observed with the cationic side chains of an unfused intercalator,[7] the amidine groups of DAPI cannot sterically fit into the minor groove but can fit quite well into the DNA major groove in a CG intercalation site (not shown). The phenyl and indole rings of DAPI stack well with base pairs at the intercalation site, and the cationic amidines associate with phosphate groups on opposite chains of the complex by H-bonding and electrostatic interactions.

Our results clearly demonstrate that DAPI binds to polyd(G-C)$_2$ by intercalation with binding strength and kinetics in the range typical of intercalators. More limited results indicate that DAPI binds to polyd(A-C)·polyd(G-T) in a manner similar to that for polyd(G-C)$_2$ but quite different from its groove-binding mode with polyd(A-T)$_2$. This is consistent with observations that groove-binding of DAPI requires three to four consecutive AT base pairs.[5] DAPI can thus intercalate at a broad range of sites, with little specificity, as with most other intercalators. More GC and mixed base-pair intercalation sites are available than consecutive AT base-pair, groove-binding sites on any natural DNA sequence. DAPI should thus be viewed as an intercalator that has unusual and very favorable interactions in the minor groove at AT sequences. The intercalation binding mode would not be easily detected by methods such as DNA footprinting due to its short lifetime. Preliminary modeling studies with other classical AT specific-groove-binding molecules suggest that they can also bind to GC base pairs by intercalation.

Acknowledgment. This research was supported by Grants NSF-8603566 and NIH-NIAID AI-27196 and by an NSF equipment grant for the VXR 400. We thank Dr. Clark Still for the MACROMODEL program and Dr. Mike Cory for assistance in modeling intercalation sites with the program.

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(15) Molecular mechanics calculations were conducted on a MicroVaxII-Evans and Sutherland PS390 system with the program MACROMODEL (Professor Clark Still, Columbia University). DAPI was docked in a central CG intercalation site (to be described elsewhere) in the dodecamer sequence d(CGTACGTACG) and minimized to a gradient of less than 0.1 kcal/mol·Å. Various orientations of DAPI, with the amidine groups in both the minor and the major grooves, were considered in the initial docking experiments. In all minor groove complexes the DAPI was forced out of the intercalation site by unfavorable van der Waals contacts.

Metalloradical Activation of CO: Formation and Carbonyl Coupling of a Bent 17-Electron M-CO Unit

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Carbonyl carbon centered radical reactivity in organotransition-metal complexes has been previously observed only for transient 19-electron species.[1-3] Abstraction of hydrogen from metal hydrides by $[\mathrm{Fe(CO)_5}]^-$ to form an intermediate 18-electron formyl complex, $[\mathrm{Fe(CO)_4CHO}]^-$, is a prominent example of this type of reactivity.[1] The characteristic reactions of 17-electron metal carbonyl species are one-electron reduction, M–M and M–X bond formation which occur at the metal center to produce 18-electron species.[4-7] Studies of rhodium porphyrins with CO that produce metalloformyl,[8-10] dimetal ketones,[11,12] and dimetal α-diketones[12] have suggested that a 17-electron metalloorganic radical, (por)Rh–$\dot{\mathrm{C}}$O,[10] may function as an intermediate, but this type of species has eluded direct observation. This article reports on the reversible reaction of tetramesitylporphyrinrhodium(II), (TMP)Rh$^\bullet$, **1**, with CO to form (TMP)Rh–$\dot{\mathrm{C}}$O, **2**, which dimerizes by C–C bond formation. EPR and reactivity studies of **2** indicate the presence of a bent CO fragment with a partially rehybridized CO unit that facilitates one-electron reactions at the carbonyl carbon center.

