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A SERIES OF MONOHAPTO PYRAZOLATES OF IRIDIUM(I) AND IRIDIUM(III)

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Summary

The reaction of *trans*-$IrCl(CO)L_2$ with pz^- * gives *trans*-Ir(pz-*N*)$(CO)L_2$, where pzH is 3,5-dimethyl-, 3,5-dimethyl-4-nitro- or 3,5-bis(trifluoromethyl)-pyrazole, and $L = PPh_3$. The nitrogen atom not involved in coordination can be protonated with HBF_4 to give the corresponding $[Ir(CO)L_2(pzH\text{-}N)]^+$ cation. The iridium(I) pyrazolates undergo oxidative addition, yielding $Ir(H)_2(pz\text{-}N)(CO)L_2$ species, while gaseous HCl cleaves the Ir–N bond, affording $IrH(Cl)_2(CO)L_2$. The iridium(I) derivatives can be obtained in several solid-state forms, each characterized by a slightly different CO stretching frequency. The presence of a monodentate pyrazolato ligand in *trans*-$Ir(3,5\text{-}(CF_3)_2pz\text{-}N)(CO)L_2$, in the form with ν(CO) at 1975 cm^{-1}, is supported also by an X-ray crystal structure determination. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with cell dimensions $a = 21.106(6)$, $b = 19.700(5)$, $c = 9.437(2)$ Å, and $\beta = 94.34(2)°$ and $Z = 4$.

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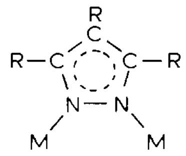
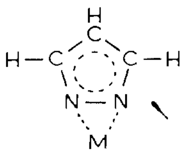
* Throughout this paper, 1-unsubstituted pyrazole ($C_3H_4N_2$) is indicated by PzH, while pzH indicates a generic pyrazole on which ring substituents may be present (e.g. $3,5\text{-}Me_2\text{-}4\text{-}NO_2pzH$ is 3,5-dimethyl-4-nitropyrazole).

Introduction

The investigations on the pyrazolato anion, pz^-, developed by Trofimenko [1] in the late Sixties, have been of growing interest in the field of transition metal chemistry [1,2] because of the different coordination modes displayed by the ligands [1–3],


exo-bidentate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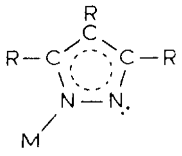

monodentate

and because of their use in the synthesis of polymetallic system.

During our previous investigations in this field, compounds of gold [4], platinum [5], palladium [5], and rhodium [4,6] were obtained where the azolato group could be exobidentate or monodentate, or even ionic [6]. Complexes containing monodentate pyrazolato groups (pz-*N*) (e.g. $M(pz\text{-}N)_2(L\text{-}L)$; M = Pd, Pt and L–L may be either 2,2′-bipyridyl or $Ph_2E(CH_2)_n\ EPh_2$ where $n = 1, 2$, or 3 and E = P or As) [5a,7] can be used to prepare hetero-polynuclear pyrazolato-bridged compounds such as $[Ni\{(\mu\text{-}Pz\text{-}N,N')_2Pt(Ph_2PCH_2)_2\}_2][BF_4]_2$ or $Pd(2,2'\text{-bipyridyl})(\mu\text{-}3,5\text{-}Me_2pz\text{-}N,N')ZnBr_2$. The assembling of these molecules requires that the ligand contain an inert coordination centre, such as, typically, platinum(II) or, sometimes, palladium(II), in order to prevent scrambling of ligands between the two coordination centers, as experienced, for instance, in the reaction 1 and 2 [4b].

$$2\,Au(pz\text{-}N)(PPh_3) + [RhCl(CO)_2]_2 = [Rh(\mu\text{-}pz\text{-}N,N')(CO)_2]_2 + 2\,AuCl(PPh_3) \tag{1}$$

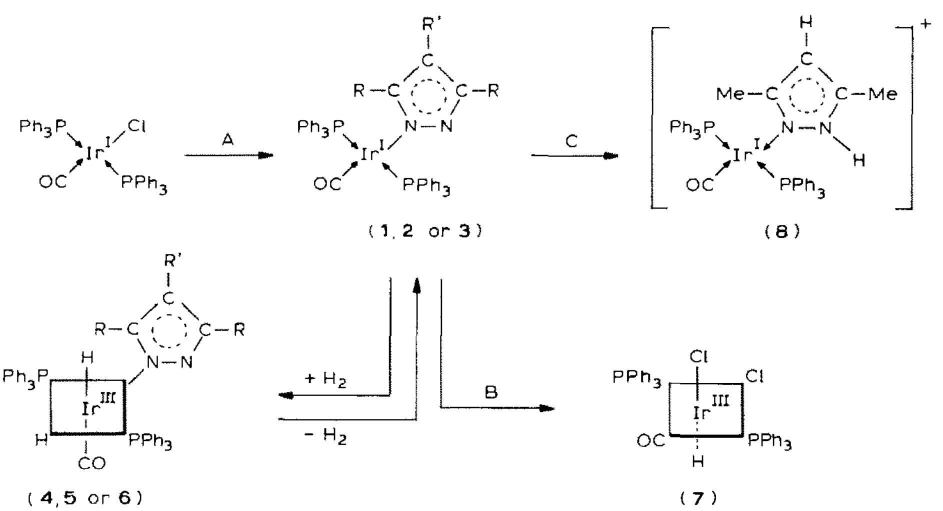
$$\begin{aligned} 2\,Au(pz\text{-}N)(PPh_3) + AgBF_4 = {} & [Au_2(\mu\text{-}pz\text{-}N,N')(PPh_3)_2][BF_4] \\ & + 1/n[Ag(\mu\text{-}pz\text{-}N,N')]_n \end{aligned} \tag{2}$$

As a development of our researches, we investigated the preparation and reactivity of iridium(I) monodentate pyrazolate complexes which are likely to be rather inert, and thus possibly useful starting materials for obtaining hetero-bimetallic complexes or, upon oxidative addition, a series of iridium(III) derivatives. Several pyrazoles were employed because it is now well established that the presence of substituents on the heterocyclic ring has a remarkable influence on the stability of the metal derivatives [6]. In our study we determined the first X-ray structure of a metal complex with a monodentate pyrazolato ligand, *trans*-$Ir[3,5\text{-}(CF_3)_2pz\text{-}N](CO)(PPh_3)_2$ [8]. Another group has obtained X-ray crystal structures of several binuclear iridium complexes having exobidentate pz^- ligands [9].

