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Multiple Bonds between Main-Group Elements and Transition Metals. 104.[†] (σ-Aryl)trioxorhenium(VII) Complexes: Syntheses, Structural Characterization, and Properties

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Reaction of arylzinc reagents with 2 equiv of Re$_2$O$_7$ in THF affords in good yields the (σ-aryl)trioxorhenium(VII) complexes MesReO$_3$ (1) (Mes = 2,4,6-trimethylphenyl), XyReO$_3$ (2) (Xy = 2,6-dimethylphenyl), Ph(THF)ReO$_3$ (4) (Ph = phenyl), and TolReO$_3$ (5) (Tol = 4-methylphenyl). The weakly coordinated THF in 4 is easily removed to afford PhReO$_3$ (3). Complexes 3 and 4 are in a fast equilibrium, which is shifted toward 3, even in the presence of excess THF. The reaction of (Ph$_f$)$_2$Zn (Ph$_f$ = pentafluorophenyl) with Re$_2$O$_7$ is catalyzed by ZnCl$_2$ and produces, after addition of quinuclidine, the five-coordinate complex (Ph$_f$)(quin)ReO$_3$ (6) (quin = N(CH$_2$CH$_2$)$_3$CH). The new organozinc reagent (Me$_3$SiO-Xy)ZnCl(THF) (7) (Me$_3$SiO-Xy = 2,6-dimethyl-4-(trimethylsiloxy)phenyl) reacts with Re$_2$O$_7$ to yield the deep yellow complex (Me$_3$SiO-Xy)ReO$_3$ (8) in high yields. Reaction of 8 with HCl gives the first, pale yellow hydroxyphenyl complex (HO-Xy)ReO$_3$ (9) (HO-Xy = 2,6-dimethyl-4-hydroxyphenyl). The Lewis acidity of the Re center in the RReO$_3$ complexes depends on both electronic and steric factors of the aryl group R. Thus, 1 does not form adducts with THF and quinuclidine, whereas 6 is isolable only as a quinuclidine adduct. Compound 3 forms the labile THF adduct 4 and the strong quinuclidine adduct Ph(quin)ReO$_3$ (10). All compounds have been characterized by IR and ^{1}H, ^{13}C, and ^{17}O NMR spectroscopy. The ^{13}C NMR data for the series 1–3 and 5 indicate that the ReO$_3$ group is a strong electron-withdrawing substituent. Complexes 1, 4, and 8 have been characterized by single-crystal X-ray diffraction. Complex 1 crystallizes in two different space groups: monoclinic $P2_1/m$ (type 1A) and orthorhombic *Pnma* (type 1B), from diethyl ether and *n*-pentane, respectively. Structure 1A has two different molecules, 1A1 and 1A2, in the unit cell, differing by the relative orientation of the phenyl plane to the ReO$_3$ fragment (1A: a = 8.210 (1) Å, b = 22.924 (3) Å, c = 8.141 (1) Å, β = 102.21 (1)°, Z = 6. 1B: a = 7.343 (2) Å, b = 10.166 (2) Å, c = 13.600 (3) Å, Z = 4). Complex 4: monoclinic $P2_1/c$, a = 8.580 (1) Å, b = 11.562 (1) Å, c = 12.407 (2) Å, β = 109.34 (7)°, Z = 4. Complex 8: monoclinic $P2_1/m$, a = 8.245 (1) Å, b = 7.492 (1) Å, c = 11.991 (2) Å, β = 100.83 (<1)°, Z = 2. Molecules 1A, 1B, and 8 are pseudotetrahedral. In comparison, the rhenium center in 4 has a distorted trigonal-bipyramidal coordination geometry, with the three oxo ligands defining the equatorial plane. The Re–C bond length is noticeably shorter in molecule 1A1 (2.006 (9) Å) than in 1A2 (2.063 (7) Å), 1B (2.075 (8) Å), and 8 (2.04 (1) Å). The different geometry in 4 has no influence on the Re–C bond length (2.071 (3) Å). Thermal degradation of 3 at 60–80 °C gives only biphenyl, indicating an intermolecular decomposition pathway. In comparison, 1 and 2 are stable up to 200 °C. This remarkable difference in thermal stability can be attributed to increased steric hindrance, thus avoiding intermolecular coupling decomposition.

Introduction

In recent years there has been considerable interest in developing convenient synthetic routes to polyaryl, aryl–halogeno, or aryl–oxo transition metal complexes, as the preparation and isolation of these compounds, especially those containing the simplest aryl radical, i.e., the phenyl group, has proved to be difficult.[1,2] These difficulties do not appear to arise from thermodynamic factors as some phenyl–transition metal complexes are known to be stable. However, kinetically favored decomposition pathways are often accessible for such complexes. Two major routes of decomposition are now well accepted. The first one involves reductive coupling of the aryl groups, resulting in the formation of a biaryl product.[3] The second is initiated by an ortho hydrogen abstraction to give a benzyne complex, which may then further rearrange or otherwise react.[4] These studies have been complicated by the fact that the metal–aryl bonds are also reactive toward protic reagents to produce the corresponding arene, thereby yielding no information about the actual mechanism of decomposition related to the metal–aryl bond.

To overcome these problems, ortho-substituted aryls such as 2,4,6-trimethylphenyl (Mes), 2,6-dimethylphenyl, 2-methylphenyl, and 2-methoxyphenyl have successfully been used. This has lead to the syntheses of stable aryl complexes of Ti, Zr, Hf, V, Mo, W, Re, and Os in higher oxidation states.[1-4] Even so, complexes containing the simple phenyl group are not numerous; examples include Os^{IV}(σ-C$_6$H$_5$)$_4$,[2] (σ-C$_6$H$_5$)Re^{VII}Cl$_2$(N^{t}Bu)$_2$,[5] (σ-C$_6$H$_5$)$_2$Mo^{VI}O$_2$(bpy),[6] (σ-C$_6$H$_5$)V^{V}O(O^{i}Pr)$_2$,[7] the paramagnetic complex (σ-C$_6$H$_5$)V^{III}(salen),[8] and (σ-C$_6$H$_5$)V^{V}OCl$_2$, for which the decomposition pathway has been reported in detail.[9] Interestingly, the series Mes$_2$MO$_2$ is known for

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[‡] Alexander von Humboldt Junior Research Fellow, 1990–1991. On leave from the CNRS-Université Louis Pasteur de Strasbourg, France.

[§] Alexander von Humboldt Junior Research Fellow, 1991–1992.

(1) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243.

(2) (a) Stavropoulos, P.; Savage, P. D.; Tooze, R. P.; Wilkinson, G.; Hussain, B.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1987, 557. (b) Koschmieder, S. U.; Wilkinson, G. *Polyhedron* **1991**, *10*, 135.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 1137.

(4) (a) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (b) For a recent introduction to benzyne complexes see: Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Organometallics* **1989**, *8*, 415 and references cited therein.

(5) Danopoulos, A. A.; Longley, C. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1989**, *8*, 2657.

(6) Schrauzer, G. N.; Zhang, X.; Liu, N. H.; Schlemper, E. O. *Organometallics* **1988**, *7*, 279.

(7) Choukroun, R., Sabo, S. *J. Organomet. Chem.* **1979**, *182*, 221.

(8) Rosset, J.-M.; Floriani, C.; Mazzani, M.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1990**, *29*, 3991.

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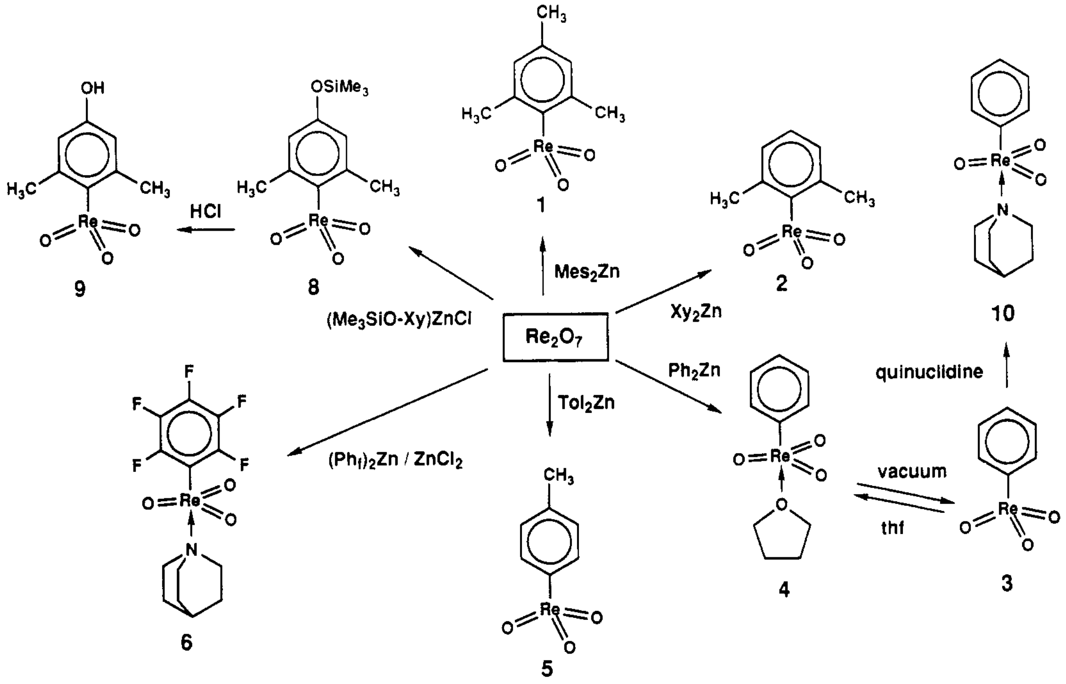
Scheme I



Mo,[10] Re, and Os,[11] whereas no phenyl analogues could be isolated despite numerous attempts.

