(LiR′ or MgR′X), i.e. wherein one or two Cu centers are replaced by Li or MgX. The trinuclear unit has a reactive site to which we anticipate that the alkene function of enones would coordinate, i.e. the initial reaction step proposed for their copper(I)-catalyzed reaction with organometallic reagents.[13,22,23] This coordination does not occur in $[Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]$ since the strength of the side-on alkynyl to copper bond favors a hexanuclear structure. However, with phosphines as two-electron donors, trinuclear compounds $[Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)\{P(OMe)_3\}]$ are formed.

Four fluxional processes in hexanuclear and trinuclear alkynylcopper arenethiolates have been observed. In order of increasing free energy of activation energy (ΔG^{*}), these are the boat-to-boat conformation flip of the Cu_3S_2C ring (±40 kJ/mol), inversion of configuration at sulfur and Cu–N dissociation (both ±50 kJ/mol), and hexanuclear to trinuclear dissociation via breaking of the side-on alkynyl to copper interactions (±58 kJ/mol).

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Supplementary Material Available: For **3** and **4**, tables of fractional coordinates of all atoms, bond distances and angles, and anisotropic thermal parameters (23 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Mononuclear Pyrazolyl Complexes of Palladium(II) and Platinum(II). Crystal Structures of $[NBu_4][M(C_6F_5)_2(pyrazole)(pyrazolato)]$ (M = Pd, Pt)

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Pyrazolyl complexes of the types $[MR_2(HX)_2]$ (M = Pd, R = C_6F_5, HX = pyrazole (Hpz) (**1**), 3,5-dimethylpyrazole (Hdmpz) (**2**); M = Pd, R = C_6Cl_5, HX = Hpz (**3**), Hdmpz (**4**); M = Pt, R = C_6F_5, HX = Hpz (**5**), Hdmpz (**6**); M = Pt, R = C_6Cl_5, HX = Hdmpz (**7**)) and $[NBu_4][M(C_6F_5)_2Cl(Hpz)]$ (M = Pd (**8**), Pt (**9**)) have been prepared by reaction of *cis*-$[MR_2(PhCN)_2]$ and $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}Cl)\}_2]$, respectively, with HX (1:2 mole ratio). Deprotonation by NBu_4OH of complexes **1**, **3**, and **5**, and **6** leads to the formation of the pyrazole–pyrazolato complexes $[NBu_4][MR_2X(HX)]$ (M = Pd, X = pz, R = C_6F_5 (**10**), C_6Cl_5 (**11**); M = Pt, R = C_6F_5, X = pz (**12**), dmpz (**13**); M = Pt, R = C_6Cl_5, X = pz (**14**)). The IR and NMR data for complexes **10**–**14** show that both pyrazolyl ligands are identical, and the X-ray structure determinations of **10** and **12** have established the existence of a intramolecular hydrogen bond between the two pyrazolyl rings, the coordination at palladium and platinum being essentially square planar. The structures are isomorphous, and both compounds are tetragonal, space group $P4_32_12$. Crystal data for **10**: $a = b = 17.022$ (2) Å, $c = 12.466$ (3) Å, $Z = 4$, 2146 reflections, $R = 0.045$. Crystal data for **12**: $a = b = 17.088$ (2) Å, $c = 12.466$ (4) Å, $Z = 4$, 2540 reflections, $R = 0.029$.

Introduction

Pyrazole-type heterocycles represent an important class of ligands in organometallic chemistry,[1-3] and the coordination chemistry of these ligands has been the subject of an excellent review by Trofimenko.[1] They can act as neutral monodentate (pyrazole-*N*), anionic monodentate (pyrazolato-*N*), or exo-bidentate anionic ligands (pyrazolato-*N,N′*) on coordination to metal centers.

The syntheses of a number of organometallic binuclear nickel, palladium, and platinum complexes of the types $[R_2M(\mu\text{-}X)_2MR_2]^{2-}$, $[R_2M(\mu\text{-}OH)(\mu\text{-}X)MR_2]^{2-}$, and $[R(PPh_3)M(\mu\text{-}OH)(\mu\text{-}X)M(PPh_3)R]$ (R = C_6F_5, C_6Cl_5, $C_6H_2F_3$-2,4,6; X = exo-bidentate pyrazolate-type ligand; M = Ni,[4,5] Pd,[6-9] Pt[10]) have been reported recently. Nonorganometallic pyrazolato palladium and platinum complexes of general formula $[(L\text{-}L)MX_2]$ (L-L = various bis(diphenylphosphines) and bis(diphenylarsines), 2,2′-

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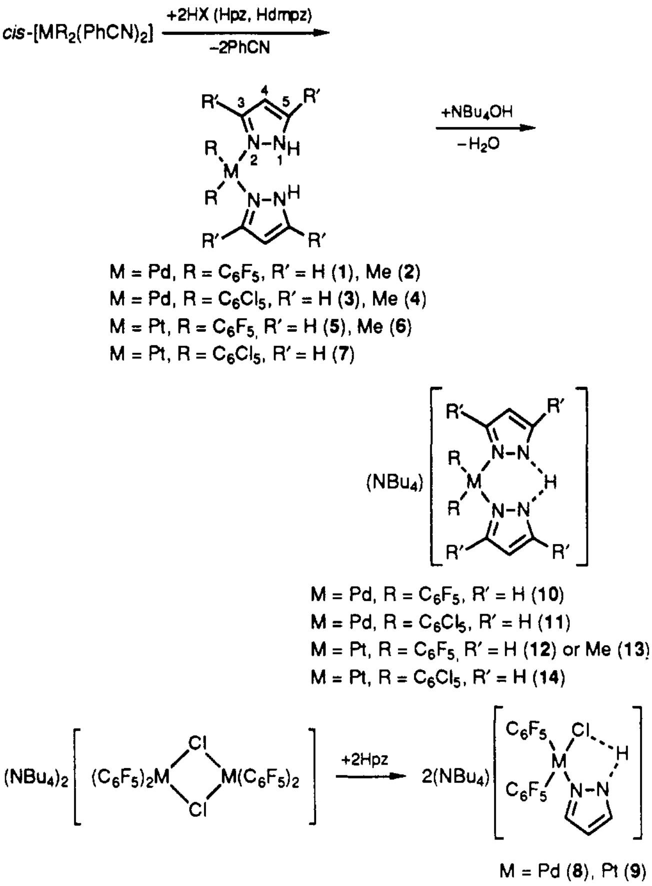
Scheme I



bipyridine; X = pz, dmpz; M = Pd,[11] Pt[11-13]) are also known. Protonation of the free nitrogen atom of monodentate coordinated pyrazolate in [(L-L)MX$_2$] by HBF$_4$ and substitution of the chloride ligands in [(L-L)MCl$_2$] by the neutral pyrazole HX are the common methods used for the preparation of palladium and platinum complexes containing pyrazoles as ligands. Similar methods have been applied to the preparation of pyrazole (HX) complexes of rhodium(III),[14] iridium(III),[14-16] and ruthenium(II).[17-19]

In this article we describe the synthesis of some bis(azole) and chloride–azole Pd(II) and Pt(II) complexes. Deprotonation of the bis(azole) complexes by OH$^-$ leads to the formation of the first reported palladium and platinum azole–azolato complexes, which may be used as precursors for the synthesis of azolato-bridged bimetallic complexes.

