pronounced upfield shift for these signals and the smaller coupling constant observed for **6** compared to the corresponding data for the monoadducts suggest that the transannular S–S bond is broken upon coordination of the second proton. The dimethylated derivative $[1,5\text{-}Ph_4P_2N_4S_2Me_2{}^{2+}][CF_3SO_3{}^-]_2$ was also generated in solution by treatment of **2** (R = Ph) with an excess of $CF_3SO_3Me$, and the $^{31}P$ NMR spectrum indicated a similar mixture of isomers (Table I). The interconversion of these isomers in solution was monitored by $^{31}P$ NMR spectroscopy. It was observed for the diprotonated derivative that **6** converts into **5** whereas the reverse process occurs for the dimethylated adduct.

The lack of regiospecificity found for the formation of diadducts by **2** (R = Ph) is in contrast to the behavior observed for **1** (R = Ph). Ab initio Hartree–Fock–Slater SCF calculations of the interaction of the model system **2** (R = H), from the experimental geometry for **2** (R = Ph),[3] with two protons to give either **5** or **6** reveal very little difference in the total interaction energy for these two systems.[26] The values are −104 and −108 kcal mol$^{-1}$ for **5** and **6**, respectively, with the difference being primarily due to a slightly larger electrostatic contribution to the interaction energy for **6**. In light of these calculations the lack of regiospecificity in the formation of diadducts of **2** and their tendency to interconvert are not surprising.

**Conclusion.** The folded structure of **2** (R = Ph) is maintained in monoadducts with Lewis or Brønsted acids, and the transannular S–S interaction is strengthened. A similar enhancement of the S–S bond was predicted for the protonation of $S_4N_4$,[8] but the cage structure of $S_4N_4H^+$ is unstable with respect to a planar form. This major structural change has been attributed to the polarization of the $\pi^*$-electron density of the $\pi$-electron-rich ring into the skeletal bonds to the protonated nitrogens. The limited conformational change observed for **2** (R = Ph) upon adduct formation is reminiscent of the behavior of the $\pi$-electron-precise cyclotetraphosphazenes. In the limiting case of a full cross-ring S–S bond, **2** (R = Ph) can be viewed as a $\pi$-electron-precise system and in practice the $\pi^*$-electron density is much lower than that in binary S–N rings. Consequently, the polarization of the $\pi$ system induced by coordination to an electrophile has a smaller disruptive influence on the skeletal bonds. The nonregiospecific formation of adducts with stoichiometries other than 1:1 is an interesting feature of the Lewis base behavior of **2** that deserves further investigation.

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**Supplementary Material Available:** Tables listing crystallographic and thermal parameters, positional and isotropic thermal parameters for H atoms, all bond lengths and bond angles for non-H atoms, and least-squares planes (9 pages); a table of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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[26] For a description of the theoretical method and a definition of the components of the interaction energy, see ref 9.

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# Monomeric Rhenium(IV) Phenoxides and Their Development from Mononuclear Rhenium Halides with Oxygen and Sulfur Donor Ligands

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The homoleptic phenoxide complexes $Re(DIPP)_4$ (**1**, DIPP = 2,6-diisopropylphenoxide) and $Re(DMP)_4$ (**2**, DMP = 2,6-dimethylphenoxide) have been prepared by the reaction of $ReCl_4(THF)_2$ with $Li(DIPP)\cdot OEt_2$ and $Li(DMP)\cdot THF$, respectively. $Re(DIPP)_4$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 22.657$ (3) Å, $b = 11.498$ (2) Å, $c = 18.605$ (3) Å, $\beta = 110.62$ (1)°, $V = 4536.2$ Å$^3$, and $Z = 4$ with final $R = 0.035$ and $R_w = 0.044$. While $Re(DIPP)_4$ does not react with the internal acetylenes $RC\equiv CR$ (R = Me, Et, Ph), less crowded $Re(DMP)_4$ reacts with $RC\equiv CR$ to form the adducts $Re(RC\equiv CR)(DMP)_4$ (**3**, R = Me; **4**, R = Et; **5**, R = Ph). The new monomeric halides *trans*-$ReBr_4(THT)_2$ (**6**) and *trans*-$ReCl_4(THT)_2$ (**7**, THT = tetrahydrothiophene) have been prepared in high yield by refluxing $K_2ReX_6$ in concentrated HX (X = Br, Cl) and THT. Reducing $ReX_4(THT)_2$ with zinc in neat THT yields compounds of the formula *mer*-$ReX_3(THT)_3$ (**8**, X = Br; **9**, X = Cl). *mer*-$ReBr_3(THT)_3$ crystallizes in the orthorhombic space group *Pbca* with $a = 15.300$ (2) Å, $b = 14.976$ (2) Å, $c = 16.969$ (2) Å, $V = 3888.3$ Å$^3$, and $Z = 8$ with final $R = 0.046$ and $R_w = 0.051$. Cyclic voltammetry studies on compounds **1**–**9** reveal that the Re(III)–Re(IV) couple is accessible for all compounds, and it is seen to shift to more negative potentials as THT is replaced by halide followed by phenoxide.

## Introduction

Next to those of molybdenum and tungsten, rhenium catalysts are probably the most widely used for olefin metathesis[1] and remain the catalysts of choice for metathesizing certain functionalized olefins.[2] Compared to that of the group 6 metals, however, the synthetic and mechanistic rhenium chemistry related to metathesis is considerably less developed. Two important principles have emerged from the well-studied group 5[3] and 6[4,5] homogeneous olefin and acetylene metathesis systems: (i) the d$^0$ configuration seems to be the only relevant oxidation state in either

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[5] For acetylene metathesis by Mo and W, see: (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (b) Freudenberger, H. J.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Ibid.* **1984**, *3*, 1563.

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reaction;[6] (ii) metathesis is often not a *catalytic* process until halide ligands are replaced by better $\pi$-donor ligands, typically alkoxides.[3,5a,7] In contrast to the group 5[3] and 6[4] $d^0$ complexes, however, $d^0$ rhenium(VII) alkylidenes are poor olefin metathesis catalysts.[8] With the exception of $Re(\equiv CCMe_3)(=CHCMe_3)(OCMe_3)_2$, which engages in a few turnovers before metathesis ceases,[9] no other homogeneous $d^0$ rhenium species are reported to metathesize olefins actively.[49] This feature of rhenium chemistry is puzzling since $d^0$ rhenium alkylidynes and metallacyclobutadienes have been shown to participate in acetylene metathesis.[10]

Of particular relevance to this question are two recent reports implicating *intermediate oxidation state* rhenium species in both olefin and acetylene metathesis. First, Re(III) complexes $ReCl_3L_3$ (L = $PMePh_2$, $P(OEt)_3$, pyridine) form well-characterized Re(V)–oxo species $ReOCl_3L_2$ in the presence of $O_2$ and, with $EtAlCl_2$ as cocatalyst, have been shown to metathesize 2-pentene.[11,12] Second, another report documents a high acetylene metathesis activity for systems comprised of $Re_2Cl_4(dppm)_2$ (dppm = bis(diphenylphosphino)methane) and $Al(OR)_3$ (OR = $OCH(CF_3)_2$, $OCH(CH_3)_2$), implicating, among other possibilities, midvalent *rhenium alkoxides* as catalytically active species.[13,14]

The discovery that the replacement of halide ligands with better $\pi$-donor ligands can impart metathesis activity to early metal alkylidene and alkylidyne complexes[3,7] *and* the possible implication of intermediate oxidation state species,[11] including alkoxides,[13] as active catalysts in rhenium metathesis systems led us to consider the combination of these features in designing rhenium compounds relevant to metathesis. Herein, we report rare examples of monomeric $ReX_4$ species (where X is a monodentate anionic ligand), viz. the phenoxide compounds $Re(O\text{-}2,6\text{-}C_6H_3R_2)_4$, and undertake an examination of their redox chemistry and their reactions with acetylenes. As a part of this effort, we have developed preparative routes to new rhenium halides of the general formula $ReX_4(THT)_2$ and $ReX_3(THT)_3$ (THT = tetrahydrothiophene; X = Cl, Br) and also report these results, including electrochemical and structural studies. A portion of this work has been communicated.[15]

## Results

**Preparation and Properties of $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ and $Re(O\text{-}2,6\text{-}C_6H_3Me_2)_4$.** The known compounds of rhenium that contain alkoxide ligands are usually either dimeric[16] or contain the oxo ligand.[17] The only exception seems to be the compound $Re(OPh)_4(PMe_3)_2$, synthesized in low yield by adding $PMe_3$ to the residue obtained from reacting $ReOCl_4$ and NaOPh.[17b] To our knowledge, there are only three reports in the literature of homoleptic rhenium alkoxides, namely unstable $Re(OMe)_6$[18], a rhenium(VI) tris(catecholate) complex,[19] and the recently reported trinuclear compound $Re_3(O\text{-}i\text{-}Pr)_9$.[20] Although Druce reported obtaining $Re(OEt)_3$ in 1937,[21a] many workers since have failed to reproduce his original results.[21b] We turned to 2,6-dialkyl-substituted phenoxides, which are useful ancillary ligands for group 5 and 6 metathesis catalysts,[3a,5a] in order to impart monomeric behavior to the desired homoleptic compounds.