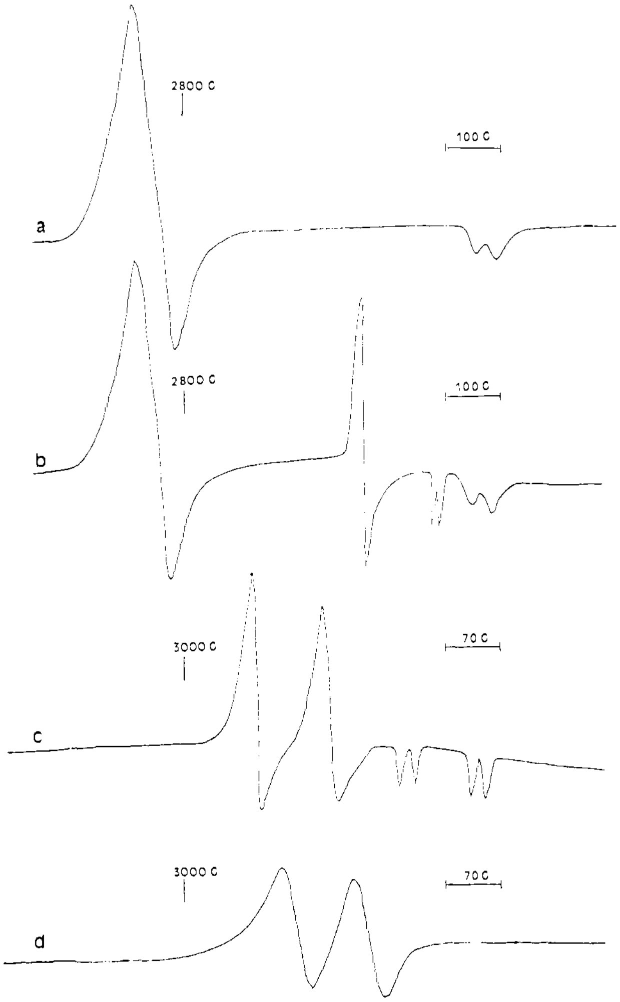

Figure 1. EPR spectra for (TMP)Rh$^{\mathrm{II}}$ and (TMP)Rh–$\dot{\mathrm{C}}$O in toluene. (a) Anisotropic EPR spectrum for (TMP)Rh$^{\mathrm{II}}$ (90 K) [$g_{1,2} = 2.65$, $g_3 = 1.915$; $A^{103}\mathrm{Rh}(g_{1,2}) = 197$ MHz, $A^{103}\mathrm{Rh}(g_3) = 158$ MHz]. (b) Anisotropic EPR spectrum that results from exposing a frozen solution of (TMP)Rh$^{\mathrm{II}}$ to ^{12}CO ($P_{\mathrm{CO}} = 200$ Torr, $T = 100$ K), warming to 195 K and refreezing to 100 K. (c) Anisotropic EPR spectrum for (TMP)-Rh–$^{13}\dot{\mathrm{C}}$O (90 K) [$g_1 \simeq 2.17$, $A^{13}\mathrm{C}(g_1) \simeq 307$ MHz; $g_2 = 2.14$, $A^{13}\mathrm{C}(g_2) = 330$ MHz; $g_3 = 1.995$, $A^{13}\mathrm{C}(g_3) = 299$ MHz; $A^{103}\mathrm{Rh}(g_3) = 67$ MHz]. (d) Isotropic EPR spectrum for (TMP)Rh–$^{13}\dot{\mathrm{C}}$O (90 K) [$\langle g\rangle_{\mathrm{iso}} = 2.101$; $\langle A^{13}\mathrm{C}\rangle = 312$ MHz].

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[1] (a) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926. (b) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49.

[2] (a) Amatore, C.; Verpeaux, J. N.; Krusic, P. J. *Organometallics* **1988**, *7*, 2426. (b) Crocker, L. S.; Heinekey, D. M.; Schulte, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 405. (c) Pan, Y. H.; Ridge, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 1151.

[3] (a) Fairhurst, S. A.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1982**, *77*, 5872. (b) Fairhurst, S. A.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1982**, *76*, 234.

[4] Lee, K. W.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3269. (b) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496. (c) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700.

[5] (a) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575. (b) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

[6] (a) Shi, Q. Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71. (b) Richmond, T. G.; Shi, Q. Z.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 76. (c) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *110*, 4942.

[7] Halpern, J. *Acc. Chem. Res.* **1970**, 386 and references therein.

[8] Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700.

[9] Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302.

[10] Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

[11] Wayland, B. B.; Woods, B. A.; Coffin, V. L. *Organometallics* **1986**, *5*, 1059.

[12] (a) Coffin, V. L.; Brennen, W.; Wayland, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 6063. (b) Wayland, B. B.; Sherry, A. E.; Coffin, V. L. *J. Chem. Soc., Chem. Commun.* **1989**, in press.

