Table IV. Selected Bond Angles (deg)

atom 1	atom 2	atom 3	angle
Cl(1)	Zn	Cl(2)	119.7 (1)
Cl(1)	Zn	O(1)	103.2 (2)
Cl(1)	Zn	N(3)	105.4 (2)
Cl(2)	Zn	O(1)	113.9 (2)
Cl(2)	Zn	N(3)	121.4 (2)
O(1)	Zn	N(3)	87.3 (2)
O(1)	P	O(2)	123.6 (3)
O(1)	P	C(1)	105.3 (3)
O(1)	P	C(10)	102.9 (3)
O(2)	P	C(1)	105.5 (3)
O(2)	P	C(10)	110.9 (3)
C(1)	P	C(10)	107.7 (3)
Zn	O(1)	P	115.2 (3)
Zn	N(3)	C(10)	112.4 (5)
Zn	N(3)	C(11)	140.9 (6)
C(10)	N(3)	C(11)	106.7 (7)
C(10)	N(4)	C(12)	104.4 (7)

drolysis of 8-quinolinyl phosphate[11] and 2-pyridylmethyl hydrogen phthalate,[12] while a nucleophilic role for $M^{2+}(OH^-)$ has often been proposed as an important pathway in metal-promoted hydrolyses.[12,13] However, insofar as we are aware, this case represents the first example whereby Zn^{2+} catalyzes the hydrolytic cleavage of a P–C bond.[14]

(14) (a) We have observed (Brown, R. S.; Huguet, J., unpublished results) that when an equimolar mixture of tris(4,5-diisopropyl-1-methyl-imidazol-2-yl)carbinol and ZnBr₂ is allowed to crystallize by controlled evaporation, crystals of [bis(4,5-diisopropyl-1-methylimidazol-2-yl)ketone]dibromozinc(II)[15] are deposited. Such a reaction requires a molecule of 4,5-diisopropyl-1-methylimidazole to be expelled from the carbinol, a process formally similar to the one reported in the present study. (b) It is noteworthy that the related silicon species behave similarly. For example (1-methylimidazol-2-yl)trimethylsilane hydrolyzes readily to produce 1-methylimidazole and trimethylsilanol. Mechanistically, the reaction involves OH⁻ attack on the N-protonated (imidazol-2-yl)trimethylsilane, the leaving group being the neutral zwitterion of N-protonated 1-methylimidazol-2-yl anion. Since OH⁻ does not attack the neutral (1-methylimidazol-2-yl)trimethylsilane, it is clear that in order for hydrolysis to occur the imidazole sp²-nitrogen lone pair must be associated with H⁺, a process formally akin to M²⁺ binding by the species reported herein: Brown, R. S.; Slebocka-Tilk, H.; Buschek, J. M.; Ulan, J. *J. Am. Chem. Soc.*, in press.

(15) For a crystal structure of [bis-(4,5-diisopropyl-1-methylimidazol-2-yl)ketone]dibromozinc(II), see: Read, R. J.; James, M. N. G. *Acta Crystallogr., Sect. B* **1980**, *B36*, 3100.

(b) Structure Description. Overall, the Zn^{2+} in the complex is coordinated approximately tetrahedrally by two Cl⁻'s and by N(3) of an imidazole and O(1) of the phosphinic acid as in Figure 1. From Table III, the Zn^{2+}–Cl distances (2.243 (2) and 2.160 (3) Å) and the Zn^{2+}–N(3) distance of 2.025 (6) Å compare favorably with those seen in [tris(4,5-diisopropylimidazol-2-yl)phosphine]dichlorozinc[16] (Zn–Cl = 2.170 (2) Å and Zn–N = 2.057 (2) Å, respectively). As is evidenced from the bond angles given in Table IV, the four-coordinate Zn^{2+} lies in a highly distorted tetrahedral environment, in which the angles vary from 87.3 (2)° (N(3)–Zn^{2+}–O(1)) to 121.4 (2)° (Cl(2)–Zn^{2+}–N(3)).

The bond lengths and angles in the two diisopropyl-imidazol-2-yl groups compare very well, as do the P–C distances, with those observed in a related tris structure.[16] The P–O distances of 1.487 (5) and 1.474 (5) Å agree nicely with the P–O distances in $Zn(OPPh_3)_2Cl_2$.[17] That the Zn–O distance of 2.037 (5) Å is somewhat longer than that in Zn-$(OPPh_3)_2Cl_2$ is not surprising considering the stereochemical constraints imposed by the nature of the chelating ligand.

From an examination of the intermolecular distances and a packing diagram, Figure 2 (see supplementary material), the only contacts of any significance are between O(3) of the water of crystallization and N(4) and O(2) (2.68 (1) and 2.71 (1) Å, respectively) of symmetry-related molecules, which may indicate the presence of a weak hydrogen-bonding network.

Registry No. **2**, 89210-50-4; **3**, 90481-58-6; ZnCl₂, 7646-85-7.

(16) Read, R. J.; James, M. N. G. *J. Am. Chem. Soc.* **1981**, *103*, 6947.
(17) Rose, M. P.; Lalancette; R. A.; Portenza, J. A.; Schugar, H. J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2409.

Contribution from the Department of Chemistry, University of California, Davis, California 95616

Redox-Active Binuclear Complexes. Preparation, Oxidation, and Structure of Rh₂(Ph₂PCH₂PPh₂)₂(1,2-O₂C₆Cl₄)(CO)

