

Structural and Electrochemical Characterization of the Novel Ortho-Metalated Dirhodium(II) Compounds



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The complex $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{CH}_3\text{CO}_2\text{H}$, **1**, was obtained by reaction of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{MeOH}$ with triphenylphosphine in acetic acid. The purple crystals belong to the monoclinic system, space group $C2/c$ with unit cell dimensions of $a = 10.111(3) \text{ \AA}$, $b = 19.653(10) \text{ \AA}$, $c = 21.033(8) \text{ \AA}$, $\beta = 97.63(3)^\circ$, $V = 4142(3) \text{ \AA}^3$, and $Z = 4$. The molecule consists of a dirhodium unit bridged by two cisoid acetate ligands and by triphenylphosphine ligands in which orthometalation has occurred at one of the phenyl rings on each phosphine, with a molecule of acetic acid in each axial site. The electrochemical reactivity of this novel dirhodium(II) compound was investigated in three organic solvents in the presence of potential donor ligands, such as pyridine, *p*-dithiane, and PMe_2Ph . In each experiment a one-electron oxidation was observed at potentials between +0.25 and +1.04 V vs. Ag-AgCl. In addition, two ill-defined reductions were observed at potentials in excess of -0.60 V. The pyridine adduct $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, **2**, was prepared independently and was shown, by X-ray crystallography, to contain the same general arrangement of ligands. It too forms monoclinic crystals in space group $C2/c$ with unit cell dimensions $a = 24.289(4) \text{ \AA}$, $b = 10.391(3) \text{ \AA}$, $c = 23.056(5) \text{ \AA}$, $\beta = 131.85(2)^\circ$, $V = 4334(2) \text{ \AA}^3$ and $Z = 4$. Both compounds are unusual in that the Rh-Rh distances, 2.508(1) \AA in **1** and 2.556(2) \AA in **2**, are significantly greater than those reported for any of the dirhodium tetracarboxylates $\text{Rh}_2(\text{O}_2\text{CR})_4 \cdot 2\text{L}$.

Introduction

In recent years the chemical and electrochemical properties of dinuclear rhodium(II) complexes have received considerable attention in the literature.¹⁻³ The majority of complexes investigated have, however, been of the type " $\text{Rh}_2(\text{XYZ})_4$ " where all four bridging ligands were of the same type. There are, to the best of our knowledge, only two examples in the literature of dirhodium(II) complexes containing a mixed-ligand bridging system, where the structures have been unequivocally identified by X-ray crystallography. These are the mixed-carboxylate $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{O}_2\text{CCPh}_3)_2(\text{CH}_3\text{CN})_2 \cdot \text{C}_7\text{H}_8$ ⁴ and the 6-methyl-2-hydroxypyridine complex $\text{Rh}_2(\text{mhp})_2(\text{O}_2\text{CCH}_3)_2(\text{Im})$.⁵ The range of complexes available has now been extended to include molecules of the general formula $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{L}$,⁶ where the bridging ligands are acetate and ortho-metalated triphenylphosphine anions.

The electrochemistry of $\text{Rh}_2(\text{O}_2\text{CR})_4$ in nonaqueous media has been studied⁷ as a function of solvent and the nature of the substituent group R. In all solvents the electrooxidation could be characterized as a one-electron abstraction to yield a $\text{Rh}(2.5+)$ complex. Such mixed-valence dimers have been characterized by a variety of techniques.⁸⁻¹² More recently, the electrochemical characterization of the amidato-bridged dimer $\text{Rh}_2(\text{ONHCCF}_3)_4$ was reported.¹³ This also exhibited a one-electron oxidation, the potential of which was solvent dependent. A subsequent report¹⁴ on the closely related $\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4$ was consistent with the previous results. Indeed, the oxidation to the radical cation $[\text{Rh}_2(\text{C}_6\text{H}_5\text{NOCCH}_3)_4]^+$ occurs at $0.54 \pm 0.01 \text{ V}$ vs. SCE, and unlike almost all other known dirhodium(II) complexes this species undergoes a further reversible one-electron oxidation. Most recently the electrochemical properties of a series of dirhodium(II) complexes, $\text{Rh}_2(\text{O}_2\text{CCH}_3)_n(\text{HNOCCH}_3)_{4-n}$ [$n = 0-4$], have been reported by Bear and co-workers.¹⁵

This paper reports the synthesis and X-ray characterization of the new dirhodium(II) complex $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{CH}_3\text{CO}_2\text{H}$, **1**, its conversion to the bis(pyridine) adduct $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, **2**, which has also been crystallographically characterized, and the results of our electrochemical studies on **1** in the presence of several donor ligands.

Experimental Section

$\text{Rh}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{MeOH}$ was prepared by a literature method.¹⁶ All other reagents were purchased from normal commercial suppliers. Solvents used were of analytical grade and were distilled under nitrogen prior to use.

