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 $n = 1 \ll n = 2 > n = 3$, 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 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]

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

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

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

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Table I. Infrared Data[a] of the $Rh_4Cl_4(CO)_4(O_2)_2P_2$ Complexes

Assign-ment	PPh_3	PPh_2(O-*i*-Bu)	Poly-$OPPh_2$[b]	$PPhEt_2$	PEt_3
C=O	1980, 2030	1990[c], 2070[c]	1990, 2060	1972, 2010	1962, 2005
P-C	1095, 1125	1095, 1120	1110, 1130	1096, 1130	1030
P-O-C		1000	1015		
Rh-Cl	320	320		310	310

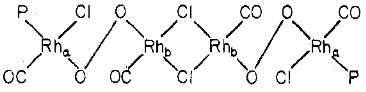
[a] cm^{-1} in Nujol; generally rather broad bands. [b] ν(P=O) bands are observed at 1220 cm^{-1} (see eq 5). [c] Same value in CH_2Cl_2; 1980 and 2030 cm^{-1} in DMA.

and analyze correctly for formulation as $Rh_2Cl_2(CO)_2(O_2)P$. They are formed according to the stoichiometry of eq 2, which

$$4RhCl(CO)P_2 + 5O_2 \rightarrow Rh_4Cl_4(CO)_4(O_2)_2P_2 + 6P{=}O \qquad (2)$$

was established by gas uptake measurement in toluene (~1.3 mol of O_2/Rh) and recovery of the phosphine oxides (~1.4 mol/Rh). A molecular weight of 1040, measured by the osmotic method for the PEt_3 complex, which was moderately soluble in 1,2-dichloroethane, is consistent with the tetranuclear formulation (calcd: 966). Further confirmation of the formulation of the complexes has been obtained by detailed studies[14] of their reactions with both H_2 and O_2. The complexes are generally insoluble in solvents other than coordinating ones such as CH_3CN, dimethylformamide, and DMA. Infrared data for the Rh_4 complexes are given in Table I. The spectra show no bands attributable to coordinated phosphine oxide or peroxide (800–900 cm^{-1}).

A plausible structure for the complexes is **1**, containing



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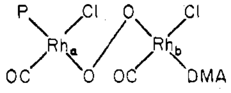
bridging chloride and peroxo (or superoxo) ligands. Interestingly, the molecular weight of the PPh_2(O-*i*-Bu) complex in DMA was found to be 675, consistent with cleavage of the bridged chlorides of **1** and formation of a dimer **2** with co-



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ordinated DMA (calcd: 710). No O_2 evolution occurs on dissolution of the Rh_4 species in DMA.[15] The two ν(CO) bands in the solid state are the same in CH_2Cl_2, where the tetranuclear structure is maintained, while in DMA significant shifts are observed (Table I). The higher wavenumber band is likely due to the CO coordinated to Rh_b, and the greater lowering of 40 cm^{-1} at this center on replacement of chloride by DMA seems reasonable. We have been unable to detect the bridging chlorides by IR due to poorly resolved spectra. A bridging peroxide or superoxide moiety should be detectable in the 800- and 1100-cm^{-1} regions, respectively, but the bands are invariably weak, and the latter region is in any case complicated here by the presence of the phosphines. The diamagnetism is best explained by invoking bridging superoxides which implies an average metal oxidation state of 1.5 and a formulation with monovalent Rh_a and divalent Rh_b, the latter being involved with some antiferromagnetic coupling with the superoxide or with each other.

The $^{31}P\{H\}$ NMR for the oxidized $PPhEt_2$ complex in DMA at 20 °C shows a doublet centered at −122.5 ppm (J_{Rh-P} = 65 Hz), and on comparison with data for the *trans*-RhCl(CO)P_2 complexes (Table II) this seems consistent with structure **2**. We consider a

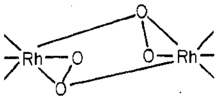
$$Rh-\overset{O}{\underset{O}{\|}}-Rh$$

Table II. $^{31}P\{H\}$ NMR Data of the *trans*-RhCl(CO)P_2 Complexes

P	δ,[a] ppm	J_{Rh-P}, Hz
PPh_2(O-*i*-Bu)	115.4	138
$PPhEt_2$	23.9	120
PEt_3	34.0	115
PPh_3	29.1[b]	124[b]

[a] Signals are doublets measured in DMA at 20 °C and are downfield shifts from an external H_3PO_4 reference. [b] Reference 16.

geometry unlikely,[17] although bonding of the type found in the unusual dioxygen-bridged structure **3** for the [RhCl-

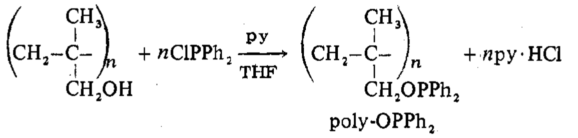


3

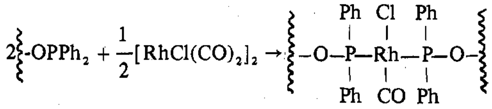
$(PPh_3)_2(O_2)]_2$ complex[6] remains a possibility.