Results and discussion

Iridium(I) pyrazolates. Vaska's compound, *trans*-$IrCl(CO)(PPh_3)_2$, was chosen as the starting material because its preparation, properties, and reactivity have been widely investigated [10]. According to Scheme 1, this compound was treated in benzene solution (step A) with a pyrazolato anion formed by the action of potassium hydroxide on a methanol solution of a pyrazole. The corresponding *trans*-Ir(pz-*N*)(CO)(PPh_3)$_2$ compounds (**1**: R = Me, R′ = H; **2**: R = Me, R′ = NO_2; **3**: R = CF_3, R′ = H) were identified through elemental analyses (Table 1) and the spectral data reported in the Tables 2 and 3.

SCHEME 1



The reaction products are yellow, crystalline compounds which are air-stable in the solid state. In benzene solution those compounds having electron withdrawing substituents (**2**, **3**) did not react with oxygen, even after a fortnight in the case of **3**, while the benzene solution of **1** became green upon standing in contact with the atmosphere: the green powder left after evaporation could not be purified. Similarly, green-coloured, unidentified by-products accompanied the formation of the yellow

TABLE 1

ANALYTICAL DATA

Compound [a]	m.p. (dec.) (°C)	Found (calcd.) (%)		
		C	H	N
1 Ir(3,5-Me_2pz)(CO)L_2 [b]	150	60.27 (60.07)	4.78 (4.41)	3.47 (3.34)
2 Ir(3,5-Me_2-4-NO_2pz)(CO)L_2	207	57.33 (57.01)	4.22 (4.07)	4.49 (4.75)
3 Ir(3,5-(CF_3)$_2$pz)(CO)L_2 [c]	205	53.27 (53.22)	3.24 (3.27)	2.71 (2.96)
4 IrH_2(3,5-Me_2pz)(CO)L_2	150–170	60.21 (59.93)	4.60 (4.64)	2.90 (3.33)
5 IrH_2(3,5-Me_2-4-NO_2pz)(CO)$L_2 \cdot C_6H_6$	170–203	59.15 (59.75)	4.58 (4.56)	4.36 (4.35)
6 IrH_2(3,5-(CF_3)$_2$pz)(CO)L_2	170–185	53.85 (53.11)	3.83 (3.48)	2.77 (2.95)
7 $IrHCl_2$(CO)$L_2 \cdot 1/3C_6H_6$	220	55.55 (55.58)	4.12 (3.92)	0.0 (0.0)
8 [Ir(3,5-Me_2pzH)(CO)L_2][BF_4] [d]	230	54.06 (54.38)	4.46 (4.10)	2.92 (3.02)

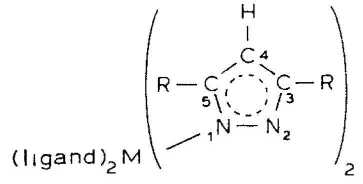
[a] L is triphenylphosphine; the compounds **1** – **3** and **8** are yellow, **4** – **7** white. [b] Molecular weight by osmometry in benzene (0.94% w/w): Found 700, calcd. 839. [c] Molecular weight by osmometry in benzene (1.56% w/w): Found 950, calcd. 947. [d] Λ = 29 ohm^{-1} cm^2 mol^{-1} in dichloromethane at 17 °C (2.5×10^{-4} *M*); Λ = 150 ohm^{-1} cm^2 mol^{-1} at 27 °C (0.4×10^{-3} *M*) in acetone.

compound **1**. The amount of green material was reduced, and the yield of **1** was increased, when the reaction was carried out under nitrogen. With unsubstituted potassium pyrazolate, KPz, unidentified green species were obtained by reaction in THF under nitrogen: in no case were any binuclear red species [9] observed under our experimental conditions.

The NMR spectra are in agreement with the structures proposed. In particular the following points are worth mentioning:

(1) The presence of only one ^{31}P signal in the spectra of the compounds **1**–**3** is in agreement with a *trans*-arrangement of the phosphine ligands; the chemical shift is comparable to that observed in other iridium(I) derivatives [11].

(2) The presence of separate signals for the protons (compound **2**), or for the fluorines (compound **3**), respectively, of the substituents in the 3- and 5-position of the heterocyclic ring suggests that the pyrazolato ligand is monodentate. Analogous behavior was previously reported for several palladium(II) and platinum(II) complexes, where the presence of $^4J(^{195}Pt-^1H)$ allowed, in addition, the assignment of the signals due to 3- or 5-substituents, e.g. in the series $Pt(3,5\text{-}Me_2pz\text{-}N)_2(Ph_2E(CH_2)_nE'Ph_2)$ ($E = E' = P$, $n = 1$, 2, or 3; $E = E' = As$, $n = 2$; $E = P$, $E' = As$, $n = 2$) [5b,12].



(3) In the 3,5-dimethylpyrazolato-derivative, **1**, evidence of the monodentate nature of the pz^- ligand is given by two sharp signals, due to the 3- and 5-methyl groups, observed in $CDCl_3$ below 273 K. At room temperature, both in $CDCl_3$ and in C_6D_6, the two separate signals are replaced by a broad absorption. In the field of the metal(pz-*N*) species, fluxionality had already been reported: in the case of *trans*-$Rh[3,5(CF_3)_2pz\text{-}N](CO)(PPh_3)_2$ at room temperature [6], and in other instances even at low temperatures, e.g. $Sn(n\text{-}Bu)_3(3,5\text{-}Me_2pz\text{-}N)$ [13] or $Au(3,5\text{-}Me_2\text{-}4\text{-}NO_2\text{-}pz\text{-}N)(PPh_3)$ [4b]. In these derivatives fluxionality may be explained by a fast exchange between species where the metal is attached to one, or to the other, nitrogen atom.

The IR spectra show the absorptions required by the presence of phosphine, pyrazolato, and carbonyl ligands. The pattern observed in the carbonyl stretching region requires some comment, because compounds **1**, **2**, and **3** exist in more than one solid-state form, each characterized by a definite value of the single $\nu(CO)$ band (see Table 2).