Synthesis of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{CH}_3\text{CO}_2\text{H}$, **1.** A 0.15-g quantity of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{MeOH}$ was added to a 15-mL volume of acetic acid under a dinitrogen atmosphere. Triphenylphosphine, 0.15 g, was added and the mixture refluxed for 45 min in which time the blue coloration was replaced by red-brown and then dark purple. The solution was concentrated to half its initial volume, and the purple solid deposited was then

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[†] Dedicated to the memory of Earl L. Muetterties

Table I. Crystallographic Parameters for 1 and 2

	Rh ₂ (O ₂ CCH ₃) ₂ [(C ₆ H ₅) ₂ P(C ₆ H ₄)] ₂ · 2CH ₃ CO ₂ H	Rh ₂ (O ₂ CCH ₃) ₂ [(C ₆ H ₅) ₂ P(C ₆ H ₄)] ₂ · 2C ₅ H ₅ N
formula	Rh ₂ P ₂ O ₈ C ₄₄ H ₄₂	Rh ₂ P ₂ O ₄ N ₂ C ₅₀ H ₄₄
fw	968.59	1004.68
space group	C2/c	C2/c
systematic absences	<i>hkl</i> , <i>h</i> + <i>k</i> = 2 <i>n</i> ; <i>h0l</i> , <i>l</i> = 2 <i>n</i> (<i>h</i> = 2 <i>n</i>); 0 <i>ko</i> , <i>k</i> = 2 <i>n</i>	<i>hkl</i> , <i>h</i> + <i>k</i> = 2 <i>n</i> ; <i>h0l</i> , <i>l</i> = 2 <i>n</i> (<i>h</i> = 2 <i>n</i>); 0 <i>ko</i> , <i>k</i> = 2 <i>n</i>
<i>a</i> , Å	10.111 (3)	24.289 (4)
<i>b</i> , Å	19.653 (10)	10.391 (3)
<i>c</i> , Å	21.033 (8)	23.056 (5)
α, deg	90.0	90.0
β, deg	97.63 (3)	131.85 (2)
γ, deg	90.0	90.0
<i>V</i> , Å ³	4142 (3)	4334 (2)
<i>Z</i>	4	4
<i>d</i> _{calcd} , g/cm ³	1.55	1.54
cryst size, mm	0.4 × 0.25 × 0.15	0.2 × 0.3 × 0.1
μ(Mo Kα), cm ⁻¹	9.10	8.68
data collectn instrument	Syntax P1	Syntax P1
radiatn (monochromated in incident beam)	Mo Kα	Mo Kα
orientatn reflctns, number, range (2θ)	15, 25 < 2θ < 34	15, 25 < 2θ < 32
temp, °C	22 ± 2	22 ± 2
scan method	ω-2θ	ω-2θ
data col range, 2θ, deg	5-50	5-50
no. of unique data, total with <i>F</i> _o ² > 3σ(<i>F</i> _o ²)	2923, 2508	2210, 1762
no. of parameters refined	253	271
<i>R</i> ^a	0.046	0.050
<i>R</i> _w ^b	0.070	0.065
quality of fit indicator ^c	1.432	1.184
largest shift/esd, final cycle	0.10	0.12
largest peak, e/Å ³	0.81	0.73

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $R_w = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

filtered off: yield 0.17 g, 60%; mp 221 °C; IR (Nujol) 1670, 1570, 1560, 1555, 1410, 1287, 1230, 1182, 1150, 1120, 1091, 1038, 1020, 930, 911, 890, 748, 740, 722, 695 cm⁻¹; electronic spectrum (THF solvent), λ_{max} 584 nm (ε 290 M⁻¹ cm⁻¹); ¹H NMR δ 1.14 (s, [O₂C-CH₃]⁻, 6 H), 2.07 (s, CH₃CO₂H, 6 H), 6.3-7.7 (m, [(C₆H₅)₂P(C₆H₄)]₂, 28 H) (signal due to CH₃CO₂H was not observed).

Synthesis of Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2C₅H₅N, 2. A 0.1-g sample of Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2CH₃CO₂H was added to a solution of 0.4 mL of pyridine in 20 mL of methanol. The solution was stirred for 10 min and then allowed to evaporate over a period of 6 days in an oxygen atmosphere. A near quantitative yield of red rhombohedral crystals was realized: mp >260 °C; IR (Nujol) 1587, 1573, 1558, 1303, 1256, 1229, 1211, 1181, 1148, 1120, 1097, 1079, 1065, 1033, 998, 971, 936, 743, 730, 719, 697, 685 cm⁻¹; electronic spectrum (neat pyridine), λ_{max} 483 nm (ε 1050 M⁻¹ cm⁻¹); ¹H NMR δ 1.19 (s, [O₂CCH₃]⁻, 6 H); 8.56, 7.78 (m, C₅H₅N, 4 H, 2 H) (third set of resonances from pyridine ring lie under phenyl resonances), 7.5-6.3 ([C₆H₅)₂P(C₆H₄)]₂, 32 H).

