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Preparation, Properties, and Reactions of Five-Coordinate Re(VII) Dioxo and Diimido Complexes

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The reactions of aliphatic and aromatic 1,2-diamines, diols, and dithiols with CH_3ReO_3 (**1**), $\{CH_3Re(NAr)_2O\}_2$ (**2**, Ar = 2,6-diisopropylphenyl), and $\{CH_3Re(NAr)_2S\}_2$ (**3**) have been studied. Two of the reaction products, $[CH_3Re(O)_2\{1,2\text{-}(NH)_2C_6H_4\}]_2\{\mu\text{-}1,2\text{-}(NH_2)_2C_6H_4\}$ (**4a′**) and $CH_3Re(NAr)_2(SCH_2CH_2S)$ (**5c**), have been structurally characterized. The former is a binuclear species in which each rhenium is six-coordinate with a pseudo-octahedral structure. The bridging phenylenediamine ligand can be replaced by pyridine and its derivatives. Unlike the known catecholato complex $CH_3Re^{VII}(O)_2(1,2\text{-}O_2C_6H_4)(Py)$, the Re^{V}-benzoquinonediimine resonance form contributes noticeably to the overall structure of **4a′**. The five-coordinate diimido complex **5c** does not interact with coordinating ligands such as pyridines. The initial reactions of **2** with catechol and ethylene glycol lead to $CH_3Re(NAr)_2(1,2\text{-}O_2C_6H_4)$ (**5b′**) and $CH_3Re(NAr)_2(OCH_2CH_2O)$ (**5b**), respectively. Further hydrolysis of **5b** affords $CH_3Re(NAr)(O)(OCH_2CH_2O)$ (**6b**). Compound **3**, a sulfur analogue of **2**, condenses only with dithiols. The high reactivity of **2** is likely due to the presence of a four-coordinate monomeric form in solution and the formation of H_2O with strong O−H bonds as a byproduct.

Introduction

Five-coordinate dioxo- and diimidorhenium(VII) species have been proposed as intermediates in ligand exchange reactions, eq 1. For example, $CH_3Re(O)_2(OH)(\mathbf{O}H)$ is believed to be involved in the oxygen exchange between CH_3ReO_3 (**1**) and $H_2\mathbf{O}$.[1−3] Analogous intermediates, such as $CH_3Re(O)_2(OH)(SH)$[4] and $CH_3Re(NR)_2(EH)(YH)$ (R = 1-adamantyl and 2,6-diisopropylphenyl; E = NR or O; Y = S, O, NPh),[5] were also proposed to lie on the pathway for hydrolysis, hydrosulfidolysis, and aminolysis. None of the above-mentioned five-coordinate intermediates has been directly observed.

$$CH_3ReX_3 + H_2E \rightarrow [CH_3ReX_2(XH)(EH)] \rightarrow CH_3ReX_2(E) + H_2X \quad (1)$$

$$(X = O, NR; E = O, S, NR)$$

Here we report our studies on the condensation reactions of CH_3ReX_2Y, comprising CH_3ReO_3, $\{CH_3Re(NAr)_2O\}_2$ (**2**), and $\{CH_3Re(NAr)_2S\}_2$ (**3**) with aliphatic and aromatic 1,2-diamines, diols, and dithiols:

$$CH_3ReX_2Y + HE(CH_m)_nEH \rightarrow CH_3ReX_2\{E(CH_m)_nE\} + H_2Y \quad (2)$$

$$(X = Y = O; X = NAr, Y = O, S; E = O, S, NH; m = 1, n = 6; m = 2, n = 2, 3)$$

The rhenium products (see Chart 1) have been identified spectroscopically and two of them, $[CH_3Re(O)_2\{1,2\text{-}(NH)_2C_6H_4\}]_2\{\mu\text{-}1,2\text{-}(NH_2)_2C_6H_4\}$ (**4a′**) and $CH_3Re(NAr)_2(SCH_2CH_2S)$ (**5c**, Ar = 2,6-diisopropylphenyl), have also been structurally characterized. Their isolation and full characterization provide support for the previously formulated intermediates. The properties of these condensation products may allow them to be anchored onto solid supports.[6]

Herrmann and co-workers investigated the reactions of **1** with $1,2\text{-}(OH)(EH)C_6H_4$ (E = O, S, NH), $1,2\text{-}(SH)_2C_6H_4$, 8-hydroxyquinoline, and $HOCX_2CX_2OH$ (X = CH_3, CF_3).[7−9] The structures of $CH_3Re(O)_2\{OC(Me)_2C(Me)_2O\}$[10] and $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)(C_5H_5N)$[7] have been determined. Danopoulos, Wong, and Wilkinson observed that **1** reacts with 1,2-phenylenediamine to form $CH_3Re(O)_2\{1,2\text{-}(NH)_2C_6H_4\}$, a compound with a trigonal bipyramidal geometry about rhenium.[11] It is

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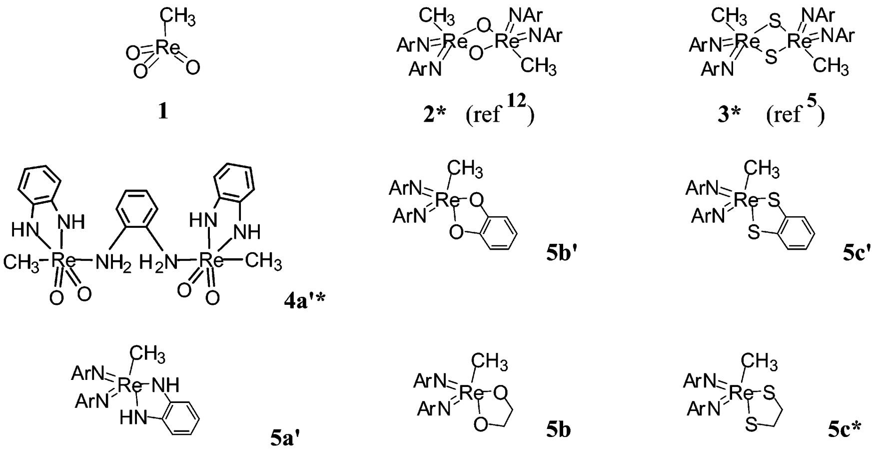
Chart 1. Structural Formulas of Rhenium Compounds[a]



