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(Pentamethylcyclopentadienyl)bis(pyrazolato)(pyrazole)iridium(III) as a Metal-Complex Ligand. Synthesis, Characterization, and Reactivity of Heterodinuclear IrM [M = Cu(I), Ag(I), Au(I), Rh(I)] and Heterotrinuclear $IrAg_2$ and IrRhAg Derivatives

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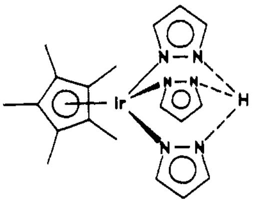
Heterodinuclear complexes of formula $[(\eta^5\text{-}C_5Me_5)Ir(pz)_3M(PPh_3)]$ [M = Cu (**2**), Ag (**3**), Au (**4**)] have been prepared by treating the mononuclear iridium pentamethylcyclopentadienyl pyrazolate complex $[(\eta^5\text{-}C_5Me_5)Ir(pz)_2(Hpz)]$ (**1**) with the corresponding halide triphenylphosphine complex $[MCl(PPh_3)]_x$ (x = 4, M = Cu, Ag: x = 1, M = Au) and KOH. Complexes **2**–**4** are fluxional: at room temperature the $MPPh_3$ fragment exchanges fast among the three free nitrogen atoms of the pyrazolate ligands. The molecular structure of complex **3** has been determined. Crystals are monoclinic, space group $P2_1/n$, with cell parameters a = 9.6171 (4) Å, b = 14.2115 (7) Å, c = 26.229 (2) Å, β = 91.90 (1)°, and Z = 4. The structure was solved and refined to R and R_w values of 0.0269 and 0.0289, respectively, with the use of 5498 reflections. In the solid state, this molecule exhibits two bridging pyrazolate groups between both metals; the iridium atom coordinates an additional terminal pyrazolate ligand and an η^5-pentamethylcyclopentadiene ring; the silver metal completes its trigonal-planar coordination by being bonded to a PPh_3 group. No direct intermetallic interaction is observed, the Ir···Ag distance being 3.8601 (2) Å. Complex **3** reacts with $AgBF_4$ and PPh_3, rendering $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)_3\{Ag(PPh_3)\}_2]BF_4$ (**5**), in which both $AgPPh_3$ exchange rapidly at room temperature. Complex **1** reacts with [Rh(acac)(COD)] to yield the complex $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2Rh(COD)]$ (**6**) in 80% yield. Carbonylation of **6** gives $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2Rh(CO)_2]$ (**7**), which in turn reacts with mono or diphosphines rendering $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2Rh(CO)(PR_3)]$ [$PR_3 = PPh_3$ (**8**), $P(OMe)_3$ (**9**)] or $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2Rh(PP)]$ [PP = dppe (**10**), R-prophos (**11a**,**b**)]. Compounds **6**–**8** can be protonated by HBF_4 at one pyrazolate group, yielding the corresponding cationic complexes $[(\eta^5\text{-}C_5Me_5)(Hpz)Ir(\mu\text{-}pz)_2RhL_2]$ (**12**–**14**). The heterotrinuclear IrRhAg derivatives $[(\eta^5\text{-}C_5Me_5)Ir\{(\mu\text{-}pz)Ag(PPh_3)\}\{(\mu\text{-}pz)_2RhL_2\}]BF_4$ [L_2 = COD (**15**); CO, PPh_3 (**16**)] have been prepared by adding equimolar amounts of $AgBF_4$ and PPh_3 to complexes **6** and **8**.

Introduction

In 1986 we described the preparation and characterization of the iridium pentamethylcyclopentadienyl pyrazolate complex $[(\eta^5\text{-}C_5Me_5)Ir(pz)_2(Hpz)]$ (Hpz = pyrazole) (**1**), in which, according to spectroscopic measurements, a dynamic hydrogen bonding between the three pyrazolates was proposed.[1]



1

Complex **1** may be compared with the protonated polypyrazolylborates $RB(pz)_2(Hpz)$ (R = H, pz) reported by Trofimenko some years ago.[2] Although the exact structure of these free acids has not been determined, very recently the molecular structure of the related hydrogen tetrakis(3,5-dimethyl-1-pyrazolyl)borate, $B(Me_2pz)_3(Me_2pzH)$, has been communicated.[3] As a solid and at −53 °C in CD_2Cl_2, the NH proton of $B(Me_2pz)_3(Me_2pzH)$ is located on one nitrogen atom, but at room temperature in CD_2Cl_2 the NMR spectrum shows that the NH proton is scrambling among four equivalent 3,5-dimethylpyrazolate groups.[3]

An extensive complex chemistry has been developed by using the $[RB(pz)_3]^-$ anions derived from these acids as ligands including most transition-metal ions.[4–6] These anions usually function as tridentate ligands or in a bidentate fashion and in solution often undergo rapid exchange of the coordinated and uncoordinated pz groups. In particular, in the tetrahedral Cu(I)[7–9] and Ag(I)[9,10] de-

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(1) Carmona, D.; Oro, L. A.; Lamata, M. P.; Elguero, J.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1114.

(2) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

(3) Bradley, D. C.; Hursthouse, M. B.; Newton, J.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1984**, 188.

(4) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

(5) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.

(6) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *734*, 115.

(7) Bruce, M. I.; Ostazewski, A. P. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433.

(8) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051.

(9) Abu Salah, O. M.; Bruce, M. I. *J. Organomet. Chem.* **1975**, *87*, C15.

(10) Abu Salah, O. M.; Ashby, G. S.; Bruce, M. I.; Pederzolli, E. A.; Walsh, J. D. *Aust. J. Chem.* **1979**, *32*, 1613.

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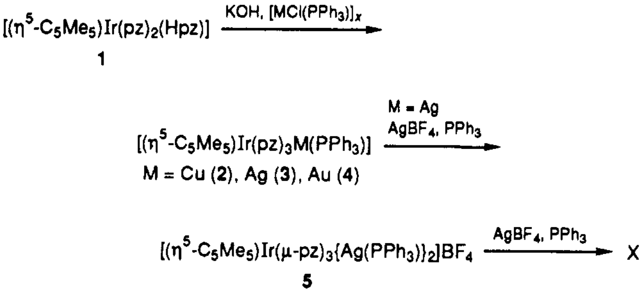
Table I. NMR Spectroscopic Data[a] for Complexes 2–5

	^1H					
		pyrazolates				
complex	C_5Me_5	$H_{3/5}$	$H_{5/3}$	H_4	PPh_3	^{31}P
2 (room temperature)	1.47 (s, 15 H)	6.77 (bs, 3 H)	*b*	6.05 (bs, 3 H)	7.45 (m, 15 H)	2.6 (bs)
2 (213 K)	1.42 (s, 15 H)	6.67 (bs, 1 H) 6.78 (bs, 2 H)	7.75 (bs, 1 H) 7.28 (bs, 2 H)	6.09 (bs, 1 H) 6.06 (bs, 2 H)	7.52 (m, 15 H)	1.8 (s)
3 (room temperature)	1.45 (s, 15 H)	6.72 (bs, 3 H)	*b*	6.08 (bs, 3 H)	7.49 (m, 15 H)	15.7 (d, *J*(AgP) = 575)[c]
4 (room temperature)	1.45 (s, 15 H)	6.90 (bs, 3 H)	*b*	6.05 (bs, 3 H)	7.46 (m, 15 H)	31.5 (s)
5 (room temperature)	1.31 (s, 15 H)	*b*	*b*	6.24 (bs, 3 H)	7.35 (m, 30 H)	17.5 (d, *J*(AgP) = 607)[c]
5 (213 K)	1.27 (s, 15 H)	*b*	8.04 (bs, 1 H)	6.42 (bs, 1 H)	7.16 (m, 30 H)	15.5 (d, *J*(^{107}AgP) = 573, *J*(^{109}AgP) = 662)
		6.77 (bs, 2 H)	*b*	6.19 (bs, 2 H)		19.8 (d, *J*(^{107}AgP) = 636, *J*(^{109}AgP) = 733)

[a] Measured in $CDCl_3$ (^1H) or in $CDCl_3/CHCl_3$ (1/1, v/v) (^{31}P) solutions. Chemical shifts in ppm from TMS (^1H) or from 85% H_3PO_4 in D_2O (^{31}P) as external standards. *J* in Hz. Abbrevations: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet. [b] Obscured by the PPh_3 protons. [c] No well-resolved doublet (see text).

