Synthesis, Characterization, and Reactivity of Heterodinuclear RuM (M = Cu(I), Ag(I), Au(I), Rh(I), and Ir(I)) and Heterotrinuclear RuAg₂ and RuRhAg **Compounds Derived from the Metal-Complex Ligand** Bis(pyrazolato)(p-cymene)(pyrazole)ruthenium(II)

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The reaction of the mononuclear ruthenium p-cymene pyrazolate complex $[(\eta^6-p-cymene) Ru(pz)_2(Hpz)](1)$ (p-cymene = p-isopropylmethylbenzene; Hpz = pyrazole, $C_3H_4N_2$) with the halide triphenylphosphine complexes $[MCl(PPh_3)]_x$ and KOH led to the corresponding heterodinuclear compounds $[(\eta^6-p-cymene)Ru(pz)_3M(PPh_3)]$ (M = Cu (2), Ag (3), Au (4)). In solution, complexes 2-4 showed a dynamic behavior consisting of exchange between terminal and bridging pyrazolate groups accompanied by dissociation of the phosphine ligand. Complex 3 reacted with AgBF₄ and PPh₃ to yield the heterotrinuclear RuAg₂ complex $[(\eta^6$ p-cymene)Ru(μ -pz)₃{Ag(PPh₃)}₂]BF₄ (**5**) which was also fluxional. Heterodinuclear derivatives of formula $[(\eta^6-p-\text{cymene})(\text{pz})\text{Ru}(\mu-\text{pz})_2\text{ML}_2]$ (M = Rh; L₂ = 1,5-cyclooctadiene (COD) (6), $(CO)_2$ (7). $M = Ir; L_2 = (CO)_2$ (8)) have been prepared by treating complex 1 with the appropriate $[M(acac)L_2](acac = acetylacetonate)$ compounds. The carbonyl complexes 7 and **8** reacted with mono- or diphosphines, rendering $[(\eta^6 - p - \text{cymene})(\text{pz})\text{Ru}(\mu - \text{pz})_2\text{ML}_2]$ (M = Rh; $L_2 = CO, PPh_3$ (9), CO, P(OMe)₃ (10), CO, bis(diphenylphosphino)methane (dppm) (11), dppm (14), 1,2-bis(diphenylphosphino)ethane (dppe) (15), cis-1,2-bis(diphenylphosphino)ethylene (dppen) (16), (R)-(+)-1,2-bis(diphenylphosphino)propane (R-prophos) (17a,b). M = Ir; L₂ = CO, PPh₃ (12), CO, dppm (13), dppe (18)). Protonation of 6-9 and 12 with HBF₄ afforded the corresponding cationic complexes $[(\eta^6-p-\text{cymene})(\text{Hpz})\text{Ru}(\mu-\text{pz})_2\text{ML}_2]\text{BF}_4$ (M = Rh; L₂ = $COD(19), (CO)_2(20), CO, PPh_3(21).$ $M = Ir; L_2 = (CO)_2(22), CO, PPh_3(23)).$ The molecular structure of complex 22 has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, with cell parameters a = 7.9909(6) Å, b = 17.0590(9) Å, c =19.083(2) Å, $\beta = 93.94(1)^{\circ}$, and Z = 4. The molecule exhibits two bridging pyrazolate groups between the metals. No direct intermetallic interaction is observed, the Ru...Ir distance being 3.6770(6) Å. In the solid state, a clear hydrogen bond is present between one fluorine atom of the tetrafluoroborate anion and the pyrazole ligand. The heterotrinuclear RuRhAg cationic derivatives $[(\eta^6-p-cymene)Ru\{(\mu-pz)Ag(PPh_3)\}\{(\mu-pz)_2RhL_2\}]BF_4$ (L₂ = COD (24), CO, PPh_3 (25)) have been prepared on the addition of equimolar amounts of AgBF₄ and PPh₃ to complexes 6 and 9, respectively.

Introduction

A large area of coordination and organometallic chemistry has been developed around polypyrazolylborate anions which includes most transition-metal ions.¹ These anions usually function as tridentate or bidentate ligands and, in solution, often undergo rapid exchange of the coordinated and uncoordinated pyrazolate groups.² Very recently the activation of C-H bonds by pyrazolylborate complexes of rhodium and iridium has received particular attention.^{2e,3} On the other hand, the site of protonation of tripyrazolylborates of rhodium and iridium can not be previously determined. Thus, while protonation of the rhodium complex [HB(Me2pz)3Rh- $(CO)_2$] by HBF₄ takes place at a pyrazolate nitrogen,

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Table 1. ¹H and ³¹P NMR Data^a for Complexes 2-5

			'H						
	<i>p</i> -cymene			pyrazolate ^b				³¹ P	
complex	Me	<i>i</i> -Pr	H _{AA'} /H _{BB'}	H _{3/5}	H _{5/3}	H ₄	PPh ₃	293 K	213 K
2	1.51 (s)	1.00 (d, J = 7.0) 2.25 (sp)	5.20, 5.53 (J = 6.0)	6.61 (bs)	C'	6.05 (bs)	7.5 (m)	1.5 (bs)	0-2 (bs)
3	1.46 (s)	0.97 (d, J = 6.9) 2.17 (sp)	5.26, 5.59 ($J = 6.1$)	6.61 (bs)	С	6.08 (bs)	7.5 (m)	15 (bs)	$15.8 (d, J(^{107}AgP) = 565, J(^{109}AgP) = 653)$
4	1.62 (s)	0.94 (d, J = 6.8) 2.50 (sp)	5.29, 5.62 ($J = 6.0$)	6.60 (bs)	с	6.03 (bs)	7.5 (m)	31.3 (s)	
5	1.39 (s)	0.93 (d, J = 6.8) 2.50 (sp)	5.23, 5.39 ($J = 6.0$)	С	С	6.25 (bs)	7.5 (m)	17.4 (d) J(AgP) = 640	$15.8 (d, J(^{107}AgP) = 573, J(^{109}AgP) = 661), 19.1 (d, J(^{107}AgP) = 641, J(^{109}AgP) = 641, J(^{109}AgP) = 740)$

^a Measured in CDCl₃ at room temperature (¹H) or in CDCl₃/CHCl₃ (1/1, v/v) at 293 or 213 K (³¹P). Chemical shifts in ppm from TMS (¹H) or from 85% H₃PO₄ in D₂O (³¹P) as external standards. J values in hertz. Abbreviations: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; sp, septet; m, multiplet; bm, broad multiplet. ${}^{b} J(H_{3}H_{4}) \approx J(H_{4}H_{5})$. Obscured by the PPh₃ protons.

leading to the cationic compound [HB(Me₂pz)₂(Me₂pzH)-Rh(CO)₂]BF₄, protonation of the homologous iridium complex [HB(Me₂pz)₃Ir(CO)₂], by the same acid, affords the iridium(III) cationic hydride [HB(Me₂pz)₃IrH(CO)₂]-BF₄.⁴ Nevertheless, the iridium complex [HB(Me₂pz)₃Ir-(COD)] (COD = 1,5-cyclooctadiene) is protonated by CF₃SO₃H at a pyrazolate nitrogen, rendering [HB(Me₂ $pz)_2(Me_2pzH)Ir(COD)]CF_3SO_3$.^{2d}

We have recently described the preparation and characterization of the bis(pyrazolato)pyrazole complexes $[(\eta^5 - C_5 Me_5)Ir(pz)_2(Hpz)]^5$ and $(\eta^6 - p$ -cymene)Ru- $(pz)_{2}(Hpz)$ (*p*-cymene = *p*-isopropylmethylbenzene) (1).⁶ From a coordination point of view, these compounds are comparable to protonated tripyrazolylborates and, in fact, we have shown that the iridium anion $[(\eta^5-C_5-$ Me₅)Ir(pz)₃]⁻ (the deprotonated form of $[(\eta^5-C_5Me_5)Ir-$ (pz)₂(Hpz)]) can act as metalloligand toward a variety of metallic fragments showing η^2 or η^3 coordination modes.⁷

