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Heterobimetallic Complexes from the Reaction of Iridium(I) and Iridium(III) 3,5-Dimethylpyrazolates with Gold(I) or Gold(III)

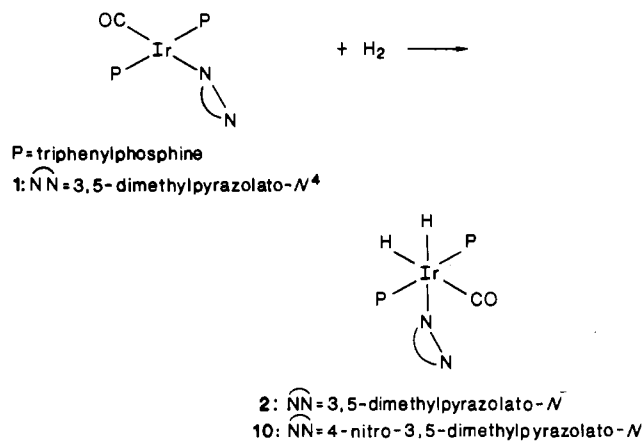
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The reaction of iridium(I) and iridium(III) pyrazolates, IrP₂(CO)(pz-*N*) (1), IrP₂(CO)(H)₂(pz-*N*) (2), and IrP₂(CO)(H)₂(pz'-*N*) (10) (P = triphenylphosphine; pzH = 3,5-dimethylpyrazole and pz'H = 4-nitro-3,5-dimethylpyrazole), with Au(tht)X (tht = tetrahydrothiophene; X = Cl, Br) affords iridium(I)-gold(I) and iridium(III)-gold(I) derivatives IrP₂(CO)(μ-pz-*N,N'*)AuX (X = Cl (3), X = Br (4)) and IrP₂(CO)(H)₂(μ-pz-*N,N'*)AuCl (8). The reaction between 1 and Au(tht)Cl₃ gives an unstable yellow bimetallic intermediate, IrAuP₂(CO)(pz)Cl₃ (5), which is easily decomposed to (AuPz)_n (6) and IrP₂(CO)Cl₃ (7). Iridium(III) cationic pyrazole derivatives [IrP₂(CO)(pzH-*N*)(H)₂][A] (A = AuCl₄ (9), A = BF₄ (12)) and [IrP₂(CO)(pz'H-*N*)(H)₂][A] (A = AuCl₄ (11), A = BF₄ (13)) are obtained by reaction of 2 or 10 with Au(tht)Cl₃ or tetrafluoroboric acid. Infrared and NMR (¹H and ³¹P{¹H}) data show that compounds 8, 12, and 13 are able to exist in two different forms: in both of them the geometry around the iridium atom is the same with a cis hydride and trans phosphine arrangement. In one of the conformers, 8A, the resonance for the hydride trans to CO is observed at unusually low field (δ -3.72 in deuteriobenzene), suggesting the existence of a Au...H interaction. Complex 8A crystallizes in the monoclinic space group P2₁/n with a = 13.385 (2) Å, b = 16.229 (3) Å, c = 18.376 (3) Å, and β = 101.60 (2)°. Complex 12c is monoclinic, space group P2₁/c, with a = 9.874 (2) Å, b = 23.951 (4) Å, c = 21.029 (6) Å, and β = 101.25 (2)°. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares; R values are 0.044 (for 3954 reflections) and 0.038 (for 4118 reflections) for 8A and 12c, respectively. In 8A a Au...H separation of 2.28 Å was calculated, against a value of 2.90 Å resulting from the sum of van der Waals radii.

Introduction

In preceding papers of ours we described the preparation of metal-containing ligands, e.g. (L-L)Pt{C(OR)=NR'}₂ or (L-L)Pt(pyrazolato-*N*)₂ (L-L = chelating diphosphine),² and we used them as bidentate nitrogen donors, so that di- or trinuclear derivatives could be obtained and characterized.^{1b,2b} More recently we described also some iridium(I) and iridium(III) species that are expected to act as monodentate metal-containing ligands;³ among them are some pairs of derivatives, such as 1 and 2, that are strictly related, the latter being obtained by oxidative addition of dihydrogen to the former:

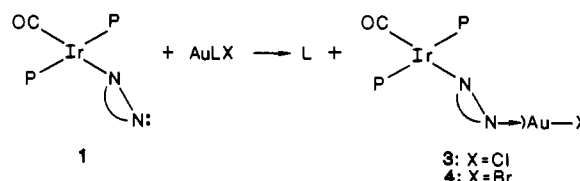


It was then decided to investigate the reactions of the couple of compounds 1 and 2 with AuLCl and with AuLCl₃, where L is an easily displaced ligand such as tetramethylene sulfide, in the hope of obtaining a series of binuclear pyrazolato-*N,N'*-bridged compounds having Au(I) in the presence of either Ir(I) or Ir(III) and Au(III) in the presence of either Ir(III) or Ir(I). Such heterobinuclear species are of interest because each metal center may be involved separately in the process of activating other molecules. In addition, ligand-bridged heterobinuclear complexes

where each metal is capable of existence in two different and well-characterized oxidation states have been traditionally the subject of studies on inner-sphere reaction mechanisms.⁵

Results and Discussion

The reaction of 1 with AuLX (X = Cl or Br) gave 3 or 4, respectively, which can be obtained with good yields if the operating temperature is lowered to 3–4 °C.



Besides the absorptions due to the phosphine and to the pyrazolato ligand, the infrared spectrum of 3 in Nujol mull showed two carbonyl stretching frequencies (1991 and 1986 cm⁻¹) that become one (at 1976 cm⁻¹) in dichloromethane solution; in the lower frequency region the AuCl stretching vibration can be assigned. Comparison with the same C=O vibration in the parent compound, 1963 cm⁻¹ in dichloromethane, shows that only a slight increase takes place upon formation of the nitrogen-gold bond. This is in line with some electron density removal from iridium toward the gold atom through the several intervening bonds. However, no speculation should be made on this because it has the same order of magnitude or is lower than the difference observed between two crystalline forms of some of the iridium(I) pyrazolates, e.g. 1.³

The NMR spectra (Table II) of 3, or of 4, were carried out in deuteriochloroform and support the structures proposed. By comparison, in the starting compound 1 both the CH and the methyl groups give broad signals at room temperature and neat

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- (2) (a) Minghetti, G.; Banditelli, G.; Bonati, F. *Chem. Ind. (London)* 1977, 123. *J. Chem. Soc., Dalton Trans.* 1979, 1851. (b) Bandini, A. L.; Banditelli, G.; Minghetti, G.; Bonati, F. *Can. J. Chem.* 1979, 57, 3237.
- (3) Bandini, A. L.; Banditelli, G.; Bonati, F.; Minghetti, G.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* 1984, 269, 91.
- (4) Throughout this paper, pzH indicates 3,5-dimethylpyrazole and pz'H indicates 4-nitro-3,5-dimethylpyrazole.
- (5) For example: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1210 and references therein.

