50}H_{40}F_6IIrN_5OP_3$: C, 47.95; H, 3.20; N, 5.60%).

Reaction of complexes (4)—(6) *with* $AgPF_6$. In a typical procedure, to a solution of the appropriate $[Ir(NO)(dppn)(PPh_3)_2X][PF_6]$ complex (0.10 mmol) in acetonitrile (20 cm^3) was added the stoicheiometric amount of $AgPF_6$ in acetonitrile (1 cm^3). After filtration of AgX, the yellow solution was evaporated under reduced pressure until a yellow precipitate formed. This was collected by filtration and vacuum dried (quantitative yield). Spectroscopic properties indicate that the product is identical with complex (1).

$[(Ph_3P)Cl_2Ir(\mu\text{-dppn})(\mu\text{-NO})PdCl][PF_6]$ (7). A solution of $[PdCl_2(PhCN)_2]$ (0.050 g, 0.13 mmol) in acetonitrile (10 cm^3) was added to a suspension of complex (5) (0.150 g, 0.13 mmol) in acetonitrile (5 cm^3) and the resultant green solution stirred at room temperature for 1 h. The yellow precipitate formed was removed by filtration and vacuum dried. This product (yield 15%) was identified as $[PdCl_2(PPh_3)_2]$ by comparison with an authentic sample. The solution was evaporated under reduced pressure until light green microcrystals formed. These were collected by filtration, washed with ethanol, and dried under vacuum; yield 78% (Found: C, 36.15; H, 2.30; N, 6.00. Calc. for $C_{32}H_{25}Cl_3F_6IrN_5OP_2Pd$: C, 35.7; H, 2.35; N, 6.50%). Traces of the same compound were separated also from the decomposition products of (2) in acetonitrile.

Reaction of complexes (2) *and* (7) *with* PPh_3. Triphenylphosphine (0.022 g, 0.085 mmol) was added to a solution of complex (2) (0.050 g, 0.035 mmol) in dichloromethane (10 cm^3) and the mixture was stirred at room temperature for 3 h. The pale yellow precipitate formed was filtered off and dried under vacuum. This product (yield 68%) was identified as $[PdCl_2(PPh_3)_2]$. Complex (1) was recovered in quantitative yield from the solution by slow evaporation of the solvent at reduced pressure, filtration, and drying under vacuum.

In a similar reaction between PPh_3 (0.035 g, 0.13 mmol) and complex (7) (0.04 g, 0.037 mmol) in dichloromethane (8 cm^3) $[PdCl_2(PPh_3)_2]$ (80% yield) and complex (4) (quantitative yield) were recovered.

$[(Ph_3P)I_2Ir(\mu\text{-dppn})(\mu\text{-NO})PtI][PF_6]\cdot 0.5C_2H_5OH$ (8). To a solution of complex (1) (0.100 g, 0.079 mmol) in dichloromethane (5 cm^3) was added a solution of $[PtI_2(1,5\text{-cod})]$ (0.045 g, 0.079 mmol) in dichloromethane (5 cm^3). The resulting red mixture was stirred at room temperature for 2 d. The red-brown solid formed was filtered off, washed with diethyl ether, and crystallized from acetonitrile–ethanol (yield, 53%) (Found: C, 27.75; H, 1.80; N, 4.70. Calc. for $C_{32}H_{25}F_6I_3IrN_5OP_2Pt\cdot 0.5C_2H_5OH$: C, 27.1; H, 1.95; N, 4.80%).

Acknowledgements

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