[a] An asterisk (*) identifies the X-ray structure.

worth noting that compound **2** mainly exists as a monomer in solution at room temperature as demonstrated by variable-temperature ^{17}O NMR.[12]

Experimental Section

Materials and Instrumentation. The diamines, diols, and dithiols were purchased from Aldrich, CIL, or Fluka, as were the NMR solvents, acetone-d_6, benzene-d_6, dimethyl sulfoxide-d_6, methylene chloride-d_2, and toluene-d_8. These compounds were used without further purification. Anhydrous benzene, acetonitrile, methylene chloride, and hexanes used as solvents for synthesis were purchased from Aldrich. Compounds **1**,[13] $\boldsymbol{CH_3}$Re(NAr)(O)$_2$,[12] **2**,[12] and **3**[5] were prepared according to the literature procedures. Unless stated otherwise, the ^{1}H and ^{13}C NMR spectra were collected at 298 K with the use of a Bruker DRX-400 spectrometer, and the chemical shifts were measured relative to the residual ^{1}H and ^{13}C resonances in the deuterated solvents; the reference peaks are the following: C_6D_5H ($\delta_H = 7.16$ ppm, $\delta_C = 128.4$ ppm), $CDHCl_2$ ($\delta_H = 5.32$ ppm), $CD_3S(O)CD_2H$ ($\delta_H = 2.50$ ppm, $\delta_C = 39.5$ ppm), $CD_3C(O)CD_2H$ ($\delta_H = 2.05$ ppm), and CD_2HCN ($\delta_H = 1.94$ ppm, $\delta_C = 1.4$ ppm). The UV−visible spectra and kinetic data were recorded at 298 K with the use of a Shimadzu UV 3101PC or an Applied Photophysics DX 17MV stopped-flow spectrophotometer. Elemental analyses were performed by Desert Analytics and the ISU Chemical Instrumentation Facility.

{CH$_3$Re(O)$_2$[1,2-(NH)$_2$C$_6$H$_4$]}$_2$[1,2-(NH$_2$)$_2$C$_6$H$_4$] (4a′). To 10 mL of a solution of 1,2-phenylenediamine (100 mg, 0.925 mmol) in acetonitrile was added 100 mg of CH_3ReO_3 (0.401 mmol). The solution was stirred for 16 h at room temperature and dark black microcrystals were collected after filtration. The solid was washed with cold acetonitrile and dried under vacuum, yielding 140 mg (36%) of product. ^{1}H NMR (CD_2Cl_2): δ 10.9 (br, 4N$\boldsymbol{H}$), 7.12 (m, 4H), 6.75 (m, 4H), 6.66 (s, 4H), 3.39 (br, 2N$\boldsymbol{H}_2$), 1.62 (s, 6H). Anal. Calcd for $C_{20}H_{26}N_6O_4Re_2$ (FW = 786.86): C, 30.53; H, 3.33; N, 10.68. Found: C, 30.56; H, 3.41; N, 10.93.

CH$_3$Re(O)$_3$(en) (4a). To 10 mL of a methylene chloride solution of **1** (100 mg, 0.401 mmol) was added 2 mL of a methylene chloride solution containing 0.80 mmol of ethylenediamine at room temperature. A yellow precipitate was obtained (110 mg, 88%) after filtration and washing with 3 × 2 mL of methylene chloride and 2 × 2 mL of hexanes. NMR (DMSO-d_6): ^{1}H, δ 4.29 (s, 4H), 2.87 (s, 4H), 0.85 (s, 3H); ^{13}C, δ 41.4 (N$\boldsymbol{C}$H$_2$$\boldsymbol{C}H_2$N), 26.0 (Re-$\boldsymbol{C}H_3$). Anal. Calcd for $C_3H_{11}N_2O_3Re$ (FW = 309.34): C, 11.65; H, 3.58; N, 9.06. Found: C, 11.91; H, 3.87; N, 8.98.

CH$_3$Re(NAr)$_2$(SCH$_2$CH$_2$S) (5c). Just 59 μL of 1,2-ethanedithiol (0.704 mmol) was added to 100 mL of a methylene chloride solution of {CH$_3$Re(NAr)$_2$O}$_2$ (400 mg, 0.352 mmol). The solution was stirred for 16 h at room temperature and the solvent was then removed under vacuum. The residue was recrystallized with hexane, yielding 300 mg of product (66%). NMR (C_6D_6): ^{1}H, δ 7.04 (m, 2H), 6.95 (d, $J = 7.2$ Hz, 4H), 3.78 (br s, 2H), 3.74 (sept, $J = 6.8$ Hz, 4H), 3.50 (br s, 2H), 2.72 (s, 3H), 1.14 (m, 24 H); ^{13}C, δ 46.1 (SCH$_2$$\boldsymbol{C}H_2$S), 42.5 (S$\boldsymbol{C}H_2CH_2$S), 29.0 ($\boldsymbol{C}HMe_2$), 16.1 (Re-$\boldsymbol{C}H_3$). Anal. Calcd for $C_{27}H_{41}N_2ReS_2$ (FW = 643.98): C, 50.36; H, 6.42; N, 4.35; S, 9.96. Found: C, 50.38; H, 6.52; N, 4.34; S, 10.11.

The compounds CH$_3$Re(NAr)$_2$(SCH$_2$CH$_2$CH$_2$S), CH$_3$Re(NAr)$_2$(1,2-O$_2$C$_6$H$_4$) (**5b′**), and CH$_3$Re(NAr)$_2$(1,2-S$_2$C$_6$H$_4$) (**5c′**) were not isolated. The ^{1}H NMR spectra showed that the reactions formed a single rhenium product.

