# Novel Types of Pyrazolyl Amidine Complexes: Mechanistic Aspects of Their Syntheses and Exchange Reactions with Acetonitrile

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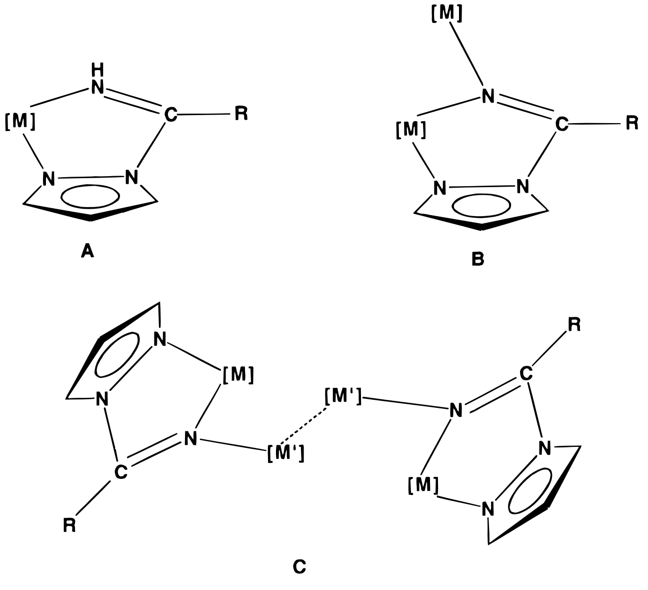
The bis(pyrazolato) pyrazole complex [($\eta^5$-$C_5Me_5$)Ir(pz)$_2$(Hpz)] (**1**) reacts with $AgBF_4$ and nitriles N≡CR to give the tetranuclear $Ir_2Ag_2$ pyrazolyl amidine complexes [{($\eta^5$-$C_5Me_5$)Ir($\mu$-pz)($\mu$-N=C(R)pz)Ag}$_2$][$BF_4$]$_2$ [R = Me (**2**), Ph (**3**), Bz (**4**)]. In acetonitrile solution, complexes **3** and **4** are converted into **2** by exchange of the nitrile moiety. Protonation of complexes **2** and **4** affords the mononuclear pyrazolyl amidines [($\eta^5$-$C_5Me_5$)Ir(Hpz)[HN=C(R)pz][$BF_4$]$_2$ [R = Me (**5**), Bz (**6**)], respectively, which in turn, in basic media, react with $AgBF_4$ to yield **2** and **4**. The molecular structure of **3** has also been elucidated. The tetranuclear cation contains an inversion center which relates the two bimetallic halves of the molecule. The iridium atoms display half-sandwich pseudooctahedral environments while the coordination around the silver is almost linear, the distortion from linearity most probably arising from an intermetallic Ag···Ag interaction (Ag···Ag separation 2.965(1) Å).

## Introduction

Some years ago, we described the preparation and characterization of the bis(pyrazolato) pyrazole complex [($\eta^5$-$C_5Me_5$)Ir(pz)$_2$(Hpz)] (**1**)[1] and subsequently, studied its coordinative properties as metalloligand.[2] Thus, for example, it reacts with the Rh(COD)$^+$ fragment yielding [($\eta^5$-$C_5Me_5$)(pz)Ir($\mu$-pz)$_2$Rh(COD)][2a] or with M(PPh$_3$)$^+$ (M = Cu, Ag, Au) cations rendering the pyrazolato-bridged [($\eta^5$-$C_5Me_5$)Ir(pz)$_3$M(PPh$_3$)] compounds.[2a]

Interestingly, when **1** was allowed to react with the silver nitrile cations Ag(NCR)$^+$, in which the coordinated nitrile ligand is susceptible to interact with pyrazole,[3] the reaction yields new types of $Ir_2Ag_2$ pyrazolyl amidine compounds of formula [{($\eta^5$-$C_5Me_5$)Ir($\mu$-pz)($\mu$-N=C(R)-pz)Ag}$_2$][$BF_4$]$_2$ (R = Me (**2**), Ph (**3**), Bz (**4**)) with a novel stereochemistry around the pyrazolyl amidine ligand (Chart 1C).