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Table I. Analytical, Infrared, and Other Data

no.	compd ^a	mp (dec), °C	anal. found (calcd)					Ir data, ^{b,c} cm ⁻¹
			C	H	N	Ir	Au	
3	IrL ₂ (CO)(μ-pz-N,N)AuCl ^{d,e}	>150	47.09 (47.04)	3.69 (3.48)	2.50 (2.61)	16.9 (17.92)	18.16 (18.37)	1991 vs, 1986 vs; ^f 1526 w; 365 w, 342 w
4	IrL ₂ (CO)(μ-pz-N,N)AuBr ^e	>170	45.78 (45.16)	3.35 (3.35)	2.53 (2.51)			1985 vs, 1968 vs; 1527 w
5	IrAuL ₂ (CO)(pz)Cl ₃ ^g	>135	43.64 (44.12)	3.19 (3.27)	2.41 (2.45)	15.8 (16.81)	16.80 (17.23)	2077 m, 2051 s; 1574 w, 1532 w; 349 w br, 331 w
6	(Au(μ-pz-N,N)) _n		19.70 (20.56)	2.41 (2.42)	9.05 (9.59)			1532 ms
7	IrL ₂ (CO)Cl ₃	>180	51.06 (52.21)	3.58 (3.56)		20.4 (22.58)		2077 s; 327 m, 324 m, 303 w
8	IrL ₂ (CO)(H) ₂ (μ-pz-N,N)AuCl ^h	>110 >120	46.67 (46.95)	3.65 (3.67)	2.60 (2.61)	16.40 (17.89)	18.30 (18.33)	(A) 2157 m, 2095 s; 1985 vs; 1537 vw ^{f,i} (B) 2153 m br; 2018 s; 1535 w; 352 w ^f
9	[IrL ₂ (CO)(H) ₂ (pzH-N)][AuCl ₄] ^j		42.33 (42.68)	3.24 (3.42)	2.49 (2.37)	15.4 (16.27)	17.0 (16.67)	3335 m; 2189 vw; 2122 s; 2016 s; 1574 m; 359 m
11	[IrL ₂ (CO)(H) ₂ (pz'H-N)][AuCl ₄] ^k	>100 250 fus	41.00 (41.10)	3.27 (3.18)	3.40 (3.42)			3270 m br, 2183 m, 2110 vs, 2039 sh, 2015 s; 1587 s, 1506 s; 363 m, 346 sh
12a	[IrL ₂ (CO)(H) ₂ (pzH-N)][BF ₄ ·Et ₂ O	>100 250 fus	55.39 (55.18)	4.48 (4.99)	2.84 (2.80)			3334 m br; 2173 m br; 2032 s; ^j 1579 m
12b	12-C ₆ H ₆	>120 250 fus	57.32 (57.19)	4.35 (4.61)	2.77 (2.78)			3313 ms; 2166 w, 2126 m; 2002 s; 1579 m ^l
13	[IrL ₂ (CO)(H) ₂ (pz'H-N)][BF ₄]		50.61 (51.75)	4.06 (4.04)	4.32 (4.31)			3480 w br; 2184 mw, 2118 ms; 2035 sh, 2019 ms; 1594 ms; 1511 ms

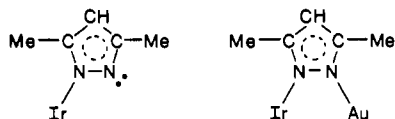
^aL is triphenylphosphine, pzH is 3,5-dimethylpyrazole, and pz'H is 3,5-dimethyl-4-nitropyrazole. Compounds 3 and 4 are orange, 5, 9 and 11 are yellow, and 6, 7, 8, 12, and 13 are white. ^bNujol mull. ^cComparison data from ref 3. IrL₂(CO)(pz-N) (1): 1975 s, 1964 s, 1954 s, 1520 w cm⁻¹. IrL₂(CO)(H)₂(pz-N) (2): 2199 m, 2107 s, 2020 vs, 1515 m cm⁻¹. IrL₂(CO)(H)₂(pz'-N) (10): 2153 w, 2127 s, 2020 vs, 1515 m cm⁻¹. ^dM_r by osmometry in chloroform (0.73% w/w): 1064 (1072.4). ^eNot an electrolyte in dichloromethane. ^fData (cm⁻¹) in dichloromethane solution: for 3, 1967 vs; for 12a, 2180 sh, 2100 m, 2030 sh, 2020 s; for 8A,B, 2140 w, 2080 m, 2005 sh, 1990 s. Data (cm⁻¹) in benzene solution: for 8, 2140 w, 2080 w, 2005 m, 1985 s, 1950 sh. ^gCl = 9.05 (9.30). ^hM_r by osmometry in chloroform (0.62% w/w): 909 (1074.4); Cl = 4.37 (3.30). ⁱCrystalline sample after X-ray crystal structure determination. ^jCl = 12.9 (12.00); Λ_M = 101 Ω⁻¹ cm² mol⁻¹ in methanol at 18 °C (0.37 mM). ^kΛ_M = 47 Ω⁻¹ cm² mol⁻¹ at 23 °C in dichloromethane. ^lIdentical with the data for crystalline sample [IrL₂(CO)(pzH-N)(H)₂][BF₄·2CH₂C₆H₅] (12c), after X-ray crystal structure determination.

Table II. ¹H and ³¹P{¹H} NMR Data^a

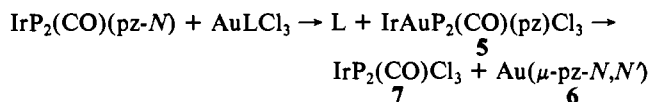
compd	solvent	¹ H ^b									
		Ar ^d	4-CH ^e	3,5-Me ^e	hydride ^f						NH ^{g,h}
					trans CO	² J _{PH}	² J _{HH}	trans pz	² J _{PH}		
1 ^h	CDCl ₃	7.9–6.9	5.2 br	2–1.3 br							24.1
	C ₆ D ₆	8–6.9	5.54	2 br							22.8
2 ^h	CDCl ₃	7.6–7.1	5.0	2.1, 1.0	-8.3	18.4	4.5	-17.3	16.3		
	C ₆ D ₆	7.9–7.4	5.5	2.6, 1.4	-8	18	4.7	-16.8	16		10.0
		7.3–6.7									
3	CDCl ₃	7.85–7.15	5.40	1.65, 1.45							22.3
4	CDCl ₃	7.9–7.5	5.4	1.67, 1.46							22.64
		7.5–7.2									
5	CDCl ₃	8.1–7.1	5.56	2.29							
7	CDCl ₃	8.2–7									-18
8A	CDCl ₃										10.28
	CD ₂ Cl ₂	7.3	5.26	1.66, 1.53	-4.66	14.8	4.2	-17.84	15.3		
	C ₆ D ₆ ⁱ	7.9–7.55	5.31	1.75	-3.72	14.7	4.2	-17.44	15.5		10.62
		7.4–6.9									
8B	CDCl ₃										11.25
	CD ₂ Cl ₂	8.1–6.5	5.02	1.95, 1.2	-8.33	17	4	-18.6	l		
	C ₆ D ₆ ^m	8.0–7.5	5.18	2.17, 1.50	-8.17	17	4.5	-18.17	15		
		7.4–6.9									
9	CDCl ₃	7.7–7.2	5.3	1.9–1.5 br	-7.63	17.5	3.7	-18.22	14.5	9.2	11.2
10 ^h	C ₆ D ₆	7.8–7.4		2.78, 1.72	-8.2	18	4.7	-17.4	15		12.1
		7.1–6.8									
	CD ₂ Cl ₂	7.6–7.1		2.24, 1.2	-8.5	18	4.7	-17.9	15		
11	CDCl ₃	7.8–7.3		2.19	-7.30	17	3.4	-18.54	13.6	10.38	
12A ⁿ	CDCl ₃	7.8–7.1	5.2	1.77, 1.79	-7.2	l	l	-18.3	l	10.05	12.57
					-7.3	17.4	3.9	-18.1	14.6		
12B ^o	CDCl ₃	7.8–7	5.04	2.1, 1.35	-7.9	l	l	-18.3	l	10.75	13.54
					-8.05	16.5	4.1	-18.38	14.4		
13A	C ₆ D ₆	8–7.4, 7.3–7		2.3, 1.9	-6.53	16.8	3.4	-18.47	14.3	11.71	14.58
13B ^l		k		2.7, 1.75	-8.06	~15	~4	-18.92	~13	12.6	14.72

