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Notes

An Organometal Hydroxide Route to $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$

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Introduction

Many (diene)rhodium(I) and -iridium(I) derivatives of early transition metal and main group polyoxoanions are known,[2−7] and several of them have proven to be sufficiently stable to allow chemical transformation and/or dissociation of the organic ligand without dissociation of the polyoxoanion supporting ligand.[8−11] Nonetheless, the ease with which the bond between the noble metal and the polyoxoanion ligand can be cleaved is problematical,[6] and the availability of complexes containing more basic supporting ligands might allow the reaction chemistry of this class of compounds to be expanded. One approach to such complexes might involve avoiding the W^{VI}-, Mo^{VI}-, Nb^{V}-, V^{V}-, and P^{V}-based supporting ligands that have been employed to date[2−7] and utilizing instead an oxide ligand containing only group 4 metal centers. Here, a pathway to titanium(IV) derivatives is explored using the organometal hydroxide route successfully employed for preparing organometallic vanadates[12] and molybdates.[13] The intent was to prepare $(C_8H_{12})Rh^I$ derivatives, C_8H_{12} = 1,5-cyclooctadiene, by reacting the organometal hydroxide $[(C_8H_{12})Rh(OH)]_2$ with $Ti(OPr^n)_4$ schematically according to eq 1 in order to prepare

$$(C_8H_{12})RhOH + TiOPr^n \rightarrow (C_8H_{12})RhOTi + Pr^nOH \tag{1}$$

organometallic titanium oxide alkoxides $\{[(C_8H_{12})Rh]_w[Ti_xO_y(OR)_z]\}$ as the ultimate products. As will be shown below, however, such compounds were not obtained. Instead, the organometallic alkoxide $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ (**1**) was formed, a titanium *n*-propoxide analogue of the known tin ethoxide complex $\{[(C_8H_{12})Rh]_2[Sn(OEt)_6]\}$ (**2**).[14]

Experimental Section

Reagents, Solvents, and General Procedures. The following chemicals were purchased from commercial sources and used without further purification: $RhCl_3{\cdot}3H_2O$ (Johnson-Mathay), $Ti(OPr^n)_4$ (98%, Aldrich), and KOH (Mallinckrodt). Literature procedures were used for the preparation of $[(C_8H_{12})RhCl]_2$[15] and $[(C_8H_{12})Rh(OH)]_2$;[16] both compounds were prepared in a dry nitrogen atmosphere. Only reagent grade solvents were used. Hexane (Baxter) and heptane (Baxter) were distilled from sodium benzophenone ketyl under nitrogen; toluene (Fisher) was distilled from sodium metal; toluene-d_8 and chloroform-d_1 were purchased from Cambridge Isotope Laboratories and dried over 3 Å molecular sieves (Linde). The sieves were activated by heating at 350 °C for 24 h and cooling under vacuum. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk and drybox techniques.

Analytical Procedures. Elemental analyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Proton NMR spectra were recorded at 300 MHz on a General Electric QE-300 spectrometer, and chemical shifts were internally referenced to solvent resonances, δ 2.09 for toluene-d_8 and δ 7.26 for chloroform-d_1.

Preparation of $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$. A solution of $Ti(OPr^n)_4$ (474 mg, 1.67 mmol) in 6 mL of toluene was added to a yellow suspension of $[(C_8H_{12})Rh(OH)]_2$ (249 mg, 0.546 mmol) in 15 mL of toluene with stirring. The suspension became a clear, orange solution during the addition. Ten minutes after the addition was completed, the solvent was removed under vacuum, yielding an orange-yellow oil, which was dried under vacuum for 4 h. The resulting glassy solid was then dissolved in hexane (4 mL), and a trace amount of insoluble powder was removed by filtration. The reaction flask was rinsed with hexane (1 mL) twice, and the filtrate and the washes were combined and concentrated in vacuum to *ca.* 1.5 mL. The resulting orange-yellow solution was then cooled to −15 °C for 3 days to afford a yellow crystalline solid. The solid was collected by filtration at −20 °C and washed with cold hexane (0.5 mL) three times. It was then dried in vacuum at 25 °C for 24 h to yield 175 mg of product (0.212 mmol, 39% based on Rh). Single crystals suitable for X-ray diffraction studies were obtained by following the procedure just described but using heptane in place of hexane. Anal. Calcd for $C_{34}H_{66}TiRh_2O_6$: C, 49.52; H, 8.07; Ti, 5.81. Found: C, 49.62; H, 8.14; Ti, 5.43.