In this paper we describe the synthesis and characterization of heterodinuclear RuM (M = Cu(I), Ag(I), Au-(I), Rh(I), Ir(I)) complexes in which the $[(\eta^6-p-cymene) Ru(pz)_3$]⁻ anion is acting as metal-complex ligand. Their general formulae are $[(\eta^6-p-\text{cymene})\text{Ru}(\text{pz})_3\text{M} (PPh_3)$] (M = Cu (2), Ag (3), Au (4)) and [(η^6 -p $cymene)(pz)Ru(\mu-pz)_2ML_2] (M = Rh, L_2 = COD (6);$ (CO)₂ (7); CO, PPh₃ (9); CO, P(OMe)₃ (10); CO, bis-(diphenylphosphino)methane (dppm) (11); dppm (14); 1,2-bis(diphenylphosphino)ethane (dppe) (15); cis-1,2bis(diphenylphosphino)ethylene (dppen) (16); (R)-(+)-1,2-bis(diphenylphosphino)propane (*R*-prophos) (17a,b). $M = Ir, L_2 = (CO)_2$ (8); CO, PPh₃ (12); CO, dppm (13); dppe (18)). Taking into account the different possibilities of protonation of these compounds, we also report the reactivity of some of them with HBF_4 to give the cationic complexes $[(\eta^6-p-cymene)(Hpz)Ru(\mu-pz)_2ML_2]$ - BF_4 (M = Rh, L₂ = COD (19); (CO)₂ (20); CO, PPh₃ (21); $M = Ir, L_2 = (CO)_2 (22); CO, PPh_3 (23))$ as well as the preparation of the trinuclear cationic derivatives [$(\eta^{6}$ p-cymene)Ru(μ -pz)₃{Ag(PPh₃)}₂]BF₄ (5) and [(η^6 -pcymene) $Ru{(\mu-pz)Ag(PPh_3)}{(\mu-pz)_2RhL_2}]BF_4 (L_2 = COD$ (24); CO, PPh₃ (25)). The molecular structure of the RuIr complex $[(\eta^6-p-\text{cymene})(\text{Hpz})\text{Ru}(\mu-\text{pz})_2\text{Ir}(\text{CO})_2]\text{BF}_4$ (22) is also described.

Results and Discussion

Heterometallic Complexes $[(\eta^6 - p - Cymene)Ru$ - $(pz)_{3}M(PPh_{3})$] (M = Cu, Ag, Au) and [(η^{6} -p-Cymene) $Ru(\mu - pz)_3 \{Ag(PPh_3)\}_2 BF_4$. The reaction in acetone or methanol of the mononuclear ruthenium complex $[(\eta^6-p\text{-cymene})\text{Ru}(\text{pz})_2(\text{Hpz})]$ (1)⁶ with the chloride compounds $[MCl(PPh_3)]_x$ (x = 4, M = Cu,⁸ Ag;⁹ x = 1, $M = Au^{10}$) and equimolar amounts of KOH afforded the heterobinuclear complexes $[(\eta^6-p-\text{cymene})\text{Ru}(\text{pz})_3\text{M} (PPh_3)$] (M = Cu (2), Ag (3), Au (4)) in yield ranging from 75 to 89%. The new compounds have been characterized by elemental analyses¹¹ (see Experimental Section) and IR and NMR spectroscopy. In particular, the IR spectra showed the characteristic bands of the pyrazolate (ca. 1050 cm^{-1})¹² and triphenylphosphine (ca. 500 cm^{-1})¹³ ligands and the absence of the N-H vibration of the starting material. ¹H and ³¹P{¹H} NMR data are recorded in Table 1. The ¹H NMR spectra, in $CDCl_3$ at room temperature, showed the expected resonances for the protons of the *p*-cymene, pyrazolate, and PPh₃ ligands and indicated the presence of only one type of pyrazolate group. On cooling to 213 K, two pyrazolate environments in a 2/1 ratio were observed but the slow-exchange limiting spectra were not achieved

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Scheme 1. Proposed Mechanism for the Fluxional Processes of 2-4



M = Cu(I), Ag(I), Au(I)

in any case. Their ${}^{31}P{}^{1}H$ spectra showed, at room temperature, broad signals centered at 1.5 and 15 ppm for 2 and 3, respectively, and a sharp singlet at 31.3 ppm for 4. At 213 K the spectrum of complex 2 was similar to that registered at ambient temperature and showed a broad signal in the 0-2 ppm region. However, the spectrum of complex 3 consisted of two doublets of similar intensity centered at 15.8 ppm $({}^{1}J({}^{107}AgP) =$ 565, ${}^{1}J({}^{109}\text{AgP}) = 653 \text{ Hz})$ consistent with direct Ag-P bonding.¹⁴ The spectrum of the RuAu complex 4 did not show significant changes on varying the temperature from 293 to 213 K.

We have recently determined the molecular structure of the related IrAg complex $[(\eta^5-C_5Me_5)Ir(pz)_3Ag(PPh_3)]$ by single-crystal X-ray analysis. In this molecule two pyrazolate groups bridge the iridium and silver atoms and the third pyrazolate is terminal and only coordinates to iridium.^{7a} Interestingly, the spectroscopic data of $[(\eta^5 - C_5 Me_5)Ir(pz)_3Ag(PPh_3)]$ are comparable to those of 3 and, therefore, both compounds probably adopt similar structures. The spectroscopic observations can be accounted for by assuming that, at room temperature, there is a rapid equilibrium between structures which exchange bridging and terminal pyrazolate groups through an intermediate in which M is tetracoordinate as depicted in Scheme 1. Additionally, an equilibrium of dissociation of the triphenylphosphine must be invoked to account for the observed ${}^{31}P{}^{1}H$ NMR spectra. In fact, the ³¹P{¹H} NMR spectrum of **3**, at room temperature, in the presence of 1 equiv of PPh₃, consisted of a peak at 4.8 ppm without coupling to silver, indicative of a fast exchange between free and coordinated PPh₃. Fluxional processes involving exchanges between free and coordinated pyrazolate groups have been observed in polypyrazolylborate complexes of Cu(I)¹⁵ and Ag(I),^{15c} and lability of PR3 groups is a phenomenon commonly observed.¹⁶ The activation energies for the rupture of $P{-}Ag$ bonds are in the zone of barriers that can be measured by NMR spectroscopy, and, very recently, we have determined by a complete NMR line shape analysis that the rupture activation energy in complex 3 is 46kJ mol⁻¹, comparable to those determined for other phosphorus-metal bonds.¹⁷

As commented above, complexes 2-4 contain one pyrazolate ligand in which one nitrogen atom is capable of subsequent coordination. In order to probe this capacity, we performed the reaction of $[(\eta^6-p-cy$ mene) $Ru(pz)_3Ag(PPh_3)$] with AgBF₄ and PPh₃. When 3 was treated with equimolar amounts of $AgBF_4$ and PPh₃, a yellow solid characterized as the trinuclear complex $[(\eta^6-p-cymene)Ru(\mu-pz)_3 \{Ag(PPh_3)\}_2]BF_4(5)$ was obtained in 77% isolated yield. Subsequent addition of $AgBF_4$ and PPh₃ to **5** did not produce the corresponding reaction, and complex 5 remained unchanged. At room temperature, the ¹H NMR spectrum of complex 5 (Table 1) showed a unique environment for the pyrazolate groups. The ³¹P{¹H} NMR spectrum of 5, at room temperature, showed two very broad signals centered at 17.4 ppm and separated by ca. 640 Hz, which we assigned to directly bound to silver PPh₃ groups. At 213 K the ¹H NMR showed a slight broadening of the pyrazolate signal, whereas the ${}^{31}P{}^{1}H$ spectrum consisted of four doublets. Two were centered at 15.8 ppm, with coupling constants ${}^{1}J({}^{107}\text{AgP}) = 573$ and ${}^{1}J({}^{109}\text{AgP})$ = 661 Hz, and the other two at 19.1 ppm, with ${}^{1}J({}^{107}\text{AgP}) = 641$ and ${}^{1}J({}^{109}\text{AgP}) = 740$ Hz. These spectral data could be explained by assuming that a fluxional process consisting of the rotation of the two $AgPPh_3$ groups of molecule 5 around the three free

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Scheme 2. Proposed Mechanism for the Fluxional Processes of Complex 5. Ag₁ and Ag₂ Represent the Two AgPPh₃ Groups of the Cation and N_1 , N_2 , and N₃ the Three Pyrazolate Nitrogen Atoms Not

Coordinated to Ruthenium (See Text)



nitrogen atoms of the $(\eta^6$ -p-cymene)Ru(pz)₃ moiety was occurring in a concerted way as it is schematically represented in Scheme 2. So, the static structure proposed for 5 consists of a trigonal silver atom coordinated to two bridging pyrazolates and one PPh₃ group and one digonal Ag atom bound to one bridging pyrazolate group and one PPh₃ ligand (Figure 1). The chemical shifts and the coupling constants of the two phosphorus nuclei of 5 in the low-temperature limiting spectrum have been assigned by comparison with those of the precursor **3** at the same conditions.