Measurements. Infrared spectra were recorded on a Perkin-Elmer 785 spectrometer. Visible spectra were obtained by using a Cary 17D spectrophotometer. ¹H NMR spectra were recorded in CDCl₃ on a Varian EM390 spectrometer. Chemical shifts are quoted to high frequency of Me₄Si (internal lock). Electrochemical measurements were made with a Bioanalytical Systems Inc., Model BAS100 electrochemical analyzer instrument in connection with a Bausch and Lomb, Houston Instruments Model DMP 40 digital plotter. Experiments were carried out in a variety of solvents (see Table VI) containing 0.1 M (NBu₄)BF₄ as supporting electrolyte. A three-electrode cell configuration was employed using a platinum disk, Model BAS MF 2032, and platinum wire as working and auxiliary electrodes, respectively, and a BAS MF 2020 Ag-AgCl cell as a reference electrode (against which ferrocene is oxidized at *E*_{1/2} = +0.45 V). All potentials were referenced to the Ag-AgCl electrode at 22 ± 2 °C with full positive feedback resistance compensation. All voltammetric measurements were made under a dry argon atmosphere.

The Rh₂(O₂CCH₃)₂(PPh₂C₆H₄)₂·2CH₃CO₂H was dissolved in each of three solvents (THF, CH₂Cl₂, CH₃OH) and the potential measured before and after addition of the axial ligands (C₄H₉S₂, C₅H₅N, PMe₂Ph). In each case a characteristic color is developed

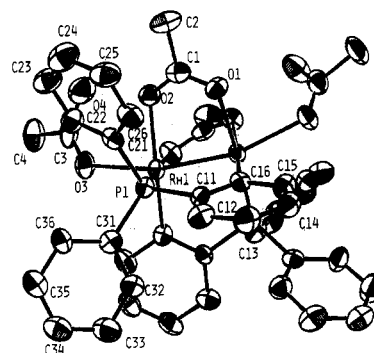


Figure 1. An ORTEP drawing of Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2CH₃CO₂H (1). Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labeling scheme in one crystallographically independent half of the molecule is defined.

on addition of the ligand: C₄H₉S₂, orange; C₅H₅N, deep red; PMe₂Ph, yellow. The solution in pure THF is blue. On addition of an additional quantity of the crystalline diadduct to a solution containing ligand, which in each case had the appropriate color, no change in the appearance of the solution could be seen nor was any new feature observed electrochemically.

X-ray Crystallographic Procedures. The structures of 1 and 2 were determined by applying the general procedures described elsewhere.^{17,18} A detailed description is available as part of the supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Tables II and III list the atomic

(17) Calculations were done on the VAX-11/780 computer at Department of Chemistry, Texas A&M University, College Station, TX, with VAX-SDP software package.

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Table II. Positional Parameters and Their Estimated Standard Deviations for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{CH}_3\text{CO}_2\text{H}$ (1)^a

atom	x	y	z	B, Å ²
Rh(1)	0.00759 (5)	0.24332 (3)	0.19099 (3)	2.13 (1)
P(1)	0.3349 (2)	0.32656 (9)	0.67806 (9)	2.21 (4)
O(1)	0.6737 (5)	0.1892 (3)	0.7103 (3)	3.0 (1)
O(2)	0.3841 (5)	0.1653 (3)	0.6927 (3)	3.1 (1)
O(3)	0.5307 (6)	0.2234 (3)	0.5861 (3)	3.9 (1)
O(4)	0.4541 (7)	0.1164 (3)	0.5914 (3)	5.5 (2)
C(1)	0.3101 (7)	0.1571 (4)	0.7379 (4)	3.2 (2)
C(2)	0.6981 (9)	0.3962 (4)	0.2286 (5)	4.9 (2)
C(3)	0.5211 (8)	0.1646 (5)	0.5656 (4)	4.2 (2)
C(4)	0.586 (1)	0.1416 (5)	0.5079 (4)	5.1 (2)
C(11)	0.6979 (7)	0.3627 (3)	0.7464 (3)	2.4 (1)
C(12)	0.2941 (7)	0.0845 (4)	0.2461 (4)	3.2 (2)
C(13)	0.6748 (8)	0.0606 (4)	0.3134 (4)	3.8 (2)
C(14)	0.7596 (8)	0.4117 (4)	0.6298 (4)	3.5 (2)
C(15)	0.6642 (8)	0.3605 (4)	0.6312 (4)	3.3 (2)
C(16)	0.6341 (6)	0.3346 (4)	0.6902 (4)	2.2 (1)
C(21)	0.3167 (7)	0.2185 (4)	0.3561 (4)	2.5 (1)
C(22)	0.3141 (8)	0.2589 (4)	0.4105 (4)	3.4 (2)
C(23)	0.4266 (8)	0.2971 (4)	0.4355 (5)	4.1 (2)
C(24)	0.5408 (9)	0.2946 (5)	0.4056 (5)	4.9 (2)
C(25)	0.5443 (8)	0.2547 (4)	0.3510 (5)	4.3 (2)
C(26)	0.4357 (7)	0.2165 (4)	0.3262 (4)	3.4 (2)
C(31)	0.3412 (7)	0.4004 (4)	0.6256 (4)	2.6 (1)
C(32)	0.4135 (9)	0.4571 (4)	0.6486 (4)	3.6 (2)
C(33)	0.4265 (9)	0.5141 (4)	0.6094 (5)	4.3 (2)
C(34)	0.6305 (8)	0.4874 (4)	0.4550 (5)	4.0 (2)
C(35)	0.297 (1)	0.4555 (5)	0.5213 (5)	4.8 (2)
C(36)	0.2845 (9)	0.3999 (4)	0.5610 (4)	3.6 (2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