Preparation of $[(C_8H_{12})Rh(OPr^n)]_2$. Method 1. A solution of $Ti(OPr^n)_4$ (63 mg, 0.22 mmol) in 2 mL of toluene was added to a solution of $[(C_8H_{12})Rh(OH)]_2$ (100 mg, 0.219 mmol) in 4 mL toluene with stirring, yielding a clear, orange solution. After 30 min, the solvent was removed under vacuum to yield an orange oil. Addition of 5 mL of hexane to this oil gave a suspension, which was filtered, and the resulting clear, orange filtrate was concentrated to *ca.* 1 mL under vacuum and cooled to −15 °C for 2 d. The needle-shaped crystals which formed from the solution were isolated by filtration, washed with 2 × 0.5 mL of hexane, and dried under vacuum for 24 h to yield 60 mg of product (0.11 mmol, 50% based on Rh). Anal. Calcd for $C_{22}H_{38}Rh_2O_2$: C, 48.90; H, 7.09; Rh, 38.09. Found: C, 49.01; H, 7.09; Rh, 37.92. ^1H NMR (300 MHz, toluene-d_8, 20 °C): δ 3.53 (s, br, 8H, $-CH{=}CH-$), 2.62 (t, 4H, $OCH_2CH_2CH_3$), 2.35 (m, 8H, $=CHCH_2-$), 1.54 (overlapping m, 12H, $=CHCH_2-$, and $OCH_2CH_2CH_3$), 0.90 (t, 6H, $OCH_2CH_2CH_3$).

Method 2. A solution of $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ (13 mg, 0.016 mmol) in 0.5 mL of hexane was cooled to −15 °C for 12 h. The needle-shaped, yellow crystals that formed from the solution were isolated by

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Table 1. Summary of Crystallographic Data for $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$

empirical formula	$\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$
color of crystal	yellow
crystal dimensions (mm)	0.34 × 0.62 × 0.80
crystal system	monoclinic
space group	$C2/c-C_{2h}^6$ (No. 15)
cell dimensions	
a (Å)	11.265(2)
b (Å)	18.843(4)
c (Å)	18.731(4)
β (deg)	100.28(2)
Z (formula units)	4
volume (Å^3)	3912(1)
calculated density (g/cm^3)	1.400
wavelength (Å)	0.710 73
molecular weight	824.59
linear absorption coefficient (mm^{-1})	1.07
scan type	ω
average ω-scan width at half-height	0.42
scan speed (deg/min)	8.0−3.0
scan width (deg)	1.00
2θ range (deg)	3.0−48.3
total no. of reflns collected	3236
no. of unique reflns	3130
no. with $I > 3\sigma(I)$	1870
absorption correction	6 ψ scans
range of relative transmission factors	0.920−1.000
R (unweighted, based on *F*)	0.039
R_w (weighted, based on *F*)	0.048
data to parameter ratio	9.3:1
goodness of fit for the last cycle	1.090
largest and mean shift/error	0.290, 0.008
largest difference peaks (e/Å^3) (within 0.93Å of Rh atom)	0.53−0.39

filtration, washed with 0.5 mL of hexane, and dried under vacuum for 24 h. Yield: 5.0 mg (0.0093 mmol, 58% based on Rh). The ^{1}H NMR spectrum of this material was identical to that of the solid prepared by method 1.

Solution ^{1}H NMR Study of $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$. A solution prepared from $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ (9.5 mg, 0.012 mmol) in 0.6 mL of toluene-d_8 was placed in a 5 mm o.d. NMR sample tube under dry argon. The NMR sample tube was then sealed with a rubber septum. The 300 MHz ^{1}H NMR spectrum shown in Figure 2 was measured at 25 °C about 10 min after tube was sealed; the same spectrum was observed 10 h later.