**Table I.** Details of the X-ray Diffraction Studies for $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ and $ReBr_3(SC_4H_8)_3$

| | | |
|---|---|---|
| mol formula | $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ | $ReBr_3(SC_4H_8)_3$ |
| $M_r$ | 895.27 | 690.44 |
| space group | $P2_1/c$ | *Pbca* |
| $V$, Å$^3$ | 4536.2 | 3888.3 |
| $a$, Å | 22.657 (3) | 15.300 (2) |
| $b$, Å | 11.498 (2) | 14.976 (2) |
| $c$, Å | 18.605 (3) | 16.969 (2) |
| $Z$ | 4 | 8 |
| $\beta$, deg | 110.62 (1) | 90 |
| calcd dens, g cm$^{-3}$ | 1.31 | 2.36 |
| data collcn temp, °C | 23 ± 1 | 23 ± 1 |
| Mo K$\alpha$ radiation $\lambda$, Å | 0.71073 (graphite monochromator) | |
| abs coeff, cm$^{-1}$ | 27.5 | 127.4 |
| $R$ | 0.035 | 0.046 |
| $R_w$ | 0.044 | 0.051 |

**Table II.** Selected Interatomic Distances (Å) and Angles (deg) for $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$[a]

| | | | |
|---|---|---|---|
| Re–O(10) | 1.867 (4) | Re–O(30) | 1.868 (4) |
| Re–O(20) | 1.879 (4) | Re–O(40) | 1.864 (4) |
| O(10)–Re–O(20) | 89.4 (2) | O(30)–Re–O(40) | 90.5 (2) |
| O(10)–Re–O(30) | 173.9 (2) | Re–O(10)–C(11) | 138.1 (4) |
| O(10)–Re–O(40) | 88.6 (2) | Re–O(20)–C(21) | 141.9 (4) |
| O(20)–Re–O(30) | 90.6 (2) | Re–O(30)–C(31) | 143.8 (4) |
| O(20)–Re–O(40) | 170.6 (2) | Re–O(40)–C(41) | 138.5 (4) |

[a] Atoms are labeled as in Figure 1. Numbers in parentheses are estimated standard deviations in the least significant digits.

The reaction between $ReCl_4(THF)_2$ and Li(DIPP)·$OEt_2$ (DIPP = $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) proceeds smoothly in diethyl ether according to eq 1, in spite of $ReCl_4(THF)_2$ being almost insoluble in the

$$ReCl_4(THF)_2 + 4Li(DIPP){\cdot}OEt_2 \xrightarrow{Et_2O} \underset{\mathbf{1},\ 75\%}{Re(DIPP)_4} + 4LiCl \tag{1}$$

reaction solvent. Reaction 1 is complete after 24 h at ambient

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**Table III.** Atomic Positional Parameters and Their Estimated Standard Deviations for Selected Atoms in $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Re | 0.24554 (1) | 0.11451 (2) | 0.07470 (2) | 2.649 (4) |
| O(10) | 0.1701 (2) | 0.0329 (4) | 0.0312 (3) | 3.6 (1) |
| O(20) | 0.2048 (2) | 0.2503 (4) | 0.0255 (3) | 3.7 (1) |
| O(30) | 0.3229 (2) | 0.1921 (4) | 0.1089 (3) | 3.3 (1) |
| O(40) | 0.2862 (2) | −0.0270 (4) | 0.1077 (3) | 3.3 (1) |
| C(11) | 0.1506 (3) | −0.0811 (6) | 0.0140 (4) | 3.6 (2) |
| C(21) | 0.1494 (3) | 0.2885 (6) | −0.0275 (4) | 3.6 (2) |
| C(31) | 0.3530 (3) | 0.2933 (6) | 0.1018 (4) | 3.1 (2) |
| C(41) | 0.3465 (3) | −0.0734 (6) | 0.1278 (4) | 3.4 (2) |

temperature, and dark red-brown $Re(DIPP)_4$ (**1**) is isolated in 75% yield. The $^1H$ NMR spectrum of $Re(DIPP)_4$ shows sharp resonances in spite of the compound's paramagnetism ($\mu_{eff} = 1.50\ \mu_B$). The only broad signal at $\delta$ 9.05 is assigned to the methine protons ($C\mathit{H}Me_2$) on the *o*-isopropyl groups. The paramagnetic contact shift is also greatest for these protons, which is not surprising, since crystal structures of DIPP complexes have shown them to be the protons closest to the metal center.[22] The meta protons on the phenoxide ligands also experience large Knight shifts and result in the usual second-order $A_2B$ spectrum for the aryl protons becoming a first-order $A_2X$ pattern. The infrared spectrum of **1** shows no strong peaks around 980 cm$^{-1}$, indicating the absence of any oxo ligands, and a sharp resonance of medium intensity at 450 cm$^{-1}$ is assigned to the Re–O stretch. The magnetic and solubility properties of $Re(DIPP)_4$ (**1**) are consistent with monomeric behavior in solution, which is borne out in a structural study (vide infra).

The reaction between $ReCl_4(THF)_2$ and Li(DMP)·THF (DMP = $O\text{-}2,6\text{-}C_6H_3Me_2$) in diethyl ether also proceeds smoothly, and $Re(DMP)_4$ (**2**) can be isolated as a dark brown crystalline solid in 77% yield (reaction 2). Combustion analysis confirms that

$$ReCl_4(THF)_2 + 4Li(DMP){\cdot}THF \xrightarrow{Et_2O} \underset{\mathbf{2},\ 77\%}{Re(DMP)_4} + 4LiCl \qquad (2)$$

**2** is not a dinitrogen compound. The $^1H$ NMR spectrum of $Re(DMP)_4$ shows three broad, featureless resonances downfield of 8 ppm in the ratio 6:2:1. No new resonances are seen to appear upon cooling the sample to 243 K. This, together with solution molecular weight measurements, leads us to believe that $Re(DMP)_4$ is also monomeric in solution.

Attempts to prepare complexes of the general formula $Re(OR)_nCl_{4-n}$ (OR = DIPP, DMP) by using 3 or fewer equivalents of the lithium phenoxides gave dark red-brown, intractable oils. These oils were characterized by $^1H$ NMR spectra that showed, inter alia, phenoxide ligand resonances and infrared spectra that contained peaks assignable to Re–Cl stretches. Although these oils were treated with both THT and pyridine in attempts to produce crystalline materials, in no case was this approach successful. While $Me_3Si$–OR or $Me_3Si$–OAr reagents are often used to prepare alkoxide and phenoxide derivatives of transition metals not normally accessible with the use of alkali-metal salts,[23] it was found that $ReCl_4(THF)_2$ is unreactive toward such reagents, even after refluxing in toluene for 7 days.

**X-ray Structural Study of $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$.** Single crystals of $Re(DIPP)_4$ suitable for X-ray analysis were grown from dichloromethane. A summary of the crystal data is given in Table I, selected bond distances and angles are given in Table II, and the atomic positional parameters of selected atoms are given in Table III. Two views of $Re(DIPP)_4$ are shown in Figure 1.