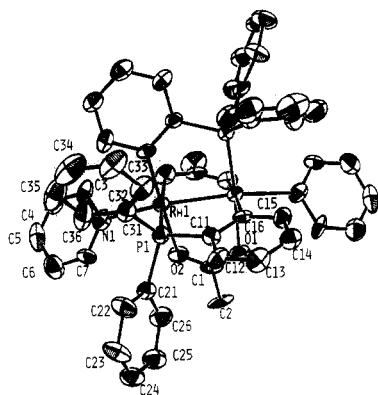


Figure 2. An ORTEP drawing of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ (2). Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labelling scheme in one crystallographically independent half of the molecule is defined.

coordinates of 1 and 2, respectively. Tables IV and V list important bond distances and angles, respectively. Complete tables of bond lengths and angles as well as anisotropic thermal parameters and structure factor data are available as supplementary material. Figures 1 and 2 show molecules 1 and 2, respectively. Both compounds crystallize in the monoclinic space group $C2/c$, with half of the molecule in the asymmetric unit. In each case the molecule resides on a twofold axis, which bisects the Rh-Rh bond. The position of the rhodium atom was in each case derived from a three-dimensional Patterson map and the remainder of each structure obtained by using least-squares refinement and difference Fourier maps.

Results and Discussion

The goal of obtaining a dimetal complex in which the metal-metal bond is bridged by an ortho-metallated ligand has long been an objective of ours. The first example of

Table III. Positional Parameters and Their Estimated Standard Deviations for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ (2)^a

atom	x	y	z	B, Å ²
Rh(1)	0.03297 (4)	0.17682 (9)	-0.17780 (4)	2.08 (2)
P(1)	-0.0463 (1)	0.0312 (3)	-0.2008 (1)	2.35 (7)
O(1)	0.1072 (3)	0.3106 (8)	-0.1632 (3)	3.3 (2)
O(2)	0.0337 (3)	0.3488 (7)	-0.2898 (3)	2.8 (2)
N(1)	0.0894 (4)	0.2446 (9)	-0.0551 (4)	3.2 (3)
C(1)	0.0880 (4)	0.373 (1)	-0.2201 (5)	2.9 (3)
C(2)	0.1345 (5)	0.493 (1)	-0.2010 (6)	4.7 (4)
C(3)	0.1630 (5)	0.273 (1)	-0.0067 (5)	3.4 (3)
C(4)	0.1983 (6)	0.333 (1)	0.0648 (6)	4.3 (3)
C(5)	0.1617 (7)	0.359 (1)	0.0890 (6)	4.9 (4)
C(6)	0.0847 (5)	0.330 (2)	0.0389 (5)	4.7 (3)
C(7)	0.0521 (4)	0.272 (1)	-0.0324 (5)	3.1 (3)
C(11)	-0.1125 (4)	-0.017 (1)	-0.3023 (5)	2.4 (3)
C(12)	-0.1689 (5)	-0.105 (1)	-0.3273 (5)	3.2 (3)
C(13)	-0.2207 (6)	-0.143 (1)	-0.4053 (6)	3.8 (4)
C(14)	-0.2141 (5)	-0.090 (1)	-0.4579 (5)	3.4 (3)
C(15)	-0.1580 (5)	-0.006 (1)	-0.4328 (5)	3.2 (3)
C(16)	0.1053 (4)	0.036 (1)	-0.1465 (5)	2.3 (2)
C(21)	-0.1100 (4)	0.071 (1)	-0.1852 (5)	2.6 (3)
C(22)	-0.1294 (5)	-0.022 (1)	-0.1573 (5)	4.3 (3)
C(23)	-0.1841 (5)	0.010 (1)	-0.1537 (6)	4.8 (3)
C(24)	-0.2168 (5)	0.131 (1)	-0.1765 (6)	4.0 (3)
C(25)	-0.1986 (5)	0.221 (1)	-0.2054 (6)	4.1 (3)
C(26)	-0.1446 (5)	0.190 (1)	-0.2088 (6)	4.0 (3)
C(31)	-0.0043 (5)	-0.117 (1)	-0.1442 (5)	2.8 (3)
C(32)	-0.0094 (5)	-0.231 (1)	-0.1793 (6)	3.7 (3)
C(33)	0.0290 (6)	-0.345 (1)	-0.1336 (7)	5.3 (4)
C(34)	0.0671 (7)	-0.339 (1)	-0.0555 (8)	6.1 (5)
C(35)	0.0726 (6)	-0.227 (2)	-0.0192 (7)	5.6 (4)
C(36)	0.0366 (6)	-0.113 (1)	-0.0629 (6)	4.8 (4)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table IV. Some Important Bond Distances (Å) in $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{CH}_3\text{CO}_2\text{H}$ (1) and $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ (2)