0002-7863/89/1511-5010$01.50/0

Toluene solutions of (TMP)Rh$^{\bullet}$, **1**, are generated by photolysis of (TMP)Rh–CH_3.[13] Exposure of **1** to CO results in the appearance of an EPR spectrum for a new $S = {}^1/_2$ species, **2** (Figure 1). Anisotropic EPR spectra for the ^{12}C and ^{13}C derivatives of **2** obtained at nonequilibrium conditions (Figure 1 (parts b and c)) reveal doublet splittings due to coupling with both ^{103}Rh and ^{13}C nuclei which identifies **2** as a complex with a 1:1 Rh/CO stoichiometry. Large reductions in the g values for **2** compared to **1** result from elevation of the metal d_{z^2} and delocalization of the odd electron to CO.[14,15] The large isotropic ^{13}C hyperfine coupling constant for **2** (312 MHz, Figure 1d) is similar to that reported for the formyl radical (377 MHz)[16] and corresponds to a C2s spin density of 0.10 and a total carbon spin density of 0.2–0.3.[17]

The anisotropic EPR spectrum of (TMP)Rh–$^{13}\dot{C}O$ in toluene glass appears similar to that expected for an axially symmetric complex, but analysis of the EPR parameters indicates that **2** is a lower symmetry species. The isotropic **g** and $\mathbf{A}^{13}C$ values [$\langle \mathbf{g} \rangle = 2.101$; $\langle \mathbf{A}^{13}C \rangle = 312$ MHz] are not accurately accounted for by the two clearly defined transitions [$\mathbf{g}_2 = 2.14$, $\mathbf{A}^{13}C(\mathbf{g}_2) = 330$ MHz, $\mathbf{g}_3 = 1.995$, $\mathbf{A}^{13}C(\mathbf{g}_3) = 299$ MHz] in the toluene glass spectrum (Figure 1) which suggests that a third overlapping transition ($\mathbf{g}_1 \simeq 2.17$, $\mathbf{A}^{13}C(\mathbf{g}_1) \simeq 307$ MHz) is also present. Observation of a smaller $\mathbf{A}^{13}C$ hyperfine coupling on the smaller **g** value transition [$\mathbf{A}^{13}C(\mathbf{g}_3)$ (299 MHz) compared to ($\mathbf{A}^{13}C(\mathbf{g}_2)$ (330 MHz)] is also incompatible with the **g** and **A** tensors having a common principal axis,[17] which is a requirement for species possessing axial symmetry.[18] EPR parameters for (TMP)Rh–$\dot{C}O$ indicate the presence of a bent M–CO unit and a spin density distribution intermediate between that of a metal or a carbonyl carbon centered radical.

Isotropic EPR spectral intensities for **2** were studied as a function of CO pressure and temperature (Figure 2). Solutions of **1** ($0.8–2.0 \times 10^{-3}$ M) with CO ($P_{CO} \simeq 0.1–1.0$ atm) show an increase in the EPR intensity of **2** ($T = 290$ K) as the P_{CO} increases up to 0.3 atm and then remains constant as P_{CO} is further increased. We associate this CO pressure dependence with the formation of **2** from **1** and CO where effectively all of **1** is consumed at $P_{CO} > 0.3$ atm. When the temperature of these solutions is lowered ($T = 290–200$ K), the EPR intensity of **2** regularly decreases (Figure 2) which we ascribe to an equilibrium with a diamagnetic species **3** which has the same CO/Rh stoichiometry as **2**. At temperatures below 230 K virtually all of **2** is converted to **3** and frozen solutions of **1** with CO prepared by slow cooling are EPR silent.