JUDITH A. LADD, MARILYN M. OLMSTEAD, and ALAN L. BALCH*

Treatment of [Ph₄As][Rh(1,2-O₂C₆Cl₄)(CO)₂] or a mixture of [Ph₄As][Rh(1,2-O₂C₆Cl₄)(CO)₂] and Rh₂(μ-Cl)₂(CO)₄ with bis(diphenylphosphino)methane (dpm) yields orange Rh₂(μ-dpm)₂(1,2-O₂C₆Cl₄)(CO). This compound crystallizes in the space group P1̄ (No. 2) with two molecules per unit cell of dimensions a = 11.126 (3) Å, b = 11.759 (3) Å, c = 20.065 (5) Å, α = 91.82 (2)°, β = 101.41 (2)°, γ = 92.23 (2)° at 140 K. Full-matrix least-squares refinement yielded R = 0.054. The structure consists of two distinct rhodium atoms: one five-coordinate and square pyramidal (with bonds to two oxygen atoms, two phosphorus atoms, and one out-of-plane rhodium atom) and the other four-coordinate and nearly planar (with bonds to two phosphorus atoms, one carbonyl carbon atom, and one rhodium atom). The Rh–Rh distance is 2.637 (1) Å. The two bridging bis(phosphine) ligands are arranged in an unusual fashion so that they are trans to one another at one rhodium, while they are cis to each other at the other rhodium. Rh₂(μ-dpm)₂(1,2-O₂C₆Cl₄)(CO) is reversibly oxidized electrochemically or chemically to a monocation, [Rh₂(μ-dpm)₂(1,2-O₂C₆Cl₄)(CO)]⁺, which has been characterized by electronic, infrared, and electron spin resonance spectra.

Introduction

There has been considerable development of the chemistry of binuclear rhodium complexes bridged by bis(diphenyl-phosphino)methane (dpm).[1-34] This work has shown that a

trans-Rh₂(μ-dpm)₂ unit is remarkably stable and can undergo a variety of reactions while retaining its structural integrity.

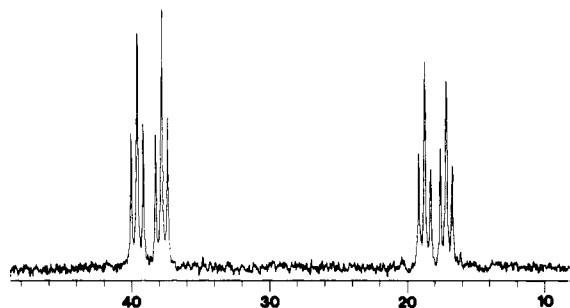(1) Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1969**, *8*, 119.

Figure 1. 81-MHz $^{31}P\{^1H\}$ NMR spectrum of a dichloromethane solution of $Rh_2(\mu\text{-dpm})_2(1,2\text{-}O_2C_6Cl_4)(CO)$.

As a result a number of unusual structures (variously known as face-to-face dimers, molecular A-frames, double A-frames) have been encountered and a variety of novel reactions (some catalytic) have been discovered. All of the reactions encountered so far have involved net two-electron changes, and all the dinuclear complexes reported are diamagnetic.

In order to take advantage of the enhanced reactivity of odd-electron molecules, we have undertaken the preparation of binuclear compounds that are capable of one-electron oxidation–reduction. One way to do this is to place a redox-active center into the complex either coordinated as a separate ligand or incorporated into the bridging bis(phosphine). Here we report on an example of the first type.

For this a catecholate (dioxolene, if oxidation state is not to be specified) ligand has been employed. Previous work has shown that stable catecholate complexes of rhodium may be prepared[35] and that these undergo reversible one-electron oxidation to produce complexes involving coordinated semi-quinones.[36,37] These paramagnetic species are stable enough
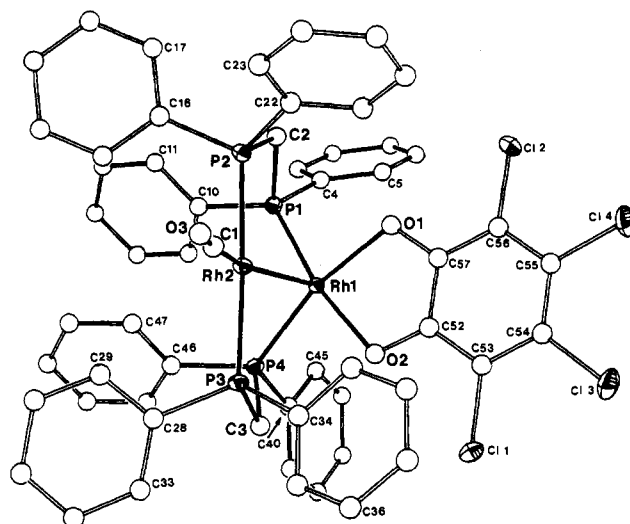

Figure 2. Prespective drawing of the structure of $Rh_2(\mu\text{-dpm})_2$-$(1,2\text{-}O_2C_6Cl_4)(CO)$.

to be observed spectrocopically, particularly by electron spin resonance techniques, and can be re-reduced in essentially quantitative yield.

Results

Synthesis and Spectroscopic Characterization of $Rh_2(\mu$-dpm$)_2(1,2\text{-}O_2C_6Cl_4)(CO)$. Two routes to the formation of $Rh_2(\mu\text{-dpm})_2(1,2\text{-}O_2C_6Cl_4)(CO)$ (1), have been found.
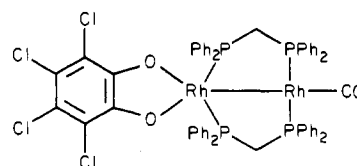
1

Treatment of $[Ph_4As][Rh(CO)_2(1,2\text{-}O_2C_6Cl_4)]$ with dpm in dichloromethane gave a mixture of compounds from which 1 could be isolated in low yield after a prolonged reaction period. Work on isolation and identification of the other products continues. After 1 had been structurally identified, a somewhat more rational route to it was devised. For this a mixture of $[Ph_4As][Rh(CO)_2(1,2\text{-}O_2C_6Cl_4)]$ and $Rh_2(\mu$-Cl$)_2(CO)_4$ was treated in dichloromethane solution with dpm. This procedure leads to 1 in somewhat higher yield in a shorter period of time. The new compound 1 has been isolated as orange needles that have good solubility in dichloromethane, acetone, and benzene but are essentially insoluble in ether and saturated hydrocarbons. The spectroscopic features of the molecule are fully in accord with the structure determined by X-ray diffraction (vide infra). The infrared spectrum of 1 in a mineral oil mull indicates that one terminal carbon group, $\nu(CO) = 1960$ cm^{-1}, is present. Bands due to the coordinated catechol[35] (at 1260, 968, 805, and 785 cm^{-1}, as well as dpm, are also present. The $^{31}P\{^1H\}$ NMR spectrum of 1 is shown in Figure 1. It consists of two doublets of triplets, and clearly two phosphorus environments are present. The spectrum can be analyzed to yield the following parameters: δ_1, 38.6; δ_2, 17.9; $J(Rh_1,P_1)$, 143 Hz; $J(Rh_2,P_2)$, 127. However, it is of the deceptively simple variety. From the known molecular geometry (vide infra) it is of the AA′BB′XY (A, B = P; X, Y = Rh) type. The appearance of triplets in the spectrum could be accommodated by an accidental equivalence of J-(A,B) and J(A′,B), but it is more likely that it arises from a virtual coupling phenomenon that has as its origin the large

