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Synthesis and Structure of $ReO(PMe_3)(CH_2SiMe_3)_3$ and Reaction with Carbon Monoxide

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The reactive d^2 square-pyramidal complex $ReO(PMe_3)(CH_2SiMe_3)_3$ has been prepared by the addition of 3 equiv of Me_3SiCH_2MgCl to $ReO(OEt)Cl_2(py)_2$ in the presence of PMe_3 (63% yield) and by the reaction of an excess of PMe_3 with $Re_2O_3(CH_2SiMe_3)_6$ (86% yield). The complex $ReO(PMe_3)(CH_2SiMe_3)_3$ reacts rapidly in pentane with CO to give purple $ReO(PMe_3)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$ in 86% yield. An analogous pyridine complex, $ReO(py)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$, is prepared by adding CO to an equilibrium mixture of $Re_2O_3(CH_2SiMe_3)_6 + py = ReO(py)(CH_2SiMe_3)_3 + ReO_2(CH_2SiMe_3)_3$. The complex $Re_2O_3(CH_2SiMe_3)_6$ also reacts with O_2, DMSO, or pyridine *N*-oxide to yield the yellow oil $ReO_2(CH_2SiMe_3)_3$, which is proposed to have a trigonal-bipyramidal geometry with the oxo ligands in the equatorial plane. Photolysis of $ReO_2(CH_2SiMe_3)_3$ in hydrocarbon solvents gives the d^1–d^1 dimer $Re_2O_4(CH_2SiMe_3)_4$ as a dark yellow oil. Crystal data for $ReO(PMe_3)(CH_2SiMe_3)_3$ at −161 °C: $a = 12.090$ (3) Å, $b = 20.288$ (7) Å, $c = 19.950$ (6) Å, $Z = 8$, $d_{calcd} = 1.466$ g cm^{-3}, and space group *Pbca*.

Introduction

The metal-centered reactivity of complexes in which there are strongly π-donating ancillary ligands (e.g., alkoxides and amides) is an important area of chemical research since such cases may reveal transformations that differ from those observed with traditional soft π-acceptor ligands. One strongly π-donating ligand that has not received much attention as an ancillary group is the terminal oxo ligand. The terminal oxo ligand is a potential 4- or 6-electron donor, the donor ability depending upon the energy and symmetry of the empty orbitals available on the metal center. In this respect the oxo ligand differs from the alkoxide and amide ligands (2- or 4-electron donors) but is similar to an imide ligand.

We are interested in both the ligand and metal–oxygen bond reactivity in metal–oxo complexes. In order to establish a pattern of reactivity we wanted to study simple, well-characterized complexes with terminal oxygen ligands. Additionally, in order to enhance substrate binding to the metal center via π-back-bonding and to allow for the possibility of electron oxidation of the metal, we felt it important to have a d^n metal center, $n > 0$. With these criteria in mind we chose as our synthetic goal oxo–alkyl complexes of rhenium. Alkyl ligands were chosen because they have an available reactive metal–carbon bond, can be changed to provide for a variety of steric restrictions at the metal center, and can be varied to increase or decrease solubility. Rhenium was chosen since it was apparent from the literature that the rhenium–oxygen bond is not so strong to preclude reactivity under mild conditions[1] and rhenium in its lower oxidation states can be supported by an oxo ligand.[2]

Commonly, the synthesis of oxo–alkyl complexes is accomplished by one of three methods: (a) oxidizing an existing alkyl complex with NO, O_2, or a similar oxygen donor,[3] (b) hydrolyzing alkyl complexes,[4] or (c) alkylating oxo–halide, oxo–alkoxide, or oxo complexes with Grignard, alkyllithium, alkylzinc, or alkylaluminum reagents.[5] There

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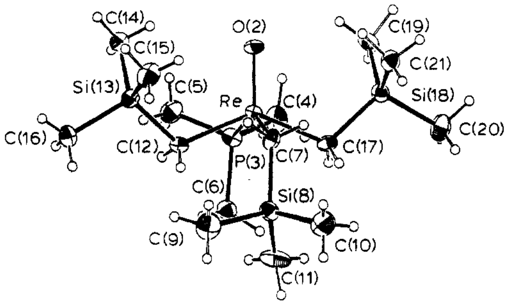

Figure 1. ORTEP drawing of $ReO(PMe_3)(CH_2SiMe_3)_3$ (1) showing the atom numbering scheme used in the tables.

are relatively few examples of method c in which simple substitution of metal chloride or alkoxide is accomplished by reaction with an alkylating agent. This is presumably due to complicating side reactions where the oxo ligand is abstracted by the alkylating agent.

In this report we establish the synthesis of the reactive d^2 oxo–alkyl complex $ReO(PMe_3)(CH_2SiMe_3)_3$ by method c and describe its reaction with carbon monoxide. We also report the synthesis of $ReO(PR_3)(CH_2SiMe_3)_3$ (PR_3 = PMe_3 or PMe_2Ph) from $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ by oxo ligand abstraction with phosphine. This latter synthetic method has not been reported for the specific case of oxo–alkyl complexes but is a well-established method for other types of oxo complexes.[6] In addition, we report on some related reactions involving $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$.

Results and Discussion

Synthesis and Structure of $ReO(PMe_3)(CH_2SiMe_3)_3$. The synthesis of $ReO(PMe_3)(CH_2SiMe_3)_3$ (1) is accomplished by the reaction of $ReO(OEt)Cl_2(py)_2$ (py = pyridine)[7] with 3 equiv of Me_3SiCH_2MgCl and 1 equiv of PMe_3 in THF/ether. Removal of the THF/ether under reduced pressure followed by two separate extractions of the residue yields a green solution from which 1 crystallizes at −80 °C as brown blocks in 63% yield. An analysis of the room-temperature ^1H and ^{13}C NMR spectra for 1 in benzene-d_6 indicates the presence of two types of (trimethylsilyl)methyl groups, two related by a mirror plane and one in a mirror plane, as well as one PMe_3 group. The IR spectrum shows a band at 997 cm^{-1} ($\nu(Re^{18}O)$ = 926 cm^{-1}) that is assigned to a Re=O stretch.[8] These data are consistent with d^2 square-pyramidal or trigonal-bipyramidal $ReO(PMe_3)(CH_2SiMe_3)_3$, and in order to confirm this expectation we performed an X-ray structure determination.