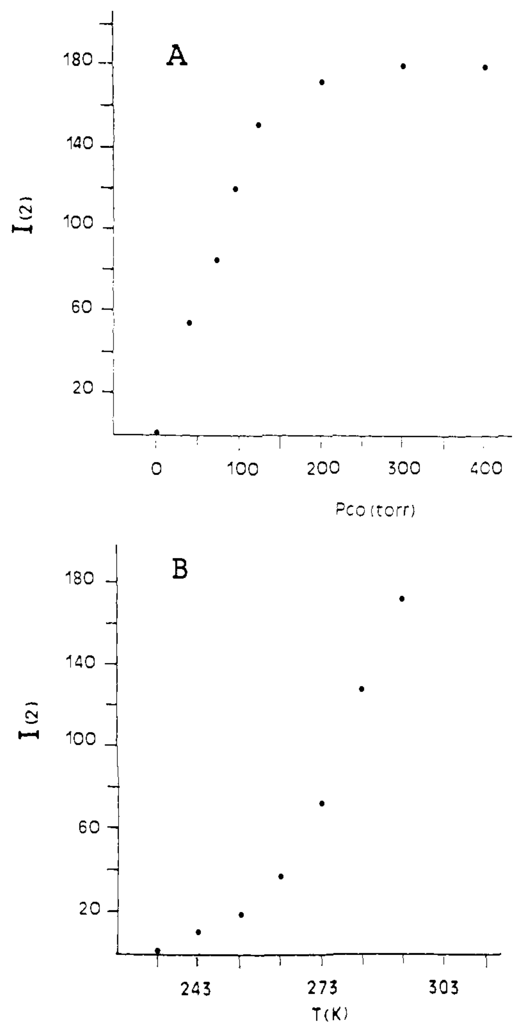

Figure 2. EPR intensities for (TMP)Rh–$\dot{C}O$, $I_{(2)}$, as a function of temperature and CO pressure {$[(TMP)Rh^{\bullet}]_0 \simeq 1 \times 10^{-3}$M}. (A) Variation of $I_{(2)}$ with CO pressure. (B) Variation of $I_{(2)}$ with temperature ($P_{CO} = 300$ Torr).

^1H and ^{13}C NMR for species **3** were obtained at conditions ($P_{CO} > 0.3$ atm, $T < 230$ K) where virtually all of the paramagnetic species (**1** and **2**) are converted to **3**. An AA′XX′ ^{13}C NMR pattern resulting from pairs of chemically equivalent but magnetically inequivalent ^{13}C and ^{103}Rh nuclei is similar to that reported for related dionyl species[12] and clearly identifies **3** as the C–C bonded dimer of **2**.[19]

Reaction of **1** with CO results in equilibria that involve a 17-electron mono-CO complex, (TMP)Rh–$\dot{C}O$, and the C–C bonded dimer (TMP)Rh–C(O)–C(O)–Rh(TMP) (eq 1 and 2).

$$(TMP)Rh^{\bullet} + CO \rightleftarrows (TMP)Rh–\dot{C}O \qquad (1)$$

$$2(TMP)Rh–\dot{C}O \rightleftarrows (TMP)Rh–C(O)–C(O)–Rh(TMP) \qquad (2)$$

Temperature dependence of the relative EPR intensity for (TMP)Rh–CO (Figure 2) provides a measurement of ΔH^0 for

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(13) (TMP)Rh–CH_3 is prepared by reaction of CH_3I with $(TMP)Rh^-$ in by established methods (see: Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461): ^1H NMR (δ in C_6D_6) 8.75 (s, 8 H, pyrrole), 2.26 (s, 12 H, *o* CH_3), 1.73 (s, 12 H, *o′*CH_3), 7.20 (s, 4 H, *m* phenyl), 7.07 (s, 4 H, *m′* phenyl), 2.43 (s, 12 H, *p* phenyl); MS, *m/e* = 898. (TMP)Rh$^{\bullet}$ is prepared by photolysis of (TMP)Rh–CH_3 in benzene or toluene solution ($\lambda \geq 350$ nm): ^1H NMR (δ in C_6D_6, $T = 296$ K) 18.25 (br s, pyrrole, 8 H), 3.57 (br s, 24 H, *o* CH_3), 8.87 (s, 8 H, *m* phenyl), 3.51 (s, 12 H, *p* CH_3); EPR (90 K, toluene glass) $\mathbf{g}_{x,y} = 2.65$, $\mathbf{g}_z = 1.915$, $\mathbf{A}^{103}Rh(\mathbf{g}_{x,y}) = 197$ MHz, $\mathbf{A}^{103}Rh(\mathbf{g}_z) = 158$ MHz; MS, *m/e* = 883.

(14) (a) Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4850. (b) McGarvey, B. R. *Can. J. Chem.* **1975**, *53*, 2498.

(15) (a) Tsay, F. D.; Gray, H. B.; Danon, J. *J. Chem. Phys.* **1971**, *54*, 3760. (b) Wayland, B. B.; Mohajer, D. *J. Am. Chem. Soc.* **1971**, *93*, 5295. (c) Wayland, B. B.; Minkiewicz, J. V.; Abd-Elmageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 2745.

