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Polynuclear Rhodium(II) Compounds with Phosphino–Phenoxide Ligands

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The syntheses, spectral properties, and molecular structures of compounds isolated from the reaction of $Rh_2(O_2CCF_3)_4(acetone)_2$ with the ether phosphine tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) are described. Two products are formed, the relative yields of which are determined by reaction conditions and stoichiometry. The tetranuclear compound $[\{Rh_2(O_2CCF_3)_3[\{C_6H_2(OMe)_3\}_2P\{C_6H_2(OMe)_2O\}]_2$ (**1**) is favored under mild conditions with 2 equiv of phosphine ligand whereas the dinuclear product $Rh_2(O_2CCF_3)_2\{C_6H_2(OMe)_3\}_2P\{C_6H_2(OMe)_2O\}_2$ (**2**) is obtained from further reaction of **1** with TMPP or by reaction of the trifluoroacetate complex with 4 equiv of TMPP. The excess phosphine in these reactions aids in the demethylation of an ortho-methoxy substituent and, if absent, results in a low yield of substitution products. Compound **1** crystallizes as a CH_2Cl_2 solvate in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 14.718(7) Å, b = 24.040(5) Å, c = 24.260(6) Å, β = 98.78(3)°, V = 8484(5) Å^3, and Z = 4. Final refinement of 937 parameters gave residuals of R = 0.058 and R_w = 0.090 with a quality-of-fit = 3.06. An X-ray structure revealed that the molecule exhibits a new binding mode for the TMPP ligand wherein a phenoxide bridge spans two dirhodium units to give a "dimer-of-dimers". The compound dissolves in coordinating solvents with disruption of the intermolecular Rh–phenoxide bonds to give two molecules of the dinuclear species $Rh_2(O_2CCF_3)_3$(TMPP-*O*)(S) (S = solvent). The tetranuclear structure of **1** is in equilibrium with the dimer form in noncoordinating solvents such as $CHCl_3$, as evidenced by two independent sets of phosphine resonances in the ^1H NMR and ^{31}P NMR spectra. Compound **2** crystallizes as a CH_2Cl_2 solvate in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 14.146(4) Å, b = 19.56(1) Å, c = 23.822(6) Å, β = 101.90(2)°, V = 6449(4) Å^3, and Z = 4. Residuals of R = 0.066 and R_w = 0.099 were obtained with 805 parameters and a quality-of-fit = 2.94. In **2**, each Rh center is bonded to a face-capping TMPP (η^3-P,O,O) and to *cis*-trifluoroacetate ligands in the usual bridging mode. The solid-state structure of **2** is preserved in solution, as judged by NMR spectroscopy, which reveals one type of TMPP ligand with magnetically inequivalent arene groups. The results of these studies are in contrast to previous findings for the the corresponding reactions of $Rh_2(O_2CCH_3)_4$ with TMPP that produce a dinuclear complex with the ligand arrangement found in **1** but no tetranuclear or bis-substituted products. Details of the syntheses, full characterization of compounds **1** and **2**, and a comparison of this work to related chemistry are described.

Introduction

It has been known for quite some time that phosphine ligands with ortho-methoxy phenyl substituents undergo dealkylation reactions to give phosphino–phenoxide ligands.[1] Such chemistry may be viewed as undesirable, if one is attempting to avoid noninnocent ligands, or as an opportunity, if one opts to take advantage of the driving force for ligand-based reactions to access interesting new compounds. In the context of this ortho-methoxy metalation chemistry, it is important to note that ortho-metalation reactions of phosphines with metal–metal-bonded systems have been a topic of interest for years. In the first documented case of ortho-metalation at a dinuclear unit, Cotton and co-workers reported a novel reaction of PPh_3 with dirhodium tetraacetate wherein the ligand exhibited an η^2,μ binding mode.[2] Extensive follow-up studies by Lahuerta *et al.* established numerous ortho-metalation reactions of various derivatives of PPh_3 such as (o-$XC_6H_5)P(C_6H_5)_2$ (X = Cl, Br) with $Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2CCF_3)_4$ both in solution and in the solid state.[3] A number of products were structurally characterized and found to contain an η^3,μ arrangement of the phosphine. Recently, the same group compared reactions of PPh_3 with $Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2CCF_3)_4$ and observed that metalation of the phosphine was considerably faster in $Rh_2(O_2CCF_3)_4$ than in $Rh_2(O_2CCH_3)_4$, giving rise to doubly metalated compounds under mild conditions. This is explained by the fact that the weaker base, $CF_3CO_2^-$, is more easily displaced by the incoming ligand. In analogous work, Morrison and Tocher used mixed alkyl–arylphosphines to demonstrate that orthometalation chemistry also occurs with these systems.[4]

We have been exploring the coordination and organometallic chemistry of the phosphine ligand tris(2,4,6-trimethoxyphenyl)-phosphine (TMPP) whose main characteristics are high basicity (p$K_a \approx 11$) and steric bulk (cone angle = 184°).[5,6] Owing to the presence of both oxygen and phosphorus donor atoms, this ligand displays a wide variety of geometries and hapticities, the particular arrangement assumed being influenced by the steric and electronic requirements of the metal center(s). Schematic diagrams depicting the binding modes for transition metal complexes of TMPP and its anionic phenoxide derivative are shown in Figure 1. The present study is an investigation of the substitution

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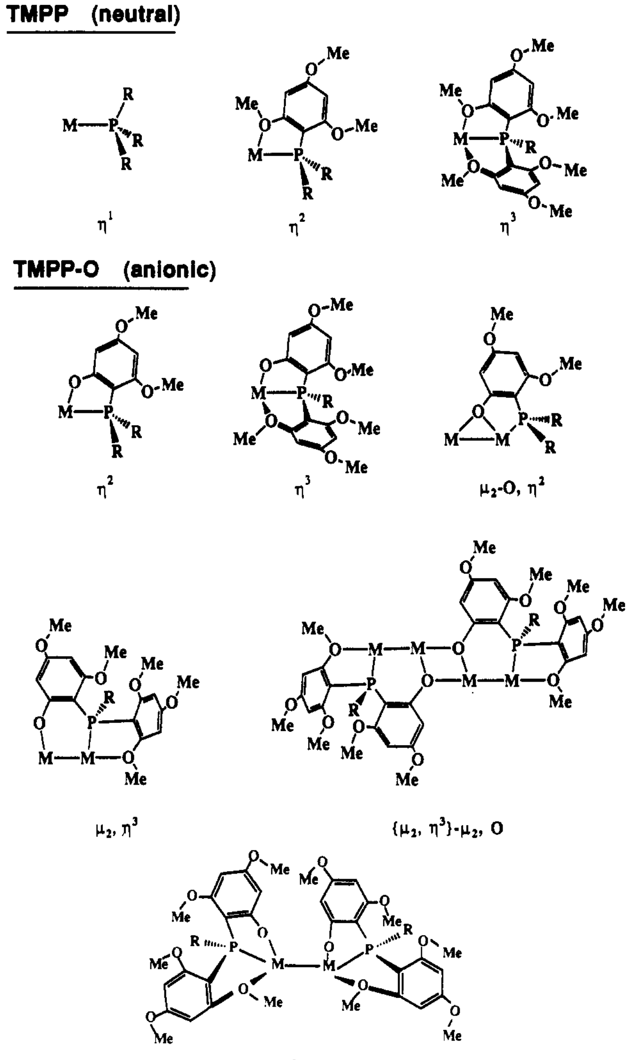

Figure 1. Schematics depicting the crystallographically determined binding modes for (2,4,6-trimethoxyphenyl)phosphine and its phenoxide derivative.

