JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 3
1983

Synthesis and Crystal Structure of the Mixed Iridium(III) and Copper(II) Complex, $[IrCl(PPh_3)_2(\mu\text{-dppn})(\mu\text{-NO})CuCl][PF_6]_2$, [dppn = 3,6-bis(2′-pyridyl)pyridazine], with a Nitrosyl Group bridging Two Different Metals

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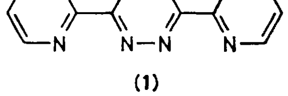
The mixed Ir–Cu complex, $[IrCl(PPh_3)_2(dppn)(NO)CuCl][PF_6]_2$, [dppn = 3,6-bis(2′-pyridyl)pyridazine], has been synthesised starting from $[Ir(NO)(dppn)_3(PPh_3)_2][PF_6]_2$, a complex with a linearly bound nitrosyl group; *X*-ray structural analysis has shown that both dppn and nitrosyl ligands bridge the metal atom and this is the first example of a nitrosyl group bridging two different metals.

Dinuclear complexes which have small molecules (*e.g.* CO, SO_2, acetylenes) bound to both metal centres have recently been the subject of much interest[1–4] but, hitherto, mixed complexes containing the NO group have not been described. We now report the synthesis and the *X*-ray structure determination of the first mixed iridium–copper complex containing a nitrosyl group bridging two different metal atoms. The previously described[5] iridium nitrosyl complex $[Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2$ reacts in absolute ethanol with 3,6-bis(2′-pyridyl)pyridazine, dppn, (1), giving, in 95% yield, the penta-co-ordinate mononuclear complex $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$, (2), as an air-stable pale yellow precipitate, equation (1). Complex (2), crystallized from acetone–benzene, is analytically pure and shows the following characterizing data: i.r., $\nu(NO)$ 1795 cm^{-1} (KBr); n.m.r., $^{31}P\{^1H\}$ −10.84 p.p.m. ($MeNO_2$); conductivity, Λ_M 182.0 ohm^{-1} mol^{-1} cm^2 ($MeNO_2$, 10^{-3} M). Comparison of these values with those of the related compound $[Ir(NO)(1,10\text{-phenanthroline})(PPh_3)_2][PF_6]_2$[$\nu(NO)$ 1805 cm^{-1} in KBr; $^{31}P\{^1H\}$ −11.40 p.p.m. in $MeNO_2$; Λ_M 195.9 ohm^{-1} mol^{-1} cm^2 ($MeNO_2$, 10^{-3} M)], whose structure is known,[6] leads us to propose a trigonal bipyramidal geometry for complex (2) with the NO group linearly bonded to the metal in the plane of the dppn ligand, and two apical triphenylphosphines.

$$\begin{array}{c} [Ir(NO)(MeCN)_3(PPh_3)_2][PF_6]_2 + \text{dppn} \\ \downarrow \\ [Ir(NO)(dppn)(PPh_3)_2][PF_6]_2 \\ \textbf{(2)} \end{array} \qquad (1)$$



(1)

A dichloromethane solution of (2) reacts with a stoicheiometric amount of $CuCl_2{\cdot}2H_2O$, dissolved in ethanol, giving the dinuclear complex (3), equation (2). The mixed Ir–Cu complex (3) crystallizes from the reaction mixture in good (90—95%) yield as air-stable blue microcrystals. Remarkably, product (3), a 1 : 2 electrolyte[7] (Λ_M 177.5 ohm^{-1} mol^{-1} cm^2, 10^{-3} M in $MeNO_2$), shows a very low NO stretching frequency at 1525 cm^{-1} (KBr) and two absorptions in the M–Cl region at 356 and 325 cm^{-1} (Nujol). Crystals of (3) suitable for X-ray analysis were obtained by re-crystallization from a mixture of dichloromethane–chloroform and ethanol.

$$\begin{array}{c} [Ir(NO)(dppn)(PPh_3)_2][PF_6]_2 + CuCl_2{\cdot}2H_2O \\ \downarrow \\ [IrCl(PPh_3)_2(dppn)(\mu\text{-NO})CuCl][PF_6]_2 \\ \textbf{(3)} \end{array} \qquad (2)$$

