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Preliminary communication

PREPARATION AND MOLECULAR STRUCTURE OF BIS(*cis*-1,2-BIS(DIPHENYLPHOSPHINO)ETHYLENE)DISULFUR DINITRIDE IRIDIUM(III) TETRAPHENYLBORATE

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Summary

The square-planar iridium(I) complex [(dppen)$_2$IrCO] BPh$_4$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene) reacts with S_4N_4 to give the iridium(III) octahedral complex [(dppen)$_2$Ir(S_2N_2)] BPh$_4$ $\cdot$0.5(CH$_3$)$_2$CO, whose molecular structure has been established by a complete X-ray structure determination.

Tetrasulfur tetranitride is readily attacked and degraded by nucleophilic agents [1]. Thus reaction of this molecule towards a wide range of low oxidation state metal complexes can be expected, but to date only a few organometallic-sulfur-nitrogen complexes have been reported. Moreover, these have been usually isolated in low yield, by chromatographic means, from complex mixtures obtained by drastic reactions [2].

Recently the dimeric complexes [(PPh$_3$)M(μ-S_2N_2)]$_2$, where M = Pt, Pd, were obtained in high yield in these laboratories by treating S_4N_4 with d^{10} tricoordinated platinum and palladium complexes, under mild conditions [3]. We now report the reaction of S_4N_4 with the d^8 iridium(I) complex [(dppen)$_2$IrCO] BPh$_4$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene, Ph$_2$PCH=CHPPh$_2$). Cleavage of the S_4N_4 ring again takes place in this case, with formation of the iridium(III) disulfur-dinitrogen heterocycle complex [(dppen)$_2$Ir(S_2N_2)] BPh$_4$ $\cdot$ 0.5(CH$_3$)$_2$CO. The latter compound was prepared by reaction of a THF solution of [(dppen)$_2$IrCO] BPh$_4$* and S_4N_4, at 50°C, under nitrogen. Orange-brown crystals were obtained (in 60% yield) by recrystallization from acetone/n-butyl ether (The analytical data are in good agreement with the proposed

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*The compound [(dppen)$_2$IrCO] BPh$_4$ was prepared by treating dppen with (PPh$_3$)$_2$IrCOCl in a benzene/tetrahydrofuran solution in presence of NaBPh$_4$. Orange crystals can be obtained by recrystallization from dichloromethane/benzene.

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formula.) The compound is soluble in polar solvents such as dichloromethane, acetone, in which it behaves as 1:1 electrolyte. The structure of the compound was established by a single crystal X-ray diffraction study.

Crystal data: $C_{77.5}H_{67}BIrN_2O_{0.5}P_4S_2$, M = 1425.4; monoclinic, space group $P2_1/n$, a 26.458(12), b 23.688(10), c 12.045(6) Å, β 102.36(5)°, U 7374.1 Å^3, D_{calcd} 1.284 g cm^{-3}, Z = 4, μ(Mo-K_α) 19.83 cm^{-1}. Diffraction data were collected on a Philips PW 1100 four-circle automatic diffractometer, using the ω—2θ scan technique and graphite monochromated Mo-K_α radiation (λ 0.7107 Å). The structure was solved by the heavy-atom method and refined by full matrix least-squares cycles to R and R_w factors both of 0.066 for the 4186 reflections ($2\theta \leqslant 45°$) having $I \geqslant 3\sigma(I)$*.