^aAt room temperature unless otherwise stated. ^bδ units, Me₄Si as internal standard. ^cIn ppm from 85% H₃PO₄ as external standard; positive shifts are downfield. ^dAlways multiplet. ^eAlways singlet. ^fTriples of doublets; coupling constants are in Hz. ^gDisappears with D₂O. ^hFrom ref 3 for 1, in deuteriochloroform at 230 K: δ 7.7–7.2 m; 5.12 s; 1.86 s, 1.34 s. ⁱAt 333 K: 8.3–6.9 m; 5.34 s; 1.81 s, 1.76 s; -3.74, -17.5 td. In perdeuteriotoluene at room temperature the hydrido region is unchanged. ^j³¹P{¹H} NMR: 11.7 s ppm. The signals attributable to 8B were not detected from 323 to 229 K. ^kMinor component. ^lIdentical. ^mUnresolved. ⁿNMR at 243 K in perdeuteriotoluene: ¹H (hydrido region), δ -8.2 td (²J_{PH} = 17, ²J_{HH} = 4.3 Hz), -18.2 td (²J_{PH} = 15 Hz); ³¹P{¹H}, 12.7 ppm. The spectra are unaffected from 243 to 273 K; at room temperature the A form, which is predominant at 333 K, is present. ^oAlways mixtures of isomers A and B with ca. 2:1 ratio, either from 12a or 12b, no significantly change was observed from 223 to 298 K. ^pAt 273 K the hydrido signals are well resolved.

signals only below it: this suggests a fluxional behavior of the pyrazolato ligand with reference to the Ir–N bond. In **3** or in **4** the molecule becomes more rigid than in **1** or in **2** because the pyrazolato ligand now has the AuX moiety attached to it: thus one sharp signal for each methyl is recorded already at room temperature. It is often observed that, upon coordination of an azole to a metal, the ring protons are shifted to lower field than in the free ligand. With **3** or **4** this is true for the CH protons, while the methyl groups get closer, in keeping with a less asymmetric placement of the pyrazolato group:

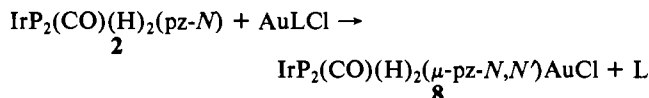


The difference between Au(III) and Au(I) as acceptor with reference to the donor **1** is underlined by the reaction of **1** with AuCl₃. This reaction gave a yellow product, **5**, which is easily decomposed, affording two white compounds identified as oligomeric (3,5-dimethylpyrazolato-*N,N'*)gold(I) (**6**)⁶ and as bis-(triphenylphosphine)(carbonyl)trichloroiridium(III) (**7**).⁷ The formulation of **5** rests upon the analytical data and the isolation of the decomposition products, which allows the following reaction path to be proposed:



The fast decomposition hindered the full spectroscopic characterization and a conclusive formulation of **5** as Ir(I)–Au(III) or Ir(III)–Au(I) complex such as, e.g., IrP₂(CO)(μ-pz)AuCl₃ or IrP₂(CO)(Cl)₂(μ-pz)AuCl. These last molecules are comparable with those considered in the ligand-bridged or inner-sphere reactions.⁵

The reaction of **2** with AuCl gave **8**:



Compound **8** was found to give two isomers, **8A** and **8B**, each of which can be obtained pure under different experimental conditions (see Experimental Section) and characterized by different spectra.

In the 2000-cm⁻¹ region compound **8A** has three strong absorptions (2157, 2095, and 1985 cm⁻¹), while compound **8B** has only two (2153, and 2018 cm⁻¹). The three highest values (ca. 2100 cm⁻¹) are assigned to Ir–H and the two lowest values to C≡O stretching vibrations by comparison with the values observed in the starting compound **2** (Ir–H, 2199 m and 2107 s cm⁻¹; C≡O, 2020 vs cm⁻¹ in Nujol mull). In the proton NMR spectrum (hydrido region) each of the isomers shows two triplets of doublets with different shifts; this allows both detection and quantitative identification. According to these spectra in perdeuteriotoluene isomer A does not change when the temperature is raised from 229 to 323 K, a mixture of A and B does not change when the temperature is lowered to 213 K, but pure B, observed at 243 K, gives a mixture of A and B when the solution is heated to room temperature: thus A seems capable of existence in a broader range of temperatures. In deuteriobenzene the hydride signals lie at δ –3.72 and –17.44 or δ –8.17 and –18.17 for the A or B isomer, respectively. In each isomer the signal observed in the region typical for a trans H–Ir–N arrangement⁸ shifts to higher field

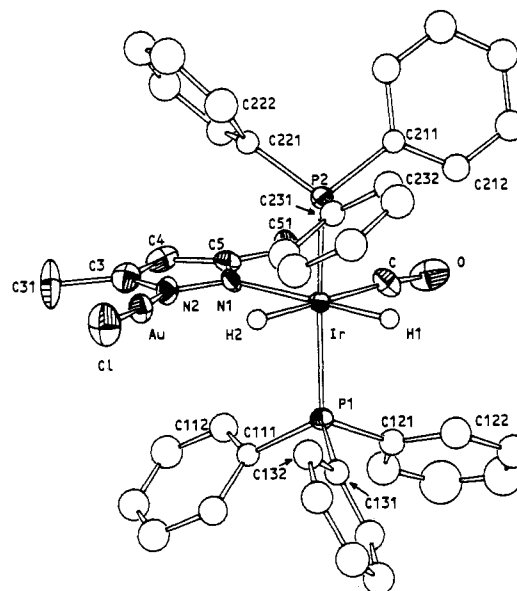
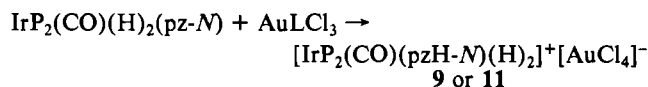


Figure 1. ORTEP view of **8A**. Thermal ellipsoids are drawn at 30% probability.

than in the parent compound **2** (δ –16.8). On the other hand, by comparison with the parent molecule **2** (δ –8.0) the lower signal, corresponding to trans H–Ir–CO, is at the usual, expected position in isomer B (δ –8.17) and is at lower field in the isomer A (δ –3.72); i.e. in a region where signals due to gold hydride derivatives were recently found.⁹ Although in A and B the chemical shifts of the hydride resonances are different, the hydride pattern is the same and also the coupling constants are nearly the same. The multiplicity and the coupling constants agree well with those expected for cis hydride and trans phosphine ligands; in addition only one singlet is observed in the hydrogen-decoupled ³¹P NMR spectrum. Therefore the two species must have the same arrangement of ligands around the idealized octahedron surrounding the iridium atom; consequently the two species are likely to be conformers. The structure of **8A** has been determined and is presented in Figure 1. The conformation in **8B** must therefore be the opposite, namely, with the AuCl group “cis” to the CO group.

The existence of two conformers may be ascribed to hindered rotations on the Ir–N axis, as e.g. in the case of iridium(I) pyrazolates,³ or, less likely, on the Ir–P axis.