Scheme I



rivatives [RB(pz)$_3$ML] [R = H, pz; L = CO (M = Cu) and various group 15 ligands] the ligands are tridentate and exhibit fluxionality in the NMR spectra. In the rhodium complexes [B(pz)$_4$Rh(diolefin)] [diolefin = 1,5-cyclooctadiene (COD), norbornadiene (NBD)] the ligands are bidentate and the metal has square-planar coordination in the solid state;[11] in solution the complexes are pentacoordinated, showing only one type of pz group, at room temperature.[12]

On the other hand, interesting and important reactions have been very recently reported for tris(3,5-dimethyl-1-pyrazolyl)borate complexes of rhodium. Thus, [HB(Me$_2$pz)$_3$Rh(CO)$_2$][13,14] photochemically activates aromatic and saturated hydrocarbons[15] and thermally activates benzene.[16] Protonation of [HB(Me$_2$pz)$_3$Rh(CO)$_2$] with $HBF_4 \cdot OEt_2$ takes place at a pyrazolate nitrogen, affording the cationic complex [HB(Me$_2$pz)$_2$(Me$_2$pzH)Rh(CO)$_2$]BF$_4$.[17] Irradiation of the closely related bis(isocyanide) complex [HB(Me$_2$pz)$_3$Rh(CNR)$_2$] (R = neopentyl) in benzene affords the benzene oxidative addition adduct [HB(Me$_2$pz)$_3$Rh(Ph)H(CNR)].[18]

Taking advantage of the formal similarity between the tris(pyrazolyl)borate anion and the deprotonated form of the iridium complex **1**, we have attempted the preparation of heterodinuclear complexes by using **1** as building block. This paper describes the synthesis and structural characterization of heterodinuclear IrM [M = Cu(I), Ag(I), Au(I), Rh(I)] complexes derived from **1** of general formulas [(η^5-C$_5$Me$_5$)Ir(pz)$_3$M(PPh$_3$)] [M = Cu (**2**), Ag (**3**), Au (**4**)] and [(η^5-C$_5$Me$_5$)(pz)Ir(μ-pz)$_2$RhL$_2$] [L$_2$ = COD (**6**); (CO)$_2$ (**7**); CO, PPh$_3$ (**8**); CO, P(OMe)$_3$ (**9**); 1,2-bis(diphenylphosphino)ethane (dppe) (**10**), *R*-1,2-bis(diphenylphosphino)propane (*R*-prophos) (**11a**,**b**)], as well as the reactivity of some of them toward the protic acid HBF$_4$. The preparation and characterization of the trinuclear cationic complexes [(η^5-C$_5$Me$_5$)Ir(μ-pz)$_3${Ag(PPh$_3$)}$_2$]BF$_4$ (**5**) and [(η^5-C$_5$Me$_5$)Ir{(μ-pz)Ag(PPh$_3$)}{(μ-pz)$_2$RhL$_2$}]BF$_4$ [L$_2$ = COD (**15**); CO, PPh$_3$ (**16**)] are also described. The molecular structure of the IrAg derivative [(η^5-C$_5$Me$_5$)Ir(pz)$_3$Ag(PPh$_3$)] (**3**) is also reported.

Results and Discussion

Heterometallic Complexes [(η^5-C$_5$Me$_5$)Ir(pz)$_3$M(PPh$_3$)] (M = Cu, Ag, Au) and [(η^5-C$_5$Me$_5$)Ir(μ-pz)$_3${Ag(PPh$_3$)}$_2$]BF$_4$. The mononuclear iridium complex [(η^5-C$_5$Me$_5$)Ir(pz)$_2$(Hpz)] (**1**)[1] readily reacts with the chloride compounds [MCl(PPh$_3$)]$_x$ (x = 4, M = Cu,[19] Ag;[20] x = 1, M = Au[21]) in the presence of equimolecular amounts of KOH, affording the pale yellow heterodinuclear complexes [(η^5-C$_5$Me$_5$)Ir(pz)$_3$M(PPh$_3$)] [M = Cu (**2**), Ag (**3**), Au (**4**)] (Scheme I). Complexes **2**–**4** have been characterized by elemental analysis (see Experimental Section),[22] spectroscopic measurements, and by the X-ray crystal structure determination of complex **3** (see below). Their IR spectra show absorptions corresponding to the pyrazolate (ca. 1050 cm^{-1})[23] and triphenylphosphine[24] groups and the disappearance of the N–H band of the starting material.[1] Table I collects the ^1H and $^{31}P\{^1H\}$ NMR data for these complexes. Besides the expected resonances for the protons of the C_5Me_5 and PPh_3 groups, the ^1H NMR

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[11] Cocivera, M.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O'Sullivan, D. J.; Paarvez, M.; Ruhl, B. *Organometallics* **1982**, *1*, 1132.

[12] Cocivera, M.; Ferguson, G.; Lalor, F. J.; Szczecinski, P. *Organometallics* **1982**, *1*, 1139.

[13] Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 1372.

[14] May, S.; Reinsalu, P.; Powell, J. *Inorg. Chem.* **1980**, *19*, 1582.

[15] Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726.

[16] Ghosh, C. K.; Rodgers, D. P. S.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 1511.

[17] Ball, R. G.; Ghosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341.

[18] Jones, W. D.; Duttweiler, R. P.; Feher, F. J.; Hessell, E. T. *New J. Chem.* **1989**, *13*, 725.

[19] Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1065.

[20] Teo, B.-K.; Calabrese, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1256.

[21] Malvaho, L. *Atti. Acad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1908**, *17*, 857.

[22] Satisfactory microanalytical data could not be obtained for **2**, most probably due to the presence of traces of Cu(II) oxidation products. Pale yellow solutions of **2** rapidly become green in air.

[23] Usón, R.; Oro, L. A.; Esteban, M.; Cuadro, A. M.; Navarro, P.; Elguero, J. *Transition Met. Chem.* **1982**, *7*, 234.

[24] Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; Vol. 1, p 358.

Table II. Fractional Atomic Coordinates[a] ($\times10^4$) for the Non-Hydrogen Atoms for [(η^5-C_5Me_5)(pz)Ir(μ-pz)$_2$Ag(PPh_3)] (3)

atom	x/a	y/b	z/c
Ir	27503 (2)	13019 (1)	64660 (1)
Ag	25658 (4)	27999 (3)	52380 (1)
P	3092 (1)	3269 (1)	4411 (1)
N(1)	1047 (4)	1406 (2)	5964 (1)
N(2)	1122 (4)	1681 (3)	5472 (1)
N(3)	3030 (4)	2749 (2)	6447 (1)
N(4)	3076 (4)	3283 (2)	6021 (1)
N(5)	1264 (4)	1560 (2)	7009 (1)
N(6)	734 (5)	840 (3)	7288 (2)
C(1)	−78 (7)	1449 (4)	5235 (2)
C(2)	−918 (7)	993 (6)	5561 (3)
C(3)	−182 (6)	977 (5)	6016 (2)
C(4)	3410 (6)	4159 (3)	6169 (2)
C(5)	3625 (6)	4199 (3)	6686 (2)
C(6)	3375 (5)	3296 (3)	6852 (2)
C(7)	−361 (6)	1201 (4)	7523 (2)
C(8)	−564 (5)	2131 (4)	7411 (2)
C(9)	474 (5)	2325 (3)	7074 (2)
C(10)	4457 (5)	750 (3)	6040 (2)
C(11)	3475 (5)	5 (3)	6108 (2)
C(12)	3368 (5)	−150 (3)	6641 (2)
C(13)	4282 (5)	488 (3)	6907 (2)
C(14)	4969 (5)	1034 (3)	6544 (2)
C(15)	4967 (7)	1088 (5)	5535 (3)
C(16)	2714 (6)	−522 (4)	5697 (2)
C(17)	2517 (7)	−903 (3)	6883 (2)
C(18)	4502 (8)	501 (5)	7482 (2)
C(19)	6073 (6)	1775 (5)	6644 (3)
C(20)	2441 (5)	2480 (3)	3911 (2)
C(21)	1526 (6)	2740 (4)	3530 (2)
C(22)	1037 (7)	2080 (4)	3162 (2)
C(23)	1492 (8)	1170 (4)	3181 (3)
C(24)	2440 (8)	899 (4)	3558 (3)
C(25)	2898 (7)	1548 (4)	3928 (3)
C(26)	4947 (5)	3309 (3)	4304 (2)
C(27)	5868 (7)	3441 (4)	4719 (2)
C(28)	7293 (7)	3448 (5)	4645 (4)
C(29)	7782 (7)	3336 (5)	4168 (4)
C(30)	6916 (7)	3221 (4)	3758 (3)
C(31)	5472 (6)	3195 (3)	3822 (2)
C(32)	2367 (5)	4406 (3)	4221 (2)
C(33)	1091 (6)	4654 (4)	4403 (2)
C(34)	464 (8)	5485 (5)	4258 (3)
C(35)	1095 (11)	6074 (5)	3942 (4)
C(36)	2347 (10)	5844 (5)	3747 (3)
C(37)	3005 (7)	5005 (4)	3892 (2)

[a] Atomic coordinates for Ir and Ag are expressed $\times10^5$.