X-ray Crystallographic Study of $\{[(C_8H_{12})Rh)_2[Ti(OPr^n)_6]\}$. Single crystals of $\{[(C_8H_{12})Rh]_2[Ti(O\text{-}n\text{-}C_3H_7)_6]\}$ (**1**) are, at 20 ± 1 °C, monoclinic, space group $C2/c-C_{2h}^6$ (No. 15) with $a = 11.265(2)$ Å, $b = 18.843(4)$ Å, $c = 18.731(4)$ Å, $\beta = 100.28(2)°$, $V = 3912(1)$ Å^3, and $Z = 4$ dimeric formula units $\{d_{calcd} = 1.400$ g cm^{-3}; μ_a(Mo Kα) = 1.07 mm$^{-1}\}$. The computer programs and procedures used for data collection, data reduction, and structure solution and refinement of **1** have been reported elsewhere;[17] a summary of the crystallographic data for the present study is given in Table 1. A total of 3236 independent reflections having 2θ(Mo Kα) < 48.3° (the equivalent of 0.7 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (1.00°-wide) ω scans and graphite-monochromated Mo Kα radiation. The data were corrected empirically for variable absorption effects using ψ scans for six reflections having 5.1° < 2θ(Mo Kα) < 18.6°; the relative transmission factors ranged from 0.920 to 1.000. The structure was solved using "direct methods" techniques with the Siemens SHELXTL-PC software package. The resulting structural parameters have been refined to convergence $\{R_1$-(unweighted, based on *F*) = 0.039 for 1870 independent reflections having 2θ(Mo Kα) < 48.3° and $I > 3\sigma(I)\}$ using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for all hydrogen atoms. Two of the three methyl groups (carbon atoms C_{13} and C_{23} with their hydrogens) refined satisfactorily as rigid rotors with sp^3-hybridized geometry and a C−H bond length of 0.96 Å. The initial orientation of both refined methyl groups were determined from difference Fourier positions for the hydrogen atoms. The final orientation of each refined methyl group was determined by three rotational parameters. The refined positions for these rigid-rotor methyl groups gave C−C−H angles which ranged from 103 to 114°. Since all attempts to refine the remaining methyl group as a rigid rotor resulted in unacceptably small C−C−H angles, it was included in the structure factor calculations as a fixed idealized (staggered) tetrahedral group.

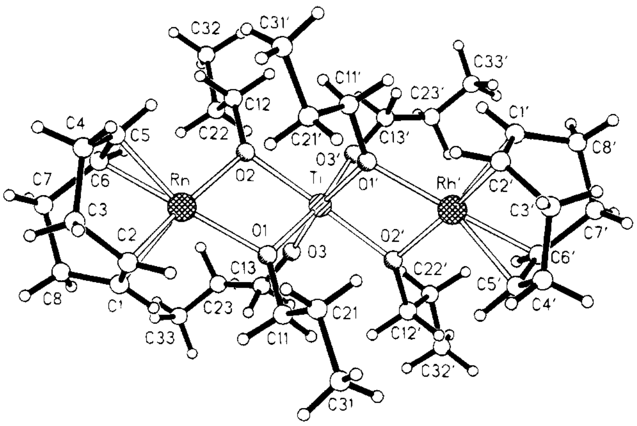

Figure 1. Perspective drawing of the solid-state structure for $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$, **1**. Rhodium and titanium atoms are represented by large-sized cross-hatched and diagonally-lined spheres, respectively; oxygen atoms are represented by medium-sized shaded spheres; and carbon and hydrogen atoms are represented by medium-sized and small open spheres, respectively. Atoms labeled with a prime are related to those labeled without primes by the crystallographic C_2 axis which passes through the Ti atom.

Results and Discussion

Synthesis and Structure of $\{[(C_8H_{12})(Rh]_2[Ti(OPr^n)_6]\}$. Reaction of $[(C_8H_{12})Rh(OH)]_2$ with 3 equiv of $Ti(OPr^n)_4$ in toluene followed by removal of solvent and crystallization of the resulting solid from hexane solution yielded analytically pure, crystalline $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$, **1**, in 39% yield based on rhodium. A structure determination using X-ray diffraction techniques revealed that single crystals of **1** are composed of discrete trinuclear $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ molecules (Figure 1) which possess rigorous crystallographic C_2 symmetry. The central d^0 Ti^{IV} ion lies on this C_2 axis and is octahedrally bonded to four μ_2-*n*-propoxy and two *cis* terminally-bonded *n*-propoxy ligands; the four μ_2-*n*-propoxy ligands provide two pairs of *cis* bridges between the Ti and the two square-planar d^8 Rh^I centers. Each Rh completes its square planar coordination by π-bonding to the two C=C bonds of a single 1,5-cyclooctadiene ligand. Fractional atomic coordinates for all non-hydrogen atoms of **1** are given with estimated standard deviations in Table 2. Selected bond lengths and angles involving non-hydrogen atoms of **1** are given in Table 3. Anisotropic thermal parameters for all non-hydrogen atoms, fractional coordinates for hydrogen atoms, and a complete set of bond lengths and angles for **1** have been deposited as supplementary material.[18]