Indeed, in the case of the compound **3** only one strong carbonyl stretching absorption was observed both in solution (1977 cm^{-1}, in benzene or dichloromethane) and in the crystal on which the X-ray crystal structure determination was carried out (1975 cm^{-1}) i.e. the yellow compound **3(G)**. Another yellow sample of **3**, indicated as **3(F)**, prepared in exactly the same way and characterized through C,H,N analyses and NMR spectra, had $\nu(CO)$ at 1981 in Nujol and at 1979 cm^{-1} in benzene solution, while no other significant difference was apparent in the IR spectrum of the two samples in the NaCl region. Remarkably, this small difference,

TABLE 2

SELECTED IR SPECTRAL DATA (cm^{-1})

Compound [a]	CO stretching region		Hydride stretching		Other [b]
	Nujol	Solution	Nujol	Solution	
1 (**A**)	1975s	1963, CH_2Cl_2			1520w
1 (**B**)	1964s	1963s, CH_2Cl_2 1970s, C_6D_6			1520w
1 (**C**)	1954s	*c*			1520w
2 (**D**)	1971s	1974s, CH_2Cl_2			1538m [d]
2 (**D**+**E**)	1995s, 1972s	*c*			1538m [d]
3 (**F**)	1981s [e]	1979s,[f] C_6D_6			1540sh, 1522w
3 (**G**)	1974s [g]	1977s,[f] C_6H_6			1540sh, 1522w
3 (**F**+**H**)	1980s, 1962s	1977s, CH_2Cl_2			1540sh, 1522w
3 (**G**+**H**)	1975s, 1962s	1976s, CH_2Cl_2			1540sh, 1522w
4	2020vs	2010s,[f] C_6H_6	2199m, 2107s	2100br,[f] C_6H_6	1515m
5	2020vs	2017vs, CH_2Cl_2 2015vs,[f] C_6H_6	2153w, 2127s	2121br, CH_2Cl_2 2110br,[f] C_6H_6	1532m [d]
6	2028vs	2030vs, CH_2Cl_2 2040vs,[f] C_6H_6	2217w 2150m	2150br,CH_2Cl_2 2160br,[f] CH_2Cl_2	1538w, 1519w
7	2021vs	*c*	2237s	*c*	312m, 266m ν(Ir–Cl)
8 (**L**) [h]	1981vs	1991s, CH_2Cl_2			1581m; 3260 broad, ν(NH)
8 (**M**) [i]	1987vs, 1976vs	1991s, CH_2Cl_2			1581m; 3260 broad, ν(NH)

[a] The number refers to the compound listed in Table 1; the letter indicates the crystalline form. Two letters indicate the presence of two crystalline forms. [b] Ring-breathing mode of the pz ring, if not otherwise indicated (Nujol mull). [c] Not recorded; in the case of **7** because of limited solubility. [d] Nitro-group vibration is expected to overlap with ring-breathing mode. [e] Crystalline sample after X-ray powder study. [f] Beckmann 4210 instrument. [g] Crystalline sample after X-ray structure determination. [h] Sample obtained upon concentration of a benzene extract. [i] Sample undissolved in benzene.

which is bigger than the confidence limit of the instrument used, was accompanied by a different X-ray powder pattern of the two samples (**3**(**F**) and **3**(**G**)), thus establishing the existence of two crystalline forms of **3**; in addition, a third form, **3**(**H**), is suggested from the IR spectra of mixtures, i.e. **3**(**F** + **H**) and **3**(**G** + **H**). Unfortunately, attempts to determine the conditions required for the reproducible isolation of the single forms were unsuccessful: in several preparations, different mixtures of the various forms were obtained in the solid state and all gave the same IR spectrum in solution. Crystals of **3**(**F**) were obtained once, but they were unsuitable for X-ray structure determination because of twinning.

Similar observations were made on **1**, *trans*-Ir(3,5-Me_2pz-*N*)(CO)(PPh_3)$_2$, which yielded three forms, indicated as **1**(**A**), **1**(**B**), and **1**(**C**), each of them being characterized in the solid state by a different value of ν(CO) (Table 2). Also in this case, attempts to obtain reproducibly one of the forms, e.g. by repeated crystallization of mixtures from benzene/methanol or benzene/petroleum ether, gave only a random increase of intensity of one of the carbonyl stretching bands, and a sample

TABLE 3

^{1}H, ^{19}F, and ^{31}P-NMR DATA

Compound	Solvent	Proton and fluorine[a]				$^{31}P\{^{1}H\}$[b]
		Aryl[c]	Pyrazole ring		Hydride[e] and others	
			4-CH[a]	3,5-R_2[d]		
1	C_6D_6	2–3.1	4.46	8br		22.8s
1	$CDCl_3$[f]	2.1–3.1	4.8br	8–8.7br		
1	$CDCl_3$[g]	2.3–2.8	4.88	8.14, 8.66		24.1s
2	C_6D_6	2.2–3	–	7.6br, 7.9		24.3s
2	$CDCl_3$	2.2–2.9	–	7.93, 8.23		
3	C_6D_6	1.9–3.4	3.7	–57.1, –60.4[h]		24.8s
3	CD_2Cl_2	2.3–2.9	4.0			
4	C_6D_6	2.1–2.6, 2.7–3 3	4.5	7.4, 8.6	18td ($J = 18$), 26.8td ($J = 16$), ($J = 4$ 7)	10.0s
4	$CDCl_3$	2.4–2.9	5.0	7.9, 9.0	18.3td ($J = 18$ 4), 27.3td ($J = 16.3$), ($J = 4.5$)	
5	C_6D_6	2.2–2.6, 2.9–3.2	–	7.22, 8.28	18.2td ($J = 18$), 24.7td ($J = 15$), ($J = 4.7$)	12.1s
5	CD_2Cl_2	2 4–2 9	–	7 76, 8.8	18 5td ($J = 18$), 27.9td ($J = 15$), ($J = 4.7$)	
6	C_6D_6	2.0–2.6, 2.8–3.3	3.7	–57.6, –60.0[h]	17 7br ($J = 14$), 28.2td ($J = 16$), ($J = 4.0$)	13.2s
7	$CDCl_3$	2–2.8	–	–	25 35t ($^{2}J(P-H) = 13$)	–2.35s
8	$CDCl_3$	2–3	4.8	8.20, 8.30	–0 66 (NH), disappears on deuteration	24 4s

[a] Proton NMR spectra in τ units, reference internal tetramethylsilane. ^{19}F Spectra in ppm from internal $CFCl_3$ Abbreviations are: br = broad, t = triplet, td = triple doublet. [b] In ppm from external 85% phosphoric acid; positive shifts are downfield; s = singlet. [c] Always multiplet. [d] Always singlet [e] The first and second J are $^{2}J(P-H)$, the last one is $^{2}J(H-H)$. [f] At 298 K. [g] At 230 K [h] Fluorine signals.