Previous synthetic strategies for the compounds quoted above use lithium, magnesium, zinc, mercury, or cadmium aryl reagents and a metal halide or oxo halide precursor. In the case of substituted phenyl derivatives, these methods can afford good yields. Therefore, a strategy to isolate high-valent metal phenyl complexes is to suppress any decomposition pathway involving the phenyl group. This might be achieved through the preparation of complexes containing only *one* phenyl ligand to prevent intramolecular reductive elimination (note that intermolecular coupling is still possible but should be slower than the intramolecular process) and having a d^0 transition-metal center to avoid oxidative addition of a C–H bond in the ortho position. Such complexes should also possess an uncrowded coordination sphere and require smooth workup conditions to avoid benzyne formation.

The ready availability of the methyl-[12a,b] and (pentamethylcyclopentadienyl)trioxorhenium,[12c] containing rhenium in the highest oxidation state (VII) as well as the uncrowded coordination sphere of methyltrioxorhenium(VII) ("MTO"),[13] prompted us to verify the σ-phenyl and other σ-aryl derivatives. In addition, we were interested to bind an aryl group to the trioxorhenium moiety to determine whether any resonance would occur within the molecule (as in nitrobenzene) and whether this resonance could be enhanced through an appropriate para functionalization of the aromatic group toward electronic "push–pull systems". Here, we report the preparation and the characterization of (σ-phenyl)trioxorhenium(VII) and a series of substituted and functionalized (σ-aryl)trioxorhenium(VII) complexes and compare their properties. A preliminary account of this work has been published previously.[14]

Results and Discussion

Synthesis. Reaction of Re_2O_7 with Mes_2Zn in a molar ratio of 2 to 1 in tetrahydrofuran (THF) affords the organorhenium(VII) complex $MesReO_3$ (1) in 30% yield based on rhenium (60% of the theory). Concomitant formation of the zinc perrhenate $Zn(ReO_4)_2(THF)_2$ (47%) is observed in this reaction (eq 1, Scheme I).

$$Mes_2Zn + 2\,Re_2O_7 \xrightarrow{thf} \underset{1}{2\,MesReO_3} + Zn(ReO_4)_2(thf)_2 \quad (1)$$

The same method was used for the preparation of $XyReO_3$ (2) (Xy = 2,6-dimethylphenyl). Complexes 1 and 2 are obtained as thermally stable, light yellow crystalline solids after crystallization from *n*-pentane at −20 °C. They are characterized by spectroscopic (IR; ^1H, ^{13}C, ^{17}O NMR; MS) and analytical methods. The crystal structure of 1 was determined by X-ray diffraction (see below).

Complexes 1 and 2 slowly decompose upon long exposure to light to give insoluble, dark residues.[15] However,

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(9) (a) Carrick, W. L.; Reichle, W. T.; Pennella, F.; Smith, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3887. (b) Reichle, W. T.; Carrick, W. L. *J. Organomet. Chem.* **1970**, *24*, 419.

(10) Heyn, B.; Hoffmann, R. *Z. Chem.* **1976**, *16*, 195.

(11) (a) Stavropoulos, P.; Edwards, P. G.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 169. (b) Longley, C. J.; Savage, P. D.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1079.

(12) (a) Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem.* **1988**, *100*, 420; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394. (b) Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351. (c) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383. (d) Herrmann, W. A.; Weichselbaumer, G.; Herdtweck, E. *J. Organomet. Chem.* **1989**, *372*, 371.

(13) Reviews and recent accounts on organorhenium oxides in general: (a) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111. (b) Herrmann, W. A.; Herdtweck, E.; Flöel, J. K.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297. (d) Herrmann, W. A. *J. Organomet. Chem.* **1990**, *382*, 1. (e) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.*, **1991**, *113*, 6527.

(14) (a) Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1989**, *371*, C13. (b) Herrmann, W. A.; Romao, C.; Fischer, R.; Kiprof, P.; de Méric de Bellefon, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185.

(15) Studies on the photochemistry of $RReO_3$ complexes are in progress; see: Kunkely, H.; Türk, T.; Teixeira, C.; de Méric de Bellefon, C.; Herrmann, W. A.; Vogler, A. *Organometallics* **1991**, *10*, 2090.

they appear to be thermally quite stable. Thus, crystals of **1** and **2** melt without decomposition at ca. 100 and 77 °C, respectively. They may be also heated to 200 °C for 2 h in tetradecane solutions without showing significant decomposition.

Because 1 equiv of rhenium is "lost" as perrhenate in the reaction illustrated in eq 1, attempts were made to find a more efficient route for the preparation of complexes **1** and **2**. Therefore, Re_2O_7 was reacted with 1 equiv or excess Mes_2Zn in the hope that *all* rhenium would be converted to compound **1**. However, the yields of $MesReO_3$ (**1**) (23%) and $Zn(ReO_4)_2(THF)_2$ (45%) were found to be similar to those obtained from the stoichiometry of the reaction in eq 1, showing that arylation of perrhenate under these reaction conditions does not occur. This was checked independently by the unsuccessful attempts to react $Zn(ReO_4)_2(THF)_2$ or $NaReO_4$ with Mes_2Zn. In addition, reduction of rhenium was observed in the above reaction as shown by the appearance of the known[11] complex Mes_2ReO_2 albeit only in 10% yield (eq 2.)

$$Mes_2Zn + Re_2O_7 \xrightarrow{thf} \underset{1}{MesReO_3} + Zn(ReO_4)_2(thf)_2 + Mes_2ReO_2 \quad (2)$$

Complex $Me_3SiOReO_3$ is also a useful precursor for the preparation of (σ-aryl)ReO_3 complexes as shown by the reaction with Mes_2Zn to afford complex **1** in 29% yield. In comparison, reaction of MesMgBr results in extensive reduction to give Mes_2ReO_2 (Re^{VI}) as the major product (33%). In the latter reaction, complex **1** is also obtained but in low yield (11%).

None of these methods appear to present significant advantages over that of eq 1. The latter reaction was then extended to less bulky organic groups. When 1 equiv of Ph_2Zn (Ph = phenyl) was reacted with 2 equiv of Re_2O_7 in THF at −78 °C to room temperature, the new parent σ-aryl complex $PhReO_3$ (**3**) was formed. In contrast to complex **1**, the isolation of **3** by extraction of the reaction mixture with *n*-pentane followed by crystallization was not straightforward, because the new THF adduct $Ph(THF)ReO_3$ (**4**) was obtained as white crystals in 18% yield instead of compound **3**. However, **3** is obtained by removal of the THF from **4** under vacuum (Experimental Section). The derivative $TolReO_3$ (**5**) (Tol = 4-methylphenyl) was prepared similarly from Tol_2Zn and Re_2O_7. Compounds **3–5** have been characterized by spectroscopic and analytical methods, and the structure of $Ph(THF)ReO_3$ (**4**) has been studied by X-ray diffraction. Complex **3** is a colorless *liquid* (although often bluish because of decomposition) at room temperature, while **4** and **5** are colorless *solids*. They are similarly light-sensitive as their methyl-substituted congeners **1** and **2**, but they appear to be thermally less stable than the latter. Thus, **3** and **4** decompose rapidly at 60–80 °C in tetradecane or toluene solutions to afford selectively biphenyl. An insoluble dark material is also formed in this decomposition.

Monitoring of the decomposition of complexes **1–5** is facilitated by the fact that they survive the conditions of conventional gas chromatography with surprisingly short retention times in spite of their relatively high molecular weights (t_r = 14.30 min for **2**; 12.2 min for **3**, fused silica HP-1 50 m, 200 kPa of He, 120–180 °C, 20 °C/min, 180–200 °C, 40 °C/min).

The reaction scheme of eq 1 was applied to the electron-withdrawing pentafluorophenyl group. When 1 equiv of $(Ph_f)_2Zn$ (Ph_f = pentafluorophenyl) was allowed to react with 2 equiv of Re_2O_7 in THF, no products were formed even under severe reaction conditions (refluxing THF). However, we found that addition of catalytic amounts of $ZnCl_2/Et_2O$ to the arylation reagent $(Ph_f)_2Zn$ results in a nearly quantitative formation of $Zn(ReO_4)_2(THF)_2$ (47%, based on Re) and of the expected complex $(Ph_f)(THF)ReO_3$. Despite numerous attempts, this THF adduct escaped isolation in the pure state. Addition of quinuclidine to the *n*-pentane extract of the reaction mixture and crystallization at −30 °C affords the isolable adduct $(Ph_f)(quin)ReO_3$ (**6**) as a light yellow powder. **6** is less stable than **1–5**, decomposing during GC characterization to selectively yield perfluorobiphenyl $C_{12}F_{10}$. However, *n*-pentane solutions of **6** can be handled over several hours without noticeable decomposition.