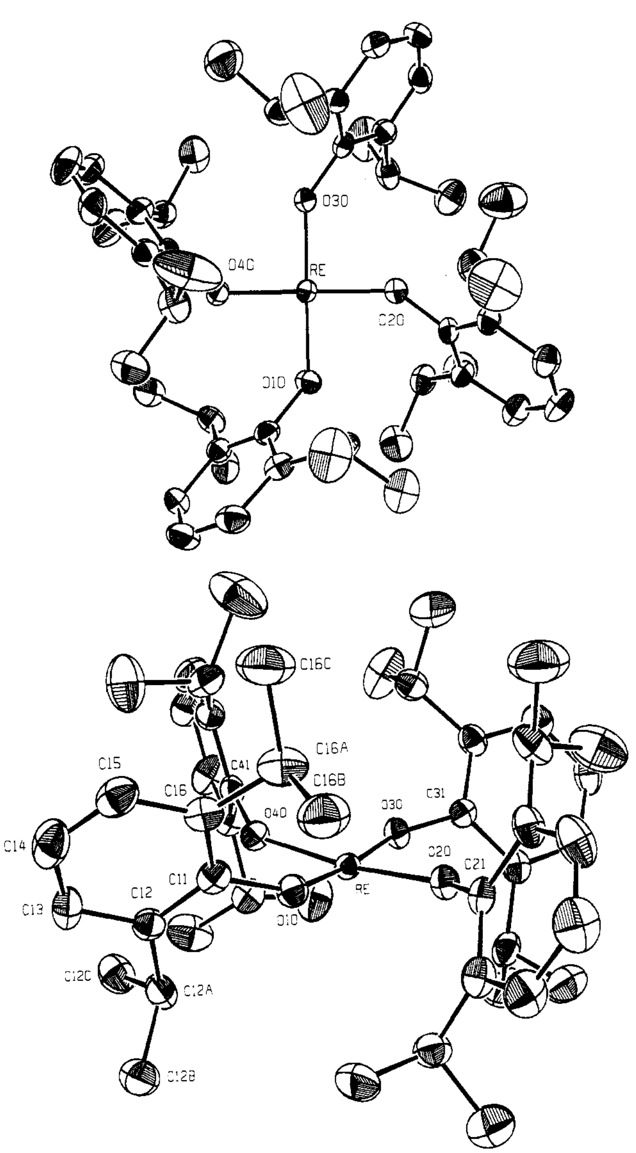

**Figure 1.** Molecular structure of $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$, with atoms shown as 30% probability ellipsoids.

The geometry about the rhenium atom in $Re(DIPP)_4$ is square planar with *trans*-O–Re–O angles of 173.9 (2) and 170.6 (2)° and *cis*-O–Re–O angles averaging 89.8°. In Figure 1, the rhenium atom is displaced 0.13 Å below the plane defined by the four oxygen atoms, while all of the $C_{ipso}$ atoms are located above this plane (0.31 Å on average). Metal–oxygen bond lengths are considered to be normal and vary from 1.864 (4) to 1.879 Å, and Re–O–$C_{ipso}$ angles fall in a narrow range between 138.1 (4) and 143.8 (4)°. The metal center is well protected from above and below the $ReO_4$ square plane by the *o*-isopropyl groups of the phenoxide ligands; the methine hydrogen atoms are projected toward the rhenium atom. The $C_6$ rings are twisted so that the angles between the normals to these planes and the normal to the $O_4$ plane average 67.5°.

This d$^3$ rhenium complex can be compared to the related d$^2$ complexes $W(DIPP)_4$ and $W(DMP)_4$, both of which are also square planar.[24] The precise geometry about the rhenium center is closer to that in $W(DMP)_4$ than $W(DIPP)_4$, the latter compound having a slight tetrahedral distortion. The observed geometry in $Re(DIPP)_4$ (like $W(OR)_4$) is no doubt electronic in origin. In a qualitative orbital analysis of $Re(DIPP)_4$, we consider the ligand $\pi$ interactions as perturbations on the d-orbital energies in a square-planar configuration ($d_{xz,yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$). The

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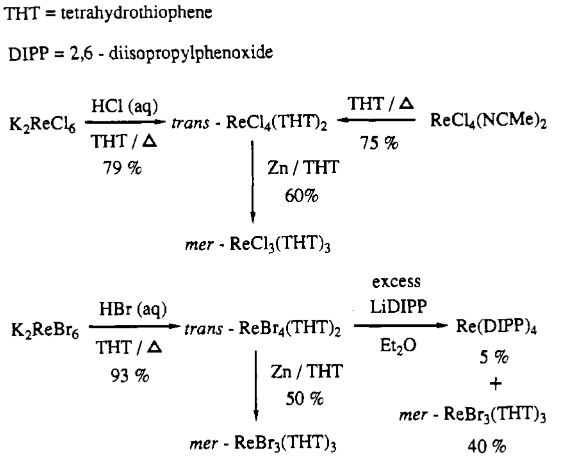
[22] See, for example: (a) Wexler, P. A.; Wigley, D. E. *J. Chem. Soc., Chem. Commun.* **1989**, 664. (b) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (c) Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4569.

[23] See, for example: (a) Handy, L. B.; Sharp, K. G.; Brinckman, F. E. *Inorg. Chem.* **1972**, *11*, 523. (b) Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1988**, *7*, 2217.

[24] (a) Listemann, M. L.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 7207. (b) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264.

**Scheme I**



oxygen p$\pi$ orbitals perpendicular to the $ReO_4$ plane (the "p$\pi\perp$" set) interact strongly with the metal, but the p orbitals on oxygen which lie in that plane are conjugated with the aryl $\pi$ system and interact less efficiently.[25] This $\perp$ p$\pi$ set interacts strongly with $d_{xz}$ and $d_{yz}$ orbitals, pushing them above the $d_{z^2}$ in energy. Therefore, the $d^3$ metal center will have two electrons in the Re $d_{z^2}$ orbital, and the remaining unpaired electron probably occupies the destabilized ($d_{xz}$, $d_{yz}$) set, which is metal–ligand $\pi^*$ in nature. Thus, the preference for a square-planar structure over tetrahedral can be traced to two principal factors: (i) the maximum stabilization afforded the oxygen p$\pi$ orbitals from the strong $\pi$ interactions with Re $d_{xz}$ and $d_{yz}$; (ii) the loss of all $\pi^*$ character in the metal $d_{z^2}$ in going from tetrahedral to square planar, which stabilizes the $d_{z^2}$ as a nonbonding, purely metal-based orbital. These arguments have been put forth recently in a quantitative MO analysis of tetrahedral vs square planar $Mo(OH)_4$.[26]

To our knowledge, the only other monomeric $ReX_4$ compound (where X is a monodentate, anionic ligand) synthesized is the recently reported $Re(2\text{-}MeC_6H_4)_4$.[27] In this compound $\pi$ interactions, such as those described above, are not possible and an X-ray structural study revealed a tetrahedral geometry about the metal center.

**Reactions of $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ and $Re(O\text{-}2,6\text{-}C_6H_3Me_2)_4$.** Discrete rhenium alkyne complexes only recently have been examined in detail.[28,29] In a series of experiments $Re(DIPP)_4$ and $Re(DMP)_4$ were each treated with 1 equiv of 2-butyne, 3-hexyne, and diphenylacetylene. No reaction was seen to occur in those experiments involving $Re(DIPP)_4$, a behavior which parallels that of the related $W(DIPP)_4$.[24] $Re(DMP)_4$, like $W(DMP)_4$, reacts with acetylenes to give acetylene adducts of the general formula $Re(RC{\equiv}CR)(DMP)_4$ (**3**, R = Me; **4**, R = Et; **5**, R = Ph) according to reaction 3. Addition of more than 1 equiv of 2-butyne or 3-hexyne to the reaction results in the formation of polymer, and no metal-containing products can be isolated.

$$Re(DMP)_4 + RC{\equiv}CR \xrightarrow{Et_2O} \underset{\textbf{3},\ 59\%;\ \textbf{4},\ 52\%;\ \textbf{5},\ 35\%}{Re(RC{\equiv}CR)(DMP)_4} \quad (3)$$

**Preparation and Properties of *trans*-$ReCl_4(SC_4H_8)_2$ and *trans*-$ReBr_4(SC_4H_8)_2$.** In the course of our studies we were recovering rhenium as $KReO_4$ and were interested in transforming this material into a compound of the general formula $ReX_4L_2$ without the need for its complete reduction to rhenium metal followed by chlorine oxidation to $ReCl_5$. The most likely (and easily accessible) precursors to such complexes are the hexahalogenorhenate(IV) $[ReX_6]^{2-}$ salts, to which $KReO_4$ can be easily recycled. Allen[30] reported that the reaction between $K_2ReBr_6$ in HBr with 1,4-dithiane in toluene gave a low yield of a compound formulated as $ReBr_4(1,4\text{-dithiane})_2$. We have found that by substituting neat tetrahydrothiophene (THT) for the organic phase the reaction can be driven to completion within 1 h and a near-quantitative yield of $ReBr_4(THT)_2$ (**6**) can be isolated (Scheme I). This air-stable compound is relatively insoluble in most organic solvents, but it may be recrystallized from dichloromethane solution to yield dark red crystals.