The reaction of **2** with AuCl₃ or with Au₂Cl₆ was carried out in several solvents



In spite of the precautions used, some moisture was still present and a yellow compound, **9** or **11**, was obtained when **2** or its nitro-substituted derivative **10**, respectively, was used; the products are formulated as the tetrachloroaurate(III) salt of protonated **2** or of protonated **10**. The same cations were present in the tetrafluoroborate **12** or **13**, isolated readily by reaction of **2** in benzene solution or **10** in methanol solution, respectively, with ethereal or aqueous tetrafluoroboric acid. Alternatively complex **12** can be obtained also by oxidative addition of dihydrogen to the corresponding Ir(I) derivative [IrP₂(CO)(pzH-*N*)]⁺[BF₄]⁻.

As already observed in the case of **1** with tetrafluoroboric acid,³ with **12** and **13** two forms are also found. Compounds **12a** and **12b** show different infrared spectra, especially in the carbonyl and M–H stretching region: the absorptions are at 2173 and 2032 cm⁻¹ and at 2166, 2126, and 2002 cm⁻¹, respectively.

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Table III. Selected Bond Distances (Å) and Angles (deg)^a

	8A	12c		8A	12c
Ir-C	1.893 (14)	1.921 (11)	N(1)-Ir-C	99.1 (4)	100.3 (4)
C-O	1.156 (14)	1.125 (10)	P(1)-Ir-N(1)	96.4 (2)	92.2 (2)
Ir-P(1)	2.319 (3)	2.336 (2)	P(2)-Ir-N(1)	97.8 (2)	92.4 (2)
Ir-P(2)	2.337 (3)	2.325 (2)	P(1)-Ir-C	94.1 (4)	99.6 (3)
Ir-N(1)	2.168 (8)	2.163 (7)	P(2)-Ir-C	98.9 (4)	98.5 (3)
N(1)-N(2)	1.368 (11)	1.375 (9)	P(1)-Ir-P(2)	158.9 (1)	160.16 (8)
N(2)-C(3)	1.328 (14)	1.371 (11)	Ir-C-O	175.4 (11)	174.6 (10)
C(3)-C(4)	1.376 (17)	1.386 (13)	Ir-N(1)-N(2)	121.4 (6)	120.1 (5)
C(4)-C(5)	1.359 (15)	1.414 (12)	Ir-N(1)-C(5)	130.3 (7)	133.9 (6)
C(5)-N(1)	1.387 (13)	1.350 (10)	N(1)-N(2)-C(3)	107.7 (9)	113.0 (7)
C(3)-C(31)	1.535 (16)	1.484 (14)	N(2)-C(3)-C(4)	109.7 (10)	103.7 (9)
C(5)-C(51)	1.497 (15)	1.504 (13)	C(3)-C(4)-C(5)	107.4 (10)	109.2 (9)
P(1)-C(1i1) ^b	1.816	1.824	C(4)-C(5)-N(1)	107.1 (10)	108.1 (8)
P(2)-C(2i1) ^b	1.820	1.817	C(5)-N(1)-N(2)	108.1 (8)	106.0 (7)
Au-N(2)	2.001 (9)		N(2)-C(3)-C(31)	121.2 (12)	121.8 (9)
Au-Cl(1)	2.262 (3)		C(4)-C(3)-C(31)	129.2 (12)	134.5 (9)
B-F(1)		1.368 (14)	N(1)-C(5)-C(51)	122.6 (10)	122.6 (8)
B-F(2)		1.358 (14)	C(4)-C(5)-C(51)	130.3 (11)	129.3 (9)
B-F(3)		1.309 (14)	N(1)-N(2)-Au	125.2 (6)	
B-F(4)		1.340 (14)	N(2)-Au-Cl(1)	176.7 (2)	
B-F ^b		1.344	Au-N(2)-C(3)	126.4 (8)	

^aStandard deviations on the least significant digit or digits are given in parentheses. ^bAveraged values.

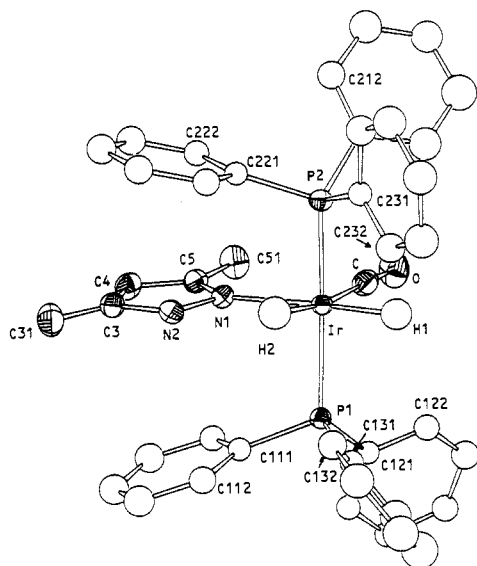


Figure 2. ORTEP view of the IrL₂(CO)(pzH-N)(H)₂⁺ cation. Thermal ellipsoids are drawn at 30% probability.

The proton and phosphorus NMR spectra (in deuteriochloroform) of **12a** and **12b** show that for both products two species are present in ca. 2:1 ratio; variable temperature (from -50 to +50 °C) spectra reveal that their ratio is slightly temperature dependent. The existence of the two species can be rationalized if conformers are considered, which in this case are stabilized by hydrogen bonding between the N-H group and the fluoroborate anion.

In all the cases where two isomers could be detected in solution the hydrido region of the proton NMR spectrum afforded quantitative evaluation. In addition this spectrum allows each isomer to be assigned, by analogy with **8A** and **8B**. The hydrido signal belonging to the trans H-Ir-N-N-Z (Z = H or AuCl) moiety is always found at higher field than in the parent compound, **2** or **10** (see Table II), for both the isomers of the same compound; the shift $\Delta\delta$ ($|\delta_{\text{parent}} - \delta_{\text{isomer}}|$) is lower in the case of isomer A than in the case of isomer B. For this last species the low-field signal is not markedly displaced from the value recorded for the parent molecule, **2** or **10** (see Table II), while the $\Delta\delta$ of the other isomer (A) is the same or larger than expected when another ligand having a different trans influence is present.

These relevant $\Delta\delta$ values may be rationalized by a long-range shielding effect of the -N-N-Z ligand and/or an interaction of the Z moiety with the hydrido group: in the case of **8A** (i.e. the

Table IV. Crystal Data and Intensity Collection Parameters

	8A	12c
formula	C ₄₂ H ₃₉ AuClIr ₂ N ₂ OP ₂	C ₄₂ H ₄₀ BF ₄ Ir ₂ N ₂ OP ₂ · 2CH ₃ C ₆ H ₅
fw	1074.36	1114.04
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /c
a, Å	13.385 (2)	9.874 (2)
b, Å	16.229 (3)	23.951 (4)
c, Å	18.376 (3)	21.029 (6)
β , deg	101.60 (2)	101.25 (2)
V, Å ³	3910 (2)	4878 (4)
Z	4	4
d _{calcd} , g cm ⁻³	1.825	1.517
F(000)	2064	2248
μ (Mo K α), cm ⁻¹	73.12	28.46
transmissn factors	0.38-1.00	0.80-1.00
cryst dimens, mm	0.10 × 0.05 × 0.15	0.20 × 0.16 × 0.12
octants in the reciprocal space explored	$\pm h, +k, +l$	$\pm h, +k, +l$
scan mode	ω	ω
θ range, deg	3-25	3-25
ω -scan width, deg	1.3 + 0.35 tan θ	1.0 + 0.35 tan θ
prescan speed, deg min ⁻¹	5	5
prescan acceptance	0.66	0.66
$\sigma(I)/I$		
requested $\sigma(I)/I$	0.03	0.03
maximum scan time, s	35	40
no. of measd reflns	7440	8525
no. of unique obsd reflns ($I \geq 3\sigma(I)$)	3954	4118
R, ^a R _w ^b	0.044, 0.050	0.038, 0.044
GOF ^c	1.489	1.248