(2) Sanger, A. R. *J. Chem. Soc., Chem. Commun.* **1975**, 893.
(3) Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049.
(4) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120.
(5) Balch, A. L.; Tulyathan, B. *Inorg. Chem.* **1977**, *16*, 2840.
(6) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 6129.
(7) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 2628.
(8) Cowie, M.; Dwight, S. K.; Sanger, A. R. *Inorg. Chim. Acta* **1978**, *31*, L407.
(9) Yaneff, P. V.; Powell, J. *J. Organomet. Chem.* **1979**, *179*, 101.
(10) Olmstead, M. M.; Lindsay, C. H.; Benner, L. S.; Balch, A. L. *J. Organomet. Chem.* **1979**, *179*, 289.
(11) Cowie, M. *Inorg. Chem.* **1979**, *18*, 286.
(12) Balch, A. L.; Labadie, J. W.; Delker, G. *Inorg. Chem.* **1979**, *18*, 1224.
(13) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.
(14) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.
(15) Kubiak, C. P.; Eisenberg, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 3637.
(16) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 209.
(17) Cowie, M., Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.
(18) Kubiak, C. P.; Eisenberg, R. J. *Inorg. Chem.* **1988**, *19*, 2726.
(19) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2508.
(20) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1980**, *19*, 3743.
(21) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* **1980**, *193*, C46.
(22) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1980**, *198*, C20.
(23) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1981**, 228.
(24) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1981**, *214*, 233.
(25) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682.
(26) Fordyce, W. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 985.
(27) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246.
(28) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.
(29) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. J. *Inorg. Chem.* **1982**, *21*, 2119.
(30) Woodcock, C.; Eisenberg, R. J. *Organometallics* **1982**, *1*, 886.
(31) Ceriott, A.; Ciani, G.; Garlaschelli, L.; Sartorelli, U.; Sironi, A. *J. Organomet. Chem.* **1982**, *229*, C9.
(32) Mondal, J. U.; Young, K. G.; Blake, D. M. *J. Organomet. Chem.* **1982**, *240*, 447.
(33) McKeer, I. R.; Cowie, M. *Inorg. Chim. Acta* **1982**, *65*, L107.
(34) Mague, J. T. *Inorg. Chem.* **1983**, *22*, 45.
(35) Sohn, Y. S.; Balch, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 1144.
(36) Balch, A. L. *J. Am. Chem. Soc.* **1973**, *95*, 2723.

(37) Girgis, A. Y.; Sohn, Y. S.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2327.

Table I. Atom Coordinates ($\times 10^4$) and Temperature Factors (A, $\times 10^3$) for $Rh_2(\mu\text{-dpm})_2(1,2\text{-}O_2C_6Cl_4)(CO)$