An ORTEP view of $ReO(PMe_3)(CH_2SiMe_3)_3$ is shown in Figure 1, and selected bond distances and angles are given in Table I. The structure of 1 is best described as square pyramidal with the Re atom displaced by 0.74 Å from the basal plane defined by C(7), C(12), C(17), and P(3) in the direction of the apical oxygen atom. There is a slight distortion toward a trigonal-bipyramidal geometry with P(3) and C(7) as the apical atoms (P(3)–Re–C(7) = 145.7 (3)° and C(12)–Re–C(17) = 135.3 (3)°). The Re–O, Re–C and Re–P distances are within the ranges of distances observed previously.[9]

Table I. Bond Distances (Å) and Angles (deg) for $ReO(PMe_3)(CH_2SiMe_3)_3$ (1)

Bond Distances			
Re–O(2)	1.688 (5)	Si(8)–C(10)	1.854 (12)
Re–P(3)	2.413 (2)	Si(8)–C(11)	1.839 (11)
Re–C(7)	2.121 (8)	Si(13)–C(12)	1.871 (9)
Re–C(12)	2.130 (9)	Si(13)–C(14)	1.855 (10)
Re–C(17)	2.117 (9)	Si(13)–C(15)	1.874 (10)
P(3)–C(4)	1.817 (9)	Si(13)–C(16)	1.882 (10)
P(3)–C(5)	1.807 (11)	Si(18)–C(17)	1.881 (9)
P(3)–C(6)	1.828 (10)	Si(18)–C(19)	1.861 (10)
Si(8)–C(7)	1.875 (9)	Si(18)–C(20)	1.862 (10)
Si(8)–C(9)	1.881 (11)	Si(18)–C(21)	1.863 (10)
Bond Angles			
P(3)–Re–O(2)	108.19 (20)	C(7)–Si(8)–C(11)	113.5 (4)
P(3)–Fe–C(7)	145.72 (25)	C(9)–Si(8)–C(10)	105.9 (6)
P(3)–Re–C(12)	83.21 (26)	C(9)–Si(8)–C(11)	108.4 (6)
P(3)–Re–C(17)	85.34 (27)	C(10)–Si(8)–C(11)	108.3 (6)
O(2)–Re–C(7)	106.1 (3)	C(12)–Si(13)–C(14)	112.7 (5)
O(2)–Re–C(12)	112.2 (3)	C(12)–Si(13)–C(15)	111.6 (5)
O(2)–Re–C(17)	112.5 (3)	C(12)–Si(13)–C(16)	106.4 (5)
C(7)–Re–C(12)	83.3 (4)	C(14)–Si(13)–C(15)	109.0 (5)
C(7)–Re–C(17)	82.4 (4)	C(14)–Si(13)–C(16)	107.7 (5)
C(12)–Re–C(17)	135.3 (3)	C(15)–Si(13)–C(16)	109.2 (6)
Re–P(3)–C(4)	118.4 (4)	C(17)–Si(18)–C(19)	114.4 (5)
Re–P(3)–C(5)	115.8 (4)	C(17)–Si(18)–C(20)	107.5 (5)
Re–P(3)–C(6)	111.3 (3)	C(17)–Si(18)–C(21)	109.9 (4)
C(4)–P(3)–C(5)	101.1 (5)	C(19)–Si(18)–C(20)	107.3 (5)
C(4)–P(3)–C(6)	103.1 (5)	C(19)–Si(18)–C(21)	108.7 (5)
C(5)–P(3)–C(6)	105.5 (5)	C(20)–Si(18)–C(21)	108.9 (5)
C(7)–Si(8)–C(9)	111.2 (5)	Re–C(7)–Si(8)	125.2 (5)
C(7)–Si(8)–C(10)	109.2 (5)	Re–C(12)–Si(13)	116.3 (4)
		Re–C(17)–Si(18)	114.3 (4)

The Grignard reaction described above is not a general route to d^2 oxo–alkyl complexes. For instance, we attempted to prepare $ReO(PPh_3)(CH_2SiMe_3)_3$ by the reaction of $ReOCl_3(PPh_3)_2$ with Me_3SiCH_2MgCl, but this did not yield the desired compound cleanly. Instead, we obtained a mixture of $ReO(PPh_3)(CH_2SiMe_3)_3$, $ReO(CH_2SiMe_3)_4$, $Re_2O_3(CH_2SiMe_3)_6$, and PPh_3 that we could not separate.[5b] In addition, we attempted to prepare $ReO(PMe_3)R_3$ (R = Me or CH_2CMe_3) by reaction of $ReO(OEt)Cl_2(py)_2$ with the appropriate Grignard reagent and phosphine but in both cases found no evidence for their formation.

An alternate synthesis of 1 involves the Re(VI) complex $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ (2).[5c,10] Complex 2 reacts with

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an excess of PMe_3 in pentane at room temperature to give a light brown solution and a fine white precipitate (Me_3PO by ^{31}P NMR[11]) (reaction 1). Filtration of the mixture and

$$Re_2O_3(CH_2SiMe_3)_6 + 3PMe_3 \rightarrow 2ReO(PMe_3)(CH_2SiMe_3)_3 + Me_3PO \quad (1)$$

then crystallization from pentane at -80 °C affords crystals of **1** in 86% yield. A similar procedure with PMe_2Ph produces $ReO(PMe_2Ph)(CH_2SiMe_3)_3$ in 72% yield. Although straightforward, the synthesis of **1** by reaction 1 is not as convenient as the Grignard reaction described above because the synthesis of $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ is time-consuming and not easily performed on a large scale.