^aR = $[\sum(F_o - k|F_c|)/\sum F_o]$. ^bR_w = $[\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}$; w = $1/\sigma^2(F_o)$. ^cGOF = $[\sum w(F_o - k|F_c|)^2/(N_{\text{observns}} - N_{\text{params}})]^{1/2}$. Minimized function in least squares: $\sum w(F_o - k|F_c|)^2$.

species having the biggest $\Delta\delta$) these data are in agreement with an estimated Au...H separation in the solid state of 2.28 Å, a value lower than the sum of van der Waals radii, 2.90 Å.¹⁰

Structures in the Solid State for Complexes 8A and 12c. The atomic positional parameters for **8A** and **12c** are listed in Tables V and VI, respectively. The atomic labeling scheme and the molecular structure for compound **8A** and for the [IrL₂(CO)(pzH-N)(H)₂]⁺ cation are reported in Figures 1 and 2, respectively. Crystals of **8A** consist of a packing of discrete molecules with no specific intermolecular interactions. Compound **12c** crystallizes with toluene molecules trapped in the crystal lattice with a molar

(10) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

Table V. Fractional Coordinates for Non-Hydrogen Atoms in 8A

atom	x	y	z
Au	0.29035 (4)	0.24222 (3)	0.80380 (3)
Ir	0.19191 (4)	0.31480 (3)	0.96547 (3)
Cl	0.2047 (3)	0.2491 (3)	0.6846 (2)
P(1)	0.1224 (2)	0.1869 (2)	0.9820 (2)
P(2)	0.2084 (2)	0.4447 (2)	0.9144 (2)
O	0.2074 (8)	0.3622 (6)	1.1278 (5)
N(1)	0.3460 (7)	0.2716 (5)	0.9685 (5)
N(2)	0.3736 (7)	0.2378 (6)	0.9072 (6)
C	0.205 (1)	0.3459 (8)	1.0663 (8)
C(3)	0.470 (1)	0.2130 (8)	0.9269 (8)
C(4)	0.506 (1)	0.2299 (8)	1.0009 (8)
C(5)	0.4288 (9)	0.2660 (7)	1.0274 (7)
C(31)	0.525 (1)	0.172 (1)	0.8708 (8)
C(51)	0.424 (1)	0.294 (1)	1.1044 (8)
C(111)	0.1992 (9)	0.0977 (7)	0.9720 (7)
C(112)	0.297 (1)	0.0911 (8)	1.0112 (8)
C(113)	0.359 (1)	0.0251 (9)	1.0012 (9)
C(114)	0.320 (1)	-0.0349 (9)	0.9514 (9)
C(115)	0.224 (1)	-0.0331 (9)	0.9104 (9)
C(116)	0.160 (1)	0.0343 (8)	0.9207 (8)
C(121)	0.089 (1)	0.1779 (3)	1.0721 (7)
C(122)	0.013 (1)	0.2290 (9)	1.0873 (9)
C(123)	-0.020 (1)	0.2247 (9)	1.1558 (9)
C(124)	0.027 (2)	0.171 (1)	1.207 (1)
C(125)	0.106 (2)	0.122 (1)	1.195 (1)
C(126)	0.136 (1)	0.122 (1)	1.1254 (9)
C(131)	-0.0009 (9)	0.1680 (7)	0.9197 (7)
C(132)	-0.018 (1)	0.1952 (8)	0.8482 (8)
C(133)	-0.111 (1)	0.1793 (9)	0.7985 (8)
C(134)	-0.180 (1)	0.131 (1)	0.8241 (9)
C(135)	-0.163 (1)	0.1009 (9)	0.8935 (8)
C(136)	-0.072 (1)	0.1174 (9)	0.9423 (8)
C(211)	0.2047 (9)	0.5317 (7)	0.9765 (7)
C(212)	0.145 (1)	0.5294 (8)	1.0295 (8)
C(213)	0.141 (1)	0.5954 (9)	1.0758 (8)
C(214)	0.195 (1)	0.6650 (9)	1.0702 (9)
C(215)	0.250 (1)	0.6692 (9)	1.0142 (9)
C(216)	0.257 (1)	0.6043 (8)	0.9684 (8)
C(221)	0.3206 (8)	0.4644 (7)	0.8754 (6)
C(222)	0.314 (1)	0.508 (1)	0.8092 (9)
C(223)	0.404 (1)	0.529 (1)	0.786 (1)
C(224)	0.494 (1)	0.505 (1)	0.8232 (9)
C(225)	0.503 (1)	0.4615 (9)	0.8872 (9)
C(226)	0.414 (1)	0.4431 (8)	0.9152 (8)
C(231)	0.1013 (9)	0.4639 (7)	0.8379 (7)
C(232)	0.037 (1)	0.5306 (8)	0.8371 (8)
C(233)	-0.047 (1)	0.5417 (9)	0.7787 (9)
C(234)	-0.067 (1)	0.4874 (9)	0.7226 (8)
C(235)	-0.002 (1)	0.4230 (9)	0.7221 (9)
C(236)	0.082 (1)	0.4100 (9)	0.7788 (8)

ratio, $[\text{IrL}_2(\text{CO})(\text{pzH-N})(\text{H})_2][\text{BF}_4]/\text{CH}_3\text{C}_6\text{H}_5$, of 1/2.

The octahedral coordination typical of Ir(III) complexes is appreciably distorted because of the very different bulkiness of the ligands, among which the hydrides have an estimated cone angle of only 75° .¹¹ Consequently the other ligands are shifted from the ideal positions so as to occupy the portion of space not filled by the hydrides. In detail, the two trans triphenylphosphine groups are arranged so that the P-Ir-P angle is much smaller than 180° ; both the N-Ir-P and the C-Ir-P angles are bigger than 90° , and even the Ir-C-O moiety is slightly bent (see Table III). It is worth noting that the ideal values were nearly reached in a strictly related iridium(I) compound, namely *trans*-bis(triphenylphosphine)carbonyl(3,5-bis(trifluoromethyl)pyrazolato-N)iridium(I) (**14**),³ where there is no similar crowding of the ligands, i.e. $176.1 (1)^\circ$ for P-Ir-P, 89.1° plus $92.5 (1)^\circ$ or $89.0 (2)^\circ$ plus $89.5 (2)^\circ$ for the N-Ir-P or C-Ir-P angles, and $177.2 (6)^\circ$ for the Ir-C-O moiety. By comparison with the last species a longer Ir-C or Ir-N distance is expected and found (1.893 (14) and 1.921 (11) Å or 2.168 (8) and 2.163 (7) Å, respectively), for both **8A** and **12c**, since here the iridium atom reaches a higher coordination number; for **14** the Ir-C or Ir-N lengths are 1.811