	1	2
Rh(1)-Rh(1)	2.508 (1)	2.556 (2)
-P(1)	2.210 (2)	2.216 (3)
-O(1)	2.136 (4)	2.118 (8)
-O(2)	2.190 (4)	2.182 (7)
-C(16)	1.996 (6)	2.011 (11)
-O(3)	2.342 (5)	
-N(1)		2.281 (9)
P(1)-C(11)	1.811 (6)	1.814 (11)
-C(21)	1.832 (6)	1.854 (11)
-C(31)	1.830 (7)	1.827 (12)
C(11)-C(16)	1.384 (9)	1.417 (14)
O(1)-C(1)	1.252 (8)	1.246 (13)
O(2)-C(1)	1.294 (8)	1.248 (13)
C(1)-C(2)	1.536 (9)	1.530 (15)
O(3)-C(3)	1.232 (9)	
O(4)-C(3)	1.323 (10)	
C(3)-C(4)	1.522 (10)	
N(1)-C(3)		1.367 (13)
C(3)-C(4)		1.40 (2)
C(4)-C(5)		1.35 (2)
C(5)-C(6)		1.43 (2)
C(6)-C(7)		1.40 (2)
C(7)-N(1)		1.348 (13)

such a complex was $\text{Re}_2\text{Cl}_3(\text{Ph}_2\text{Ppy})_2[(\text{Ph})(\text{py})\text{P}(\text{C}_6\text{H}_4)]$ ^{19,20} in which the triply bonded Re_2^{4+} core is bridged by a Ph_2Ppy ligand in a novel tridentate mode as a result of orthometalation having occurred at one of the phenyl rings.

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Table V. Some Important Bond Angles (deg) in Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2CH₃CO₂H (1) and Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2C₅H₅N (2)

	1	2
Rh(1)-Rh(1)-P(1)	88.31 (5)	89.95 (8)
-O(1)	87.8 (1)	86.2 (2)
-O(2)	82.7 (1)	82.9 (2)
-C(16)	97.5 (2)	96.1 (3)
-O(3)	163.6 (1)	
-N(1)		162.0 (2)
P(1)-Rh(1)-O(1)	176.1 (1)	175.7 (2)
-O(2)	93.9 (1)	98.6 (2)
-C(16)	91.1 (2)	90.1 (3)
-O(3)	103.5 (1)	
-N(1)		102.4 (3)
O(1)-Rh(1)-O(2)	85.6 (2)	82.9 (3)
-C(16)	89.4 (2)	88.4 (3)
-O(3)	80.3 (2)	
-N(1)		81.8 (3)
O(2)-Rh(1)-C(16)	175.0 (2)	171.2 (4)
-O(3)	85.1 (2)	
-N(1)		82.3 (3)
C(16)-Rh(1)-O(3)	93.6 (2)	
-N(1)		96.9 (4)
O(1)-C(1)-O(2)	123.7 (6)	125 (1)
-C(2)	117.6 (7)	116 (1)
O(2)-C(1)-C(2)	118.7 (7)	119 (1)
P(1)-C(11)-C(16)	118.2 (5)	118.0 (8)
O(3)-C(3)-O(4)	123.3 (7)	
-C(4)	122.3 (8)	
O(4)-C(3)-C(4)	114.4 (8)	
N(1)-C(3)-C(4)		120 (1)
C(3)-C(4)-C(5)		121 (1)
C(4)-C(5)-C(6)		119 (1)
C(5)-C(6)-C(7)		117 (1)
C(6)-C(7)-N(1)		123 (1)
C(7)-N(1)-C(3)		119 (1)

In the course of our investigations of the reactions of the osmium(III) carboxylates with triphenylphosphine we isolated complexes with the stoichiometry Os₂(O₂CR)₂[(C₆H₅)₂P(C₆H₄)]₂Cl₂.⁶ Crystal structure determinations (for R = CH₃, C₂H₅) showed that the osmium-osmium triple bond was bridged by two triphenylphosphine ligands in which orthometalation had occurred at one phenyl ring of each phosphine.

In order to determine how general this reaction might be, we set about investigating the reactions of triphenylphosphine with other dimetal tetracarboxylato compounds. One of the first candidates examined was Rh₂(O₂CCH₃)₄·2MeOH. The reaction of dirhodium carboxylates with triphenylphosphine in a weakly coordinating solvent such as an alcohol, under mild conditions, readily gives the 2:1 adducts Rh₂(O₂CR)₄(PPh₃)₂.²¹⁻²⁴ However, the conditions employed here, refluxing acetic acid, are sufficiently different that the isolation of a different final product need not be considered surprising. Mixing of the reactants at room temperature rapidly gives a red-brown suspension characteristic of simple adduct formation. However, refluxing for 30 min gives a deep purple solution from which 1 can be isolated (see Experimental Section). The electronic spectrum, in THF solution, contains only one band, in the visible region, at 584 nm, characteristic of the Rh₂⁴⁺ core. The infrared spectrum contains bands in the region 1540-1570 cm⁻¹ that may be tentatively assigned to the ortho-metalated ligand.²⁵ As the identity

of the complex could not be unequivocally established from the spectral data, recourse was had to X-ray crystallography. This showed the complex to be Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2CH₃CO₂H in which there are two bridging phosphine ligands, orthometalation having occurred at one phenyl ring of each phosphine. The complex readily reacts with Lewis bases to give the type of adduct well-known for the tetracarboxylates. One typical example, Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2C₅H₅N, has been isolated and characterized by X-ray crystallography.