Reaction 1 is related to the reactions employed by McDonald and co-workers for the synthesis of d^2 $MoO(S_2XR_2)_2$ (X = CN or P) complexes from $MoO_2(S_2XR_2)_2$ and PPh_2Et.[6,12] McDonald and co-workers proposed reactions 2 and 3 as a mechanism to account for the reduction product.

$$MoO_2(S_2XR_2)_2 + PPh_2Et \rightarrow MoO(S_2XR_2)_2 + OPPh_2Et \quad (2)$$

$$Mo_2(\mu\text{-}O)O_2(S_2XR_2)_4 \rightleftharpoons MoO(S_2XR_2)_2 + MoO_2(S_2XR_2)_2 \quad (3)$$

In this scheme, $MoO_2(S_2XR_2)_2$ is reduced by phosphine to give $MoO(S_2XR_2)_2$, which rapidly combines with starting material in an equilibrium reaction to give $Mo_2(\mu\text{-}O)O_2(S_2XR_2)_4$. The equilibrium product $MoO_2(S_2XR_2)_2$ is reduced by phosphine, and $Mo_2(\mu\text{-}O)O_2(S_2XR_2)_4$ is consumed as the equilibrium is shifted to the right. Evidence for equilibrium 3 comes from a UV-vis study of isolated $Mo_2(\mu\text{-}O)O_2(S_2XR_2)_4$ compounds in which it was found that the spectra did not obey Beer's law. Importantly, it was also observed that for the $Mo_2(\mu\text{-}O)O_2L_4$ compounds where Beer's law was obeyed and there was no evidence for an equilibrium analogous to (3), e.g., L = acac, the reaction between MoO_2L_2 and an excess of phosphine stopped at $Mo_2(\mu\text{-}O)O_2L_4$. Thus, it was shown that the $Mo_2(\mu\text{-}O)O_2L_4$ complexes that do not dissociate cannot be further reduced by phosphine and that direct reduction of the $Mo_2(\mu\text{-}O)O_2L_4$ complexes does not occur. On the basis of this, it was proposed that the $Mo_2(\mu\text{-}O)O_2(S_2XR_2)_4$ complexes are also not reduced directly by phosphine.

Given these facts, it would appear from the results of reaction 1 that $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ is in equilibrium with the dissociation products $ReO_2(CH_2SiMe_3)_3$ and $ReO(CH_2SiMe_3)_3$ and is consumed as $ReO_2(CH_2SiMe_3)_3$ is reduced. However, the following evidence suggests that this is not the case. (a) A UV-vis study for **2** in hexanes reveals the spectra do obey Beer's law. (b) Complex **2** reacts very slowly with an excess of PPh_3 (25% conversion to $ReO(PPh_3)(CH_2SiMe_3)_3$ in 5 d at 23 °C) yet $ReO_2(CH_2SiMe_3)_3$, prepared as described below, reacts rapidly with an excess of PPh_3 in benzene to give only phosphine oxide and **2**, reaction 4 (>95% conversion in <5 h at 23 °C; ^1H NMR in benzene-d_6 vs. internal standard). Furthermore, we find that addition of pyridine to a solution of **2** sets up equilibrium 5 ($K_{eq} = 10^{-2}$ at 23 °C in benzene-d_6) and that addition of PPh_3 to the equilibrium mixture gives only $ReO(py)(CH_2SiMe_3)_3$, Ph_3PO, and pyridine (^1H NMR vs. internal standard).

$$2ReO_2(CH_2SiMe_3)_3 + PPh_3 \rightarrow Re_2O_3(CH_2SiMe_3)_6 + Ph_3PO \quad (4)$$

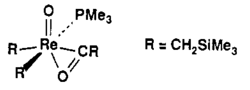
$$Re_2O_3(CH_2SiMe_3)_6 + py \rightleftharpoons ReO(py)(CH_2SiMe_3)_3 + ReO_2(CH_2SiMe_3)_3 \quad (5)$$

These results suggest that as in the case of the $Mo_2(\mu\text{-}O)O_2(S_2XR_2)_4$ system, $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ is not reduced directly by phosphine but is consumed as the dissociation product $ReO_2(CH_2SiMe_3)_3$ is reduced. Unlike the $Mo_2(\mu\text{-}O)O_2(S_2XR_2)_4$ system, however, $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ does not dissociate spontaneously but must be assisted by ligand. The difference can be rationalized by examining the coordination geometries. The complex $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ has open coordination sites at each Re center trans to the terminal oxo ligands,[5c] whereas the octahedrally coordinated Mo centers in the $Mo_2(\mu\text{-}O)O_2L_4$ complexes have no open sites.[13] Thus, ligands can attack at one open coordination site of $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ and facilitate dissociation to $ReO(ligand)(CH_2SiMe_3)_3$ and $ReO_2(CH_2SiMe_3)_3$, with subsequent reduction of $ReO_2(CH_2SiMe_3)_3$ by external phosphine. Our results suggest that PPh_3 is not as effective as pyridine or PMe_2R (R = Me or Ph) at bringing about the dissociation.

Reaction of $ReO(PMe_3)(CH_2SiMe_3)_3$ with CO. The complex $ReO(PMe_3)(CH_2SiMe_3)_3$ reacts readily with carbon monoxide. Bubbling CO through a pentane solution of $ReO(PMe_3)(CH_2SiMe_3)_3$ at room temperature, reaction 6, results in a rapid color change to purple. Short reaction times (ca. 5 min) permit the isolation of purple crystalline $ReO(PMe_3)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$ (**3**) in 86% yield.

$$ReO(PMe_3)(CH_2SiMe_3)_3 + CO \rightarrow ReO(PMe_3)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2 \quad (6)$$