atom	x	y	z	U^a	atom	x	y	z	U^a
Rh(1)	2258 (1)	2432 (1)	7662 (1)	12 (1)*	C(24)	6520 (7)	6693 (6)	9096 (4)	25 (2)
Rh(2)	4030 (1)	3651 (1)	7285 (1)	14 (1)*	C(25)	6520 (7)	7087 (7)	9346 (4)	26 (2)
P(1)	3605 (2)	1427 (2)	8352 (1)	14 (1)*	C(26)	4551 (7)	6365 (7)	9336 (4)	31 (2)
P(2)	5283 (2)	3506 (2)	8332 (1)	14 (1)*	C(27)	4493 (7)	5267 (7)	9063 (4)	26 (2)
P(3)	2837 (2)	3741 (2)	6203 (1)	15 (1)*	C(28)	3668 (6)	3588 (6)	5503 (4)	16 (2)
P(4)	1996 (2)	1521 (2)	6659 (1)	14 (1)*	C(29)	4937 (6)	3637 (6)	5636 (4)	17 (2)
Cl(1)	−1139 (2)	4849 (2)	6608 (1)	27 (1)*	C(30)	5583 (7)	3575 (6)	5122 (4)	24 (2)
Cl(2)	1684 (2)	4944 (2)	9620 (1)	25 (1)*	C(31)	4958 (7)	3449 (6)	4452 (4)	24 (2)
Cl(3)	−1643 (2)	6767 (2)	7642 (1)	29 (1)*	C(32)	3701 (7)	3359 (6)	4302 (4)	25 (2)
Cl(4)	−144 (2)	6875 (2)	9145 (1)	24 (1)*	C(33)	3035 (7)	3405 (6)	4825 (3)	17 (2)
O(1)	2111 (4)	3459 (4)	8485 (2)	15 (1)	C(34)	2065 (6)	5095 (6)	6075 (4)	17 (2)
O(2)	882 (4)	3417 (4)	7193 (2)	18 (1)	C(35)	1510 (7)	5471 (6)	5446 (4)	23 (2)
O(3)	5552 (5)	5687 (4)	7081 (3)	31 (1)	C(36)	953 (7)	6503 (7)	5414 (4)	35 (2)
C(1)	5004 (7)	4853 (6)	7150 (4)	20 (2)	C(37)	898 (7)	7157 (7)	5992 (4)	34 (2)
C(2)	4687 (6)	2480 (6)	8866 (3)	15 (2)	C(38)	1452 (7)	6797 (7)	6611 (4)	29 (2)
C(3)	1607 (6)	2605 (6)	6022 (3)	16 (2)	C(39)	2044 (7)	5777 (6)	6657 (4)	26 (2)
C(4)	2929 (6)	721 (6)	9006 (4)	16 (2)	C(40)	603 (6)	599 (6)	6537 (3)	15 (2)
C(5)	2167 (6)	1349 (6)	9354 (4)	20 (2)	C(41)	−256 (7)	446 (6)	5933 (4)	23 (2)
C(6)	1633 (7)	838 (6)	9851 (4)	22 (2)	C(42)	−1321 (7)	−221 (6)	5891 (4)	25 (2)
C(7)	1833 (7)	−269 (7)	10008 (4)	27 (2)	C(43)	−1537 (8)	−737 (7)	6460 (4)	33 (2)
C(8)	2578 (7)	−899 (7)	9667 (4)	34 (2)	C(44)	−703 (7)	−613 (7)	7072 (4)	30 (2)
C(9)	3124 (7)	−404 (6)	9179 (4)	25 (2)	C(45)	359 (7)	55 (6)	7108 (4)	22 (2)
C(10)	4503 (6)	302 (6)	8078 (3)	14 (2)	C(46)	3122 (6)	699 (6)	6310 (4)	15 (2)
C(11)	5764 (7)	273 (6)	8278 (4)	22 (2)	C(47)	4351 (6)	1064 (6)	6473 (4)	21 (2)
C(12)	6389 (7)	−632 (7)	8068 (4)	29 (2)	C(48)	5212 (7)	484 (6)	6202 (4)	25 (2)
C(13)	5739 (7)	−1518 (7)	7661 (4)	26 (2)	C(49)	4848 (7)	−477 (7)	5771 (4)	27 (2)
C(14)	4482 (7)	−1507 (6)	7464 (4)	23 (2)	C(50)	3633 (7)	−857 (7)	5627 (4)	27 (2)
C(15)	3850 (7)	−604 (6)	7669 (3)	16 (2)	C(51)	2779 (7)	−268 (6)	5897 (4)	24 (2)
C(16)	6818 (6)	3063 (6)	8307 (3)	11 (2)	C(52)	630 (6)	4209 (6)	7616 (4)	16 (2)
C(17)	7701 (6)	3021 (6)	8906 (4)	20 (2)	C(53)	−288 (7)	4965 (6)	7435 (4)	20 (2)
C(18)	8848 (7)	2633 (6)	8886 (4)	22 (2)	C(54)	−535 (7)	5798 (6)	7902 (4)	19 (2)
C(19)	9126 (7)	2234 (7)	8277 (4)	27 (2)	C(55)	108 (7)	5833 (6)	8570 (4)	20 (2)
C(20)	8261 (6)	2279 (6)	7676 (4)	20 (2)	C(56)	985 (6)	5022 (6)	8772 (4)	17 (2)
C(21)	7123 (7)	2697 (6)	7695 (4)	22 (2)	C(57)	1271 (6)	4222 (6)	8305 (4)	16 (2)
C(22)	5480 (6)	4865 (6)	8804 (3)	14 (2)					
C(23)	6499 (7)	5591 (6)	8823 (4)	19 (2)					

^{a} Asterisks denote equivalent isotropic U values, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

value (ca. 300 Hz) that is anticipated for $J(A,A')$ for the trans pair of phosphine ligands. The experimental spectrum can be satisfactorily simulated with use of a variety of parameters, and as a consequence $J(A,A')$, $J(B,B')$, and $J(A,B')$ cannot be meaningfully evaluated. The ^1H NMR spectrum of **1** shows a complex set of phenyl resonances in the region 6.5–8 ppm The protons of the methylene group of dpm appear as a 1:4:7:8:7:4:1 septet at 5.1 ppm and an equally intense but broad apparent triplet at 3.8 ppm. Thus the two methylene protons of each dpm ligand are inequivalent as required by structure **1**. The low-field septet results from $J(H,H) = 2J(P,H)$, and the values of $J(H,H) = 6.2$ Hz and apparent $J(P,H) = 3.1$ Hz are consistent with the corresponding values for other compounds. The poorer resolution of the upfield methylene resonances probably results from overlapping of the 10 or more possible lines of the multiplet particularly if $J(P,H)$ has a value smaller than $^1/_2 J(H,H)$.

Crystal and Molecular Structure of $Rh_2(\mu\text{-dpm})_2(1,2\text{-}O_2C_6Cl_4)(CO)$. The compound **1** crystallizes with one molecule in the asymmetric unit and no unusual contacts between molecules. A view of the entire molecule with atomic labels is shown in Figure 2. Table I records the positional parameters while Tables II and III, give selected interatomic distances and angles, respectively. While the molecule possesses no crystallographically imposed symmetry, there is a virtual mirror plane, which would bisect the O(1)–Rh(1)–O(2) angle and pass through the two rhodium atoms.

Each of the two rhodium atoms resides in a unique environment. The coordination about these two metal centers is best appreciated by turning to Figure 3, which shows just the inner coordination of the two metal centers. Rh(1) is five-coordinate. Its ligands include the chelating pair of catecholate oxygens and two phosphorus atoms from each of the two

Table II. Selected Interatomic Distances (Å) for $Rh_2(\mu\text{-dpm})_2(1,2\text{-}O_2C_6Cl_4)(CO)$

	At Rh(1)		
Rh(1)–Rh(2)	2.637 (1)	Rh(1)–O(1)	2.051 (5)
Rh(1)–P(1)	2.230 (2)	Rh(1)–O(2)	2.052 (5)
Rh(1)–P(4)	2.212 (2)		

	At Rh(2)		
Rh(2)–Rh(1)	2.637 (1)	Rh(2)–P(3)	2.317 (2)
Rh(2)–P(2)	2.296 (2)	Rh(2)–C(1)	1.808 (7)