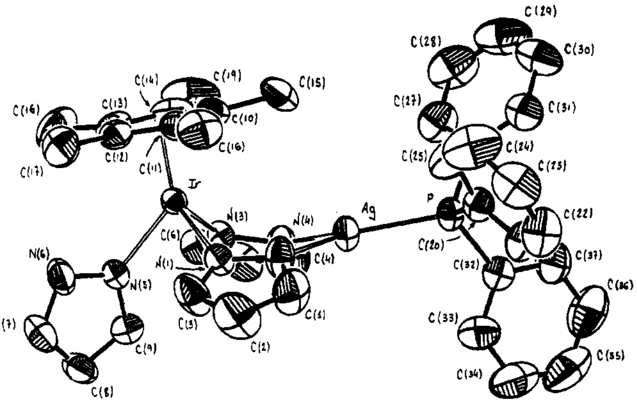

Figure 1. ORTEP view of [(η^5-C_5Me_5)Ir(pz)$_3$Ag(PPh_3)] (3) showing the atom-labeling scheme.

Table III. Selected Bond Distances (Å) and Angles (deg) for 3

Ir–N(1)	2.073 (3)	N(3)–N(4)	1.353 (4)
Ir–N(3)	2.075 (3)	N(3)–C(6)	1.349 (6)
Ir–N(5)	2.083 (3)	N(4)–C(4)	1.340 (5)
Ir–C(10)	2.163 (5)	N(5)–N(6)	1.366 (6)
Ir–C(11)	2.193 (5)	N(5)–C(9)	1.341 (6)
Ir–C(12)	2.192 (4)	N(6)–C(7)	1.340 (8)
Ir–C(13)	2.176 (5)	C(1)–C(2)	1.360 (10)
Ir–C(14)	2.170 (5)	C(2)–C(3)	1.367 (9)
Ag–P	2.341 (1)	C(4)–C(5)	1.366 (7)
Ag–N(2)	2.211 (4)	C(5)–C(6)	1.379 (6)
Ag–N(4)	2.205 (3)	C(7)–C(8)	1.367 (8)
P–C(20)	1.821 (5)	C(8)–C(9)	1.383 (7)
P–C(26)	1.816 (5)	C(10)–C(11)	1.434 (6)
P–C(32)	1.823 (5)	C(10)–C(14)	1.453 (7)
N(1)–N(2)	1.353 (4)	C(11)–C(12)	1.422 (7)
N(1)–C(3)	1.341 (7)	C(12)–C(13)	1.429 (7)
N(2)–C(1)	1.334 (7)	C(13)–C(14)	1.410 (7)
N(1)–Ir–N(3)	90.8 (1)	Ag–N(2)–N(1)	121.8 (3)
N(1)–Ir–N(5)	82.9 (1)	Ag–N(2)–C(1)	126.1 (3)
N(1)–Ir–Cp[a]	126.1 (1)	N(1)–N(2)–C(1)	107.5 (4)
N(3)–Ir–N(5)	86.2 (1)	Ir–N(3)–N(4)	125.7 (2)
N(3)–Ir–Cp	126.0 (1)	Ir–N(3)–C(6)	125.5 (3)
N(5)–Ir–Cp	130.7 (1)	N(4)–N(3)–C(6)	108.3 (3)
P–Ag–N(2)	128.3 (1)	Ag–N(4)–N(3)	125.6 (2)
P–Ag–N(4)	136.6 (1)	Ag–N(4)–C(4)	127.1 (3)
N(2)–Ag–N(4)	95.0 (1)	N(3)–N(4)–C(4)	107.2 (3)
Ir–N(1)–N(2)	124.1 (3)	Ir–N(5)–N(6)	120.7 (3)
Ir–N(1)–C(3)	125.7 (3)	Ir–N(5)–C(9)	129.4 (3)
N(2)–N(1)–C(3)	107.7 (3)	N(6)–N(5)–C(9)	108.4 (4)

[a] Cp is the centroid of the C_5Me_5 ring.

spectra of complexes 2–4, in $CDCl_3$ at ambient temperature, only show one type of pyrazolate environment. On cooling to 213 K, the spectrum for the IrCu complex 2 shows two pyrazolate environments in a 2/1 ratio. Two pyrazolate groups are coordinated to silver in the solid-state structure of the IrAg complex 3 (see below). It is likely therefore that the signals of intensity 2, in the spectrum at 213 K of complex 2, can be assigned to the protons of two bridging pyrazolate groups, with the others being resonances of a terminal pyrazolate ligand. At room temperature, the three pyrazolate groups interchange rapidly on the NMR time scale, probably by an associative mechanism. On cooling to 213 K, only broadening of the room-temperature resonances was observed for the IrAg and IrAu complexes 3 and 4, respectively. Thus, the fluxional process is more facile for these complexes than for the IrCu complex 2 and the exchange rates are rapid for them even at 213 K. A similar behavior has been found in the related polypyrazolylborate complexes [B(pz)$_4$M{P(OMe)$_3$}] (M = Cu or Ag), the dynamic process being easier with silver than with copper.[9].

At room temperature, the $^{31}P\{^1H\}$ NMR spectra of complexes 2 and 3 consist of a broad singlet at 2.6 ppm and two broad signals centered at 15.7 ppm and separated by 575 Hz, respectively. At 213 K the resonances (now centered at 1.8 and 15.5 ppm) become sharp and the splitting by coupling to the silver for complex 3 can be accurately measured. The magnitudes of the coupling constants, $J(^{107}AgP)$ = 565 and $J(^{109}AgP)$ = 653 Hz, are consistent with direct Ag–P bonding.[25] A second dynamic process that could be responsible for the observed $^{31}P\{^1H\}$ NMR spectra is the flipping of configurations of the six-membered IrN_4M rings. Inversion of the BN_4M boat conformation has been previously reported for various polypyrazolylborate derivatives.[9,26]

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(25) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979; pp 107–109.

(26) Herring, F. G.; Patmore, D. J.; Storr, A. *J. Chem. Soc., Dalton Trans.* **1975**, 711.

In order to gain more structural information about these systems, the determination of the molecular structure of complex **3** by X-ray diffraction methods was undertaken. The crystal structure of **3** contains discrete molecules separated by normal van der Waals distances. Figure 1 shows the molecular structure and numbering scheme. Atomic coordinates are listed in Table II, and derived bond distances and angles are in Table III. The molecule is heterodinuclear with an iridium and a silver atom connected by two bridging pyrazolate groups. The iridium–silver separation, 3.8601 (2) Å, excludes any significant intermetallic interaction. An η^5-coordinated pentamethylcyclopentadienyl ligand and a terminal pyrazolate group complete the pseudooctahedral coordination of the iridium atom. The trigonal-planar coordination around the silver metal is completed by the phosphorus atom of a triphenylphosphine ligand. The separation between the iridium and the centroid of the cyclopentadienyl ring is 1.808 (2) Å, which compares well with the reported value, 1.800 (7) Å, for the related mononuclear iridium pyrazolate complex $[(\eta^5\text{-}C_5Me_5)Ir(Me_2pz)_2(Me_2pzH)]$.[1] The Ir–C(ring) distances range from 2.163 (5) to 2.193 (5) Å, in good agreement with literature reports.[27-29] The methyl substituents are bent away from the iridium atom; displacements for C(15), C(16), C(17), C(18), and (C19) from the mean plane through the C_5 ring are 0.101 (7), 0.033 (6), 0.088 (6), 0.054 (7), and 0.062 (6) Å, respectively.

The Ir–N(bridging pyrazolate) bond distances [Ir–N(1) = 2.073 (3) and Ir–N(3) = 2.075 (3) Å] are similar to the Ir–N(terminal pyrazolate) [Ir–N(5) = 2.083 (3) Å] bond length and compare well with the Ir–N(bridging pyrazolate) bond distances found in the dinuclear bis(μ-hydrido)(μ-pyrazolate) complex $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2(\mu\text{-}H)_2(\mu\text{-}pz)]BF_4$ [2.098 (10) and 2.065 (11) Å][29] and in the heterodinuclear pyrazolate-bridged IrRh compound $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)(\mu\text{-}I)_2Rh(CO_2Me)I(CO)]$ [2.095 (8) Å][30] and with the Ir–N(terminal pyrazolate) bond length found in the mononuclear iridium compound $[(\eta^5\text{-}C_5Me_5)Ir(Me_2pz)(Me_2pzH)]$ [2.085 (6) Å].[1]

The six-membered IrN_4Ag ring adopts a boat conformation with the bow at Ir and the stern at Ag. The description of the magnitude of the deformation from the ideal boat could be accomplished with the Cremer and Pople parameters (Q = 0.874 (2), φ = −171.0 (3), and θ = 102.5 (2)°).