The mass spectra of the tetranuclear phenylphosphine complexes all gave peaks at *m/e* 355, 378, 201, 199, and 183, which could be due, respectively, to fragments such as $RhCl(O_2)(PPh_2)$, $RhCl(O_2)(PPh)$, $RhCl(O_2)P$, $RhCl(O_2)P$, $RhCl(CO)(O_2)$, and RhCl(CO)(O).

The polyphosphinite ligand (poly-$OPPh_2$) and complex were made in terms of their potential for a polymer-supported homogeneous catalyst.[18] The ligand synthesis is outlined in eq 3. The insoluble rhodium complex (eq 4) shows 8.2% Rh

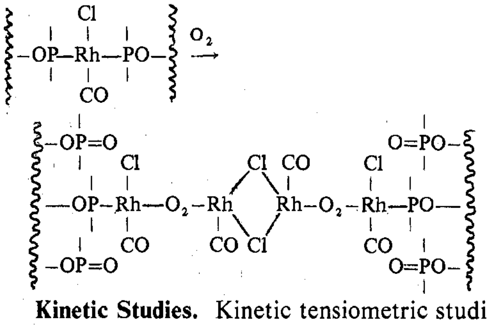


$$\left(CH_2-\underset{CH_2OH}{\overset{CH_3}{C}}-\right)_n + nClPPh_2 \xrightarrow[THF]{py} \underset{\text{poly-}OPPh_2}{\left(CH_2-\underset{CH_2OPPh_2}{\overset{CH_3}{C}}-\right)_n} + n\,py\cdot HCl \qquad (3)$$



$$2\,\text{-}OPPh_2 + \frac{1}{2}[RhCl(CO)_2]_2 \rightarrow -O-\underset{Ph}{\overset{Ph}{P}}-\underset{CO}{\overset{Cl}{Rh}}-\underset{Ph}{\overset{Ph}{P}}-O- \qquad (4)$$

and 9.8% P, equivalent to a P:Rh ratio of 4.0. Oxidation by refluxing as a suspension in benzene under O_2 shows no loss of rhodium, and the IR data (Table I) are consistent with the tetranuclear formulation. Despite the very low number of coordinated phosphinites, the oxidized complex is still completely insoluble in all solvents, suggesting that the cross-linking has been maintained (eq 5). Phosphine oxide bands are detected in the IR at 1220 cm^{-1}.



(5)

Kinetic Studies. Kinetic tensiometric studies on reaction 2 for the $RhCl(CO)(PPh_2O\text{-}i\text{-}Bu)_2$ complex in DMA at 60 °C reveal a first-order dependence on Rh and an O_2 dependence that goes from first order at low pressure to less than first, and approaches zero order at ~700 Torr. Since we were unable to detect an intermediate $RhCl(CO)P_2O_2$ dioxygen complex, even at low temperatures, where their formation is thermodynamically favored,[19] a dissociative mechanism such as shown in eq 6, where L = P or Cl^-, seems likely. Testing

$$RhCl(CO)P_2 \underset{k_{-1},\,+L}{\overset{k_1,\,-L}{\rightleftarrows}} \text{solvated Rh} + O_2 \xrightarrow{k_2} \text{products} \qquad (6)$$

such a mechanism (rate law, eq 7), which requires an inverse

$$-d[O_2]/dt = k_1k_2[Rh][O_2]\,(k_{-1}[L] + k_2[O_2]) \qquad (7)$$

dependence on L at lower O_2 pressures, proved impossible since the addition of chloride led to decomposition to metal and green solutions (probably[20] via $2Rh^I \rightleftharpoons Rh^0 + Rh^{II}$), while addition of phosphinite led to its catalytic oxidation (see below).