Table 1. Crystal Data for $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2{\cdot}1.2CH_2Cl_2$ (**1**) and $Rh_2(O_2CCF_3)_2(TMPP\text{-}o)_2{\cdot}CH_2Cl_2$ (**2**)

formula	$Rh_2P_2C_{65.2}O_{30}F_{18}H_{62.4}Cl_{2.4}$	$Rh_2P_2F_6C_{57}O_{22}H_{62}Cl_2$
fw	2226.62	1551.76
space group	$P2_1/n$	$P2_1/n$
a, Å	14.718(7)	14.146(4)
b, Å	24.040(5)	19.56(1)
c, Å	24.260(6)	23.822(6)
α, deg	90.0	90.0
β, deg	98.78(3)	101.90(2)
γ, deg	90.0	90.0
V, Å^3	8484(5)	6449(4)
Z	4	4
d_{calc}, g/cm^3	1.743	1.598
μ(Mo Kα), cm^{-1}	9.79	7.24
radiation (monochromated in incident beam) (λ_α, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
temp, °C	−95	−100
transm factors: max, min	1.00, 0.79	1.00, 0.82
R^a	0.058	0.066
$R_w{}^b$	0.090	0.099

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

chemistry of tetrakis(trifluoroacetato)dirhodium(II) with TMPP, work that builds on earlier findings that the corresponding acetate chemistry yields the unusual compound $[Rh_2(\mu\text{-}O_2CCH_3)_3(TMPP\text{-}O)]$ where TMPP-O = $\{C_6H_2(OMe)_3\}_2P\{C_6H_2(OMe)_2O^-\}$ with the dirhodium unit spanned by three acetate groups and one combination bridging/chelating TMPP-O ligand.[5c,f] This observation aroused our curiosity regarding the potential use of TMPP as a ligand for other polynuclear frameworks, since, in spite of its size, the ligand appears to be quite compatible with metal–metal-bonded structures. We therefore turned our attention to the chemistry of TMPP with dirhodium(II) tetrakis(trifluoroacetate), as this compound is considerably more soluble and reactive than the acetate derivative. Herein, we report the syntheses, spectroscopic studies, and X-ray structures of two new compounds obtained from the reaction of $Rh_2(O_2CCF_3)_4$ with TMPP. One product contains an η^3-TMPP ligand acting jointly as an intra- and intermolecular bridging ligand, and a second product possesses two η^3-capping TMPP groups, one on each Rh center. These results suggest that the demethylated TMPP ligand, *viz.*, the phenoxide anion $(Ph)'_2P(C_6H_2(OMe)_2O)^-$ = TMPP-O, is an excellent ligand for stabilizing metal–metal-bonded compounds and may even be useful in constructing oligomeric or polymeric frameworks.

Experimental Section

General Procedures. The starting materials $Rh_2(O_2CCF_3)_4(acetone)_2$[7] and TMPP[8] were prepared according to literature methods. Solvents were dried over appropriate drying agents and freshly distilled under nitrogen prior to use. All reactions were carried out under an argon atmosphere by using standard Schlenk-line techniques.

A. Preparation of $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2$ (1). A suspension of $Rh_2(O_2CCF_3)_4(acetone)_2$ (0.100 g, 0.152 mmol) and TMPP (0.162 g, 0.304 mmol) in THF (15 mL) was stirred at ambient temperature for 20 min to give a clear green solution. The completion of the reaction was verified by thin-layer chromatography using hexanes/acetone (2:3 v/v) as eluent. The solvent was reduced to *ca.* 2 mL under vacuum, and the resulting solution was chromatographed on a silica-coated glass plate using the same eluent as was used for TLC. A green band (R_f = 0.85) was removed from the plate and extracted with THF to give 0.15 g (95%) of **1**. IR (CsI plates, Nujol mull, cm^{-1}): 1658 s, 1581 s, 1406 m, 1340 m, 1201 s, 1159 s, 1116 m, 1089 m, 1030 w, 945 w, 854 w, 819 w, 779 w. UV–visible [CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 656 (2.93 × 10^2).

Preparation of $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2$ (2). In a typical experiment, a suspension of $Rh_2(O_2CCF_3)_4(acetone)_2$ (0.100 g, 0.152 mmol) and TMPP (0.3236 g, 0.607 mmol) in THF (15 mL) was refluxed for ~6 h, during which time the solution turned dark green. The solution was concentrated to *ca.* 3 mL and chromatographed on silica-coated glass plates using a 1:1 (v/v) solution of acetone:hexanes as eluent. A green band corresponding to **1** and an olive-green band (R_f = 0.65) were collected and extracted with THF; yield of **2** 0.95 g (43%). Compound **2** may also be prepared in ~60% yield by the direct reaction of **1** with 2 equiv of TMPP in refluxing THF. Anal. Calcd for $C_{56}H_{60}F_6O_{22}P_2Rh_2$: C, 45.81; H, 4.09. Found: C, 45.14; H, 5.28. IR (CsI plates, Nujol mull; cm^{-1}): 1668 m, 1597 s, 1209 m, 1151 m, 1120 w, 1084 w, 1037 w, 949 w, 862

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Table 2. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2\cdot 1.2CH_2Cl_2$