**Chart 1**



Usually, the addition of pyrazoles to coordinated nitriles affords mononuclear N,N′-chelated pyrazolyl amidines complexes[3a−e] (Chart 1A), and exceptionally, a binuclear ruthenium compound has been reported, namely [($\eta^4$-$C_8H_{12}$)$_2$Ru$_2$H{$\mu$-N=C(Me)pz}($\mu$-pz)($\mu$-H)],[3f] in which the resulting amidine acts as chelate toward a metal and, simultaneously, bridges both metals through its deprotonated imine nitrogen atom, as depicted in Chart 1B.

In this paper we discuss the synthetic route to **2**−**4** as well as a possible pathway for the exchange of the iminic moiety "N=CR" that these compounds undergo in acetonitrile-$d_3$ to give **2-*d*₃**.

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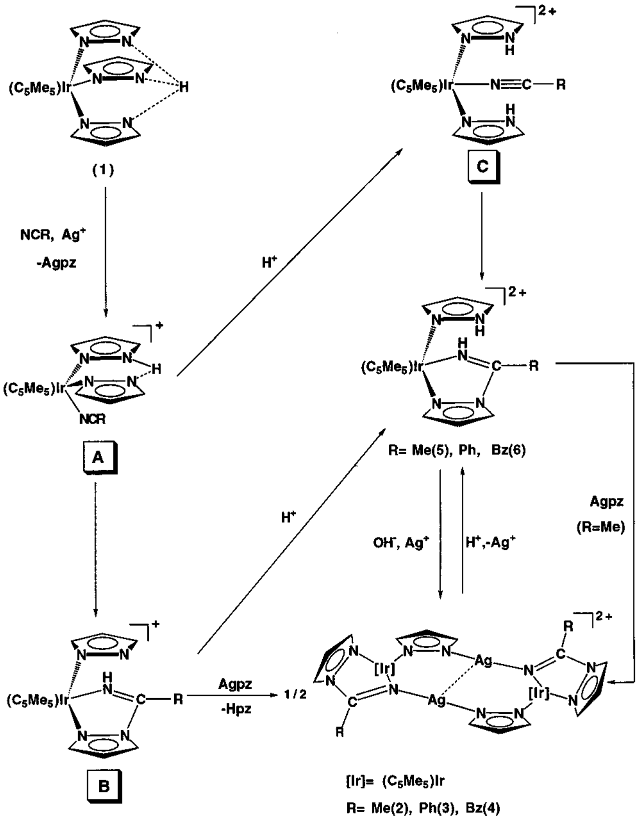
**Scheme 1**



## Results and Discussion

The reaction of **1** with $AgBF_4$ in the presence of excess of organic nitriles, N≡CR (R = Me, Ph, Bz), afforded the pyrazolyl amidine compounds $[\{(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-pz})(\mu\text{-N=C(R)pz)Ag}\}_2][BF_4]_2$ (R = Me (**2**), Ph (**3**), Bz (**4**)) (Scheme 1). During the process the precipitation and subsequent redisolution of a white powder, identified as Ag(pz) by microanalyses and IR spectroscopy, was observed.[4]

The infrared spectra of compounds **2**−**4** showed a strong band at *ca.* 1625 $cm^{-1}$ [$\nu$(C=N)] suggestive of an amidine ligand system arising from pyrazolyl−nitrile couplings.[2] However, no $\nu$(NH) bands were detected and, consistently, their $^1H$ NMR spectra showed no NH protons. The remaining NMR data (see Experimental Section) were in good agreement with the proposed stoichiometry as well as the mass spectra which showed an envelope of peaks at *m/z* 1307, 1431, and 1458 for **2**−**4**, respectively, with isotopic distributions that matched those calculated for the tetranuclear formulation aforementioned.

In order to inequivocally establish the molecular structure of the products, the X-ray crystal structure of complex **3** has been determined. Figure 1 shows a molecular representation of the cation, and the most relevant bond lengths and angles are given in Table 1. The tetranuclear cation contains an inversion center which relates the two bimetallic halves of the molecule. The structure confirms the presence of the amidine ligand (N(1)−C(11) 1.268(8) Å), which forms an iridacycle of five members through coordination of one of the nitrogens of the pyrazole moiety and the imine nitrogen. The latter nitrogen atom and a pyrazolate anion bridge the iridium to two different, but symmetry related, silver atoms. The coordination around the silver metal is almost linear [N(1)−Ag−N(5′) 170.6(4)°]; this distortion most likely arises from an intermetallic Ag⋯Ag interaction as evidenced by the short Ag⋯Ag separation observed, 2.965(1) Å. An $\eta^5$-$C_5Me_5$ ligand completes the coordination sphere of the iridium. The iridium atoms are stereogenic centers, and the molecule has the $R_{Ir}S_{Ir}$ configuration of a *meso* form.[5]