Heterometallic Complexes [(η^{6} -*p*-Cymene)- $(\mathbf{pz})\mathbf{Ru}(\mu - \mathbf{pz})_2\mathbf{ML}_2$ (M = Rh, Ir). The ruthenium complex $[(\eta^6-p\text{-cymene})\text{Ru}(pz)_2(\text{Hpz})]$ (1) reacted with equimolar amounts of $[M(acac)L_2]$ (M = Rh; L₂ = COD,¹⁸ $(CO)_2$.¹⁹ M = Ir; L₂ = $(CO)_2^{20}$) to give the corresponding heterodinuclear complexes $[(\eta^6-p-cymene)(pz)Ru(\mu-pz)_2 ML_2$] (M = Rh; L_2 = COD (6), (CO)₂ (7). M = Ir; L_2 = $(CO)_2$ (8)). With $[Ir(acac)(COD)]^{21}$ the above reaction led to a mixture of $[Ir(\mu-pz)(COD)]_2^{22}$ and unidentified p-cymene-ruthenium products, which were probably formed by fragmentation of the unstable dinuclear intermediate $[(\eta^6-p-\text{cymene})(\text{pz})\text{Ru}(\mu-\text{pz})_2\text{Ir}(\text{COD})]$. The dicarbonyl RuRh derivative 7 could also be prepared upon bubbling CO through dichloromethane or tetrahydrofuran solutions of complex 6. The very high solubility of complex 8, even in hydrocarbon solvents, precluded its isolation. Its formation was inferred from IR solution data and from its chemical reactivity. The structures of 6 and 7 were assigned on the basis of elemental microanalyses and IR and NMR spectroscopic measurements. In the IR spectra the absence of the bands corresponding to the acac group²³ and to the ν -(NH)¹² vibration of the starting materials was observed. Furthermore, complexes 7 and 8 showed the characteristic cis-dicarbonyl bands²⁴ at ca. 2000 and 2080 cm⁻¹.



Figure 1. Schematic structure of complex **5** with ${}^{31}P{}^{1}H{}$ NMR data assignments.

The ¹H NMR spectra of complexes **6** and **7**, in $CDCl_3$ at room temperature, showed, besides the expected resonances of the *p*-cymene and diolefin ligands, two sets of pyrazolate signals in a 2/1 ratio. As the temperature was increased, a slight broadening of the signals was observed although, until 363 K in toluene- d_8 , the fast exchange limiting spectra were not achieved. These data indicated that in solution a dynamic equilibrium between structures that slowly exchange the two types of chemically inequivalent pyrazolates was taking place above room temperature. Three static structures (excluding the uncommon one with a tricoordinate rhodium atom) are compatible with the spectral data (Figure 2). In structure A two pyrazolates are bridging the two metals while the third pyrazolate is only coordinated to ruthenium. In structures **B** and **C** a triple pyrazolate bridge connects the two metals, rendering M fivecoordinated and displaying square-pyramidal (B) or trigonal-bipyramidal (C) geometries. In the first case, an exchange between free and coordinated pyrazolate groups can be postulated to explain the fluxional process, whereas an exchange between axial and equatorial nitrogen atoms would account for the spectral data in the case of structures \mathbf{B} and \mathbf{C} . Both types of dynamic processes have been reported for the related complexes [B(pz)₄Rh(diolefin)],^{2b} exchange between axial and equatorial sites occurring faster than that involving mono- and bidentate ligands. In our case, as the dynamic processes involving complexes 6 and 7 were still slow at 363 K, we propose they adopt structure A with the M atom being four-coordinated. This proposal was also supported by the shift to higher field observed for the resonance of the H_5 proton of the terminal pyrazolate ring in 6 and 7 (Table 2). Most probably this shielding is produced by the electronic ring current of the bridging pyrazolates^{5,7} which is only possible in structure A. In fact, the molecular structure of the related complex $[(\eta^6-p-\text{cymene})(\text{Hpz})\text{Ru}(\mu-\text{pz})_2\text{Ir}(\text{CO})_2]$ - BF_4 (22) (see below) exhibits an azolate ligand disposition comparable to that of **A**. Finally, the reactivity shown by complexes 6-8 also corroborates the proposed structure.

Reactivity of Complexes $[(\eta^6 - p - Cymene)(pz)Ru$ - $(\mu$ -pz)₂M(CO)₂]. (a) With Mono- or Bidentate Phosphorus Donor Ligands. The dicarbonyl complexes 7 and 8 reacted with monodentate phosphorus donor ligands or dppm to give the monocarbonyl dinuclear complexes $[(\eta^6-p-cymene)(pz)Ru(\mu-pz)_2M(CO)L]$ (M = Rh; $L = PPh_3$ (9), P(OMe)₃ (10), dppm (11). M = Ir; L

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⁽²⁰⁾ $[Ir(acac)(CO)_2]$ can be prepared by bubbling CO at atmospheric pressure through *n*-hexane solutions of [Ir(acac)(COD)]. The starting yellow solutions became dark in a few seconds, and a brown-blue solid began to precipitate which, after filtering and drying, is characterized began to precipitate which, after intering and drying, is characterized as the dichroic [Ir(acac)(CO)₂]. Yield: 90%. Ir (Nujol) ν(CO) 2050 (vs), 1990 (vs) cm⁻¹. Anal. Caled for C₇H₇IrO₄: C, 24.20; H, 2.03. Found: C, 24.12; H, 1.95. ¹H NMR (CDCl₃, δ): 5.76 (s, 1H), 2.09 (s, 6H). (21) Robinson, S. D.; Shaw, B. L. J. Chem. Soc. 1965, 4997. (22) Coleman, A. W.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J.; Atwood, J. L. J. Am. Chem. Soc. 1982, 104, 922. (20) Birthy, W. Lee, H. B. Pacilar, P. M. ACD wave the A. Maithia.

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Figure 2. Possible static structures for complexes 6-8.

Table 2.	¹ H NMR	Data ^a for	Complexes	6-25
			COMPLEX.	