	In the Catecholato Ligand		
O(1)–C(57)	1.327 (8)	O(2)–C(52)	1.316 (9)
C(52)–C(53)	1.382 (10)	C(53)–C(54)	1.406 (11)
C(54)–C(55)	1.388 (10)	C(55)–C(56)	1.402 (10)
C(56)–C(57)	1.396 (10)	C(57)–C(52)	1.423 (9)
C(53)–Cl(1)	1.737 (7)	C(54)–Cl(3)	1.727 (7)
C(55)–Cl(4)	1.725 (8)	C(56)–Cl(2)	1.733 (7)

	At Phosphorus		
P(1)–C(2)	1.833 (6)	P(2)–C(2)	1.829 (7)
P(1)–C(4)	1.841 (8)	P(2)–C(16)	1.814 (7)
P(1)–C(10)	1.824 (7)	P(2)–C(22)	1.814 (7)
P(3)–C(3)	1.849 (7)	P(4)–C(3)	1.837 (7)
P(3)–C(28)	1.837 (8)	P(4)–C(40)	1.827 (7)
P(3)–C(34)	1.839 (7)	P(4)–C(46)	1.842 (8)
P(1)···P(2)	3.024 (3)	P(3)···P(4)	2.971 (3)

	In the Carbonyl Group	
C(1)–O(3)	1.160 (9)	

bridging bis(phosphine) ligands. This group of five atoms (Rh(1), O(1), O(2), P(1), P(4)) forms a planar array. In addition, Rh(1) is bound to Rh(2), which lies above the plane. The Rh(2)–Rh(1) vector is aligned nearly perpendicular (84.7°) to the plane of the ligands, P(1), P(4), O(1), O(2), surrounding Rh(1). While the Rh(1)–Rh(2) separation of 2.637 (1) Å falls below the range of 2.73–2.84 Å found for

| At Rh(1)			
Rh(2)-Rh(1)-P(1)	91.8 (1)	O(1)-Rh(1)-O(2)	81.5 (2)
Rh(2)-Rh(1)-P(4)	86.9 (1)	P(1)-Rh(1)-O(1)	88.8 (1)
Rh(2)-Rh(1)-O(1)	96.8 (1)	P(4)-Rh(1)-O(2)	84.6 (1)
Rh(2)-Rh(1)-O(2)	94.7 (1)	P(1)-Rh(1)-O(2)	168.9 (2)
P(1)-Rh(1)-P(4)	104.8 (1)	P(4)-Rh(1)-O(1)	165.8 (1)
At Rh(2)			
Rh(1)-Rh(2)-C(1)	161.3 (2)	Rh(1)-Rh(2)-P(3)	89.9 (1)
P(2)-Rh(2)-P(3)	177.0 (1)	C(1)-Rh(2)-P(3)	91.9 (2)
Rh(1)-Rh(2)-P(2)	91.3 (1)	C(1)-Rh(2)-P(2)	87.8 (2)
At the Catecholato Ligand			
Rh(1)-O(1)-C(57)	110.5 (4)	Rh(1)-O(2)-C(52)	111.3 (4)
O(1)-C(57)-C(56)	122.0 (6)	O(2)-C(52)-C(53)	123.0 (6)
O(1)-C(57)-C(52)	118.8 (6)	O(2)-C(52)-C(57)	117.0 (6)
C(52)-C(53)-C(54)	121.4 (6)	C(53)-C(54)-C(55)	119.8 (7)
C(54)-C(55)-C(56)	119.3 (7)	C(55)-C(56)-C(57)	121.2 (6)
C(56)-C(57)-C(52)	119.2 (6)	C(57)-C(52)-C(53)	118.9 (7)
Cl(1)-C(53)-C(52)	117.7 (6)	Cl(1)-C(53)-C(54)	120.8 (5)
Cl(2)-C(56)-C(57)	118.3 (5)	Cl(2)-C(56)-C(55)	120.4 (6)
Cl(3)-C(54)-C(55)	120.4 (6)	Cl(3)-C(54)-C(53)	119.8 (6)
Cl(4)-C(55)-C(54)	120.6 (6)	Cl(4)-C(55)-C(56)	120.1 (5)
At the Carbonyl Ligand			
Rh(2)-C(1)-O(3)	173.8 (7)		
At the Phosphine Ligands			
P(1)-C(2)-P(2)	111.3 (3)	P(3)-C(3)-P(4)	107.4 (3)
Rh(1)-P(1)-C(2)	105.7 (2)	Rh(1)-P(4)-C(3)	106.0 (2)
Rh(1)-P(1)-C(10)	125.3 (2)	Rh(1)-P(4)-C(46)	127.7 (2)
C(2)-P(1)-C(4)	101.7 (3)	C(3)-P(4)-C(40)	103.6 (3)
C(2)-P(1)-C(10)	107.3 (3)	C(3)-P(4)-C(46)	102.1 (3)
C(4)-P(1)-C(10)	101.7 (3)	C(40)-P(4)-C(46)	105.8 (3)
Rh(2)-P(2)-C(2)	113.3 (2)	Rh(2)-P(3)-C(3)	112.4 (2)
Rh(2)-P(2)-C(16)	114.7 (2)	Rh(2)-P(3)-C(28)	115.2 (2)
Rh(2)-P(2)-C(22)	110.9 (2)	Rh(2)-P(3)-C(34)	112.5 (2)
C(2)-P(2)-C(16)	104.7 (3)	C(3)-P(3)-C(28)	104.4 (3)
C(2)-P(2)-C(22)	106.6 (3)	C(3)-P(3)-C(34)	106.1 (3)
C(16)-P(2)-C(22)	106.0 (3)	C(28)-P(3)-C(34)	105.5 (3)
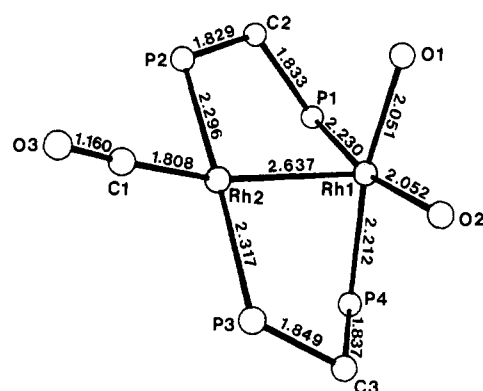
Figure 3. Diagram of the inner coordination environments of the rhodium atoms in $Rh_2(\mu\text{-dpm})_2(1,2\text{-}O_2C_6Cl_4)(CO)$.