The corresponding reaction between $K_2ReCl_6$ and THT is considerably slower and is only 90% complete after 1 week. However, the yellow-green complex $ReCl_4(THT)_2$ (**7**) can be isolated in nearly 80% yield based on the quantity of $K_2ReCl_6$ consumed (Scheme I). This difference in reaction rates is entirely consistent with the observed labilities of the halogens in the $[ReX_6]^{2-}$ ions.[21b] $ReCl_4(THT)_2$ can also be prepared from $ReCl_4(NCMe)_2$ by ligand exchange. The acetonitrile adduct dissolves in neat THT easily, upon heating, to yield a dark yellow solution from which **7** can be isolated in good yield.

The infrared spectra of these compounds show the features associated with coordinated THT ligands, and metal halide stretches were observed at 269 $cm^{-1}$ for the bromide **6** and 322 $cm^{-1}$ for the chloride **7**. In both cases the single $\nu$(Re–X) mode is consistent with a trans arrangement of the THT ligands. Neither compound exhibits any features in their $^1H$ NMR spectra; relaxation of the protons appears to be so rapid that the peaks are broadened into the base line. Magnetic moments of these compounds were measured by the Evans method;[31] values of $\mu_{eff} = 5.40\ \mu_B$ and $\mu_{eff} = 4.98\ \mu_B$ were obtained for the bromide **6** and the chloride **7**, respectively. These values are much greater than that expected from the spin-only formula (3.87 $\mu_B$) and probably reflect a large orbital contribution to the moment, possibly due to a HOMO with considerable sulfur character. Our measurements of the magnetic moment of $ReCl_4(THF)_2$ provide a value (3.40 $\mu_B$) that is comparable to literature values obtained by Guoy measurements.[30]

**Preparation and Properties of *mer*-$ReBr_3(SC_4H_8)_3$ and *mer*-$ReCl_3(SC_4H_8)_3$.** Since $WCl_4(SMe_2)_2$ is the starting material for preparing $W(OR)_4$ complexes,[24] and since alkoxide compounds have been reported to *not* be isolated from reactions involving $ReCl_4(THF)_2$,[17b] we originally prepared the sulfur donor complexes **6** and **7** as potential precursors to $Re(OR)_4$ compounds (Scheme I). Thus, the reaction of $ReBr_4(THT)_2$ with 4 equiv of $Li(DIPP)\cdot OEt_2$ (24 h, $Et_2O$ solution) provides a small quantity (ca. 5%) of $Re(DIPP)_4$, along with a much larger quantity (ca. 40%) of a yellow, ether-insoluble powder. This yellow compound's $^1H$ NMR, $^{13}C$ NMR, and IR spectra suggested the formulation *mer*-$ReBr_3(THT)_3$ (**8**). This complex can be synthesized in higher yield by reducing $ReBr_4(THT)_2$ with zinc in neat THT; *mer*-$ReCl_3(THT)_3$ (**9**) can be prepared in an analogous manner from $ReCl_4(THT)_2$. The $^1H$ NMR spectra of compounds **8** and **9** show four featureless peaks in intensity ratios 2:1:2:1 ($C_\alpha$, $C_\alpha'$, $C_\beta$, $C_\beta'$) consistent with a *mer* geometry for the THT ligands. These peaks show large contact shifts for protons on the $\alpha$-carbon (consistent with a $d^4$ configuration) and are broad for all protons, contrasting sharply with the spectra obtained for compounds of the type $ReX_3(PR_3)_3$.[32] The $^{13}C$ NMR spectra of **8** and **9** show only four

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(25) (a) Coffindaffer, T. W.; Rothwell, I. P.; Huffmann, J. C. *Inorg. Chem.* **1983**, *22*, 2906. (b) The four oxygen p$\pi$ orbitals that lie in the $ReO_4$ plane will destabilize the Re $d_{xy}$ orbital to a lesser extent than the "p$\pi\perp$" set will destabilize the $d_{xz,yz}$ set. See ref 26.

(26) Cayton, R. H.; Chisholm, M. H.; Clark, D. L.; Hammond, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 2751.

(27) Savage, P. D.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 669.

(28) Boag, N. M.; Kaesz, H. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 4 pp, 161–242.

(29) See, for example: (a) de Boer, E. J. M.; de With, J.; Orpen, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 8271. (b) Mayer, J. M.; Tulip, T. H. *Ibid.* **1984**, *106*, 3878. (c) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *Ibid.* **1985**, *107*, 7454. (b) Mayer, J. M.; Tulip, T. H.; Calabrese, J. C.; Valencia, E. *Ibid.* **1987**, *109*, 157. (e) Valencia, E.; Santarsiero, B. D.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *Ibid.* **1987**, *109*, 6896. (f) Einstein, F. W. B.; Tyers, K. G.; Sutton, D. *Organometallics* **1985**, *4*, 489.

(30) Allen, E. A.; Johnson, N. P.; Rosevear, D. T.; Wilkinson, W. *J. Chem. Soc. A* **1969**, 788.

(31) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(32) (a) Shaw, D.; Randall, E. W. *J. Chem. Soc., Chem. Commun.* **1965**, 82. (b) Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg) for $ReBr_3(SC_4H_8)_3$[a]

| | | | |
|---|---|---|---|
| Re–Br(1) | 2.503 (2) | Re–S(1) | 2.396 (4) |
| Re–Br(2) | 2.566 (2) | Re–S(2) | 2.425 (5) |
| Re–Br(3) | 2.509 (2) | Re–S(3) | 2.400 (5) |
| Br(1)–Re–Br(2) | 93.19 (7) | Br(3)–Re–S(1) | 88.9 (2) |
| Br(1)–Re–Br(3) | 177.62 (7) | Br(3)–Re–S(2) | 90.4 (2) |
| Br(2)–Re–Br(3) | 89.17 (7) | Br(3)–Re–S(3) | 89.9 (2) |
| Br(1)–Re–S(1) | 88.7 (1) | S(1)–Re–S(2) | 91.7 (1) |
| Br(1)–Re–S(2) | 90.0 (1) | S(1)–Re–S(3) | 91.5 (1) |
| Br(1)–Re–S(3) | 89.8 (1) | S(2)–Re–S(3) | 176.8 (1) |
| Br(2)–Re–S(1) | 178.1 (1) | C(11)–S(1)–C(14) | 92.2 (9) |
| Br(2)–Re–S(2) | 88.1 (1) | C(21)–S(2)–C(24) | 93.2 (9) |
| Br(2)–Re–S(3) | 88.7 (1) | C(31)–S(3)–C(34) | 92.6 (9) |

[a] Atoms are labeled as in Figure 2. Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table V.** Atomic Positional Parameters and Their Estimated Standard Deviations for Selected Atoms in $ReBr_3(SC_4H_8)_3$

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Re | 0.30600 (5) | 0.46754 (5) | 0.35807 (5) | 2.49 (1) |
| Br(1) | 0.3559 (1) | 0.5272 (2) | 0.2278 (1) | 4.04 (5) |
| Br(2) | 0.4289 (1) | 0.3512 (1) | 0.3644 (2) | 4.32 (5) |
| Br(3) | 0.2504 (2) | 0.4117 (2) | 0.4881 (1) | 3.88 (4) |
| S(1) | 0.1898 (3) | 0.5747 (3) | 0.3566 (3) | 3.26 (9) |
| S(2) | 0.4027 (3) | 0.5711 (3) | 0.4251 (3) | 3.4 (1) |
| S(3) | 0.2171 (3) | 0.3593 (3) | 0.2913 (3) | 3.3 (1) |

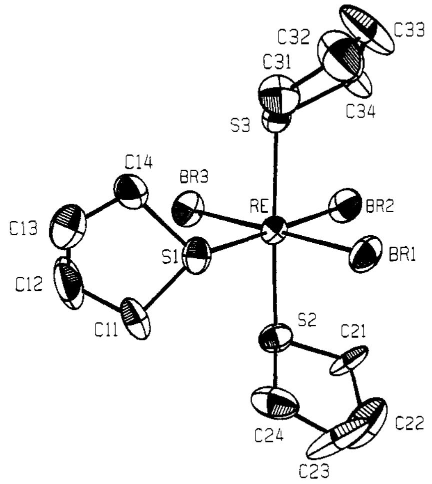

**Figure 2.** Molecular structure of *mer*-$ReBr_3(THT)_3$ (THT = tetrahydrothiophene), with atoms shown as 50% probability ellipsoids.