atom	*x*	*y*	*z*	*B*(eq)[a]	atom	*x*	*y*	*z*	*B*(eq)[a]
Rh1	0.26436(8)	0.31407(5)	0.36506(4)	1.92(5)	C9	0.050(1)	0.4434(7)	0.0958(7)	2.4(8)
Rh2	0.23435(8)	0.34046(5)	0.26633(4)	1.78(5)	C10	0.049(1)	0.5060(7)	0.0854(7)	4(1)
Rh3	0.06768(7)	0.34501(5)	0.16309(4)	1.85(5)	C11	0.041(1)	0.2329(6)	0.1306(7)	2.1(8)
Rh4	0.03864(8)	0.32931(5)	0.06192(5)	2.08(6)	C12	0.024(1)	0.1715(7)	0.1433(7)	3.2(9)
P1	0.1211(3)	0.3065(2)	0.3755(1)	2.0(2)	C13	0.058(1)	0.3794(6)	0.2924(6)	1.7(7)
P2	0.1827(3)	0.3253(2)	0.0510(2)	2.0(2)	C14	0.010(1)	0.4222(6)	0.2673(6)	2.3(7)
F1	0.5614(9)	0.3783(9)	0.3514(5)	13(1)	C15	−0.034(1)	0.4588(6)	0.2988(6)	2.2(7)
F2	0.564(1)	0.3072(8)	0.3139(8)	14.1(6)	C16	−0.022(1)	0.4529(6)	0.3561(7)	2.6(8)
F3	0.5379(8)	0.3739(9)	0.2669(5)	14(1)	C17	0.028(1)	0.4085(6)	0.3817(6)	1.8(7)
F4	0.3716(8)	0.1603(5)	0.2739(5)	7.2(7)	C18	0.065(1)	0.3688(6)	0.3500(6)	2.0(7)
F5	0.2513(7)	0.1539(4)	0.2183(4)	5.1(5)	C19	−0.099(1)	0.5106(8)	0.2189(8)	6.0(5)
F6	0.255(1)	0.1299(4)	0.3017(5)	7.4(7)	C20	0.028(2)	0.444(1)	0.473(1)	8.1(6)
F7	0.3350(9)	0.5114(4)	0.3636(5)	7.8(7)	C21	0.210(1)	0.2994(6)	0.4862(6)	1.9(7)
F8	0.229(1)	0.4990(4)	0.4113(4)	7.4(7)	C22	0.217(1)	0.2969(6)	0.5434(6)	2.7(8)
F9	0.2004(8)	0.5220(4)	0.3258(4)	6.7(6)	C23	0.137(1)	0.2955(6)	0.5667(6)	2.7(3)
F10	−0.2455(7)	0.3539(6)	0.1632(5)	8.2(7)	C24	0.055(1)	0.2949(6)	0.5335(6)	2.6(8)
F11	−0.2756(7)	0.3411(7)	0.0794(6)	9.7(8)	C25	0.051(1)	0.2979(6)	0.4763(6)	2.5(8)
F12	−0.225(1)	0.4161(6)	0.1088(5)	8.5(3)	C26	0.128(1)	0.3011(6)	0.4510(5)	2.1(7)
F13	0.0934(8)	0.5320(4)	0.1290(4)	5.4(5)	C27	−0.109(1)	0.3090(7)	0.4613(7)	3.7(4)
F14	−0.0375(7)	0.5231(4)	0.0804(4)	5.4(5)	C28	0.217(1)	0.2946(8)	0.6568(8)	5.6(5)
F15	0.0800(6)	0.5213(4)	0.0403(4)	4.6(5)	C29	0.371(1)	0.3102(8)	0.4916(8)	5.6(5)
F16	0.0515(7)	0.1551(3)	0.1932(4)	4.4(5)	C30	0.056(1)	0.2449(6)	0.3487(6)	2.3(7)
F17	−0.0662(7)	0.1644(4)	0.1356(5)	6.2(6)	C31	0.091(1)	0.1932(6)	0.3689(5)	1.6(3)
F18	0.0557(9)	0.1384(4)	0.1081(4)	6.7(6)	C32	0.048(1)	0.1443(6)	0.3512(6)	2.8(8)
O1	0.4055(6)	0.3274(4)	0.3607(4)	3.1(5)	C33	−0.033(1)	0.1480(6)	0.3160(6)	2.7(8)
O2	0.3713(6)	0.3434(4)	0.2676(4)	2.4(4)	C34	−0.073(1)	0.1966(6)	0.2975(6)	2.3(7)
O3	0.2798(6)	0.2352(4)	0.3372(4)	2.1(5)	C35	−0.027(1)	0.2453(6)	0.3147(6)	2.2(3)
O4	0.2376(6)	0.2581(4)	0.2466(4)	2.0(4)	C36	−0.147(1)	0.0920(7)	0.2599(8)	4.8(4)
O5	0.2401(6)	0.4213(4)	0.2951(4)	2.2(5)	C37	−0.151(1)	0.2998(7)	0.2768(7)	4.6(4)
O6	0.2616(7)	0.3957(4)	0.3873(4)	2.4(5)	C38	0.195(1)	0.1434(7)	0.4349(7)	3.8(4)
O7	−0.0701(6)	0.3456(4)	0.1606(4)	2.4(4)	C39	0.240(1)	0.3896(5)	0.1418(6)	1.8(7)
O8	−0.1032(6)	0.3395(4)	0.0667(4)	3.2(5)	C40	0.282(1)	0.4346(6)	0.1715(5)	1.9(3)
O9	0.0607(6)	0.4280(4)	0.1453(4)	2.3(5)	C41	0.316(1)	0.4765(6)	0.1416(6)	2.4(3)
O10	0.0427(6)	0.4147(4)	0.0517(4)	2.4(5)	C42	0.304(1)	0.4768(6)	0.0840(6)	2.8(7)
O11	0.0669(6)	0.2610(4)	0.1741(4)	2.2(4)	C43	0.263(1)	0.4321(6)	0.0556(6)	2.0(7)
O12	0.0241(7)	0.2470(4)	0.0810(4)	2.6(5)	C44	0.2371(9)	0.3866(5)	0.0837(5)	1.3(6)
O13	0.0976(6)	0.3441(3)	0.2591(3)	1.7(4)	C45	0.377(1)	0.5235(7)	0.2277(7)	4.2(4)
O14	−0.0834(7)	0.5046(4)	0.2784(4)	3.8(5)	C46	0.261(1)	0.4781(8)	−0.0320(8)	5.2(4)
O15	0.0425(8)	0.4031(4)	0.4374(4)	4.0(6)	C47	0.094(1)	0.3235(5)	−0.0594(6)	2.1(3)
O16	−0.0287(6)	0.2964(4)	0.4395(4)	2.4(5)	C48	0.086(1)	0.3264(6)	−0.1172(6)	2.9(7)
O17	0.1355(7)	0.2934(5)	0.6232(4)	3.7(5)	C49	0.166(1)	0.3281(6)	−0.1400(7)	3.2(3)
O18	0.2852(6)	0.2984(4)	0.4592(4)	2.5(5)	C50	0.249(1)	0.3294(6)	−0.1081(6)	2.7(3)
O19	−0.0707(7)	0.0951(4)	0.3007(4)	3.8(5)	C51	0.253(1)	0.3281(6)	−0.0506(6)	2.5(7)
O20	−0.0641(6)	0.2955(4)	0.3035(4)	3.1(5)	C52	0.177(1)	0.3272(6)	−0.0245(6)	1.9(7)
O21	0.1677(7)	0.1942(4)	0.4075(4)	2.8(5)	C53	0.414(1)	0.3403(7)	−0.0364(7)	4.1(4)
O22	0.2046(6)	0.3490(4)	0.1702(4)	1.9(4)	C54	0.083(1)	0.3337(8)	−0.2322(9)	6.2(5)
O23	0.3579(7)	0.5231(4)	0.1668(4)	3.7(5)	C55	−0.068(1)	0.3188(7)	−0.0665(7)	4.4(4)
O24	0.2517(7)	0.4304(4)	−0.0007(4)	3.6(5)	C56	0.245(1)	0.2622(6)	0.0707(5)	1.9(7)
O25	0.3330(7)	0.3280(4)	−0.0144(4)	2.9(5)	C57	0.211(1)	0.2121(6)	0.0458(6)	2.5(8)
O26	0.1664(7)	0.3305(6)	−0.1968(4)	5.2(6)	C58	0.255(1)	0.1621(6)	0.0578(6)	2.7(8)
O27	0.0179(6)	0.3209(4)	−0.0331(4)	2.7(5)	C59	0.334(1)	0.1599(6)	0.0940(6)	2.2(7)
O28	0.1352(6)	0.2180(4)	0.0081(4)	2.2(4)	C60	0.372(1)	0.2079(6)	0.1181(6)	2.1(7)
O29	0.3720(7)	0.1093(4)	0.1011(4)	3.4(5)	C61	0.329(1)	0.2593(6)	0.1059(6)	2.6(8)
O30	0.3667(7)	0.3082(4)	0.1250(4)	3.2(5)	C62	0.106(1)	0.1736(7)	−0.0259(7)	3.8(4)
C1	0.421(1)	0.3397(6)	0.3129(7)	2.5(3)	C63	0.452(1)	0.1058(7)	0.1419(7)	3.8(4)
C2	0.521(1)	0.3553(8)	0.3096(8)	4.4(4)	C64	0.454(1)	0.3086(7)	0.1552(7)	3.5(3)
C3	0.264(1)	0.2250(6)	0.2855(7)	2.0(7)	Cl1	0.5332(8)	0.4409(5)	0.0620(5)	11.8(3)
C4	0.284(1)	0.1671(7)	0.2697(7)	2.9(9)	Cl2	0.5984(8)	0.4541(5)	0.1799(5)	12.4(3)
C5	0.251(1)	0.4292(6)	0.3471(7)	2.4(8)	C65	0.550(2)	0.476(1)	0.125(1)	6.9(7)
C6	0.253(1)	0.4895(8)	0.3644(8)	4.8(4)	Cl3	0.775(1)	0.5556(7)	0.3895(7)	9.9(4)
C7	−0.121(1)	0.3464(6)	0.1147(7)	2.4(3)	Cl4	0.758(1)	0.448(1)	0.426(1)	13.7(6)
C8	−0.217(1)	0.3619(6)	0.1179(7)	2.9(8)	C66	0.731(4)	0.500(3)	0.367(2)	10(2)