The solid-state structure of **1** is quite similar to that observed for its Sn^{IV} ethoxide analogue,[14] $\{[(C_8H_{12})Rh]_2[Sn(OEt)_6]\}$, **2**, when differences between d^0 Ti^{IV} and d^{10} Sn^{IV} are taken into account. While the structure of **1** possesses rigorous crystallographic C_2 symmetry in the solid state, the structure of **2** only approximates this idealized symmetry. The most noticeable

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(18) See paragraph at the end of the paper regarding supplementary material.

Table 2. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$[a]

atom[b]	fractional coordinates 10^4x	10^4y	10^4z	equiv isotropic thermal param B (Å^2 × 10)[c]
Rh	−2332(1)	3654(1)	1646(1)	41(1)
Ti	0[d]	4471(1)	2500[d]	45(1)
O_1	−491(4)	3689(3)	1740(2)	46(1)
O_2	−1742(4)	4299(2)	2538(3)	45(1)
O_3	−165(5)	5122(3)	1787(4)	75(2)
C_1	−2785(8)	3449(5)	545(4)	65(3)
C_2	−2671(7)	2802(5)	910(5)	62(3)
C_3	−3732(8)	2354(6)	1020(6)	81(4)
C_4	−4180(9)	2542(6)	1700(6)	85(4)
C_5	−3939(7)	3292(5)	1939(5)	57(3)
C_6	−4186(6)	3895(5)	1520(5)	61(3)
C_7	−4818(8)	3875(7)	733(5)	95(4)
C_8	−3963(9)	3805(7)	214(5)	94(4)
C_{11}	242(7)	3339(5)	1322(5)	60(3)
C_{21}	771(8)	2670(5)	1667(6)	83(4)
C_{31}	1655(11)	2342(9)	1215(8)	134(6)
C_{12}	−2452(6)	4681(4)	2968(4)	52(2)
C_{22}	−2796(7)	5415(4)	2700(5)	62(3)
C_{32}	−3522(9)	5782(6)	3193(7)	95(4)
C_{13}	−452(14)	5389(13)	1197(12)	244(13)
C_{23}	−1328(19)	5756(11)	857(10)	179(10)
C_{33}	−1804(16)	5721(16)	234(11)	259(16)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [d] This is a symmetry-required value and is therefore listed without an estimated standard deviation.

Table 3. Selected Bond Lengths (Å) and Angles (deg) Involving Non-Hydrogen Atoms in Crystalline $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$[a,b]