Table I. NMR Spectroscopic Data[a] for the Neutral Complexes 1–7

complex	^{1}H	^{19}F
1[b]	12.49 (br s, 2 H, NH)	−115.4 (d, 4 F$_o$, J_{om} = 26.0)
	7.86 (br d, 2 H, 5-H, $J_{54} \approx 2.2$)	−163.3 (t, 2F$_p$, J_{mp} = 19.5)
	7.41 (br s, 2 H, 3-H)	−165.5 (m, 4 F$_m$)
	6.42 (br s, 2 H, 4-H)	
2[c]	9.82 (br s, 2 H, NH)	−117.6 (d, 4 F_o, J_{om} = 26.8)
	5.76 (br d, 2 H, 4-H, $J \approx 1.2$)	−161.7 (t, 2 F$_p$, J_{mp} = 19.8)
	2.19 (s, 6 H, 5-Me)	−164.1 (m, 4 F$_m$)
	2.11 (s, 6 H, 3-Me)	
3[b]	12.36 (br s, 2 H, NH)	
	7.83 (d, 2 H, 5-H, J_{54} = 2.5)	
	7.27 (d, 2 H, 3-H, J_{34} = 1.9)	
	6.34 (pseudotriplet, 2 H, 4-H)	
4[b]	11.46 (br s, 2 H, NH)	
	5.87 (br s, 2 H, 4-H)	
	2.11 (s, 6 H, 5-Me)	
	2.08 (s, 6 H, 3-Me)	
5[b]	12.68 (br s, 2 H, NH)	−119.0 (d, 4 F$_o$, J_{om} = 20.3, J_{PtF_o} = 479)
	7.91 (d, 2 H, 5-H, J_{54} = 2.5)	
	7.50 (d, 2 H, 3-H, J_{34} = 2.2, J_{HPt} = 10.3)	−165.0 (t, 2 F$_p$, J_{mp} = 19.2)
	6.46 (pseudotriplet, 2 H, 4-H)	−166.7 (m, 4 F$_m$)
6[c]	10.37 (br, 2 H, NH)	−121.1 (d, 4 F$_o$, J_{om} = 25.2, J_{PtF_o} = 493)
	5.78 (br s, 2 H, 4-H)	
	2.16 (s, 6 H, 5-Me)	−163.4 (t, 2 F$_p$, J_{mp} = 19.7)
	2.12 (s, 6 H, 3-Me)	−165.3 (m, 4 F$_m$)
7[b,d]	12.56 (br s, 2 H, NH)	
	7.88 (2 H, 5-H)	
	7.32 (2 H, 3-H)[e]	
	6.42 (2 H, 4-H)	

[a] Chemical shifts in ppm from TMS (^{1}H) or from CFCl$_3$ (^{19}F); J values in Hz. Abbreviations: br, broad; s, singlet; d, doublet. [b] In (CD$_3$)$_2$CO. [c] In CDCl$_3$. [d] For explanation see text. [e] Unresolved ^{195}Pt satellites.

Results and Discussion

Neutral Bis(pyrazole) Complexes *cis*-[MR$_2$(HX)$_2$]. The benzonitrile complexes *cis*-[MR$_2$(PhCN)$_2$] (M = Pd,[7,8,20-23] Pt;[24] R = C$_6$F$_5$, C$_6$Cl$_5$) have been shown to be good precursors for synthetic work. The reaction of *cis*-[MR$_2$(PhCN)$_2$] with HX (X = pz, dmpz) in chloroform gives the neutral bis(pyrazole-*N*) complexes 1–7 (Scheme I). The replacement of PhCN by HX takes place without isomerization, and the reaction products are the cis isomers. The new complexes 1–7 have been characterized on the basis of partial elemental analysis and IR and NMR (^{1}H and ^{19}F) spectroscopy.

The IR spectra of the bis(pentahalophenyl) derivatives show the absorptions attributed to the C$_6$F$_5$ (1630, 1490, 1460, 1050, and 950 cm^{-1})[25] or the C$_6$Cl$_5$ (1315, 1285, 1220, and 670 cm^{-1})[26] groups. Moreover, an absorption located at ca. 800 cm^{-1} in the spectra of the bis(pentafluorophenyl) derivatives[27,28] or at ca. 830 cm^{-1} for the bis(pentachloro-

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phenyl) derivatives[29] has previously been used for structural elucidation. It is derived from the so-called halogen-sensitive mode in C_6F_5 and C_6Cl_5 halogen molecules[30-32] and in square-planar MR_2L_2 (R = C_6F_5, C_6Cl_5) complexes is related to the skeletal symmetry of the entire molecule[33] and behaves like a ν(M–C) band. This absorption is observed as a split band in complexes **1**–**7**, which is characteristic of the *cis*-MR_2 fragment (C_{2v} symmetry). In the spectra of the bis(pentachlorophenyl) derivatives **3**, **4**, and **7** a split band at ca. 610 cm^{-1}, assigned to ν(M–C),[26] also supports the cis geometry. All the bis(pyrazole) complexes present an intense ν(N-H) band in the 3460–3380-cm^{-1} region.

The ^{19}F NMR spectra of compounds **1**, **2**, **5**, and **6** (Table I) show the expected three signals (relative intensities 2:1:2) corresponding to the ortho, para, and meta fluorine atoms of two equivalent C_6F_5 groups freely rotating around the carbon–metal bond. The ^1H NMR spectra (Table I) consist of four resonances with relative intensities of 2:2:2:2 which is some cases appear as broad or incompletely resolved signals. The resonances at δ 12.7–9.8 and 6.5–6.3 in the spectra of complexes **1**, **3**, **5**, and **7** are unambiguously assigned to 1-H and 4-H atoms, respectively (with the numbering given in Scheme I, i.e., considering the heterocyclic ring as a 1*H*-azole coordinated to the metal atom through the 2-N lone pair).[17] The resonance at δ 7.5–7.2 should be assigned to 3-H because this signal is flanked by ^{195}Pt satellites in the spectra of compounds **5** and **7**. By comparison, the low-field methyl resonance is assigned to 5-Me in complexes **2**, **4**, and **6**. The splitting pattern observed for 5-H, 3-H, and 4-H in the spectrum of compound **7** was quite different from those of the other compounds. The two-dimensional spectroscopy (COSY) homonuclear (^1H–^1H) experiment showed the couplings 5-H/4-H and 3-H/4-H, but only NH irradiation gave clear evidence for the coupling of 1-H with the 5-, 3-, and 4-H atoms, when the 1-H signal collapsed and the 5-, 3-, and 4-H resonances were observed as a doublet (J_{54} = 2.4 Hz), a doublet (J_{34} = 1.8 Hz), and a pseudotriplet, respectively. The coupling constants J_{15}, J_{13}, and J_{14} could not be determined.