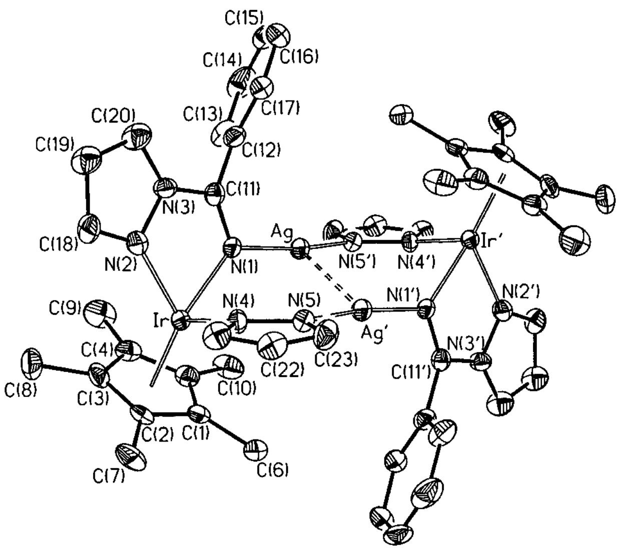


**Figure 1.** Perspective drawing of the cation of complex **3**.

**Table 1. Bond Lengths (Å) and Selected Angles (deg) for the Cationic Part of $[\{(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-pz})(\mu\text{-N=C(Ph)pz)Ag}\}_2][BF_4]_2$ (3)[a]**

| | | | |
|---|---|---|---|
| Ag−N(1) | 2.120(5) | Ir−C(1) | 2.174(6) |
| Ag−N(5′) | 2.089(5) | Ir−C(2) | 2.184(6) |
| Ir−N(1) | 2.081(5) | Ir−C(3) | 2.183(6) |
| Ir−N(2) | 2.069(5) | Ir−C(4) | 2.168(7) |
| Ir−N(4) | 2.084(5) | Ir−C(5) | 2.179(7) |
| N(1)−C(11) | 1.268(8) | N(5)−C(23) | 1.351(8) |
| N(2)−N(3) | 1.355(7) | C(1)−C(2) | 1.462(9) |
| N(2)−C(18) | 1.328(8) | C(1)−C(5) | 1.428(9) |
| N(3)−C(11) | 1.428(8) | C(2)−C(3) | 1.422(9) |
| N(3)−C(20) | 1.358(8) | C(3)−C(4) | 1.452(9) |
| N(4)−N(5) | 1.370(7) | C(4)−C(5) | 1.438(10) |
| N(4)−C(21) | 1.338(8) | C(11)−C(12) | 1.489(9) |
| N(1)−Ag−N(5′) | 170.6(2) | | |
| N(1)−Ir−N(2) | 77.8(2) | N(2)−N(3)−C(11) | 115.5(5) |
| N(1)−Ir−N(4) | 90.9(2) | N(2)−N(3)−C(20) | 110.4(5) |
| N(1)−Ir−Cp* | 129.5(3) | C(11)−N(3)−C(20) | 134.1(6) |
| N(2)−Ir−N(4) | 84.1(2) | Ir−N(4)−N(5) | 125.1(4) |
| N(2)−Ir−Cp* | 132.8(3) | Ir−N(4)−C(21) | 125.0(4) |
| N(4)−Ir−Cp* | 126.2(3) | N(5)−N(4)−C(21) | 108.6(5) |
| Ir−N(1)−Ag | 130.3(3) | Ag′−N(5)−N(4) | 129.8(4) |
| Ir−N(1)−C(11) | 115.2(4) | Ag′−N(5)−C(23) | 123.9(4) |
| Ag−N(1)−C(11) | 114.4(4) | N(4)−N(5)−C(23) | 106.2(5) |
| Ir−N(2)−N(3) | 113.5(4) | N(1)−C(11)−N(3) | 117.7(5) |
| Ir−N(2)−C(18) | 139.4(5) | N(1)−C(11)−C(12) | 126.6(6) |
| N(3)−N(2)−C(18) | 106.9(5) | N(3)−C(11)−C(12) | 115.4(5) |

[a] Cp* represents the centroid of the pentamethylcyclopentadienyl ligand. Primed atoms (Ag′ and N(5′)) are related to the unprimed ones by the following symmetry transformation: −*x* + 1, −*y* + 1, −*z* + 1.