	<i>p</i> -cymene			terminal pz ^b			bridging pz ^b			
complex	Me	i-Pr	H _{AA'} /H _{BB'}	H ₃	H ₅	H ₄	H ₃	H ₅	H ₄	others
6	1.71 (s)	1.11 (d, $J = 6.9$) 2.32 (sp)	5.97, 6.12 ($J = 5.8$)	7.61 (d)	5.56 (d)	5.86 (t, $J = 1.5$)	7.41 (d)	6.56 (d)	6.00 (t, J = 1.8)	4.43 (m), 3.95 (m), 2.66 (m), 2.00 (m) (COD)
7	1.70 (s)	1.08 (d, J = 7.0) 2.40 (sp)	5.70, 5.89 ($J = 5.9$)	7.64 (bs)	5.83 (d)	5.92 (t, $J = 1.8$)	7.54 (d)	6.68 (d)	6.13 (t, $J = 2.1$)	(000)
9 ¢	1.71 (s)	1.03 (d, J = 6.8) 1.14 (d, J = 6.8) 2.52 (sp)	5.22 (t) ^d 6.22, 6.38 ($J = 5.7$)	7.63 (d)	5.61 (d)	5.86 (t, $J = 1.7$)	7.68 (d) 6.73 (d)	6.66 (t) 6.60 (d)	$\begin{array}{l} 6.11 \; (\mathbf{q}, J = 2.0^e) \\ 5.76 \; (\mathbf{t}, J = 1.8) \end{array}$	7.4 (m, PPh ₃)
10 ^c	1.68 (s)	1.07 (d, J = 6.8) 2.38 (sp)	5.68, 5.83 (J = 6.0) 5.17, 6.20 (J = 6.0)	7.63 (bs)	5.82 (bs)	5.99 (t, $J = 1.8$)	7.63 (s) 7.44 (bs)	6.73 (t) 6.53 (bs)	6.12 (q, $J = 1.9^{e}$) 5.91 (bs)	3.79 (d, J(PH) = 12.0, OMe)
11 ¢	1.61 (s)	0.93 (d, J = 7.0) 1.08 (d, J = 6.9) 2.40 (sp)	5.17, 6.32 (J = 6.0)	f	5.60 (d)	5.85 (t, $J = 1.9$)	f f	6.64 (bs) 6.54 (d)	$6.10 \text{ (bs)} \\ 5.81 \text{ (t, } J = 1.9)$	3.5 (m), 7–8 (m, dppm)
12 ^c	1.70 (s)	1.01 (d, $J = 6.8$) 1.11 (d, $J = 6.8$) 2.50 (sn)	5.19, f(J = 5.8) 6.16, 6.31 (J = 6.0)	7.59 (d)	5.74 (d)	5.83 (t, $J = 1.9$)	7.77 (d) 6.80 (d)	6.68 (t) 6.58 (d)	$\begin{array}{l} 6.11 \; (\mathbf{q}, J = 2.1^{e}) \\ 5.55 \; (\mathbf{t}, J = 1.9) \end{array}$	7.4 (m, PPh ₃)
13 ^c	1.61 (s)	$\begin{array}{l} 2.56 \text{ (sp)} \\ 0.93 \text{ (d, } J = 6.8) \\ 1.05 \text{ (d, } J = 6.9) \\ 2.43 \text{ (sp)} \end{array}$	5.14, 6.27 $(J = 6.0)$	f	5.54 (d)	5.82 (t, $J = 1.9$)	${f \over f}$	6.65 (bs) 6.54 (d)	6.10 (bs) 5.81 (t)	3.4 (m), 4.2 (m), 7-8 (m) (dppm)
14	1.18 (s)	0.91 (d, J = 6.6) 1.97 (sp)	5.59, 5.94 ($J = 6.0$)	f	5.59 (d)	5.89 (bm)	f	6.54 (d)	5.89 (bm)	3.5 (m), 4.3 (m), 7-8 (bm, dppm)
15	0.79 (s)	0.90 (d, J = 6.8) 2.12 (sp)	5.32 $(t)^d$	f	5.63 (d)	5.81 (t, $J = 1.5$)	f	6.47 (d)	5.89 (t, $J = 1.9$)	1.8 (m), 2.1 (m), 7-8 (bm) (dppe)
16	0.58 (s)	0.85 (d, J = 6.8) 1.67 (sp)	5.16 (bm) ^d	f	5.69 (d)	5.82 (t, $J = 1.5$)	f	6.47 (d)	5.84 (t, $J = 1.9$)	1.7 (m), 2.7 (m), 7-8 (bm) (dppen)
18 ^g	0.82 (s)	0.90 (d, J = 6.8) 2.70 (sp)	5.26, 5.30 (J = 6.2)	f	5.63 (d)	5.81 (t, $J = 1.5$)	f	6.47 (d)	5.84 (t, $J = 1.9$)	1.8 (m), 2.5 (m), 7-8 (bm) (dppe)
19	1.76 (s)	1.12 (d, $J = 6.8$) 2.25 (sp)	$6.28 (s)^d$	7.87 (d)	5.85 (d)	6.08 (t, J = 1.8)	7.44 (d)	6.51 (d)	6.08 (t, $J = 2.1$)	1.9 (m), 2.6 (m), 3.9 (m), 4.4 (m) (COD), 12.1 (bs. NH)
20	1.74 (s)	1.11 (d, J = 6.9) 2.25 (sp)	6.00, 6.11 ($J = 6.2$)	7.98 (d)	5.96 (d)	6.16 (t, $J = 1.9$)	7.60 (d)	6.67 (d)	6.24 (t, $J = 2.2$)	12.4 (bs, NH)
21 ^c	1.68 (s)	1.05 (d, J = 6.9) 1.10 (d, J = 6.8) 2.20 (sp)	5.46, 6.35 $(J = 6.1)$ 5.66, 6.40 $(J = 5.9)$	7.89 (d)	5.80 (bs)	6.10 (t, $J = 2.5$)	7.70 (d) 6.81 (d)	6.51 (t) 6.58 (d)	6.18 (q, $J = 2.1^{e}$) 5.87 (t, $J = 2.2$)	12.2 (bs, NH), 7.5 (m, PPh ₃)
22	1.77 (s)	1.12 (d, J = 6.9) 2.33 (sp)	6.08, 6.17 (<i>J</i> = 5.9)	8.04 (s)	5.87 (d)	6.14 (d)	7.75 (d)	6.75 (d)	6.29 (t, <i>J</i> = 1.9)	12.4 (bs, NH)
23°	1.68 (s)	1.03 (d, $J = 6.9$) 1.07 (d, $J = 6.8$) 2.20 (sp)	5.46, 6.35 $(J = 6.1)$ 5.66, 6.40 $(J = 5.9)$	7.80 (s)	5.66 (bs)	6.07 (t, $J = 2.5$)	7.90 (d) 6.88 (d)	6.58 (t) 6.54 (d)	6.19 (q, $J = 2.1^{e}$) 5.86 (t, $J = 2.2$)	12.2 (bs, NH), 7.5 (m, PPh ₃)

	<i>p</i> -cymene			Ru-pz-Ag ^b			Ru-pz-Rh ^b			
complex	Me	<i>i</i> -Pr	H _{AA'} /H _{BB'}	H ₃	H_5	H ₄	H ₃	H ₅	H ₄	others
25 ^c	1.68 (s)	1.05 (d, J = 6.9) 1.10 (d, J = 6.8) 2.20 (sp)	5.47, 6.36 (J = 5.9) 5.67, 6.41 (J = 6.4)	7.93 (t)	5.76 (t)	6.10 (q, $J = 1.9^{e}$)	7.70 (d) 6.81 (d)	6.51 (t) 6.59 (d)	$6.19 (q, J = 2.0^{e})$ 5.87 (t, J = 2.1)	7.5 (m, PPh ₃)

"All conditions as stated in footnote *a* in Table 1. ^{*b*} For labeling of pyrazolate protons, see Figure 2. $J(H_3H_4) \approx J(H_4H_5)$. ^{*c*} Pyrazolate protons assigned through selective decoupling experiments. The first set of bridging pyrazolate resonances corresponds to the pyrazolate group *trans* to the phosphorus ligand. ^{*d*} Four aromatic protons. ^{*e*} $J(HP) \approx J(H_3H_4) \approx J(H_4H_5)$. ^{*f*} Obscured by the phosphorus ligand protons. ^{*s*} In (CD₃)₂CO.

= PPh₃ (12), dppm (13)). The non-carbonyl-containing derivatives $[(\eta^6-p\text{-cymene})(pz)\text{Ru}(\mu\text{-}pz)_2M(\text{LL})]$ (M = Rh; LL = dppm (14), dppe (15), dppen (16), *R*-prophos (17a,b). M = Ir; LL = dppe (18)) were obtained by treating 7 and 8 with the appropriate diphosphine ligand. Complexes 14–18 were most probably formed via the monocarbonyl intermediates $[(\eta^6-p\text{-cymene})(pz)\text{-}$ $\text{Ru}(\mu\text{-}pz)_2M(\text{CO})(\text{LL})]$, which we have been able to isolate in the case of the dppm derivatives 11 and 13. Monocarbonyl complexes **9–13** have been characterized by microanalyses (see Experimental Section) and IR and ¹H and ³¹P{¹H} NMR spectroscopies (Table 2). The IR spectra showed a strong ν (CO) band in the 1950–2000 cm⁻¹ region, characteristic of four-coordinated square-planar monocarbonyl rhodium or iridium-(I) complexes. Moreover, their ¹H NMR spectra, at room temperature, showed three different AMX systems corresponding to the three pyrazolate groups. The chemical shifts and the relative intensities of the signals were in accord with a structure containing two bridging and one terminal pyrazolate ligand, the rhodium or iridium atoms being four-coordinated. The ${}^{31}P{}^{1}H{}$ NMR spectra of the dppm complexes 11 and 13 showed one high-field doublet (at -25.7 ppm) and one doublet of doublets for the RuRh complex 11 and two doublets (one of them at -26.3 ppm) for the RuIr complex 13, which unequivocally established the monodentate coordination of the diphosphine.

The ¹H NMR spectra of complexes **14**–**18** showed two sets of signals, in a 2/1 ratio, assigned to two bridging and one terminal pyrazolate. The ³¹P{¹H} spectra showed the equivalence of both phosphorus nuclei and consisted of one doublet with characteristic phosphorus– rhodium coupling constants (complexes **14**–**16**) or one singlet (compound **18**). The ruthenium atom in the monocarbonyl complexes **9**–**13** and in the *R*-prophos derivative **17** is a chiral center. Thus, we have prepared complexes **9**–**13** as racemic mixtures of the two possible enantiomers. In the case of the chiral *R*-prophos ligand, the two diastereomers $R_{\rm Ru}R_{\rm C}$ and $S_{\rm Ru}R_{\rm C}$ (**17a,b**) were stereoselectively formed, the diastereomeric excess being 33%.

All the data described so far allowed assignment of dinuclear structures of the A type (see Figure 2) to complexes 9-18.