TABLE 4

PRINCIPAL INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) WITH ESD'S FOR *trans*-Ir[3,5-$(CF_3)_2$pz-*N*](CO)$(PPh_3)_2$

Ir–P(1)	2.328(2)	C(1)–F(2)	1.284(10)
Ir–P(2)	2.336(2)	C(1)–F(3)	1.329(8)
Ir–N(1)	2.079(5)	C(5)–C(4)	1.477(10)
Ir–C	1.811(7)	C(5)–F(4)	1.283(10)
C–O	1.155(9)	C(5)–F(5)	1.332(10)
N(1)–N(2)	1.360(7)	C(5)–F(6)	1.297(9)
N(1)–C(2)	1.347(8)	P(1)–C(111)	1.818(5)
C(2)–C(3)	1.384(9)	P(1)–C(121)	1.827(5)
C(3)–C(4)	1.377(9)	P(1)–C(131)	1.824(5)
C(4)–N(2)	1.340(8)	P(2)–C(211)	1.834(5)
C(1)–C(2)	1.484(10)	P(2)–C(221)	1.825(5)
C(1)–F(1)	1.344(9)	P(2)–C(231)	1.819(4)
P(1)–Ir–P(2)	176.1(1)	C(3)–C(4)–N(2)	113.9(6)
C–Ir–N(1)	177.2(2)	C(4)–N(2)–N(1)	105.1(5)
C–Ir–P(1)	89.0(2)	N(1)–C(2)–C(1)	122.2(6)
C–Ir–P(2)	89.5(2)	C(1)–C(2)–C(3)	126.7(6)
N(1)–Ir–P(1)	89.1(1)	C(2)–C(1)–F(1)	113.1(6)
N(1)–Ir–P(2)	92.5(1)	C(2)–C(1)–F(2)	115.3(6)
Ir–C–O	177.2(6)	C(2)–C(1)–F(3)	111.1(6)
Ir–N(1)–N(2)	118.0(3)	C(3)–C(4)–C(5)	128.6(6)
Ir–N(1)–C(2)	133.5(4)	N(2)–C(4)–C(5)	117.6(6)
C(2)–N(1)–N(2)	108.5(5)	C(4)–C(5)–F(4)	117.1(7)
N(1)–C(2)–C(3)	111.1(6)	C(4)–C(5)–F(5)	112.8(7)
C(2)–C(3)–C(4)	101.4(6)	C(4)–C(5)–F(6)	113.5(6)

with only one ν(CO) has never been obtained. In any case, the presence of only one ν(CO) in solution, as well as the fact that the NMR spectra of different forms are the same for each compound, prove that the existence of the various forms is due to solid state effect(s), although the isolation of single forms of **1**, **2** or **3** has been erratic from the preparative point of view.

Crystal structure of 3(G). Crystals of the compound result from the packing of

TABLE 5

WEIGHTED LEAST-SQUARES PLANES FOR *trans*-Ir[3,5-$(CF_3)_2$pz-N](CO)$(PPh_3)_2$ IN THE FORM $Ax + By + Cz + D = 0$

(a) Equations of planes through selected groups of atoms

Plane	Atoms	*A*	*B*	*C*	*D*
1	Ir, P(1), P(2), C, N(1)	4.869	−9.208	7.866	−2.425
2	C(2), C(3), C(4), N(2), N(1)	20.308	−2.453	−2.966	−4.385

(b) Distances of selected atoms from the planes

Plane	Atoms distances $(\text{Å} \times 10^3)$
1	Ir −3(0), P(1) 70(2), P(2) 70(2), C −65(8), N(1) 7(5)
2	C(2) −7(7), C(3) 1(7), C(4) 3(7), N(1) 4(5), N(2) −3(5), C(1) −22(8), C(5) 11(8)

monomeric molecules, separated by normal Van der Waals contacts (shortest H · · · H contact 2.31 Å). Selected bond distances and angles are reported in Table 4. The iridium atom is in an essentially square planar environment (see Fig. 1). Minor deviations from the planarity are observed for the atoms Ir, P(1), P(2), C, and N(1) (Table 5), which may arise from packing effects. The Ir–P(av), Ir–C, and C–O bond lengths (2.332, 1.811(7), 1.155(9) Å, respectively) are very close to those found in *trans*-Ir(benzotriazenido-N_1)(CO)(PPh_3)$_2$ (2.322, 1.821(6), and 1.150(7) Å, respectively) [11], and in the monoclinic form of RhCl(CO)(PPh_3)$_2$ (2.326, 1.810(7), and 1.144(8) Å) [14a]. The similarity of the Rh–C (in RhCl(CO)(PPh_3)$_2$) and Ir–C (in the present compound) bond lengths shows that the *trans*-influence of the pyrazolato-*N* ligand is weak, and is comparable to that of the chloride ion, a result previously suggested in a series of pyrazolato-derivatives of platinum(II) on the basis of NMR parameters alone, namely $^1J(^{195}Pt-^{31}P)$ [12]. The Ir–N bond length (2.079(5) Å) is statistically identical to that found in the benzotriazenido-derivative, 2.074(4) Å [11a]. Significantly shorter Ir–N distances were found when multiple bond character is present: see for instance, Ir–N = 1.824(6) Å in IrCl(tetrachlorodiazacyclopentadiene)(PPh_3)$_2$ [15].