other dpm-bridged rhodium dimers with Rh–Rh bonds,[10,11,16,19,24,25,29] it is within normal limits found for other types of Rh–Rh-bonded compounds.[38] Rh(2) has approximately planar coordination. It is bonded to a trans pair of phosphorus atoms from the bridging phosphine ligands, the terminal carbonyl group, and the other rhodium atom. While the P(2)–Rh(2)–P(3) unit is nearly linear (angle of 177.0 (1)°), the Rh(1)–Rh(2)–C(1) group is bent to an angle of 161.3 (2)°. The carbonyl group is, however, nearly linearly bound to Rh(1) with the Rh(2)–C(1)–O(3) angle being 173.8 (7)°.

The bis(phosphine) ligands are arranged in an unusual fashion. While they are trans to one another at Rh(2), they

are cis to each other at Rh(1) with the P(1)–Rh(1)–P(4) angle being 104.8 (1)°. In contrast all other compounds containing the $Rh_2(dpm)_2$ unit have the bis(phosphines) trans to each other at both metal centers. Other examples of compounds with the two dpm ligands arranged in a trans/cis fashion like this are $Pt_2(\mu\text{-dpm})_2(CH_3)_3^{+}$[39] and $(PhC_2)_2Pt(\mu\text{-dpm})_2AgI$.[40] Despite the unorthodox arrangement of the bis(phosphine), the bonded Rh–Rh and nonbonded P···P separations in the molecule are within normal limits.

The dioxolene ligand is capable of existing in three states; the dianion shown in **2**, the semiquinone form shown in **3**, and the quinone form shown in **4**. In $Rh_2(\mu\text{-dpm})_2(1,2\text{-}$

$O_2C_6Cl_4)(CO)$ the dimensions of the dioxolene ligand are consistent with nearly exclusive catecholato (**2**) contribution with no semiquinone (**3**) or quinone (**4**) character. Thus the C–O bond lengths, 1.327 (8) and 1.316 (9) Å, are longer than the C=O bond length in tetrachloro-*p*-quinone (1.20 (1) Å)[41] and only slightly shorter than those in tetrachloro-*o*-hydroquinone (1.35 (1) Å).[42] The C–C bond lengths in the ring are, within experimental error, equal and show no evidence for the bond length alternation that would be found in a quinoid type structure. The measurements of the dioxolene ligand in **1** are overall quite similar to those found for $(Ph_3P)_2Pd(1,2\text{-}O_2C_6Cl_4)$[43] and $(Ph_3P)Ir(NO)(1,2\text{-}O_2C_6Br_4)$,[44] both of which have been formulated as catecholato complexes.

While the overall geometric pattern of **1** differs significantly from that of all other binuclear, dpm-bridged rhodium compounds, it is closely related structurally to two other binuclear rhodium complexes, **5**[45] and **6**.[46] All of these possess two
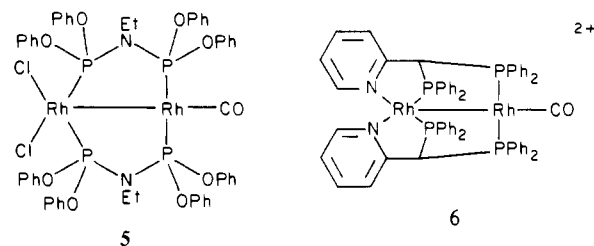
distinct rhodium environments, one five-coordinate and square pyramidal, the other four-coordinate and nearly planar. The Rh–Rh separations in **5** (2.661 Å) and **6** (2.674 Å) are quite similar to that in **1** (2.637 (1) Å). Bonding in these molecules is undoubtedly similar. Two descriptions can be given. The five-coordinate rhodium, Rh(1), can be assigned an oxidation state of 2 while the four-coordinate rhodium, Rh(2), then must be given a formal oxidation state of 0. Spin pairing between the d^7 and d^9 metal centers produces the Rh–Rh single bond. Alternatively, both rhodium ions may be formulated in oxidation state 1. In this case the five-coordinate rhodium, Rh(1), must act as a donor toward the four-coordinate rhodium,

(38) Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182.

(39) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500.

(40) McDonald, W. S.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 861.

(41) Chu, S.; Jeffrey, G. A.; Sakurai, T. *Acta Crystallogr.* **1962**, *15*, 661.

(42) Sikka, S. K.; Chidambaran, R. *Acta Crystallogr.* **1967**, *23*, 107.

(43) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1975**, *14*, 343.

(44) Shorthill, W. B.; Buchanan, R. M.; Pierpont, C. G.; Ghedini, M.; Dolcetti, G. *Inorg. Chem.* **1980**, *19*, 1803.

(45) Haines, R. J.; Meintjies, E.; Laing, M. *Inorg. Chim. Acta* **1979**, *36*, L403.

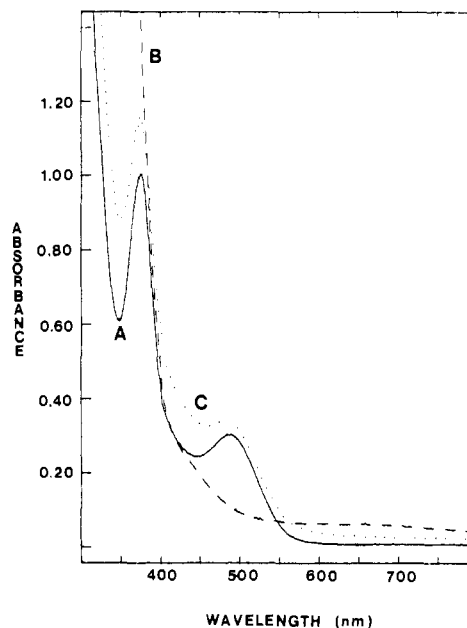(46) Anderson, M. P.; Pignolet, L. H. *Organometallics* **1983**, *2*, 1246.