Following the discovery that $ZnCl_2$ *catalyzes* the reaction of Re_2O_7 with $(Ph_f)_2Zn$, probably via the species $[(Ph_f)ZnCl]$, to afford the complex $(Ph_f)(THF)ReO_3$ in solution (only small amounts of $ClReO_3$ are formed, EI-MS evidence), another organozinc reagent of the type RZnCl was prepared and reacted with Re_2O_7: $(Me_3SiO\text{-}Xy)ZnCl(THF)$ (**7**) (Me_3SiO-Xy = 2,6-dimethyl-4-(trimethylsiloxy)phenyl) can be made from $(Me_3SiO\text{-}Xy)MgBr$ and $ZnCl_2$. It reacts with 1 equiv of Re_2O_7 in THF to give the new functionalized σ-aryl complex $(Me_3SiO\text{-}Xy)ReO_3$ (**8**) in 37% isolated yield (eq 3).

$$\underset{7}{[Me_3SiO\text{-}Xy]ZnCl(thf)} + Re_2O_7 \xrightarrow{thf} \underset{8}{[Me_3SiO\text{-}Xy]ReO_3} + 1/2\, Zn(ReO_4)_2(thf)_2 + 1/2\, ZnCl_2 \quad (3)$$

Interestingly, **7** does not reduce Re_2O_7; no Re^{VI} species such as $(Me_3SiO\text{-}Xy)_2ReO_2$ was formed even when an excess of **7** was used. Complex **8** was characterized by spectroscopic, analytical, and X-ray methods. It is a thermally very stable, yellow, crystalline material that melts at 73 °C to give an orange liquid. Decomposition starts at temperatures above 150 °C. However, owing to the reactivity of the Me_3SiO group, **8** could not be detected by gas chromatography. The reactivity of the trimethylsiloxy group of **8** toward protic reagents has been verified by treatment of **8** with HCl/Et_2O. The first known σ-hydroxyphenyl complex, $(HO\text{-}Xy)ReO_3$ (**9**) (HO-Xy = 2,6-dimethyl-4-hydroxyphenyl), could be thus obtained as a light yellow powder (eq 4).

$$\underset{8}{(Me_3SiO\text{-}Xy)ReO_3} + HCl \xrightarrow{Et_2O} \underset{9}{(HO\text{-}Xy)ReO_3} + Me_3SiCl \quad (4)$$

Attempts to prepare Mes_fReO_3 (Mes_f = 2,4,6-tris(trifluoromethyl)phenyl) from $(Mes_f)_2Zn$ and Re_2O_7 were unsuccessful, even in the presence of $ZnCl_2$.

THF and quinuclidine have been shown to form adducts with $PhReO_3$ (**3**) and $(Ph_f)ReO_3$ to afford $Ph(THF)ReO_3$ (**4**) and $(Ph_f)(quin)ReO_3$ (**6**), respectively. By contrast, no adduct was formed when quinuclidine was added to $MesReO_3$ (**1**), probably owing to the steric hindrance of the mesityl group. In comparison, the sterically less crowded $PhReO_3$ (**3**) and $Ph(THF)ReO_3$ (**4**) react with quinuclidine to afford $Ph(quin)ReO_3$ (**10**) as a yellow, microcrystalline powder.

Discussion

The preparation of high oxidation state σ-aryl complexes of the type $ArReO_3$ is possible by using organozinc compounds as arylating reagents and the simple rhenium oxide Re_2O_7 as the precursor for the ReO_3 moiety. Good yields are normally obtained.[32] So far, treatment of Re_2O_7 or $[(CH_3)_3NH][ReO_4]$ with Grignard reagents has been a route to these compounds, but yields are low due to extensive reduction of the rhenium. No phenyl complexes could be isolated.[11]

Due to the "loss" of 1 equiv of rhenium as $Zn(ReO_4)_2(THF)_2$ in this preparation (eqs 1–3), attempts were made to use $Me_3SiO–ReO_3$ as a more efficient precursor for the fragment ReO_3.[11b] However, this compound can only be used successfully in the case of ortho-substituted aryls. It reacts with Mes_2Zn to afford $MesReO_3$ (**1**) in good yields but gives only trace amounts of $PhReO_3$ (**3**) or $TolReO_3$ (**5**) when reacted with Ph_2Zn or Tol_2Zn, respectively. Nevertheless, $Me_3SiO–ReO_3$ will develop as a precursor compound in this chemistry because its oxidation power is very low.[32]

The imido analogue $Me_3SiO–Re(NR)_3$ (R = ${}^tBu$, Ar),[16] has been used more extensively to obtain complexes of the type $R'Re(NR)_3$ (R′ = Me, Et, $CH_2{}^tBu$, *o*-tolyl, xylyl, mesityl, σ-allyl, σ-phenylacetylide), by reaction with organolithium and Grignard reagents, without extensive reduction at the metal center.[11b,17,18] This confirmed reports that imido ligands (=NR) stabilize electron-poor metal centers through better σ/π donation than oxo ligands (=O), thus minimizing reduction at the rhenium center.[19] Thus, $Me_3SiO–ReO_3$ reacts with PhMgBr and with *p*-TolMgBr to give only intractable products which probably arise from rhenium reduction, even at low temperatures, and by decomposition upon workup. Note that the Re(VI) complexes Ph_2ReO_2 and $Ph_2Re_2O_4$ have not yet been reported.

Even the favorable case MesMgBr, with the bulky mesityl group, reduces $Me_3SiO–ReO_3$, Mes_2ReO_2 being the major product. The desired product, $MesReO_3$ (**1**), is isolated in low yields (<10%). Similar behavior has been observed for the reaction of XylMgBr with $Me_3SiO–ReO_3$.[11b] Thus, $Me_3SiO–ReO_3$ is a reasonable precursor for the preparation of complexes of the type $RReO_3$ only when reacted with organozinc compounds bearing sterically hindered organic groups such as Mes, Xy, CH_2SiMe_3, or $C_5(CH_3)_5$.[20]

The combination $Re_2O_7–Ar_2Zn$ is normally preferred in the synthesis of (σ-aryl)ReO_3 complexes. However, the yields depend on the precise stoichiometry of the reagents and on the electronic nature of the organic substituent. When the reaction of Re_2O_7 with Ph_2Zn is carried out with a 2:1 stoichiometry, typical yields vary from 30 to 40%, whereas for a 1:1 stoichiometry only very small amounts of $PhReO_3$ are formed. With the less reactive Mes_2Zn, yields are comparable for both stoichiometries (ca. 30%), with ca. 10% of the rhenium(VI) reduction product Mes_2ReO_2 being formed. By contrast, the functionalized arylzinc reagent $(Me_3SiO-Xy)ZnCl(THF)$ (**7**) does not reduce the rhenium even with the 1:2 stoichiometry that is needed to obtain better yields. Interestingly, Mes_2ReO_2 is not formed via reduction of $MesReO_3$ or $Zn(ReO_4)_2\cdot 2(THF)$ with excess Mes_2Zn, even at ambient temperature. By contrast, the analogous $[Me_2ReO(\mu-O)]_2$ is formed by reduction of $MeReO_3$ with Me_2Zn at the same temperatures at which $MeReO_3$ is formed from the reaction of Re_2O_7 with Me_2Zn.[12a] This shows that, for a given organozinc reagent, nucleophilic substitution of X by R in $XReO_3$ (X = ReO_4, Me_3SiO) to yield $RReO_3$ is faster than reduction at the Re center. The reverse process, i.e., oxidation of Re(VI) to Re(VII), has also been observed: $MesReO_3$ is formed in good yields from Mes_2ReO_2 and NO_2.[21]

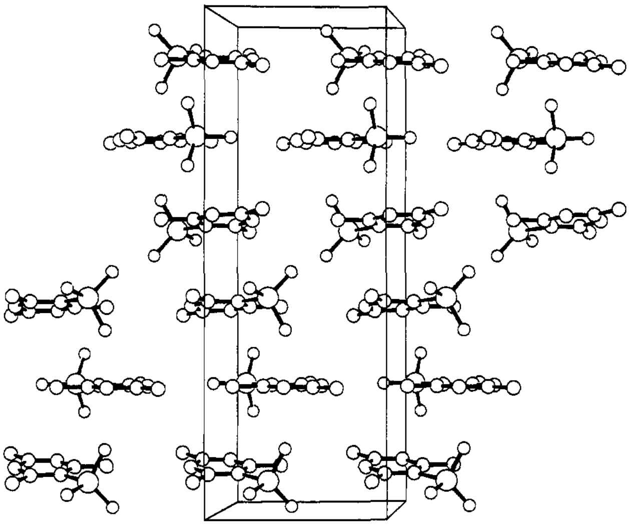

Figure 1. Cell packing diagram of structure **1A**. Hydrogen atoms are omitted for clarity.

Crystal Structure Determinations

The single-crystal X-ray structures of compounds **1**, **4**, and **8** have been determined. Structure **1A** was reported in a preliminary communication.[14] We have since then found that compound **1** crystallizes in two different forms: **1A** in the monoclinic space group $P2_1/m$ and **1B** in the orthorhombic space group *Pnma*. Structure **1A** contains six molecules in the unit cell: two type 1 molecules with mirror symmetry (the mesityl ligand, Re, and O atoms lying within the mirror plane at $y = {}^1/_4$) and four type 2 molecules having no molecular symmetry, lying in general positions (Figure 1).

Molecular mirror symmetry in molecule 2 is lost due to a slight rotation about the Re–C bond with respect to the ligand plane (torsion angle C(22)–C(21)–Re–O(5) = 9.7°). Structure **1B** involves only one type of molecule. The unit cell in this case contains four molecules, in each of which the mesityl ligand as well as the Re and one O atom lie within the mirror plane at $y = {}^1/_4$.

Complex **8** crystallizes in the monoclinic space group $P2_1/m$, but in this case the cell contains only two equivalent molecules, which lie with the aromatic ring and the Re and one O atom within the mirror plane at $y = {}^1/_4$.

There is very little variation in the coordination geometry about the Re atom in structures **1A**, **1B**, and **8** (Figures 2 and 3).

The Re–C bond for molecule 1 in structure **1A** is slightly shorter than that seen for the other molecules (2.006 (9) (**1A**, 1), 2.063 (7) (**1A**, 2), 2.075 (8) (**1B**), 2.04 (1) Å (**8**), but this fact can be correlated neither with the molecular configuration associated with the rotation of the ReO_3 unit nor to an electronic effect. The Re–O bond lengths range from 1.674 (8) to 1.703 (6) Å, O(1)–Re–O(1,2) bond angles vary from 109.7 (3) to 112.2 (2)°, and the O–Re–C angles vary from 105.9 (3) to 108.2 (3)°. Selected bond distances and angles are listed in Table I.