Anionic Complexes $[NBu_4][MR_2Cl(HX)]$ and $[NBu_4][MR_2X(HX)]$. The chloro–pyrazole complexes **8** and **9** (Scheme I) were obtained when the chloro-bridged binuclear complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ (M = Pd, Pt) were treated with Hpz (1:2 mole ratio) in chloroform. In acetone solution both complexes behave as 1:1 electrolytes,[34] in accordance with the formulas given. The IR spectra show the split band of the C_6F_5 group which is characteristic of the *cis*-$\{M(C_6F_5)_2\}$ fragment, as well as a strong band at 3250 cm^{-1} for the N–H stretching vibration of coordinated Hpz; the lower wavenumber of this band compared with that of the bis(pyrazole) complexes may be attributed to the presence of the hydrogen bond N–H···Cl.[17] The ^{19}F NMR patterns are consistent with the presence of two nonequivalent C_6F_5 groups, one C_6F_5 trans to Cl and one C_6F_5 trans to Hpz (Table II). The assignment of the ^1H NMR spectroscopic data (Table II) were made on the basis of the same numbering given above for the coordinated azole ring.

Table II. NMR Spectroscopic Data[a] for the Anionic Complexes 8–14

complex	^1H[b]	^{19}F
8[c]	12.43 (br, 1 H, NH)	−114.6 (d, 2 F_o, J_{om} = 30.1)
	7.43 (br s, 1 H, 5-H)	−115.0 (d, 2 F_o, J_{om} = 30.2)
	6.70 (br s, 1 H, 3-H)	−162.7 (t, F_p, J_{mp} = 20.3)
	6.14 (pseudoquartet, 1 H, 4-H)[d]	−164.3 (t, F_p, J_{mp} = 19.8)
		−164.9 (m, 2 F_m)
		−166.0 (m, 2 F_m)
9[c]	12.61 (br, 1 H, NH)	−118.1 (d, 2 F_o, J_{om} = 26.2, J_{PtF_o} = 488.2)
	7.50 (br s, 1 H, 5-H)	−118.9 (d, 2 F_o, J_{om} = 26.0, J_{PtF_o} = 484.3)
	7.20 (br s, 1 H, 3-H)	−164.5 (t, 1 F_p, J_{mo} = 20.0)
	6.16 (br s, 1 H, 4-H)	−165.9 (m, 1 F_p + 2 F_m)
		−166.8 (m, 2 F_m)
10[e]	7.60 (d, 2 H, 5-H, J_{54} = 2.1)	−113.3 (d, 4 F_o, J_{om} = 28.2)
	6.65 (d, 2 H, 3-H, J_{34} = 1.9)	−164.7 (t, 2 F_p, J_{mp} = 20.0)
	6.05 (pseudotriplet, 2 H, 4-H)	−166.0 (m, 4 F_m)
11[e]	7.57 (d, 2 H, 5-H, J_{54} = 1.9)	
	6.64 (d, 2 H, 3-H, J_{34} = 1.7)	
	6.02 (pseudotriplet, 2 H, 4-H)	
12[e]	7.61 (d, 2 H, 5-H, J_{54} = 2.0)	−116.7 (d, 4 F_o, J_{om} = 26.2, J_{PtF_o} = 489.1)
	6.91 (d, 2 H, 3-H, J_{34} = 1.8, J_{HPt} = 15)	−166.5 (t, 2 F_p, J_{mp} = 19.2)
	6.07 (pseudotriplet, 2 H, 4-H)	−167.3 (m, 2 F_m)
13[c]	5.62 (s, 2 H, 4-H)	−119.3 (d, 4 F_o, J_{om} = 27.0, J_{PtF_o} = 493)
	2.23 (s, 6 H, 5-Me)	−165.2 (t, 2 F_p, J_{mp} = 20.2)
	1.97 (s, 6 H, 3-Me)	−166.6 (m, 4 F_m)
14[e]	7.61 (d, 2 H, 5-H, J_{54} = 1.9)	
	6.83 (d, 2 H, 3-H, J_{34} = 1.7, J_{HPt} = 10.7)	
	6.05 (pseudotriplet, 2 H, 4-H)	

[a] See footnote *a* in Table I. [b] Additional peaks from $[NBu_4]^+$ are found at δ ca. 3.3 (t, NCH_2), 1.7 (m, NCH_2CH_2), 1.4 (m, CH_2CH_3), and 1.0 (t, CH_3), the relative intensities being 8:8:8:12. [c] In $CDCl_3$. [d] As with complex **7** (see Table I and text), the pseudoquartet is due to coupling of 4-H with NH, 5-H, and 3-H. After NH irradiation the original signals converted to a doublet (J_{54} = 2.2), a doublet (J_{34} = 1.7), and a pseudotriplet for 5-, 3-, and 4-H, respectively, when the NH resonance collapsed. [e] In $(CD_3)_2CO$.

Proton abstraction by NBu_4OH of complexes **1**, **3**, and **5**–**7** in acetone (1:1 mole ratio) leads to the formation of the corresponding pyrazole–pyrazolato complexes **10**–**14** with the concomitant release of water (Scheme I). It is worth mentioning that further addition of NBu_4OH (i.e. 1:2 mole ratio) did not cause abstraction of the remaining proton in the neutral azole ligand. The IR data for the pentahalophenyl ligands indicate the presence of the *cis*-MR_2 moiety, but no absorption assignable to ν(N–H) was found in the 3500–3000-cm^{-1} region. In similar complexes of iridium[15] and ruthenium[17] a broad, medium band centered at 2800 cm^{-1} was assigned to ν(N–H), but in the spectra of our complexes this spectral region is obscured by the C–H stretching vibrations arising from the $[NBu_4]^+$ cation. The analytical data, the values of the molar conductivities in acetone solution (1:1 electrolytes),[34] and the NBu_4^+:pyrazolyl mole ratio (1:2) shown by the ^1H NMR spectra make it necessary to postulate the presence of the "extra" hydrogen atom at one of the coordinated azoles of compounds **10**–**14**.