CH$_3$Re(NAr)$_2$[1,2-(NH)$_2$C$_6$H$_4$] (5a′). ^{1}H NMR (C_6D_6, 298 K): δ 9.82 (s, 2H), 7.18 (m, 4H), 7.02 (m, 2H), 6.61 (dd, 2H), 6.35 (dd, 2H), 3.47 (sept, $J = 6.8$ Hz, 4H), 1.87 (s, 3H), 1.25 (d, $J = 6.8$ Hz, 12H), 1.18 (d, $J = 6.8$ Hz, 12H). ^{13}C NMR (C_6D_6, 298 K): δ 29.4 ($\boldsymbol{C}$HMe$_2$), 24.3 and 23.9 [CH($\boldsymbol{C}$H$_3$)$_2$], 5.4 (Re-$\boldsymbol{C}$H$_3$).

CH$_3$Re(NAr)$_2$(OCH$_2$CH$_2$O) (5b). ^{1}H NMR (C_6D_6, 298 K): δ 7.0 (m, 6H), 4.75 (s, 4H), 3.62 (sept, $J = 6.8$ Hz, 4H), 2.38 (s, 3H), 1.13 (m, 24H). ^{13}C NMR (C_6D_6, 298 K): δ 78.7 (O$\boldsymbol{C}$H$_2$$\boldsymbol{C}H_2$O), 29.0 ($\boldsymbol{C}HMe_2$), 27.5 (Re-$\boldsymbol{C}H_3$).

CH$_3$Re(NAr)(O)(OCH$_2$CH$_2$O) (6b). ^{1}H NMR (C_6D_6, 298 K): δ 6.98 (s, 3H), 4.61 (unresolved m, 2H), 4.39 (unresolved m, 2H), 3.67 (sept, $J = 6.8$ Hz, 2H), 2.19 (s, 3H), 1.15 (d, 12H). ^{13}C NMR (C_6D_6, 298 K): δ 78.2 (O$\boldsymbol{C}$H$_2$$\boldsymbol{C}H_2$O), 29.3 (Re-$\boldsymbol{C}H_3$), 29.0 ($\boldsymbol{C}HMe_2$).

CH$_3$Re(NAr)$_2$(1,2-O$_2$C$_6$H$_4$) (5b′). ^{1}H NMR (C_6D_6, 298 K): δ 7.30 (dd, 2H), 6.93 (m, 6H), 6.85 (dd, 2H), 3.47 (sept, $J = 6.8$ Hz, 4H), 2.69 (s, 3H), 1.06 (d, $J = 6.8$ Hz, 12H), 0.98 (d, $J = 6.8$ Hz, 12H). ^{13}C NMR (C_6D_6, 298 K): δ 29.1 ($\boldsymbol{C}$HMe$_2$), 26.5 (Re-$\boldsymbol{C}$H$_3$).

CH$_3$Re(NAr)$_2$(1,2-S$_2$C$_6$H$_4$) (5c′). ^{1}H NMR (C_6D_6, 298 K): δ 7.69 (m, 2H), 6.81 (m, 2H), 3.64 (sept, $J = 6.8$ Hz, 4H), 2.80 (s, 3H), 1.09 (d, $J = 6.8$ Hz, 12H), 1.03 (d, $J = 6.8$ Hz, 12H). ^{13}C NMR (C_6D_6, 298 K): δ 29.4 ($\boldsymbol{C}$HMe$_2$), 23.8 [CH($\boldsymbol{C}$H$_3$)$_2$], 16.8 (Re-$\boldsymbol{C}$H$_3$).

CH$_3$Re(NAr)$_2$(SCH$_2$CH$_2$CH$_2$S). ^{1}H NMR (C_6D_6, 298 K): δ 7.03 (m, 2H), 6.96 (d, $J = 7.2$ Hz, 4H), 3.82 (sept, $J = 6.8$ Hz, 4H), 3.81 (m, 2H), 3.52 (m, 2H), 2.48 (s, 3H), 2.01 (m, 2H), 1.15 (m, 24 H). ^{13}C NMR (C_6D_6, 298 K): δ 31.9 (SCH$_2$$\boldsymbol{C}H_2CH_2$S), 31.1 (S$\boldsymbol{C}H_2CH_2CH_2$S), 30.7 (SCH$_2CH_2$$\boldsymbol{C}H_2$S), 29.1 ($\boldsymbol{C}HMe_2$), 26.5 (Re-$\boldsymbol{C}H_3$), 24.2 [CH($\boldsymbol{C}H_3$)$_2$].

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X-ray Crystallography. A dark red crystal (**4a′**) with approximate dimensions 0.40 × 0.34 × 0.26 mm^3 and a dark black crystal (**5c**) with approximate dimensions 0.2 × 0.2 × 0.1 mm^3 were selected under ambient conditions. The crystals were mounted and centered in the X-ray beam with the use of a video camera. The crystal evaluation and data collection were performed at 173 K on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation at a detector-to-crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames for **4a′** and 30 frames for **5c** collected at intervals of 0.3° in a 6° for **4a′** and 10° for **5c** range about ω with the exposure time of 10 s per frame. A total of 78 and 114 reflections for **4a′** and **5c**, respectively, were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6667 and 5526 strong reflections from the actual data collection for **4a′** and **5c**, respectively. The data were collected using the hemisphere routine. For **4a′**, a total of 22943 data were harvested by collecting four sets of frames with 0.3° scans in ω with an exposure time of 20 s per frame. For **5c**, a total of 9013 data were harvested by collecting four sets of frames with 0.3° scans in ω with an exposure time of 10 s per frame. These datasets were corrected for Lorentz and polarization effects. The absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements[14] using SADABS software.[15]

The systematic absences in the diffraction data were consistent with the space group $P2_1/c$ for **4a′** and $P2_1$ for **5c**[15] that yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map for **4a′**. The position of the heavy atom was found by the Patterson method for **5c**. In both cases, the remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. There are six hydrogen bonding interactions in the structure of **4a′** as shown in Table S-1. For **4a′**, the final least-squares refinement of 291 parameters against 4829 independent reflections resulted in R (based on F^2 for $I \geq 2\ \sigma$) and wR (based on F^2 for $I \geq 2\sigma$) of 0.0171 and 0.0403, respectively. For **5c**, the final least-squares refinement of 297 parameters against 4688 independent reflections converged to R (based on F^2 for $I \geq 2\ \sigma$) and wR (based on F^2 for $I \geq 2\sigma$) of 0.023 and 0.058, respectively. Crystallographic data for **4a′** and **5c** are given in Table 1.