[a] The equivalent isotropic temperature factor (Fischer; Tillmanns. *Acta Crystallogr.* **1988**, *C44*, 775–776) is defined as follows:

$$B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\vec{\mathbf{a}}i\cdot\vec{\mathbf{a}}_j.$$

w, 806 w, 781 w. UV–visible [CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 711 (3.69×10^2).

Physical Measurements. ^1H NMR and $^{31}P\{1H\}$ NMR spectra were obtained on a Varian VXR 300-MHz spectrometer with an internal deuterium lock and were referenced to the deuterated impurity in the solvent for ^1H and to external 85% H_3PO_4 for $^{31}P\{^1H\}$. Infrared spectra were recorded on a Perkin-Elmer 599 or a Nicolet 740 FT-IR spectrophotometer. Fast atom bombardment (FAB) mass spectrometry studies were performed on a JEOL HX 110 double-focusing mass spectrometer housed in the National Institutes of Health/ Michigan State University Mass Spectrometry Facility; samples were dissolved in a 3-nitrobenzyl alcohol matrix.

X-ray Crystallographic Procedures. The solid-state structures of $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2$ (**1**) and $[Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2]$ (**2**) were determined by application of general procedures fully described elsewhere.[9] Geometric and intensity data were collected on a Rigaku

Table 3. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2{\cdot}CH_2Cl_2$

atom	*x*	*y*	*z*	*B*(eq)[a]	atom	*x*	*y*	*z*	*B*(eq)[a]
Rh1	0.37376(7)	0.27514(5)	0.58330(4)	2.28(4)	C15	0.438(1)	0.2791(8)	0.8016(6)	4.1(7)
Rh2	0.27738(7)	0.19280(5)	0.50937(4)	2.29(4)	C16	0.340(1)	0.3818(8)	0.7934(6)	4.2(8)
P1	0.2649(2)	0.3315(2)	0.6189(1)	2.4(1)	C17	0.282(1)	0.3673(7)	0.7387(6)	3.5(7)
P2	0.2690(2)	0.2402(2)	0.4246(1)	2.6(1)	C18	0.327(1)	0.3486(7)	0.6936(5)	3.0(6)
F1	0.371(1)	0.1061(6)	0.7237(5)	8.6(7)	C19	0.572(1)	0.336(1)	0.6657(6)	4.6(8)
F2	0.2646(9)	0.0510(7)	0.6700(6)	10.9(8)	C20	0.459(2)	0.405(1)	0.901(1)	8(1)
F3	0.404(1)	0.0410(7)	0.6573(7)	13(1)	C21	0.129(1)	0.388(1)	0.7682(7)	6(1)
F4	0.6436(7)	0.1718(7)	0.5135(6)	9.2(8)	C22	0.124(1)	0.2566(7)	0.6582(6)	3.1(6)
F5	0.5655(8)	0.0765(6)	0.5043(7)	11.1(8)	C23	0.027(1)	0.2416(8)	0.6616(6)	3.9(7)
F6	0.623(1)	0.1192(8)	0.5881(7)	12(1)	C24	−0.048(1)	0.2738(8)	0.6247(6)	3.8(7)
O1	0.2603(7)	0.1338(5)	0.5832(4)	3.4(4)	C25	−0.030(1)	0.3182(8)	0.5828(6)	3.7(7)
O2	0.3867(6)	0.1919(5)	0.6384(4)	2.9(4)	C26	0.065(1)	0.3321(7)	0.5803(6)	3.3(6)
O3	0.4082(6)	0.1435(5)	0.5160(4)	3.6(4)	C27	0.1419(9)	0.3038(7)	0.6179(5)	2.6(5)
O4	0.5016(6)	0.2345(5)	0.5569(4)	3.1(4)	C28	0.189(1)	0.1965(9)	0.7453(6)	4.6(8)
O5	0.3814(6)	0.3583(4)	0.5352(3)	2.6(4)	C29	−0.219(1)	0.285(1)	0.5922(8)	7(1)
O6	0.3218(7)	0.5982(5)	0.5127(4)	3.7(4)	C30	0.017(1)	0.4164(8)	0.5090(7)	5.3(8)
O7	0.1643(7)	0.4659(5)	0.6334(4)	4.0(5)	C31	0.0957(9)	0.2502(7)	0.4532(5)	2.6(5)
O8	0.4703(6)	0.3290(5)	0.6610(4)	3.4(4)	C32	−0.006(1)	0.2596(7)	0.4441(5)	2.7(6)
O9	0.5014(8)	0.3934(6)	0.8547(4)	5.7(6)	C33	−0.056(1)	0.2850(7)	0.3925(6)	3.4(6)
O10	0.1828(7)	0.3682(5)	0.7271(4)	3.6(4)	C34	−0.008(1)	0.3012(7)	0.3475(6)	3.3(6)
O11	0.2022(7)	0.2263(5)	0.6921(4)	3.5(4)	C35	0.090(1)	0.2921(7)	0.3567(6)	3.0(6)
O12	−0.1385(7)	0.2555(6)	0.6306(4)	4.9(5)	C36	0.1432(9)	0.2675(7)	0.4089(5)	2.5(5)
O13	0.0861(6)	0.3700(5)	0.5378(4)	3.4(4)	C37	−0.206(1)	0.2728(8)	0.4194(8)	4.7(8)
O14	0.1424(6)	0.2243(4)	0.5036(3)	2.5(4)	C38	0.093(1)	0.3258(9)	0.2609(6)	5.0(8)
O15	−0.1509(6)	0.2973(6)	0.3798(4)	4.3(5)	C39	0.239(1)	0.1021(7)	0.3953(6)	3.4(7)
O16	0.1431(7)	0.3024(5)	0.3152(4)	3.8(4)	C40	0.227(1)	0.0422(8)	0.3630(7)	5.0(8)
O17	0.2203(7)	0.1010(5)	0.4501(4)	3.7(5)	C41	0.243(1)	0.045(1)	0.3101(9)	6(1)
O18	0.232(1)	−0.0087(8)	0.2700(5)	7.5(7)	C42	0.274(1)	0.106(1)	0.2871(6)	5(1)
O19	0.3132(7)	0.2269(7)	0.3032(4)	5.0(6)	C43	0.286(1)	0.164(1)	0.3197(6)	4.1(7)
O20	0.4637(7)	0.2085(8)	0.4143(5)	5.5(6)	C44	0.2666(9)	0.1635(9)	0.3774(6)	3.6(7)
O21	0.544(1)	0.4141(8)	0.3300(6)	7.7(8)	C45	0.221(2)	0.0370(9)	0.4776(8)	7(1)
O22	0.2495(8)	0.3931(5)	0.4074(4)	4.3(5)	C46	0.193(2)	−0.070(1)	0.287(1)	9(1)