Crystal data: $C_{50}H_{40}Cl_2CuF_{12}IrN_5OP_4{\cdot}CHCl_3{\cdot}H_2O$, $M = 1542.84$, monoclinic, space group $P2_1/a$, $a = 35.777(17)$, $b = 12.393(9)$, $c = 13.481(8)$ Å, $\beta = 100.65(7)°$, $U = 5874(6)$ Å^3, $Z = 4$, $D_c = 1.74$ g cm^{-3}; $F(000) = 3036$, $\mu(\text{Mo-}K_\alpha) = 30.35$ cm^{-1}. The intensities of 7849 independent reflections were collected rapidly on a Siemens AED diffractometer (with θ in the range 3—22°), as a notable decay in the intensity of the standard reflection was observed (the last intensity measured had decreased to 40% of the starting one). Nb-filtered Mo-K_α radiation and the θ–2θ scan technique were used. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis

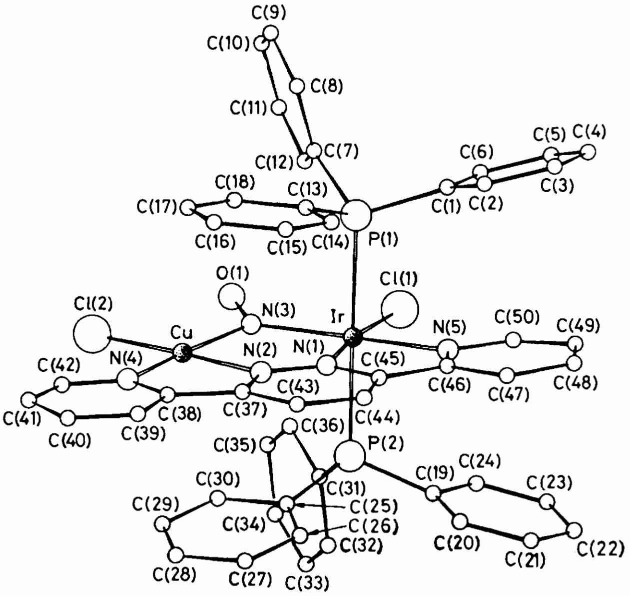


Figure 1. A view of the cation $[IrCl(PPh_3)_2(dppn)(NO)CuCl]^{2+}$. Important bond distances and angles: Ir–Cl(1) 2.33(1), Ir–P(1) 2.42(1), Ir–P(2) 2.39(1), Ir–N(1) 1.98(2), Ir–N(3) 2.01(2), Ir–N(5) 2.03(2), Cu–Cl(2) 2.15(1), Cu–N(2) 1.99(2), Cu–N(3) 2.01(2), Cu–N(4) 1.98(2), N(3)–O 1.16(3) Å; N(1)–Ir–N(5) 78(1), N(2)–Cu–N(4) 80(1), Ir–N(3)–Cu 117(1)°.

of 4335 observed reflections [having $I \geqslant 2\sigma(I)$] to an R value of 9.1%.†

The structure of the mixed metal cation $[IrCl(PPh_3)_2(dppn)(NO)CuCl]^{2+}$ is shown in Figure 1 together with the more significant bond distances and angles. The dppn molecule, acting as a tetradentate ligand, chelates both Ir and Cu metals through one pyridyl and one pyridazine nitrogen atoms. This bonding of the dppn ligand has already been observed in the dinuclear copper(II) complex $[Cu_2(dppn)Cl_3(OH)(H_2O)]$.[8] The nitrosyl group bridges the two metals symmetrically [Ir–N(3) and Cu–N(3) bonds are 2.01(2) Å] with a Cu · · · Ir separation of 3.416(5) Å. The square planar co-ordination of the Cu atom is completed by a chlorine atom; the octahedral co-ordination of the Ir atom is completed by a chlorine atom (in the equatorial plane) and by two PPh_3 ligands in the apical positions. Except for the PPh_3 ligands all the atoms of the cation are nearly coplanar. It is noteworthy that for the cation to be formed a chlorine atom must migrate from the copper to the iridium atom and the nitrosyl ligand changes from a linear to a bridging group.

We are grateful to the Italian C.N.R., for financial support for this research.

Received, 27th September 1982; Com. 1134

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23529 (27 pp.) from the British Library Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index Issues.