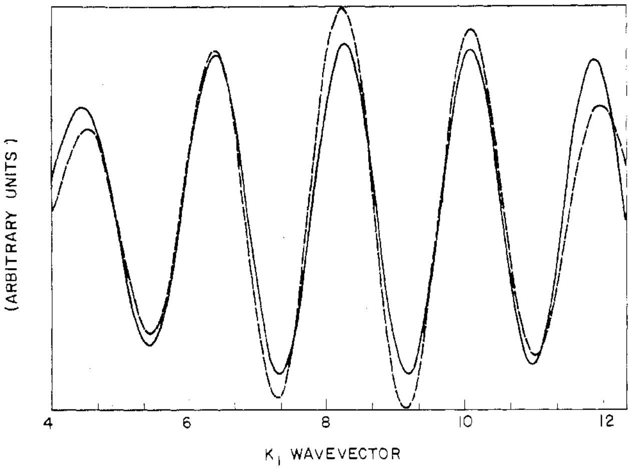

Figure 3. The fit (- - -) of the EXAFS data (—) for $TiCl_3$.

theoretical phase shifts was also used.

Results and Discussion

The results of the fitting technique (Figure 3) gave a Ti–Cl bond distance of 2.22 (1) Å. The empirical method gave a Ti–Cl interatomic distance of 2.21 (2) Å. The data support the argument that all the Ti–Cl bonds are equal in distance from the Ti atom. It has previously been shown that theoretical phase shifts and amplitudes can be used to accurately predict interatomic distances by EXAFS to ±0.01 Å in known structures.[16b,17] The measured distance of 2.21 Å is considerably shorter than the 2.40-Å bond distance that would result from a Ti^{3+}–Cl^- ionic bond, indicating the strong covalent nature of the bonding in $TiCl_3$. The techniques and results reported herein demonstrate the practical application of EXAFS to the solution of structural problems. This analysis technique supplements single-crystal x-ray diffraction as another tool for the resolution of structural problems for which x-ray crystallography could not or has not been applied.

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Base Strengths of (ω-Methoxyalkyl)triphenyl- and (ω-Methoxyalkyl)diphenylmethylsilanes

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It has been suggested that the nature of the substituents directly bound to the silicon atom will determine to a large extent which resonance interactions will be of prime importance.[1-3] We had previously examined the base strengths of $CH_3O(CH_2)_nSiR_3$ (R = H, Cl, and CH_3) compounds and suggested that lowered basicity (R = H and Cl) and the lack of such an effect when R = CH_3 is consistent with a trend that lowered basicities result when the substituent is able to induce a positive charge on the silicon.[4,5] In order to test this hypothesis we prepared the analogous compounds in which R = C_6H_5.

Experimental Section

$CH_3OCH_2Si(C_6H_5)_2CH_3$. This new compound was prepared from the addition of chloromethyl methyl ether to diphenylmethylsilyllithium. In a typical reaction, a solution of 48.0 g (0.198 mol) of $(C_6H_5)_2CH_3SiCl$ in 75 mL of anhydrous THF was added dropwise to 3.1 g (0.45 mol) of Li clippings in 75 mL of THF. After the reaction mixture was stirred for 3.5 h, the dark red lithium reagent was filtered from excess Li and cooled to −15 °C, and a solution of 17 g (0.21 mol) of CH_3OCH_2Cl in 50 mL of THF was added dropwise. After 15 min, the reaction mixture turned yellow-brown, and a white precipitate was observed. The solution was then allowed to slowly warm to 20 °C and stirred for an additional 1.5 h. The reaction mixture was hydrolyzed with a saturated NH_4Cl solution, extracted with diethyl ether, and dried over $CaCl_2$. Removal of the solvent in vacuo yielded a mixture consisting of a yellow oil and a white solid $[(C_6H_5)_4(CH_3)_2Si_2]$. The oil was distilled under reduced pressure and chromatographed on a 2 ft × 1 in alumina (Brockman activity II) column. Petroleum ether (bp 40–60 °C) was used as the elutant. The yield based on $(C_6H_5)CH_3SiCl$ was 40%.

Proton chemical shifts for this and the compounds listed below are given in Table I.