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[16] Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965.

[17] Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489.

[18] Horton, A. D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841.

[19] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley, New York, 1988; p 246.

[20] (a) Herrmann, W. A.; Taillefer, M.; de Méric de Bellefon; C.; Behm, *J. Inorg. Chem.* **1991**, *30*, 3247. (b) Herrmann, W. A.; Romao, C. C.; Kiprof, P.; Behm, J.; Cook, M.; Taillefer, M. *J. Organomet. Chem.* **1991**, *413*, 11.

[21] McGilligan, B. S.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2465.

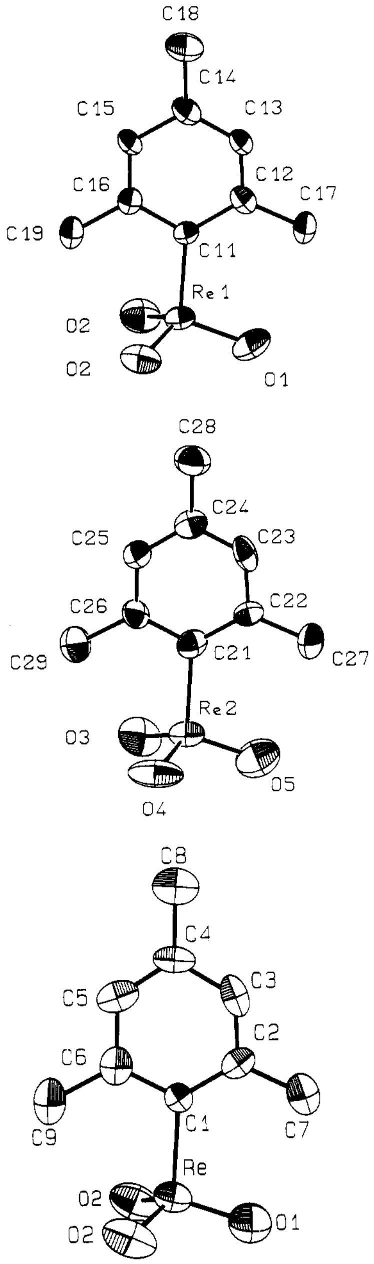


Figure 2. ORTEP drawings of molecules (a, top) **1A1**, (b, center) **1A2**, and (c, bottom) **1B**, found in two different crystal forms of (2,4,6-trimethylphenyl)ReO$_3$ (**1**), with 50% probability ellipsoids, showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Table I. Bond Lengths and Angles for (σ-Aryl)rhenium(VII) Oxides 1A1, 1A2, 1B, and 8

	1A2	1A	1B	8
Bond Lengths around Re (Å)				
Re–O(1,3)	1.681 (5)	1.682 (8)	1.674 (8)	1.703 (6)
Re–O(2,4)	1.683 (5)	1.697 (5)	1.688 (5)	1.696 (8)
Re–O(2′,5)	1.700 (6)			
Re–C(1)	2.063 (7)	2.006 (9)	2.075 (8)	2.04 (1)
Bond Angles at Re (deg)				
O(1,3)–Re–O(2,4)	109.7 (3)	111.7 (2)	112.2 (2)	111.5 (2)
O(1,3)–Re–O(1′,5)	111.7 (3)			110.9 (5)
O(2,4)–Re–O(2′,5)	111.9 (3)	110.1 (2)	110.8 (3)	
O(1,3)–Re–C(1)	107.4 (3)	108.1 (4)	105.9 (3)	108.0 (3)
O(2,4)–Re–C(1)	107.8 (3)	107.6 (2)	107.7 (2)	106.9 (4)
O(2′,5)–Re–C(1)	108.2 (3)			
Coordination Angles of Aryl Ring to Re (deg)				
Re–C(1)–C(2)	124.0 (5)	125.4 (7)	124.1 (6)	114.7 (8)
Re–C(1)–C(6)	116.0 (5)	117.4 (6)	114.4 (7)	125.4 (8)

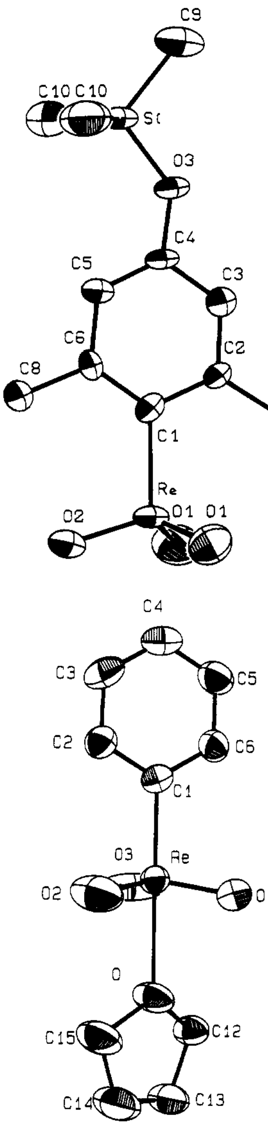


Figure 3. ORTEP drawings of (a, top) the [2,6-dimethyl-4-(trimethylsiloxy)phenyl]ReO$_3$ (**8**) and (b, bottom) Ph(THF)ReO$_3$ (**4**) molecules with 50% probability ellipsoids, showing the atom-labeling schemes. Hydrogen atoms are omitted for clarity.

In each of the above molecules the σ-aryl ligand is tilted away from the oxygen atom which lies in or near to the ring plane. This can be seen in the Re–C(1)–C(2,6) angles: 124.0 (5), 116.0 (5); 125.4 (7), 117.4 (6); 124.1 (6), 114.4 (7); 125.4 (8), 114.7 (8)° for molecules **1A2**, **1A1**, **1B**, and **8**, respectively. In addition, there are distorsions in the mesityl ligand angles by up to 4°, such that the methyl groups in the 2- and 6-positions are bent away from the ReO$_3$ moiety. This apparent flexibility in the ligand presumably allows free rotation of the ReO$_3$ moiety about the Re–C bond in solution as observed in the low-temperature (−90 °C) ^{1}H NMR of **1** and **8**. As the hydrogen positions could not be refined for all of these structures, the preference for the observed molecular geometries cannot be attributed with certainty to hydrogen–oxygen contacts.

This distortion appears to be a common feature in compounds bearing the mesityl ligand, such as in Mes$_2$ReO$_2$, Mes$_2$OsO$_2$, and Mes$_4$ReO, and has been explained in terms of steric repulsions between the oxygen atoms and the methyl groups, minimum carbon–oxygen distances being about 3.00 Å.[11] In complexes **1** and **8**, the C(7)–O(1,5) and C(8)–O(2) distances range from 2.89 (1) Å in molecule **1B** to 3.00 (1) Å in molecule **8**, and their

Table II. Bond Lengths and Angles of Trioxo(σ-phenyl)rhenium-Tetrahydrofuran (1/1) (4)

Bond Lengths (Å)			
Re-O(1)	1.674 (3)	Re-C(1)	2.071 (3)
Re-O(2)	1.683 (3)	Re-O(THF)	2.420 (2)
Re-O(3)	1.658 (3)		
Bond Angles (deg)			
O(1)-Re-O(2)	120.4 (2)	O(THF)-Re-O(1)	80.0 (1)
O(1)-Re-O(3)	115.8 (3)	O(THF)-Re-O(2)	80.2 (2)
O(2)-Re-O(3)	117.3 (3)	O(THF)-Re-O(3)	84.4 (1)
O(1)-Re-C(1)	98.6 (1)	O(THF)-Re-C(1)	175.8 (1)
O(2)-Re-C(1)	97.2 (1)	Re-C(1)-C(2)	120.3 (3)
O(3)-Re-C(1)	99.8 (1)	Re-C(1)-C(6)	120.4 (2)

"couterparts", C(9)-O(2,3,4) and C(7)-O(1), range from 3.40 (1) to 3.12 (1) Å. Thus, the mesityl ligand is distorted in order to minimize the "in-plane" methyl-oxo interaction because, as shown in molecule **1A2**, rotation about the ReO_3 fragment does not significantly release the methyl-oxo repulsions.

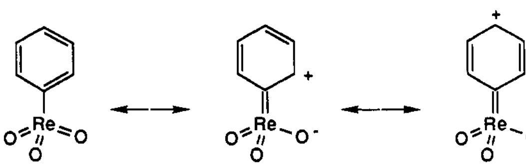
Although the NMR spectra of the (σ-aryl)ReO_3 compounds show evidence of Re-THF interactions in solution, compound **4** is the first crystalline adduct of these compounds with tetrahydrofuran to be structurally characterized. The metal environment is a distorted trigonal bipyramid, with an O(THF)-Re-C angle of 175.8 (1)° and Re-O(THF) distance of 2.420 (2) Å. The cell is monoclinic $P2_1/c$, and the molecules lie on general positions, there being no local molecular symmetry. Table II gives selected bond distances and angles for compound **4**.

While there are only small changes in the (σ-aryl)ReO_3 bond lengths observed for these compounds on moving from four- to five-coordinate heptavalent rhenium, it is interesting to note that a rotation about the Re-C bond has occurred in the THF adduct relative to the mesityl derivatives. When $PhReO_3$ is considered as a separate moiety, with the torsional angles C(2)-C(1)-Re-O(3) = 90.8 (5)°, C(2)-C(1)-Re-O(2) = -28.6 (5)°, and C(6)-C(1)-Re-O(1) = 26.3 (5)° and the coordination angles Re-C(1)-C(2,6) = 120.3 (3)° and 120.4 (2)°, then this moiety can be seen to have approximate mirror symmetry, but in this case the mirror plane lies perpendicular to the plane of the phenyl ligand. The coordination of the THF disturbs the overall molecular symmetry. It would therefore be of interest to obtain Ph(pyridine)ReO_3 to determine whether a similar $PhReO_3$ symmetry is also observed and, in addition, the manner of coordination of the pyridine molecule. One might expect the pyridine ring to lie perpendicular to the phenyl ring to allow maximum orbital overlap with Re and therefore conjugation of electron density throughout the molecule.