The coordination of the silver atom is trigonal planar, the angles around adding to 359.8 (1)°. The two Ag–N bond lengths 2.211 (4) and 2.205 (3) Å are comparable to one another, in contrast to those found in the three-coordinated bis(pyrazolyl)borate compound $[\{Ph_2B(pz)_2\}Ag\{P(C_6H_4Me\text{-}p)_3\}]$, in which the $Ph_2B(pz)_2$ ligand is strongly bound to silver by only one nitrogen atom [Ag–N = 2.194 (4) and 2.411 (4) Å].[31] The Ag–N bond distances in the three-coordinated complex **3** fall between the Ag–N bond lengths reported for the azole complexes $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3\cdot 2THF$ (THF = tetrahydrofuran) [Ag–N(average) = 2.085 (1) Å][32] and $[Ag(ImH)_2]NO_3$ [Ag–N = 2.12 Å],[33] in which the silver is two-coordinated, and the Ag–N bond distances reported for the compounds $[\{Me_2C(pz)_2\}_2Ag]ClO_4$ [Ag–N(average) = 2.323 (4) Å][34] and $[Ag(pyridine)_4]ClO_4$ [Ag–N = 2.322 (3) Å],[35] in which the silver is four-coordinated, and may be compared to those reported for other complexes in which the silver is three-coordinated: Ag–N = 2.243 (3) Å in the pyrazole complex[36] $[Ag\{1\text{-}Ph,3,5\text{-}Me_2pz\}_3]NO_3$ and 2.239 (4) Å in the heterotetranuclear derivative[37] $[(Ph_3P)(O_3ClO)AgN(Ph_2PAuPPh_2)_2NAg(OClO_3)(PPh_3)]$. The Ag–P bond length in complex **3**, 2.341 (1) Å, is comparable with that found in the mononuclear three-coordinated bis(pyrazolyl)borate complex $[\{Ph_2B(pz)_2\}Ag\{P(C_6H_4Me\text{-}p)_3\}]$ [Ag–P = 2.351 (1) Å].[31] The structural features within the C_5Me_5, PPh_3, and pz ligands are normal.

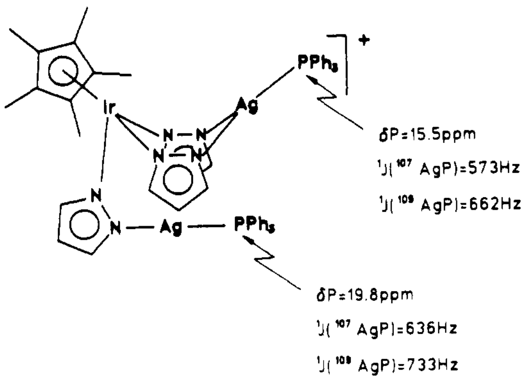

Figure 2.

The crystal structure of complex **3** shows that, in the solid state, there is a free nitrogen atom whose lone electron pair can be potentially used to further coordination. In effect, complex **3** readily reacts with equimolecular amounts of $AgBF_4$ and PPh_3, affording the trinuclear complex $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)_3\{Ag(PPh_3)\}_2]BF_4$ (**5**). Subsequent addition of $AgBF_4$ and PPh_3 to **5** does not produce an ulterior reaction; complex **5** remaining unchanged. At room temperature, the ^1H NMR spectrum of **5** (Table I) shows three-proton resonance centered at 6.24 ppm that can be assigned to the three H_4 protons of the three equivalent pyrazolate groups. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows, at room temperature, two broad signals separated by 607 Hz that can be assigned to PPh_3 groups directly bound to silver. These spectral data indicate that, at room temperature, a fluxional process is occurring which renders the three pyrazolate and the two $AgPPh_3$ groups equivalent. When the temperature is lowered, the signals broaden and at 213 K two resonances at 6.42 and 6.19 ppm in 1/2 ratio are observed in the 6.0–6.5 ppm region of the ^1H NMR spectrum. At the same temperature four sharp doublets emerge in the $^{31}P\{^1H\}$ NMR spectrum of **5**. Two are centered at 15.5 ppm [$^1J(^{107}AgP)$ = 573 Hz, $^1J(^{109}AgP)$ = 662 Hz] and the other two at 19.8 ppm [$^1J(^{107}AgP)$ = 636 Hz, $^1J(^{109}AgP)$ = 733 Hz]. An exchange process that satisfies the experimental data involves the rotation of the two $AgPPh_3$ units of complex **5** in a concerted fashion around the arrangement formed by the three free nitrogen atoms of the $(\eta^5\text{-}C_5Me_5)Ir(pz)_3$ moiety, each silver alternatively being coordinated to one and to two nitrogen

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(27) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1.

(28) Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1747.

(29) Oro, L. A.; Carmona, D.; Puebla, M. P.; Lamata, M. P.; Foces-Foces, C.; Cano, F. H. *Inorg. Chim. Acta* **1986**, *112*, L11.

(30) Carmona, D.; Lahoz, F. J.; Oro, L. A.; Reyes, J.; Lamata, M. P. *J. Chem. Soc., Dalton Trans* **1990**, 3551.

(31) Bruce, M. I.; Walsh, J. D.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 956.

(32) Murray, H. H.; Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 26.

(33) Acland, C. B.; Freeman, H. C. *J. Chem. Soc., Chem. Commun.* **1971**, 1016.

(34) Lorenzotti, A.; Bonati, F.; Cingolani, A.; Gioia Lobbia, G.; Leonesi, D.; Bovio, B. *Inorg. Chim. Acta* **1990**, *170*, 199.

(35) Nilsson, K.; Oskaarsson, A. *Acta Chem. Scand., Ser. A* **1982**, *36*, 605.

(36) Francisco, R. H. P.; Mascarehnas, Y. P.; Lechat, J. R. *Acta Crystallogr., Sect. B* **1979**, *35*, 177.

(37) Usón, R.; Laguna, A.; Laguna, M.; Gimeno, M. C.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1986**, 509.

Table IV. NMR Spectroscopic Data[a] for Complexes 6–16

	$^1H^b$								
		terminal pyrazolate			bridging pyrazolates				
complex	C_5Me_5	H_3	H_4	H_5	$H_{3/5}$	$H_{5/3}$	H_4	others	$^{31}P^b$
6	1.82 (s)	7.51 (bs, J = 1.4)	5.80 (t)	5.46 (d)	6.75 (d, J = 1.9)	7.39 (d)	6.00 (t)	2.50 (m), 3.94 (m), 4.48 (m) (COD)	
7	1.69 (s)	7.59 (bs, J = 1.5)	5.94 (t)	6.07 (d)	6.82 (d, J = 1.6)	7.50 (d)	6.14 (t)		
8[c]	1.78 (s)	7.56 (bs, J = 1.9)	5.83 (t)	5.46 (d)	6.61 (t, J = 2.0)[d]	6.89 (d)	5.77 (t)	7.2–7.6 (m, PPh_3)	39.2 (d, J(RhP) = 155)
					6.50 (d, J = 1.9)	7.60 (d)	6.08 (t)		
9[c]	1.72 (s)	7.57 (ABX system, J(AB) = 1.8, J(AX) = 1.9)	5.88	5.84	6.84 (t, J = 1.8)[e]	7.57 (bs)	6.13 (t)	3.73 (d, $P(OMe)_3$, J(PH) = 11.8)	137.1 (d, J(RhP) = 244)
					6.61 (d, J = 1.90)	7.41 (bs)	5.97 (t)		
10	1.32 (s)	f (J = 1.9)	5.76 (t)	5.29 (d)	6.56 (d, J = 1.8)	f	5.81 (t)	1.7 (m), 2.2 (m), 7.2–7.7 (m, dppe)	70.1 (d, J(RhP) = 172.5)
11a	1.29 (s)	f (J = 1.6)	5.74 (t)	5.18 (d)	6.25 (d, J = 1.8)	f	5.76 (t)	1.02 (dd, CH_3 Prophos), J(PH) = 10.5, J(HH) = 4.0)	54.7 (dd, J(RhP) = 168, J(PP) = 45)
					6.81 (d, J = 1.7)	f	5.83 (t)		77.0 (dd, J(RhP) = 173)
11b	1.37 (s)								60.9 (dd, J(RhP) = 172, J(PP) = 44)
									78.8 (dd, J(RhP) = 171)

	$^1H^b$								
		terminal pyrazole			bridging pyrazolates				
complex	C_5Me_5	H_3	$H_{4/5}$	$H_{5/4}$	$H_{3/5}$	$H_{5/3}$	H_4	others	^{31}P
12	1.84 (s)	7.86 (bs)	6.00 (bs)	6.11 (bs)	6.81 (d, J = 2.0)	7.44 (d)	6.11 (t)	10.66 (bs, NH)	
13	1.70 (s)	8.05 (bs)	6.21 (bs)	6.34 (bs)	6.88 (d, J = 1.9)	7.56 (d)	6.26 (t)	11.23 (bs, NH)	
14[c]	1.76 (s)	7.67 (bs)	6.13 (bs)	6.22 (bs)	6.65 (bs, J = 2.1)	6.84 (d)	5.81 (t)	10.73 (bs, NH)	38.6 (d, J(RhP) = 155)
					6.71 (bs)	7.90 (bs)		6.13 (bs)	