**Table VI.** Voltammetric Data for Compounds of Re(IV) and Re(III)[a]

| complex | $E_{1/2}$(ox) | $E_{p,a}$(ox) | $E_{1/2}$(red) |
|---|---|---|---|
| $Re(DIPP)_4$ (**1**)[b] | +0.49 (120) | | −0.72 (155) |
| $Re(DMP)_4$ (**2**)[b] | | +0.84 | −0.52 (110) |
| Re(MeC≡CMe)$(DMP)_4$ (**3**)[b] | | +0.80 | −0.57 (120) |
| Re(EtC≡CEt)$(DMP)_4$ (**4**)[b] | | +0.76 | −0.67[d]<br>−0.92[d] |
| Re(PhC≡CPh)$(DMP)_4$ (**5**)[b] | | +0.63 | −0.51[d]<br>−0.70[d] |
| *trans*-$ReBr_4(THT)_2$ (**6**)[c] | | | +0.14 (70) |
| *trans*-$ReCl_4(THT)_2$ (**7**)[c] | | +2.08 | +0.01 (80) |
| *mer*-$ReBr_3(THT)_3$ (**8**)[c] | +0.67 (60) | | −0.92 (60) |
| *mer*-$ReCl_3(THT)_3$ (**9**)[c] | +0.66 (70) | | −1.07 (70) |

[a] In volts vs Ag/AgCl, recorded at a Pt-disk electrode on solutions that are 0.1 M in *n*-$Bu_4NPF_6$ supporting electrolyte. $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 150 mV/s are given in parentheses. [b] Recorded in $CH_2Cl_2$ solution. [c] Recorded in $CH_3CN$ solution. [d] $E_{p,c}$(red) reported.

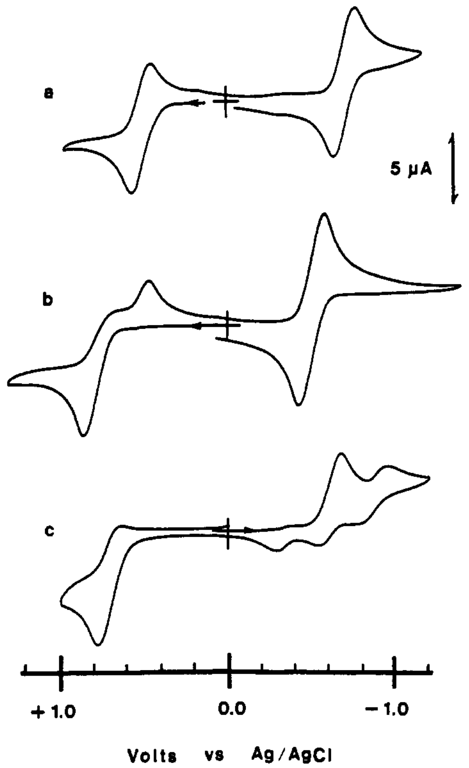

**Figure 3.** Cyclic voltammograms of 0.1 M *n*-$Bu_4NPF_6/CH_2Cl_2$ solutions of (a) Re(O-2,6-$C_6H_3$-*i*-$Pr_2)_4$ (**1**), (b) Re(O-2,6-$C_6H_3Me_2)_4$ (**2**), and (c) Re(EtC≡CEt)(O-2,6-$C_6H_3Me_2)_4$ (**4**), recorded at 150 mV/s.

lines, with large paramagnetic contact shifts for the α-carbons ($\delta(C_\alpha)$ 140–150 ppm). The magnetic moments of the complexes were measured in chloroform solution by the Evans method.[31] The observed values of $\mu_{eff} = 2.60\ \mu_B$ for *mer*-$ReBr_3(THT)_3$ (**8**) and $\mu_{eff} = 2.55\ \mu_B$ for *mer*-$ReCl_3(THT)_3$ (**9**) are only slightly lower than the spin-only value of 2.83 $\mu_B$ of a triplet ground state and are similar to those of other $ReX_3L_3$ complexes.[21b]

Both of these new Re(III) compounds appear remarkably stable. In an attempt to prepare rhenium(III) phenoxides, solutions of both the chloride and the bromide were stirred with Li(DIPP)·$OEt_2$ or Li(DMP)·THF but in no case was reaction seen to occur and the starting material was recovered in nearly quantitative yield. The reaction of these rhenium(III) halides with K(DMP) or K(DIPP) yielded dark green solutions from which no tractable products could be isolated.

**X-ray Structural Study of *mer*-$ReBr_3(SC_4H_8)_3$.** Single crystals of the bromide suitable for X-ray analysis were grown from dichloromethane/diethyl ether (1:1). A summary of the crystal data is given in Table I, bond distances and angles are given in Table IV, and atomic positional parameters of selected atoms are given in Table V.

Figure 2 presents the molecular structure of $ReBr_3(THT)_3$ (**8**) and confirms the meridional configuration consistent with the NMR data. Re–Br, S–C, and C–C bond lengths are all considered normal. The Re–S bond distances vary between 2.396 (4) and 2.425 (5) Å, which suggests that the bonding between the sulfur ligands and the rhenium center is predominantly a σ interaction: these bond lengths are significantly longer than those of simple rhenium(III) thiolate compounds.[33] The orbital geometry about the sulfur atoms is distorted tetrahedral, and the C–S–C angles of approximately 93° are normal for the THT ligand. Recently, Clark has reported the structure of the analogous rhodium compound $RhCl_3(THT)_3$,[34] which shows a similar twisting of the THT ligands away from each other; however, the two structures are not superimposable. Unlike in the rhodium compound, the trans THT ligands lie on either side of a mirror plane defined by the three bromines and the rhenium atom.

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(33) (a) Dilworth, J. R.; Neaves, B. D.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L223. (b) Blower, P. J.; Dilworth, J. R.; Hutchinson, J.; Nicholson, T.; Zubieta, J. *Ibid.* **1984**, *90*, L27. (c) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.

(34) Clark, P. D.; Machin, J. H.; Richardson, J. F.; Dowling, N. I.; Hyne, J. B. *Inorg. Chem.* **1988**, *27*, 3526.

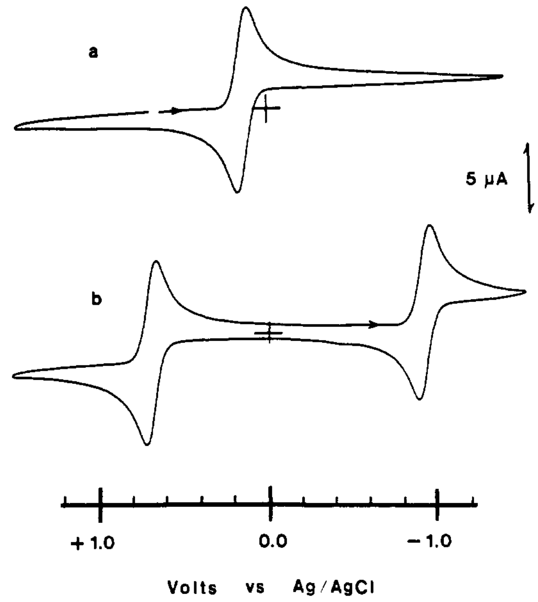

**Figure 4.** Cyclic voltammograms in 0.1 M $n$-$Bu_4NPF_6/CH_3CN$ solutions of (a) *trans*-$ReBr_4(THT)_2$ (**6**) and (b) *mer*-$ReBr_3(THT)_3$ (**8**), recorded at 150 mV/s.