The penta-atomic pyrazolato ring is strictly planar (see Table 5) and approximately normal to the metal coordination plane (dihedral angle 85.8°). This arrange-

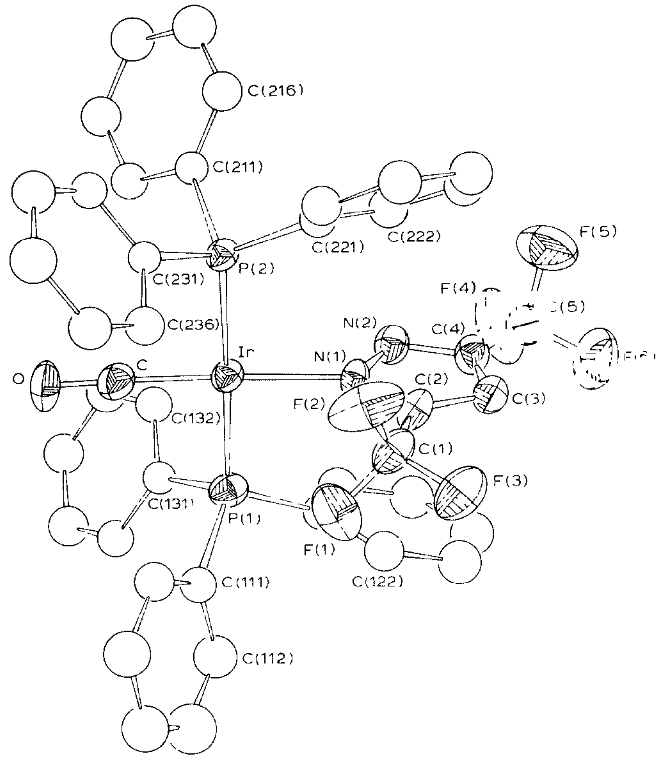
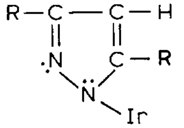


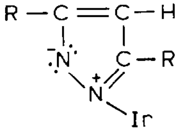
Fig. 1. ORTEP view of *trans*-Ir(3,5-(CF_3)$_2$pz-*N*)(CO)(PPh_3)$_2$ (3) with hydrogen atoms omitted for clarity. The numbering of the phenyl carbons continues around the ring as indicated, with the third subscript as the running index.

ment results in relief of the non-bonding repulsions between this bulky pyrazolato-ligand and the phenyl rings. The corresponding dihedral angle in the derivative of benzotriazene, a planar and less bulky heterocyclic ligand, is slightly smaller (78.4°).

Several structures are known of molecules involving a pyrazole ring. In addition to pyrazole itself [16], they include, for example, 1-substituted organic derivatives such as 1-*o*-nitrophenyl-3-methyl-5-t-butylpyrazole [17], and various metal derivatives, e.g.: $[M(\mu\text{-}3,5\text{-}Me_2pz\text{-}N,N')(NO)_2]_2$ (M = Fe, Co), and $Ni[Ni(C_3H_5)(\mu\text{-}3,5\text{-}Me_2pz\text{-}N,N')_2]_2$ [18]. Furthermore, several structures of uranium(IV) derivatives were reported for which an *endo*-bidentate pyrazolato ligand was proposed [3], the metal–azolate interaction being interpreted as mainly ionic [3].

Our structure is the first where a monodentate pyrazolato ligand is found and, therefore, comparison with some of these compounds is detailed in Table 6. The N–N distance, for example, is 1.360(7) and this is in the range observed for pyrazole (1.341(6)) [16], a substituted pyrazole (1.372(3)) [17], μ-pyrazolates (1.368–1.381) [18], or *endo*-bidentate pyrazolates (1.348 or 1.349 or 1.318) [3]. In any case, the aromatic character of the pyrazolato ring in the compound **3** seems to be quite evident, even if its amount cannot be evaluated precisely; indeed both the two C–C and the two C–N distances in the ring are statistically equal. In the valence bond language, this might be expressed by saying that the weight of the two following canonical forms is approximately equal.





The *trans*-phosphine ligands display a conformation which is intermediate between staggered and eclipsed, as can be seen from the dihedral angle (33.1°) between the planes C(111)–P(1)–Ir and C(211)–P(2)–Ir. It is of interest to recall that $RhCl(CO)(PPh_3)_2$ has been shown to crystallize in both a triclinic [14b] and a monoclinic [14a] form. The only significant difference in the molecular parameters of the two polymorphs concerns the conformation of the phosphine groups, which are staggered in the triclinic and eclipsed in the monoclinic form. The change of conformation is accompanied by a change of the value of $\nu(CO)$ from 1965 (triclinic) to 1980 cm^{-1} (monoclinic) [14a]. This or another, similar packing effect [19] may explain the existence of the various forms, each with a different $\nu(CO)$, observed in the present series of *trans*-$Ir(pz\text{-}N)(CO)(PPh_3)_2$ complexes.

TABLE 6

COMPARISON OF RING DISTANCES IN PYRAZOLE AND PYRAZOLE DERIVATIVES, $-N_1-N_2-C_3-C_4-C_5$

Compound	N_1-N_2	N_1-C_5	N_2-C_3	C_5-C_4	C_4-C_3	Ref.
Pyrazole	1.341(6)	1.333(10)	1.329(10)	1.376(10)	1.382(10)	16b
1-(o-$NO_2C_6H_4$)-3-Me-5-t-Bupz	1.372(3)	1.374(4)	1.324(4)	1.371(4)	1.390(4)	17
$Fe(\mu\text{-}3,5\text{-}Me_2pz\text{-}N,N')(NO)_2)_2$	1.381(2)	1.347(2)	1.351(2)	1.377(3)	1.382(3)	18b
$U(C_5Me_5)_2(\eta^2\text{-}pz)Cl$	1.348(7)	1.367(9)	1.354(9)	1.343(10)	1.318(10)	3b
$Ir(3,5\text{-}(CF_3)_2pz\text{-}N)(CO)(PPh_3)_2$	1.360(7)	1.347(8)	1.340(8)	1.384(9)	1.377(9)	this work

Reactions of iridium(I) pyrazolates. The reactivity of the pyrazolates, **1**–**3**, was investigated towards acids and hydrogen; their behavior with oxygen, or air, was mentioned above.