	$^1H^b$								
		Ir–pz–Ag			Ir–pz–Rh				
complex	C_5Me_5	$H_{3/5}$	$H_{5/3}$	H_4	$H_{3/5}$	$H_{5/3}$	H_4	others	$^{31}P^g$
15	1.70 (s)	7.16 (bs)	7.93 (bs)	6.27 (bs)	6.79 (bs)	6.99 (bs)	6.07 (bs)	7.3–7.7 (m, PPh_3), 3.9 (m), 4.1 (m, COD)	16.4 (d, $J(^{107}AgP)$ = 635, $J(^{109}AgP)$ = 733)
16[h]	1.66 (s)	5.75 (bs), 6.02 (bs)	6.27 (bs)	6.35 (bs)	6.75 (bs)	6.80 (bs)	7.97 (bs)	6.9–7.5 (m, PPh_3)	37.3 (d, J(RhP) = 152.5), 16.3 (d, $J(^{107}AgP)$ = 638, $J(^{109}AgP)$ = 736)

[a] See footnote *a* in Table I. [b] For labeling of pyrazolate protons see Figure 3. J represents the $^3J(H_3H_4) = {}^3J(H_4H_5)$ coupling constants in the pyrazolate ring. [c] Pyrazolate protons assigned through selective decoupling experiments. [d] $J(PH) = {}^3J(H_3H_4) = {}^3J(H_4H_5)$ = 2.0 Hz. [e] $J(PH) = {}^3J(H_3H_4) = {}^3J(H_4H_5)$ = 1.8 Hz. [f] Obscured by the phenyl protons. [g] Measured at 213 K. [h] Pyrazolate protons not assigned.

atoms. Then, the static structure of **5** should contain a trigonal arrangement around one silver atom of two bridging pyrazolates and a PPh_3 ligand and one digonal silver atom coordinated to one bridging pyrazolate group and a PPh_3 ligand, as is schematically shown in Figure 2. It is noteworthy to point out the similarity of the NMR parameters of the resonance centered at 15.5 ppm of complex **5** and the low-temperature limiting ^{31}P NMR spectrum of complex **3** (see above), which indicates a similar structural disposition for both $AgPPh_3$ fragments.

Iridium–Rhodium Heterometallic Complexes. Addition of equimolecular amounts of [Rh(acac)(COD)] (Hacac = acetylacetone)[38] to methanolic solutions of **1** causes the instantaneous precipitation of a yellow solid analytically and spectroscopically characterized as the heterometallic iridium–rhodium complex [(η^5-C_5Me_5)(pz)Ir(μ-pz)$_2$Rh(COD)] (**6**). In this reaction the acidic NH proton of **1** is abstracted by the basic acac ligand, which is displaced from the rhodium coordination sphere as the weakly coordinating neutral acetylacetone molecule. The generated vacancies at rhodium are occupied by the free nitrogen atoms of the resulting (η^5-C_5Me_5)Ir(pz)$_3$ entity. This synthetic strategy has been previously used by us to prepare homo- and heterodinuclear complexes.[39-42] In the reaction, the formation of small amounts of the previously reported dimer[13] [Rh(pz)(COD)]$_2$ was also observed. Most probably this complex proceeds from the fragmentation of **6** to give (η^5-C_5Me_5)Ir(pz)$_2$ and Rh(pz)(COD) moieties, the latter giving rise to [Rh(pz)(COD)]$_2$ by dimerization. In fact, the reaction in methanol of **1** with the homologous iridium complex [Ir(acac)(COD)][43] affords the dark red dimer[44] [Ir(pz)(COD)]$_2$ and the previously reported[45] diiridium(III) cation [{(η^5-C_5Me_5)Ir}$_2$(μ-pz)$_2$(μ-OH)]$^+$ as the only identified species.

Besides the C_5Me_5 singlet and the characteristic olefin resonances, the ^1H NMR spectrum of **6**, at room temperature, in $CDCl_3$ (Table IV), shows two pyrazolate environments in a 2/1 ratio. Due to the great tendency of rhodium(I) to give four-coordinated square-planar 16e$^-$ complexes,[46] we propose for complex **6** the coordination

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(38) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.

(39) Oro, L. A.; Fernández, M. J.; Modrego, J.; Foces-Foces, C.; Cano, F. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 913.

(40) Oro, L. A.; Ciriano, M. A.; Villarroya, B. E.; Tiripicchio, A.; Lahoz, F. J. *J. Chem. Soc., Chem. Commun.* **1984**, 521.

(41) Oro, L. A.; Carmona, D.; Lamata, M. P.; Tiripicchio, A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1986**, 15.

(42) Oro, L. A.; Carmona, D.; Reyes, J.; Foces-Foces, C.; Cano, F. H. *J. Chem. Soc., Dalton Trans.* **1986**, 31.

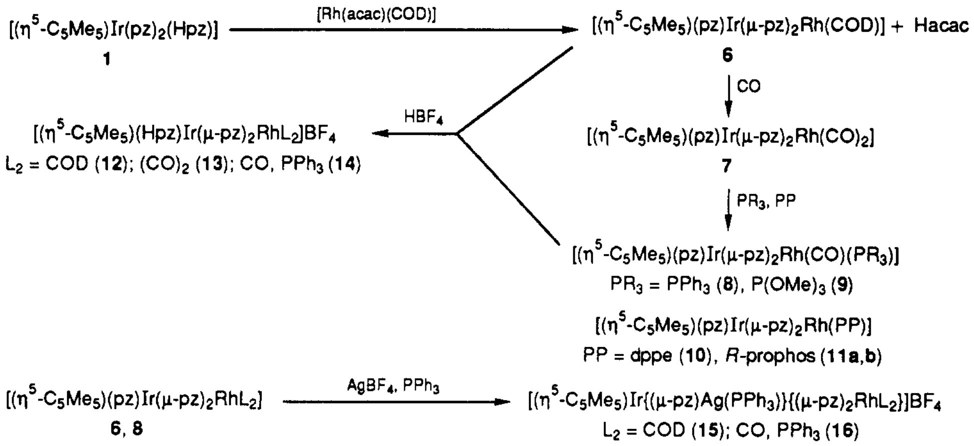
(43) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1965**, 4997.

(44) Coleman, A. W.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 922.

(45) Carmona, D.; Oro, L. A.; Lamata, M. P.; Puebla, M. P.; Ruiz, J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 639.

(46) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 5.

Scheme II



of two of the pyrazolate groups to the rhodium, becoming bridging ligands, the third pyrazolate remaining only coordinated to the iridium atom. However, on the basis of line width behavior and the change in chemical shifts of the signals as the temperature increases, a slow exchange between the three pyrazolate groups takes place in **6**. The fast-exchange limiting spectrum has not been achieved in toluene-d_8, at 100 °C. It seems interesting to point out that, at room temperature, the related polypyrazolylborate diolefin rhodium complexes [{RB(pz)$_3$}Rh(diolefin)] (R = H, pz; diolefin = COD, NBD) and, at 60 °C, the duroquinone derivative [{B(pz)$_4$}Rh(duroquinone)] only present one type of pyrazolate environment,[47] most probably due to an intramolecular exchange between coordinated and free pyrazolyl groups.[12] Consequently, the rate of exchange of the free and coordinated pyrazolate groups is much slower in **6** than in the related [{RB(pz)$_3$}Rh(diolefin)] complexes.

Complex **6** reacts with carbon monoxide (room temperature, atmospheric pressure) with displacement of the diolefin coordinated to the rhodium and formation of the dicarbonyl derivative [(η^5-C$_5$Me$_5$)(pz)Ir(μ-pz)$_2$Rh(CO)$_2$] (**7**). The IR spectrum of **7** in Nujol shows two sharp ν(CO) bands at 2010 and 2070 cm^{-1}, characteristic of *cis*-dicarbonylrhodium complexes.[15,48,49] No bridging ν(CO) bands could be detected in this reaction. The formation of **7** from **6** parallels the preparation of [{H$_2$B(pz)$_2$}Rh(CO)$_2$] from the diolefin compound [{H$_2$B(pz)$_2$}Rh(COD)].[47] The related monomeric tris(3,5-dimethylpyrazolyl)borate dicarbonyl derivative [{HB(Me$_2$pz)$_3$}Rh(CO)$_2$] has been previously reported.[13,14] Nevertheless, the reaction of [{RB(pz)$_3$}Rh(COD)] (R = H, pz) with CO at atmospheric pressure gives the bridging carbonyl polynuclear compounds[47] [{RB(pz)$_3$}$_2$Rh$_2$(μ-CO)$_3$]$_n$. In a similar way, the related tris(pyrazolyl)methane (tpzm) cationic rhodium complex [(tpzm)Rh(COD)]ClO$_4$ reacts with carbon monoxide to afford the dinuclear bridging carbonyl compound [(tpzm)$_2$Rh$_2$(μ-CO)$_3$](ClO$_4$)$_2$ via the mononuclear dicarbonyl derivative[50] [(tpzm)Rh(CO)$_2$]ClO$_4$.