The proposed structure of **3** is shown below and is based upon its ^1H, ^{13}C and ^{31}P NMR and IR spectra and elemental analysis. Specifically, the η^2-C(O)R ligand is identified by the existence of a resonance at 285.4 ppm in the ^{13}C NMR spectrum and a C–O stretch at 1505 cm^{-1} ($\nu(^{13}CO) \simeq 1460$ cm^{-1}) in the IR spectrum.[14] There is no symmetry in the proposed structure **3**, and accordingly the ^{13}C and ^1H NMR spectra show three inequivalent (trimethylsilyl)methyl ligands. The methylene carbon of one of the (trimethylsilyl)methyl groups is coupled strongly to ^{13}C in $ReO(PMe_3)(\eta^2\text{-}^{13}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$ (J_{CC} = 28 Hz) and can be assigned to the $\eta^2\text{-}^{13}C(O)CH_2SiMe_3$ ligand. The methylene group protons of the (trimethylsilyl)methyl ligands for the unlabeled complex should appear as six doublets in the ^1H NMR spectrum, members of AB quartets. In fact the spectrum is complex due to overlapping resonances and coupling to phosphorus. It was finally interpreted by 2D J-resolved NMR and is consistent with the proposed structure. The Re=O bond is intact



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since free CO_2 is not detected by gas chromatography in the reaction mixture and the Re═O stretch has been identified by oxygen-18 labeling (ν(ReO) = 970 cm^{-1}, ν($Re^{18}O$) = 915 cm^{-1}). It is noteworthy that no ^{18}O scrambling is observed in the reaction of CO with $Re(^{18}O)(PMe_3)(CH_2SiMe_3)_3$. Complex **3** appears to be only the second example of an oxo–acyl complex and is a rare example of an acyl–alkyl complex.[15,16]

The pyridine complex analogous to **3** is prepared by exploiting the equilibrium shown in (5). Addition of CO to $Re_2O_3(CH_2SiMe_3)_6$ partially dissolved in pyridine-d_5 initially gives a green solution that by ^1H and ^{13}C NMR contains $ReO(py)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$ (**4**) and $ReO_2(CH_2SiMe_3)_3$ (see below) in the expected ratio based upon reactions 5 and 7. Consistent with this formulation

$$ReO(py)(CH_2SiMe_3)_3 + CO \rightarrow ReO(py)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2 \quad (7)$$

of the mixture, the addition of an excess of PMe_3 to the product mixture gives $ReO(PMe_3)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$, $ReO(PMe_3)(CH_2SiMe_3)_3$, and $P(O)Me_3$. All attempts to isolate **4** have failed due to loss of pyridine with decomposition under vacuum.

The mechanism of the insertion reactions 6 and 7 is not known. We assume that the square-pyramidal complex $ReO(CO)(CH_2SiMe_3)_3$ is involved, although we have not been able to detect any intermediates by monitoring reaction 6 with ^1H NMR at low temperature.[17]

For both reactions 6 and 7 long CO contact times result in complex reaction mixtures (for **3**, $t_{1/2} \sim 8$ h), and, even in the absence of excess CO, $ReO(py)(C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$ is not indefinitely stable in solution at room temperature. Complex **1** also reacts with isocyanides to give a mixture of products, but, interestingly, ethylene does not react with **1**. This is presumably for steric reasons since in the initially formed complex, i.e., square-pyramidal $ReO(C_2H_4)(CH_2SiMe_3)_3$, the organic ligand would have to lie in the xy plane (x and y axes along the $Re\text{–}CH_2SiMe_3$ vectors) in order for π-bonding between the π^* MO of the organic ligand and the metal center HOMO, d_{xy}, to occur. The bulky (trimethylsilyl)methyl ligands should prevent this, and we are trying to prepare analogues of **1** with smaller alkyl ligands to avoid the steric congestion.

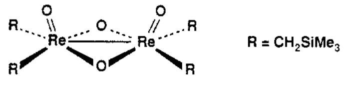
Synthesis of $ReO_2(CH_2SiMe_3)_3$ and $Re_2O_4(CH_2SiMe_3)_4$. In order to better define equilibrium 5 we have prepared $ReO_2(CH_2SiMe_3)_3$ (**5**) independently by reacting $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ with O_2, DMSO, or, most cleanly, pyridine N-oxide (reaction 8).[18] Addition of PPh_3

$$Re_2O_3(CH_2SiMe_3)_6 + C_5H_5NO \rightarrow 2ReO_2(CH_2SiMe_3)_3 + C_5H_5N \quad (8)$$

to a solution of **5** rapidly regenerates $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$ (plus Ph_3PO, reaction 4) and addition of PMe_3 gives $ReO(PMe_3)(CH_2SiMe_3)_3$. Complex **5** is a bright yellow photosensitive oil. If reaction 8 is carried out in the absence of light, **5** is produced quantitatively as judged by ^1H NMR (vs. CH_3CN internal standard).

The ^1H and ^{13}C NMR spectra for **5** reveal resonances assignable to two different types of alkyl ligands. In the ^1H NMR spectrum two singlets are observed in a ratio of 2:1 for the methylene protons, indicating the alkyl ligands all lie in a mirror plane. The IR spectrum shows bands at 989 and 941 cm^{-1}, the latter of greater intensity, that are assigned to the symmetric and antisymmetric stretches, respectively, of the cis dioxo group.[8,13] Thus the spectroscopic data suggests that **5** has a tbp geometry with the two oxygen atoms in the equatorial plane. A similar structure has been proposed for the analogous imido complexes.[19]

In the absence of oxygen, $ReO_2(CH_2SiMe_3)_3$ in benzene or pentane is photolyzed ($t_{1/2}$ = 5–6 h) by Pyrex-filtered fluorescent light to give $Re_2O_4(CH_2SiMe_3)_4$ (**6**) as a dark yellow oil. The proposed structure of **6** is shown below and is based upon the similarity between its spectroscopic properties and those of the structurally characterized derivative $Re_2(\mu\text{-}O)_2O_2(CH_2CMe_3)_4$.[20] It is noteworthy that the photolysis reaction of **5** is different from the photolysis of $Re(NCMe_3)_2(CH_2SiMe_3)_3$, which is reported to give the alkylidene complex $Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$ by α-hydrogen abstraction.[19]