Table VI. Fractional Coordinates for Non-Hydrogen Atoms in 12c

atom	x	y	z
Ir	0.08974 (4)	0.10152 (2)	0.36177 (2)
P(1)	0.0273 (2)	0.0612 (1)	0.2591 (1)
P(2)	0.0701 (3)	0.1465 (1)	0.4575 (1)
F(1)	-0.4251 (8)	0.1995 (4)	0.2148 (4)
F(2)	-0.3906 (7)	0.2756 (3)	0.2737 (4)
F(3)	-0.297 (1)	0.2693 (4)	0.1890 (4)
F(4)	-0.2174 (8)	0.2175 (4)	0.2720 (5)
O	0.3538 (8)	0.0371 (3)	0.4137 (4)
N(1)	0.1675 (7)	0.1759 (3)	0.3227 (3)
N(2)	0.0771 (7)	0.2156 (3)	0.2922 (3)
C	0.260 (1)	0.0624 (4)	0.3927 (5)
C(3)	0.142 (1)	0.2595 (4)	0.2691 (5)
C(4)	0.281 (1)	0.2456 (4)	0.2854 (5)
C(5)	0.2950 (9)	0.1940 (4)	0.3187 (4)
C(31)	0.064 (1)	0.3067 (5)	0.2339 (5)
C(51)	0.424 (1)	0.1620 (5)	0.3468 (6)
C(111)	0.0393 (9)	0.1104 (4)	0.1945 (4)
C(112)	-0.078 (1)	0.1358 (5)	0.1586 (5)
C(113)	-0.066 (1)	0.1747 (5)	0.1113 (5)
C(114)	0.064 (1)	0.1893 (5)	0.1010 (5)
C(115)	0.181 (1)	0.1657 (5)	0.1373 (5)
C(116)	0.167 (1)	0.1256 (4)	0.1842 (5)
C(121)	0.1240 (9)	0.0007 (4)	0.2411 (4)
C(122)	0.167 (1)	-0.0388 (4)	0.2872 (5)
C(123)	0.231 (1)	-0.0877 (5)	0.2736 (5)
C(124)	0.253 (1)	-0.0973 (5)	0.2119 (5)
C(125)	0.209 (1)	-0.0582 (4)	0.1640 (5)
C(126)	0.146 (1)	-0.0094 (4)	0.1780 (4)
C(131)	-0.1511 (9)	0.0353 (4)	0.2430 (4)
C(132)	-0.255 (1)	0.0666 (5)	0.2580 (5)
C(133)	-0.392 (1)	0.0465 (6)	0.2453 (6)
C(134)	-0.420 (1)	-0.0045 (6)	0.2173 (6)
C(135)	-0.320 (1)	-0.0354 (6)	0.2020 (6)
C(136)	-0.181 (1)	-0.0173 (5)	0.2137 (5)
C(211)	0.200 (1)	0.1326 (4)	0.5299 (4)
C(212)	0.273 (1)	0.1732 (5)	0.5690 (5)
C(213)	0.367 (1)	0.1592 (6)	0.6259 (6)
C(214)	0.384 (1)	0.1063 (5)	0.6432 (5)
C(215)	0.314 (1)	0.0637 (6)	0.6071 (6)
C(216)	0.218 (1)	0.0772 (5)	0.5484 (6)
C(221)	0.0640 (9)	0.2220 (4)	0.4464 (4)
C(222)	0.186 (1)	0.2520 (4)	0.4433 (4)
C(223)	0.178 (1)	0.3070 (5)	0.4274 (5)
C(224)	0.053 (1)	0.3333 (5)	0.4126 (5)
C(225)	-0.066 (1)	0.3045 (5)	0.4153 (5)
C(226)	-0.061 (1)	0.2495 (4)	0.4316 (5)
C(231)	-0.0872 (9)	0.1317 (4)	0.4860 (4)
C(232)	-0.188 (1)	0.0959 (5)	0.4546 (5)
C(233)	-0.310 (1)	0.0865 (5)	0.4784 (6)
C(234)	-0.328 (1)	0.1136 (5)	0.5329 (6)
C(235)	-0.232 (1)	0.1493 (5)	0.5650 (5)
C(236)	-0.110 (1)	0.1578 (5)	0.5427 (5)
B	-0.331 (1)	0.2405 (6)	0.2365 (6)

(7) or 2.079 (5) Å, respectively.

The two Ir-P bonds in both compounds are only slightly different as a result of packing effects: their mean values (2.328 and 2.330 Å in **8A** and **12c**, respectively) are in the range 2.248–2.452 Å listed for iridium-phosphorus distances in the compilation of ref 12.

The conformation of the two mutually trans triphenylphosphine ligands is almost eclipsed, the phenyl rings being arranged so to minimize any interactions with the pyrazolato ligand and its appendage (either a chlorogold or a HFBF_3 moiety) and with the other equatorial ligands.

The intramolecular Au-Ir contact found in **8A** (3.68 Å), which is longer than that observed for the hydrido-bridged Au-Ir bond in $[\text{AuPPH}_3(\mu\text{-H})\text{Ir}(\text{PPh}_3)_3(\text{H})_2]^+$ (2.765 (1) Å^{9a}) clearly indicates the absence of a metal-metal bond. The Au-H(2) calculated contact, 2.28 Å, is longer than the gold-hydrogen bond (1.72 (11) Å) in $\text{Au}(\text{PPh}_3)(\mu\text{-H})\text{Cr}(\text{CO})_5$,^{9b} although shorter than the sum of the van der Waals radii for gold and hydrogen ($r_{\text{Au}} = 1.70$ Å;

(11) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(12) Robertson, G. B.; Tucker, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 317.

$r_H = 1.20 \text{ \AA}$);¹⁰ these features are indicative of a weak interaction in agreement with the proton NMR spectra.

In spite of the various substituents, in both cases (**8A** and **12c**) the heterocyclic ring, strictly planar, lies approximately in the plane Ir, C, N(1); in contrast in the related compound **14** the pyrazolato ring is approximately normal to the metal coordination plane. Inside the ring the pattern of the bond distances is unexceptional,³ thus indicating that its aromatic character is maintained also upon coordination to a second metal. This dative Au–N bond is not different from the bond between an amine nitrogen and a two-coordinate gold(I), thus suggesting that the substitution of the 1-hydrogen in a pyrazole by a (ligand)_nIr moiety does not change the main behavior of the 2-nitrogen. Indeed, while N–Au bond lengths as short as 1.93 (2) \AA ¹³ or as long as 2.077 (9) \AA ¹⁴ are documented for tris(μ -3,5-bis(trifluoromethyl)pyrazolato-*N,N'*)trigold(I) or for 1-AuL-6-methylpyridone-2 (L = triphenylphosphine), the value of 2.001 (9) for Au–N(2) is comparable with those found for various amine derivatives: 2.00 (2) \AA for [AuL(pzH-N)]⁺ (L = triphenylphosphine),¹⁵ 2.018–2.045 \AA for tris(*p*-tolylimino)(ethoxy)methyl]trigold(I),¹⁶ 2.038 (4) \AA for AuL(adeninate-*N9*) (L = triphenylphosphine),¹⁷ or 2.07 (2) \AA for (piperidine)chlorogold(I).¹⁸

Similarly, while the Au–Cl bond may range between 2.256 (8) \AA in (piperidine)chlorogold(I)¹⁸ and 2.305 (6) \AA in (AuCl)₂Ph₂P(CH₂)₃PPh₂(AuCl),¹⁹ the length here reported, 2.262 (3) \AA , shows that the trans influence of the 1-irradiated pyrazole is as low as that of an amine. The N–Au–Cl angle, 176.7 (2)°, is only slightly lower than 180°, as found often, e.g. 176.0 (5)°,¹⁸ probably because of packing effects.