With acids the behavior changes as a function of the nucleophilic character of the conjugate anion. If this is good nucleophile both replacement of the pz^- ligand and oxidative addition of the H–X molecule takes place, as, in fact, observed in the reaction of **3** with hydrogen chloride (pathway B of the scheme) in benzene: the nitrogen-free iridium(III) compound $IrH(Cl)_2(CO)(PPh_3)_2$ (**7**) [20] was obtained in good yield, and characterized. On the other hand, if the conjugate anion is a poor ligand (e.g. BF_4^-) the heterocycle undergoes protonation and a cationic iridium(I) species is formed according to pathway C: thus the reaction of **1** with fluoboric acid in methanol gave **8** smoothly. In solution this compound showed the CO stretching frequency at a value which is higher than the average value found in the starting material, in agreement with the cationic character established independently through conductivity measurements. In the IR spectrum it also showed the expected broad ν(NH) at 3260 cm^{-1} and the typical ring-breathing vibration at 1581 in place of 1520 cm^{-1} observed in the pyrazolato-*N* compound. The pyrazole-associated ring vibration was not affected by solid state effects, while ν(CO) was: indeed this strong vibration could be observed either at 1981 (**8(L)**) or at 1987 plus 1976 cm^{-1} (**8(M)**), although the same IR spectrum, having only one ν(CO), was observed in solution. The proton NMR spectrum of **8** showed two signals, due to non-equivalent methyl groups; consequently, while in the starting pyrazolato compound the anion pz^- is fluxional, here the protonated ligand, pzH, is not.

All the compounds **1**–**3** reacted slowly in benzene solution with gaseous hydrogen, affording the corresponding dihydrido-derivatives of iridium(III), the white complexes **4**–**6**. From these the yellow starting compounds can be regenerated, either by bubbling nitrogen through a benzene solution, or, in the case of **3**, even in the solid state by just allowing a sample of **6** to stand in contact with the atmosphere for 1–2 months. The formation of the hydrides from the starting iridium(I) derivatives and vice versa can be followed by IR or by NMR spectroscopy. For example, when the hydrogenation time was not sufficient, or the accumulation time of an NMR spectrum of a hydride was too long, the simultaneous presence of both iridium(I) and iridium(III) derivatives, e.g. **6** and **3**, could be ascertained.

In their IR spectrum the hydrides **4**–**6** showed, besides the bands associated with PPh_3 and pz^- ligands, two Ir–H and one CO stretching bands; the last was found at ca. 2020 cm^{-1}, that is at a value higher than in the starting iridium(I) compounds. The ν(CO) and ν(Ir–H) values are in agreement with a *trans*-(anion)IrH and a *trans*-(OC)IrH arrangement [21]. Such an arrangement is supported also by the shift of ν(Ir–H) upon change of the pyrazolato group. This arrangement of ligands, which implies a *cis*-addition of hydrogen, is confirmed by the proton NMR spectra. Indeed, in the hydride region two different signals are observed at ca. 18 and 26.8–28.2 τ; each of them is split into a triplet (^2J(P–H) 14–18 Hz) by coupling with two equivalent P nuclei, and is further split into a doublet (^2J(H–H) 4–5 Hz) by coupling with the other hydride. Irradiation of each triplet of doublets reduced the other set of hydrido signals into a simple triplet. In agreement with *trans*-arrangement of the phosphine ligand, the $^{31}P\{^1H\}$ NMR spectrum showed only one singlet which became a pseudo-triplet with $^2J(P–H) \cong 14$ Hz when, in the case of **5**, the non-hydrogen-decoupled spectrum was recorded. Finally, the presence of two methyl (or of two CF_3) signals in the spectra of the compounds **4** and **5** (or of **6** respectively) agrees with a monodentate pyrazolato ligand also in solution.

Experimental

For the compounds obtained, the analytical data and molecular weight determinations are reported in Table 1; selected IR data are located in Table 2, while the NMR data are in Table 3. The IR spectra were recorded on Beckmann 4210 or on Nicolet MX-1 FT instruments. The NMR spectra were recorded on a Bruker instrument operating at 80 (^1H), 32.4 (^{31}P), or 56 MHz (^{19}F).

3,5-Dimethylpyrazole (Fluka) was a commercial product, while potassium pyrazolate, potassium 3,5-dimethylpyrazolate [22], 3,5-dimethyl-4-nitropyrazole [23], and 3,5-bis(trifluoromethyl)pyrazole [24], and Vaska's complex [25] were prepared and purified according to the literature methods.

Evaporation was always carried out under reduced pressure (water aspirator). All of the analytical samples were obtained by crystallization from benzene/n-pentane or n-hexane or from benzene/methanol, and were pumped to constant weight under vacuum (ca. 1 Torr).

Iridium(I) pyrazolates (1–3). To a stirred solution of Vaska's compound (730 mg, 0.94 mmol), 3,5-bis(trifluoromethyl)pyrazole (212 mg, 1.04 mmol), and then potassium hydroxide in methanol (3.5 ml of a 0.37 *M* solution) were added. After 0.5 h, the solution was concentrated and filtered; upon addition of n-hexane, a yellow precipitate of **3** (805 mg 85%) was obtained, which was purified from benzene/methanol. The sample of **3(G)** used for the X-ray crystal structure determination was obtained from a saturated solution in diethyl ether to which n-pentane was then added (1/1); slow evaporation (3 d) gave the sample used. The compounds **1** and **2** were obtained exactly as **3** (35 and 75% yield respectively). In all cases, by repeated crystallization, samples were obtained which had the same m.p., analytical and solution spectral data but differed in the solid state IR spectrum, as detailed in the Table 2 and discussed in the text.

$Ir(3,5\text{-}Me_2pz\text{-}N)(CO)(PPh_3)_2$ (1). Under a nitrogen blanket, to a stirred solution of Vaska's compound (957 mg) in anhydrous tetrahydrofuran (0.15 l) a solution of potassium 3,5-dimethylpyrazolate in the same solvent (10 ml, 0.2 *M*) was added. After 5 min the yellow solution was evaporated to dryness; the greenish-yellow residue was extracted with benzene (ca. 30 ml), and n-pentane was added until a greenish precipitate formed in the extract. This was then filtered and the yellow solution was evaporated to dryness to afford a yellow, oily residue, which became solid after stirring under n-pentane. The crude product was crystallized twice from benzene/n-pentane to give the analytical sample (750 mg, 68%), identical to the one obtained as described above, according to analytical and solution spectral data.

Neither this nor the preceding reaction pattern afforded isolation of the analogous iridium derivative of pyrazole, $C_3H_4N_2$. When the reaction time was 0.5 h unreacted Vaska's complex was isolated, according to IR and spectral evidence; with a reaction time of up to two days no pure product could be isolated from the greenish solution.