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[4] Undoubtedly, Ag(pz) has a more complex formulation. Reedijk *et al.* reported that solid Ag(pz) is "at least trimeric but polymeric forms cannot be excluded": Okkersen, H.; Groeneveld, W. L.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 945. The molecular structure of the related trimer $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ has been recently reported by Fackler *et al.*: Murray, H. H.; Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 26.

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The $^1$H NMR spectra of compounds **3** and **4**, in acetone, deserve some comments. They showed the presence, in both cases, of a 3/2 molar ratio mixture of two related compounds. These results can be explained by assuming that a dissociation of the tetranuclear $Ir_2$-$Ag_2$ cations into two dinuclear IrAg *monomers* was taking place in solution by cleavage of two symmetry related N−Ag bonds (N(1)−Ag and N(1′)−Ag′ or N(5′)−Ag and N(5)−Ag; see Figure 1). Alternatively, the observed NMR signals can be attributed to a mixture of *meso* and *RR* and/or *SS* diastereomers of the complexes. In the solid state, complexes **3** and **4** could be the pure *meso* forms as found in the crystal structure of **3** (for just a single crystal) or a mixture of diastereomers (*RS* and *SS* and/or RR). If solids are the pure *meso* forms, when dissolved in acetone, an epimerization process should occur at the iridium centers. We have not additional experimental evidence in order to discriminate between these two explanations.[6] Complex **2** is not soluble enough in acetone to carry out NMR measurements.

Complex **4** was quantitatively converted into the new mononuclear pyrazolyl amidine compound $[(\eta^5\text{-}C_5Me_5)\text{Ir(NH=C(Bz)pz)(Hpz)}][BF_4]_2$ (**6**), by $HBF_4$ protonation (Scheme 1). Its formation has been confirmed by preparing it from the solvated compound $[(\eta^5\text{-}C_5Me_5)\text{Ir(NCBz)}_3]^{2+}$ following an experimental procedure similar to that reported by McCleverty *et al.* for related ruthenium pyrazolyl amidine compounds.[3b] The methyl complex $[(\eta^5\text{-}C_5Me_5)\text{Ir(NH=C(Me)pz)(Hpz)}][BF_4]_2$ (**5**) was also prepared by this latter route, as well as by $HBF_4$ protonation of an acetonitrile solution of complex **2**, the only usual organic solvent in which **2** is soluble enough. The reaction can be reversed. Thus, addition of equimolar quantities of $AgBF_4$ and KOH to compounds **5** or **6** afforded the corresponding tetranuclear complexes **2** or **4** in quantitative yield.

Scheme 1 shows a suggested preparative route to **2**−**4** in which Ag(pz) plays a critical role. A pz anion is eliminated as Ag(pz) by interaction of **1** with $Ag^+$, and a nitrile molecule coordinates to the iridium rendering A. Intramolecular nucleophilic attack of the pyrazole to the nitrile affords the pyrazolyl amidines B, according to a similar mechanism to that proposed for the formation of amidine derivatives from primary[7a,b] or secondary[7c] amines and Pt(II) nitrile complexes. The previously formed Ag(pz) is able to deprotonate the NH amidine group in B, and most probably, the resulting metalloligand coordinates Ag. Subsequent dimerization afforded the final products **2**−**4**. Alternatively, these tetranuclear complexes could be formed through the protonated species C or **5**, **6**, or the related phenyl derivative. These intermediates would be formed by protonation of A or B by residual protic impurities. In fact, in an independent experiment, we have proved spectroscopically that the addition of Ag(pz) to **5** produces **2**. We have not been able to isolate and characterize the proposed intermediates A−C, either from **1** or from **5** or **6**. When, in the preparation of compounds **2**−**4**, Ag(pz) was filtered off from the reaction medium, a mixture of $C_5Me_5$- and pyrazolate-containing species was isolated. Among them, the mononuclear complexes $[(\eta^5\text{-}C_5Me_5)\text{Ir(NH=C(R)pz)(Hpz)}][BF_4]_2$ (R = Me (**5**), Ph, Bz (**6**)) were the only identified compounds. Addition of base (KOH, $NEt_3$) to these latter compounds also affords similar mixtures of unidentified $C_5Me_5$- and pyrazolate-containing species.