(b) With Tetrafluoroboric Acid. Complexes 6-18 could potentially be protonated either at nitrogen of the terminal pyrazolate group or at M metal. Both types of processes have been reported in the polypyrazolylborate chemistry of these metals.⁴ In order to determine where protonation occurs in these complexes, we have reacted some of them with HBF₄. When complexes [$(\eta^6$ p-cymene)(pz)Ru(μ -pz)₂ML₂] (M = Rh; L₂ = COD (6), $(CO)_2$ (7), CO, PPh₃ (9). M = Ir; L₂ = $(CO)_2$ (8), CO, PPh_3 (12)) in THF or diethyl ether were treated with equimolar amounts of HBF₄, the cationic derivatives $[(\eta^6 \text{-}p\text{-}cymene)(Hpz)Ru(\mu\text{-}pz)_2ML_2]BF_4$ (M = Rh; L₂ = COD (19), $(CO)_2$ (20), CO, PPh_3 (21). $M = Ir; L_2 = (CO)_2$ (22), CO, PPh₃ (23)) were obtained. The IR spectra of complexes 19-23 showed broad bands in the region of 3300 cm⁻¹ assigned to ν (NH) stretching vibrations as well as the characteristic bands due to the BF₄ anion under T_d symmetry.²⁵ The frequencies of their $\nu(CO)$ bands were very similar to those found for their corresponding precursors, and the values of the resonances and coupling constans of the phosphorus nuclei of complexes 21 and 23 were comparable to those of their respective parents 9 and 12 (see Experimental Section). The ¹H NMR spectra of **19–23** showed a broad resonance at low field but nothing below the TMS signal. The AMX systems of the pyrazolate protons appeared slightly more withdrawn than the respective protons in the neutral precursors. All these spectroscopic observations strongly support the fact that protonation occurs at the uncoordinated nitrogen atom of the terminal pyrazolate as confirmed by the determination of the molecular structure of compound 22 by X-ray diffraction methods (see below). Interestingly, protonation takes place on the pyrazolate group even in the iridium complexes 8 and 12. This behavior contrasted with that found in the related tripyrazolylborate complexes [HB-



Figure 3. ORTEP view of the cation of the complex $[(\eta^6 - p\text{-cymene})(\text{Hpz})\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{CO})_2]\text{BF}_4$ (22).

Table 3.	Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Ir and Ru
Atoms) and	d Equivalent Isotropic Displacement Coefficients
	$(Å^2 \times 10^3)$ for 2^2

	(7)			
atom	x/a	y/b	z/c	U(eq)"
Ir	13608(3)	8714(1)	11255(1)	58(1)
Ru	27432(5)	28992(3)	14706(2)	41(1)
O(1)	2849(9)	-164(3)	70(3)	108(3)
O(2)	1591(9)	-393(4)	2203(4)	121(3)
N(1)	1165(5)	3859(3)	1224(3)	53(2)
N(2)	1681(6)	4601(3)	1145(3)	67(2)
N(3)	646(5)	2391(3)	1889(2)	47(2)
N(4)	267(6)	1616(3)	1813(2)	54(2)
N(5)	1731(6)	2492(3)	500(2)	50(2)
N(6)	1157(6)	1751(3)	387(2)	54(2)
C(1)	2297(10)	225(4)	470(4)	77(3)
C(2)	1504(11)	87(5)	1795(5)	88(3)
C(3)	-491(8)	3886(4)	1095(4)	75(3)
C(4)	-1018(8)	4649(4)	945(4)	80(3)
C(5)	378(10)	5079(4)	996(4)	81(3)
C(6)	-304(7)	2680(4)	2381(3)	58(2)
C(7)	-1324(7)	2098(4)	2617(3)	64(2)
C(8)	-916(8)	1444(4)	2259(3)	65(2)
C(9)	1513(9)	2881(4)	-105(3)	67(2)
C(10)	798(10)	2416(5)	-611(3)	83(3)
C(11)	607(9)	1708(5)	-296(4)	78(3)
C(12)	4734(7)	2037(4)	1729(4)	60(2)
C(13)	4211(7)	2376(4)	2358(3)	55(2)
C(14)	4256(7)	3200(4)	2460(3)	55(2)
C(15)	4776(6)	3667(3)	1897(3)	49(2)
C(16)	5279(7)	3331(4)	1270(3)	53(2)
C(17)	5267(7)	2512(4)	1189(3)	60(2)
C(18)	5766(10)	2137(5)	526(4)	91(3)
C(19)	3749(9)	3540(5)	3134(3)	72(3)
C(20)	3086(12)	4372(6)	3088(4)	102(4)
C(21)	5201(12)	3478(5)	3691(4)	104(4)
В	4965(15)	5908(6)	1169(6)	93(3)
$F(1a)^b$	4784(16)	5233(8)	686(8)	110(4)
F(2a) ^b	4678(17)	5675(7)	1910(6)	114(4)
F(3a) ^b	6311(13)	6302(7)	1115(7)	98(3)
F(4a) ^b	3703(16)	6419(8)	1067(8)	133(5)
$F(1b)^b$	4951(12)	5152(6)	923(6)	66(3)
F(2b) ^b	3886(21)	5884(8)	1657(8)	119(5)
F(3b) ^b	6664(14)	6132(7)	1405(7)	85(4)
F(4b) ^b	4003(22)	6389(11)	594(12)	172(8)

^{*a*} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{*b*} This group of atoms, involved in disorder, were refined with isotropic displacement parameters. The refined occupancy factors were 0.54(2) for a-labeled atoms and 0.46(2) for b-labeled ones.

 $(dmpz)_3M(CO)_2]\,(M=Rh,\,Ir).$ While protonation of the rhodium complex takes place at the nitrogen of the free pyrazolate group, protonation of the iridium complex occurs at the metal.⁴

Molecular Structure of $[(\eta^6-p-Cymene)(Hpz)Ru(\mu-pz)_2Ir(CO)_2]BF_4$ (22). Figure 3 shows a view of the cationic complex, together with the atom labeling used.

⁽²⁵⁾ Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds, 2nd ed.; John Wiley and Sons: 1970; p 110.

 Table 4.
 Selected Bond Distances (Å) and Angles (deg)

 for 22

	101		
Ir-C(1)	1.862(8)	Ru-N(1)	2.101(5)
Ir-C(2)	1.849(8)	Ru-N(3)	2.093(5)
Ir - N(4)	2.062(5)	Ru - N(5)	2.088(4)
Ir = N(6)	2.058(5)	Ru-G"	1.697(5)
C(1) = O(1)	1.125(10)	C(2) - O(2)	1.128(11)
N(1) - N(2)	1.343(7)	N(3) - N(4)	1.362(7)
N(1) - C(3)	1.330(7)	N(3) - C(6)	1.341(8)
N(2) - C(5)	1.337(9)	N(4) - C(8)	1.346(8)
C(3) - C(4)	1.391(11)	C(6) - C(7)	1.379(9)
C(4) - C(5)	1.333(10)	C(7) - C(8)	1.360(10)
N(5) - N(6)	1.357(7)	N(5) - C(9)	1.332(8)
N(6) - C(11)	1.348(8)	C(9) - C(10)	1.347(10)
C(10)-C(11)	1.362(11)		
C(1) = Ir = C(2)	91.5(3)	N(1) = Ru = N(3)	85.7(2)
C(1) = Ir = N(4)	177.3(3)	N(1) - Ru - N(5)	82.5(2)
C(1) - Ir - N(6)	89.3(3)	N(3) - Ru - N(5)	85.9(2)
C(2) - Ir - N(4)	90.8(3)	$N(1)=Ru=G^{a}$	131.4(3)
C(2) - Ir - N(6)	178.9(3)	$N(3)-Ru-G^{a}$	126.4(3)
N(4) - Ir - N(6)	88.3(2)	$N(5)=Ru=G^{a}$	129.0(2)

"G represents the centroid of the p-cymene ring.