Phosphine dissociation from $RhCl(CO)(PPh_3)_2$ has been proposed recently[7] for a photoinduced O_2 oxidation; here, however, the oxidation of coordinated CO to CO_2 was photoinduced, and the isolated oxidized complex was formulated as $[RhCl(O_2)(OPPh_3)_{0.67}]_x$. This process almost certainly involves radical pathways via hydroperoxides, since Harvie and McQuillin[21] have reported the oxidation of CO in $RhCl(CO)(PPh_3)_2$ to CO_2 by reaction with hydroperoxides. Our system is a "dark" reaction and is unaffected by the presence of added hydroquinone.

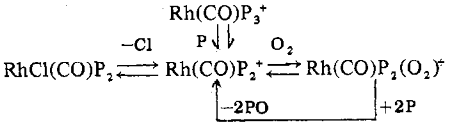
The catalytic phosphinite oxidation was very rapid at 60 °C and 1 atm of O_2; ~0.3 M phosphinite solutions being converted to the oxide in ~15 min using ~10^{-3}M $RhCl(CO)(PPh_2O\text{-}i\text{-}Bu)_2$. Kinetic studies at 30 °C show that the initial reaction rates are *independent* of the [Rh], even though the metal complex is a necessary catalyst. Such behavior indicates a radical process involving decomposition of adventitious hydroperoxides. Addition of hydroquinone (HQ) in a 1:1 ratio to Rh did not affect the oxidation rates, but increasing the [HQ] by ten to a hundred times that of the Rh (in fact, to concentrations approaching that of the phosphinite) reduced the rates by as much as a hundred. The radical mechanism could be initiated by reaction 8, where I is formed sponta-

$$Rh^I + I \xrightarrow{O_2} Rh^{II} + IOO\cdot \qquad (8)$$

neously on exposing the reaction mixture to O_2; an extremely low concentration of I can result in zero-order dependence on Rh. The fact that 10^{-3} M HQ does not inhibit the reaction implies that HQ is consumed and, since the phosphinite is the reagent in large excess, this is the likely source of I. All the reagents were completely negative to tests for peroxides. A possible hydroperoxide source is hydrogen abstraction from the phosphinite by traces of a $Rh\text{–}O_2$ adduct.[22]

In the presence of ~10^{-1} M HQ, the efficient radical pathway is stopped, and the kinetics of the catalytic oxidation show first order in Rh and between first and zero order in O_2 and in phosphinite at 1 atm of O_2. At low O_2 pressure, an inverse phosphinite dependence is observed. Triphenylphosphine oxidation catalyzed by $Pt(PPh_3)_n$ and $RuCl_2(PPh_3)_3$ are thought to involve attack of uncoordinated phosphine on an intermediate O_2 adduct.[23,24] Reaction Scheme I for phosphinite oxidation invokes such a pathway and qualitatively accounts for the kinetics. Addition of chloride to the system again produces metal and thwarts attempts to substantiate the mechanism.

Scheme I



The main conclusion is that the catalytic phosphinite oxidation occurs mainly via a radical (or at least peroxide) pathway and not via oxygen atom transfer from coordinated dioxygen. Of interest is Halpern's[25] suggestion that the Pt(O)-catalyzed O_2 oxidation of Ph_2PMe via a molecular dioxygen complex involves free peroxide in solution.

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Registry No. *trans*-$RhCl(CO)[PPh_2(O\text{-}i\text{-}Bu)]_2$, 64740-76-7; *trans*-$RhCl(CO)(PPhEt_2)_2$, 15691-93-7; *trans*-$RhCl(CO)(PEt_3)_2$, 15631-52-4; *trans*-$RhCl(CO)(PPh_3)_2$, 15318-33-9; *trans*-$RhCl(CO)(\text{poly-}OPPh_2)_2$, 64740-85-8; O_2, 7782-44-7; $Rh_4Cl_4(CO)_4(O_2)_2(PPh_3)_2$, 64740-77-8; $Rh_4Cl_4(CO)_4(O_2)_2[PPh_2(O\text{-}i\text{-}Bu)]_2$, 64740-78-9; $Rh_4Cl_4(CO)_4(O_2)_2(\text{poly-}OPPh_2)_2$, 64740-83-6; $Rh_4Cl_4(CO)_4(O_2)_2(PPhEt_2)_2$, 64740-79-0; $Rh_4Cl_4(CO)_4(O_2)_2(PEt_3)_2$, 64740-80-3; **2**, 64740-81-4.

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A Mössbauer Effect Study of the Bonding in η^5-Cyclopentadienyliron Carbonyl Complexes[1]

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The series of complexes $CpFe(CO)_2X$, where Cp is $\eta^5\text{-}C_5H_5$ and X is a one-electron ligand such as a halide, an alkyl group, or $SiCl_3$, etc., undergoes substitution reactions in which either