As there is no significant lengthening of the Re-O bond in the current THF adduct **4**, one is tempted to assume that the coordination of the THF is relatively weak. We have found no comparable five-coordinate complexes L(THF)$Re^{VII}O_3$ in the literature. However, a six-coordinate Re(VII) complex of 1,4-dioxane has been reported, with Re-O(dioxane) bond distances of 2.469 and 2.486 (5) Å.[22] In addition, [Re_2O_7(pyridine)$_3$] containing a five-coordinate Re(VII) is known; here, the Re-N distance is 2.44 (1) Å.[23] Our Re-O(THF) distance of 2.420 (2) Å is therefore what might be expected for five-coordinate Re(VII) in this type of adduct.

In conclusion, only minor differences in the Re-O and Re-C bond lengths are evident in these four structures. Changes occur upon addition of THF: increase of the O-Re-O angles by 6-8° (to ca. 116-120°), reduction of the O-Re-C angles by about 9° (to ca. 97-100°), and rotation about the Re-C bond in the case of σ-mesityl compounds. No significantly short intermolecular distances are observed in any of these structures.

Scheme II



Spectroscopic Studies in Solution

The ^{1}H NMR spectra of complexes **1-10** reveal the expected features (see the Experimental Section). The chemical shift of the aromatic protons in the σ-aryl complexes **1-3**, **5**, and **8** are solvent-dependent, appearing ca. 0.6-0.9 ppm at lower field in polar solvents (THF, $CDCl_3$, or CH_2Cl_2) as compared to benzene. This effect is also noticeable but less pronounced for the methyl protons.

Addition of THF (up to 20-fold excess) to a C_6D_6 solution of the σ-phenyl complex **3** induces a downfield shift from 7.10, 6.75, and 6.67 ppm for the ortho, meta, and para protons to 7.50, 6.85, and 6.80 ppm, respectively. The meta protons in the σ-mesityl complex **1** follow the same trend (shift from 6.57 ppm (C_6D_6) to 7.22 ppm (THF-d_8). A large excess of THF is needed in order to observe a significant shift of the aromatic protons. When only a stoichiometric amount of THF is being added to solutions of complex **3**, or when the ^{1}H NMR spectra of complex **4** are recorded in C_6D_6 or CD_2Cl_2, the same spectra features are observed as for complex **3**.

These data strongly support the presence of equilibria between the free complex (e.g., **3**) and solvated derivatives (e.g., **4**) (eq 5). At room temperature, the solvent-free species predominate. The observation of averaged NMR signals indicates fast equilibration rates.

$$\underset{\mathbf{3}}{PhReO_3} + thf \rightleftharpoons \underset{\mathbf{4}}{Ph(thf)ReO_3} \qquad (5)$$

Further evidence of a weakly coordinated THF ligand in complex **4** is its ready displacement from the rhenium center by quinuclidine, a stronger Lewis base. A color change from colorless to yellow and a strong absorption at 922 cm^{-1} in the solution IR spectrum, typical for $RReO_3$(quin) complexes,[14b] indicate that a stable quinuclidine complex Ph(quin)ReO_3 (**10**) is obtained.

Electronic Ligand Effects

A ^{13}C NMR study was performed to gain information about the electronic properties of the ReO_3 moiety with respect to the aryl groups. The chemical shift of the ortho carbon in $PhReO_3$ (**3**) does not reveal information of significance.[24] However, the ReO_3 group appears to be a strong electron-withdrawing substituent when compared with a series of monosubstituted benzene derivatives. Shielding induced by donors and deshielding arising from acceptors are clearly related to the chemical shift of the para carbon of monosubstituted benzene.[25] The donor properties of typical substituents may then be classified as follows: $NH_2 < OR \leq OH < F < CH_3 < Cl < COOR \leq H < SO_3H < CN < COOH < NO_2$. The Sp criterion (Sp = $\delta(p\text{-}C(C_6H_5X)) - \delta(C_6H_6)$) is used as a basis for this order.[25] Strong electron-releasing groups are in the order

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[22] Fischer, D.; Krebs, B. *Z. Anorg. Allg. Chem.* **1982**, *491*, 73.

[23] Johnson, J. W.; Brody, J. F.; Ansell, G. B.; Zentz, S. *Acta Crystallogr.* **1984**, *C40*, 2040.

[24] Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH press: Weinheim, Germany, 1988; p 255.

Table III. ^{17}O **NMR and IR Data for Selected Complexes of Type** $RReO_3$

complex[a]	NMR: $\delta(^{17}O)$, ppm				IR: ν(ReO), cm^{-1} CS$_2$	
	THF	*n*-pentane	$CDCl_3$	C_6D_6		
CH_3ReO_3	870	835	829	823	1001 (w)	965 (vs)
$MesReO_3$ (**1**)	836		811	809	986 (m)	953 (vs)
$PhReO_3$ (**3**)	912	872		856		
$(Ph_f)(quin)ReO_3$ (**6**)				978	921 (vs)	
$(Me_3SiO\text{-}Xy)ReO_3$ (**8**)	821	813	800	805	975 (m)	951 (vs)
$Ph(quin)ReO_3$ (**10**)	947				922 (vs)	

[a] Key: Mes = 2,4,6-trimethylphenyl; Ph = phenyl; Ph_f = pentafluorophenyl; quin = quinuclidine, $N[(CH_2CH_2)_3]CH$; Me_3SiO-Xy = 2,6-dimethyl-4-(trimethylsiloxy)phenyl.

of Sp = −10.0 (NH_2) while the strongly electron-withdrawing group NO_2 appears at Sp = +6.1. With an Sp value of +7.0 (135.5 − 128.5 ppm), the ReO_3 group is classified as a strong electron-withdrawing group. As such, it compares well to the sulfonium ion $[SMe_2]^+$ (Sp = +7.6) and to the phosphonium ion $[PPh_3]^+$ (Sp = +7.4). Carbocations are found at more positive Sp values, e.g., Sp = +27.4 for $[CMe_2]^+$.[25]

Very little NMR data on σ-phenyl high oxidation state metal complexes are available in the literature, and comparison of the electron-withdrawing properties of the ReO_3 group with other fragments such as $VOCl_2$ (e.g., in the compound $(\sigma\text{-}C_6H_5)VOCl_2$) is not possible. However, there is a clear difference in the NMR spectra for low oxidation state phenyl complexes such as $(\sigma\text{-}C_6H_5)Re(CO)_5$ (Sp = −4.2) and, more surprisingly, of other high oxidation state complexes such as $(\eta^5\text{-}C_5H_5)_2Ti(\sigma\text{-}C_6H_5)_2$, in which the metal center exhibits electron-releasing properties according to the Sp criterion.[26]

Returning to the equilibrium shown in eq 5, we believe that the complexes of the type $RReO_3$ generally undergo such equilibria with weak Lewis bases. For example, the protons in CH_3ReO_3 are shifted downfield in THF as compared to C_6D_6.[12d] In order to gain further information about the equilibrium of eq 5, these complexes were studied by ^{17}O NMR spectroscopy, in the hope that the change of electron density at rhenium induced by coordination of THF would be reflected in the chemical shift of the oxo ligands.[19] We have studied the spectra of four selected complexes, **1**, **3**, **8**, and CH_3ReO_3, in four different solvents, *n*-pentane, benzene, chloroform, and THF, all presenting very different polarity and coordination ability, in order to separate solvent effects due to polarity and coordination. In all cases have we found that THF has the strongest shift effect, more for the sterically less hindered σ-phenyl and methyl complexes **3** and CH_3ReO_3, respectively, than for **1** and **8** (Table III). Interestingly, *n*-pentane induces a larger shift than $CDCl_3$ and C_6D_6. These results demonstrate that the solvent dependence of the ^{17}O chemical shift for these complexes is *not* related to the polarity of the solvent but rather to metal coordination of the latter (THF) and thus support the equilibria shown in eq 5.

The ^{17}O chemical shifts are also affected by the electronic nature of groups R: In C_6D_6, the oxo resonances are shifted upfield if electron-donating groups are present, such as methyl (in **1**) or methyl and siloxy (in **8**), and downfield in the σ-phenyl complex **3** and in the perfluorophenyl complex **6** (Table III). This supports the rhenium centers in **1** and **8** being less Lewis acidic than in compounds **3** and **6**.

We have also used IR spectroscopy together with ^{17}O NMR to further confirm the equilibrium of eq 5. Compound **10**, which has a trigonal-bipyramidal coordination as in $(C_2H_5)(quin)ReO_3$,[14b] displays a ^{17}O NMR signal at 947 ppm in THF, a surprisingly deshielded value in view of the low ν(Re=O) IR absorption (922 cm^{-1}, CS_2). This shows that the rhenium–oxo bands cannot be correlated with the ^{17}O chemical shift. With this information, the ^{17}O NMR signal at 912 ppm for **3** in THF (ca. 60 ppm downfield from the value found in C_6D_6) is not surprising, since under these solution conditions the observed species is more likely to be the THF adduct **4**. This is supported by IR measurements of solutions of $PhReO_3$ (**3**) in mixtures of CS_2 and THF (pure THF cannot be used because of strong absorptions between 1100 and 800 cm^{-1}), which show bands due to **3** and an absorption attributed to **4** at 939 cm^{-1}, the intensity of the latter band increasing with increasing THF concentration.