Bond Lengths, Å			
$Ti-O_1$	2.054(5)	$Rh-O_1$	2.050(4)
$Ti-O_2$	2.003(4)	$Rh-O_2$	2.077(4)
$Ti-O_3$	1.798(7)	$Rh\cdots Ti$	3.214(1)
$Rh-C_1$	2.071(8)	$Rh-C_5$	2.097(8)
$Rh-C_2$	2.106(9)	$Rh-C_6$	2.109(7)
$Rh-C_{1,2}$	1.969(−)[c]	$Rh-C_{5,6}$	1.986(−)[c]
C_1-C_2	1.391(14)	C_5-C_6	1.379(13)
C_1-C_8	1.518(13)	C_4-C_5	1.494(14)
C_2-C_3	1.507(13)	C_6-C_7	1.518(13)
C_3-C_4	1.494(16)	C_7-C_8	1.492(15)
Bond Angles, deg			
O_1TiO_2	76.4(2)	$O_3TiO_{2'}$	93.2(2)
$O_1TiO_{1'}$	88.5(3)	$O_3TiO_{3'}$	93.9(4)
O_1TiO_3	89.7(2)	O_2TiO_3	99.5(2)
$O_2TiO_{1'}$	90.2(2)		
$O_2TiO_{2'}$	161.4(3)	$O_3TiO_{1'}$	169.4(2)
O_1RhO_2	74.9(2)	$C_{1,2}RhC_{5,6}$	88.1(−)[c]
$O_1RhC_{1,2}$	99.1(−)[c]	$O_2RhC_{5,6}$	98.5(−)[c]
$O_1RhC_{5,6}$	170.7(−)[c]	$O_2RhC_{1,2}$	171.4(−)[c]
RhO_1Ti	103.1(2)	RhO_2Ti	103.9(2)
RhO_1C_{11}	128.7(4)	RhO_2C_{12}	128.2(4)
TiO_1C_{11}	127.8(4)	TiO_2C_{12}	126.2(4)
TiO_3C_{13}	160.2(12)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] $C_{1,2}$ and $C_{5,6}$ are used to denote the midpoints of the $C_1{=}C_2$ and $C_5{=}C_6$ olefinic bonds, respectively. These values are therefore listed without estimated standard deviations.

difference between **1** and **2** is the different bonding modes for the two terminally-bonded alkoxides which have a nearly linear 160(1)° $M^{IV}-O-C$ linkage in **1** and a more bent 125.5° linkage in **2**. The $M^{IV}-O$ distances to terminal alkoxides average[19] 1.798(7) Å in **1** and 1.980(5,1,1,2) Å in **2**. For the bridging alkoxide ligands, the $M^{IV}-O$ distances *trans* to the terminal alkoxides average 2.054(5) Å in **1** and 2.101(4,3,3,2) Å in **2** while the $M^{IV}-O$ distances which are *cis* to the terminal alkoxides but *trans* to each other average 2.003(4) Å in **1** and 2.079(4,4,4,2) Å in **2**. The large 0.256 Å difference in bond length between the *trans* $Ti-O_1$ and $Ti-O_3$ bonds in **1** is presumably a consequence of $O_{2p}-Ti$ 3d π bonding, and it establishes a pattern of bond alternation which is propagated throughout the molecule.[20] Although the Rh−O bonds in **1** average 2.064(4,14,14,2) Å and those in **2** average 2.067(4,7,15,4) Å, the Rh−O bonds in **1** are of two distinct types based on length. The $Rh-O_1$ bond in **1** which is adjacent to the "longer" bridging $Ti-O_1$ bond is 0.027 Å shorter than the $Rh-O_2$ bond which is adjacent to the "shorter" bridging $Ti-O_2$ bond. The coordination sphere(s) of **1** are congested: each oxygen and α-carbon of an *n*-propoxide ligand is involved in intramolecular intraligand O⋯O, O⋯C, or C⋯C contacts which are shorter than or equal to the respective sum of van der Waals radii.[21]

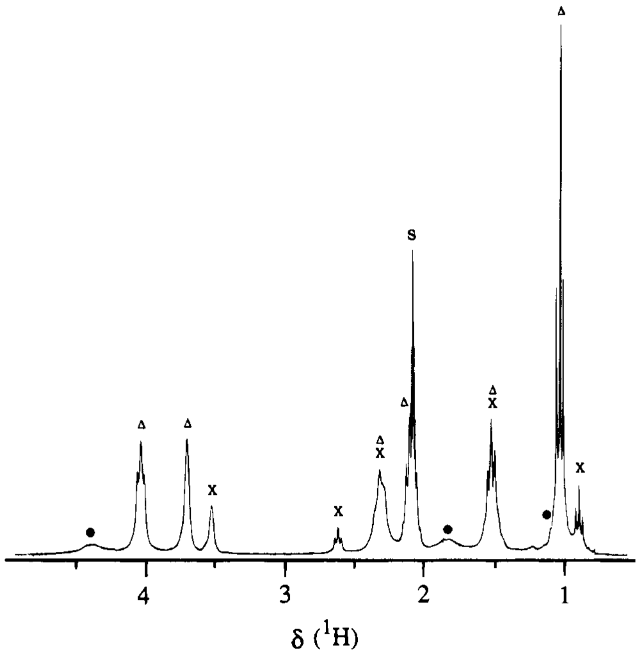

Figure 2. 300 MHz ^1H FTNMR spectrum of a 0.02 M solution of $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ in toluene-d_8 at 25 °C. Resonances assigned to $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ are labeled with triangles, resonances assigned to $\{[(C_8H_{12})Rh(OPr^n)]_2\}$ are labeled with crosses, and resonances assigned to $Ti(OPr^n)_4$ are labeled with dots. The solvent resonance is labeled with the letter "s".