$IrH_2(pz\text{-}N)(CO)(PPh_3)_2$ (4–6). Hydrogen was bubbled for 20 h through a solution of compound **2** (280 mg, 0.316 mmol) in benzene (40 ml). After the addition of n-pentane (40 ml) the solution was concentrated, affording a precipitate which was

washed with few drops of benzene to give **5** (210 mg, 75%), which could be purified by benzene/n-pentane. The compounds **4** and **6** were obtained similarly (ca. 70% yield) after bubbling hydrogen for 2 or for 6 days, respectively.

Reactions with acids. (a) Dry hydrogen chloride was bubbled through a benzene solution of the compound **3** (150 mg); the solution turned colorless immediately and afforded a white precipitate, **7** (134 mg), upon concentration.

(b) A methanol solution of fluoboric acid (0.13 ml of a 0.56 *M* solution) was added to a methanol suspension (15 ml) of the compound **3** (60 mg, 0.071 mmol). After 10 min the solution was evaporated to dryness and the residue was washed with benzene which, upon concentration, afforded **8(L)** (20 mg, 30%). The part of the residue which was benzene-insoluble was crystallized from dichloromethane/diethyl ether, affording **8(M)** (45 mg, 68%). The samples **8(L)** and **8(M)** have the same analytical and solution spectroscopic data (see Table 2 and discussion in the text).

Crystal structure determination

Preliminary precession photographs revealed that the yellow crystals of the compound **3(G)** belong to the monoclinic system, with systematic absences characteristic of the space group $P2_{1/n}$–C_{2h}^5 ($h\ 0\ l$: $h + l$, $0\ k\ 0$: $k = 2n + 1$). A prismatic specimen was mounted on a BASIC diffractometer [26] with the *a* axis approximately parallel to the ϕ-axis of the instrument. Cell constants were obtained by least-squares refinement of the θ values (in the range 8–16°) of 24 accurately centered reflections. These and other crystallographic data are listed in the Table 7.

TABLE 7

CRYSTAL AND INTENSITY COLLECTION DATA FOR *trans*-Ir[3,5-$(CF_3)_2$pz-*N*](CO)$(PPh_3)_2$

Formula	$C_{42}H_{31}F_6IrN_2OP_2$
Formula weight	947.9
a (Å)	21.106(6)
b (Å)	19.700(5)
c (Å)	9.437(2)
β (deg)	94.34(2)
V (Å^3)	3912(3)
Z	4
D (calcd) (g cm^{-3})	1.61
Space group	$P2_1/n$
Crystal size	0.20 × 0.20 × 0.36 mm
Radiation source, λ (Å)	Mo-K_α (graphite-monochromated) 0.71069
Absorption coefficient, μ(cm^{-1})	35.4
Transmission factors	0.560 (min)–0.653 (max)
Scan rate (deg min^{-1})	3
Scan range (deg)	1
Background time	= scan time
2θ limits (deg)	6–50
No. unique data ($I > 3\sigma(I)$)	4474
Final no. variables	244
R [a]	0.036
R_w [b]	0.038
GOF [c]	1.365

[a] $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = \{(\Sigma w(|F_o| - |F_c|))^2/(\Sigma w|F_o|)^2\}^{1/2}$. $w = 1/(\sigma^2(F_o) + 0.015(F_o)^2)$.
[c] Goodness of fit, GOF $= \{\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})\}^{1/2}$

TABLE 8

ATOMIC COORDINATES ($\times 10^4$)

Atom	x	y	z
Ir	2510(0)	520(0)	2135(0)
P(1)	1512(0)	652(0)	2998(2)
P(2)	3521(0)	325(0)	1372(2)
C	2239(3)	−266(3)	1303(8)
O	2053(2)	−753(2)	729(6)
F(1)	2002(2)	2003(2)	629(5)
F(2)	2956(2)	2072(2)	134(4)
F(3)	2492(2)	2924(2)	893(5)
F(4)	3151(3)	1907(3)	7220(5)
F(5)	3978(2)	2230(3)	6424(6)
F(6)	3245(3)	2900(2)	6570(5)
N(1)	2780(2)	1447(2)	3046(5)
N(2)	2983(2)	1455(2)	4450(5)
C(1)	2575(3)	2259(3)	1057(8)
C(2)	2780(3)	2089(3)	2554(6)
C(3)	2994(3)	2538(3)	3612(7)
C(4)	3108(3)	2108(3)	4752(7)
C(5)	3348(3)	2275(4)	6222(8)
C(111)	869(2)	851(3)	1672(5)
C(112)	293(2)	1106(2)	2066(4)
C(113)	−199(2)	1232(2)	1035(6)
C(114)	−116(2)	1103(3)	−388(5)
C(115)	459(2)	848(2)	−782(4)
C(116)	952(2)	722(2)	248(6)
C(121)	1452(2)	1300(2)	4365(5)
C(122)	1402(1)	1977(2)	3950(4)
C(123)	1427(2)	2488(1)	4971(5)
C(124)	1502(2)	2322(2)	6408(5)
C(125)	1552(1)	1645(2)	6823(4)
C(126)	1527(2)	1134(1)	5802(5)
C(131)	1268(2)	−121(2)	3871(4)
C(132)	1736(1)	−483(2)	4666(5)
C(133)	1577(2)	−1066(2)	5392(4)
C(134)	949(2)	−1287(2)	5323(4)
C(135)	480(1)	−925(2)	4528(5)
C(136)	640(2)	−341(2)	3803(4)
C(211)	3971(2)	−321(2)	2422(5)
C(212)	3651(1)	−895(2)	2845(5)
C(213)	3987(2)	−1420(2)	3548(5)
C(214)	4643(2)	−1369(2)	3827(5)
C(215)	4962(1)	−794(2)	3403(5)
C(216)	4626(2)	−270(2)	2700(5)
C(221)	4071(2)	1040(2)	1358(3)
C(222)	4215(2)	1390(2)	2622(3)
C(223)	4607(2)	1958(1)	2640(3)
C(224)	4856(2)	2176(2)	1394(3)
C(225)	4712(2)	1826(2)	129(3)
C(226)	4320(2)	1258(1)	111(3)
C(231)	3493(2)	9(2)	−441(3)
C(232)	3879(2)	−518(2)	−847(4)
C(233)	3878(2)	−700(2)	−2272(5)
C(234)	3491(2)	−354(2)	−3292(3)
C(235)	3106(2)	173(2)	−2887(4)
C(236)	3107(2)	355(2)	−1461(5)

Intensity data were collected by the ω-scan method, with background counts measured at each end of the scan range for a total time equal to the time of scan. The intensity of three standard reflections were measured after every 128 reflections; these showed no appreciable decay during data collection. A total of 8 831 intensity data in the $\pm h$, $+k$, $+l$ quadrant of the reciprocal space were measured. The data were corrected for Lorentz and polarization effects and for absorption, the latter by the numerical integration method with a gaussian grid of $8 \times 8 \times 8$. After averaging the equivalent reflections a set of 4474 unique data having $I \geqslant 3\sigma(I)$ was used in subsequent calculations.