6

Concluding Remarks. Two syntheses of the reactive monomeric d^2 oxo–alkyl complex **1** are reported. In the one case, we were able to prepare **1** by reaction of $ReO(OEt)Cl_2(py)_2$ with Me_3SiCH_2MgCl in the presence of PMe_3. We have not been able to develop this method as a general route for other alkyl ligands. The other synthesis of **1** involves phosphine reduction of the Re(VI) complex $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$. The evidence suggests that this reduction proceeds subsequent to attack by phosphine and is therefore different from the related Mo reductions.[6,12]

Complex **1** reacts with carbon monoxide to give the oxo–acyl complex $ReO(PMe_3)(\eta^2\text{-}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$ (**3**). Complex **3** appears to be only the second example of an oxo–acyl complex, the other being $W(\eta^5\text{-}C_5H_5)(O)(C(O)Me)(C_2H_2)$,[14] and is one of only a few examples of an acyl–alkyl complex.[15] Further studies concerning the reactivity of complexes **1** and **3** are in progress.

Experimental Section

General Techniques. All experiments were performed under prepurified nitrogen or argon atmosphere by using standard Schlenk techniques or a Vacuum Atmospheres drybox. Solvents used in the preparations were purified by standard techniques and were dry and oxygen-free. The various NMR spectra were recorded on Bruker instruments (AM-500, AM-300, AM-250, and WM-300-WB (^{31}P NMR) spectrometers). The ^1H NMR chemical shifts are reported relative to the ^1H impurity in the solvent (benzene-d_6, δ 7.15; $CDCl_3$, δ 7.24), and ^{13}C NMR chemical shifts are reported relative to the ^{13}C triplet of benzene-d_6 set at δ 128.0. Phosphorus NMR spectra are referenced to external H_3PO_4 with positive chemical shifts downfield. Infrared spectra are referenced externally to the 1601 cm^{-1} band of polystyrene. Microanalyses were performed by Dornis and Kolbe, Federal Republic of Germany, or Galbraith Microanalytical Laboratory, Knoxville, TN.

$Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$.[5c,10] To a cold solution (0 °C) of $Al(CH_2SiMe_3)_3$ (6.5 mL, 20.7 mmol) in hexane (30 mL) was added $ReO_3(OSiMe_3)$ (2.23 g, 6.9 mmol) via solid-addition tube over a period of 45 min. After the addition was complete, the dark reaction mixture was allowed to warm to room temperature. It was stirred for 5 h and then chromatographed under N_2 on Al_2O_3

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[15] Alt, H. G.; Hayen, H. I. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 497–498.

[16] Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723–2728.

[17] The d^2 complex $W(O)Cl_2(CO)(PMePh_2)_2$ has recently been prepared: Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545–3547.

[18] $ReO_2(Me)_3$ is known: See ref 3b.

[19] Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505–1513.

[20] Cai, S.; Hoffman, D. M.; Woo, H.-G.; Huffman, J. C. *Inorg. Chem.*, in press. See also ref 5d.

(activity grade V, hexane eluant). Crystallization from hexane at −20 °C afforded red blocks (yield 1.08 g, 33%).

UV–vis (hexanes; λ_{max}, nm (ϵ, L M^{-1} cm^{-1})): 458 (14 300), 358 (2600), 318 (2550).

$ReO(PMe_3)(CH_2SiMe_3)_3$. Method A. In a Schlenck reaction flask, $ReO(OEt)Cl_2(py)_2$ (0.80 g, 1.68 mmol)[7] was dissolved in THF (125 mL). The solution was frozen (−196 °C), and PMe_3 (2 mmol) was condensed into the flask via a calibrated vacuum manifold. The mixture was allowed to warm to room temperature, and an ether solution of Me_3SiCH_2MgCl (5.04 mmol) was added via syringe. The blue solution gradually changed to dark brown over a period of 48 h. The volatiles were removed under reduced pressure, and the residue was extracted with toluene (5 × 20 mL) and filtered. After the toluene was removed under reduced pressure, the residue was extracted with pentane (6 × 20 mL) and filtered and the solution then reduced in volume. Cooling at −80 °C for 12 h produced brown crystals that were isolated by removing the supernatant via a cannula (yield 0.567 g, 63%). **Method B.** A red solution of $Re_2O_3(CH_2SiMe_3)_6$ (0.356 g, 0.38 mmol) in pentane (50 mL) was frozen (−196 °C) and the flask evacuated. PMe_3 (1.5 mmol) was then condensed into the flask via a calibrated vacuum manifold. After the mixture was allowed to warm to room temperature, it was stirred in the absence of light for 12 h. The brown reaction mixture was then filtered through a glass frit to remove a fine white precipitate. The filtrate was reduced in volume (ca. 5 mL) and placed in a freezer at −20 °C for 4 h and then −80 °C for 12 h. This produced brown crystals that were isolated by decanting the supernatant liquid via cannula (yield 0.350 g, 86%). Anal. Calcd for $ReSi_3POC_{15}H_{42}$: C, 33.37; H, 7.84; Si, 15.61. Found: C, 33.45; H, 7.87; Si, 15.86.