C1	0.326(1)	0.1428(7)	0.6255(6)	3.4(7)	C47	0.337(1)	0.234(1)	0.2472(6)	7(1)
C2	0.345(1)	0.0850(9)	0.6685(8)	5.1(9)	C48	0.445(1)	0.273(1)	0.3993(6)	4.0(7)
C3	0.487(1)	0.177(1)	0.5376(7)	4.2(8)	C49	0.501(1)	0.314(1)	0.3739(7)	6(1)
C4	0.582(1)	0.135(1)	0.536(1)	6(1)	C50	0.478(1)	0.378(1)	0.3597(7)	5.0(9)
C5	0.3348(8)	0.4135(6)	0.5468(5)	2.1(5)	C51	0.394(1)	0.4119(9)	0.3699(7)	5.1(8)
C6	0.356(1)	0.4763(7)	0.5228(5)	2.8(6)	C52	0.331(1)	0.369(1)	0.3947(6)	4.4(8)
C7	0.308(1)	0.5339(7)	0.5344(6)	3.0(6)	C53	0.353(1)	0.3027(9)	0.4067(5)	3.6(7)
C8	0.244(1)	0.5341(7)	0.5721(6)	3.2(6)	C54	0.526(1)	0.168(1)	0.386(1)	8(1)
C9	0.225(1)	0.4732(7)	0.5963(6)	3.1(6)	C55	0.528(2)	0.477(1)	0.3182(9)	9(1)
C10	0.2712(9)	0.4133(6)	0.5849(5)	2.4(5)	C56	0.207(1)	0.454(1)	0.3851(8)	7(1)
C11	0.405(1)	0.6062(7)	0.4876(6)	3.7(7)	Cl1	0.8924(5)	0.1297(4)	0.5361(3)	9.2(2)
C12	0.125(1)	0.5257(9)	0.6518(7)	4.7(8)	Cl2	1.0257(6)	0.0735(4)	0.6320(4)	12.2(2)
C13	0.426(1)	0.3464(7)	0.7067(6)	3.3(7)	C57	1.028(2)	0.114(1)	0.560(1)	8.5(6)
C14	0.485(1)	0.3613(8)	0.7584(6)	3.7(7)					

[a] The equivalent isotropic temperature factor (Fischer; Tillmanns. *Acta Crystallogr.* **1988**, *C44*, 775–776) is defined as follows:

$$B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}\mathrm{U}_{ij}a_i{}^*a_j{}^*\vec{\mathbf{a}}_i{\cdot}\vec{\mathbf{a}}_j.$$

AFC-6S diffractometer with graphite-monochromated Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å) radiation and were corrected for Lorentz and polarization effects. Calculations were performed with the Texsan crystallographic software package of the Molecular Structure Corp.[10] Crystal parameters and basic information pertaining to data collection and structural refinement are summarized in Table 1. Positional parameters and equivalent isotropic displacement parameters for 1 and 2 are listed in Tables 2 and 3, respectively. Complete tables of bond distances and angles and anisotropic thermal parameters are available as supplementary material.

$[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2{\cdot}1.2CH_2Cl_2$. Thin platelets of **1** were grown by slow evaporation of a CH_2Cl_2 solution of **1** layered with hexanes at ambient temperature. A green crystal of dimensions 0.55 × 0.41 × 0.25 mm^3 was selected and mounted on the tip of a glass fiber with silicone grease and placed in a stream of N_2(g) at −95 ± 1 °C. A monoclinic cell was determined from 20 reflections with 2θ values between 26 and 28°. Intensity data were collected over the range 6–47° in 2θ using an ω–2θ scan mode. Three standard reflections were measured after every 150 reflections during intensity data collection with no significant loss in intensity; thus a correction was not applied. After averaging of equivalent reflections, 8322 unique data remained, of which 5934 were observed with $F_o{}^2 > 3\sigma(F_o)^2$. The positions of the Rh atoms were obtained from a solution provided by the direct-methods program in SHELXS-86. The remaining non-hydrogen atoms were located through a sequence of successive difference Fourier maps and least-squares cycles. Two areas of electron density in the lattice were assigned to two CH_2Cl_2 molecules of crystallization at a total occupancy of 1.2. Hydrogen atoms were generated by the programs within the TEXSAN package and were included in the structure factor calculations but not refined. The last cycle of full-matrix refinement involved 937 parameters and 5934 data points with residuals R = 0.058 and R_w = 0.090 and a quality-of-fit of 3.06. The somewhat high residuals are attributed to mosaic spread in the diffraction peaks due to partial loss of interstitial CH_2Cl_2. Unfortunately, higher quality crystals were not obtained even after repeated attempts at screening independent batches. The final difference Fourier map showed a highest peak of 1.38 e/Å^3, which is close to F2 of the CF_3 group. A summary of important crystallographic parameters is presented in Table 1.