Major peaks in the IR spectrum occur at 3071, 3050, 2975, 2925, 2843, 2810 (m), 1430 (s), 1251 (m), 1107 (vs), 985 (m), 820, 788, 733, 700, 487 (s), and 470 (m) cm^{-1}. Mass spectral peaks in >10% relative abundance occur at *m/e* values of 44 (15.9%), 105 (11.1%, $C_6H_5Si^+$), 151 (47.7%, $(C_6H_5)CH_3SiOCH_3^+$ (R)), 197 (100%, $(C_6H_5)_2SiCH_3^+$), and 198 (19.1%, $(C_6H_5)_2SiO^+$ (R)). Anal. Calcd: C, 74.32; H, 7.49. Found: C, 74.55; H, 7.35.

$CH_3O(CH_2)_2Si(C_6H_5)_2CH_3$. This new compound was obtained in 40% yield from the addition of 2-chloro-1-methoxyethane in THF to a −10 °C solution of diphenylmethylsilyllithium in THF. The product was purified in a manner similar to that for $CH_3OCH_2Si(C_6H_5)_2CH_3$. Major peaks in the IR spectrum occur at 3072, 3051, 3020, 2925, 2896, 2870, 2823, 1485, 1456 (m), 1425 (s), 1380, 1255, 1205, 1187, and 1157 (m) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 32 (66.1%), 105 (16.0%), 121 (12.3%), 151 (100%), 152 (13.2%), 179 (15.9%), 183 (13.4%), 197 (52.8%), 198 (12.3%), 213 (59.2%), and 214 (11.7%). Anal. Calcd: C, 74.94; H, 7.86. Found: C, 74.94; H, 7.66.

$CH_3O(CH_2)_3Si(C_6H_5)_2CH_3$. This new compound was obtained in 45% yield by reacting 3-chloro-1-methoxypropane with diphenylmethylsilyllithium in THF. The product was purified in a manner similar to that for $CH_3OCH_2Si(C_6H_5)_2CH_3$. Major peaks in the IR spectrum occur at 3070, 3052, 3015 (m), 2927 (s), 2825, 1480, 1456 (m), 1431, 1423 (s), 1380, 1256, 1210, 1180, 1150 (m), 1111 (s), 1059 (m), 787, 730, 701 (s), 485, 475, and 434 (m) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 28 (14.3%), 44 (10.8%), 105 (19.4%), 121 (10.4%), 151 (56.2%), 181 (11.6%), 183 (11.1%), 193 (100%), 194 (16.9%), 195 (13.2%), 197 (82.5%), 198 (17.7%), and 213 (27.8%). Anal. Calcd: C, 75.50; H, 8.20. Found: C, 75.53; H, 8.46.

$CH_3O(CH_2)_4Si(C_6H_5)_2CH_3$. This new compound was obtained in ca. 10% yield from the dropwise addition of 4-bromo-1-methoxybutane

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Table I. Proton Chemical Shifts for $CH_3O(CH_2)_nMR_3$ Compounds[a]

Compound	$C\text{-}M(C_6H_5)_3$	$C\text{-}M(C_6H_5)_2$	$C\text{-}M(C_6H_5)_2\text{-}CH_3$	MCH_2	CH_2O	OCH_3
		M = Carbon				
$CH_3OCH_2C(C_6H_5)_3$	7.08				4.24	3.30
$CH_3O(CH_2)_2C(C_6H_5)_3$	7.21			*d*	3.0[b]	3.13
$CH_3O(CH_2)_3C(C_6H_5)_3$	7.14			2.63[b]	3.24	3.26
		M = Silicon				
$CH_3OCH_2Si(C_6H_5)_3$	7.35[c]				3.77	3.38
$CH_3O(CH_2)_2Si(C_6H_5)_3$	7.38[c]			1.71	3.47	3.14
$CH_3OCH_2Si(C_6H_5)_2CH_3$		7.32[c]	0.53		3.50	3.36
$CH_3O(CH_2)_2Si(C_6H_5)_2CH_3$		7.49[c]	0.54	1.43	3.48	3.23
$CH_3O(CH_2)_3Si(C_6H_5)_2CH_3$		7.29[c]	0.52	*d*	3.23	3.20
$CH_3O(CH_2)_4Si(C_6H_5)_2CH_3$		7.31[c]	0.51	*d*	3.24	3.19

[a] Observed δ values relative to internal Me_4Si standard. Samples run as 0.20 and 0.80 M solutions in CCl_4 were identical. [b] Second-order spectrum was observed. δ value measured to midpoint of multiplet. [c] Very broad resonance. [d] Not discernible as distinct multiplet, but overlaps other $C\text{–}(CH_2)_x\text{–}C$ protons: $\delta(CH_3O(CH_2)_3Si(C_6H_5)_2CH_3) = 0.76\text{–}1.88$; $\delta(CH_3O(CH_2)_4Si(C_6H_5)_2CH_3) = 0.82\text{–}1.68$.