^1H NMR (C_6D_6): δ 0.05 (s, 9, $CH_2Si\mathit{Me}_3$), 0.42 (s, 18, $CH_2Si\mathit{Me}_3$), 0.95 (d, 9, J_{PH} = 9.4 Hz, $P\mathit{Me}_3$), 3.20 (dd, 2, J_{HH} = 8 Hz, J_{PH} = 6.8 Hz, $C\mathit{H}_2SiMe_3$), 3.61 (dd, 2, J_{HH} = 8 Hz, J_{PH} = 14 Hz, $C\mathit{H}_2SiMe_3$), 4.29 (d, 2, J_{PH} = 2.8 Hz, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (C_6D_6): δ 33.24 (t of d, J_{PC} = 21 Hz, J_{CH} = 117 Hz, $\mathit{C}H_2SiMe_3$), 28.63 (t, J_{CH} = 117 Hz, $\mathit{C}H_2SiMe_3$), 13.88 (q of d, J_{PC} = 29 Hz, J_{CH} = 130 Hz, $P\mathit{Me}_3$), 4.25 (q, J_{CH} = 118 Hz, $CH_2Si\mathit{Me}_3$), 2.70 (q, J_{CH} = 118 Hz, $CH_2Si\mathit{Me}_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −1.68 (s). IR (Nujol, CsI, cm^{-1}): ν(Re=O) 997 s (ν(Re=^{18}O) 926), 1426 m, 1286 m, 1252 m, 1239 s, 1166 vw, 1011 m, 959 s, 944 s, 836 vs, 778 m, 755 m, 745 m, 729 s, 706 m, 675 m, 608 w, 543 w, 508 w, 491 w, 354 w, 292 w, 274 w.

$ReO(PMe_2Ph)(CH_2SiMe_3)_3$. The preparation is analogous to the method B preparation of the PMe_3 complex except that crystallization is from CH_3CN (yield 72%). Anal. Calcd for $ReSi_3POC_{20}H_{44}$: C, 39.90; H, 7.37; Si, 14.00. Found: C, 39.44; H, 7.05; Si, 13.97.

^1H NMR (C_6D_6): δ 7.12 (m, 2, $PMe_2\mathit{Ph}$), 7.02 (m, 3, $PMe_2\mathit{Ph}$), 4.47 (d, 2, J_{PH} = 2.7 Hz, $C\mathit{H}_2SiMe_3$), 3.79 (dd, 2, J_{HH} = 8 Hz, J_{PH} = 14.7 Hz, $C\mathit{H}_2SiMe_3$), 3.17 (dd, 2, J_{HH} = 8 Hz, J_{PH} = 6.8 Hz, $C\mathit{H}_2SiMe_3$), 1.22 (d, 6, J_{PH} = 8.9 Hz, $P\mathit{Me}_2Ph$), 0.30 (s, 18, $CH_2Si\mathit{Me}_3$), 0.09 (s, 9, $CH_2Si\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 131.0 (d, 2, J_{PC} = 8.8 Hz, $PMe_2\mathit{Ph}$), 129.4 (s, 1, $PMe_2\mathit{Ph}$), 128.8 (d, 2, J_{PC} = 9.4 Hz, $PMe_2\mathit{Ph}$), 32.7 (d, 1, J_{PC} = 22.0 Hz, $\mathit{C}H_2SiMe_3$), 29.1 (s, 2, $\mathit{C}H_2SiMe_3$), 12.6 (d, 2, J_{PC} = 30.8 Hz, $P\mathit{Me}_2Ph$), 4.33 (s, 3, $CH_2Si\mathit{Me}_3$), 2.61 (s, 6, $CH_2Si\mathit{Me}_3$). IR (Nujol, CsI, cm^{-1}): 1487 m, 1434 s, 1416 w, 1409 vw, 1337 w, 1316 w, 1295 s, 1283 s, 1251 s, 1238 vs, 1189 vw, 1157 vw, 1130 vw, 1103 s, 1068 vw, 1001 vs, 968 m, 939 s, 909 s, 905 s, 823 vs, 774 m, 744 w, 734 m, 724 m, 707 m, 699 w, 686 m, 673 s, 608 m, 540 w, 483 s, 416 s, 329 w, 272 w.

$ReO(PMe_3)(C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$. Excess carbon monoxide was added via a needle to a solution of $ReO(PMe_3)(CH_2SiMe_3)_3$ (0.283 g, 0.52 mmol) in pentane (20 mL). The solution quickly turned purple. After the solution was stirred for 5 min, the CO was removed and the volume reduced to 5 mL under reduced pressure. The remaining pentane solution was warmed to redissolve some purple precipitate that had formed on reducing the volume, cooled, and then placed in a freezer at −80 °C for 12 h. This produced purple crystals that were isolated by removing the supernatant liquid via a cannula (yield 0.253 g, 86%). Anal. Calcd for $ReSi_3PO_2C_{16}H_{42}$: C, 33.84; H, 7.45. Found: C, 33.89; H, 7.71.

^1H NMR (C_6D_6, 2D *J* resolved): δ 3.62 (d, 1, J_{HH} = 14.8 Hz, $C\mathit{H}_2SiMe_3$), 3.42 (dd, 1, J_{HH} = 11.4 Hz, J_{PH} = 3.3 Hz, $C\mathit{H}_2SiMe_3$), 2.62 (dd, 1, J_{HH} = 10.8 Hz, J_{PH} = 14.8 Hz, $C\mathit{H}_2SiMe_3$), 2.56 (dd, 1, J_{HH} = 10.8 Hz, J_{PH} = 19.7 Hz, $C\mathit{H}_2SiMe_3$), 2.52 (dd, 1, J_{HH} = 14.8 Hz, J_{PH} = 2.3 Hz, $C\mathit{H}_2SiMe_3$), 2.43 (dd, 1, J_{HH} = 11.4 Hz, J_{PH} = 3.3 Hz, $C\mathit{H}_2SiMe_3$), 0.86 (d, 9, J_{PH} = 9.7 Hz, $P\mathit{Me}_3$), 0.44, 0.40, 0.19 (s, 9, $CH_2Si\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 42.94 (s, $\mathit{C}H_2SiMe_3$), 34.17 (d, J_{PC} = 45 Hz, $\mathit{C}H_2SiMe_3$), 21.02 (s, $\mathit{C}H_2SiMe_3$), 14.78 (d, J_{PC} = 28 Hz, $P\mathit{Me}_3$), 3.43, 2.35, 0.34 (s, $CH_2Si\mathit{Me}_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −25.5 (s). IR (Nujol, CsI, cm^{-1}): ν(CO) 1505 m (ν(^{13}CO) ~1460), ν(Re=O) 970 s (ν(Re=^{18}O) 915), 1306 w, 1288 m, 1281 m, 1249 s, 1234 s, 1209 m, 1076 w, 1028 m, 1006 m, 945 s, 925 m, 839 s, 763 m, 744 m, 735 m, 715 m, 706 m, 672 m, 606 w, 528 w, 512 w, 342 w.