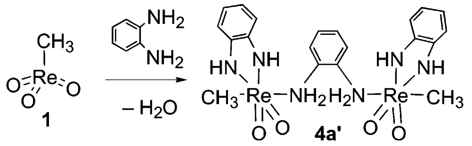
Table 1. Crystallographic Data for $\{CH_3Re(O)_2[1,2\text{-}(NH)_2C_6H_4]\}_2[1,2\text{-}(NH_2)_2C_6H_4]$ (4a′) and $CH_3Re(NAr)_2(SCH_2CH_2S)$ (5c, Ar = 2,6-Diisopropylphenyl)[a]

	4a′	5c
empirical formula	$C_{20}H_{26}N_6O_4Re_2$	$C_{27}H_{41}N_2ReS_2$
formula weight	786.86	643.94
temperature/K	173(2)	173(2)
wavelength/Å	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$
unit cell dimens		
a/Å	9.3301 (5) Å	10.3930 (9) Å
b/Å	11.6534 (6) Å	9.1030 (8) Å
c/Å	21.7439 (11) Å	19.2160 (9) Å
β/deg	92.372 (2)°	100.284 (2)°
vol/Å^3	2362.1(2)	1435.4(2)
Z	4	2
density (calcd)/Mg/m^3	2.213	1.490
abs coeff/mm^{-1}	10.278	4.395
F(000)	1480	648
R indices (all data)	R1 = 0.0214, wR2 = 0.0412	R1 = 0.0238, wR2 = 0.0589

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

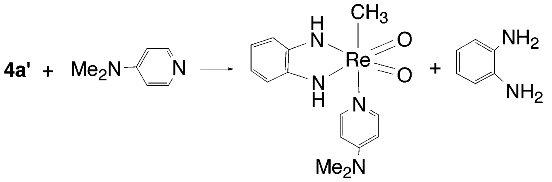
Results

Reactions with Diamines: **(a) 1,2-Phenylenediamine.** The ^{1}H NMR spectrum of the isolated product for the reaction of **1** with 1,2-phenylenediamine is in agreement with the formula $\{CH_3Re(O)_2[1,2\text{-}(NH)_2\text{-}C_6H_4]\}_2[1,2\text{-}(NH_2)_2C_6H_4]$ (**4a′**):



(3)

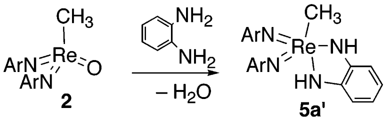
The chemical shift of the amido protons (N***H***) in **4a′** was at 11.52 ppm in CD_3CN. Such strongly deshielded amido protons have been observed in similar compounds.[7] The N$\boldsymbol{H}_2$ protons of the bridging phenylenediamine ligand were observed at 3.65 ppm. The presence of a bridging ligand is consistent with the elemental analysis and was confirmed by X-ray diffraction studies, see below. Acetone-d_6 was the solvent for studies of the substitution reactions because **4a′** is more soluble in it than in C_6D_6, CD_2Cl_2, or CD_3CN. Free phenylenediamine is released upon addition of 4-(dimethylamino)pyridine to an acetone solution of **4a′**:



(4)

The resonance for the Re-C***H***$_3$ protons in **1** occurs at 1.36 ppm, but at 0.51 ppm in **4a′**. A similar upfield shift of the Re-C***H***$_3$ resonance was also found when pyridine or pyridine-*N*-oxide was added, Figure S-1 (Supporting Inforamtion). Separate signals for the coordinated pyridine or its derivatives were not observed; evidently the dynamic binding is faster than the NMR time scale at room temperature. The results of the UV–vis experiments are consistent with the NMR data. The change of λ_{max} in the electronic spectrum of **4a′** in CH_3CN upon addition of pyridine and 4-(dimethylamino)pyridine is illustrated in Figure 1.

When **2** and 1,2-phenylenediamine were mixed in C_6D_6 at starting concentrations of 5 and 20 mM, respectively, no **2** was detected by ^{1}H NMR spectroscopy after an hour. The resulting rhenium product was formulated as $CH_3Re(NAr)_2\{1,2\text{-}(NH)_2C_6H_4\}$ (**5a′**) on the basis of the chemical shifts and multiplicities of the ^{1}H NMR signals, eq 5. The strongly deshielded amido



(5)

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[14] Blessing, R. H. *Acta Crystallogr. A* **1995**, *51*, 33.

[15] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, B. A. X.-r. S., Madison, WI).

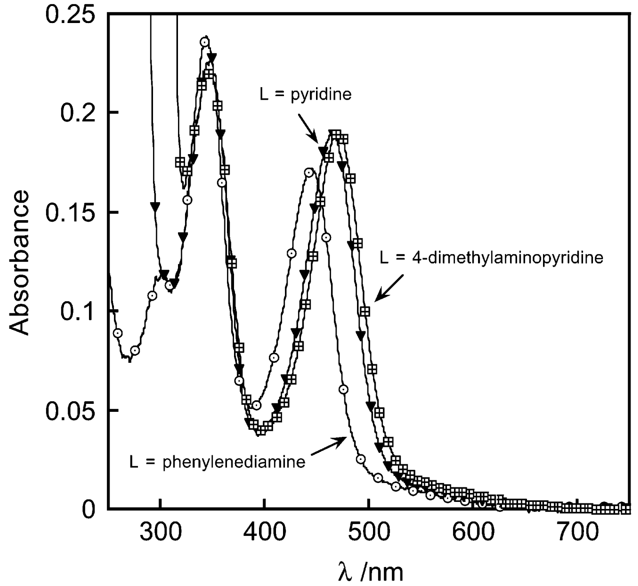
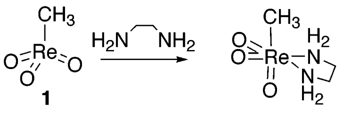