In addition to the C$_5$Me$_5$ singlet, at 1.69 ppm, the ^{1}H NMR spectrum of **7** at room temperature, in CDCl$_3$, shows two pyrazolate environments in a 2/1 ratio, which we assign to two bridging and one terminal pyrazolate groups, respectively. At higher temperatures, in toluene-d_8, the ^{1}H NMR spectral data indicate that the pyrazolate groups exchange but the fluxional processes responsible for this exchange are slow, even at 100 °C.

The carbon monoxide groups in **7** can be partially or completely removed by reaction with monodentate or bidentate phosphorus donor ligands, respectively. Thus, addition of PPh$_3$ or P(OMe)$_3$ to **7** gives the monocarbonyl derivatives [(η^5-C$_5$Me$_5$)(pz)Ir(μ-pz)$_2$Rh(CO)(PR$_3$)] [PR$_3$ = PPh$_3$ (**8**), P(OMe)$_3$ (**9**)] and addition of dppe or *R*-prophos gives the no-carbonyl-containing complexes [(η^5-C$_5$Me$_5$)(pz)Ir(μ-pz)$_2$Rh(PP)] [PP = dppe (**10**), *R*-prophos (**11a,b**)]. In the reaction of **7** with *R*-prophos, two diastereomers **11a** and **11b** could be obtained. Both are formed, but the process is largely diastereoselective. The formation ratio (measured by integration of the ^{1}H NMR signals of the C$_5$Me$_5$ groups in the crude reaction mixture) is **11a**/**11b** = 90/10.

The IR spectra of the monocarbonyl derivatives **8** and **9** show strong ν(CO) bands at 1990 and 2000 cm^{-1}, respectively. These absorptions are at lower frequencies than those of the precursor **7**, as expected for the substitution of a CO group by better σ-donor ligands such as PPh$_3$ or P(OMe)$_3$. Scheme II summarizes all these reactions.

The room-temperature ^{1}H NMR spectra of complexes **8**–**11** show the characteristic AMX patterns for the pyrazolate protons. In all cases the spectral data are consistent with the presence of two bridging and one terminal pyrazolate groups, the rhodium being tetracoordinate (Figure 3). The high-temperature ^{1}H NMR spectrra of complexes **8** and **9** in toluene-d_8 indicate that the rate of exchange between coordinated and free pyrazolate groups are slower than those found for complexes **6** and **7**. The ^{1}H NMR spectra of **10** and **11** do not shown any significant change from −60 to +50 °C in CDCl$_3$ solution[51] (complex **10**) nor from −90 to +100 °C in toleuene-d_8 solution (complex **11**).

It is noteworthy to point out the low values of the chemical shift of the H$_5$ protons of the free pyrazolate group of the neutral IrRh complexes **6**–**11**. Their resonances appear at lower values than those of the corresponding H$_4$ protons in complexes **6** and **8**–**11**. In complex **9** the H$_4$ and H$_5$ protons give an AB spin system and in complex **7** the doublet assigned to the H$_5$ proton is centered at 6.07 ppm while the H$_4$ proton triplet is centered at 5.94 ppm (Table IV). These low values could be explained by assuming that the terminal pyrazolate ligand is in such a conformation that its H$_5$ proton lies above one

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[47] Cocivera, M.; Desmond, T. J.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O'Sullivan, D. J. *Organometallics* **1982**, *1*, 1125.

[48] Usón, R.; Oro, L. A.; Claver, C.; Garralda, M. A. *J. Organomet. Chem.* **1976**, *105*, 365.

[49] Usón, R.; Oro, L. A.; Artigas, J.; Sariego, R. *J. Organomet. Chem.* **1979**, *179*, 65.

[50] Esteruelas, M. A.; Oro, L. A.; Claramunt, R. M.; López, C.; Lavandera, J. L.; Elguero, J. *J. Organomet. Chem.* **1989**, *366*, 245.

[51] The low solubility of **10** in toluene precludes an NMR study for it in this solvent.

bridging pyrazolate ring, so that it is being shielded by the ring current. A similar ^1H NMR behavior has been previously found for the Me_5 protons of the (3,5-dimethylpyrazole)iridium derivative [(η^5-C_5Me_5)Ir(dmpz)(Hdmpz)$_2$]BF_4, in which the solid-state structure reveals that the Me_5 group of the "free" pyrazolate lies just above one pyrazolate ring.[1]

The $^{31}P\{^1H\}$ NMR spectral data for complexes 8–11 are collected in Table IV. As expected, all resonances show the splitting due to coupling to the ^{103}Rh nucleus (spin $^1/_2$, natural abundance 100%).

Addition of 1 equiv of aqueous HBF_4 to complexes 6–8 in acetone affords the yellow cationic compounds [(η^5-C_5Me_5)(Hpz)Ir(μ-pz)$_2$RhL_2]BF_4 [L_2 = COD (12); (CO)$_2$ (13); CO, PPh_3 (14)]. Complex 13 shows two ν(CO) bands at 2000 and 2070 cm^{-1}, and complex 14 presents one ν(CO) band at 1980 cm^{-1}. The shifts of the ν(CO) bands to slightly lower frequencies, with respect to their parent complexes 7 and 8, are consistent with the presence of a positive charge in the complexes and exclude a protonation at rhodium. A broad ν(NH) absorption band at 3380 (12), 3370 (13), and 3400 (14) cm^{-1} and a broad ^1H NMR singlet centered at 10.66 (12), 11.23 (13), and 10.73 (14) ppm, strongly indicate that a pyrazolate nitrogen has been protonated. Consistently, the values of the phosphorus chemical shift, 38.6 ppm, and of the rhodium–phosphorus coupling constant, 155 Hz, in complex 14 are very similar to those found for its parent complex 8, 39.2 ppm and 155 Hz, respectively.

Again, the pyrazolate ring in complexes 12–14 is in such a conformation that its H_5 proton is shielded by the ring current of one of the bridging pyrazolate rings (Table IV).

The protonation of the free nitrogen atom of monodentate coordinated pyrazolate ligands by HBF_4 has been previously reported for mononuclear palladium[52] and platinum[52,53] complexes of general formula *cis*-[(LL)M(Pz)$_2$] (LL = various bis(diphenylphosphines) or arsines and 2,2′-bipyridine, Pz = Me_2pz, pz). In this context, it seems interesting to point out that the protonation of the rhodium tris(pyrazolyl)borate complex [HB(Me_2pz)$_3$Rh(CO)$_2$] by HBF_4 takes place at a pyrazole nitrogen, leading to the tetracoordinated cationic complex [HB(Me_2pz)$_3$(HMe_2pz)Rh(CO)$_2$]BF_4, while the protonation of the homologous iridium compound [HB(Me_2pz)$_3$Ir(CO)$_2$] by the same acid affords the iridium(III) cationic hydride [HB(Me_2pz)$_3$Ir(H)(CO)$_2$$BF_4$.[17]

The free nitrogen atom of complexes 6 and 8 is capable of coordination to the cationic moiety AgPPh_3, which is isolobal to the proton. Thus, the addition of equimolecular amounts of AgBF_4 and PPh_3 to acetone suspensions of 6 or 8 affords the heterotrinuclear complexes [(η^5-C_5Me_5)Ir$\{$(μ-pz)Ag(PPh_3)$\}\{$(μ-pz)$_2$Rh$L_2$$\}$]$BF_4$ [L_2 = COD (15); CO, PPh_3 (16)]. These complexes have been characterized by elemental analysis (see Experimental Section) and spectroscopic means (Table IV). The values of the ^{107}AgP and ^{109}AgP coupling constants, 635 and 733 Hz (complex 15) and 638 and 736 Hz (complex 16), respectively, can be compared with those found for the triphenylphosphine bound to the digonal silver in complex 5 (Figure 2) and suggest this type of coordination for the silver in complexes 15 and 16.

The resonance of the H_5 proton of the Ir–Ag bridging pyrazolate group in 15 is shifted at least 1.70 ppm downfield with respect to the same proton in its parent complex 6. Most probably, the presence of the bulky substituent AgPPh_3 on the nitrogen prevents this H_5 proton from being shielded by the ring current of the other pyrazolate groups.