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(9) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(10) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

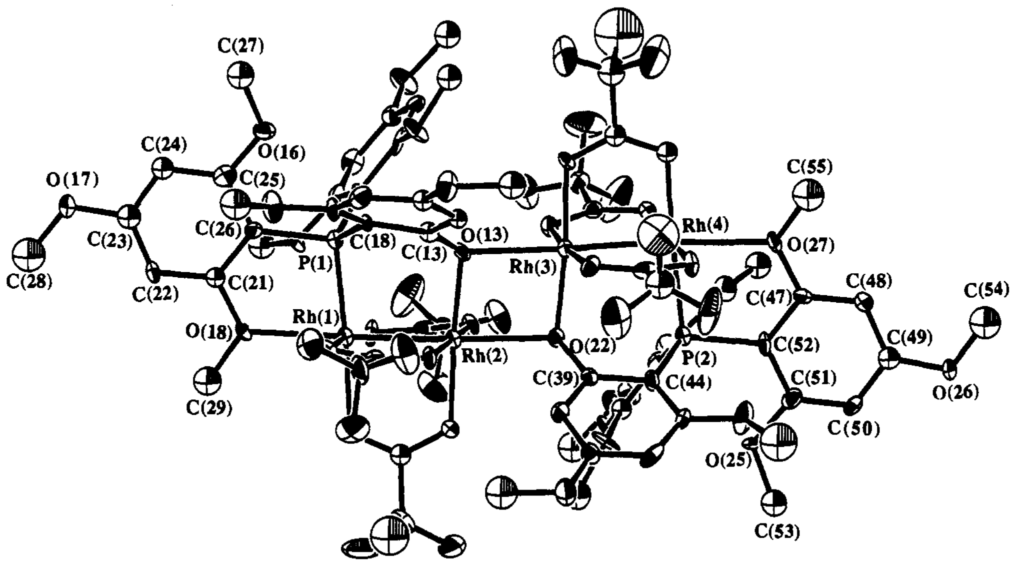

Figure 2. ORTEP plot of $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2$ (1) with thermal ellipsoids represented at the 40% level and a partial labeling scheme for the sake of clarity.

$Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2{\cdot}CH_2Cl_2$ (2). Brown-green crystals of **2** were grown by slow evaporation of CH_2Cl_2 solution of **2** layered with hexanes at room temperature. A crystal of approximate dimensions 0.79 × 0.48 × 0.22 mm^3 was mounted on the tip of a glass fiber with a high-viscosity oil and cooled to -100 ± 1 °C in a stream of $N_2(g)$. A monoclinic cell was determined for 20 reflections with 2θ values between 20 and 24°. Data were collected using an ω–2θ scan motion to a maximum 2θ value of 47°. Periodic monitoring of three standard reflections during data collection revealed no decay in crystal quality. Of the 10253 reflections that were collected, 5886 were in the category $F_o^2 > 3\sigma(F_o)^2$. The positions of the Rh atoms were determined by the direct-methods program in SHELXS-86; all other non-hydrogen atoms were located through successive difference Fourier maps and least-squares cycles and refined anisotropically with the exception of a C and a Cl atom belonging to an interstitial CH_2Cl_2 molecule. Hydrogen atom positions were generated and included in the structure factor calculations but were not refined. The final full-matrix refinement involved 5886 data and 805 parameters with residuals of $R = 0.066$ and $R_w = 0.099$ and quality-of-fit of 2.94. These residuals reflect a rather low data-to-parameter ratio. The final difference Fourier map showed a highest peak of 0.95 e/Å^3. Table 1 lists important crystallographic parameters.

Results

Synthetic Approach. Reaction of $Rh_2(O_2CCF_3)_4(acetone)_2$ with 2 equiv of tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) in THF at ambient temperatures produces the compound $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2$ (1) where TMPP-*O* is a phenoxide derivative of the phosphine ligand. Reaction of **1** with additional quantities of TMPP in refluxing THF yields $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2$ (**2**) along with unreacted starting material. Alternatively, **2** can be prepared by reacting $Rh_2(O_2CCF_3)_4(acetone)_2$ with 4 equiv of TMPP in refluxing THF. Higher molar excesses of TMPP result in shorter reaction times but do not affect the course of the reaction. Free phosphine acts as a nucleophile in these reactions to assist in demethylation of the coordinated TMPP, an established side reaction encountered in the chemistry of this ligand.[5,11] If excess TMPP is deliberately avoided, as in the reaction of $Rh_2(O_2CCF_3)_4(acetone)_2$ with 1 equiv of TMPP, very low yields of **1** are produced, with no evidence for a simple substitution product containing neutral TMPP.

It is interesting to note that the chemistry of $Rh_2(O_2CCF_3)_4(acetone)_2$ with TMPP is quite different from that observed for $Rh_2(O_2CCH_3)_4(MeOH)_2$ under the same conditions of solvent, phosphine stoichiometry, and temperature. In earlier investigations of the acetate complex, we observed that no reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with TMPP occurs in THF even after prolonged reflux times of up to 1 week, although reactions performed in alcohols readily give $[Rh_2(\mu\text{-}O_2CCH_3)_3(TMPP\text{-}O)]$. These reactivity differences, while not entirely surprising given the much weaker donor properties of CF_3COO^- versus CH_3COO^-, reveal that solvent assistance is required for dirhodium acetate substitution chemistry with this ligand. There appears to be no such requirement for the trifluoroacetate chemistry, as reactions proceed under mild conditions in THF or alcohol solvents to give more highly substituted products.

Solid-State and Solution Structural Studies. (a) $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2$ (1). Fast atom bombardment mass spectrometry (FAB) of **1** revealed a parent ion peak at $m/z = 1062$ corresponding to the formula $Rh_2(O_2CCF_3)_3(TMPP\text{-}O)$ where TMPP-*O* = $\{C_6H_2(OMe)\}_2P\{C_6H_2(OMe)_2O\}$. The results of single-crystal X-ray diffraction studies support the FAB data and reveal an additional aspect of the molecular structure, namely that the compound crystallizes as a "dimer-of-dimers".[12] An ORTEP plot of the molecule with a partial atom-labeling scheme depicted in Figure 2 clearly shows that the molecule consists of a dirhodium unit bridged by three trifluoroacetate ligands and one TMPP ligand that forms two separate metallacycle rings within the structure. The ligand arrangement is similar to that encountered in $[Rh_2(O_2CCH_3)_3(TMPP\text{-}O)]$ but with one important difference; namely, the phenoxide oxygen involved in the six-membered ring Rh–Rh–P–C–C–O is further bonded to another unit of $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]$ to give a tetranuclear structure. The two metal atoms, Rh2 and Rh3, and the two oxygen atoms form a parallelogram defined by the bonds Rh2–O22 = 2.316(9) Å, Rh3–O13 = 2.303(8) Å, Rh2–O13 = 1.995(9) Å, and Rh3–O22 = 1.999(9) Å. The significant differences in axial versus equatorial Rh–phenoxide bond distances reflect weak intermolecular association, which is supported by ^{1}H NMR studies that reveal facile cleavage of the tetranuclear unit occurs in coordinating solvents (vide supra). The equatorial Rh–phenoxide bond distances (1.99 Å) are also significantly shorter than the axial ether interactions Rh1–O18 = 2.289(9) and Rh4–O27 = 2.287(9) as expected. The metal–metal separations of 2.452(2) Å for Rh1–Rh2 and 2.455(2) Å for Rh3–Rh4 are slightly longer than the corresponding distance in the tetrakis(trifluoroacetate) complex $Rh_2(O_2CCF_3)_4(EtOH)_2$, for which Rh–Rh = 2.409(2) Å.[3] The substantial distortions associated with angles involving phosphorus are a consequence of the formation of the five- and six-membered metallacycles Rh–P–C–C–O and Rh–