Solution Stability of $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$. Attempts to crystallize $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ from dilute hexane solutions led to the isolation of a different compound, $[(C_8H_{12})Rh(OPr^n)]_2$, in 58% yield based on rhodium. This complex, which could be directly synthesized from $[(C_8H_{12})Rh(OH)]_2$ and 1 equiv of $Ti(OPr^n)_4$ in 50% yield, was characterized by elemental analysis as well as ^1H NMR spectroscopy and was assigned a dimeric $[(C_8H_{12})Rh(\mu_2\text{-}OR)_2Rh(C_8H_{12})]$ structure by analogy with the structurally-characterized methoxy analogue.[22]

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(19) The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

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Solution ^{1}H NMR spectra of $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ in toluene showed that decomposition was occurring principally according to eq 2. The δ 4.4, 1.85, and 1.07 resonances labeled

$$\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\} = [(C_8H_{12})Rh(OPr^n)]_2 + (1/n)[Ti(OPr^n)_4]_n \quad (2)$$

with dots in Figure 2 were assigned to $Ti(OPr^n)_4$, which displayed δ 4.45, 1.78, and 1.00 resonances in toluene solution. The δ 3.53, 2.62, 2.32, 1.52, and 0.89 resonances labeled with crosses in Figure 2 were then assigned to $[(C_8H_{12})Rh(OPr^n)]_2$ by comparison of their chemical shifts with those of pure material in toluene solution (see Experimental Section). Resonances at δ 4.03 and 3.70, the δ 2.10 multiplet overlapping with the solvent resonance, and resonance intensity in the δ 2.32, 1.52, and 1.03 resonances in excess of that which could be ascribed to $Ti(OPr^n)_4$ and $[(C_8H_{12})Rh(OPr^n)]_2$ remained to be assigned. These resonances, labeled with triangles in Figure 2, were assigned to $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ as follows. First, the δ 3.70, 2.32, and 1.52 resonances were assigned to the C_8H_{12} group since the tin analogue $\{[(C_8H_{12})Rh]_2[Sn(OEt)_6]\}$,[14] which does not decompose in solution, displays a methine resonance at δ 3.69 and two methylene resonances at δ 2.17 and 1.41. The remaining resonances at δ 4.03, 2.10, and 1.03 were assigned to the *n*-propoxide OCH_2 methylene protons, CH_3CH_2 methylene protons, and methyl protons, respectively. An alternative assignment of the δ 2.10 resonance to C_8H_{12} methylene protons and the δ 2.32 resonance to CH_3CH_2 methylene protons could be ruled out on the basis of integrated intensities. Only one type of *n*-propoxide group was observed instead of the three types implied by the solid state structure shown in Figure 1. As was the case for the tin analogue,[14] this is presumably a consequence of ligand exchange, either intra- or intermolecular, that is rapid on the NMR time scale.

Conclusions

The organometal hydroxide $\{[(C_8H_{12})Rh(OH)]_2\}$ reacts with 1 equiv of $Ti(OPr^n)_4$ to form $\{[(C_8H_{12})Rh(OPr^n)]_2\}$. In the presence of excess $Ti(OPr^n)_4$, the $Ti(OPr^n)_4$ adduct $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ is formed. The reaction between $\{[(C_8H_{12})Rh(OH)]_2\}$ and $Ti(OPr^n)_4$ proceeds, therefore, not as in eq 1 with elimination of alcohol, but instead by alkoxide/hydroxide exchange. In other words, the organometal hydroxide behaves not as a Brønsted acid but as a Brønsted base.

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Supplementary Material Available: The crystal structure analysis report, tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, bond lengths, and bond angles, and an ORTEP plot for $\{[(C_8H_{12})Rh]_2[Ti(OPr^n)_6]\}$ (13 pages). Ordering information is given on any current masthead page.

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