Figure 1. UV−visible spectra in CH_3CN for $\{CH_3Re(O)_2[1,2\text{-}(NH)_2C_6H_4]\}_2[1,2\text{-}(NH_2)_2C_6H_4]$ (**4a′**, 7 μM) and its adducts with C_5H_5N (40 mM) and $4\text{-}Me_2NC_5H_4N$ (40 mM).

protons of **5a′** appear as a broad singlet centered at 9.82 ppm. Two sets of the aromatic protons of the phenylenediamido moiety occur at 6.62 and 6.35 ppm, and they were coupled to each other. The $^1H-^1H$ 2D COSY experiment also showed that the only septet at 3.47 ppm was coupled to the doublets at 1.25 and 1.18 ppm. The NMR data point to a square-pyramidal structure of **5a′** with *cis*-diimido and phenylenediamido ligands on the basal plane. However, one cannot rule out a trigonal-bipyramidal isomer that undergoes rapid Berry pseudorotation to interconvert trigonal-bipyramidal and square-pyramidal forms. In general, however, a multiple bond between nitrogen and rhenium will disfavor ligand occupancy in a position trans to it. Unlike the case of **4a′**, the ^1H NMR spectra of **5a′** did not change upon addition of pyridine or its derivatives, such as 4-(dimethylamino)pyridine, indicating that compound **5a′** likely remains five-coordinate.

(b) 1,2-Ethylenediamine. A yellow precipitate was immediately formed upon mixing $H_2NCH_2CH_2NH_2$ and **1** in acetone, acetonitrile, benzene, and methylene chloride; in all of these solvents the solubilities of the resulting product are very low. NMR data in $Me_2SO\text{-}d_6$ are consistent with the formula of $CH_3ReO_3(en)$, eq 6;

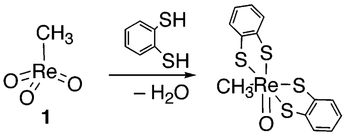


(6)

i.e., addition without condensation. The intensities of three slightly broadened singlets at 4.29, 2.87, and 0.85 ppm are in a ratio of 4:4:3, and the ^{13}C resonances of the latter two are at 41.4 and 26.0 ppm. The elemental analysis agrees with this formulation. It is likely that the compound $CH_3ReO_3(en)$ possesses a structure similar to that of the bipyridine adduct of **1**, $CH_3ReO_3(bpy)$.[2]

The resonance of the Re-C***H***$_3$ protons in **2** in C_6D_6 remains unshifted upon addition of en, suggesting negligible interaction between them at the start. No ethylenic proton resonance for the expected initial condensation product, $CH_3Re(NAr)_2(en)$, was initially observed. However, a new species slowly appeared over the course of several hours. The ratio of the Re-C***H***$_3$ protons to the methine protons of the isopropyl groups indicated that an adduct of $CH_3Re(NAr)(O)_2(en)$ had been produced. Addition of excess en to an authentic sample of $CH_3Re(NAr)(O)_2$ in C_6D_6 caused a similar shift for the methyl resonance of ***CH***$_3$Re(NAr)(O)$_2$, from 1.86 to 1.55 ppm for ReC***H***$_3$ and from 11.9 to 16.6 ppm for Re***C***H$_3$. Specially dried 1,2-ethylenediamine and solvents were not used since water would in any event be the byproduct of condensation.

Reactions with Dithiols: (a) 1,2-Benzenedithiol. The reactions of **1** with thiophenol and 1,2-benzenedithiol have been studied by Herrmann and co-workers, eq 7;[8] the reactions with aliphatic dithiols are being investigated.[16] When 1,2-benzenedithiol was added to a C_6D_6 solution of **2**, a singlet at 2.80, a septet at 3.58, two doublets at 1.09 and 1.03 ppm, and two multiplets in the aromatic region were built up, with intensities in accordance with the formula $CH_3Re(NAr)_2(1,2\text{-}S_2C_6H_4)$ (**5c′**), eq 8. The lack of an observable interaction between **5c′** and pyridine was indicated by an unshifted Re-C***H***$_3$ resonance upon the addition of 40 mM pyridine. The similarity between the ^1H NMR spectra of **5a′** and **5c′** suggests that they have analogous structures.



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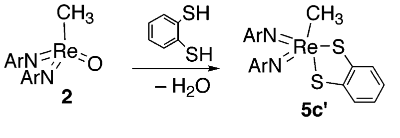
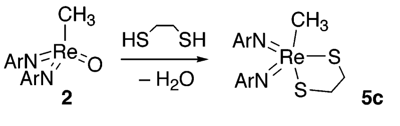


(8)

(b) 1,2-Ethanedithiol. ^1H NMR studies in C_6D_6 showed a clean reaction between $HSCH_2CH_2SH$ and **2**. The intensities of the septet at 3.74 ppm, due to the methine protons of the isopropyl moieties and a singlet at 2.72 ppm from the Re-C***H***$_3$ group, established that two arylimido ligands are present for each rhenium methyl group. The rhenium product was thus formulated as $CH_3Re(NAr)_2(SCH_2CH_2S)$ (**5c**) in accordance with the intensities of the inequivalent methylene protons of the ethane dithiolato moiety, eq 9.



(9)

The signal of the slightly broad methylene protons at 3.50 ppm was coupled to the one at 3.78 ppm, and the corresponding ^{13}C chemical shifts were at 42.5 and 46.1 ppm, respectively, Figure 2. Because the two ^1H-resonances arise from protons attached to different carbon atoms, a trigonal-bipyramidal structure is indicated. Variable-temperature ^1H NMR studies in C_7D_8 showed that the broad peak at 3.50 ppm resolved into a triplet at 278 K. The other broad peak (at 3.78 ppm) was not well-defined owing to its overlap with the methine

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(16) Shan, X.-P.; Espenson, J. H. Unpublished information.