Although these compounds are formulated as pyrazole–pyrazolato complexes, *cis*-$[MR_2X(HX)]$, the ^{19}F NMR data for complexes **10**, **12**, and **13** clearly indicate both pyrazolyl rings to be equivalent and the same conclusion is inferred from the ^1H spectra of **10**–**14** (Table II), since only one set of proton resonances is observed for the substituents on the 3-, 4-, and 5-positions of the hetero-

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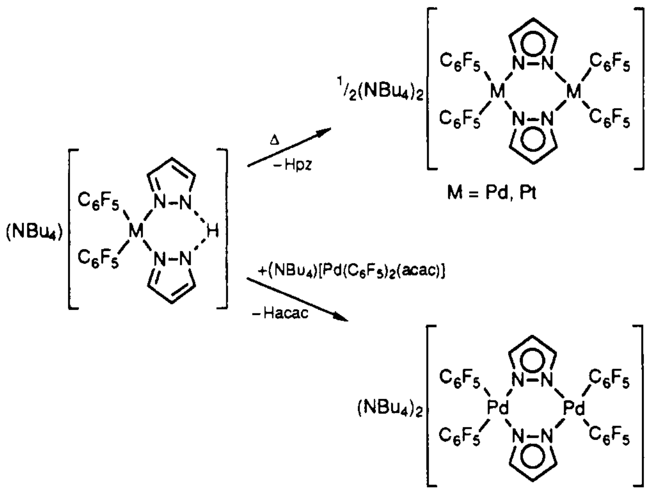
Scheme II



cyclic ring (with the same numbering as above). All of these data taken together strongly suggest the structure shown in Scheme I for the anions in compounds **10**–**14**. This "chelated proton" structure should be similar to that proposed for some $(\eta^5\text{-}C_5H_5)$(perfluoroalkyl)$Co(C_3H_3N_2)_2H$ derivatives[35] and that crystallographically established in $[(\eta^5\text{-}C_5Me_5)$(dmpz)Ir(dmpz)(Hdmpz)].[15]

The ^{1}H NMR data of complexes **10**–**14** indicate that in solution there is a fast (on the ^{1}H and ^{19}F NMR time scales) proton exchange between the 1-N atoms of both pyrazolate rings. The presence of the hydrogen bond N–H···N in the solid state has been established by X-ray diffraction studies for compounds **10** and **12**. In rigorously dried solvents no signal attributable to NH (in the 12–10 ppm region) is observed in the ^{1}H spectra of **10**–**14** because of H/D exchange between $CDCl_3$ or $(CD_3)_2CO$ and the pyrazolyl complex. In solvents which are not completely water-free a broad resonance signal is observed in the 5–3 ppm region but the exact position of the signal depends not only on the identities of the complex and the solvent but also on the concentration of the solution, indicating that H exchange takes place between NH and H_2O.

When they are heated under an atmosphere of nitrogen, all the azole–azolato complexes **10**–**14** decompose, the final decomposition product being metallic palladium or platinum, but the thermogravimetric curves of complexes **10** and **12** showed the formation of stable intermediate species (see Scheme II) in the temperature ranges 158–266 and 198–290 °C, respectively. As described in the Experimental Section, these species were isolated and identified as the previously reported pyrazolato-bridged complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-pz})\}_2]$ (M = Pd,[6] Pt[10]) resulting from the loss of one Hpz molecule in **10** and **12** and subsequent dimerization to regenerate the four-coordination of the metal atom.

It is worth mentioning that proton abstraction by NBu_4OH from $[PdR_2(Hdmpz)_2]$ (R = C_6F_5, C_6Cl_5) does not lead to the reaction products $[NBu_4][PdR_2$(dmpz)(Hdmpz)] (this is the reason these compounds are lacking in Scheme I). Instead the complex $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-dmpz})\}_2]$ or a mixture of $[NBu_4]_2[\{Pd(C_6Cl_5)_2(\mu\text{-dmpz})\}_2]$ (identified by ^{1}H NMR spectroscopy; see Experimental Section) and the previously reported[8] $[NBu_4]_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-OH})(\mu\text{-dmpz})]$ are formed. It is likely that the expected reaction products $[PdR_2$(dmpz)(Hdmpz)$]^-$, if formed, dissociate to give $[R_2Pd(\mu\text{-dmpz})_2PdR_2]^{2-}$ + Hdmpz, and partial hydrolysis of the pentachlorophenyl derivative accounts for the presence of the μ-OH–μ-dmpz complex.

Table III. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for 10

	x	y	z	U_{eq}[a]
Pd	3415.0 (3)	3415.0	0	45.81 (8)
F1	2295 (2)	2662 (2)	−1859 (3)	71 (3)
F2	747 (3)	2725 (3)	−2142 (4)	99 (3)
F3	−172 (2)	3487 (3)	−672 (4)	104 (3)
F4	493 (3)	4161 (3)	1058 (4)	94 (3)
F5	2040 (2)	4098 (3)	1350 (3)	76 (3)
N1	3413 (3)	4609 (3)	−429 (4)	52 (3)
N2	4084 (3)	5039 (3)	−472 (4)	55 (3)
N3	1358 (3)	1358	5000	75 (2)
C1	2858 (4)	5049 (4)	−910 (6)	64 (4)
C2	3169 (4)	5749 (4)	−1239 (6)	61 (4)
C3	3942 (4)	5712 (4)	−951 (6)	60 (4)
C4	2250 (3)	3381 (4)	−244 (5)	48 (3)
C5	1869 (4)	3047 (4)	−1106 (5)	54 (4)
C6	1074 (4)	3077 (4)	−1276 (6)	63 (4)
C7	614 (3)	3459 (5)	−554 (6)	68 (4)
C8	943 (4)	3799 (4)	331 (6)	64 (4)
C9	1762 (4)	3741 (4)	471 (5)	50 (4)
C10	637 (5)	1371 (5)	5715 (5)	80 (5)
C11	−145 (5)	1311 (5)	5197 (7)	91 (6)
C12	−755 (6)	1291 (6)	6081 (8)	113 (7)
C13	−1561 (7)	1153 (7)	5719 (9)	139 (8)
C14	2078 (5)	1341 (6)	5757 (7)	98 (6)
C15	2883 (6)	1343 (7)	5275 (8)	122 (8)
C16	3499 (7)	1225 (7)	6198 (8)	140 (8)
C17	4273 (8)	1221 (9)	5842 (11)	171 (12)
HN	4654 (50)	4654	0	125 (52)[b]

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] U_{iso}.

Homobimetallic azolate-bridged nickel,[5] palladium,[6] and platinum[10] complexes have been prepared by the reaction between the basic $[R_2M(\mu\text{-OH})_2MR_2]^{2-}$ and the acidic azole, and homo- or heterobimetallic $\{M(\mu\text{-pz})_2M'\}$ can be obtained by reaction between a {M(pz)(HPz)} or $\{M(Hpz)_2\}$ complex and a {M′(acac)} complex with the concomitant release of Hacac (acac = acetylacetonate). This is a synthetic strategy widely and successfully applied by Oro et al. to rhodium and iridium chemistry.[16,36] In methanol complex **10** reacts with $[NBu_4][Pd(C_6F_5)_2(acac)]$, affording $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-pz})\}_2]$ in good yield (Scheme II). It should be noted that when the same reaction is carried out in acetone it does not go to completion (see Experimental Section), probably because in acetone the reverse reaction, in which the di-μ-pz complex is attacked by Hacac, is competing.