Atomic positional parameters and selected bond lengths and angles are presented in Tables 3 and 4, respectively. The cation consists of one ruthenium and one iridium atom bridged by two pyrazolate groups. The ruthenium atom completes its pseudooctahedral coordination through bonding to an η^6 -*p*-cymene ring and to a terminal pyrazole ligand. The Ru-*p*-cymene bond distance, 1.697(5) Å, falls in the upper range of those found in p-cymene-ruthenium complexes with pyra-zolate ligands.^{6,26,27} Two carbon monoxide terminal groups complete the square-planar coordination of the iridium, angles around it adding 359.9°. The sixmembered RuN₄Ir cyclic core is bent into a boat conformation, which brings the two metals to 3.6770(6)Å from one another. This intermetallic separation excludes any significant metal-metal interaction. The Ru-N(3) and Ru-N(5) (mean 2.090(4) Å) and Ir-Nbond distances (mean 2.060(4) Å) compare well with the averaged bond distances found in related compounds of these metals with pyrazolate bridging ligands such as $[(\eta^6-p-\text{cymene})ClRu(\mu-pz)_2M(CO)_2]$ (M = Ir; Ru-N = 2.083(3) Å, Ir-N = 2.062(3) Å. M = Rh; Ru-N = 2.086- $(2) Å)^{26} [{(\eta^6-p-cymene)Ru}_2(\mu-pz)_2(\mu-OH)]BPh_4 (Ru-N)^{-1}$ $= 2.086(2) \text{ Å})^{27} [\{(\eta^{6}\text{-benzene})\text{Ru}\}_{2}(\mu\text{-pz})_{2}(\mu\text{-Cl})]\text{Cl} (\text{Ru}-\text{N}) \\= 2.083(3) \text{ Å})^{28} [\text{Ir}(\mu\text{-pz})(\text{CO})(\text{PPh}_{3})]_{2} (\text{Ir}-\text{N}) = 2.07(1) \\$ Å),²⁹ $[Ir(\mu-pz)(COD)]_2$ $(Ir-N = 2.081(8) Å).^{30}$ Complex 22 has been prepared by protonation of the neutral compound [$(\eta^6$ -p-cymene)(pz)Ru(μ -pz)₂Ir(CO)₂] with HBF₄. The N(2) $\cdot \cdot F(1b)$ separation, 2.836(11) Å, is indicative of the existence of a $N-H \cdot \cdot F$ interaction. Furthermore, the C-C bond distances (1.333(10) vs 1.391(10) Å)within the terminal pyrazole ring suggest a partial localization of the electronic density toward a N=C-C=C-NH bond distribution as expected for a protonated pyrazole. These structural data along with the spectroscopic data, reported above, strongly sup-





Figure 4. Schematic structure proposed for complexes 24 and 25.

ported the fact that the free nitrogen of the terminal pyrazole of the parent complex has been protonated in the reaction. However, although from the crystallographic data a N-H···F interaction is evident, no significant shift to lower energies of the ν (NH) stretching frequency (3320 cm⁻¹, Nujol mull) has been observed.

(c) With AgBF₄ and PPh₃. The free nitrogen atom of the neutral complexes $[(\eta^6-p-\text{cymene})(pz)Ru(\mu-pz)_2-$ ML₂] could be coordinated to unsaturated metallic fragments as, for example, the cationic moiety AgPPh₃⁺. Thus, addition of equimolar amounts of AgBF₄ and PPh₃ to THF solutions of 6 (M = Rh, $L_2 = COD$) or 9 (M = Rh, $L_2 = (CO)$, PPh₃) afforded the cationic heterotrinuclear complexes $[(\eta^6-p-\text{cymene})\text{Ru}\{(\mu-\text{pz})\text{Ag}(\text{PPh}_3)\}\{(\mu-\mu)\}$ $pz_{2}RhL_{2}$]BF₄ (M = Rh, L₂ = COD (24); CO, PPh₃ (25)). Adequate analyses and ¹H NMR data were not obtained for complex 24 because it was impurified by small amounts of the dimer $[Rh(\mu-pz)(COD)]_2$ and other pcymene-containing unidentified products which we were not able to efficiently separate. Its ${}^{31}P{}^{1}H$ NMR spectrum consisted of two doublets centered at 18.2 ppm with characteristic phosphorus-silver coupling constants, ${}^{1}J({}^{107}\text{AgP}) = 639$ and ${}^{1}J({}^{109}\text{AgP}) = 736$ Hz. Complex 25 has been completely characterized by elemental analyses and spectroscopic means (Table 2). Its IR spectrum indicated its ionic character (BF₄absorptions) and showed, along with the characteristic bands of the PPh₃ ligand, a very strong absorption at 1990 cm⁻¹ corresponding to the ν (CO) stretching vibration of the terminal carbonyl group. The ¹H NMR spectrum showed two doublets and two AB systems for the isopropyl methyl and aromatic protons of the p-cymene, respectively, which demonstrated that the ruthenium atom was linked to three chemically different pyrazolates.³¹ Accordingly, nine resonances corresponding to nine different pyrazolate protons were also observed. Finally, the ³¹P{¹H} NMR spectrum of 25 consisted of a doublet at 41.2 ppm with ${}^{1}J(\text{RhP}) = 152$ Hz and two doublets centered at 17.4 ppm with coupling constants ${}^{1}J({}^{107}\text{AgP}) = 640 \text{ Hz and } {}^{1}J({}^{109}\text{AgP}) = 738 \text{ Hz},$ according to the proposed structure drawn in Figure 4. As expected, the values of the coupling constants ${}^{1}J(AgP)$ in 24 and 25 are comparable to those found for the phosphorus atom bound to digonal silver in complex $[(\eta^6-p\text{-cymene})\text{Ru}(\mu\text{-pz})_3\{\text{Ag}(\text{PPh}_3)\}_2]\text{BF}_4(\mathbf{5}), \text{supporting}\}$ a similar coordination mode for the silver in all three complexes.

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Conclusions

The bis(pyrazolato)(pyrazole) complex 1 has successfully been used to build heteropolynuclear compounds of transition-metal ions of the 9 and 11 groups. Its deprotonated form $[(\eta^6 - p - \text{cymene}) \text{Ru}(\text{pz})_3]^-$ behaves as the tripyrazolylborate anion in some respects. Thus, coordinates $M(PPh_3)$ (M = Cu, Ag, Au) and the resulting heterodinuclear compounds showed exchange between terminal and bridging pyrazolate groups. The RuAg complex incorporates a second Ag(PPh₃) moiety, and in the new complex the two Ag(PPh₃) groups rotate in a concerted way around the three nitrogen atoms of the $[(\eta^6 - p - cymene)Ru(pz)_3]^-$ anion. This type of fluxionality involving changes in the hapticity is characteristic of polypyrazolylborate ligands. In the heterodinuclear derivatives $[(\eta^6 - p - \text{cymene})(\text{pz})\text{Ru}(\mu - \text{pz})_2\text{ML}_2]$ (M = Rh, Ir), the $[(\eta^6-p-\text{cymene})\text{Ru}(pz)_3]^-$ ligand is bidentate in the ground state and the exchange between coordinated and uncoordinated pyrazolate groups is slow even at 363 K in toluene- d_8 . The CO groups in $[(\eta^6-p-\text{cymene})(\text{pz}) Ru(\mu-pz)_2M(CO)_2$ can be partially or completely removed by mono- and ditertiary phosphines and electrophiles such as H^+ or $Ag(PPh_3)^+$ attack the lone pair of the uncoordinated nitrogen of the terminal pyrazolate, rendering the corresponding cationic products. Protonation occurs at nitrogen even in the RuIr complexes as it has been unequivocally demonstrated by spectroscopic and crystallographic methods.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer (range $4000-200 \text{ cm}^{-1}$) using Nujol mulls between polyethylene sheets or dichloromethane solutions between NaCl plates. Proton and ³¹P{¹H} NMR spectra were recorded on a Varian Unity 300 spectrometer (300.0 (¹H) and 121.4 (³¹P) MHz). The C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. All solvents were dried and distilled before use.

Preparation of $[(\eta^{6}$ -*p*-**Cymene**)**Ru**(**pz**)₃**Cu**(**PPh**₃)] (2). Under nitrogen, to a solution of 1 (0.140 g, 0.32 mmol) in acetone (25 mL) were added [CuCl(PPh₃)]₄ (0.116 g, 0.08 mmol) and KOH (2.0 mL, 0.16 N, 0.32 mmol) in MeOH. After stirring for 30 min, the solution was vacuum-evaporated to 0.5 mL. Slow addition of hexane led to the precipitation of a yellow solid which was filtered off, washed with hexane, and dried under vacuum. Yield: 83%. Anal.¹¹ Calcd for C₃₇H₃₈N₆-CuPRu: C, 58.68; H, 5.03; N, 11.05. Found: C, 56.63; H, 5.11; N, 10.82.

Complexes **3** and **4** were prepared similarly in MeOH as solvent. **3**. Yield: 75%. Anal. Calcd for $C_{37}H_{38}N_6AgPRu$: C, 55.11; H, 4.83; N, 10.45. Found: C, 55.63; H, 5.12; N, 10.00. **4**. Yield: 89%. Anal. Calcd for $C_{37}H_{38}N_6AuPRu$: C, 49.62; H, 4.33; N, 9.41. Found: C, 48.93; H, 4.21; N, 8.93.