The $^1$H NMR spectrum of an acetonitrile-$d_3$ solution of compound **2** showed two interesting features: (i) It contained only one set of signals and (ii) it showed all the expected resonances, with the appropriate intensities, but that of the amidine methyl group. Point (i) implied that complex **2** does not dissociate or epimerize in acetonitrile. The second point was indicative that an exchange between the nondeuterated and the deuterated acetonitrile has occurred. This exchange is more general since the $^1$H NMR espectra of compounds **3** and **4** in acetonitrile-$d_3$ showed their quantitative conversion to **2-*d*₃** and to the corresponding free nitrile. This behavior can be accounted for by assuming the reversibility of the preparative route from the final products **2**−**4** to A or C (Scheme 1). The latter would exchange the coordinated nitrile to the deuterated acetonitrile solvent and, subsequently, generate **2-*d*₃**. The quantitative formation of $[(\eta^5\text{-}C_5Me_5)\text{Ir(NH=C(CD}_3\text{)pz)(Hpz)}][BF_4]_2$ (**5-*d*₃**) by dissolving **5** in acetonitrile-$d_3$, as assayed by $^1$H NMR spectroscopy, supported this proposal.

Further work is in progress to determine the generality of the reported method for the preparation of heterotetranuclear pyrazolyl amidine compounds, to study their chemical reactivity, and to elucidate their mechanism of formation and nitrile exchange.

## Experimental Section

**General Comments.** All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried over appropriate drying agents, distilled under $N_2$, and degassed prior to use. Infrared spectra were recorded on Perkin-Elmer 783 and 1330 spectrophotometers. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer 240B microanalyzer. $^1$H NMR spectra were recorded on a Varian UNITY 300 spectrometer operating at 299.95 MHz. Chemical shifts are expressed in ppm upfield from $SiMe_4$. Coupling constants $J$ are given in hertz. Mass spectra were measured on a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode. Ions were produced with the standard $Cs^+$ gun at *ca.* 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as a matrix.

**Preparation of $[\{(\eta^5\text{-}C_5Me_5)\text{Ir}(\mu\text{-pz})(\mu\text{-N=C(Ph)pz)Ag}\}_2][BF_4]_2$ (3).** Under nitrogen, to a solution of $[\text{Ir}(\eta^5\text{-}C_5Me_5)(\text{pz})_2\text{(Hpz)}]$ (150.0 mg, 0.28 mmol) in 25 mL of acetone was added benzonitrile (0.2 mL) and $AgBF_4$ (55.2 mg, 0.28 mmol). The precipitation of a white powder was observed immediately. The resulting suspension was stirred for 3 h, in the absence of light. During this time most of the precipitate redisolved. The suspension was filtered over Kiesselguhr, and the resulting solution was concentrated under reduced pressure. The addition of diethyl ether led to the precipitation of a pale yellow solid, which was filtered off, washed with the same solvent, and air-dried. Complexes **2** and **4** were prepared similarly but using neat acetonitrile (**2**) or THF (**4**) as solvents. In both cases the tetranuclear complexes precipitated spontaneously after 5 min of reaction. Complex **2**: Yield, 81%. Anal. Calcd for $C_{36}H_{48}N_{10}Ag_2B_2F_8Ir_2$: C, 31.00; H, 3.47; N, 10.04. Found: C, 31.21; H, 3.32; N, 10.19. IR (Nujol): 1625 cm$^{-1}$ [s, $\nu$(C=N)]; 1000−1100 (vb, $BF_4$). $^1$H NMR ($CD_3CN$): 1.70 s (30H, $C_5Me_5$); 6.21 bs (2H, pz); 6.82 bs (2H, pz); 7.23 bs (2H, pz); 7.59 bs

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[6] We acknowledge the suggestion of the dissociative proposal by a reviewer.