(Frinton Laboratories) to a −10 °C solution of diphenylmethylsilyllithium in THF. After hydrolysis and ether extraction, the crude material was distilled through a 6-ft Vigreaux column under reduced pressure, eluted through a 2 ft × 1 in alumina (Brockman activity III) column with anhydrous hexane, and again distilled at reduced pressure through a 6-in Vigreaux column. Major peaks in the IR spectrum occur at 3068, 3050, 3015, 2975 (m), 2895 (s), 2865 (s), 2810, 1455, 1430, 1402, 1383, 1253, 1202, 1180, 1160, 1145 (m), 1114 (s), 1064 (m), 1019 (m), 1000 (m), 791 (s), 732 (s), 701 (s), 490, 470, and 435 (m) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 45 (11.7%), 105 (14.8%), 151 (15.5%), 197 (100%), 198 (20.7%), 207 (65.4%), 208 (11.9%), and 213 (29.2%). Anal. Calcd: C, 76.00; H, 8.50. Found: C, 75.80; H, 8.22.

$CH_3OCH_2Si(C_6H_5)_3$. (Methoxymethyl)triphenylsilane, a white solid, was obtained in 35% yield from the addition of chloromethyl methyl ether to triphenylsilyllithium by a procedure similar to that described for $CH_3OCH_2Si(C_6H_5)_2CH_3$. Major peaks in the infrared spectrum occur at 3078, 3043, 3001, 2966, 2929, 2898, 2843, 2813, 2798, 1481 (m), 1426 (s), 1293, 1260, 1212, 1181, 1155 (m), 1117, 1094, 1086 (s), 1080, 1065 (sh), 1026, 992 (m), 925, 785 (s), 733, 699, 510, 489, and 410 (m) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 105 (16.2%), 155 (13.1%), 180 (16.6%), 181 (49.6%), 182 (13.6%), 213 (67.1%), 214 (15.4%), 259 (100%), and 260 (27.9%). Anal. Calcd: C, 78.90; H, 6.62. Found: C, 78.60; H, 6.68.

$CH_3O(CH_2)_2Si(C_6H_5)_3$. This new compound was obtained in 25% yield from the addition of 2-chloro-1-methoxyethane in THF to a 0 °C solution of triphenylsilyllithium in THF. The yellow, oily filtrate was subjected to high-pressure liquid chromatography on a silver styrene–divinylbenzenesulfonate column. Major peaks in the infrared spectrum occur at 3070, 2921, 2877, 2810, 1485 (m), 1430 (s), 1382, 1213, 1186 (m), 1112, 1098, 1000, 946 (m), 735, 720 (s), 702 (vs), and 499 (s) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 18 (16.7%), 28 (23.6%), 45 (11.4%), 213 (100%), 214 (19.1%), and 259 (31.1%). Anal. Calcd: C, 79.19; H, 6.96. Found: C, 78.95; H, 6.75.

$CH_3OCH_2C(C_6H_5)_3$. (Methoxymethyl)triphenylmethane was prepared in 26% yield by the addition of chloromethyl methyl ether to triphenylmethylsodium, which was prepared by the addition of 7.0 g (0.025 mol) of triphenylchloromethane in 0.125 L of anhydrous ether to 200 g of 1% sodium amalgam, freshly prepared according to the procedure of Renfrow and Hauser.[6] To separate the sodium reagent from the amalgam, the ether solution of $(C_6H_5)_3CNa$ was forced by means of positive nitrogen pressure through a U-shaped tube into a receiving flask. After the $(C_6H_5)_3CNa$ solution was cooled to 0 °C, 2.3 g (0.029 mol) of chloromethyl methyl ether in anhydrous ether was added dropwise. The solution was allowed to warm to ambient temperature and was stirred overnight. The reaction mixture was hydrolyzed with a saturated NH_4Cl solution and extracted with ether. The ether extracts were washed with water and dried over $CaCl_2$. Elution with 10% benzene in hexane followed by 20% benzene in hexane yielded $(C_6H_5)_3CCH_2OCH_3$. Major peaks in the IR spectrum occur at 3085, 3051, 3032, 3020, 2970, 2923, 2890, 2825, 2808, 1605 (m), 1500, 1453 (s), 1392, 1199, 1165 (m), 1122 (s), 1093, 1035, 1001, 930, 889 (m), 774, 770, 761 (s), 717 (m), 709 (s), 658, 629, 621 (m), 617 (s), 529, and 513 (m) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 45 (33.1%), 165 (39.7%), 243 (100%), and 244 (20%). Anal. Calcd: C, 79.19; H, 6.96. Found: C, 79.95; H, 6.75.