(16) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1966**, *44*, 4626.

(17) The anisotropic ^{13}C coupling constants for an axially symmetric complex are given by the following expression:

$$\mathbf{A}(\mathbf{g}_z) = \mathbf{A}_{iso} + 2(\mathbf{A}_{dip} + \mathbf{A}_{aniso})$$

$$\mathbf{A}(\mathbf{g}_{x,y}) = \mathbf{A}_{iso} - (\mathbf{A}_{dip} + \mathbf{A}_{aniso})$$

The isotropic ^{13}C coupling constant, $\mathbf{A}_{iso}$ in **2** is dominated by C_{2s} spin density ($\mathbf{A}_{iso} = \rho C2s$ (3, 110) MHz) and must be positive. The anisotropic ^{13}C coupling constant ($\mathbf{A}_{aniso}$) is determined by the C_{2p} spin density ($\mathbf{A}_{aniso} = \rho C2p$ (90.8) MHz) and is positive for ^{13}C, and the metal-centered dipolar contribution ($\mathbf{A}_{dip}$) is also positive for ^{13}C. In an axially symmetric complex $\mathbf{A}^{13}C(\mathbf{g}_z)$ must be larger than $\mathbf{A}^{13}C(\mathbf{g}_{x,y})$ which is not experimentally observed for (TMP)Rh–CO, **2**. See: *Advances in Inorganic and Radiochemistry*; *Vol. 13*; Academic: New York, 1970; pp 170–173, and ref 18.

(18) (a) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, 1977; pp 339–340. (b) Chien, J. C. W.; Dickerson, L. C. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 2783.

(19) (TMP)Rh–C(O)–C(O)–Rh(TMP), **3**: ^1H NMR (δ in C_6D_6) 8.27 (s, 16 H, pyrrole), 1.93 (s, 24 H, *o* CH_3), 1.12 (s, 24 H, *o′* CH_3), 2.42 (s, 24 H, *p* CH_3), *m* phenyl hydrogens are obscured by the solvent (7.155); ^{13}C NMR (δ in toluene-d_8 at −80 °C) 164.9 (AA′XX′, 2 ^{13}C, dionyl unit), six transitions are observed at ±12, ±17, and ±25 Hz relative to the center at δ 164.9 ppm. Attempts to obtain satisfactory IR data for **3** have thus far been unsuccessful due to limited solubility of the complex in organic solvents and the propensity for **3** to lose CO. However, IR stretching bands at 1778 and 1767 cm^{-1} have been obtained for the related (TXP)Rh–C(O)–C(O)–Rh(TXP) complex (see ref 12b).

reaction 2 ($\Delta H^0_2 = -18.5 \pm 0.8$ kcal/mol).[20] Reversible dimerization of **2** through C–C bond formation to produce a 1,2-ethanedionyl bridged complex (eq 2) can be viewed as being related to formyl radical coupling ($2H\dot{C}O \rightarrow H(O)C{-}C(O)H$). However, dimerization of (TMP)Rh–$\dot{C}$O must involve substantially larger electronic and structural rearrangement of the Rh–CO unit compared to that required for H$\dot{C}$O as evidenced by the small ΔH^0 for reaction 2. Rehybridization and reduction of the CO fragment of **2** is completed only when a second covalent bond is formed with the carbonyl center as occurs in the formation of **3**. This work also supports previous indications that the carbonyl carbon in (por)Rh–CO species functions as a site for one-electron reactions such as hydrogen atom transfer from a metallohydride to produce a metalloformyl species[10] and reaction with a second metalloradical to form dimetal ketone complexes.[11,12] Rhodium porphyrin systems are currently unique in providing metalloradical activated carbonyl species at equilibrium, where one-electron reactions at the carbonyl center can be more fully exploited.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation and the Department of Energy, Division of Chemical Sciences, Offices of Basic Energy Sciences through Grant DE-FG02-86ER13615. We also thank Dr. P. Krusic for helpful discussions relating to this work.