Conclusions

The mononuclear iridium compound 1 is a good precursor for the synthesis of heteronuclear compounds. The structural similarity and isolobal relationship between the proton and the group 11 MPPh_3^+ cations explain the preparation of the heterodinuclear complexes 2–4 from 1. A metallotropism for the MPPh_3 fragment is observed in 2–4 comparable to the prototropism described for 1. In these complexes the anion of 1, [(η^5-C_5Me_5)Ir(pz)$_3$]$^-$, behaves as a tridentate ligand while it acts as a bidentate ligand toward different RhL_2^+ moieties. As has been found for the related [$\{$RB(pz)$_3$$\}$Rh(diolefin)] complexes the [(η^5-C_5Me_5)(pz)Ir(μ-pz)$_2$RhL_2] (6–9) compounds are fluxional in solution, exchanging the terminal and bridging pyrazolate groups. These fluxional processes are slower than those of the [$\{$RB(pz)$_3$$\}$Rh(diolefin)] compounds. The free nitrogen atom in [(η^5-C_5Me_5)(pz)Ir(μ-pz)$_2$RhL_2] could be used to build the heterotrinuclear derivatives 15 and 16, as well as one of the nitrogen in [(η^5-C_5Me_5)(pz)$_3$Ag(PPh_3)] can be coordinated to a second AgPPh_3^+ unit rendering complex 5. In 5 both AgPPh_3 fragments exchange rapidly at room temperature. Protonation of the complexes [(η^5-C_5Me_5)(pz)Ir(μ-pz)$_2$RhL_2] (6–8) takes place at the free pyrazolate group, affording the corresponding cationic derivatives [(η^5-C_5Me_5)(Hpz)Ir(μ-pz)$_2$RhL_2]BF_4 (12–14). The coordinative behavior of the anion [(η^5-C_5Me_5)Ir(pz)$_3$]$^-$ closely resembles that of the polypyrazolylborates RB(pz)$_3^-$ (R = H, pz), and consequently, an extensive chemistry could be anticipated for it comparable to that reported for the RB(pz)$_3^-$ anions.

Experimental Section

All solvents were dried over appropriate drying agents, distilled under N_2, and degassed prior to use. All preparations have been carried out under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer (range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets or dichloromethane solutions between NaCl plates. The C, H, and N analyses were carried out with a Perkin-Elmer 240 B microanalyzer. Phosphorus-31 and ^1H NMR spectra were recorded on a Varian XL-200 spectrometer [80.9 (^{31}P) and 200.0 (^1H) MHz].

Preparation of [(η^5-C_5Me_5)Ir(pz)$_3$Cu(PPh_3)] (2). To a solution of 1 (150.0 mg, 0.283 mmol) in 25 mL of MeOH were added [CuCl(PPh_3)]$_4$ (102.3 mg, 0.071 mmol) and 1.64 mL of a methanolic solution of KOH (0.172 N, 0.283 mmol). The mixture was stirred for 30 min. During this time a pale yellow solid precipitated, which was filtered off, washed with water and hexane, and dried under vacuum. Yield: 90%. Anal. Calcd for $C_{37}H_{39}N_6CuIrP$: C, 52.00; H, 4.60; N, 9.83. Found:[22] C, 51.02; H, 4.68; N, 10.10.

The pale yellow complexes 3 and 4 were prepared similarly. Complex 3: yield, 95%. Anal. Calcd for $C_{37}H_{39}N_6AgIrP$: C, 49.44; H, 4.37; N, 9.35. Found: C, 49.03; H, 4.35; N, 9.24. Complex 4: yield, 61%. Anal. Calcd for $C_{37}H_{39}N_6AuIrP$: C, 44.98; H, 3.97; N, 8.50. Found: C, 44.66; H, 3.87; N, 8.47.

Preparation of [(η^5-C_5Me_5)Ir(pz)$_3$$\{$Ag($PPh_3$)$\}_2$]$BF_4$ (5). To a solution of 3 (150.0 mg, 0.166 mmol) in 25 mL of acetone were added PPh_3 (43.7 mg, 0.166 mmol) and AgBF_4 (32.4 mg, 0.166 mmol). The solution was stirred for 1 h and then was filtered to remove any remaining solid. The volume of the filtrate was reduced to 5 mL. The precipitation of a pale yellow solid was completed by addition of diethyl ether (20 mL). The solid was collected, washed with diethyl ether, and dried under vacuum. Yield: 73%. Anal. Calcd for $C_{55}H_{54}N_6Ag_2BF_4IrP_2$: C, 48.72; H, 4.01; N, 6.19. Found: C, 48.60: H, 4.26; N, 6.20.

Preparation of [(η^5-C_5Me_5)Ir(μ-pz)$_2$Rh(COD)] (6). To a solution of complex 1 (250.4 mg, 0.472 mmol) in methanol (25 mL) was added [Rh(acac)(COD)] (146.4 mg, 0.472 mmol). The

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[52] Minghetti, G.; Banditelli, G.; Bonati, F. *J. Chem. Soc., Dalton Trans.* **1979**, 1851.

[53] Banditelli, G.; Bandini, A. L.; Bonati, F.; Minghetti, G. *Inorg. Chim. Acta* **1982**, *60*, 93.

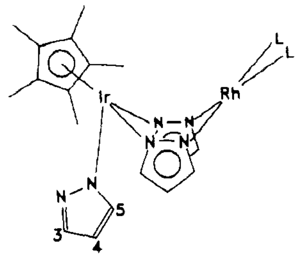

Figure 3.

instantaneous precipitation of a yellow solid was observed. The suspension was stirred during 30 min, and then the solid was filtered off, washed with methanol, and dried under vacuum. Recrystallization from dichloromethane/hexane affords pure complex 6. Yield: 80%. Anal. Calcd for $C_{27}H_{36}N_6IrRh$: C, 43.84; H, 4.90; N, 11.36. Found: C, 44.20; H, 5.30; N, 11.47.

Reaction of 1 with [Ir(acac)(COD)] in the same conditions as above gave $[Ir(pz)(COD)]_2$[18] and $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2(\mu\text{-}pz)_2(\mu\text{-}OH)]^+$ as the only identified species.

Preparation of $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2Rh(CO)_2]$ (7). At room temperature and atmospheric pressure, carbon monoxide was bubbled through a solution of complex 6 in dichloromethane (25 mL) during 30 min. The color of the solution changed from yellow to pale yellow, and the IR spectrum of the solution showed two terminal ν(CO) bands. Hexane (25 mL) was added to the solution, and bubbling of CO was continued until the precipitation of a yellow solid was observed. The solid was filtered off, washed with cold hexane, and vacuum-dried. Yield: 84%. IR (Nujol): ν(CO) 2070 (vs), 2010 (vs) cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_6IrO_2Rh$: C, 36.68; H, 3.51; N, 12.22. Found: C, 36.54; H, 3.39; N, 12.29.

Preparation of $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2Rh(CO)(PPh_3)]$ (8). To a solution of 6 (250.4 mg, 0.364 mmol) in acetone (25 mL) was added 95.6 mg (0.364 mmol) of solid PPh_3. The solution was stirred during 1 h. During this time the precipitation of a yellow solid was observed. The solid was filtered off, washed with hexane, and dried under vacuum. Yield: 82%. IR (Nujol): ν(CO) 1900 (vs) cm^{-1}. Anal. Calcd for $C_{38}H_{39}N_6IrOPRh$: C, 49.51; H, 4.26; N, 9.11. Found: C, 49.08; H, 3.96; N, 9.02.

The yellow complexes 9–11 were similarly prepared by using the appropriate phosphorus ligand. Complex 9 precipitates after concentration of the acetone solution to 2 mL and subsequent addition of hexane (25 mL).

Complex 9: yield 57%. IR (Nujol): ν(CO) 2000 (vs) cm^{-1}. Anal. Calcd for $C_{23}H_{33}N_6IrO_4PRh$: C, 35.25; H, 4.24; N, 10.72. Found: C, 35.68; H, 4.57; N, 10.61. Complex 10: yield 85%. Anal. Calcd for $C_{45}H_{48}N_6IrP_2Rh$: C, 52.47; H, 4.69; N, 8.15. Found: C, 52.43; H, 5.04; N, 7.84. Complex 11: yield 86%. Anal. Calcd for $C_{46}H_{50}N_6IrP_2Rh$: C, 52.92; H, 4.82; N, 8.04. Found: C, 52.43; H, 4.98; N, 7.68.

Preparation of $[(\eta^5\text{-}C_5Me_5)(Hpz)Ir(\mu\text{-}pz)_2Rh(COD)]BF_4$ (12). To a suspension of 6 (89.9 mg, 0.121 mmol) in acetone (25 mL) was added 24.2 μL of an aqueous solution of HBF_4 (35% w/w, 0.121 mmol). The resulting solution was stirred during 30 min and then vacuum-concentrated to ca. 2 mL. The addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 53%. IR (Nujol): ν(NH) 3380 (br) cm^{-1}. Anal. Calcd for $C_{27}H_{37}N_6BF_4IrRh$: C, 39.18; H, 4.50; N, 10.15. Found: C, 38.90; H, 4.43; N, 9.93.

The yellow complexes 13 and 14 were similarly prepared starting from complexes 7 and 8, respectively. Complex 13: yield 62%. IR (Nujol): ν(NH) 3370 (br); ν(CO) 2070 (vs), 2000 (vs) cm^{-1}. Anal. Calcd for $C_{21}H_{25}N_6BF_4IrO_2Rh$: C, 32.53; H, 3.24; N, 10.83. Found: C, 31.86; H, 3.17; N, 10.63. Complex 14: yield 63%. IR (Nujol): ν(NH) 3400 (br); ν(CO) 1980 (vs) cm^{-1}. Anal. Calcd for $C_{38}H_{40}N_6BF_4IrOPRh$: C, 45.20; H, 3.99; N, 8.32. Found: C, 44.73; H, 4.19; N, 7.97.