Conclusion

(σ-Aryl)rhenium(VII) oxides of general formula (aryl)-ReO_3 are now easily accessible from Re_2O_7 and arylzinc compounds.[32] Other arylating reagents are inferior with regard to product yields, mainly due to their reducing properties (i.e., Re(VII) → Re(VI)). The easily available siloxy derivative $Me_3SiO\text{-}ReO_3$ may be used as an alternative starting material for special cases.[32] This procedure has allowed the preparation of functionalized derivatives such as (2,6-dimethyl-4-hydroxyphenyl)trioxorhenium(VII) (**9**) and (pentafluorophenyl)trioxorhenium(VII) as the quinuclidine adduct **6** for the first time. The metal Lewis acidity (Re(VII)) depends on electronic and steric properties of the σ-aryl ligand. Thus, the σ-mesityl derivative **1** forms a weaker THF adduct than the parent σ-phenyl complex **3** and does *not* form adducts with quinuclidine, in contrast to **3**. The situation is even more pronounced with the σ-perfluorophenyl complex $(Ph_f)ReO_3$, which can be isolated only as a quinuclidine adduct. The σ-mesityl complex **1** is thermally stable up to 200 °C. By comparison, the σ-phenyl complex **3** slowly decomposes at room temperature, resulting in the *selective* formation of diphenyl. From these results, we can conclude that (i) homolytic cleavage of the rhenium–carbon bond is not the initiation step for decomposition of the aryl complexes, (ii) the remarkable increase of thermal stability of complexes **1** and **2** when compared to **3** may be attributed either to an increase steric hindrance at the rhenium center, which enhances the activation barrier for a bimolecular decomposition process, or to the absence of β-hydrogen atoms in these compounds, and (iii) intramolecular migration of the aryl group to give a phenoxyrhenium species is not likely. This is in striking contrast with the closely related example of $(\sigma\text{-}C_6H_5)VOCl_2$ which is believed to afford $(C_6H_5O)VCl_2$ upon decomposition.[9b] The latter reaction is still the only cited[27] textbook example referring to alkyl/aryl transfer from a metal to an oxo ligand,[28] a key step

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(25) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499.

(26) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London 1981.

(27) Vetter, W. M.; Sen, A. *Organometallics* **1991**, *10*, 244.

often mentioned in mechanisms of metal-catalyzed oxidation of organic substrates.[19]

Experimental Section

All reactions were performed in Schlenk flasks under oxygen- and water-free nitrogen. Solvents were dried and distilled under nitrogen: tetrahydrofuran, diethyl ether, benzene, hexane, and *n*-pentane over sodium benzophenone–ketyl; toluene and dioxane over sodium; dichloromethane and chloroform over P_2O_5. Infrared spectra were recorded on a FT-Nicolet 5 DX spectrophotometer as KBr pellets, Nujol mulls, or CS_2 or CH_2Cl_2 solutions. The ^1H, ^{13}C, and ^{17}O NMR spectra were recorded at 399.78, 100.5, and 54.21 MHz, respectively, on a FT-JEOL GX 400 instrument. The NMR spectra were externally referenced to Me_4Si and H_2O for the ^1H, ^{13}C, and ^{17}O nuclei, respectively, with downfield chemical shifts reported as positive. All NMR solvents were freeze–pump–thaw degassed and stored over molecular sieves before use. Elemental analyses were performed at the Microanalytical Laboratory in this Institute. Mass spectra were obtained with a Finnigan MAT 311 A and MAT 90 spectrometer. Gas chromatograms were recorded on a HP A-5890. The complexes Mes_2Zn, Xy_2Zn, Tol_2Zn, $(Ph_f)_2Zn$, and $(Mes_f)_2Zn$ have been prepared according to literature methods.[29] The reagents Ph_2Zn (Strem Chemicals), $ZnCl_2$ (Et_2O solution, Aldrich), and Re_2O_7 (Degussa AG) were used as received. For large-scale preparations of organozinc reagents, solid $ZnCl_2$ was dried with $SOCl_2$ (refluxed for 2 h under vacuum 10^{-2} mmHg at 80 °C overnight) prior to dissolution in Et_2O and then reaction. The new Grignard reagent $(Me_3SiO\text{-}Xy)MgBr$ was prepared as reported for [4-(trimethylsiloxy)phenyl]MgBr.[30]

(2,4,6-Trimethylphenyl)trioxorhenium(VII) (1). **(a)** A solution of Mes_2Zn (0.31 g, 1.02 mmol) in THF (20 mL) was added dropwise to a cooled (−78 °C) solution of Re_2O_7 (0.97 g, 2.00 mmol) in THF (50 mL). While the temperature was slowly raised to ambient temperature (ca. 3 h), the color changed to yellow and a white precipitate formed at −10 °C. After the mixture was stirred for 0.5 h at room temperature, the solvent was removed in vacuo and the dark solid residue was extracted with pentane (3 × 20 mL), giving a pale yellow solution that was filtered via canula. Upon concentration of this solution, yellow crystals of 1 formed. They were collected by filtration and dried in vacuo (0.43 g, 1.22 mmol, 30% based on Re, 60% of theory). The dark residue was further extracted with acetone, and pyridine was added to the extract, affording a white precipitate of $Zn(ReO_4)_2(Py)_4$ (0.83 g, 0.94 mmol, 47% based on Re). Data for 1: mp 98–108 °C; IR (CS_2) ν(ReO) 986 (m), 953 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 6.57 (s, 2 H, H-m), 2.23 (s, 6 H, CH_3-o), 1.83 (s, 3 H, CH_3-p); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 161.6 (CRe), 147.9 (C-o), 146.0 (C-p), 129.1 (C-m), 27.9 (CH_3-o), 21.2 (CH_3-p); ^{17}O NMR (C_6D_6/THF-d_8) δ 836; MS, *m/z* (EI) 354 (M^+), 119 ($M^+ - ReO_3$). Anal. Calcd for $C_9H_{11}O_3Re$ (M_r = 353.39): C, 30.59; H, 3.14; O, 13.58; Re, 52.69. Found: C, 30.50; H, 3.18; O, 13.82; Re, 52.42.

(b) A solution of Mes_2Zn (0.180 g, 0.62 mmol) in Et_2O (10 mL) was added dropwise via canula to a cooled (−78 °C) solution of $Me_3SiOReO_3$ (0.380 g, 1.17 mmol) in Et_2O (20 mL). During addition (ca. 0.5 h), the color of the solution turned slowly from colorless to light orange. The temperature was then raised to ambient temperature, and the color became darker. After 0.5 h of stirring at room temperature, the solvent was removed under vacuum and the light brown residue was extracted with *n*-pentane (3 × 5 mL) to afford a white insoluble solid (0.072 g) and a pale purple solution. This was concentrated to ca. 5 mL and upon cooling afforded yellow crystals of 1 (0.120 g, 0.34 mmol, 29% based on Re).

(c) Reaction of Re_2O_7 with 1 equiv of Mes_2Zn. A solution of Mes_2Zn (0.608 g, 2.00 mmol) in THF (30 mL) was added dropwise to a cooled (−78 °C) colorless solution of Re_2O_7 (0.970 g, 2.00 mmol) in THF (70 mL). No immediate color change occurred but when the solution was warmed to ambient temperature (2 h), it became light red and a white precipitate was formed at ca. −10 °C. The mixture was further stirred for 2 h at room temperature. The white solid was filtered off with a canula and was identified as $Zn(ReO_4)_2(THF)_2$ (0.642 g, 0.90 mmol, 45% based on Re). The THF solution was dried under vacuum, and the residue was extracted with *n*-pentane to afford a light red solution and an oily brown residue. From the pentane solution, $MesReO_3$ was obtained as yellow microcrystalline powder (0.322 g, 0.91 mmol, 23% based on Re). The oily brown residue was extracted into toluene as a red solution and recrystallized from a toluene/*n*-pentane mixture, yielding the red microcristalline powder Mes_2ReO_2 (0.120 g, 0.46 mmol, 11% based on Re).

(d) Reaction of $Me_3SiOReO_3$ with MesMgBr. Upon addition of a solution of MesMgBr (1 M in Et_2O, 0.80 mL, 0.80 mmol) to a cooled (−78 °C) solution of $Me_3SiOReO_3$ (0.260 g, 0.80 mmol) in THF (20 mL), the color changed from colorless to red. After the mixture was warmed to ambient temperature (2 h), it was further stirred for 1 h and the THF was removed under vacuum. A first extraction of the residue with *n*-pentane (2 × 10 mL) afforded a light red solution from which a light red powder was obtained upon cooling at −78 °C. This was shown to contain almost pure $MesReO_3$ (1) (IR, ^1H NMR, and EI-MS evidence; yield 0.030 g, 0.085 mmol, 11% based on Re or Mes). A second extraction with toluene yielded dark red crystals of Mes_2ReO_2 (IR, EI-MS, and ESR evidence; yield 0.120 g, 0.263 mmol, 33% based on Re, 66% based on Mes). An insoluble white powder analyzed as a mixture of the starting compound and $Zn(ReO_4)_2(THF)_2$ remained.