**Electrochemical Properties of New Rhenium(IV) and Rhenium(III) Complexes.** The electrochemical behavior of $Re(OR)_4$ compounds is presented in Table VI and Figure 3. The redox chemistry of the rhenium(IV) phenoxides contrasts to that of the rhenium(IV) halides (vide infra) in that both the Re(V) and Re(III) oxidation states are easily accessible. The oxidation of $Re(DIPP)_4$ to Re(V) occurs at $E_{1/2} = +0.49$ V, while reduction to Re(III) comes at $E_{1/2} = -0.72$ V (vs Ag/AgCl in $CH_2Cl_2$ solution) in what is probably best described as quasi-reversible processes on the CV time scale. Plots of peak anodic current vs the square root of the sweep rate ($v^{1/2}$) are linear in each case, but cathodic/anodic peak separations for both waves are between 125 and 155 mV (at 150 mV/s scan rate) and $i_{p,a}/i_{p,c}$ is *not* strictly 1.0 in either case (Figure 3).[35] A more detailed examination of the electrochemistry via bulk electrolysis reveals that in each process only 0.5 ± 0.05 electrons are consumed. Similar results have between obtained for Mo(alkyne)$(DIPP)_4$ complexes, in which it is suggested that some product of the oxidation or reduction reacts stoichiometrically with the starting material (an EC process).[36] The electrochemistry of $Re(DMP)_4$ (Figure 3 and Table VI) parallels that of $Re(DIPP)_4$ in all except one regard: the oxidation process in $Re(DMP)_4$ is completely irreversible on the CV time scale. The reactivity differences between neutral DMP and DIPP compounds—presumably due to steric influences—have been noted by us (vide supra) and others,[24] and it seems likely that this difference may be augmented in a highly reactive cation of $Re(OR)_4$.

The cyclic voltammograms of $Re(RC{\equiv}CR)(DMP)_4$ (**3**–**5**, Figure 3 and Table VI) are seen to display apparently reversible[37] reductions within the $CH_2Cl_2$ solvent range; however, bulk electrolysis reveals that they are also "half-electron" reductions. These processes are shifted to slightly more negative potentials relative to "base-free" $Re(DMP)_4$. This result is consistent with adduct formation, since one would expect the addition of an electron to be more difficult (and the removal of an electron to be more facile) in the adduct. This conclusion is only made in a general sense, since the LUMOs of $Re(OR)_4$ and Re(acetylene)$(OR)_4$ are not expected to be the same. The oxidation waves for compounds **3**–**5** are irreversible but are also shifted to slightly more negative potentials relative to those for $Re(DMP)_4$.

The cyclic voltammogram of *trans*-$ReBr_4(THT)_2$ (**6**) is reproduced in Figure 4, and electrochemical data are recorded in Table VI. Both Re(IV) compounds show a readily accessible, reversible[37] reduction near 0.0 V vs Ag/AgCl. Exhaustive electrolysis reveals that these are one-electron processes ($n = 1.00 \pm 0.05$). The cathodic/anodic peak separations are between 70 and 80 mV (at a 150 mV/s scan rate) for these reductions. In addition, an electrochemical oxidation is observed for *trans*-$ReCl_4(THT)_2$ (**7**) that appears at a potential just inside the solvent window (Table VI). This process occurs at $E_{p,a} = +2.08$ V (vs Ag/AgCl) for **7**, is possibly a two-electron process based solely upon anodic current, and is completely irreversible.

The rhenium(III) halides exhibit a well-defined electrochemistry, as both the Re(II) $\rightleftharpoons$ Re(III) and Re(III) $\rightleftharpoons$ Re(IV) couples are accessible (Figure 4 and Table VI). A one-electron reduction of both $ReBr_3(THT)_3$ (**8**) and $ReCl_3(THT)_3$ (**9**) occurs near $E_{1/2} = -1.0$ V, while the one-electron oxidation of both compounds is seen near +0.7 V (both vs Ag/AgCl in $CH_3CN$). In all of the redox processes the cathodic/anodic peak separations were between 60 and 70 mV (at a 150 mV/s scan rate), and variable-scan-rate experiments revealed electrochemical reversibility.[37]

If one examines the potentials of the Re(III) $\rightleftharpoons$ Re(IV) couple in the compounds **1**–**9**, and if one assumes the shift in potentials are a reflection of the ligand's donating ability to the metal center, it is clear that these ligands place more electron density on the metal in the order DIPP > Br > THT. This result is not unexpected as the $\pi$-donor nature of alkoxides, and to a lesser extent halides, is well established, but these electrochemical results help quantify this donor ability and demonstrate that the $d^2$ Re(V) oxidation state, implicated in many metathesis systems, is easily accessible for the alkoxide complexes.

## Discussion

Because we believe that some of the active rhenium metathesis systems involve $d^{n>0}$ complexes, and because alkoxide ligation may be important in activating these species to *catalytic* behavior, we consider the investigation of these rhenium(IV) alkoxides as relevant to metathesis chemistry. The initial reactivity studies of new $Re(OR)_4$ compounds have centered on their redox behavior and their reactions with acetylenes. In addition, midvalent rhenium alkoxides may prove important in studies of small molecule activation as has been the case for $MoX_4$ and $WX_4$ compounds (where X is a monodentate anionic ligand).[24,38] While rhenium(IV) compounds of the general formulas $ReX_4L_2$, $[ReX_6]^{2-}$ and $[ReX_5L]^-$ are common, monomeric $ReX_4$ species are quite rare.[21b,27]

The electrochemical comparisons of $Re(OR)_4$ vs $Re(RC{\equiv}CR)(DMP)_4$ seem to indicate that it is perhaps more accurate to view the metal center in $Re(OR)_4$ as behaving principally in a Lewis acidic fashion. In other words, the present data do not support the acetylene ligand in $Re(RC{\equiv}CR)(DMP)_4$ (**3**–**5**) being reduced to any extent and the metal center thereby oxidized. This behavior is analogous to that of known rhenium acetylene compounds[28,29,39] in various oxidation states and the related molybdenum compounds $Mo(RC{\equiv}CR)(OR)_4$ and $Mo(RC{\equiv}CR)(SR)_4$.[36] The reactivity of $Re(DIPP)_4$ and $Re(DMP)_4$ toward acetylenes has paralleled that of their diamagnetic analogues $W(DIPP)_4$ and $W(DMP)_4$ thus far,[24] although the paramagnetism of $Re(OR)_4$ is expected to impart different reactivity properties in many reactions.

Although the new tetrahydrothiophene complexes did *not* provide the best route to $Re(OR)_4$ compounds, these Re(III) species do represent rare examples of mononuclear $ReX_3L_3$ molecules with ancillary solvent ligands.[21b] These new $ReX_n(solvent)_{6-n}$ ($n$ = 3, 4) adducts ultimately may prove useful in

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[35] Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; John Wiley and Sons: New York, 1974.

[36] Walborsky, E. C.; Wigley, D. E.; Roland, E.; Dewan, J. C.; Schrock, R. R. *Inorg. Chem.* **1987**, *26*, 1615.

[37] The ratio $i_{p,a}/i_{p,c}$ was 1.0 in all cases, and plots of $i_p$ current vs the square root of the scan rate ($v^{1/2}$) were linear, indicating electrochemical reversibility; see ref 35.

[38] See, for example: (a) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3572. (b) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *Ibid.* **1985**, *107*, 5795.

[39] (a) Hey, E.; Welle, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 25. (b) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946.

addressing the Ziegler-type metathesis systems based upon $ReCl_5$. These systems *typically* do not employ added ligands such as phosphines, therefore only solvent molecules, substrate (acetylene or olefin), or cocatalysts can serve as stabilizing ligands.[1] By developing new mononuclear solvent adducts, we may approach actual metathesis conditions in a homogeneous Ziegler type system and perhaps substantiate and understand the role of midvalent rhenium complexes in catalytic metathesis. We intend to include olefins and typical cocatalysts in reactivity studies of these halides *and* $Re(OR)_x$ in an effort to ascertain which combination of reagents may provide a species that can initiate and propagate metathesis.

## Experimental Section

**General Details.** All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[40] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were purified under $N_2$ by standard techniques[41] and transferred to the drybox or reaction vessel without exposure to air.

**Starting Materials.** Tetrahydrothiophene, 2,6-diisopropylphenol, 2,6-dimethylphenol, and diphenylacetylene were purchased from Aldrich and distilled or recrystallized before use. Lithium salts of the phenols were prepared by adding equimolar *n*-butyllithium to pentane solutions of the phenol. The subsequent salt was converted to a solvent adduct by dissolution in the solvent, followed by solvent removal. 2-Butyne and 3-hexyne were purchased from Farchan and passed down a short column of alumina at −20 °C. Rhenium metal was purchased from Johnson Matthey and used as received. $ReCl_5$,[42] $KReO_4$,[43] $K_2ReCl_6$,[44] $K_2ReBr_6$,[44] $ReCl_4(THF)_2$,[30] and $ReCl_4(MeCN)_2$[45] were prepared by literature methods.