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**Table 2. Crystallographic Data and Structure Refinement for 3**

| | |
|---|---|
| formula | $C_{48}H_{56}Ag_2B_2Cl_4F_8Ir_2N_{10}$ |
| mol wt | 1688.59 |
| cryst syst | monoclinic |
| space group | $P2_1/c$ (No. 14) |
| $a$, Å | 10.557(2) |
| $b$, Å | 17.927(3) |
| $c$, Å | 15.222(2) |
| $\beta$, deg | 105.44(1) |
| $V$, Å$^3$ | 2776.9(8) |
| $Z$ | 2 |
| $\mu$, mm$^{-1}$ | 5.736 |
| temp, K | 150.0(2) |
| scan method | $\omega/2\theta$ |
| $\theta$ (min−max), deg | 1.79−26.02 |
| index ranges | $0 \le h \le 13$, $0 \le k \le 22$, $-18 \le l \le 18$ |
| no. measd refls | 5731 |
| no. indep refls | 5429 [$R_{int} = 0.0204$] |
| max and min transmissn | 1.000, 0.663 |
| data/param | 5429/344 |
| final $R$ indices[a] [$I > 2\sigma(I)$] | $R_1 = 0.0358$, $wR_2 = 0.0744$ |
| $R$ indices (all data) | $R_1 = 0.0520$, $wR_2 = 0.0802$ |
| goodness of fit ($S$) | 1.029[b] |

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$. [b] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; $n$ = number of reflections used in refinement, $p$ = number of parameters.

(2H, pz); 8.02 bs (2H, pz); 8.25 bs (2H, pz). MS (FAB$^+$): $m/z$ 1307 (M$^+$ + BF$_4$, 8). Complex **3**: Yield, 80%. Anal. Calcd for $C_{46}H_{52}N_{10}Ag_2B_2F_8Ir_2$: C, 36.38; H, 3.45; N, 9.22. Found: C, 36.83; H, 3.56; N, 9.07. IR (Nujol): 1625 cm$^{-1}$ [s, $\nu$(C=N)]; 1000−1100 (vb, BF$_4$). $^1$H NMR [(CD$_3$)$_2$CO]: Major isomer, 1.51 s (30H, C$_5$Me$_5$); 6.29 bs (2H, pz); 6.50 bs (2H, pz); 6.96 bs (2H, pz); 7.42 bs (2H, pz); 7.5−7.9 bm (10H, Ph; 2H, pz); 8.70 bs (2H, pz); minor isomer, 1.59 s (30H, C$_5$Me$_5$); 6.22 bs (2H, pz); 6.50 bs (2H, pz); 7.35 bs (2H, pz); 7.5−7.9 bm (10H, Ph; 6H, pz). MS (FAB$^+$): $m/z$ 1431 (M$^+$ + BF$_4$, 10). Complex **4**: Yield, 87%. Anal. Calcd for $C_{48}H_{56}N_{10}Ag_2B_2F_8Ir_2$: C, 37.27; H, 3.65; N, 9.05. Found: C, 36.86; H, 4.18; N, 9.43. IR (Nujol): 1635 cm$^{-1}$ [s, $\nu$(C=N)]; 1000−1100 (vb, BF$_4$). $^1$H NMR [(CD$_3$)$_2$CO]: Major isomer, 1.67 s (30H, C$_5$Me$_5$); 4.61, 4.86 AB system (4H, C*H*$_2$Ph); 6.30 bm (2H, pz); 6.54 bs (2H, pz); 6.56 bs (2H, pz); 6.88 bs (2H, CH$_2$*Ph*); 7.23, 7.39 AB system (8H, CH$_2$*Ph*); 7.79 bs (2H, pz); 8.09 m (2H, pz); 8.62 m (2H, pz); minor isomer, 1.72 s (30H, C$_5$Me$_5$); 4.74 m (4H, C*H*$_2$Ph); 6.30 bm (2H, pz); 6.81 bm (4H, pz); 6.88 bs (2H, CH$_2$*Ph*); 7.23, 7.30 AB system (8H, CH$_2$*Ph*); 7.67 bs (2H, pz); 8.09 m (2H, pz); 8.62m (2H, pz). MS (FAB$^+$): $m/z$ 1458 (M$^+$ + BF$_4$, 3).