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(20) $2(TMP)Rh{-}\dot{C}O \rightleftarrows ((TMP)Rh{-}(CO))_2$; $K_2 = [((TMP)Rh{-}CO)_2]/[(TMP)Rh{-}CO]^2$; $[((TMP)Rh{-}CO)_2] = [((TMP)Rh{-}CO)_2]_0 - {}^1/_2[(TMP)Rh{-}CO]$; $I_{(2)}$ = EPR intensity for **2** adjusted for the temperature dependence of the electron spin populations; $I_{(2)}[(TMP)Rh{-}CO] = X$; $K_2 = [[((TMP)Rh{-}CO))_2]_0 - {}^1/_2X]/X^2$; $X \ll [((TMP)Rh{-}CO)_2] = C$; $K_2 = C/X^2$; $X = C'(I_{(2)})$; $K_2 \simeq C/C'^2(I_{(2)})^2 = C''I_{(2)}{}^{-2}$; $\ln K_2 = -2 \ln I_{(2)} + \ln C''$. The slope of the linear relationship between $-2 \ln I_{(2)}$ and $1/T$ yields $-\Delta H_2{}^0/R$ ($\Delta H_2{}^0 = -18.5 \pm 0.8$ kcal/mol). Estimating $\Delta S_2{}^0$ as $\simeq -28$ cal/mol K yields an estimate for $\Delta G_2{}^0$ ($\Delta G_2{}^0$ (298 K) $\simeq -10.2$ kcal/mol; K_2 (298 K) $\simeq 3 \times 10^7$). These thermodynamic estimates demonstrate that the dissociation of **3** into **2** within the range of temperature and concentrations studied (230–290 K) is less than 0.5%.

Novel Trimetallic Complexes of Rhodium with Bis(difluorophosphino)methylamine: The Crystal and Molecular Structure of $[Rh_3(\mu\text{-}Cl)_3(\mu\text{-}H_3CN(PF_2)_2)_3]$

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The coordination chemistry of bis(difluorophosphino)methylamine is notable for the number of unusual structures that can be formed.[1-3] Until very recently when the mixed-valence complex $[Rh_2Cl_2(PF_3)(\mu\text{-}H_3CN(PF_2)_2)_3]$ was reported,[4] the chemistry of this ligand with rhodium and iridium has been conspicuous by its absence. We wish to report findings in this area which include the synthesis of the first *trinuclear* complex of $MeN(PF_2)_2$, $[Rh_3(\mu\text{-}Cl)_3(\mu\text{-}MeN(PF_2)_2)_3]$, shown to adopt an unprecedented cone-shaped structure.

Reaction of $MeN(PF_2)_2$ with $[RhCl(CO)_2]_2$ forms a dark green-black solution which becomes dark red-orange upon concentration under reduced pressure.[5] An X-ray crystallographic analysis[6] of the product obtained (**1**) revealed that instead of the anticipated binuclear "A-frame" species, **1** is *trimeric* with a novel *cone*-shaped structure. The inner coordination sphere of **1** is depicted in Figure 1 and although possessing no crystallographically imposed symmetry, **1** is very close to having C_{3v} symmetry. The average Rh–Rh separation of 3.0964 (4) Å is comparable to that found in binuclear Rh(I) complexes of the "A-frame" type[7,8] and does not require the presence of metal–metal bonding. It is significantly longer than the value of 2.785 (1) Å found in $[Rh_2Cl_2(PF_3)(\mu\text{-}MeN(PF_2)_2)_3]$.[4] The coordination about each metal is approximately square-planar, and there are no unusual metrical parameters.

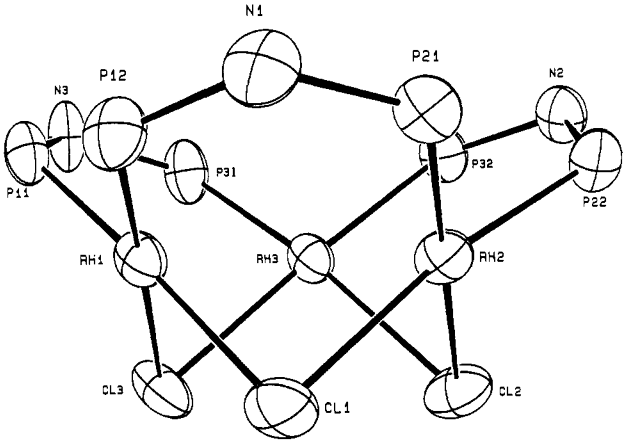

Figure 1. A perspective view of the inner coordination sphere of $[Rh_3(\mu\text{-}Cl)_3(\mu\text{-}MeN(PF_2)_2)_3]$. Thermal ellipsoids are drawn at the 50% probability level.