**Physical Measurements.** $^1H$ (250 MHz) and $^{13}C$ (62.9 MHz) NMR were recorded at probe temperature on a Bruker WM-250 spectrometer in $C_6D_6$ or $CDCl_3$ solvent. Chemical shifts are referenced to protio solvent impurities and are reported in ppm downfield of $Me_4Si$. Infrared spectra were recorded on CsI pellets in the region of 4000–180 $cm^{-1}$ by using a PE-983 spectrometer. Cyclic voltammetry experiments were performed under a nitrogen atmosphere by using a BioAnalytical Systems CV-27 voltammograph and recorded on a Houston Instruments Model 100 X-Y recorder. Measurements were taken at a Pt-disk electrode in $CH_2Cl_2$ or $CH_3CN$ solutions containing 0.1 M $n\text{-}Bu_4NPF_6$ as supporting electrolyte. Voltammograms were recorded at room temperature and at a sweep rate of 150 mV/s. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) are referenced to Ag/AgCl and are uncorrected for junction potentials. Values of *n*, where *n* is the number of equivalents of electrons transferred in an exhaustive electrolysis at a constant potential, were determined by measuring the total area under current vs time curves for the complete reaction. Redox reactions were considered one-electron processes if $n = 1.0 \pm 0.1$. Reversibility criteria have been stated.[37] Magnetic moment measurements were performed by the Evans method[31] on $C_6D_6$ or $CDCl_3$ solutions (250 MHz) at probe temperature, and frequency shifts were measured for solvent protio impurity resonances. Diamagnetic corrections ($\chi_{dia}$) were calculated from Pascal's constants.[46] X-Band ESR spectra were recorded at room temperature on THF solutions by using a Varian E-3 spectrometer. All microanalytical samples were handled under nitrogen and were combusted with $WO_3$ (Desert Analytics, Tucson, AZ).

**Preparations. $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ (1).** To a suspension of 1.0 g (2.1 mmol) of $ReCl_4(THF)_2$ in 40 mL of diethyl ether was added 2.20 g (8.6 mmol) of $LiDIPP{\cdot}OEt_2$ (DIPP = 2,6-diisopropylphenoxide). After being stirred for 24 h, the resulting dark solution was filtered through Celite and the solvent removed under reduced pressure to yield a dark solid. This solid was extracted twice with dichloromethane, and the combined extracts were pumped to dryness. The resulting solid can be recrystallized from dichloromethane/diethyl ether (2:1) to yield 1.40 g (1.56 mmol, 75%) of the product as dark brown crystals. $^1H$ NMR ($C_6D_6$): δ 11.35 (d, 2 H, $H_m$, $J_{HH}$ = 8 Hz), 9.05 (br, 2 H, $C\mathit{H}Me_2$), 6.17 (t, 1 H, $H_p$, $J_{HH}$ = 8 Hz), 1.74 (br s, 12 H, $CH\mathit{Me}_2$). $^{13}C$ NMR ($C_6D_6$): δ 203.1 (br s, $C_{ipso}$ or $C_o$), 146.4 (d, $C_m$), 127.0 (d, $C_p$), 27.0 (q, $CH\mathit{Me}_2$), 23.6 (d, $\mathit{C}HMe_2$). Magnetic moment ($C_6D_6$ solution): $\mu_{eff} = 1.50\ \mu_B$. ESR (THF solution): six-line signal at $g = 2.04$, $A_{Re} \approx 580$ Hz ($I(^{185}Re) = {}^5/_2$, 37.07% abundant; $I(^{187}Re) = {}^5/_2$, 62.93% abundant). Anal. Calcd for $C_{48}H_{68}O_4Re$: C, 64.39; H, 7.65; Cl, 0.0. Found: C, 64.26; H, 7.79; Cl, 0.0.

**$Re(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (2).** To a suspension of 1.83 g (3.88 mmol) of $ReCl_4(THF)_2$ in 60 mL of diethyl ether was added 3.10 g (16 mmol) of $LiDMP{\cdot}THF$ (DMP = 2,6-dimethylphenoxide). After being stirred for 24 h, the resulting dark solution was filtered and the resulting solid washed with a small quantity of diethyl ether. The solid was extracted thoroughly with dichloromethane and the resulting solution pumped to dryness to yield the product as a dark solid. The mother liquor from the reaction was cooled to −20 °C to yield a further crop of product. The total yield of $Re(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ was 2.0 g (2.98 mmol, 77%). The compound is sufficiently pure for further reactions but may be recrystallized from diethyl ether/dichloromethane (2:1). $^1H$ NMR [$C_6D_6$; all resonances are broad, featureless signals (first number in parentheses is peak width (Hz) at half-maximum)]: δ 10.1 (60, 1 H, $C_p$), 9.48 (65, 2 H, $C_m$), 8.73 (75, 6 H, Me). Magnetic moment ($C_6D_6$): $\mu_{eff} = 1.37\ \mu_B$. ESR (THF solution, room temperature): six-line signal at $g_{av} = 2.16$, $A_{Re} \approx 430$ Hz ($I(^{185}Re) = {}^5/_2$, 37.07% abundant; $I(^{187}Re) = {}^5/_2$, 62.93% abundant). $M_r$ (vapor pressure osmometry, $CH_2Cl_2$ solution, room temperature): 640 ± 60 (calcd 671). Anal. Calcd for $C_{32}H_{36}O_4Re$: C, 57.29; H, 5.41; N, 0.0. Found: C, 57.07; H, 5.53; N, 0.0.

**$Re(MeC{\equiv}CMe)(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (3).** A 0.25-g amount of $Re(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (0.37 mmol) was dissolved in 25 mL of diethyl ether, and the solution was cooled to −20 °C. 2-butyne (29 μL, 0.37 mmol) was added and the solution stirred and allowed to reach ambient temperature. After 45 min the solvent was removed under reduced pressure to yield a dark solid. Dissolution in 5 mL of dichloromethane/diethyl ether (1:1) and cooling to −20 °C yields 0.16 g (0.22 mmol, 59%) of **3** as dark cubes. $^1H$ NMR [$C_6D_6$; all resonances are broad, featureless signals (peak width (Hz) at half-maximum in parentheses)]: δ 12.8 (180), 11.6 (350), 9.75 (50), 6.35 (48), 6.0 (420), 4.65 (42), 1.3 (200). Magnetic moment ($C_6D_6$): $\mu_{eff} = 1.89\ \mu_B$. Anal. Calcd for $C_{36}H_{42}O_4Re$: C, 59.65; H, 5.84. Found: C, 59.59; H, 5.62.

**$Re(EtC{\equiv}CEt)(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (4).** A 0.3-g amount of $Re(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (0.45 mmol) was dissolved in 25 mL of diethyl ether, and the solution was cooled to −20 °C. 3-Hexyne (50 μL, 0.45 mmol) was added and the solution stirred and allowed to reach ambient temperature. After 45 min the solvent was removed under reduced pressure to yield a dark oily solid. Dissolution in 5 mL of pentane and cooling to −20 °C yields 0.17 g (0.23 mmol, 52%) of **4** as dark blocks. $^1H$ NMR [$C_6D_6$; all resonances are broad, featureless signals (peak width (Hz) at half-maximum in parentheses)]: δ 12.3 (165), 11.5 (300), 10.6 (70), 10.0 (300), 5.4 (330), 3.9 (130), 3.4 (150), 0.1 (70), −0.2 (140). Magnetic moment ($C_6D_6$): $\mu_{eff} = 1.78\ \mu_B$. Anal. Calcd for $C_{38}H_{46}O_4Re$: C, 60.62; H, 6.16. Found: C, 60.81; H, 5.99.

**$Re(PhC{\equiv}CPh)(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (5).** A 0.25-g amount of $Re(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (0.37 mmol) was dissolved in 15 mL of dichloromethane, and the solution was cooled to −20 °C. Diphenylacetylene (66 mg, 0.37 mmol) was added and the solution stirred and allowed to reach ambient temperature. After 2 h the solvent was removed under reduced pressure to yield a dark solid. The solid was stirred in 5 mL of pentane, and dichloromethane was added dropwise until dissolution was complete. Cooling the solution to −20 °C yields 0.11 g (0.13 mmol, 35%) of **5** as dark crystals. $^1H$ NMR [$C_6D_6$; all resonances are broad, featureless signals (peak width (Hz) at half-maximum in parentheses)]: δ 10.8 (20), 9.65 (150), 8.28 (15), 7.7–6.4 (sharp multiplets), 3.58 (20), 2.2 (135), 0.35 (60). Magnetic moment ($C_6D_6$): $\mu_{eff} = 1.82\ \mu_B$. Anal. Calcd for $C_{46}H_{46}O_4Re$: C, 65.07; H, 5.46. Found: C, 64.36; H, 5.24.