Structures of the Pyrazole–Pyrazolate Complexes 10 and 12. Good-quality colorless prismatic crystals of complexes **10** and **12** were obtained by recrstallization from CH_2Cl_2/hexane. The structures were isomorphous, and both compounds crystallized in a tetragonal unit cell. Systematic absences indicated that the space group was either $P4_12_12$ or $P4_32_12$; better R factors were obtained on refinement in $P4_32_12$. Atomic coordinates for **10** are given in Table III and for **12** in Table IV. Selected bond lengths and angles are given in Tables V and VI, respectively. The structures of the anions of **10** and **12** are shown in Figures 1 and 2.

The coordination at palladium and platinum is square-planar with interbond angles which deviate little from 90°. The hydrogen-bonded bis(pyrazolate) unit is essentially planar, and the hydrogen atom could be located in a symmetric position only for the palladium complex.

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Table IV. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³) for 12

	x	y	z	U_{eq}[a]
Pt	3415.8 (1)	3415.8	0	43.59 (4)
F1	2299 (2)	2655 (2)	−1864 (3)	71 (2)
F2	750 (3)	2703 (3)	−2134 (4)	100 (3)
F3	−187 (2)	3468 (3)	−693 (4)	105 (3)
F4	466 (3)	4161 (3)	1042 (4)	96 (3)
F5	2022 (3)	4132 (3)	1338 (3)	81 (3)
N1	3423 (3)	4604 (3)	−430 (4)	51 (3)
N2	4092 (3)	5033 (3)	−465 (4)	57 (3)
N3	1372 (4)	1372	5000	80 (2)
C1	2854 (4)	5041 (4)	−888 (6)	63 (4)
C2	3171 (4)	5751 (4)	−1218 (6)	63 (4)
C3	3942 (4)	5721 (4)	−943 (6)	59 (4)
C4	2254 (3)	3394 (4)	−247 (4)	49 (3)
C5	1872 (4)	3039 (4)	−1109 (5)	54 (4)
C6	1071 (4)	3069 (4)	−1279 (6)	67 (4)
C7	595 (4)	3449 (5)	−555 (6)	71 (4)
C8	931 (4)	3805 (4)	319 (6)	67 (4)
C9	1739 (4)	3755 (4)	456 (5)	54 (4)
C10	638 (5)	1379 (5)	5710 (6)	81 (5)
C11	−142 (5)	1304 (5)	5185 (7)	94 (6)
C12	−759 (6)	1278 (6)	6080 (9)	117 (8)
C13	−1534 (7)	1155 (8)	5734 (9)	156 (9)
C14	2071 (5)	1373 (5)	5769 (7)	99 (6)
C15	2873 (6)	1354 (6)	5280 (8)	121 (8)
C16	3492 (6)	1237 (8)	6213 (9)	141 (8)
C17	4270 (8)	1186 (9)	5824 (12)	189 (13)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Intramolecular Distances (Å) and Angles (deg) for 10, with Estimated Standard Deviations in Parentheses[a]

	(a) Distances		
Pd-N1	2.103 (5)	Pd-C4	2.007 (5)
N1-C1	1.346 (9)	N2-C3	1.314 (8)
C1-C2	1.368 (10)	N1-N2	1.356 (8)
C2-C3	1.365 (9)	N2-HN	1.31 (6)
	(b) Angles		
N1-Pd-N1′	93.9 (2)	N1-Pd-C4	89.3 (2)
N1-Pd-C4′	173.7 (2)	C4-Pd-C4′	88.1 (3)
Pd-N1-N2	122.0 (4)	Pd-N1-C1	130.7 (5)
N2-N1-C1	105.9 (5)	N1-N2-C3	109.5 (5)
N1-N2-HN	110 (2)	C3-N2-HN	141 (2)
N1-C1-C2	110.2 (6)	C1-C2-C3	104.7 (6)
N2-C3-C2	109.7 (6)	N2-HN-N2′	160 (5)

[a] The symmetry element denoted by a prime is y, x, $-z$.

Table VI. Intramolecular Distances (Å) and Angles (deg) for 12, with Estimated Standard Deviations in Parentheses[a]

	(a) Distances		
Pt-N1	2.091 (5)	Pt-C4	2.000 (5)
N1-C1	1.348 (9)	N2-C3	1.337 (8)
C1-C2	1.385 (10)	N1-N2	1.353 (7)
C2-C3	1.356 (10)		
	(b) Angles		
N1-Pt-N1′	93.1 (2)	N1-Pt-C4	89.1 (2)
N1-Pt-C4′	174.0 (2)	C4-Pt-C4′	89.2 (2)
Pt-N1-N2	122.3 (4)	Pt-N1-C1	129.6 (4)
N2-N1-C1	107.1 (5)	N1-N2-C3	109.0 (5)
N1-C1-C2	109.0 (6)	C1-C2-C3	105.7 (6)
N2-C3-C2	109.2 (6)		

[a] The symmetry element denoted by a prime is y, x, $-z$.

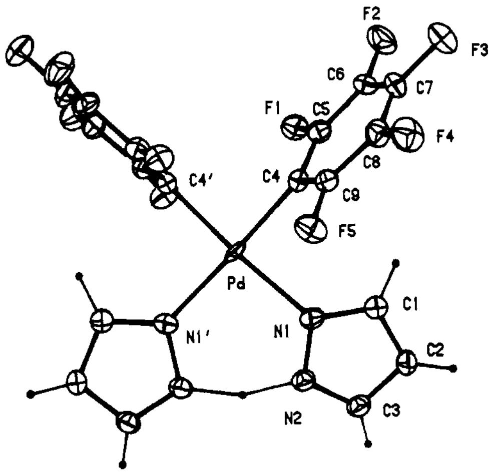

Figure 1. Structure of the anion of 10.

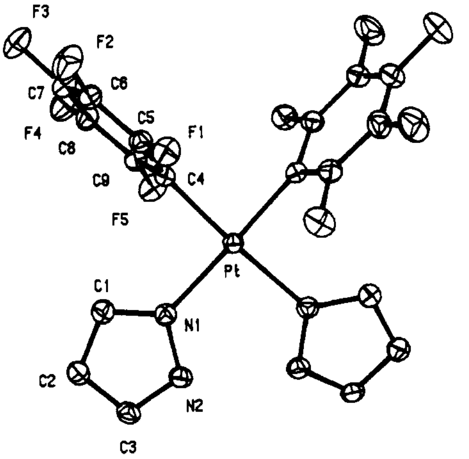

Figure 2. Structure of the anion of 12.