Table II. Crystal Data Summary for 1

color of crystal	brown
space group	*Pbca*
cell dimens	
temp, °C	−161
a, Å	12.090 (3)
b, Å	20.288 (7)
c, Å	19.950 (6)
Z (molecules/cell)	8
V, Å^3	4893.54
d_{calcd}, g cm^{-3}	1.466
wavelength, Å	0.71069
linear abs coeff, cm^{-1}	52.431
detector to sample dist, cm	22.5
sample to source dist, cm	23.5
takeoff angle, deg	2.0
av ω scan width at half-height, deg	0.25
scan speed, deg/min	4.0
scan width, deg (+ dispersion)	2.0
single bkgd time at extremes of scan, s	6
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
total no. of reflctns collected	3926
no. of unique reflections	3186
no. with $F_o > 3.00\sigma(F_o)$	2598
$R(F)$	0.0362
$R_w(F)$	0.0383
goodness of fit for last cycle	0.934
largest Δ/σ for last cycle	0.05

$ReO(PMe_3)(^{13}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$. ^1H NMR (C_6D_6, 90 atom % ^{13}CO, 2D *J* resolved): δ 3.62 (dd, 1, J_{HH} = 14.8 Hz, J_{CH} = 5.6 Hz, $^{13}C(O)C\mathit{H}_2SiMe_3$), 3.42 (dd, 1, J_{HH} = 11.7 Hz, J_{PH} = 3.9 Hz, $C\mathit{H}_2SiMe_3$), 2.62 (ddd, 1, J_{HH} = 10.8 Hz, J_{PH} = 15.3 Hz, J_{CH} = 1.5 Hz, $C\mathit{H}_2SiMe_3$), 2.56 (ddd, 1, J_{HH} = 10.8 Hz, J_{PH} = 19.4 Hz, J_{CH} = 1.5 Hz, $C\mathit{H}_2SiMe_3$), 2.52 (ddd, 1, J_{HH} = 14.8 Hz, J_{PH} = 1.9 Hz, J_{CH} = 6.7 Hz, $^{13}C(O)C\mathit{H}_2SiMe_3$), 2.43 (ddd, 1, J_{HH} = 11.7 Hz, J_{PH} = 3.9 Hz, J_{CH} = 1 Hz, $C\mathit{H}_2SiMe_3$) 0.86 (d, 9, J_{PH} = 9.7 Hz, $P\mathit{Me}_3$), 0.44, 0.40, 0.19 (s, 9, $CH_2Si\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 90 atom % ^{13}CO): δ 285.41 (d, J_{PC} = 5.0 Hz, $^{13}\mathit{C}(O)CH_2SiMe_3$), 42.83 (d, J_{CC} = 28.3 Hz, $^{13}C(O)\mathit{C}H_2SiMe_3$), 34.14 (d, J_{PC} = 45.2 Hz, $\mathit{C}H_2SiMe_3$), 20.98 (s, $\mathit{C}H_2SiMe_3$), 14.73 (d, J_{PC} = 27.9 Hz, $P\mathit{Me}_3$), 3.43, 2.35, 0.34 (s, $CH_2Si\mathit{Me}_3$).

$ReO(py)(^{13}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$. To an NMR tube containing $Re_2O_3(CH_2SiMe_3)_6$ (0.015 g) partially dissolved in pyridine-d_5 (0.5 mL) was added ^{13}CO (90 atom % ^{13}C) via a needle (ca. 1 atm pressure). The NMR data were collected after the red solution had changed to green (45 min).

^1H NMR (pyridine-d_5): δ 4.32, 2.26 (d of an AB q, 1, J_{HH} = 11.3 Hz, $C\mathit{H}_2SiMe_3$), 4.04 (dd, 1, J_{HH} = 11.0 Hz, J_{CH} = 5.2 Hz, $^{13}C(O)C\mathit{H}_2SiMe_3$), 3.43 (dd, 1, J_{HH} = 11.0 Hz, J_{CH} = 7.7 Hz, $^{13}C(O)C\mathit{H}_2SiMe_3$), 2.80 (d, 1, J_{HH} = 11.6 Hz, $C\mathit{H}_2SiMe_3$), 1.73 (dd, 1, J_{HH} = 11.6 Hz, J_{CH} = 1.3 Hz, $C\mathit{H}_2SiMe_3$), 0.31, 0.18, −0.13 (s, 9, $CH_2Si\mathit{Me}_3$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 287.50 (s, $^{13}\mathit{C}(O)CH_2SiMe_3$), 42.89 (d, J_{CC} = 30.8 Hz, $^{13}C(O)\mathit{C}H_2SiMe_3$), 36.33, 25.05 (s, $\mathit{C}H_2SiMe_3$), 2.15, 2.05, −0.83 (s, $CH_2Si\mathit{Me}_3$). Resonances assigned to $ReO_2(CH_2SiMe_3)_3$ were observed in both spectra.