Rh(2), and the metal–metal bond is a dative bond. Both schemes produce a Rh–Rh single bond. They differ principally in the polarization of that bond. Either scheme leaves the four-coordinate rhodium, Rh(2), coordinatively unsaturated with only 16 valence electrons while the five-coordinate rhodium, Rh(1), is a saturated, 18-electron center. All three complexes **1, 5,** and **6** have shorter Rh–P distances for the four-coordinate rhodium than for the five-coordinate rhodium. We disagree with Haines and co-workers in their interpretation[45] that this difference reflects a difference in rhodium oxidation states in **5**. Rather we believe that the difference in Rh–P distances results from the nature of the trans ligands. The longer Rh–P bonds in these three complexes are always found when the Rh–P bond is trans to another phosphorus. The shorter Rh–P bonds have as trans ligands chloride, nitrogen, or oxygen. Metal–phosphorus bond distances in group 8 are strongly dependent on the nature of the trans ligand.[47] It has been shown previously that Rh–P bonds trans to chloride[48] or nitrogen[38] are shorter than those trans to phosphorus.

The bend of the Rh(1)–Rh(2)–C(1) angle in **1** is less pronounced but nevertheless present in **5** (172°) and **6** (165.5°). In **1** this phenomenon can be traced to steric interaction between the carbonyl group and the phenyl rings of the bridging ligands. For **1** with its bent Rh–Rh–C group, the closest nonbonding contacts involving the carbonyl group are C(1)$\cdots$H(39) = 2.962 Å and O(3)$\cdots$H(29) = 2.962 Å. These are within normal ranges. However, if the carbonyl group is moved so that the Rh–Rh–C angle becomes linear while the Rh–C and C–O distances are held fixed at their values in **1**, then severe nonbonded contacts develop. In this hypothetical position the following short contacts are observed, C(1)$\cdots$H(29) = 2.068 Å, C(1)$\cdots$H(21) = 2.538 Å, and O(3)$\cdots$H(29) = 2.126 Å, while O(3)$\cdots$H(21) is 2.883 Å. As a consequence the carbonyl group is prevented from occupying a location directly trans to the Rh–Rh bond. However, although this analysis can explain the bending of the Rh–Rh–C angles as a consequence of nonbonded contacts, it does not explain why the Rh–Rh–C bending is preferable to rotation of the phenyl group as a means of minimizing these nonbonded contacts. We suspect that the phenyl group orientation may be dictated by nonbonded phenyl–phenyl contacts, but we have not explored the consequences of phenyl ring rotation about the C–P axes.

Oxidation of Rh$_2$(μ-dpm)$_2$(1,2-O$_2$C$_6$Cl$_4$)(CO). Compound **1** undergoes reversible one-electron oxidation to yield [Rh$_2$(μ-dpm)$_2$(1,2-O$_2$C$_6$Cl$_4$)(CO)]$^+$ (**1$^+$**), the first paramagnetic rhodium dimer in this group of compounds. The oxidation may be demonstrated electrochemically or chemically. Cyclic voltammetry in dichloromethane solution with an aqueous saturated calomel electrode reveals a nearly reversible, one-electron oxidation with E_p^{ox} = 0.52 V and a 75-mV peak-to-peak separation. For comparison, oxidation of [(OC)$_2$Rh(1,2-O$_2$C$_6$Cl$_4$)]$^-$ occurs at 0.63 V under these conditions.[37]

Chemical oxidation can be effected with use of silver trifluroracetate as the oxidant. The reaction is readily followed by UV–visible spectroscopy. The spectrum of **1** in dichloromethane solution is shown in trace A of Figure 4. Upon addition of silver trifluoroacetate and filtration to remove the precipitate of silver metal, the spectrum shown in trace B of figure 4 is obtained. The oxidized material may be reduced with hydrazine to regenerate **1**. When that is done, the spectrum shown in trace C is obtained.

Solutions of **1$^+$** show a strong electron spin resonance signal at g = 2.00 with a peak to peak separation of 10 G. Such a spectrum is typical for organometallic radicals of this type.[36,37] The lack of hyperfine coupling is consistent with earlier ob-

(47) Palenik, G. J.; Mathew, M.; Steffen, W. L.; Beran, G. *J. Am. Chem. Soc.* **1975,** *97,* 1059.
(48) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977,** *16,* 655.

Figure 4. Electronic spectra of (A) a 0.10 M dichloromethane solution of Rh$_2$(μ-dpm)$_2$(1,2-O$_2$C$_6$Cl$_4$)(CO), (B) a solution of [Rh$_2$(μ-dpm)$_2$(1,2-O$_2$C$_6$Cl$_4$)(CO)]$^+$, obtained by oxidation with silver trifluoroacetate, and (C) the solution in (B) after treatment with hydrazine.

servations on related semiquinone complexes and is indicative of localization of the odd electron on the semiquinone ligand. Previously it was demonstrated that phosphines and metal nuclei lying in the plane of the coordinated semiquinone gave no detectable hyperfine splitting due to the fact that they resided in a nodal plane of the spin-containing π orbital.[36,37] Therefore, in first order the spin density at the metal and such phosphines would be zero. Thus for **1$^+$** no hyperfine splitting due to Rh(1), P(1), and P(4) is expected. Likewise the spin density at P(2) and P(3), which lie far from the semiquinone ligand and are only indirectly connected to it, is expected to be low and consequently no hyperfine splitting due to these nuclei is likely either.