The structure adopted by **1** represents a new type for closed trinuclear complexes. The closest analogy available appears to be $[Rh_3(\mu\text{-}H)_3(P(OPr^i)_3)_6]$,[9] but, although all three metals there also have square-planar coordination, the dihedral angles between these planes and the Rh_3 plane vary considerably. More important, one bridging hydride ligand lies on the *opposite* side of the Rh_3 plane from the other two, while in **1** all three bridging chloride ligands are on the same side of the Rh_3 plane. Two other similar but less closely related species are $[Pt_3H(\mu_3\text{-}S)(\mu\text{-}DPPM)_3]BPh_4$[10] and $[Pt_3(\mu_3\text{-}CO)(dmpm)_3]PF_6$.[11] Here however two of the bridging diphosphine ligands in the former are more nearly *equatorial* than axial with respect to the Pt_3 plane, while, in the latter, all three are within 0.62 Å of this plane.

Complex **1** reacts readily with carbon monoxide and with 3 equiv of *tert*-butylisocyanide as evidenced by color changes from orange to dark blue-green and dark red-violet, respectively. A slower reaction of **1** occurs with hexafluorobut-2-yne to yield a light orange adduct (**2**) which analyzes for $[Rh_3Cl_3(C_4F_6)(H_3CN(PF_2)_2)_3]$.[12] No apparent reaction occurs under moderate conditions with either dimethylacetylene dicarboxylate or dihydrogen. In **2**, a band of medium intensity at 1612 cm^{-1} suggests the alkyne is bound as a dimetalated olefin.[13] Consistent with the expected unsymmetrical structure the ^1H NMR spectrum shows two resonances for the fluorophosphine methyl groups.[14]

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(1) King, R. B.; Shimura, M.; Brown, G. M. *Inorg. Chem.* **1984**, *23*, 1398.

(2) Newton, M. G.; King, R. B.; Chang, M.; Pantaleo, N. S.; Gimeno, J. *J. Chem. Soc., Chem. Commun.* **1977**, 531.

(3) Newton, M. G.; King, R. B.; Lee, T.-W.; Norskov-Lauritzen, L.; Kumar, V. *J. Chem. Soc., Chem. Commun.* **1982**, 201.

(4) Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 4054.

(5) A solution of 0.400 g (0.806 mmol) of $[RhCl(COD)]_2$ (COD = cycloocta-1,5-diene) in 20 mL of diethyl ether was stirred under carbon monoxide for 30 min. Dropwise addition of 0.270 g (1.612 mmol) of $MeN(PF_2)_2$ in 1 mL of hexane produced a dark yellowish green solution accompanied by gas evolution. Concentration of the solution under reduced pressure resulted in a color change to dark red orange. Filtration, dilution with hexane, and cooling at −10 °C produced dark red orange, air stable crystals.

(6) Crystal data for **1**: $C_3H_9N_3P_6F_{12}Cl_3Rh_3$, fw = 916.06; monoclinic space group $C2/c$, $a = 17.323$ (2) Å, $b = 10.998$ (2) Å, $c = 23.226$ (3) Å; $\beta = 93.03$ (1)°; $V = 4419$ (2) Å^3; $Z = 8$; $d_{calcd} = 2.76$ g/cm^{-3}; absorption coefficient = 30.8 cm^{-1}; Mo Kα radiation (graphite monochromated); scan range $\theta = 3{-}26°$; 4322 unique data with $3811 \geq 3\sigma(I)$. Solution by direct methods (MULTAN) with full-matrix refinement to convergence (271 variables); $R = 0.030$, $R_w = 0.038$, GOF = 2.72.

(7) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.

(8) Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726.

(9) Brown, R. K.; Williams, J. M.; Sivak, A. J.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 370.

(10) Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 3776.

(11) Ferguson, G.; Lloyd, R. B.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344.

(12) Anal. Calcd for $C_7H_9N_3P_6F_{18}Cl_3Rh_3$: C, 7.80; H, 0.83. Found: C, 7.7; H, 1.2.

(13) Mague, J. T. *Organometallics* **1986**, *5*, 918.

0002-7863/89/1511-5012$01.50/0