Table II. Infrared Shifts (Δν)[a] of $CH_3O(CH_2)_nM(C_6H_5)_2R$ Compounds (M = C and Si; R = CH_3 and C_6H_5)

Ether	Δν, cm^{-1}
$CH_3OCH_2C(C_6H_5)_3$	93
$CH_3O(CH_2)_2C(C_6H_5)_3$	137
$CH_3O(CH_2)_3C(C_6H_5)_3$	136
$CH_3OCH_2Si(C_6H_5)_3$	114
$CH_3O(CH_2)_2Si(C_6H_5)_3$	142
$CH_3O(CH_2)_3Si(C_6H_5)_3$	141
$CH_3OCH_2Si(C_6H_5)_2CH_3$	127
$CH_3O(CH_2)_2Si(C_6H_5)_2CH_3$	145
$CH_3O(CH_2)_3Si(C_6H_5)_2CH_3$	138
$CH_3O(CH_2)_4Si(C_6H_5)_2CH_3$	138

[a] Δν ± 2 cm^{-1}; shifts of 0.2 M solution of ether vs. 0.02 M CH_3OH in CCl_4. There was no evidence of self-association.

$CH_3O(CH_2)_2C(C_6H_5)_3$. (Methoxyethyl)triphenylmethane was prepared in 26% yield by adding 20 g of ethylene oxide to a stirred THF solution of triphenylmethylsodium. After the solution was stirred at 0 °C for 1.5 h, 2.8 mL (0.051 mol) of freshly distilled methyl bromide was added dropwise. The reaction mixture was stirred overnight and purified as described for $CH_3OCH_2C(C_6H_5)_3$. Major peaks in the IR spectrum occur at 3059, 3024, 2979, 2934, 2898, 1592 (m), 1492, 1448 (s), 1389, 1198, 1183 (m), 1109 (s), 1080, 1069, 1029, 956 (m), 765 (s), 740 (m), 704 (s), 639 (m), and 609 (s) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 18 (14.1%), 45 (13.8%), 165 (34.4%), 243 (100%), and 244 (23.8%). Anal. Calcd: C, 87.31; H, 7.33. Found: C, 87.30; H, 7.45.

$CH_3O(CH_2)_3C(C_6H_5)_3$. (ω-Methoxypropyl)triphenylmethane was obtained in 15% yield from the addition of 3-chloro-1-methoxypropane to a solution of triphenylmethylsodium in THF. Major peaks in the IR spectrum occur at 3070, 3039, 3030, 2990, 2975, 2945, 2935, 2880, 2840, 2820, 2740, 1600 (m), 1498 (s), 1460 (m), 1450 (s), 1380, 1188 (m), 1115 (s), 1093, 1080, 1070, 1065, 1028, 1001, 934, 911, 898, 842, 771 (m), 764, 750, 704 (s), 644, 622, 616, 604, and 525 (m) cm^{-1}. Mass spectral peaks at >10% relative abundance occur at *m/e* values of 165 (16.6%), 243 (100%), and 244 (16.6%).