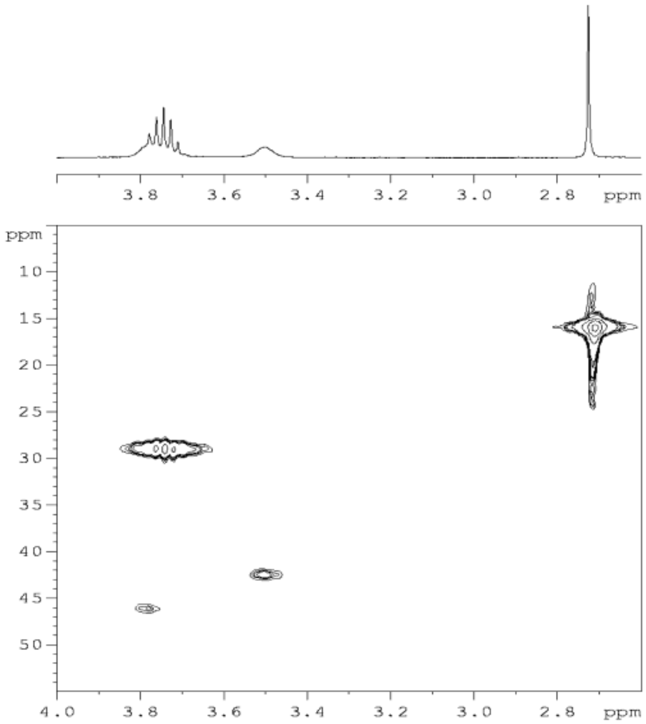
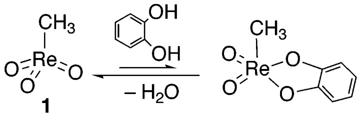


Figure 2. ^1H and $^1H-^{13}C$ 2D NMR spectra of $CH_3Re(NAr)_2(SCH_2CH_2S)$ (**5c**) in C_6D_6 at 298 K.

resonance of the isopropyl groups. At 323 K, the two methylene resonances coalesced into one, resulting in a value of $\Delta G^{\ddagger} = 64$ kJ mol^{-1} for the exchange process.

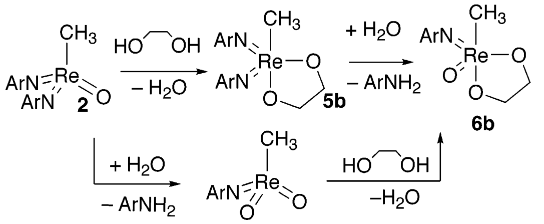
An analogous compound, $CH_3Re(NAr)_2(SCH_2CH_2CH_2S)$, was detected from the reaction of **2** with 1,3-propanedithiol. Because the signal at 2.01 ppm was coupled to both resonances at 3.81 and 3.52 ppm and the latter two were not coupled to each other, the well-resolved pentet at 2.01 ppm was assigned to the central methylene protons of the $SCH_2CH_2CH_2S$ moiety. The resonance at 3.81 ppm overlapped with the methine protons of the isopropyl group of the arylimido ligand and its pattern could not be assigned. The triplet-like resonance at 3.52 ppm was not well-resolved at room temperature. As in the case of $CH_3Re(NAr)_2(SCH_2CH_2S)$, only one set of methine protons from the arylimido ligands was seen, suggesting a symmetrical structure in solution.

Reactions with Diols: (a) Catechol. The reaction of **1** with catechol has been investigated by Herrmann and co-workers. Although pure $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)$ was not obtained, its pyridine adduct was isolated and structurally characterized.[7] To compare the reactivity of **1** with **2** and **3**, the reaction of catechol with **1** was studied in acetonitrile with the use of UV−vis and NMR techniques. An equilibrium constant of 0.59(6) for eq 10 was obtained from UV−vis data, which was in agreement with the value of 0.51 from ^1H NMR studies. The intense purple color of the $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)$ solution ($\epsilon_{552} = 9140$ M^{-1} cm^{-1}) faded rapidly upon addition of water according to the reverse reaction. No condensation products were observed between **1** and naphthalene-2,3-diol, ethane-1,2-diol, or propane-1,3-diol. This puts an upper limit $K_{10} \leq 0.05$ for the analogous reactions of any of these reagents.



(10)

Scheme 1. Favored (upper) and Disfavored Routes to 6b



Catechol equilibrates with **1**, whereas its reaction with **2** proceeds to completion. The resulting condensation product $CH_3Re(NAr)_2(1,2\text{-}O_2C_6H_4)$ (**5b′**) has two sets of aromatic protons from the catecholate ligand at 7.30 and 6.85 ppm, coupled to each other. The septet at 3.47 ppm was coupled to the doublets at 1.06 and 0.98 ppm. The NMR data indicate that **5a′**, **5b′**, and **5c′** have analogous structures in solution.

(b) Ethylene Glycol. Further hydrolysis was observed for the reaction of ethylene glycol with **2**. For example, 30 mM ethylene glycol with 10 mM **2** gave predominantly $CH_3Re(NAr)_2(OCH_2CH_2O)$ (**5b**) within 5 min. The intensities of the methylene protons of the glycolate ligand at 4.74 ppm in C_6D_6 and the rhenium methyl protons at 2.38 ppm agree with the proposed formula. The corresponding ^{13}C chemical shifts are located at 78.7 and 27.5 ppm, respectively, typical for O−C and Re(VII)−C connectivities. The initial condensation product was not stable under the experimental conditions and the hydrolyzed product, $CH_3Re(NAr)(O)(OCH_2CH_2O)$ (**6b**), was observed. Two sets of methylene protons at 4.61 and 4.39 ppm and a ^{13}C resonance at 78.2 ppm were observed. The signal of the rhenium methyl protons shifted to 2.24 ppm. A similar upfield shift was observed for the rhenium methyl protons as the imido ligand in $CH_3Re(NR)_2(O)$ (R = 1-adamantyl and 1,2-diisopropylphenyl) was replaced by the oxo counterpart.[5,12] Only one ^1H and one ^{13}C resonance was observed for the glycolate ligand in **5b**, suggesting that this compound has either a stationary square-pyramidal structure or a fluxional trigonal bipyramidal one with a low activation barrier for pseudorotation. Hydrolysis of **5b** began even before the entire quantity of the starting rhenium compound **2b** had been consumed. Since **2** is known to hydrolyze relatively slowly, **6b** is not likely to have arisen from hydrolysis of **2** followed by condensation between $MeRe(NAr)O_2$ and ethylene glycol. More likely, the sequence **2** → **5b** → **6** provides the predominant pathway. Both pathways are given in Scheme 1.