Preparation of $[(\eta^{6}$ -*p*-Cymene)**Ru**(**pz**)₃{**Ag**(**PPh**₃)}₂]**BF**₄ (5). Under nitrogen, to a solution of complex $[(\eta^{6}$ -*p*-cymene)**Ru**(**pz**)₃**Ag**(**PPh**₃)] (0.133 g, 0.16 mmol) in acetone (40 mL) were added PPh₃ (0.043 g, 0.16 mmol) and AgBF₄ (0.032 g, 0.16 mmol). After stirring for 1 h, the solution was filtered to remove any remaining solid. The filtrate was concentrated under reduced pressure, and the addition of hexane led to the precipitation of a pale yellow solid which was filtered off, washed with hexane, and dried under vacuum. Yield: 77%. Anal. Calcd for C₅₅H₅₃N₆Ag₂BF₄P₂Ru: C, 52.31; H, 4.23; N, 6.62. Found: C, 52.72; H, 4.32; N, 6.30.

Preparation of $[(\eta^6-p-Cymene)(pz)Ru(\mu-pz)_2Rh(COD)]$ (6). Under nitrogen, to a solution of 1 (0.564 g, 1.29 mmol) in acetone (40 mL) was added [Rh(acac)(COD)] (0.400 g, 1.29 mmol). The starting yellow solution became yellow-brown and after stirring for 15 min was concentrated until dryness. Addition of MeOH (20 mL) gave a yellow solid which was filtered off, washed with MeOH and cold hexane, and dried under vacuum. Yield: 70%. Anal. Calcd for $C_{27}H_{35}N_6RhRu:$ C, 50.11; H, 5.43; N, 13.01. Found: C, 49.64; H, 5.63; N, 12.67.

Preparation of $[(\eta^{6}-p\text{-}Cymene)(pz)Ru(\mu-pz)_{2}Rh(CO)_{2}]$ (7). Method 1. Under nitrogen, to a solution of 1 (0.700 g, 1.60 mmol) in THF (50 mL) was added [Rh(acac)(CO)_{2}] (0.413 g, 1.60 mmol). The starting yellow solution became yellowbrown. The isolation of solid 7 by addition of different precipitants failed due to its great solubility. So, the compound could be isolated by concentrating the solutions until dryness. The residue was then dried under vacuum during 24 h. Method 2. Bubbling of carbon monoxide (atmospheric pressure, room temperature) for 1 h through CH₂Cl₂ or THF solutions (20 mL) of compound 6 (1.000 g, 1.54 mmol) led to a yellow solution. Complex 7 was obtained by workup as above. Yield: 85%. IR (CH₂Cl₂): ν (CO) 2070 (vs), 2010 (vs) cm⁻¹. Anal. Calcd for C₂₁H₂₃N₆O₂RhRu: C, 42.51; H, 3.91; N, 14.12. Found: C, 43.11; H, 4.33; N, 14.50.

Preparation of $[(\eta^6-p-Cymene)(pz)Ru(\mu-pz)_2Rh(CO)-(PPh_3)]$ (9). To a suspension of the dicarbonyl complex 7 (0.173 g, 0.29 mmol) in diethyl ether (30 mL) prepared *in situ* by method 2 was added solid PPh₃ (0.076 g, 0.29 mmol). From the resulting solution, the precipitation of a yellow solid was observed, and after stirring for 12 h, the compound was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 70%. IR (CH₂Cl₂): ν (CO) 1985 (vs) cm⁻¹. Anal. Calcd for C₃₈H₃₈N₆OPRhRu: C, 55.03; H, 4.60; N, 10.12. Found: C, 55.43; H, 4.95; N, 9.90. ³¹P{¹H} NMR (CDCl₃/CHCl₃, 1/1, v/v, δ): 41.5 (d, $J_{RhP} = 153$ Hz).

Preparation of Complexes 10–13 and 15–18. Complexes 10, 11, and 15-17 were similarly prepared by using the appropriate phosphorus ligand. The RuIr complexes 12, 13, and 18 were prepared by the same method, starting from solutions of 8.

Complex 10. Yield: 51%. IR (CH₂Cl₂): ν (CO) 1995 (vs) cm⁻¹. Anal. Calcd for C₂₃H₃₂N₆O₄PRhRu: C, 39.93; H, 4.70; N, 12.13. Found: C, 39.23; H, 4.75; N, 11.60. ³¹P{¹H} NMR (CDCl₃/CHCl₃, 1/1, v/v, δ): 137.5 (d, $J_{RhP} = 242$ Hz).

Complex 11. Yield: 69%. IR (CH₂Cl₂): v(CO) 1985 (vs) cm⁻¹. Anal. Calcd for $C_{45}H_{45}N_6OP_2RhRu$: C, 56.83; H, 4.82; N, 8.82. Found: C, 56.64; H, 5.05; N, 8.56. ³¹P{¹H} NMR $(CDCl_3/CHCl_3, 1/1, v/v, \delta)$: 35.9 (dd, $J_{RhP} = 152 Hz$), -25.7(d, d) $J_{\rm PP} = 75$ Hz). Complex 12. Yield: 75%. IR (CH₂Cl₂): v-(CO) 1980 (vs) cm⁻¹. Anal. Calcd for $C_{38}H_{38}N_6IrOPRu$: C, 49.63; H, 4.17; N, 9.12. Found: C, 49.04; H, 4.22; N, 9.03. $^{31}P\{^{1}H\}$ NMR (CDCl₃/CHCl₃, 1/1, v/v, $\delta):$ 16.5 (s). Complex 13. Yield: 82%. IR (CH₂Cl₂): ν (CO) 1975 (vs) cm⁻¹. Anal. Calcd for C₄₅H₄₅N₆IrOP₂Ru: C, 51.93; H, 4.44; N, 8.13. Found: C, 51.90; H, 5.25; N, 8.06. ³¹P{¹H} NMR (CDCl₃/ CHCl₃, 1/1, v/v, δ): 8.2 (d, $J_{PP} = 70$ Hz), -26.3 (d). Complex 15. Yield: 75%. Anal. Calcd for C₄₅H₄₇N₆P₂RhRu: C, 57.62; H, 5.12; N, 8.93. Found: C, 57.14; H, 5.15; N, 8.66. ³¹P{¹H} NMR (CDCl₃/CHCl₃, 1/1, v/v, δ): 71.7 (d, $J_{RhP} = 170$ Hz). Complex 16. Yield: 74%. Anal. Calcd for C45H45N6P2-RhRu: C, 57.73; H, 4.92; N, 9.02. Found: C, 56.94; H, 5.00; N, 8.76. ³¹P{¹H} NMR (CDCl₃/CHCl₃, 1/1, v/v, δ): 77.5 (d, J_{RhP} = 170 Hz). Complex 17. Yield: 72%. Anal. Calcd for C₄₆H₄₉N₆P₂RhRu: C, 58.03; H, 5.22; N, 8.83. Found: C, 57.67; H, 5.35; N, 8.75. ¹H NMR (CDCl₃, δ): major isomer 7.76 (d), 6.77 (d), 6.30 (t, $J_{\rm HH} = 2.3$ Hz), 6.05, 5.99 (AB system, $J_{\rm AB} =$ 6.4 Hz), 2.34 (sp), 1.83 (s), 1.12 (d, $J_{\rm HH} = 6.8$). ³¹P{¹H} NMR $(CDCl_3/CHCl_3, 1/1, v/v, \delta)$: major isomer 78.7 (dd, $J_{RhP} = 168$, $J_{\rm PP} = 45$ Hz), 61.1 (dd, $J_{\rm RhP} = 169$ Hz); minor isomer 78.4 (dd, $J_{\text{RhP}} = 170, J_{\text{PP}} = 44 \text{ Hz}$), 56.5 (dd, $J_{\text{RhP}} = 167 \text{ Hz}$). Complex 18. Yield: 79%. Anal. Calcd for $C_{45}H_{47}N_6P_2IrRu$: C, 52.63; H, 4.62; N, 8.23. Found: C, 52.14; H, 4.65; N, 7.81. ³¹P{¹H} NMR ((CD₃)₂CO, δ): 43.1 s.