(2,6-Dimethylphenyl)trioxorhenium(VII) (2). The complex $XyReO_3$ was prepared similarly as for 1. From Xy_2Zn (0.29 g, 1.05 mmol) and Re_2O_7 (0.49 g, 1.01 mmol), yellow greenish needles of **2** were obtained (0.17 g, 0.50 mmol, 25% based on Re, 50% of theory). The following spectral and analytical data were obtained: mp 77 °C; IR (CS_2) ν(ReO) 986 (m), 954 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 6.74 (m, 3 H, H-p and H-o), 2.20 (s, 6 H, CH_3); ^{13}C NMR (CD_2Cl_2) δ 164.3 (br m, CRe), 148.2 (m, C-o), 135.3 (d, C-p, ^1J(CH)= 161 Hz), 128.7 (dm, C-m, ^1J(CH)= 161 Hz), 28.4 (qm, CH_3, ^1J(CH)= 128 Hz); MS, *m/z* (EI) 340 (M^+, 100%), 105 ($M^+ - ReO_3$, 66%). Anal. Calcd for $C_8H_9O_3Re$ (M_r = 339.36): C, 28.31; H, 2.67; O, 14.14; Re, 54.87. Found: C, 28.26; H, 2.67; O, 11.33; Re, 53.91.

Phenyltrioxo(tetrahydrofuran)rhenium(VII) (4). A colorless solution of Ph_2Zn (0.11 g, 0.50 mmol) in THF (10 mL) was added dropwise to a cooled (−78 °C) slightly yellow solution of Re_2O_7 (0.49 g, 1.00 mmol) in THF (30 mL). While the mixture was slowly warmed to ambient temperature, (ca. 2 h), the color changed to yellow and a white precipitate formed at −30 °C. After the mixture was stirred for 1 h at room temperature, the solvent was removed in vacuo and the dark solid residue was extracted with pentane (3 × 10 mL), giving a clear solution that was filtered via canula, concentrated to ca. 5 mL, and cooled for 2 h at −78 °C. This afforded white crystals of $Ph(THF)ReO_3$ (4) which were collected by filtration at low temperature and dried in vacuo (0.14 g, 0.36 mmol, 18% yield based on Re, 36% of theory). The white precipitate was identified (IR, elemental analysis) as $Zn(ReO_4)_2(THF)_2$ (0.34 g, 0.48 mmol, 48% based on Re): IR (KBr) ν(ReO), 912 cm^{-1}. Anal. Calcd for $C_8H_{16}O_{10}Re_2Zn$ (M_r = 709.91): C, 13.52; H, 2.27; O, 22.53; Re, 52.67; Zn, 9.01. Found: C, 13.62; H, 2.27; O, 22.12; Re, 52.25; Zn, 7.40. Data for $Ph(THF)ReO_3$: mp 45–47 °C; IR (CS_2) ν(ReO) 939 cm^{-1}; ^{17}O NMR (pentane, δ 0 (H_2O standard)) δ 872 (ReO_3), 24 (THF). Anal. Calcd for $C_{10}H_{13}O_4Re$ (M_r = 384.03): C, 31.25; H, 3.41. Found: C, 32.12; H, 3.50.

Phenyltrioxorhenium(VII) (3). $PhReO_3$ was obtained from $Ph(THF)ReO_3$ by removal of THF under vacuum for 2 h. Data for **3**: IR (KBr) ν(ReO) 986 (m), 956 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 7.87 (d, 2 H, H-o, *J*(HH) = 7.9 Hz), 7.69 (t, 1 H, H-p, *J*(HH) = 7.3 Hz), 7.63 (t, 2 H, H-p); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 155.5 (CRe), 142.5 (C-o), 135.5 (C-p), 130.4 (C-m); MS *m/z* (EI) 312 (M^+). Anal.

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(28) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; pp 159 and 164.

(29) Preparation of organozinc reagents: (a) Mes_2Zn: Seidel, W.; Bürger, I. *Z. Anorg. Allg. Chem.* **1981**, *473*, 166. (b) Xy_2Zn: Hofstee, H. K.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *144*, 255. (c) Tol_2Zn: de Graaf, P. W. J.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1977**, *127*, 391. (d) $(Ph_f)_2Zn$: Nützel, K. In *Methoden der Organischen Chemie*, Houben-Weyl, 4th ed.; Müller, E., Ed; Thieme-Verlag: Stuttgart, 1973; Vol. XIII/2a, p 559. (e) $(Mes_f)_2Zn$: Bertel, N. Ph.D. Thesis, Universität Göttingen, Germany, 1989. (f) Mes_fLi: Scholz, M.; Roesky, H. W.; Stalke, D.; Keller, K.; Edelmann, F. T. *J. Organomet. Chem.* **1989**, *366*, 73.

(30) Neville, R. G. *J. Org. Chem.* **1960**, *25*, 1063.

Table IV. Crystallographic Data for Structures 1A, 1B, 8, and 4

	1A	1B	8	4
Crystal Parameters				
molecular formula	$C_9H_{11}O_3Re$	$C_9H_{11}O_3Re$	$C_{11}H_{17}O_4ReSi$	$C_{10}H_{13}O_4Re$
molecular weight	354.4	354.4	427.6	383.4
crystal form	pale yellow columns	green columns	yellow plates	white columns
crystal dimens, mm	0.16 × 0.25 × 0.25	not estimated	not estimated	0.51 × 0.25 × 0.18
temp, °C	23 ± 3	23 ± 3	23 ± 3	−50 ± 3
space group	monoclinic $P2_1/m$ (No. 11)	orthorhombic *Pnma* (No. 62)	monoclinic $P2_1/m$ (No. 11)	monoclinic $P2_1/c$ (No. 14)
a, Å	8.210 (1)	7.343 (2)	8.245 (1)	8.580 (1)
b, Å	22.924 (3)	10.166 (2)	7.492 (1)	11.562 (1)
c, Å	8.141 (1)	13.600 (3)	11.991 (2)	12.407 (2)
β, deg	102.21 (1)		100.83 (<1)	109.34 (7)
Z	6	4	2	4
V, Å^3	1498	1015	728	1161
ρ(calc), g/cm^3	2.28	2.32	1.95	2.19
F(000)	984	660	408	720
λ, Å	0.7107	0.7107	1.5418	0.7107
Measurement Parameters				
scan time, s	max 60	max 60	max 60	max 60
scan width, deg	0.9	0.90 + 0.30 tan Θ	1.00 + 0.30 tan Θ	1.00 + 0.30 tan Θ
no. of reflcns	5038	1977	2657	2291
hkl	(−9/9), (−26/26), (0/9)	(−8/8), (0/12), (0/16)	(0/9), (−8/8), (−14/14)	(0/10), (0/13), (−14/14)
obsd reflcns	2426	821	1301	1899
no. used in refinement	2422 with $I > 0.0$	739 with $I > 0.5\sigma(I)$	1258 with $I > 1.0\sigma(I)$	1822 with $I > 1.0\sigma(I)$
no. reflcns/param	9.6	9.6	12.1	13.3
Refinement				
abs corr	empirical	empirical	empirical	empirical
μ, cm^{-1}	116.3	121.1	165.7	106.0
no. of parameters	253	77	104	137
R^a	0.043	0.042	0.046	0.026
$R_w{}^b$	0.028	0.022	0.034	0.023
goodness of fit^c		1.553		2.899
residual electron density (e/Å^3)	+0.85/−1.04	+0.80/−1.06	+1.18/−1.62	+1.31/−1.04

$^a R = \sum||F_o| - |F_c||/|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. $^c \mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})^2]^{1/2}$.

Calcd for $C_6H_5O_3Re$ (M_r = 311.30): C, 23.15; H, 1.62; O, 15.42; Re, 59.81. Found: C, 23.72; H, 1.82; O, 15.45; Re, 57.80.

(4-Methylphenyl)trioxorhenium(VII) (5). The complex $TolReO_3$ was prepared similarly as for 4. The following spectra and analytical data were obtained. From Tol_2Zn (0.27 g, 1.08 mmol) and Re_2O_7 (1.06 g, 2.19 mmol), a gray microcristalline powder of 5 was obtained (0.12 g, 0.37 mmol, 17% based on Re, 34% of theory): mp 66 °C; IR (CS_2) ν(ReO) 988 (m), 956 (vs) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.77 (d, 2 H, H-o, *J*(HH) = 8.2 Hz), 7.44 (d, 2 H, H-m), 2.45 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 153.5 (CRe), 147.6 (C-p), 142.4 (C-o), 131.0 (C-m), 22.3 (CH_3); MS, *m/z* (EI) 326 (M$^+$, 85%), 182 (bitolyl, 18%), 91 (M$^+$ − ReO_3, 100%). Anal. Cacld for $C_7H_7O_3Re$ (M_r = 325.34): C, 25.84; H, 2.17. Found: C, 25.21; H, 2.43.

(Pentafluorophenyl)trioxo(quinuclidine)rhenium(VII) (6). A mixture of $(Ph_f)_2Zn$ (0.722 g, 1.80 mmol) and $ZnCl_2$ (1 M in Et_2O, 0.20 mL, 0.2 mmol) in THF (10 mL) was added dropwise to a cooled (−78 °C) solution of Re_2O_7 (1.58 g, 3.26 mmol) in THF (50 mL). While the mixture was slowly raised to ambient temperature (ca. 2 h), a white precipitate formed at −40 °C and the solution darkened. The THF was removed in vacuo, and the dark solid residue was extracted with pentane (2 × 30 mL). A solution of quinuclidine (0.210 g, 1.89 mmol) in *n*-pentane was then added, causing a color change to yellow and formation of some precipitate in small quantities. Upon filtering and cooling of this solution at −30 °C, yellow needles of 6 formed (0.23 g, 0.45 mmol, 14% based on Re, 28% of theory). The white precipitate was identified (elemental analysis) as $Zn(ReO_4)_2(THF)_2$ (47% based on Re) without trace amounts of chloride. Anal. Calcd for $C_8H_{16}O_{10}Re_2Zn$ (M_r = 709.91): C, 13.52; H, 2.27; Re, 52.67; Zn, 9.0. Found: C, 11.11; H, 2.06; Re, 53.34; Zn, 9.1. Data for 6: IR (CS_2) ν(ReO) 922 (vs), $\nu(C_6F_5)$ 1635 (m) 1081 (m) 970 (s) 787 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.24 (s, br, 6 H, NCH_2), 1.01 (s br, 1 H, CH), 0.71 (s br, 6 H, CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 144 (s br, CRe), 148.0 (d br, ^1J(CF) = 249 ± 5 Hz), 137.3 (dm, ^1J(CF) = 250 ± 20 Hz), 130.2 (partially masked by the solvent), 50.1 (NCH_2), 25.6 (CH_2), 19.8 (CH); ^{17}O NMR (C_6D_6, δ 0 (H_2O standard)) δ 978 (ReO_3); MS, *m/z* (EI) 402 (M$^+$ − quinuclidine, 21%), 168 (decafluorobiphenyl, 100%).