Reactions with {$CH_3Re(NAr)_2S$}$_2$ (3). No reaction occurs between **3** and a 6-fold excess of 1,2-phenylenediamine in C_6D_6 at room temperature for 3 days. Neither catechol nor ethylene glycol reacted with **3** regardless of the presence or absence of base. However, the reaction of $HSCH_2CH_2SH$ with **3** in C_6D_6 proceeded analogously to eq 9. The formation of H_2S as well as $CH_3Re(NAr)_2(SCH_2CH_2S)$ (**5c**) was observed with the use of ^1H and ^{13}C NMR spectroscopies. As in the case of ethanedithiol, the reaction of **3** with 1,2-benzene-

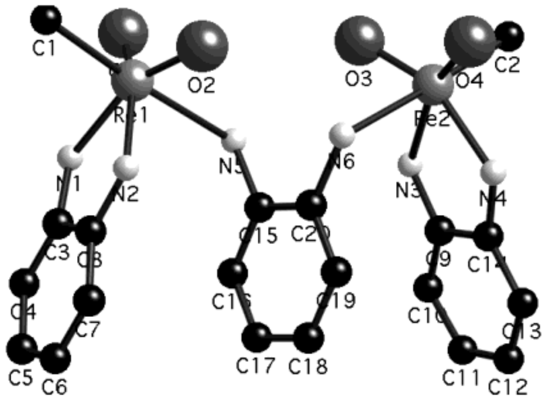


Figure 3. The molecular structure of $[CH_3Re(O)_2\{1,2\text{-}(NH)_2C_6H_4\}]_2\{\mu\text{-}1,2\text{-}(NH_2)_2C_6H_4\}$ (**4a′**) shown at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (pm) and Angles (deg) for 4a′.

Re2−O3	174.4(2)	Re1−O1	174.8(2)
Re2−O4	173.8(2)	Re1−O2	175.4(2)
Re2−C2	210.9(4)	Re1−C1	211.9(4)
Re2−N3	203.1(3)	Re1−N1	204.6(3)
Re2−N4	203.3(3)	Re1−N2	203.0(3)
Re2−N6	249.8(3)	Re1−N5	244.0(3)
C2−Re2−N6	175.6(1)	C1−Re1−N5	175.6(1)
O3−Re2−N4	155.5(1)	O1−Re1−N2	156.8(1)
O4−Re2−N3	157.9(1)	O2−Re1−N1	156.1(1)
C2−Re2−N4	98.2(2)	C1−Re1−N2	94.3(1)
C2−Re2−O4	92.9(1)	C1−Re1−O2	93.8(1)
O3−Re2−O4	115.1(1)	O1−Re1−O2	115.2(1)
N3−Re2−N4	72.8(1)	N1−Re1−N2	72.3(1)

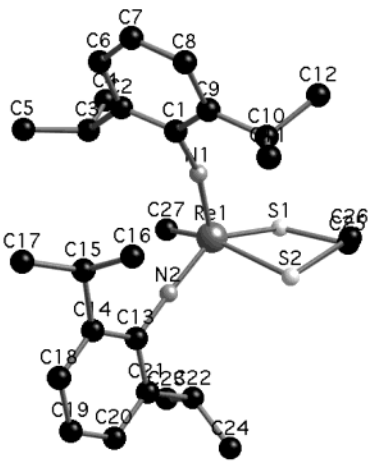


Figure 4. The molecular structure of $CH_3Re(NAr)_2(SCH_2\text{-}CH_2S)$ (**5c**). Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (pm) and Angles (deg) for 5c

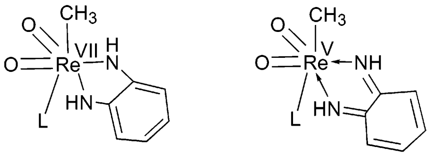
Re(1)−N(1)	174.2(3)	Re(1)−N(2)	175.0(4)
Re(1)−C(27)	218.4(5)	Re(1)−S(2)	237.39(13)
Re(1)−S(1)	239.07(11)	S(1)−C(25)	181.5(6)
S(2)−C(26)	181.5(6)	C(1)−N(1)	140.9(5)
C(13)−N(2)	137.0(6)	C(25)−C(26)	151.6(7)
N(1)−Re(1)−N(2)	114.09(17)	N(1)−Re(1)−C(27)	101.53(18)
N(2)−Re(1)−C(27)	93.2(2)	N(1)−Re(1)−S(2)	105.16(12)
N(2)−Re(1)−S(2)	90.26(14)	C(27)−Re(1)−S(2)	148.92(13)
N(1)−Re(1)−S(1)	110.42(12)	N(2)−Re(1)−S(1)	135.32(12)
C(27)−Re(1)−S(1)	74.03(14)	S(2)−Re(1)−S(1)	81.88(4)
C(1)−N(1)−Re(1)	161.1(3)	C(13)−N(2)−Re(1)	177.6(4)

dithiol was slower than that with **2** under similar conditions. Both $CH_3Re(NAr)_2(1,2\text{-}S_2C_6H_4)$ (**5c′**) and H_2S (δ 0.19) were eventually observed after hours. Unlike the reaction of **1** with 1,2-benzenedithiol, the further condensation product, $CH_3Re(NAr)(1,2\text{-}S_2C_6H_4)_2$, was not formed even in the presence of excess ligand.[8]

Structures of 4a′ and 5c. The rhenium center in **4a′** displays a pseudo-octahedral geometry with the diamido ligand and the *cis*-dioxo groups in the equatorial plane. The methyl group and the trans bridging phenylenediamine ligand (∠C1−Re1−N5 = 175.6°) occupy the axial positions, Figure 3. Selected bond distances and angles are given in Table 2. Neither a square pyramid nor a trigonal bipyramid can be used to describe the molecular structure of **5c**, depicted in Figure 4. The widest angle in **5c** is C(27)−Re(1)−S(1) of 148.9°. Key bond distances and angles are given in Table 3.