Preparation of $[(\eta^5\text{-}C_5Me_5)Ir\{(\mu\text{-}pz)Ag(PPh_3)\}\{(\mu\text{-}pz)_2Rh(COD)\}]BF_4$ (15). To a suspension of 6 (109.7 mg, 0.148 mmol) in acetone (25 mL) were added 38.9 mg (0.148 mmol) of PPh_3 and 28.9 mg (0.148 mmol) of $AgBF_4$, successively. The resulting yellow solution was stirred during 30 min and then concentrated under vacuum to ca. 2 mL. The precipitation of a yellow solid was completed by addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 64%. Anal. Calcd for $C_{45}H_{51}N_6AgBF_4IrPRh$: C, 45.16; H, 4.29; N, 7.02. Found: C, 45.17; H, 4.39; N, 7.22.

Table V. Crystal Data and Data Collection and Refinement for $[(\eta^5\text{-}C_5Me_5)(pz)Ir(\mu\text{-}pz)_2Ag(PPh_3)]$ (3)

Crystal Data	
formula	$C_{37}H_{39}AgIrN_6P$
mol wt	898.82
color and habit	yellow, prismatic block
cryst size, mm	0.46 × 0.40 × 0.56
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	9.6171 (4)
b, Å	14.2115 (7)
c, Å	26.229 (2)
β, deg	91.90 (1)
V, $Å^3$	3582.9 (4)
Z	4
D(calcd), g cm^{-3}	1.667
Data Collection and Refinement	
diffractometer	4-circle Siemens AED
λ(Mo Kα radiation), Å; technique	0.71069; bisecting geometry
monochromator	graphite oriented
μ, cm^{-1}	43.15
scan type	$\omega - 2\theta$
2θ range, deg	3–50
no. of data collcd	7021
no. of unique data	6139
unique obs data	5498 $(F_o) \geq 5\sigma(F_o)$
no. of params refined	416
R	0.0269
R_w[a]	0.0289
max/min abs corr	1.301/0.829

[a] $w = 0.8775/[\sigma^2(F_o) + 0.00020F_o^2]$.

The yellow complex 16 was similarly prepared starting from complex 8. Complex 16: yield 50%. IR (Nujol): ν(CO) 1985 (vs) cm^{-1}. Anal. Calcd for $C_{56}H_{54}N_6AgBF_4IrOP_2Rh$: C, 48.78; H, 3.94; N, 6.09. Found: C, 48.55; H, 4.33; N, 5.85.

X-ray Structure Analysis of 3. Collection and Reduction of Data. Crystals suitable for an X-ray diffraction experiment were obtained by gas diffusion of hexane into a concentrated solution of 3 in chloroform. A summary of crystal data, intensity collection procedures, and refinement data is reported in Table V. The prismatic crystal studied was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 48 reflections in the range $20 \leq 2\theta \leq 35°$. The 7021 recorded reflections $(-h,+k,\pm l)$ were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by using the DIFABS program.[54]

Structure Solution and Refinement. The structure was solved by Patterson (Ir and Ag) and conventional Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic and subsequent anisotropic thermal parameters for all non-hydrogen atoms of the molecule. Hydrogen atoms were located from difference Fourier maps for pz and PPh_3 ligands and included in calculated positions for methyls of the Cp* group (C–H 1.08 Å). All the hydrogens were refined riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Ir, Ag, and P, were taken from ref 55.

The function minimized was $\sum w([F_o] - [F_c])^2$ with the weight defined as $w = 0.8775/[\sigma^2(F_o) + 0.00020F_o^2]$. Final R and R_w values were 0.0269 and 0.0289, respectively. All calculations were performed by use of the SHELX76 system of computer programs.[56]

Acknowledgment. We thank the Dirección General

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(54) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(55) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(56) Sheldrick, G. M. *SHELX76 Program for Crystal Structure Determinations*; University of Cambridge: Cambridge, England, 1976.

de Investigación Cientifica y Técnica for financial support (Grant 87-0289).

Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates, experimental details of the X-ray study, bond distances and angles (involving non-hydrogen and hydrogen atoms), selected least-squares planes, and interatomic distances (21 pages); a table of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

Insertion of Isocyanides into Metal–Hydrogen Bonds in Triangular Hydrido–Carbonyl Clusters of Rhenium. X-ray Crystal Structures of $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}CHNR)(CO)_{10}]^-$ (R = *p*-Tolyl) and of $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CHNR)(CO)_9]^-$ (R = Cyclohexyl)

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The reaction of the unsaturated triangular cluster anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with isocyanides CNR (R = cyclohexyl or *p*-tolyl) gives in high yields $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}CHNR)(CO)_{10}]^-$, containing a formimidoyl group originated by the transfer of a hydride ligand to the C atom of the isocyanide. Upon heating, this complex looses one CO ligand, giving with good selectivity $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CHNR)(CO)_9]^-$, in a reaction that can be reversed only under high CO pressure (50 atm). The structures of these two formimidoyl species have been elucidated by single-crystal X-ray analyses of their NEt_4^+ salts: $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}CHNC_6H_4Me)(CO)_{10}]^-$ gives monoclinic crystals, space group $P2_1/c$, with a = 16.755 (5) Å, b = 12.705 (5) Å, c = 16.816 (4) Å, β = 117.5 (2)°, Z = 4, and R = 0.030; $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CHNC_6H_{11})(CO)_9]^-$ gives monoclinic crystals, space group $P2_1/a$, with a = 14.589 (7) Å, b = 12.965 (8) Å, c = 16.843 (9) Å, β = 93.99 (4)°, Z = 4, and R = 0.039. Variable-temperature ^{1}H NMR experiments showed that the triple-bridging formimidoyl group undergoes two types of dynamic processes, causing partial or total equalization of the hydrides and consisting presumably in rotations of this ligand on the Re_3 face, through the interchange of its three coordination modes (σ-C, σ-N, π) among the vertices of the triangle. Insertion reactions were observed also upon treatment of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_9(CNC_6H_{11})]^-$ with two-electron-donor molecules, as CO (50 atm) or CNC_6H_{11} itself. In the latter case, two isomers of the complex $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}CHNC_6H_{11})(CO)_9(CNC_6H_{11})]^-$ are formed, likely differing in the coordination of the CNC_6H_{11} ligand (axial syn or anti with respect to the bridging formimidoyl). In all the insertion reactions here reported, the H transfer is supposed to take place in intermediate $[Re_3(\mu\text{-}H)_3H(CO)_9(CNR)L]^-$ adducts, too reactive to be observed. The differences with respect to the analogous reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ are discussed.

Introduction

Isocyanide molecules insert into M–H bonds much more easily than the isoelectronic carbon monoxide,[1] in a reaction that represents the first step of their hydrogenation to amines. In mononuclear complexes, terminally coordinated formimidoyl groups $-C(H){=}NR$ are formed and the two valence electrons lost by the metallic center in the insertion are provided by extra ligands,[2] by the increase in donicity of a ligand,[3] or by dimerization:[4] in polynuclear complexes, in fact, the formimidoyl group itself can provide more electrons, assuming a bridging coordination. In a basic study,[5] Adams and Golembeski demonstrated that, in the triangular osmium cluster $[Os_3(\mu\text{-}H)H(CO)_{10}(CNR)]$, a hydride can be transferred to the isocyanide in two different ways. Upon heating in nondonor solvents, an intramolecular insertion process gives a μ-η^2-coordinated formimidoyl ligand, while, in donor solvents, a μ-η^1-iminyl ${=}C{=}N(H)R$ group is obtained.[6] The last reaction is base catalyzed, and a mechanism involving a proton dissociation step was assumed.[7] Upon further heating, the form-

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[1] Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. Crociani, B. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, Vol. I, 1986.

[2] Christian, D. F.; Clark, G. R.; Roper, W. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Chem. Commun.* **1972**, 458. Christian, D. F.; Roper, W. R. *J. Organomet. Chem.* **1974**, *80*, C35.

[3] Christian, D. F.; Clark, H. C. *J. Organomet. Chem.* **1975**, *85*, C9. Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* **1976**, *112*, 209.

[4] Ciriano, M.; Green, M.; Gregson, D.; Howard, J. A. K.; Spencer, J. L.; Stone, F. A. G.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1294.

[5] Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

[6] The formation of a dinuclear μ-formimidoyl complex was also reported by treatment with Me_3N of an intermediate μ-aminocarbene, formed by reaction of MeNC with $[Co_2(\mu\text{-}PPh_2)_2(\mu\text{-}H)Cp_2]^+$: Zolk, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 577.

[7] Recently, studies on kinetic isotope effects have demonstrated that, for the methyl isocyanide derivative, the conversion to the μ-η^1-iminyl group occurs also in dry benzene, through an intramolecular reaction path, with a significant tunneling component. Upon addition of base, the intermolecular mechanism via proton transfer becomes the faster one: Rosemberg, E. *Polyhedron* **1989**, *8*, 383.

0276-7333/91/2310-3131$02.50/0