Chloro[2,6-dimethyl-4-(trimethylsiloxy)phenyl](tetrahydrofuran)zinc, (Me_3SiO-Xy)ZnCl(THF) (7). A solution of 4-Bromo-3,5-dimethyl-1-(trimethylsiloxy)benzene (28.60 g, 0.105 mol) in THF (80 mL) was added dropwise to a suspension of Mg (2.82 g, 0.116 mol, 10% excess) in THF (150 mL). The reaction was induced by addition of 10 drops of 1,2-dibromoethane and then refluxed for 1 h. The solution was concentrated to ca. 50 mL by evaporation of the solvent, and Et_2O (100 ml) was added, affording a white precipitate. The solution was filtered, and a solution of anhydrous $ZnCl_2$ (15.00 g, 0.110 mol) in Et_2O (100 mL) was added dropwise to the Grignard reagent. A white precipitate formed. The mixture was stirred for 18 h, after which time the solution was filtered and the oily residue was dried under vacuum. This was extracted with toluene (30 mL), concentrated in vacuo, and cooled to −78 °C to yield a light brown oil. After the residue was washed with pentane (2 × 30 mL), a white powder of 7 was obtained (yield 19.2 g, 0.052 mol, 50% based on 4-bromo-3,5-dimethyl(trimethylsiloxy)benzene): ^{1}H NMR (C_6D_6) δ 6.81 (s, 2 H, H-m), 3.64 (br m, 4 H, THF), 2.67 (s, 6 H, Me-o), 1.17 (br m, 4 H, THF), 0.24 (s, 9 H, $SiMe_3$). Anal. Calcd $C_{15}H_{25}ClO_2SiZn$ (M_r = 366.28): C, 49.19; H, 6.88; Cl, 9.68; Si, 7.67; Zn, 17.85. Found: C, 47.70; H, 6.91; Cl, 11.20; Si, 6.88; Zn, 17.20.

[2,6-Dimethyl-4-(trimethylsiloxy)phenyl]trioxorhenium(VII), (Me_3SiO-Xy)ReO_3 (8). A colorless solution of (Me_3SiO-Xy)ZnCl(THF) (0.74 g, 2.02 mmol) in THF (10 mL) was added dropwise to a cooled (−78 °C) pale yellow solution of Re_2O_7 (0.49 g, 1.01 mmol) in THF (40 mL). While the mixture was slowly warmed to ambient temperature, (ca. 2 h), the color changed to yellow and a white precipitate formed at −20 °C. After the mixture was stirred for 1 h at room temperature, the solvent was removed in vacuo to afford an oily yellow residue. This was extracted with pentane (3 × 15 mL) to give a reddish solution which yielded a yellow crystalline material upon concentration to ca. 5 mL and cooling (−78 °C). This was recrystallized from pentane to give yellow crystals of 8 (0.32 g, 0.75 mmol, 37% yield based on Re, 74% of theory). The white solid was extracted in a mixture of acetone and H_2O (3 drops) to hydrolyze the excess organozinc reagent. The acetone solution was filtered, dried in vacuo, and washed several times with THF. The white solid was identified (IR and elemental analysis) as $Zn(ReO_4)_2(THF)_2$ (0.34 g, 0.48 mmol, 48% based on Re). Data for 8: mp 73 °C; decpt 150 °C; IR (CS_2) ν(ReO) 975 (m), 951 (s), ν(SiO) 858 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.55 (s, 2 H, H-m), 2.22 (s, 6 H, Me-o), 0.07 (s, 9 H, $SiMe_3$); MS, m/z (EI) 428 (M^+, 100%), 413 (M^+ − Me, 59%), 193 (M^+ − ReO_3, 30%). Anal. Calcd for $C_{11}H_{17}O_4ReSi$ (Mr = 427.54): C, 30.90; H, 4.01; Re, 43.55; Si, 6.57. Found: C, 30.73; H, 3.88; Re, 45.17; Si, 6.30.

(2,6-Dimethyl-4-hydroxyphenyl)trioxorhenium(VII) (9). Upon addition of anhydrous HCl (1.0 M in Et_2O, 1.0 mL, 1.0 mmol) to a yellow solution of 8 (0.25 g, 0.59 mmol) in ether (5 mL), the color changed to light yellow. The solvent was removed in vacuo, and the yellow solid was washed several times with pentane and dried in vacuo. This afforded 9 as a microcrystalline powder (0.12 g, 0.34 mmol, 58% yield based on Re): IR (CH_2Cl_2) ν(OH) 3555 (m, br), ν(ReO) 985 (s), 951 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.02 (s, 2 H, H-m), 4.41 (s, 1 H, OH), 2.18 (s, 6 H, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 162.0 (CRe), 151.7 (C-p), 125.2 (C-o), 115.6 (C-m), 28.4 (Me). Anal. Calcd for $C_8H_9O_4Re$ (M_r = 355.36): C, 27.04; H, 2.55; Re, 52.40. Found: C, 27.30; H, 3.11; Re, 52.32.

Phenyltrioxo(quinuclidine)rhenium(VII) (10). A solution of $Ph(THF)ReO_3$ in n-pentane was prepared as described above from Ph_2Zn (0.11 g, 0.50 mmol) and Re_2O_7 (0.49 g, 1.00 mmol), and a solution of quinuclidine (0.12 g, 0.10 mmol) in pentane (5 mL) was added dropwise to afford a yellow precipitate of Ph-(quin)ReO_3 (10) (0.10 g, 0.24 mmol, 11% yield on Re): mp 156 °C; IR (KBr) ν(ReO) 917 (vs), (CS_2) ν(ReO) 922 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.62 (m, 2 H), 7.29 (m, 3 H), 2.65 (s br, 6 H, NCH_2), 1.88 (s br, 1 H, CH), 1.59 (s br, 6 H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 165.2 (CRe), 140.8 (C-o), 129.7 (C-p), 129.0 (C-m), 48.5 (NCH_2), 25.6 (CH_2), 20.2 (CH). Anal. Calcd for $C_{13}H_{18}NO_3Re$ (M_r = 422.50); C, 36.96; H, 4.29; N, 3.32. Found: C, 37.02; H, 4.44; N, 3.40.

X-ray Data Collection. Crystals of 1A were obtained by crystallization from n-pentane at −30 °C, crystals of 1B were obtained by slow evaporation of a diethyl ether solution, and crystals of 4 and 8 were obtained from slow cooling of n-pentane solutions from room temperature to −30 °C over 2 weeks. Data collections were carried out with Cu Kα or Mo Kα radiation on Enraf-Nonius CAD4 diffractometers. Final cell constants were obtained by least-squares refinement of 25 automatically centered reflections at high θ angles. Data were collected in $\theta/2\theta$ scan mode for compound 8 and in ω scan mode for the other compounds within the θ range 1–65° and 1–25°, respectively. Orientation control reflections were monitored every 200 reflections, and the intensities of three reflections were checked every 3600 s. Changes in intensity for 8 were corrected. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table IV.

Structures were solved by Patterson methods and subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing $\sum w(|F_o| - |F_c|)^2$. Anomalous dispersion has been taken into account. The refinements converged at shift/error <0.001. All calculations were carried out on a MicroVAX 3100 computer with the STRUX-III system[31] including the programs ORTEP, PLATON, SCHAKAL, SDP, SHELX-76, and SHELX-86.

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Registry No. 1, 125923-26-4; 2, 125923-25-3; 3, 131457-04-0; 4, 138693-72-8; 5, 138667-87-5; 6, 138667-88-6; 7, 138667-89-7; 8, 138667-90-0; 9, 138667-91-1; 10, 138667-92-2; Re_2O_7, 1314-68-7; Mes_2Zn, 73681-65-9; $Zn(ReO_4)_2(py)_4$, 28538-51-4; $Me_3SiOReO_3$, 16687-12-0; $Zn(ReO_4)_2(THF)_2$, 125934-15-8; Mes_2ReO_2, 110781-68-5; MesMgBr, 2633-66-1; Xy_2Zn, 65797-26-4; Ph_2Zn, 1078-58-6; Tol_2Zn, 15106-88-4; $(Ph_f)_2Zn$, 1799-90-2; 4-bromo-3,5-dimethyl-1-(trimethylsiloxy)benzene, 138721-92-3.

Supplementary Material Available: Tables of atomic positions, complete sets of bond distances and angles, and anisotropic displacement parameters for 1A, 1B, 4, and 8 (36 pages); listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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(31) Kiprof, P.; Herdtweck, E.; Schmidt, R. E.; Birkhahn, M.; Massa, W. *STRUX-III, ein Programmsystem zur Verarbeitung von Röntgendaten*; Technische Universität München and Universität Marburg: Germany, 1985/89.

(32) Note added in proof. As a new efficient route for organorhenium oxides in general, we will shortly report on the reactions of $R_3CC(=O)$-$OReO_3$ with alkylating agents (Herrmann, W. A.; Kühn, F.; Thiel, W. R.; Fischer, R. W. Unpublished results).