The position of all non-hydrogen atoms were obtained by the usual Fourier and Patterson methods. Published sources were used to obtain scattering factors for the non-hydrogen atoms [27], the hydrogen atoms [28], as well as for the anomalous dispersion factors for iridium and phosphorus [29]. The phenyl rings of the triphenylphosphine ligands were constrained to D_{6h} symmetry (C–C 1.392 Å) with individual isotropic thermal parameters. In the final least-squares cycles, the contribution of all the hydrogen atoms, fixed in their expected position (C–H 1.00 Å), was included.

The final full-matrix refinement, in which anisotropic thermal parameters were assigned to all the non-hydrogen atoms except the carbon atoms of the phenyl rings, was terminated when no parameter shifted more than one third of its estimated standard deviation. The final difference-Fourier map showed no other peak of structural significance. All computations were carried out on a UNIVAC 1100/80 computer using well-checked programs from our library, partly derived from entries 7528, 7531, and 7535 of the 1966 World list of Crystallographic Programs. Johnson's ORTEP was used in preparing the drawing. Positional parameters are given in the Table 8.

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References

1 S. Trofimenko, Chem. Rev., 72 (1972) 497.

2 A. Shaver, J. Organomet. Chem. Library, 3 (1977) 157; F. Bonati, Chim. Ind. (Milan), 62 (1980) 323.

3 C.W. Eigenbrot, Jr. and K.N. Raymond, Inorg. Chem., 20 (1981) 1553; ibid., 21 (1982) 2653.

4 (a) F. Bonati, G. Minghetti and G. Banditelli, J. Chem. Soc., Chem. Commun., 88 (1974); (b) G. Minghetti, G. Banditelli and F. Bonati, Inorg. Chem., 18 (1979) 658; (c) G. Banditelli, A.L. Bandini, F. Bonati, R.G. Goel and G. Minghetti, Gazz. Chim. Ital., 112 (1982) 539.

5 (a) G. Minghetti, G. Banditelli and F Bonati, Chem Ind. (London), (1977) 123; (b) J. Chem. Soc. Dalton Trans., (1979) 1851.

6 G. Banditelli, A.L. Bandini, F. Bonati and G. Minghetti, J. Organomet. Chem., 218 (1981) 229.

7 A.L. Bandini, G. Banditelli, G. Minghetti and F. Bonati, Can. J. Chem., 57 (1979) 3237.

8 A.L. Bandini, G. Banditelli, F. Bonati, F. Demartin, M. Manassero, G. Minghetti, J. Organomet. Chem., 238 (1982) C9.

9 (a) K.A. Beveridge, G.W. Bushnell, K.R. Dixon, D.T. Eadie, S.R. Stobart, J.L. Atwood and M.J. Zaworotko, J. Am. Chem. Soc., 104 (1982) 920; (b) A.W. Coleman, D.T. Eadie, S.R. Stobart, M.J. Zaworotko and J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 922.

10 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th Ed., Wiley, New York, 1980, p. 940.

11 (a) L.D. Brown, J.A. Ibers and A.R. Siedle, Inorg. Chem., 17 (1978) 3026; (b) P.U. Kreutzer, J.C. Weis, U. Bock, J. Erbe and W. Beck, Chem. Ber., 116 (1983) 2691.

12 G. Banditelli, A.L. Bandini, F. Bonati and G. Minghetti, Inorg. Chim. Acta, 60 (1982) 93.

13 R. Gassend, J.C. Maire and J.C. Pommier, J. Organomet. Chem., 132 (1977) 69.

14 (a) A. Ceriotti, G. Ciani and A. Sironi, J. Organomet. Chem., 247 (1983) 345; (b) A. Del Pra, G. Zanotti and P. Segala, Cryst. Struct. Commun., 8 (1979) 959.

15 K.D. Schraum and J.A. Ibers, Inorg. Chem., 19 (1980) 1231.

16 T. La Cour and S.E. Rasmussen, Acta Chem. Scand., 27 (1973) 1845; (b) F.K. Larsen, M.S. Lehmann, L. Søtofte and S.E. Rasmussen, Acta Chem. Scand., 24 (1970) 3248.

17 B. Bovio, J. Cryst. Spectr. Res., 13 (1983) 89.

18 K.S. Chong, S.J. Rettig, A. Storr and R.J. Trotter, Can. J. Chem., 59 (1981) 996; idem, ibid., 57 (1979) 3119.

19 M.J. Bennett, P.B. Donaldson, Inorg. Chem., 16 (1977) 655.

20 (a) L. Vaska, J.W. DiLuzio, J. Am. Chem. Soc., 83 (1961) 2784; (b) L. Vaska, J. Am. Chem. Soc., 88 (1966) 5325.

21 J.P. Jesson, in E.L. Muetterties (Ed.), Transition Metal Hydrides, Marcel Dekker, New York, 1971, Chap. IV, pp. 129–143.

22 S. Trofimenko, J. Org. Chem., 33 (1968) 890; J. Am. Chem. Soc., 92 (1970) 5118.

23 G.T. Morgan and I. Ackermann, J. Chem. Soc., (1923) 1308.

24 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 3165.

25 J.P. Collman, C.T. Sears Jr. and H. Kubota, Inorg. Synth., 11 (1968) 102.

26 M. Angoletta, P.L. Bellon, F. Demartin and M. Manassero, J. Chem. Soc., Dalton Trans., (1981) 150.

27 D.T. Cromer and J.B. Mann, Acta Crystallogr., Sect A, 24 (1968) 321.

28 J.B. Forsyth and M. Wells, Acta Crystallogr., 12 (1959) 421.

29 D.T. Cromer, in International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4, pp. 149–150.