Molecular Structures of Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2CH₃CO₂H, 1, and Rh₂(O₂CCH₃)₂[(C₆H₅)₂P(C₆H₄)]₂·2C₅H₅N, 2. The important details of each structure are similar and hence both 1 and 2 will be discussed concurrently. The structure of each compound was solved by three-dimensional X-ray crystallographic procedures. The atomic coordinates and equivalent isotropic thermal vibration parameters for 1 and 2 are listed in Tables II and III, respectively. A diagram of each molecule is shown in Figures 1 and 2. Important bond distances and angles are listed in Tables IV and V. In each case the molecule resides on a crystallographic twofold axis of symmetry that is a perpendicular bisector of the Rh-Rh bond.

Each structure consists of a dinuclear rhodium(II) core bridge by cisoid acetate groups and triphenylphosphine ligands in which orthometalation has occurred at one of the phenyl rings of each phosphine. One phosphorus atom is bonded to each rhodium. In 1 the axial sites are occupied by molecules of acetic acid, while in 2 pyridine ligands occupy the axial positions. The geometry about each rhodium atom is distorted octahedral, with angles in the range 82-103°. The rhodium-rhodium distances at 2.508 (1) and 2.556 (2), for 1 and 2, respectively, are significantly longer than any of those reported for the tetracarboxylates^{1,2} and are more in line with the values expected for a single metal-metal bond than those found in previous structure determinations. Only the complexes Rh₂(O₂CCH₃)₂(dmg)₂(PPh₃)₂²⁶ and Rh₂(O₂CH)₂(phen)₂Cl₂,²⁷ with Rh-Rh distances of 2.618 (5) and 2.576 Å, in which there are only two bridging ligands, have longer rhodium-rhodium bonds. The Rh-O distances are in the normal range with the Rh-O bonds trans to the phosphorus atom being shorter than those trans to the carbon atom. This is in accord with the expected order of trans influence of M-P and M-C bonds. In 1 the pertinent distances are Rh(1)-O(1) = 2.136 (4) Å and Rh(1)-O(2) = 2.190 (4) Å, while in 2 Rh(1)-O(1) is 2.118 (8) Å and Rh(1)-O(2), 2.182 (7) Å. The Rh-P distances, 2.210 (2) and 2.216 (3) Å, for 1 and 2, respectively, are normal and, as expected, much shorter than those observed for weak axial coordination of a phosphine ligand; e.g., in Rh₂(O₂CCH₃)₄(PPh₃)₂, Rh-P is 2.4771 (5) Å.²³ The Rh-C distances, 1.996 (6) and 2.011 (11) Å, respectively, are of the expected magnitude.

Unlike most simple adducts of the tetracarboxylates the angle Rh-Rh-axial ligand deviates significantly from linearity. In 1 the angle Rh(1)-Rh(1)-O(3) is 163.6 (1)°, and in 2 Rh(1)-Rh(1)-N(1) = 162.0 (2)°. Similar deviations from linearity were observed for the ortho-metalated osmium compounds Os₂(O₂CR)₂[(C₆H₅)₂P(C₆H₄)]₂Cl₂.²⁸

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Table VI. Electrode Potentials (V) and ΔE_p (mV) for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_5\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_2]_2 \cdot 2\text{CH}_3\text{CO}_2\text{H}$ in Three Solvents in the Presence of Ligands^a

added ligand	solvent		
	THF	CH_2Cl_2	CH_3OH
	+0.93 (65)	+1.04 (60)	+0.73 (65)
$\text{C}_4\text{H}_8\text{S}_2$	+1.00 (60)	+0.86 (70)	+0.86 ^b
$\text{C}_5\text{H}_5\text{N}$	+0.79 (70)	+0.66 (60)	+0.66 (60)
PMe_2Ph	+0.51 (60)	+0.34 (60)	+0.25 (60)

^a Peak potentials were measured at a scan rate of 100 mV s^{-1} and at compound concentration of ca. 2.5×10^{-4} M. ^b Peak potential measured using differential pulse voltammetry.

This deformation of the structure can probably be attributed to steric interactions between the non-ortho-metalated phenyl rings and the axial ligands. In complex 2 this seems to result in a variation in the bond distances within the pyridine ring. In complex 1 the axial acetic acid molecule is hydrogen bonded through O(4) to one of the oxygen atoms, O(2), of the bridging carboxylate; O(2)–O(4) = 2.527 Å. The distortions from octahedral geometry result in, or may be due to, significant torsion angles about the metal–metal bond. In the acetic acid adduct 1, both torsion angles are large, P(1)–Rh(1)–Rh(1)′–C(16) = 12.2° and O(1)–Rh(1)′–Rh(1)–O(2) = 17.3°. However, the longer Rh–Rh distance in the pyridine adduct appears to relieve the strain present in the five-membered rings and the appropriate angles are much reduced, P(1)–Rh(1)–Rh(1)′–C(16) = 3.8° and O(1)–Rh(1)′–Rh(1)–O(2) = 14.5°. The longer Rh–Rh distance in 2 compared to 1 presumably results from the fact that pyridine is a stronger donor than the acetic acid molecule.