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[11] Dunbar, K. R.; Haefner, S. C. Manuscript in preparation.

[12] For other "dimer-of-dimers", see, for example: (a) Bartley, S. L.; Dunbar, K. R. *Angew. Chem., Int. Ed. Eng.* **1991**, *30*, 1991. (b) Cotton, F. A.; Ren, T.; Eglin, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 3439.

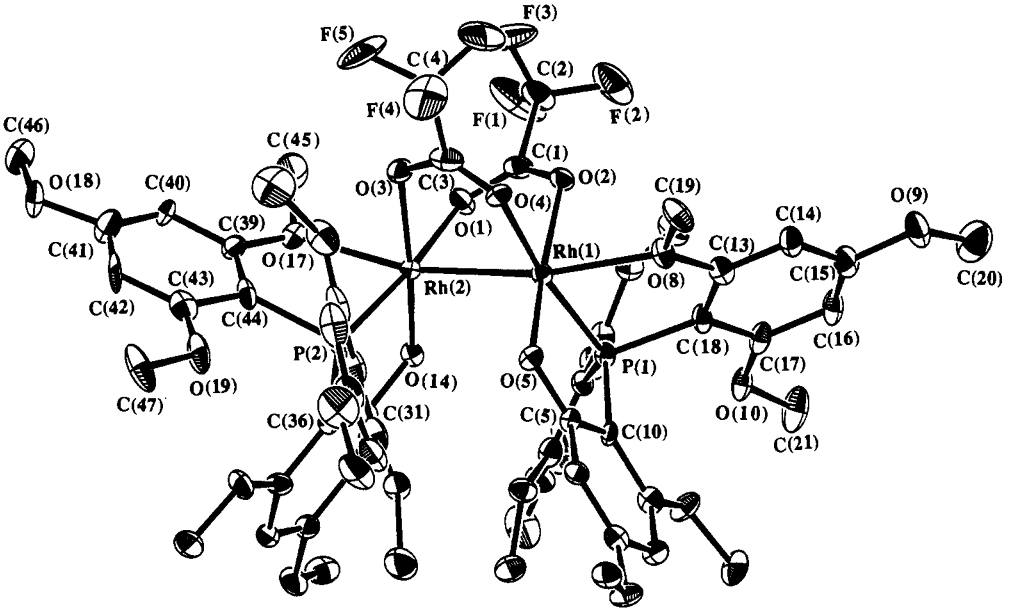

Figure 3. ORTEP diagram of $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2$ (2) with a partial labeling scheme. Thermal ellipsoids are at the 40% level for clarity.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) and Their Estimated Standard Deviations for $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2\cdot 1.25CH_2Cl_2$ (1)

	Bond Distances		
Rh1–Rh2	2.452(2)	Rh3–Rh4	2.455(2)
Rh1–P1	2.170(4)	Rh3–O7	2.019(9)
Rh1–O1	2.121(9)	Rh3–O9	2.041(9)
Rh1–O3	2.037(9)	Rh3–O11	2.307(9)
Rh1–O6	2.038(9)	Rh3–O13	2.303(8)
Rh1–O18	2.289(9)	Rh3–O22	1.999(9)
Rh2–O2	2.013(9)	Rh4–P2	2.179(4)
Rh2–O4	2.038(9)	Rh4–O8	2.123(9)
Rh2–O5	2.062(9)	Rh4–O10	2.07(1)
Rh2–O13	1.995(9)	Rh4–O12	2.05(1)
Rh2–O22	2.316(9)	Rh4–O27	2.287(9)
	Bond Angles		
Rh2–Rh1–P1	95.9(1)	Rh4–Rh3–O7	87.2(3)
Rh2–Rh1–O1	86.8(3)	Rh4–Rh3–O9	86.8(3)
Rh2–Rh1–O3	86.0(3)	Rh4–Rh3–O11	88.6(3)
Rh2–Rh1–O6	90.1(3)	Rh4–Rh3–O13	170.6(2)
Rh2–Rh1–O18	173.8(2)	Rh4–Rh3–O22	96.5(3)
Rh1–Rh2–O2	87.9(3)	Rh3–Rh4–P2	96.0(1)
Rh1–Rh2–O4	88.3(3)	Rh3–Rh4–O8	87.1(3)
Rh1–Rh2–O5	85.5(3)	Rh3–Rh4–O10	87.9(3)
Rh1–Rh2–O13	97.3(2)	Rh3–Rh4–O12	86.0(3)
Rh1–Rh2–O22	170.1(2)	Rh3–Rh4–O27	174.4(3)
Rh1–P1–C18	107.3(5)	Rh3–O13–Rh2	97.1(3)
Rh1–P1–C26	102.5(5)	Rh2–O13–C13	124.0(8)
Rh1–O18–C21	118.7(8)	O18–Rh1–P1	81.6(3)

Rh–P–C–C–O, respectively. Other distances and angles in the molecule are within usual ranges for dirhodium(II) complexes (Table 4).[13]

The ^1H NMR spectrum of **1** in $CDCl_3$ at room temperature is complicated, with a total of 12 resonances being observed in the meta region between δ 5.62 and 6.54 ppm and 16 upfield resonances between δ 3.93 and 3.21 ppm for the methoxy substituents. Within each group, there are two distinct sets of resonances whose unequal intensities clearly indicate the presence of two solution species. Likewise, the ^{31}P NMR spectrum in $CDCl_3$ shows two sets of resonances, an intense doublet centered at δ 15.34 ppm with $J(^{103}Rh\text{–}^{31}P) = 140$ Hz and a weak, broad signal at 12.42 ppm in an approximate 2:1 ratio by integration. The ^1H NMR spectrum of **1** in coordinating solvents exhibits a simplified pattern, with six resonances in the meta region between δ values of 5.6 and 6.8 ppm and eight resonances for the methoxy substituents in the range 5–7 ppm; the pattern and chemical shifts are very similar to those of the spectrum of the fully characterized dinuclear compound $[Rh_2(O_2CCH_3)_3(TMPP\text{-}O)][MeOH]_2$.[5f] Furthermore, these signals correspond closely to the minor set of resonances observed for **1** in $CDCl_3$. We take these NMR results in different solvents as evidence that disruption of the tetranuclear structure is occurring slightly in $CDCl_3$ and completely in the coordinating solvent CD_3OD.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) and Their Estimated Standard Deviations for $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2\cdot CH_2Cl_2$ (2)