Discussion

Lowered basicities in $CH_3O(CH_2)_nSiR_3$ compounds have been shown[4,5] to be most substantial for those series in which R = H or Cl and less significant when R = CH_3. Basicities of compounds synthesized in this study are given in Table II. As previously discussed, both group electronegativity[7] and bond dipole data[8,9] ($\chi_{SiCl_3} = 2.78$ and $Si^+\text{–}Cl^- = 2.5$ D) are consistent with decreased basicity of the $SiCl_3$ series, and although χ_{SiH_3} is only 2.21, the $Si^+\text{–}H^- = 1.0$ D bond dipole is surprisingly large and can account for the similarity in the observed basicities of the $SiCl_3$ and SiH_3 groups. However, the small

Table III. Mass Spectra of Metastable Ions Observed for Selected (ω-Methoxyalkyl)silanes

Organosilicon ethers	m/e		Intramolecular interaction
$CH_3OCH_2Si(C_6H_5)_2CH_3$	94.3	242→151	$CH_3OCH_2Si(C_6H_5)_2CH_3^+ \rightarrow CH_3OSi(C_6H_5)CH_3^+$
$CH_3O(CH_2)_3Si(C_6H_5)_2CH_3$	118.8	193→151	$CH_3O(CH_2)_3Si(C_6H_5)CH_3^+ \rightarrow CH_3OSi(C_6H_5)CH_3^+$
$CH_3O(CH_2)_4Si(C_6H_5)_2CH_3$	110.2	207→151	$CH_3O(CH_2)_4Si(C_6H_5)CH_3^+ \rightarrow CH_3OSi(C_6H_5)CH_3^+$
$CH_3O(CH_2)_2Si(C_6H_5)_3$	188.3	241→213	$CH_3O(CH_2)_2Si(C_6H_5)_2^+ \rightarrow CH_3OSi(C_6H_5)_2^+$

bond dipoles of SiR_3 groups ($Si^+–R^- = 0.2$ D, where R = CH_3 and C_6H_5) are consistent with the apparently lesser significance of an O→Si intramolecular interaction in compounds containing a SiR_3 group.

The mass spectra of the organosilicon ethers provide additional confirmation on an excited-state O→Si intramolecular interaction in $CH_3O(CH_2)_nSiR_3$ compounds. The spectra all show the presence of rearranged fragment ions in which the oxygen has migrated to the silicon. No analogous rearrangement ions are noted for the all-carbon analogues. Such rearrangement ions have been associated with intramolecular rearrangement ions in other studies;[4,10] moreover, metastable ions (see Table III) have been observed which show the transitions from parent ion to rearranged ion.

The relative order of increasing basicity in the $CH_3O(CH_2)_nSi(C_6H_5)_3$ and $–Si(C_6H_5)_2CH_3$ compounds (Table II) is $n = 1 << n = 2 > n = 3$, which is the same general order found for both the $–Si(CH_3)_3$ series[4] and also for several other $Y(CH_2)_nM(CH_3)_3$ series studied by Chvalovský, Voronkov, and co-workers.[11,12]

In summary, previous authors have suggested that a number of factors (d orbital participation, hyperconjugation, and inductive and steric effects) must be utilized to account for the observed behavior of organosilicon compounds.[1] The basicities of the compounds reported in this study are analogous to those of $CH_3O(CH_2)_nSi(CH_3)_3$ compounds and would seem to confirm that no single concept of those cited above but rather a combination of these effects is required to correlate observed results.

Registry No. $CH_3OCH_2Si(C_6H_5)_2CH_3$, 64666-48-4; $CH_3O(CH_2)_2Si(C_6H_5)_2CH_3$, 64666-47-3; $CH_3O(CH_2)_3Si(C_6H_5)_2CH_3$, 64666-46-2; $CH_3O(CH_2)_4Si(C_6H_5)_2CH_3$, 64666-45-1; $CH_3OCM_2Si(C_6H_5)_3$, 64666-54-2; $CH_3O(CM_2)_2Si(C_6H_5)_3$, 64666-53-1; $CH_3OCH_2C(C_6H_5)_3$, 64666-52-0; $CH_3O(CH_2)_2C(C_6H_5)_3$, 64666-51-9; $CH_3O(CH_2)_3C(C_6H_5)_3$, 64666-50-8; $CH_3O(CH_2)_3Si(C_6H_5)_3$, 64666-49-5; chloromethyl methyl ether, 107-30-2; diphenylmethylsilyllithium, 3839-30-3; 2-chloro-1-methoxyethane, 627-42-9; 3-chloro-1-methoxypropane, 36215-07-3; 4-bromo-1-methoxybutane, 4457-67-4; triphenylsilyllithium, 791-30-0; triphenylmethylsodium, 4303-71-3; ethylene oxide, 75-21-8.