In compound **12c** the pyrazolato ring interacts with the tetrafluoroborate anion *via* a hydrogen bond, the separation N–(2)–F(4) being 2.86 (1) \AA , a feature already found in all the investigated metal adducts of neutral pyrazoles, e.g. in [Au(PPh₃)(pzH-N)][BF₄]¹⁵ or in (1,2-bis(diphenylphosphino)ethane)bis(3,5-dimethylpyrazole)platinum(II)tetrafluoroborate.²⁰

Experimental Section

Aqueous HBF₄ (50%) and HBF₄·Et₂O were purchased from Hoechst and Janssen, respectively. The iridium complexes *trans*-Ir(Ph₃P)₂(CO)(pz-*N*) (**1**), Ir(Ph₃P)₂(CO)(H)₂(pz-*N*) (**2**), Ir(Ph₃P)₂(CO)(H)₂(pz-*N'*) (**10**), and [Ir(Ph₃P)₂(CO)(pzH-*N*)] [BF₄] were prepared as previously described;³ the gold derivatives AuCl₃, Au(tht)Cl₃, and Au(tht)X (tht = (CH₂)₄S; X = Cl, Br) were obtained according to the literature.²¹ The analytical samples were pumped to constant weight (ca. 0.1 Torr, 25 °C). Evaporation was always carried out under reduced pressure (water aspirator). Elemental analyses and molecular weight determinations were performed by the Microanalytical Laboratory of the University of Milano and by Mikroanalytisches Labor Pascher (Bonn, FRG). Infrared spectra were recorded on Beckmann 4210 and Nicolet MX-1 instruments; ¹H (80.13 and 200 MHz) and ³¹P{¹H} (32.4 and 80.98 MHz) NMR spectra were recorded on Bruker WP80 and Varian XL200 instruments. The reactions were carried out at room temperature. In most cases ca. 10% higher yields were observed at lower temperatures (–10 to +5 °C).

(A) **Reactions of Iridium(I) Pyrazolates.** (1) **Iridium(I)–Gold(I) Derivatives (3 and 4).** *trans*-Ir(Ph₃P)₂(CO)(μ -pz-*N,N'*)AuCl (**3**). A filtered solution of Au(tht)Cl (185 mg, 0.58 mmol) in dichloromethane (30 mL) was added under stirring to a solution of compound **1** (440 mg, 0.52 mmol) in the same solvent (40 mL). After 0.5 h the yellow solution was concentrated to ca. 20 mL; a yellow-orange product (460 mg) was precipitated by slow addition of 50 mL of diethyl ether. The crude

product was crystallized from dichloromethane (20 mL) and diethyl ether (40 mL) to give the analytical sample (382 mg; yield 66%).

trans-Ir(Ph₃P)₂(CO)(μ -pz-*N,N'*)AuBr (**4**). A suspension of Au(tht)Br (183 mg, 0.50 mmol) in benzene was added to a stirred solution of compound **1** (403 mg, 0.48 mmol) in the same solvent. After 10 min the dark orange solution was filtered and concentrated to ca. 15 mL. A red-orange product was precipitated (ca. 300 mg) by addition of *n*-pentane. The crude product was dissolved in benzene (50 mL); from the solution, after filtration and concentration (15 mL), the analytical sample was obtained by addition of *n*-pentane (250 mg; yield 47%).

(2) **Reaction of Ir(Ph₃P)₂(CO)(pz-*N*) with Au(tht)Cl₃.** (i) A filtered solution of Au(tht)Cl₃ (181 mg, 0.46 mmol) in dichloromethane (40 mL) was added to a stirred solution of compound **1** (327 mg, 0.39 mmol) in the same solvent. After 1 h the darkened solution was filtered and concentrated to ca. 20 mL. A small amount of a white precipitate was collected and washed with 20 mL of diethyl ether (compound **6**, 20 mg). By addition of diethyl ether to the clear mother solution (yellow), a second crop was precipitated (65 mg) and identified as a mixture of compounds **6** and **7**.

Compound **5** was obtained as a yellow powder from the dichloromethane/diethyl ether solution by addition of a large excess of *n*-pentane (ca. 150 mg; yield 34%).

(ii) To a suspension of compound **1** (302 mg; 0.36 mmol) in anhydrous diethyl ether a suspension of Au(tht)Cl₃ (147 mg, 0.37 mmol) in 70 mL of the same solvent was added under stirring at 0–2 °C. After 0.5 h an insoluble fraction was removed by filtration and the yellow solution concentrated to small volume (ca. 10 mL). The yellow crude precipitate was collected and washed with diethyl ether (5 mL), yielding **5** (70 mg; yield 17%).

Attempts to crystallize the crude product with different solvents failed, owing to decomposition of **5** into **6** and **7**.

(B) **Reactions of Iridium(III) Pyrazolates.** To prevent the formation of iridium(I) derivatives, dihydrogen was bubbled into the solutions of the hydrido-iridium(III) complexes before use.

(1) **Iridium(III)–Gold(I) Derivative.** Ir(Ph₃P)₂(CO)(H)₂(μ -pz-*N,N'*)AuCl (**8**). A solution of Au(tht)Cl (128 mg, 0.40 mmol) in dichloromethane (10 mL) was added to a stirred solution of compound **2** (320 mg, 0.38 mmol) in the same solvent (20 mL). After 10 min, the colorless solution was concentrated to 15 mL and filtered. After addition of diethyl ether (25 mL) the solution was concentrated to give the crude product, which was crystallized from dichloromethane/diethyl ether (140 mg; yield 34%).

Compound **8B** was isolated by carrying out the reaction at temperatures lower than 0 °C. At higher temperatures compound **8A** or mixtures of **8A** and **8B** in different ratios were obtained.

(2) **Pyrazole Derivatives of Iridium(III) (9, 11, 12, and 13).** (a) **Reactions with AuCl₃ and Au(tht)Cl₃.** [Ir(Ph₃P)₂(CO)(pzH-*N*)(H)₂][AuCl₄] (**9**). A filtered solution of Au(tht)Cl₃ (74 mg, 0.19 mmol) in dichloromethane (20 mL) was added to a stirred solution of compound **2** (151 mg, 0.18 mmol) in the same solvent. After 15 min the yellow solution was concentrated (ca. 20 mL) and filtered; after addition of a large amount of diethyl ether, a yellow solid was obtained by scratching. This was crystallized from dichloromethane (5 mL) and diethyl ether (10 mL) (40 mg; yield 19.5%).

By reaction of **2** with AuCl₃ the same compound, **9**, was obtained (yield 46%).

[Ir(Ph₃P)₂(CO)(pzH-*N*)(H)₂][AuCl₄] (**11**). Compound **11** was obtained in the same manner as **9** by reaction of Ir(Ph₃P)₂(CO)(H)₂(pz-*N*) (**10**) with AuCl₃ in chloroform solution (yield 30%).

(b) **Reactions with HBF₄.** [Ir(Ph₃P)₂(CO)(pzH-*N*)(H)₂][BF₄]·Et₂O (**12a**) and [Ir(Ph₃P)₂(CO)(pzH-*N*)(H)₂][BF₄]·C₆H₆ (**12b**). (i) A 0.029 mL (0.18-mmol) aliquot of HBF₄·Et₂O was added, under a nitrogen atmosphere, to a stirred solution of compound **2** (155 mg, 0.18 mmol) in benzene (30 mL). After 1 h the suspension was evaporated to dryness, and the resulting white solid was washed with 60 mL of benzene. The residue was dissolved in 5 mL of dichloromethane and the solution was filtered; by concentration and addition of diethyl ether the analytical sample was obtained as **12a** (100 mg; yield 54%). By concentration of the benzene extract to a small volume (ca. 10 mL), a further crop of complex **12** was obtained as **12b**.