The hydrogen bond is slightly bent. The palladium–nitrogen bond length in 10, at 2.103 (5) Å, is slightly longer than that in $[(OC)_2Rh(\mu\text{-pyrazolate})(\mu\text{-}N_3)Pd(\eta^3\text{-}C_3H_5)]$ (2.036 (14) Å),[37] $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3B\text{-}B(pz)_3\}]$ (2.049–2.088 Å),[38] or *trans*-$[PdCl_2(2\text{-ethenyl-5-methylpyrazole})_2]$ (2.039 Å).[39] A similar phenomenon is observed when we compare the Pt–N bond length in 12 with those in $[Pt(pz)_2(PMe_2Ph)_2]$,[40] $[PtCl_2(pz)_2]$,[41] and *trans*-$[PtCl_2(C_2H_4)(pz)]$.[42] Thus, the Pt-N bond lengths seen here are longer than those previously noted for either pyrazole or pyrazolate complexes, and it seems likely that these are the result of the steric demands of the aryl ligands.

Conclusions

The complexes *cis*-$[MR_2(PhCN)_2]$ and $[\{M(C_6F_5)_2(\mu\text{-}Cl)\}_2]^{2-}$ are good precursors for the synthesis of neutral *cis*-$[MR_2(HX)_2]$ and anionic *cis*-$[M(C_6F_5)_2Cl(HX)]^-$ complexes, respectively (HX = pyrazole, 3,5-dimethylpyrazole). Deprotonation of the $(HX)_2$ complexes by OH^- leads to the formation of the corresponding anionic derivatives *cis*-$[MR_2(X)(HX)]^-$. NMR spectroscopic data indicate that in acetone or chloroform solution there is a prototropic exchange between the two azolate rings of the azole–azolato complexes, and X-ray structure determinations reveal the presence of an H atom between the two N atoms not bonded to the metal center. In the thermal treatment of

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complexes **10** and **12** one molecule of Hpz is released and the binuclear anionic complexes $[(C_6F_5)_2M(\mu\text{-pz})_2M(C_6F_5)_2]^{2-}$ are formed, but this is not a general method to synthesize $\{M(\mu\text{-azoalte})_2M\}$ complexes because in similar complexes the bis(μ-azolato) complex cannot be isolated as a stable species. Deprotonation of **10** by $[Pd(C_6F_5)_2(acac)]^-$ leads to the formation of $[(C_6F_5)_2Pd(\mu\text{-pz})_2Pd(C_6F_5)_2]^{2-}$ with the concomitant release of acetylacetone, and consequently, by appropriate choice of the reactants a general method for the synthesis of $R_2M(\mu\text{-azolato})_2M'R_2$-type complexes may be anticipated.

Experimental Section

The C, H, and N analyses were carried out with a Carlo Erba Model EA 1108 microanalyzer. Conductance measurements were made with a Crison 525 conductimeter in acetone solutions ($c \approx 5 \times 10^{-4}$ mol L^{-1}). Thermal decomposition studies were carried out with a Mettler TG-50 thermobalance. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets or potassium bromide pellets. The NMR spectra were recorded on a Bruker AC 200E (^{1}H) or Varian Unity 300 (^{19}F) spectrometer. Solvents were dried by the usual methods. The starting complexes *cis*-$[MR_2(PhCN)_2]$ (M = Pd (R = C_6F_5,[20] C_6Cl_5[8]), Pt (R = C_6F_5, C_6Cl_5)[24]) and $[NBu_4]_2[\{(C_6F_5)_2M\}_2(\mu\text{-Cl})_2]$ (M = Pd,[27] Pt[43]), were prepared by procedures described elsewhere.

Preparation of Complexes $[MR_2(HX)_2]$ (1–7). To a solution of $[MR_2(PhCN)_2]$ (0.15 mmol) in chloroform (5 mL) was added either pyrazole or 3,5-dimethylpyrazole (0.31 mmol). The mixture was stirred for 30 min, and then the solution was concentrated under vacuum. The addition of hexane caused the precipitation of white crystals of compounds **1**–**7**, which were collected by filtration and air-dried.

Complex **1**: yield 75%; mp 215 °C dec; IR (Nujol, cm^{-1}) 3450 (ν(NH)), 800, 790 (Pd–C_6F_5). Anal. Calcd for $C_{18}H_8N_4F_{10}Pd$: C, 37.5; H, 1.4; N, 9.7. Found: C, 37.7; H, 1.5; N, 9.7. Complex **2**: yield 80%; mp 232 °C dec; IR (Nujol, cm^{-1}) 3460, 3440 (ν(NH)), 795, 785 (Pd–C_6F_5). Anal. Calcd for $C_{22}H_{16}N_4F_{10}Pd$: C, 41.8; H, 2.5; N, 8.9. Found: C, 41.7; H, 2.7; N, 9.1. Complex **3**: yield 96%; mp 93 °C dec; IR (Nujol, cm^{-1}) 3420 (ν(NH)), 835, 825 (Pd–C_6Cl_5). Anal. Calcd for $C_{18}H_8N_4Cl_{10}Pd$: C, 29.2; H, 1.1; N, 7.6. Found: C, 29.5; H, 1.6; N, 7.4. Complex **4**: yield 71%; mp 211 °C dec; IR (Nujol, cm^{-1}) 3425, 3405 (ν(NH)), 830, 825 (Pd–C_6Cl_5). Anal. Calcd for $C_{22}H_{16}N_4Cl_{10}Pd$: C, 33.1; H, 2.0; N, 7.0. Found: C, 32.8; H, 2.1; N, 7.3. Complex **5**: yield 70%; mp 244 °C dec; IR (Nujol, cm^{-1}) 3440 (ν(NH)), 810, 800 (Pd–C_6F_5). Anal. Calcd for $C_{18}H_8N_4F_{10}Pt$: C, 32.5; H, 1.2; N, 8.4. Found: C, 32.1; H, 1.1; N, 8.5. Complex **6**: yield 73%; mp 270 °C dec; IR (Nujol, cm^{-1}) 3460, 3430 (ν(NH)), 805, 795 (Pd–C_6F_5). Anal. Calcd for $C_{22}H_{16}N_4F_{10}Pt$: C, 36.6; H, 2.2; N, 7.8. Found: C, 36.9; H, 2.3; N, 8.0. Complex **7**: yield 95%; mp 244 °C dec; IR (Nujol, cm^{-1}) 3380 (ν(NH)), 840, 835 (Pd–C_6Cl_5). Anal. Calcd for $C_{18}H_8N_4Cl_{10}Pt$: C, 26.0; H, 1.0; N, 6.8. Found: C, 26.5; H, 1.3; N, 6.8.