	Bond Distances		
Rh1–Rh2	2.562(2)	P1–C18	1.84(1)
Rh1–P1	2.201(4)	P1–C27	1.82(1)
Rh1–O2	2.075(9)	P2–C36	1.82(1)
Rh1–O4	2.182(9)	P2–C44	1.87(1)
Rh1–O5	2.005(8)	P2–C53	1.82(1)
Rh1–O8	2.315(9)	O5–C5	1.32(1)
Rh2–P2	2.203(4)	O8–C13	1.40(2)
Rh2–O1	2.157(9)	O1–C1	1.23(2)
Rh2–O3	2.063(9)	O2–C1	1.29(2)
Rh2–O14	1.984(8)	O3–C3	1.31(2)
Rh2–O17	2.323(9)	O4–C3	1.21(2)
P1–C10	1.80(1)		
	Bond Angles		
Rh2–Rh1–P1	105.3(1)	Rh1–Rh2–O14	102.7(2)
Rh2–Rh1–O2	84.6(3)	Rh1–Rh2–O17	166.5(2)
Rh2–Rh1–O4	85.9(2)	P1–Rh1–O5	78.9(2)
Rh2–Rh1–O5	101.6(2)	P1–Rh1–O8	86.5(2)
Rh2–Rh1–O8	168.0(2)	P2–Rh2–O14	86.4(2)
Rh1–Rh2–P2	106.6(1)	P2–Rh2–O17	79.7(3)
Rh1–Rh2–O14	84.8(2)	Rh1–O8–C13	115.7(9)
Rh1–Rh2–O17	166.5(2)	Rh2–O17–C45	116.7(8)

(b) $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2$ (2). The FAB spectrum of **2** contains a molecular ion peak corresponding to $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2$ (m/z = 1467), which was confirmed by a single-crystal X-ray study. An ORTEP drawing of **2** is shown in Figure 3, and important bond distances and angles are listed in Table 5. In this molecule, each TMPP-*O* ligand is bound to a Rh center in a face-capping mode through phosphorus, an ether oxygen atom, and a phenoxide group. The η^3-TMPP-*O* ligands are *syn*, the only arrangement that easily accommodates *cis*-trifluoroacetate ligands, as a trans isomer would dictate a *mer* geometry, which the phosphino–phenoxide ligand cannot assume. The longer Rh–Rh distance of 2.562(2) Å as compared to that in $Rh_2(O_2CCF_3)_4(EtOH)_2$ (Rh–Rh = 2.409(2) Å) is unsurprising, given the loss of two of the four bridging ligands. As in other TMPP-*O*-containing compounds,[5,c,f,o] the phenoxide oxygen atom is bound more strongly to the metal than is the ether group (Rh1–O5 =

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[13] (a) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73. (b) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109.

2.005(8) and Rh2–O14 = 1.984(8) Å versus [Rh1–O8 = 2.315(9) and Rh2–O17 = 2.323(9) Å). Of further note are the C–P–C angles about phosphorus, which are considerably distorted due to the participation of the P atom in the five-membered metallacycles Rh–P–C–C–O. The Rh–P distances of 2.201(4) and 2.203(4) Å are typical for late transition metal-phosphine bonds, as are all other distances and metric parameters in the molecule.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ displays eight resonances between δ 3.00 and 3.96 ppm corresponding to the ortho- and para-methoxy substituents of two magnetically equivalent TMPP ligands. A set of six virtual triplets observed downfield between 5.3 and 6.1 ppm are attributed to meta proton–proton coupling with superimposed proton–phosphorus coupling of a comparable magnitude. The $^{31}P\{^1H\}$ spectrum in $CDCl_3$ exhibits a doublet centered at $\delta = 21.7$ ppm with $J(^{103}Rh–^{31}P) = 135$ Hz.

Discussion

In the course of our investigations involving TMPP reactions with various complexes containing M(II) and M(III) centers (M = Co, Rh, Ni),[5] we discovered that dealkylation of the TMPP ligands occurred in some cases and that such reactions could be controlled by temperature, solvent, and workup conditions. Since phenoxide chemistry of the late transition metals is not generally well-explored, we decided to further investigate reactions of TMPP with dinuclear complexes. Preliminary work led to the finding that dirhodium tetraacetate undergoes substitution of one acetate in favor of a bridging phosphino–phenoxide TMPP ligand mode.[5f] We were rather surprised by the apparent lack of steric problems associated with the presence of the TMPP ligand in this structure and were further encouraged to explore similar reactions with the more reactive dirhodium trifluoroacetate compound.

The results of the present study establish that TMPP reactions with dinuclear carboxylate compounds give rise to unusual products due to the noninnocence of the ether functionalities. This chemistry is quite different from reactions of dimetal carboxylates with nonfunctionalized tertiary phosphines and other Lewis bases which lead to products of two main types, those that are coordinated along the M–M axis (class I adducts) or those that bind perpendicular to the M–M axis (class II adducts).[14] Small basic phosphines such as PMe_3, PEt_3, and PMe_2Ph preferentially form class II adducts, whereas bulky phosphines favor class I adducts. Although TMPP has a large cone angle (184°), it gives no evidence for producing axial adducts under the experimental conditions used, presumably because of a driving force to assume multidentate coordination, a process that is facilitated by demethylation of a methoxy substituent. The bonds formed by this ligand are sufficiently strong to allow for the phosphorus and the adjacent phenoxide oxygen to span the dinuclear unit, a situation that requires the formation of a six-membered metallacycle. The fact that $[Rh_2(O_2CCF_3)_3(TMPP\text{-}O)]_2$ readily converts to $Rh_2(O_2CCF_3)_2(TMPP\text{-}O)_2$ with two facially coordinated TMPP moieties does not reflect strain associated with the bridging TMPP, as the corresponding acetate compound $Rh_2(O_2CCH_3)_3(TMPP\text{-}O)$ does not react with a second TMPP under forcing conditions although it also contains the six-membered ring Rh–Rh–P–C–C–O. Rather, it must be concluded that the reactivity differences are a consequence of electronic influences of the carboxylate ligands, a useful observation in the context of our phosphine chemistry as well as in the broader area of metal carboxylate chemistry.

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Supplementary Material Available: Descriptions of data collection and refinement procedures and full listings of atomic positional parameters and their estimated standard deviations, bond distances and angles, and anisotropic displacement parameters (54 pages). Ordering information is given on any current masthead page.

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