Infrared spectroscopy shows that the oxidized species, **1$^+$**, has a terminal carbonyl absorption of 1997 cm^{-1}, a value which is higher than that of **1** itself. The observation of this magnitude change in the carbonyl stretching frequency is wholly consistent with a ligand-centered, rather than a metal-centered, oxidation. Such shifts in the carbonyl stretching bands are, in fact, typical for the oxidation of other catecholato complexes.[36,37] For example ν(CO) increases from 2045 and 1983 cm^{-1} in Ru(1,2-O$_2$C$_6$Cl$_4$)(CO)$_2$(PPh$_3$)$_2$ to 2072 and 2022 cm^{-1} in Ru(1,2-O$_2$C$_6$Cl$_4$)(CO)$_2$(PPh$_3$)$_2$$^+$, although electron spin resonance results indicate that here also the odd electron is localized on the semiquinone ligand. The infrared data reveal that there is reduced metal–CO back-bonding in the oxidized forms of these complexes even in **1$^+$**, where the carbonyl group resides on the metal that is not attached to the semiquinone ligand. These results indicate that oxidation of the catechol ligand produces a coordinated semiquinone which must be a poorer σ donor so that the electron density at the metals is lowered upon oxidation and this effect (upon oxidation of **1** to **1$^+$**) is transmitted to Rh(2).

Experimental Section

Rh$_2$(μ-dpm)$_2$(1,2-O$_2$C$_6$Cl$_4$)(CO). Method 1. Solid bis(diphenylphosphino)methane (0.32 g, 0.831 mmol) was added to a yellow

solution of 0.520 g (0.800 mmol) of $[(C_6H_5)_4As][Rh(CO)_2(1,2-O_2C_6Cl_4)]$ in 20 mL of dichloromethane. Vigorous gas evolution was noted. The reaction mixture was stirred for 5 days at room temperature. After the solvent was removed with a rotary evaporator, the orange-brown oil was redissolved in a minium of dichloromethane and chromatographed on neutral alumina (Baker, activity grade 1) with use of dichloromethane as eluent. The bright orange band was collected and concentrated to 5 mL by evaporation. Addition of 5 mL of cyclohexane precipitated the product as orange needles, which were collected by filtration, washed with cyclohexane, and vacuum-dried; yield 0.083 g (16.6%).

Method 2. $[Rh(CO)_2Cl]_2$ (0.039 g, 0.100 mmol) and 0.130 g (0.105 mmol) of $[(C_6H_5)_4As][Rh(CO)_2(1,2-O_2C_6Cl_4)]$ were dissolved in 20 mL of dichloromethane. A second solution containing 0.154 g (0.400 mmol) of bis(diphenylphosphino)methane in 10 mL of dichloromethane was added dropwise to the first solution over a period of 10 min. After the mixture was stirred for 20 min, the solvent was removed with use of a rotary evaporator. Addition of 5 mL of acetone to the brown-orange oil induced the formation of an orange precipitate, which was collected by filtration, washed with acetone, and dried. The crude precipitate was purified by the procedure in method 1 to give 0.084 g of $Rh_2(\mu\text{-dpm})_2(1,2-O_2C_6C_4)(CO)$ after recrystallization; yield 33.2%. The products from method 1 or method 2 gave identical spectroscopic features.

X-ray Data Collection. Deep red-orange tabular prisms of $Rh_2(\mu\text{-dpm})_2(1,2-O_2C_6Cl_4)(CO)$ were grown by slow vapor diffusion of diethyl ether into a dichloromethane solution of the complex. A rectangular crystal of dimensions $0.125 \times 0.125 \times 0.27$ mm was selected, attached to a glass fiber, and coated with epoxy glue. The crystal was mounted on a Syntex $P2_1$ diffractometer with the longest crystal axis parallel to ϕ and maintained at 140 K with a modified LT-1 low-temperature apparatus. The crystal lattice was determined to be triclinic, either $P1$ (No. 1) or $P\bar{1}$ (No. 2), from axial photographs and the automatic indexing routine of the diffractometer software. Twelve centered reflections, including Friedel pairs, in the range $25° < 2\theta < 35°$ were used to obtain lattice constants of $\alpha = 11.126$ (3) Å, $b = 11.759$ (3) Å, $c = 20.065$ (5) Å, $\alpha = 91.82$ (2)°, $\beta = 101.41$ (2)°, and $\gamma = 92.23$ (2)°. The experimental density of 1.62 g cm⁻³, measured at room temperature by flotation, and the calculated density at 140 K of 1.61 g cm⁻³ were consistent with the assumption of $Z = 2$.

The data were collected at 140 K on the $P2_1$ diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å, graphite monochromator), a constant scan speed of 29.3 deg min⁻¹, and a 1.0° ω scan with 1° offset for background. In the 2θ range 0–45°, 8166 unique data were collected in the octants $(h,\pm k,\pm l)$, of which 5018 reflections with $I > 2\sigma(I)$ were used in the final refinement. The intensities of 2 standard reflections were measured after every 100 reflections and showed no decay. The usual Lorentz and polarization corrections were made. Due to the relatively uniform crystal size and small absorption coefficient (μ(Mo $K\alpha$) = 10.09 cm⁻¹) no absorption correction was made. Maximum and minumum transmission factors were 0.90 and 0.86.

Solution and Refinement of the Structure. The positions of the two rhodium atoms were deduced from the Patterson map, assuming the space group to be $P\bar{1}$. The choice of space group as $P\bar{1}$ was confirmed by successful refinement in that space group. Other atoms were located from successive difference Fourier maps. Final cycles of refinement were carried out with anisotropic thermal parameters for the rhodium, phosphorus, and chlorine atoms and isotropic thermal parameters for all remaining nonhydrogen atoms. Hydrogen atoms were included as fixed contributions. Corrections for anomalous dispersion were applied to Rh, Cl, and P.[49a] Neutral-atom scattering factors were those of Cromer and Waber.[49a] A final R value of 0.054 ($R_w = 0.046$) was obtained with no features larger than 0.84 e/ų (less than that expected for a hydrogen atom) on the final difference Fourier map.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 180 infrared spectrometer. ¹H and ³¹P{¹H} NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer at 200 and 81 MHz, respectively. An external 85% phosphoric acid reference was used for ³¹P NMR spectra, and the high-frequency positive convention, recommended by IUPAC, has been used in reporting chemical shifts. Electron spin resonance spectra were obtained with a Varian E4 ESR spectrometer and calibrated with dpph.

Supplementary Material Available: Listings of structure factor amplitudes, thermal parameters, and all bond lengths and bond angles (40 pages). Ordering information is given on any current masthead page.

(49) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 149–150; (b) pp 99–101.