Preparation of Complexes $[NBu_4][M(C_6F_5)_2Cl(Hpz)]$ (8, 9). Pyrazole (0.139 mmol) was added to a chloroform (5 mL) suspension of $[NBu_4]_2[\{(C_6F_5)_2M\}_2(\mu\text{-Cl})_2]$ (0.0695 mmol). The resulting solution was stirred for 30 min and then concentrated under vacuum. On addition of hexane a white solid precipitated, which was filtered off and air-dried.

Complex **8**: yield 90%; mp 227 °C dec; $\Lambda_M = 95\ \Omega^{-1}$ cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 3250 (ν(NH)), 795, 780 (Pd–C_6F_5). Anal. Calcd for $C_{31}H_{40}N_3F_{10}ClPd$: C, 47.3; H, 5.1; N, 5.3. Found: C, 47.0; H, 5.4; N, 5.2. Complex **9**: yield 60%; mp 261 °C dec; $\Lambda_M = 104\ \Omega^{-1}$ cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 3250 (ν(NH)), 810, 795 (Pt–C_6F_5). Anal. Calcd for $C_{31}H_{40}N_3F_{10}ClPt$: C, 42.5; H, 4.6; N, 4.8. Found: C, 42.9; H, 4.8; N, 5.0.

Preparation of Complexes $[NBu_4][MR_2X(HX)]$ (10–14). To a solution of the corresponding $(HX)_2$ complex (**1**, **3**, or **5**–**7**, respectively; 0.173 mmol) in acetone (5 mL) was added a 20% aqueous solution of NBu_4OH (0.173 mmol). After it was stirred for 30 min, the solution was concentrated under vacuum. The addition of water caused the precipitation of a white solid, which was filtered off and air-dried.

Complex **10**: yield 80%; mp 158 °C dec; $\Lambda_M = 113\ \Omega^{-1}$ cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 790, 780 (Pd–C_6F_5). Anal. Calcd for $C_{34}H_{43}N_5F_{10}Pd$: C, 49.9; H, 5.3; N, 8.6. Found: C, 50.4; H, 5.8; N, 8.2. Complex **11**: yield 81%; mp 190 °C dec; $\Lambda_M = 97\ \Omega^{-1}$ cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 830, 820 (Pd–C_6Cl_5). Anal. Calcd for $C_{34}H_{43}N_5Cl_{10}Pd$: C, 41.6; H, 4.4; N, 7.1. Found: C, 41.3; H, 4.2; N, 7.1. Complex **12**: yield 90%; mp 198 °C dec; $\Lambda_M = 87\ \Omega^{-1}$ cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 800, 790 (Pt–C_6F_5). Anal. Calcd for $C_{34}H_{43}N_5F_{10}Pt$: C, 45.0; H, 4.8; N, 7.7. Found: C, 45.5; H, 4.8; N, 7.9. Complex **13**: yield 65%; mp 235 °C dec; $\Lambda_M = 95\ \Omega^{-1}$ cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 800, 790 (Pt–C_6F_5). Anal. Calcd for $C_{38}H_{51}N_5F_{10}Pt$: C, 47.4; H, 5.3; N, 7.3. Found: C, 47.8; H, 5.5; N, 7.4. Complex **14**: yield 72%; mp 223 °C dec; $\Lambda_M = 115\ \Omega^{-1}$ cm^2 mol^{-1}; IR (Nujol, cm^{-1}) 840, 830 (Pt–C_6Cl_5). Anal. Calcd for $C_{34}H_{43}N_5Cl_{10}Pt$: C, 38.1; H, 4.0; N, 6.5. Found: C, 37.7; H, 4.1; N, 6.4.

Thermal Treatment of Complexes 10 and 12. Both complexes were heated at 160 and 200 °C in the thermobalance in a dynamic N_2 stream to constant weight. The resulting solids were characterized by C, H, and N analysis, conductance measurements in acetone solution, and IR and ^{1}H NMR spectra, these data being coincident with those of the previously reported complexes $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-pz})\}_2]$ (M = Pd,[6] Pt[10]).

Reaction of 2 with NBu_4OH. To a solution of **2** (100 mg, 0.158 mmol) in acetone (5 mL) was added NBu_4OH (0.158 mmol, ca. 0.20 mL of a 20% aqueous solution). The solution was stirred for 30 min and then was vacuum-concentrated. Addition of small portions of water resulted in the precipitation of a white solid, which was collected by filtration and air-dried: yield 75%. The product was identified to be $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-dmpz})\}_2]$ by ^{1}H NMR spectroscopy.

Reaction of 4 with NBu_4OH. The workup was like that described above for **2**. The ^{1}H NMR spectrum (in $(CD_3)_2CO$) showed the isolated solid to be a 2:3 mixture of $[NBu_4]_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-OH})(\mu\text{-dmpz})]$ (δ 5.3 (s, 4-H), 1.5 (s, 3- and 5-Me), and -1.67 (s, μ-OH))[8] and a new complex tentatively identified as $[NBu_4]_2[\{Pd(C_6Cl_5)_2(\mu\text{-dmpz})\}_2]$ (δ 5.2 (s, 4-H) and 2.1 (s, 3- and 5-Me)), respectively, which we were not able to separate.

Reaction of Complex 10 with $[NBu_4][Pd(C_6F_5)_2(acac)]$. To a suspension of **10** (100 mg, 0.122 mmol) in methanol (10 mL) was added the acac (acetonylacetonate) complex[24] (95.57 mg, 0.122 mmol). The suspension was stirred for 1 h and then filtered off to separate a white solid, which was air-dried: yield 81%. Elemental analysis (C, H, N) and spectroscopic (IR, ^{1}H NMR) data identified the solid as the previously reported $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-pz})\}_2]$. When the same reaction was carried out in acetone, the solid isolated after precipitation with water (the starting compounds as well as the reaction product are soluble in acetone) was shown to be a 2:1 mixture of unchanged **10** (two doublets at δ 7.59 and 6.66 and a pseudotriplet at δ 6.04 for the pyrazolyl ligands) and the reaction product $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-pz})\}_2]$ (one doublet at δ 7.04 and one 1:2:1 triplet at δ 5.68 for the μ-pz ligands) together with a small amount of the reactant $[NBu_4][Pd(C_6F_5)_2(acac)]$ (two singlets at δ 5.22 and 1.74 for the CH and CH_3 protons of the acac ligand).

Crystal Structure Determination and Refinement. Data were collected on an Enraf-Nonius CAD4 diffractometer: graphite-monochromated Mo Kα radiation, θ–2θ scan, $\Delta\theta = (0.8 + 0.35 \tan \theta)°$, maximum scan time 1 min, Lorenz and polarization corrections. Drawings were made using ORTEP,[44] showing the atoms as 20% vibrational ellipsoids. Data are given in Table VII.