Electrochemical Studies. Complex 1 was investigated by using cyclic voltammetry and differential pulse voltammetry at 22 °C at a platinum electrode in tetrahydrofuran, methylene chloride, and methanol, using 0.1 M $(\text{NBu}_4)\text{BF}_4$ as supporting electrolyte. Experiments were carried out both in the pure solutions and in solutions containing ligands that would coordinate axially more strongly than the solvent molecules. The maximum potential range covered was +2 to –2 V in solvent CH_2Cl_2 . The other solvents imposed narrower potential intervals. In all solvents a single reversible, or quasi-reversible, oxidation to the Rh(2.5+) radical cation was observed. In addition, two irreversible reductions were observed at negative potentials. The more facile process could be attributed to the reduction of the proton associated with the acetic acid molecules displaced by solvent from the parent complex. This was confirmed by the addition of a small amount of acetic acid to the electrochemical solution, which resulted in a growth of this irreversible peak relative to the other waves present in the voltammogram. A further highly irreversible reduction was observed at more negative potentials. This reduction was not investigated in detail, and we shall confine this discussion to the oxidations. The oxidation potential is dependent on the medium and can show dramatic shifts in the presence of various axially binding ligands. The electrode potentials observed and the peak-to-peak separations ($\Delta E_p = E_{p,a} - E_{p,c}$) are summarized in Table VI.

Electrooxidation of 1 in all three solvents produced a single oxidation peak on the forward scan and a coupled reduction peak on the backward sweep. Potential separations between the anodic peak, $E_{p,a}$, and the cathodic peak potential, $E_{p,c}$, were in the range 60–70 mV at a scan rate of 100 mV s^{-1} and increased with sweep rate above 500 mV s^{-1} . The ratio of cathodic to anodic peak current, $i_{p,c}/i_{p,a}$, was close to unity at all scan rates consistent with

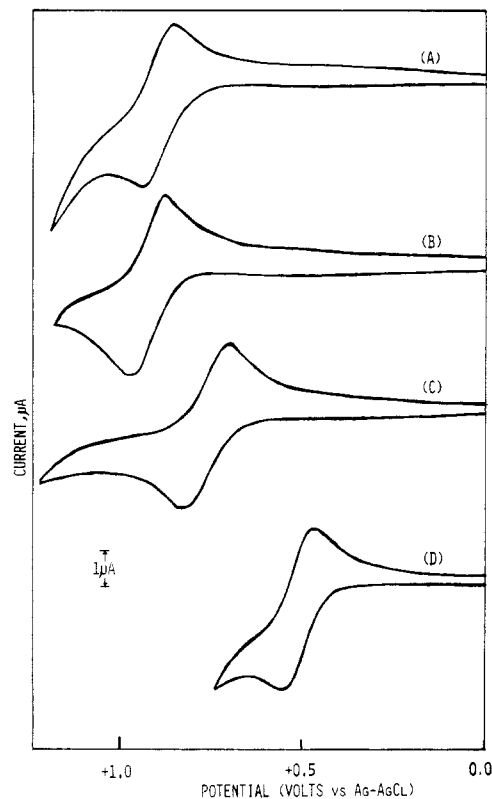


Figure 3. Cyclic voltammograms of 1 in (A) THF, 0.1 M $(\text{NBu}_4)\text{BF}_4$, with the following ligands added at approximate concentrations of 10^{-3} M: (B) *p*-dithiane, (C) pyridine, (D) dimethylphenylphosphine.

the absence of coupled chemical reactions.^{29,30} In addition, plots of $i_p/v^{1/2}$ were constant over sweep rates of 25–500 mV s^{-1} , indicating diffusion control.

The experiments were repeated in the presence of the potential ligands *p*-dithiane, pyridine, and PMe_2Ph , and shifts in oxidation potential were observed as summarized in Table VI. Figure 3 shows the cyclic voltammograms obtained for 1 in THF solution in the presence of each ligand. To confirm that we were observing the oxidation wave due to the appropriate bisadduct, genuine samples of the adduct were in several cases added to the electrochemical solution. The only change observed upon this addition was a growth in the wave height.

Previous studies have attempted to correlate the oxidation potential of $\text{Rh}_2(\text{O}_2\text{CR})_4$ ⁷ and $\text{Rh}_2(\text{ONHCCF}_3)_4$ ¹³ with the donor number, or the solvent donicity, that can be taken as a measure of the interaction of the axial ligands with the Rh^{II} ions in these complexes. However, this comparison is valid only when the starting complex is without any axial ligands.^{31,32} Although this criterion is not met in our study, since the initial complex has axially bound acetic acid molecules, some qualitative comparisons may still be made.

