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Preliminary communication

1-PYRAZOLYLIRIDIUM(I) DERIVATIVES; X-RAY EVIDENCE FOR MONODENTATE PYRAZOLATO LIGANDS

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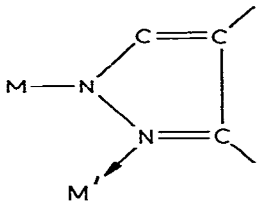
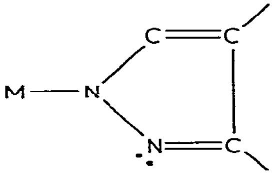
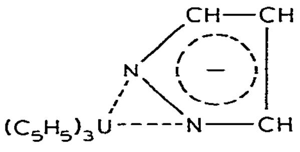
Summary

An X-ray crystal structure determination has shown that *trans*-$(Ph_3P)_2Ir(CO)$-(pyrazolato-*N*), obtained from the chloride and potassium pyrazolate, contains a monodentate azolato ligand.

The growing interest [1,2] in the field of metal derivatives of the pyrazolato anion (pz) has led to the realization that more than one coordination mode is possible for these ligands. They are generally *exo*-bidentate (A) but in a few cases they were suggested to contain monodentate [2] (B) or even *endo*-bidentate ligands (C) [3]


(A)


(B)


(C)

In the chemistry of iridium, binuclear complexes were recently described [4] in which the metal atoms are bridged in the usual way (A) by two pz ligands (e.g. $[(COD)Ir(\mu\text{-}Pz)]_2$, $[(Ph_3P)(CO)Ir(\mu\text{-}Pz)]_2$, PzH = pyrazole, and $[L(CO)Ir(\mu\text{-}3,5\text{-dimethylpyrazolato})]_2$, L = Ph_2MeP, $PhMe_2P$, $(PhO)_3P$); these complexes

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undergo several types of two centre oxidative addition reactions [4]. These reports prompted us to report the isolation of some mononuclear iridium compounds in which the azolato ligand is monodentate, namely *trans*-$(Ph_3P)_2(CO)$-Ir(pz) (pzH is 3,5-Me_2- (I), 3,5-$(CF_3)_2$- (II), or 3,5-Me_2-4-NO_2-pyrazole (III)). In the case of II the nature of the coordination of the nitrogen ligand has been ascertained through an X-ray crystal structure determination, the first one for a monodentate pyrazolato group attached to a metal (Fig. 1).