Data for **10** were collected using a piece 0.1 mm long cut from a prismatic crystal of section 0.1 × 0.1 mm. Unit cell parameters for **10** were obtained from the setting angles for 25 reflections with $16 < 2\theta < 20°$. The space group was assigned as $P4_13_12$ or $P4_32_12$ from the systematic absences of $h00$ for h odd and $00l$ for $l = 4n$. Structure solution was by heavy-atom methods using SHELXS-86[45] refinement by full-matrix least squares using

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[44] Johnson, C. K. ORTEP II; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

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Table VII. Summary of the Crystal Structure Data

	10	12
formula	$C_{34}H_{43}F_{10}N_5Pd$	$C_{34}H_{43}F_{10}N_5Pt$
recryst solvent	CH_2Cl_2/hexane	CH_2Cl_2/hexane
fw	818.1	906.83
cryst size, mm	0.1 × 0.1 × 0.1	0.4 × 0.2 × 0.15
cryst syst	tetragonal	tetragonal
space group	$P4_32_12$	$P4_32_12$
Z	4	4
a, b, Å	17.022 (2)	17.008 (2)
c, Å	12.466 (3)	12.466 (4)
V, Å^3	3612	3607
D_{exptl}, g cm^{-3}	1.50	1.66
λ(Mo Kα), Å	0.71069	0.71069
abs corr	none	DIFABS;[47] max 1.118, min 0.896
μ, cm^{-1}	20.4	40.1
2θ range, deg	4–50	4–50
hkl range	*h*, 0–20; *k*, 0–20; *l*, 0–14	*h*, 0–20; *k*, 0–20; *l*, 0–14
no. of measd rflns	3756	3572
no. of unique rflns	3196	3192
no. of obsd rflns	2146 ($\|F^2\| > 2\sigma(F^2)$)	2540 ($\|F^2\| > 2\sigma(F^2)$)
no. of variables	229	227
temp factors	C, F, N, Pd aniso	C, F, N, Pt aniso
w	$\sigma^2(F)$	$\sigma^2(F)$
R	0.045	0.029
R_w	0.050	0.033
s	1.15	0.94
$\Delta/\sigma_{\max}$	0.02	0.02
$(\Delta\rho)_{\max,\min}$ e Å^{-1}	+0.97, −1.59	0.56, 0.47
$F(000)$	1672	1800

programs from the Enraf-Nonius SDP package[46] with non-hydrogen atoms anisotropic. The hydrogen atom attached to N2 was located and freely refined with an isotropic thermal parameter, while the other hydrogen atoms were fixed at calculated positions with U_{iso} = 1.3 times the U_{eq} value for the parent atom; $w = 1/\sigma^2(F)$, and $\sum w(|F_o| - |F_c|)^2$ was minimized.

Data for 12 were collected using a prismatic crystal (0.4 × 0.2 × 0.15 mm). Unit cell parameters for 12 were obtained by a least-squares fit of 25 reflections with $8 < \theta < 12°$. The space group was assigned as $P4_32_12$ from the systematic absence of *h*00 for *h* odd and 00*l* for *l* = 4*n* and successful refinement. Original refinement in the enantiomorphous space group $P4_12_12$ (No. 92) gave a final $R = 0.047$ and $R_w = 0.065$, which were improved on refinement in $P4_32_12$. Non-hydrogen positions were taken from the isomorphous palladium complex and were refined by full-matrix least squares on F using programs from the SDS-Plus package.[46] Non-hydrogen atoms were refined anisotropically; $w = 1/\sigma^2(F)$, and $\sum w(|F_o| - |F_c|)^2$ was minimized. Hydrogen atoms were placed in calculated positions, except for the hydrogen atom involved in H-bonding. This could not be located on a difference map.

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Registry No. **1**, 143858-10-0; **2**, 143858-11-1; **3**, 143858-12-2; **4**, 143858-13-3; **5**, 143858-14-4; **6**, 143858-15-5; **7**, 143886-85-5; **8**, 143858-17-7; **9**, 143858-19-9; **10**, 143886-99-1; **11**, 143858-21-3; **12**, 143858-23-5; **13**, 143858-25-7; **14**, 143858-27-9; *cis*-Pd$(C_6F_5)_2(PhCN)_2$, 110900-60-2; *cis*-Pd$(C_6Cl_5)_2(PhCN)_2$, 136314-36-8; *cis*-Pt$(C_6F_5)_2(PhCN)_2$, 139912-62-2; *cis*-Pt$(C_6Cl_5)_2(PhCN)_2$, 139912-63-3; $(NBu_4)_2[\{(C_6F_5)_2Pd\}_2(\mu\text{-}Cl)_2]$, 74436-08-1; $(NBu_4)_2[\{(C_6F_5)_2Pt\}_2(\mu\text{-}Cl)_2]$, 90590-30-0; Hpz, 288-13-1; Hdmpz, 67-51-6.

Supplementary Material Available: Tables of hydrogen coordinates, anisotropic temperature factors, and least-squares planes for 10 and 12 and of torsion angles for 12 and plots of the NBu_4^+ cation and the unit cell packing diagram for 10 (14 pages). Ordering information is given on any current masthead page.

OM920219P

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Iron Carbonyl Promoted Conversion of α,ω-Diynes to (Cyclopentadienone)iron Complexes

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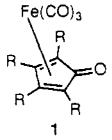
An efficient high-yielding procedure is described for the intramolecular carbonylative coupling of α,ω-diynes to give cyclopentadienone–$Fe(CO)_3$ complexes. Exchanging one CO ligand with PPh_3 affords control over the manipulation of α,α′-trimethylsilyl-substituted cyclopentadienone complexes. The preparation of α,ω-diynes with a hydroxy group adjacent to one alkyne unit leads to modest stereocontrol upon cyclization forming the $Fe(CO)_3$ complex. The hydroxy-substituted complex was oxidized to ketone. Borohydride reduction and Grignard addition to the ketone proceed anti to the $Fe(CO)_3$ moiety. The X-ray crystal structure of $C_{40}H_{31}FeO_3P$ shows that it crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions a = 12.0595 (24), b = 13.3926 (30), c = 19.0682 (38) Å, β = 93.98 (2)°, with Z = 4.

Introduction

We have developed a procedure for the synthesis of tricarbonyl(cyclopentadienone)iron complexes 1 in high yield via the intramolecular coupling of two alkyne moieties accompanied by the insertion of carbon monoxide.[1] Historically, the iron carbonyl mediated cyclization of acetylenes to form cyclopentadienone (CPD) complexes has been, with few exceptions, an inefficient process. Early reports cite the preparation of CPD tricarbonyliron complexes from phenyl- and diphenylacetylene in very low yields (<15%).[2] Only in cases where the R group is



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