**Preparation of [($\eta^5$-C$_5$Me$_5$)Ir(NH=C(Me)pz)(Hpz)][BF$_4$]$_2$ (5).** Under nitrogen, to a solution of [{Ir($\eta^5$-C$_5$Me$_5$)Cl}$_2$($\mu$-Cl)$_2$] (300.0 mg, 0.38 mmol) in 20 mL of acetone was added AgBF$_4$ (294.0 mg, 1.52 mmol). An abundant amount of AgCl precipitate was formed, which after stirring for 30 min was filtered off. To the resulting filtrate, Hpz (104.0 mg, 1.53 mmol) and acetonitrile (0.1 mL) were added. The mixture was stirred for 2h. The solution was then concentrated under reduced pressure, and the addition of diethyl ether led to the precipitation of a pale yellow solid, which was filtered off, washed with the same solvent, and air-dried. Complex **6** was prepared by the same method. Complex **5**: Yield, 54%. Anal. Calcd for $C_{18}H_{26}N_5B_2F_8Ir$: C, 31.87; H, 3.86; N, 10.32. Found: C, 31.45; H, 3.31; N, 10.24. IR (Nujol): 3300 [br, $\nu$(NH)]; 1660 [s, $\nu$(C=N)]; 1000−1100 (vb, BF$_4$) cm$^{-1}$. $^1$H NMR [(CD$_3$)$_2$CO]: 1.84 s (15H, C$_5$Me$_5$); 2.98 s (3H, Me); 6.53 q (1H, $^3J$(HH) = 2.0 Hz, pz); 7.08 t (1H, $^3J$(HH) = 2.5 Hz, pz); 7.80 bs (1H, pz); 7.95 bs (1H, pz); 8.71 d (1H, $^3J$(HH) = 3.3 Hz, pz); 8.84 d (1H, $^3J$(HH) = 1.9 Hz, pz); 11.23 bs (1H, Hpz); 12.50 bs (1H, Hpz). Complex **6**: Yield, 51%. Anal. Calcd for $C_{24}H_{30}N_5B_2F_8Ir$: C, 38.21; H, 4.01; N, 9.28. Found: C, 37.87; H, 3.88; N, 9.21. IR (Nujol): 3300 [br, $\nu$(NH)]; 1660 [s, $\nu$(C=N)]; 1000−1100 (vb, BF$_4$) cm$^{-1}$. $^1$H NMR [(CD$_3$)$_2$CO]: 1.83 s (15H, C$_5$Me$_5$); 4.74 m (2H, C*H*$_2$Ph); 6.54 q (1H, $^3J$(HH) = 2.1 Hz, pz); 7.06 t (1H, $^3J$(HH) = 2.5 Hz, pz); 7.31 m (2H, CH$_2$*Ph*); 7.39 m (2H, CH$_2$*Ph*); 7.81 t (1H, $^3J$(HH) = 1.7 Hz, pz); 7.96 t (1H, $^3J$(HH) = 2.0 Hz, pz); 8.71 d (1H, $^3J$(HH) = 2.9 Hz, pz); 8.85 d (1H, $^3J$(HH) = 2.0 Hz, pz); 11.31 bs (1H, Hpz); 12.50 bs (1H, Hpz).

**Crystal Structure Determination of [{($\eta^5$-C$_5$Me$_5$)Ir($\mu$-pz)($\mu$-N=C(Ph)pz)Ag}$_2$][BF$_4$]$_2$ (3).** A summary of crystal data and refinement parameters is reported in Table 2. A yellowish pyramidal crystal (0.31 × 0.35 × 0.49 mm) was used to collect data on a Siemens-Stoe AED-2 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.710 73 Å). A set of standard reflections were monitored every 55 min of measured time throughout data collection; no variations were observed. Data were corrected for Lorentz and polarization effects and for absorption using the DIFABS93 program.[8] The structure was solved by Patterson and difference Fourier methods (half-molecule of **3** in the asymmetric unit) and refined by full-matrix least squares on $F^2$, with anisotropic displacement parameters for all nondisordered atoms (SHELXL93).[9] One solvent dichloromethane molecule was present, and the tetrafluoroborate anion was observed disordered in two orientations. Hydrogens were found for the pyrazolate and pyrazolyl amidine ligands and placed in calculated positions for the cyclopentadienyl group. Residual peaks in the final difference map were in the range 1.588 to −0.944 e Å$^{-3}$.

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**Supporting Information Available:** Full listings of crystallographic data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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