Preparation of $[(\eta^6-p-Cymene)(pz)Ru(\mu-pz)_2Rh(dppm)]$ (14). A THF solution (50 mL) of complex 7 (0.173 g, 0.29 mmol) was heated under reflux for 1 h after adding dppm (0.115 g, 0.29 mmol). The resulting solution was evaporated to ca. 2 mL, and the slow addition of hexane led to the precipitation of a yellow solid which was filtered off, washed with the precipitant, and vacuum-dried. Yied: 58%. Anal. Calcd for $C_{44}H_{45}N_6P_2RhRu$: C, 56.71; H, 4.92; N, 9.12. Found: C, 57.24; H, 4.75; N, 8.85. ³¹P{¹H} NMR (CDCl₃/ CHCl₃, 1/1, v/v, δ): -19.6 (d, $J_{RhP} = 144$ Hz).

Preparation of $[(\eta^{6}$ -*p*-**Cymene**)(**Hpz**)**Ru**(μ -**pz**)₂**Rh**(**CO**)₂]-**BF**₄ (20). To a solution of the dicarbonyl complex 7 (ca. 0.29 mmol) in THF (30 mL) prepared *in situ* by method 2 was added HBF₄ in diethyl ether (40.6 μ L, 54% w/w, 0.29 mmol). The solution was concentrated to ca. 2 mL, and the slow addition of diethyl ether led to the precipitation of a yellow solid which was separated by filtration, washed with the precipitant and dried under vacuum. Yield: 87%. IR (Nujol) ν (NH) 3300 (br), ν (CO) 2070 (vs), 2010 (vs) cm⁻¹. Anal. Calcd for C₂₁H₂₄N₆BF₄O₂RhRu: C, 36.93; H, 3.49; N, 12.28. Found: C, 37.52; H, 3.55; N, 12.31.

Complexes **19** and **22** were similarly prepared starting from **6** and solutions of **8**, respectively. **Complex 19**. Yield: 75%. IR (Nujol): ν (NH) 3320 (br) cm⁻¹. Anal. Calcd for C₂₇H₃₆N₆BF₄RhRu: C, 44.09; H, 4.91; N, 11.37. Found: C, 44.13; H, 5.03; N, 11.52. **Complex 22**. Yield: 53%. IR (Nujol): ν (NH) 3320 (br), ν (CO) 2070 (vs), 2010 (vs) cm⁻¹. Anal. Calcd for C₂₁H₂₄N₆BF₄IrO₂Ru: C, 32.72; H, 3.12; N, 10.90. Found: C, 33.23; H, 3.13; N, 10.88.

Preparation of [(η⁶-p-Cymene)(Hpz)Ru(μ-pz)₂Rh(CO)-(**PPh**₃)]BF₄ (21). Under nitrogen, 21 μL of a solution of HBF₄ in diethyl ether (54% w/w, 0.15 mmol) was added to a solution of [(η⁶-p-cymene)(pz)Ru(μ-pz)₂Rh(CO)(PPh₃)] (9) (0.124 g, 0.15 mmol) in THF (20 mL). After 15 min of stirring, the solution was concentrated to ca. 2 mL and the slow addition of diethyl ether led to the precipitation of a yellow solid which was separated by filtration, washed with the precipitant, and dried under vacuum. Yield: 80%. IR (Nujol): ν(NH) 3330 (br), ν(CH₂Cl₂) 1985 (vs) cm⁻¹. Anal. Calcd for C₃₈H₃₉N₆BF₄-OPRhRu: C, 49.72; H, 4.33; N, 9.1. Found: C, 49.01; H, 4.75; N, 8.54. ³¹P{¹H} NMR (CDCl₃/CHCl₃, 1/1, v/v, δ): 41.2 (d, J_{RhP} = 153 Hz).

Complex 23 was similarly obtained from **12**. Yield: 53%. IR (Nujol): ν (NH) 3350 (br), ν (CO) 1995 (vs) cm⁻¹. Anal. Calcd for C₃₈H₃₉N₆BF₄IrOPRu: C, 45.32; H, 3.91; N, 8.29. Found: C, 45.03; H, 3.87; N, 7.92. ³¹P{¹H} NMR (CDCl₃/ CHCl₃, 1/1, v/v, δ): 16.7 (s).

Preparation of $[(\eta^{6}$ -**p**-**Cymene)Ru**{ $(\mu$ -**pz**)**Ag**(**PPh**₃)}{ $(\mu$ -**pz**)₂**Rh**(**CO**)(**PPh**₃)}]**BF**₄ (25). Under nitrogen and in the absence of light, PPh₃ (0.029 g, 0.11 mmol) and AgBF₄ (0.021 g, 0.11 mmol) were added to a solution of $[(\eta^{6}$ -*p*-cymene)(pz)**Ru**(μ -pz)₂**Rh**(**CO**)(**PPh**₃)] (**9**) (0.090 g, 0.11 mmol) in THF (25 mL). The resulting solution was stirred for 15 min and then was vacuum-evaporated to ca. 2 mL. Addition of hexane afforded a yellow powder which was filtered off, washed with hexane, and vacuum-dried. Yield: 85%. IR (Nujol): ν -(CO) 1990 (vs) cm⁻¹. Anal. Calcd for C₅₆H₅₃N₆AgBF₄OP₂-RhRu: C, 52.26; H, 4.12; N, 6.52. Found: C, 52.42; H, 4.54; N, 6.53. ³¹P{¹H} NMR (CDCl₃/CHCl₃, 1/1, v/v, δ): 41.1 (d, J_{RhP} = 152 Hz), 17.4 (d, $J^{107}AgP$ = 640 Hz, $J^{109}AgP$ = 738 Hz).

Complex **24** was similarly prepared starting from **6**. ³¹P-{¹H} NMR (CDCl₃/CHCl₃, 1/1, v/v, δ): 18.2 (d, $J(^{107}AgP) = 640$ Hz, $J(^{109}AgP) = 736$ Hz).

X-ray Measurements and Structure Determination for 22. An irregular crystal of dimension $0.236 \times 0.188 \times 0.603$ mm was glued to the end of a glass fiber. It was mounted on

Table 5. Crystal Data and Refinement Details for 22

formula	$C_{21}H_{24}BF_4IrN_6O_2Ru$
fw	772.5
symmetry	monoclinic, $P2_1/c$
a (Å)	7.9909(6)
b (Å)	17.0590(9)
c (Å)	19.083(2)
β (deg)	93.94(1)
$V(Å^3), Z$	2595.2(4), 4
radiation	Mo K α ($\lambda = 0.71073$ Å)
method of collcn	$\omega/2\theta$ scan
scan range (deg)	$(3 \le 2\theta \le 50)$
no. of reflns:	8528 (h - 90; k - 1712; l - 2222)
obsd	$3652 (F_0 \ge 4.0\sigma(F_0))$
μ (cm ⁻¹)	57.3
largest difference peaks	0.66 e/Å^3 , close to BF ₄
$R, {}^{\prime}R_{w}{}^{b}$	0.0316, 0.0342
S ^c (goodness-of-fit)	1.15
data-to-parameter ratio	11.5:1
-	

 ${}^{a}R = \sum ||F_{o}| - |F_{c}||/\sum |F_{o}|. {}^{b}R_{w} = \{\sum w(|F_{o}| - |F_{c}|)^{2}/\sum w|F_{o}|^{2}\}^{1/2}, w^{-1} = \sigma^{2}(F) + 0.000423F^{2}. {}^{c}S = \{\sum w(|F_{o}| - |F_{c}|)^{2}/(M - N)\}^{1/2}, \text{ where } M$ and N denote the number of data and variables, respectively.

a four-circle Siemens AED diffractometer working with graphitemonochromated Mo Ka radiation. Selected crystallographic data are collected in Table 5. Precise lattice parameters were determined by least-squares fit to 54 reflections (20 \leq 2 θ \leq 45°). Three standard reflections were monitored every hour to check crystal and instrument stability. There were no significant fluctuations of the intensities. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction 32 based on ψ scans was also applied (min and max trans fact. 0.150 and 0.261). The structure was solved by the heavy-atom method followed by difference Fourier calculations using the SHELXTL-PLUS package.³³ All non H-atoms of the cation were anisotropically refined. The tetrafluoroborate anion was isotropically refined with two orientations as disorder model. Hydrogen atoms were included in the last cycles in calculated and found positions. The hydrogen bonded to the azolate nitrogen N(2) was clearly observed in the difference Fourier map and included in the observed position. All H-atoms were refined with a common thermal parameter using the riding method. The scattering factors, with anomalous dispersion correction for heavy atoms, were taken from ref 34. All calculations were carried out on a μ -VAX 3400 computer.

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Supplementary Material Available: Full details of crystallographic and experimental data, hydrogen positional parameters, and anisotropic displacement parameters (4 pages). Ordering information is given on any current masthead page.

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