***trans*-$ReBr_4(SC_4H_8)_2$ (6).** A 1.00-g amount (1.34 mmol) of $K_2ReBr_6$, 20 mL of tetrahydrothiophene, and 10 mL of 48% hydrobromic acid solution were refluxed together for 1 h and allowed to cool. Red brown crystals of the desired compound grew within the organic phase; these were filtered off and dried in vacuo. The organic phase from the original reaction mixture was separated from the aqueous layer, dried over anhydrous sodium carbonate, and pumped to dryness. The resulting brown solid was washed with diethyl ether and dried in vacuo. Total yield of compound was 0.85 g (1.25 mmol) or 93% of theoretical. The compound is sparingly soluble in common organic solvents but may be recrystallized satisfactorily from dichloromethane at −35 °C. Anal. Calcd for $C_8H_{16}Br_4ReS_2$: C, 14.09; H, 2.36; Br, 46.85. Found: C, 14.17; H, 2.32; Br, 46.78.

***trans*-$ReCl_4(SC_4H_8)_2$ (7). From $K_2ReCl_6$.** A 1.00-g amount (2.10 mmol) of dipotassium hexachlororhenate, 20 mL of concentrated hydrochloric acid, and 50 mL of tetrahydrothiophene were refluxed together with rapid stirring for 6 days. The reaction was then allowed to cool and the dark organic phase separated. The aqueous phase was extracted

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twice with 50 mL of dichloromethane, and these extracts were combined with the organic phase. Filtration of the aqueous phase, followed by $H_2O$ removal under reduced pressure, led to the recovery of 0.10 g of $K_2ReCl_6$. The combined organic extracts were dried over anhydrous sodium carbonate before being pumped to dryness to yield a yellow-green solid residue. Washing this residue with small amounts of acetone followed by diethyl ether gave the product as a yellow solid, which can be recrystallized from 1:1 dichloromethane/diethyl ether. The yield of *trans*-$ReCl_4(SC_4H_8)_2$ was 0.75 g (1.49 mmol) or 79% of theoretical based upon $K_2ReCl_6$ consumed. Anal. Calcd for $C_8H_{16}Cl_4ReS_2$: C, 19.05; H, 3.20; Cl, 28.12. Found: C, 19.23; H, 3.22; Cl, 28.29.

**From $ReCl_4(NCMe)_2$.** A suspension of 0.73 g (1.78 mmol) of $ReCl_4(NCMe)_2$ in 15 mL of tetrahydrothiophene was heated to 80 °C for 1 h, over which time the solid dissolved to yield a dark solution. After cooling, the solution was pumped to dryness and the resulting yellow solid recrystallized from dichloromethane/diethyl ether (1:1). The yield of $ReCl_4(THT)_2$ was 0.67 g (1.33 mmol) or 75% of theoretical.

***mer*-$ReBr_3(SC_4H_8)_3$ (8).** To a solution of 0.20 g (0.29 mmol) of $ReBr_4(THT)_2$ in 15 mL of tetrahydrothiophene was added 10 mg (0.15 mmol) of zinc dust. After being stirred for 2 days, the resulting orange solution was pumped to dryness to yield a yellow solid. This solid was washed with a small amount of acetonitrile (to remove the zinc salts) and recrystallized from dichloromethane/diethyl ether (1:3). The yield of orange crystals of *mer*-$ReBr_3(SC_4H_8)_3$ was 0.1 g (0.14 mmol) or 50%. $^1H$ NMR ($CDCl_3$): $\delta$ 11.9 (br, 8 H, $\mathrm{SC}H_2\mathrm{CH}_2$), 8.9 (br, 4 H, $\mathrm{SC}H_2\mathrm{CH}_2$), 5.6 (br, 8 H, $\mathrm{SCH_2C}H_2$), 4.3 (br, 4 H, $\mathrm{SCH_2C}H_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 145.1 (t, $\mathrm{S}C\mathrm{H_2CH_2}$), 139.3 (t, $\mathrm{S}C\mathrm{H_2CH_2}$), 57.1 (t, $\mathrm{SCH_2}C\mathrm{H_2}$), 54.1 (t, $\mathrm{SCH_2}C\mathrm{H_2}$). Anal. Calcd for $C_{12}H_{24}Br_3ReS_3$: C, 20.88; H, 3.50; Br, 34.72. Found: C, 20.96; H, 3.44; Br, 34.57.

***mer*-$ReCl_3(SC_4H_8)_3$ (9).** To a solution of 0.3 g (0.59 mmol) of $ReCl_4(THT)_2$ in 15 mL of tetrahydrothiophene was added 19 mg (0.29 mmol) of zinc dust. After being stirred for 2 days, the resulting orange solution was pumped to dryness to yield an orange solid residue. The compound was purified by chromatography on activated alumina using dichloromethane/diethyl ether (1:1) as eluent. The yield of *mer*-$ReCl_3(SC_4H_8)_3$ was 0.20 g (0.36 mmol) or 60% of theoretical. $^1H$ NMR ($CDCl_3$): $\delta$ 11.85 (br, 8 H, $\mathrm{SC}H_2\mathrm{CH}_2$), 9.10 (br, 4 H, $\mathrm{SC}H_2\mathrm{CH}_2$), 5.45 (br, 4 H, $\mathrm{SCH_2C}H_2$), 3.74 (br, 8 H, $\mathrm{SCH_2C}H_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 151.0 (t, $\mathrm{S}C\mathrm{H_2CH_2}$), 140.1 (t, $\mathrm{S}C\mathrm{H_2CH_2}$), 64.8 (t, $\mathrm{SCH_2}C\mathrm{H_2}$), 58.5 (t, $\mathrm{SCH_2}C\mathrm{H_2}$). Anal. Calcd for $C_{12}H_{24}Cl_3ReS_3$: C, 25.87; H, 4.43; Cl, 19.09. Found: C, 25.97; H, 4.41; Cl, 18.81.

**X-ray Study of $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$.** A dark red block crystal of dimensions 0.16 × 0.29 × 0.56 mm was mounted in a glass capillary in a random orientation. Data were collected on a Syntex $P2_1$ diffractometer in the range $2\theta$ = 2–50° and at scan speeds of 2–8° $min^{-1}$. No crystal decay was observed during data collection. Of the 8948 reflections measured, 5163 had $I > 3\sigma(I)$. The structure was solved by the Patterson heavy-atom method, and 478 parameters were refined by full-matrix least-squares techniques. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The largest peak in the final difference-Fourier map had a height of 0.48 e/Å$^3$. All calculations were performed on a VAX computer using SDP/VAX[47] and SHELX-86.[48]

**X-ray Study of *mer*-$ReBr_3(SC_4H_8)_3$.** A golden brown rectangular crystal of dimensions 0.1 × 0.26 × 0.28 mm was mounted on a glass fiber in a random orientation. Data were collected on a Syntex $P2_1$ diffractometer in the range $2\theta$ = 2–50° and at scan speeds of 2–8° $min^{-1}$. No crystal decay was observed during the course of data collection. Of the 3946 reflections measured, 1645 had $I > 3\sigma(I)$. The structure was solved by the Patterson heavy-atom method, and the 172 parameters were refined by full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and constrained to ride on their respective carbon atoms. The largest peak in the final difference-Fourier map had a height of 0.93 e/Å$^3$. All calculations were performed on a VAX computer using SDP/VAX.[47] A numerical absorption correction was applied.

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**Supplementary Material Available:** For $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ and *mer*-$ReBr_3(THT)_3$, full details of the structure solutions, tables of crystallographic details, atomic positional and thermal parameters, bond distances and angles, torsional angles, least-squares planes, and dihedral angles, and ORTEP figures (18 pages); tables of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(49) Note Added in Proof: Since the submission of this paper, Schrock and co-workers have reported certain well-defined rhenium(VII) alkylidenes that, in the presence of Lewis acid cocatalysts, exhibit a high activity toward catalytic olefin metathesis. See: Schrock, R.; Toreki, R.; Weinstock, I.; Schofield, M. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX; American Chemical Society: Washington, DC, 1989; INOR 99.