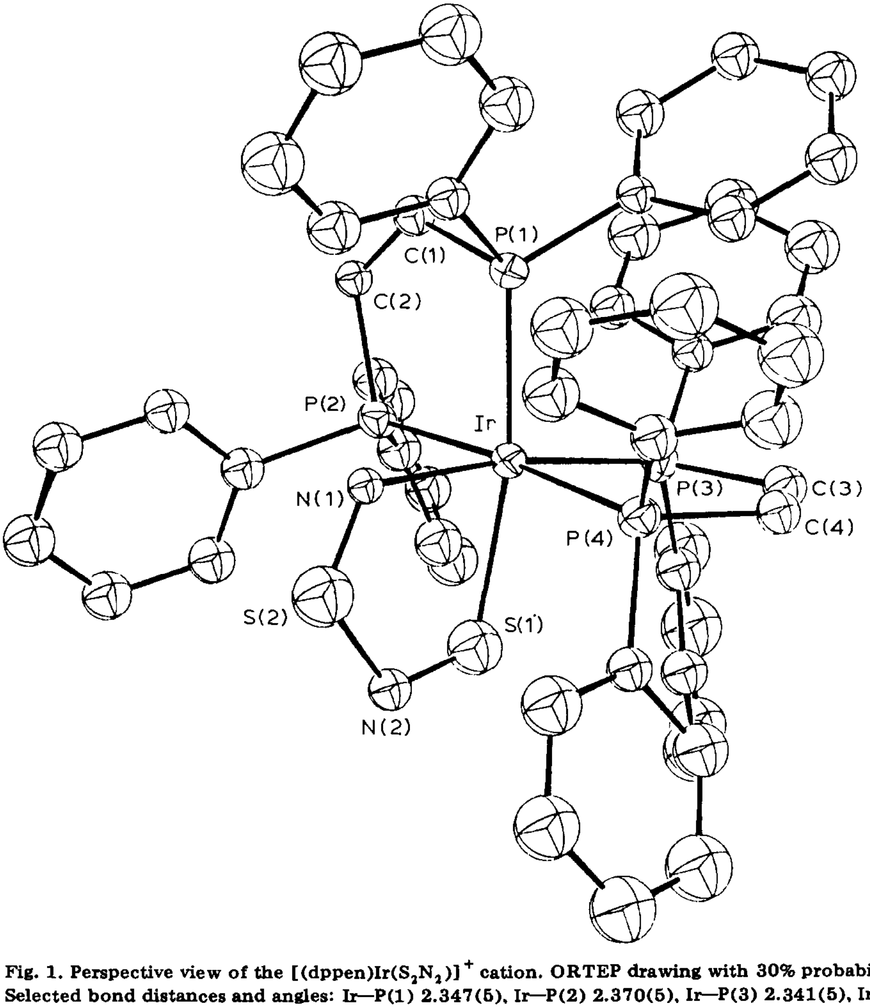

Fig. 1. Perspective view of the [(dppen)Ir(S_2N_2)]$^+$ cation. ORTEP drawing with 30% probability ellipsoids. Selected bond distances and angles: Ir—P(1) 2.347(5), Ir—P(2) 2.370(5), Ir—P(3) 2.341(5), Ir—P(4) 2.367(5), Ir—S(1) 2.379(9), Ir—N(1) 2.289(12) Å; P(1)—Ir—S(1) 169.7(2), P(3)—Ir—N(1) 169.6(3), P(2)—Ir—P(4) 174.3(2), P(1)—Ir—P(2) 84.6(2), P(1)—Ir—P(3) 95.9(2), P(1)—Ir—P(4) 98.4(2), P(1)—Ir—N(1) 91.1(3), P(2)—Ir—P(3) 100.2(2), P(2)—Ir—S(1) 87.1(2), P(2)—Ir—N(1) 88.1(3), P(3)—Ir—P(4) 84.3(2), P(3)—Ir—S(1) 91.6(3), P(4)—Ir—S(1) 89.4(2), P(4)—Ir—N(1) 87.0(3), S(1)—Ir—N(1) 82.5(4)°,

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***The atomic coordinates for this work are available on request from Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory- Lensfield Road, Cambridge CB2 1EW.**

The molecular structure consists of $[(dppen)_2Ir(S_2N_2)]^+$ cations and BPh_4^- anions with acetone molecules interspersed in the lattice. Figure 1 shows a perspective view of the cation and some important bond distances and angles. The metal atom displays a distorted octahedral geometry, being surrounded by the four phosphorus atoms of the two dppen molecules and by one sulfur atom and one nitrogen atom of the S_2N_2 ligand. The S_2N_2 group chelates the metal to form a five-membered ring, which is planar within 0.03 Å. The distortions from the octahedral geometry, as evidenced by the values of the axial angles 169.6(3), 169.7(2) and 174.3(2)°, are mainly due to the requirement of the chelating rings and to the reduced steric hindrance of the S_2N_2 group with respect to the bulky phosphines, and there is a slight bending of the phosphines toward the S_2N_2 fragment. The Ir—P bond distances ranging from 2.341(5) to 2.370(5) Å are only slightly longer than the sum of the covalent radii (2.33 Å). It is noteworthy that the phosphorus atoms *trans* to the donor atoms of the S_2N_2 group display shorter Ir—P distances. The disulfur-dinitrogen group is disordered, and so far it has been possible to refine only one model. For this reason the difference between the Ir—S and Ir—N distances is 0.09 Å instead of the expected difference of ca. 0.25 Å. Because of this disorder, the distances within the S_2N_2 group are not accurate enough to permit discussion of the bonding in the heterocycle.

These results, together with those previously reported, show that the reactions of S_4N_4 with low oxidation state platinum metal complexes give rise to a formerly similar metal-dinitrogen disulfur heterocycles. We assume that these reactions proceed by the following route: (i) addition of S_4N_4 to the unsaturated metal center, (ii) cleavage of S_4N_4 to S_2N_2*, (iii) oxidative addition of S_2N_2 to the metal.

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*Cleavage of S_4N_4 to S_2N_2 promoted by metal ions is well known [4].