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Reaction of Carbonylchlorobis(tertiary phosphine or phosphinite)rhodium(I) Complexes with Dioxygen in the Absence and Presence of Excess Phosphine (Phosphinite)

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The behavior of transition-metal complexes under oxygen atmospheres remains of considerable current interest because of the possibility of obtaining catalytic oxygenation systems in which an internal oxygen atom transfer occurs between the metal and substrate.[2-5]

The studies here are concerned with the aspects of reaction 1 in the absence and presence of excess P. Such catalytic

$$trans\text{-}RhCl(CO)P_2 + O_2 \rightarrow \text{oxidized complexes} + PO \qquad (1)$$

P = PPh_3, $PPh_2(O\text{-}i\text{-}Bu)$, $PPhEt_2$, PEt_3, and poly-$OPPh_2$ (poly(methallyl)diphenylphosphinite)

oxidation of tertiary phosphines is usually considered to go via a process involving oxygen atom transfer from a coordinated dioxygen,[2,3] but we find that oxidation of $PPh_2(O\text{-}i\text{-}Bu)$ proceeds mainly via a radical pathway. Various complexes have been isolated previously from O_2-oxidized rhodium(I) phosphine complexes in solution.[6,7]

Experimental Section

PPh_3, $PPhEt_2$, and PEt_3 were Strem products. A literature method[8] was used to obtain $PPh_2(O\text{-}i\text{-}Bu)$; bp 105 °C (0.05 mm), ν(P–O–C) 1030 cm^{-1}. Poly-$OPPh_2$ was prepared similarly[10] from low molecular weight atactic poly(methallyl) alcohol. The alcohol (3 g) was suspended in 30 mL of dry THF and 3.2 mL of pyridine under N_2. Chlorodiphenylphosphine (7.4 mL) was added dropwise with formation of py·HCl, the slurry was stirred overnight at 20 °C and filtered under N_2, and the residue was washed with THF. The filtrate was evaporated to give a white solid which partially dissolved in 100 mL of dry benzene. The filtered-off solid is oxidized poly-$OPPh_2$. The filtrate was concentrated to 50 mL and added to degassed dry petroleum ether. The precipitated white solid was filtered off, washed with the ether, and dried in vacuo. Anal. Calcd for $C_{16}H_{17}OP$: C, 74.9; H, 6.63; P, 12.1. Found: C, 74.6; H, 6.40; P, 11.6. ν(P–O–C) 1025 cm^{-1}.

trans-$RhCl(CO)P_2$ with P = PPh_3, $PPh_2(O\text{-}i\text{-}Bu)$, $PPhEt_2$, and PEt_3 were synthesized from $[RhCl(CO)_2]_2$ according to the literature.[9,10] With L = poly-$OPPh_2$, the procedure[9] precipitates the complex as a yellow cross-linked solid, insoluble in all solvents; ν(CO) 1980 cm^{-1}.

The $Rh_4Cl_4(CO)_4(O_2)_2P_2$ complexes were prepared from $RhCl(CO)P_2$ (1 mmol) by refluxing in 10 mL of benzene under O_2 (1 atm). The yellow solution darkened, and a brown solid separated over 1–5 days depending on the phosphine.[11] Concentration and addition of ether completed precipitation, and the solid was filtered, washed with ether, and vacuum-dried. The phosphine oxide was recovered from the reaction filtrate. The complexes gave correct analyses. For example, for $PPh_2(O\text{-}i\text{-}Bu)$, calcd for $C_{18}H_{19}O_5Cl_2PRh_2$: C, 34.5; H, 3.1; O(diff), 12.0; Cl, 11.4; P, 5.0; Rh, 33.1. Found: C, 34.3; H, 3.9; O, 13.3; Cl, 11,4; P, 4.7; Rh, 32.4.

Methods. The procedure for measuring gas uptake at constant pressure has been described previously.[12] Spectroscopic measurements were made on the following instruments: Perkin-Elmer 457 (IR), Varian XL 100 (^{31}P NMR), AEI MS-9 (mass spectra), Cary 14 (UV–vis at temperatures[13] from −40 to 25 °C). Magnetic measurements were made on a Gouy balance. Molecular weights in *N,N*-dimethylacetamide (DMA) were determined by Arro Laboratories, Jobet, Ill.

Results and Discussion

Characterization of the Oxidized Complexes. Reaction 1 was carried out on a preparative scale by refluxing the $RhCl(CO)P_2$ complexes in benzene, toluene, or CH_2Cl_2 under O_2. The isolated dark brown products are diamagnetic solids