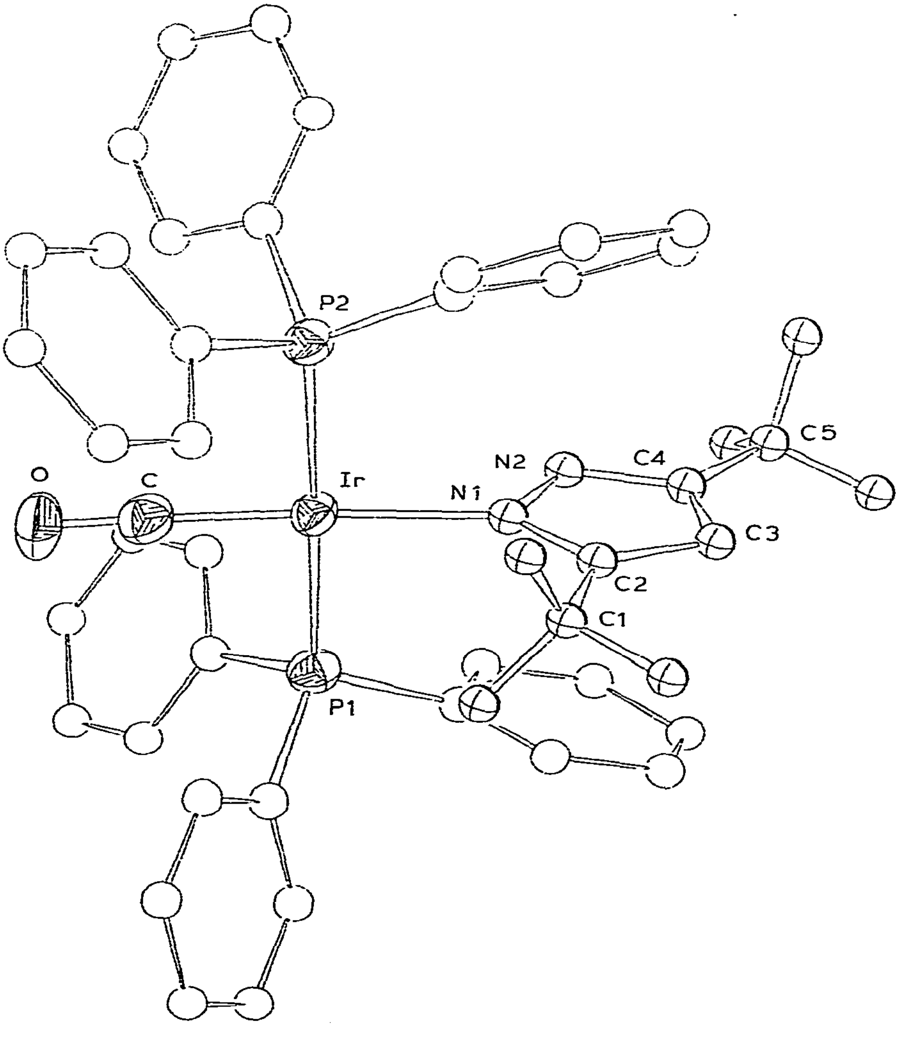

Fig. 1. ORTEP view of compound II, *trans*-$(Ph_3P)_2(OC)Ir[3,5\text{-}(CF_3)_2$-pyrazolato-*N*].

Crystal data. $C_{42}H_{31}F_6IrN_2OP_2$, $M = 947.87$, yellow monoclinic prisms, space group $P2_1/n$ (from systematic absences) a 21.106(6), b 19.700(5), c 9.437(2) Å, β 94.34°, U 3912.5 Å^3, $Z = 4$, D_c 1.609 g cm^{-3}, μ(Mo-K_α) 35.4 cm^{-1}. Intensity data were collected on a BASIC diffractometer by the ω-scan technique, with graphite monochromated Mo-K_α radiation in the 2θ range 6—50°. The structure was solved by Patterson and Fourier methods using 4474 absorption corrected reflections having $I \geqslant 3\sigma(I)$. The final full matrix least-squares refinement led to conventional R and R_w values of 0.036 and 0.038, respectively. Hydrogen atoms were introduced in calculated positions (C—H 1.00 Å) but not refined. The iridium atom is in a square-planar environment; the phosphine ligands are mutually *trans* and the planar pyrazolato ring is nearly normal to the coordination plane (dihedral angle 85.8°), an arrangement which is probably required by steric overcrowding. Principal bond distances are: Ir—P(1) 2.328(2), Ir—P(2) 2.336(2), Ir—C 1.811(7), Ir—N(1) 2.079(5), N(1)—N(2) 1.360(7), N(2)—C(4) 1.340(8), C(4)—C(3) 1.377(9), C(3)—C(2) 1.384(9), C(2)—N(1) 1.347(8), C—O 1.155(9) Å. The observed bond lengths are in keeping with the aromatic character even for the monodentate pz ligand. The shortest Ir...Ir contact is 9.44 Å.

The complexes I—III were obtained by reaction of the corresponding chloride (Vaska's complex) with potassium pyrazolate (room temperature under nitrogen: I THF, 10 min; II and III benzene, 30 min) and isolated as air-stable yellow crystals. Molecular weight determinations and spectroscopic data (IR, ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR) are all in agreement with mononuclear species also in solution. On the other hand the mass spectrum of II shows a peak at *m/z* 1368, corresponding to $[(Ph_3P)(CO)^{191}Ir(\mu\text{-pz})]_2$, and confirms the tendency of the pz anions to act as *exo*-bidentate ligands.

The isolation of I—III suggests that mononuclear species are possible with pz anions having a wide range of substituents. The mononuclear compounds reported here might be intermediates for assembling singly-bridged hetero-binuclear complexes by reaction with suitable Lewis acids, following the pattern previously employed [5] for making $M(\mu\text{-pz})_2M'$ systems (e.g. [5] M = Pt, Pd; M' = Cu, Co, Zn, Cd or Hg; or [6] M = Pt, M' = Cr), to be used in two-centre oxidative addition reactions.

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