(ii) Into a solution of [Ir(Ph₃P)₂(CO)(pzH-*N*)] [BF₄] (130 mg, 0.14 mmol) in dichloromethane, dihydrogen was bubbled for 20 h. The solution was evaporated to dryness and the white residue (110 mg) washed with 30 mL of benzene. The white crude product was dissolved in dichloromethane; after addition of benzene, compound **12b** was precipitated with diethyl ether (78 mg; yield 55%).

[Ir(Ph₃P)₂(CO)(pzH-*N*)(H)₂][BF₄] (**13**). Excess aqueous tetrafluoroboric acid (ca. 6 drops) was added to a stirred suspension of Ir(Ph₃P)₂(CO)(H)₂(pz-*N*) (**10**) in methanol (30 mL). After 1 h the white complex **13** was collected and washed with 20 mL of methanol.

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X-ray Structural Determination. Intensity data were collected at room temperature on a Nonius CAD-4 automated diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$), and corrected for absorption by the empirical method described in ref 22.

Crystal data for compounds **8A** and **12c** ($12 \cdot 2\text{CH}_3\text{C}_6\text{H}_5$) are summarized in Table IV, together with some experimental details. The unit cell parameters for both crystals were determined by least-squares refinement of the setting angles of 25 reflections. Both structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least squares as described in Table IV.

Anisotropic thermal factors were refined for all the atoms with the exception of the phenyl carbon atoms and the solvent molecules. Scattering factors and anomalous dispersion corrections were taken from ref 23. The hydrogen atoms of the phenyl rings and of the pyrazolato ligand (wherever their positioning was not ambiguous) were placed in calculated positions (C-H distance 0.95 \AA), and their contribution to the structure factors were computed. A set of three difference Fourier syntheses was finally computed at increasing values of limiting $(\sin \theta)/\lambda$, to test whether residual peaks attributable to the hydridic hydrogen atoms were present

close to the metal atom.²⁴ For compound **8A** only peaks due to a residual contribution of the metal atom were detected, so that the hydrides were introduced in approximate calculated positions in the plane N(1), Ir, C, trans to N(1) and C only for sake of clarity in the drawing. For **12c** the test reveals two peaks approximately close to the expected positions for the two hydrides at 1.66 and 1.65 \AA from the iridium atom. All computations were carried out on a PDP11/34 computer using the SDP-Plus structure determination package and the physical constants listed therein.²⁵

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Supplementary Material Available: Tables of general temperature factors, calculated positions for hydrogen atoms in **8A** and **12c**, and atomic positions for solvent molecules in **12c** (5 pages); listings of structure factors for **8A** and **12c** (55 pages). Ordering information is given on any current masthead page.

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Properties and X-ray Structure of $\text{PPN}^+[\text{cis-HFe}(\text{CO})_3\text{P}(\text{OPh})_3]^-$: An Unexpected Structural Isomer

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The preparation of $[\text{PPN}][\text{HFe}(\text{CO})_3\text{P}(\text{OPh})_3]$ (**1**) has been carried out by using an alcoholic hydroxide reaction with $\text{Fe}(\text{CO})_4\text{P}(\text{OPh})_3$; the same synthesis was reported earlier for *trans*- $\text{HFe}(\text{CO})_3\text{PR}_3^-$ salts. After spectral and chemical differences were observed between the anion of **1** and all other $\text{HFe}(\text{CO})_3\text{PR}_3^-$ anions, which have been shown to exist in a *trans* configuration of H and PR_3 (TBP geometry), an X-ray structural determination was performed. **1** crystallizes in the triclinic system, space group $P\bar{1}$, with cell parameters $a = 10.491$ (3) \AA , $b = 13.963$ (4) \AA , $c = 18.687$ (6) \AA , $\alpha = 108.19$ (2) $^\circ$, $\beta = 105.47$ (2) $^\circ$, $\gamma = 93.16$ (2) $^\circ$, $V = 2478$ (1) \AA^3 , and $Z = 2$. The hydride ligand was located in the axial position of a distorted trigonal bipyramid, but curiously the $\text{P}(\text{OPh})_3$ ligand is in the equatorial plane, *cis* to the hydride. Unique properties of **1** include its air stability and its rigidity as the *cis* isomer. The spectral properties of **1** including ion pairing and isotopic H/D exchange effects were examined. In contrast to other anion trigonal-bipyramidal complexes that show equatorial $\text{CO}\cdots\text{Na}^+$ interaction, an axial $\text{CO}\cdots\text{Na}^+$ site interaction was observed for **1**. Hydrogen/deuterium substitution in this anion revealed a large $\nu(\text{MH})$ to $\nu(\text{CO})$ coupling to the *trans* carbonyl group.

Introduction

Recently we synthesized a series of phosphine and phosphite derivatives of the well-known $\text{HFe}(\text{CO})_4^-$ anion.¹ An X-ray crystal structure determination carried out on the $\text{Et}_4\text{N}^+\text{HFe}(\text{CO})_3\text{PPh}_3^-$ salt found the anion to be of distorted trigonal-bipyramidal geometry, with the PPh_3 ligand in an axial position and *trans* to the likely position for the unlocated hydride ligand. The distortion results from a bending of the CO groups away from the PPh_3 ligand, $\angle(\text{P}-\text{Fe}-\text{CO}) = 99.5^\circ$, and into the void where the hydride ligand presumably lies. Since this angle is identical with the $\angle(\text{CO})_{\text{ax}}-\text{Fe}-(\text{CO})_{\text{eq}}$ of $\text{HFe}(\text{CO})_4^-$,² the distortion is not a result of the large steric bulk of the PPh_3 substituent.

An alternate view of the structure of $\text{HFe}(\text{CO})_3\text{PPh}_3^-$ is that of a tetrahedral $\text{Fe}(\text{CO})_3\text{PPh}_3^{2-}$ anion that has been distorted by protonation in the all-carbonyl face. As a distorted TBP the relative positioning of the ligands is as expected according to the thesis of Rossi and Hoffmann³ that the equatorial plane is the site of preference of weaker σ -donating and better π -accepting ligands in d^8 , TBP complexes.

The $\nu(\text{CO})$ infrared spectra observed for *trans*- $\text{HFe}(\text{CO})_3\text{PPh}_3^-$ was consistent with C_{3v} symmetry of the CO groups (i.e., one weak and one very strong band). Six other derivatives (PET_3 , PMe_3 , PPh_2Me , PPhMe_2 , $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$) had analogous $\nu(\text{CO})$ band patterns.¹ The proton NMR spectra of the series showed an interesting and dramatic dependence of J_{PH} on solvent polarity and temperature, varying from a maximum of $|J_{\text{PH}}| = 15 \text{ Hz}$ to a minimum of 0.0 Hz. Surprisingly, the eighth member of this series, $\text{HFe}(\text{CO})_3\text{P}(\text{OPh})_3^-$, showed anomalous spectral and chemical behavior. Whereas the other hydrides were air-sensitive as expected for anionic hydrides, the $\text{P}(\text{OPh})_3$ derivative was stable to air, even in solution for extended periods of time. The $\nu(\text{CO})$ IR spectrum was comprised of three bands, of a medium, strong, and medium (sh) pattern. Furthermore, the Fe-H stretch at 1895 cm^{-1} was surprisingly intense. The ^1H NMR hydride resonance was a doublet of $J_{\text{PH}} = 55 \text{ Hz}$, which was invariant with temperature. This derivative has also been subjected to a molecular

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