$ReO_2(CH_2SiMe_3)_3$. The following procedure is carried out in the absence of light. To a mixture of $Re_2O_3(CH_2SiMe_3)_6$ (0.100 g, 0.11 mmol) and pyridine *N*-oxide (0.010 g, 0.11 mmol) was added hexane (15 mL). Over a period of 4 days, the orange solution gradually changed to yellow. The volatiles were then removed under reduced pressure to give a yellow oil. All attempts to crystallize the oil from various solvents failed. The reaction is quantitative in benzene-d_6 by ^1H NMR (vs. CH_3CN internal standard). The IR data and elemental analysis reported below

Table III. Fractional Coordinates for the Non-Hydrogen Atoms of $ReO(PMe_3)(CH_2SiMe_3)_3$ (1)[a]

atom	*x*	*y*	*z*
Re(1)	6927.7 (3)	1798.6 (2)	1033.4 (2)
O(2)	8221 (5)	2018 (3)	805 (3)
P(3)	5648 (2)	2268 (1)	237 (1)
C(4)	5710 (8)	1990 (5)	−627 (4)
C(5)	5729 (8)	3151 (5)	130 (5)
C(6)	4216 (7)	2099 (4)	475 (4)
C(7)	7101 (7)	1230 (4)	1920 (4)
Si(8)	5929 (2)	931 (1)	2455 (1)
C(9)	5747 (10)	1467 (5)	3216 (5)
C(10)	6262 (9)	97 (5)	2777 (5)
C(11)	4601 (8)	888 (6)	2008 (5)
C(12)	6197 (7)	2496 (4)	1698 (4)
Si(13)	7141 (2)	3142 (1)	2046 (1)
C(14)	7851 (8)	3622 (5)	1383 (5)
C(15)	8204 (8)	2777 (5)	2620 (5)
C(16)	6242 (8)	3727 (5)	2534 (5)
C(17)	6447 (7)	879 (4)	625 (4)
Si(18)	7552 (2)	459 (1)	117 (1)
C(19)	8082 (8)	954 (5)	−599 (5)
C(20)	6941 (9)	−309 (5)	−236 (5)
C(21)	8738 (8)	234 (5)	668 (5)

[a] Fractional coordinates are $\times 10^4$.

are taken from a sample condensed on an H_2O-cooled coldfinger (40 °C, 10^{-4} torr). Anal. Calcd for $ReSi_3O_2C_{12}H_{33}$: C, 30.04; H, 6.93, Si, 17.56. Found: C, 30.00; H, 6.65; Si, 17.52.

^1H NMR (C_6D_6): δ 2.25 (s, 4, CH_2SiMe_3), 2.22 (s, 2, CH_2SiMe_3), 0.20 (s, 18, CH_2SiMe_3), 0.17 (s, 9, CH_2SiMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 45.00, 38.27 (s, CH_2SiMe_3), 1.95, 0.14 (s, CH_2SiMe_3). IR (Nujol, KBr, cm^{-1}): 1407 w, 1300 w, 1262 m, 1250 m, 1010 w, 989 m, 941 s, 841 s, 763 w, 753 w, 683 m, 615 w.

$Re_2(\mu\text{-}O)_2O_2(CH_2SiMe_3)_4$. In a Schlenk reaction flask, $ReO_2(CH_2SiMe_3)_3$ (0.100 g, 0.21 mmol) was dissolved in pentane (30 mL). The yellow solution was photolyzed at room temperature with Pyrex-filtered fluorescent light for 5 days. The yellow solution gradually changed to dark yellow. The volatiles were removed under vacuum to give a yellow oil. The reaction is approximately 70% in benzene-d_6 by ^1H NMR (vs. CH_3CN internal standard). The spectroscopic data and elemental analysis reported below are taken from a sample condensed on a H_2O-cooled coldfinger (60 °C, 10^{-4} torr). Anal. Calcd for $Re_2Si_4O_4C_{16}H_{44}$: C, 24.47; H, 5.65. Found: C, 24.46; H, 5.63.

^1H NMR ($CDCl_3$): δ 3.02 and 2.91 (d of an AB q, 8, J_{HH} = 11 Hz, CH_2SiMe_3), 0.15 (s, 36, CH_2SiMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 44.49 (s, CH_2SiMe_3), 1.37 (s, CH_2SiMe_3). IR (Nujol, CsI, cm^{-1}): 1410 w, 1351 w, 1304 w, 1265 s, 1251 s, 1030 s, 1020 sh, 955 m, 838 s, 778 w, 753 w, 699 m, 685 s, 620 w, 562 w, 537 w, 494 m.

Crystallography. General operating procedures and listings of programs used at the Indiana University Molecular Structure Center have been described.[21] Crystal data are summarized in Table II, and final fractional coordinates for the non-hydrogen atoms are given in Table III.

A suitable crystal of 1 was located and transferred to the goniostat under inert atmosphere. It was then cooled to −161 °C for characterization and data collection. A systematic search of reciprocal space located diffraction maxima with orthorhombic symmetry and systematic absences corresponding to the unique space group *Pbca*. Subsequent solution and refinement confirmed this choice.

Data were collected in the usual manner by using a continuous θ–2θ scan technique. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were located in a difference Fourier phased on the non-hydrogen atoms and were included in the final cycles of refinement. Non-hydrogen atoms were assigned anisotropic thermal parameters, and hydrogens were allowed to vary isotropically. Data were corrected for absorption and an isotropic extinction parameter was utilized during the refinement.

A final difference Fourier was essentially featureless, with the largest peak being 0.50 e/Å^3.

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Registry No. 1, 109889-90-9; $Re_2(\mu\text{-}O)O_2(CH_2SiMe_3)_6$, 56519-48-3; $ReO(PMe_2Ph)(CH_2SiMe_3)_3$, 109889-91-0; $ReO(PMe_3)(C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$, 109889-92-1; $ReO(PMe_3)(^{13}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$, 109889-93-2; $ReO(py)(^{13}C(O)CH_2SiMe_3)(CH_2SiMe_3)_2$, 109889-94-3; $ReO_2(CH_2SiMe_3)_3$, 109889-95-4; $Re_2O_4(CH_2SiMe_3)_4$, 109889-96-5; $Al(CH_2SiMe_3)_3$, 41924-27-0; $ReO_3(OSiMe_3)$, 16687-12-0; $ReO(OEt)Cl_2(py)_2$, 64069-70-1; PMe_3, 594-09-2; PMe_2Ph, 672-66-2; Me_3SiCH_2MgCl, 13170-43-9; pyridine-d_5, 7291-22-7.

Supplementary Material Available: Complete tables of fractional coordinates and thermal parameters (4 pages); a listing of F_o and F_c (7 pages). Ordering information is given on any current masthead page.

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(21) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.