Returning to Figure 3, we see that the oxidation process becomes more favorable as the interaction of the axial group becomes stronger; i.e., PMe_2Ph is a better donor than pyridine, which in turn is a better donor than THF. This shift of potential, to more cathodic values, with increased donor ability is an indication that the HOMO levels are destabilized with increasing ligand binding

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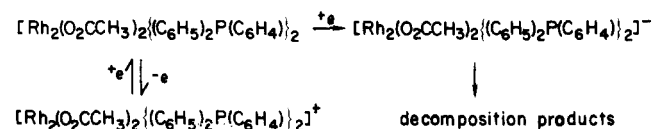
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ability. Since $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2$ is electron-rich and polarizable, it will form stronger axial bonds with ligands having a π -acceptor ability. The σ interactions with pyridine or PMe_2Ph , for example, are thus augmented by the synergistic π -acceptor abilities of these ligands. It is likely that this will destabilize both the unoccupied σ^* levels and also the π^* levels,³³ but it may be expected that the latter will be affected to a smaller extent than the former. Thus, there is a more cathodic oxidation potential as the donor ability of the axial ligands increase, in accord with the experimentally observed trend.

On the basis of data available the following description is proposed for oxidation-reduction of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2$:



(33) This assumes that the molecular orbital scheme calculated for $\text{Rh}_2(\text{O}_2\text{CR})_4$ complexes is equally applicable to the ortho-metalated complex.

Finally, although the oxidation of the PMe_2Ph adduct is facile, occurring at potentials between +0.51 and +0.25 V vs. $\text{Ag}-\text{AgCl}$, no second oxidation wave was observed. This is perhaps surprising in view of Bear and Kadish's recent results,¹⁵ which indicated that the complexes $\text{Rh}_2(\text{O}_2\text{CCH}_3)_n(\text{HNOCCH}_3)_{4-n}$ ($n = 0, 1$) underwent an initial oxidation at potentials comparable to those exhibited by our phosphine adduct and then a further reversible oxidation to the $\text{Rh}(\text{III})$ dicationic dimer at a potential about 1.3V more positive.

Clearly these ortho-metalated dimers are worthy of further study, and our investigations into their physical and chemical properties are continuing.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Registry No. 1, 91837-70-6; 2, 92669-58-4; $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2$, 92669-59-5; $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$, 30553-94-7.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters and complete lists of bond distances and bond angles (45 pages). Ordering information is given on any current masthead page.

Model Intermediates for Rhodacarborane Catalysis: Isolation of a Disubstituted *closo*-Bis(triphenylphosphine)hydridorhodacarborane¹

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Reaction of a carbon-disubstituted [*nido*-7-(R)-9-(R')-7,9- $\text{C}_2\text{B}_9\text{H}_{10}$]⁻ ($\text{R} = \text{CH}_3$; $\text{R}' = \text{C}_6\text{H}_5$) (V) ion with $[(\text{PPh}_3)_3\text{RhCl}]$ in ethanol at the reflux temperature for 24 h yielded [*closo*-2,2-(PPh_3)₂-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-Rh $\text{C}_2\text{B}_9\text{H}_9$] (VI) rather than the corresponding *exo-nido* tautomer expected. In addition to spectroscopic characterization (IR, NMR), the molecular structure of VI was determined crystallographically for $[\text{C}_{45}\text{H}_{49}\text{B}_9\text{P}_2\text{Rh}\cdot\text{C}_4\text{H}_8\text{O}\cdot\text{C}_2\text{H}_5\text{OH}]$; $M_r = 970.215$; monoclinic; space group $P2_1/n$; $a = 24.694$ (6) Å, $b = 18.714$ (6) Å, $c = 12.117$ (2) Å, $\beta = 112.33$ (2)°, $V = 5180$ (2) Å³, and $Z = 4$. The structure was refined to $R = 0.067$ and $R_w = 0.081$ using 3421 reflections (of 6396 reflections measured) with $2\theta < 43.0^\circ$ (Mo K α radiation).

Introduction

Mechanisms have recently been proposed² describing how *closo*-bis(triphenylphosphine)hydridorhodacarboranes^{3,4} and *exo-nido*-bis(triphenylphosphine)rhodacarboranes^{5,6} act as homogeneous catalyst

(1) Dedicated to the memory of our friend and colleague, Earl L. Muettterties.

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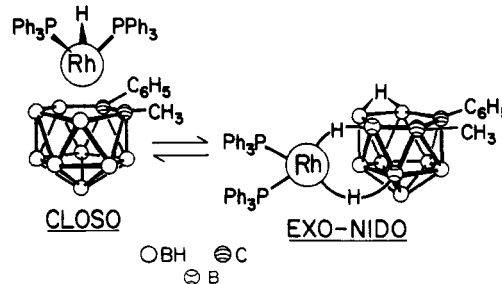
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Scheme I. Proposed Mechanistic Scheme for *Closo*-*Exo*-*Nido* Tautomerism^a



^a In this particular example, the equilibrium lies far to the right.

precursors for the hydrogenation and isomerization of alkenes. Although the several *closo*- and *exo-nido* isomers are very efficient catalysts, major emphasis for the kinetic and mechanistic studies was placed on the more stable