Discussion

Re(VII) vs Re(V). Herrmann and co-workers have shown the rich chemistry of the condensation reactions of CH_3ReO_3 (**1**) with 2-aminophenol, 2-aminothiophenol, 1,2-benzenediol, and 1,2-benzenedithiol.[7,8] For example, $MeRe(O)_2\{1,2\text{-}S(NH)C_6H_4\}(Py)$ was obtained from the reaction of **1** with 2-aminothiophenol, while $MeRe(O)\text{-}\{1,2\text{-}O(NH)C_6H_4\}_2$ and $\{CH_3Re(O)_2(8\text{-oxyquinolinato})\}_2\text{-}(\mu\text{-}O)$ were isolated from the reaction with 2-aminophenol and 8-hydroxyquinoline, respectively. The structure of $MeRe(O)_2\{1,2\text{-}(O)_2C_6H_4\}(Py)$ suggested that Re(VII)-catecholate instead of Re(V)-benzoquinone provides a better description of this rhenium compound based on the bond distances among the ring carbon atoms. The analogous compound **4a′** has a similar pseudo-octahedral structure. Since the bridging phenylenediamine serves as an internal reference, the contribution of resonance structures, **A** and **B**, could be evaluated. The average N−C distance for the chelating diamido ligands is 134.5(9) pm, noticeably shorter than 143.5(4) pm, the average distance of the N−C bonds for the bridging phenylenediamine ligand. The C−C distances of the aromatic ring for the bridging phenylenediamine ligand are nearly the same, 138.1(4) pm, except for the C15−C20 distance of 140.5(5) pm. On the other hand, the C−C bond distances of the aromatic ring for the chelating phenylenediamine ligand alternate (see the resonance structure **B**). The small variation of the C−C bond distances suggests a minor contribution from the Re(V)-benzoquinonediimine resonance to the overall structure. An interesting compound reported by Wilkinson and co-workers, $\{WCl_3[1,2\text{-}(NH),2\text{-}(H_2N)C_6H_4]\}_2[\mu\text{-}1,2\text{-}(N)C_6H_4]$, contains three bonding modes for amines.[17]



A B

TBP vs SP. Both trigonal-bipyramidal (**TBP**) and square-pyramidal (**SP**) structures can explain the ^1H NMR data for equivalent imido groups in **5**. The $^1H-^{13}C$ 2D NMR data show that the two sets of

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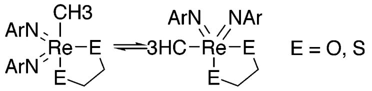
(17) Redshaw, C.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1992**, 555.

ethylene protons in $CH_3Re(NAr)_2(SC\mathbf{H}_2C\mathit{H}_2S)$ (**5c**) are from two different carbons. Thus the **TBP** structure in solution seems to fit the data better. The crystal structure of **5c** determined by X-ray diffraction studies, Figure 4, indicates that the solid-state structure is intermediate between the ideal **TBP** and **SP** geometries, and is perhaps best viewed as a distorted trigonal bipyramid. The patterns of the α-methylene protons of the chelating ligand in **5c** and $CH_3Re(NAr)_2(SC\mathbf{H}_2CH_2C\mathit{H}_2S)$ clearly suggest that a dynamic process exists in solution. Variable-temperature ^1H NMR spectra of **5c** reveal that this dynamic process, eq 11, takes place



(11)

with a $\Delta G^\ddagger$ of 64 kJ mol^{-1} at 323 K. A similar process with $\Delta G^\ddagger = 52$ kJ mol^{-1} has been observed for $CH_3Re(O)_2\{OC(Me)_2C(Me)_2O\}$.[9] In the case of **5b**, a sharp singlet is observed for the ethylene protons, suggesting that the Berry-pseudorotation barrier for **5b** is smaller than that for **5c**. Since the two sets of aromatic resonances for **5′** are similar to those for **4a′**, the structure of **5′** with an aromatic chelating backbone may possess a **SP** geometry.

Reactivity of 1, 2, and 3. The condensation reaction of **1** with diols is inherently unfavorable, but can be drawn to completion by the removal of water.[18] The aliphatic diols (1,2-ethanediol, 2,3-butanediol, 1,2-propanediol, and 1,2-cyclohexanediol), do not condense with **1** in CD_3CN. The detectable catecholate product of **1** is also fragile toward water. Without removal of the water formed, or the addition of pyridine, the major rhenium species in solution is **1**. On the other hand, the reaction of catechol with **2** easily reaches completion. Even for aliphatic diols, such as ethylene glycol, the reaction with **2** forms **5b**. The arylimido ligands significantly stabilize the condensation product, an effect that is not provided by the oxo ligands. Both electronic and steric effects may be responsible for the differences. The imido ligands are better donors, which may diminish the necessity of the 6th ligand required to stabilize the condensation product. The steric bulk of the arylimido groups may also prevent further coordination.

Although **2** reacts with diamines, diols, and dithiols, **3** reacts only with dithiols. This is likely a thermodynamic problem rather than a kinetic one because thiolate is a better nucleophile than alkoxide. That is to say, a reaction under kinetic control should proceed at least as well with a thiolate. The strong O−H bond of the byproduct water, compared to the N−H and S−H bonds of amines and thiols, plays the key role in the condensation reactions of **2** with diamines and dithiols. The reactions with **2** and dithiols are distinctly faster than those with **3**. The large driving force from the formation of H_2O, compared to H_2S, is likely responsible. Also, **2** exists mainly as a four-coordinate monomer in solution whereas **3** is a five-coordinate dimer.

Unlike **1**, **2** undergoes no further condensation to form $CH_3Re(NAr)(1,2\text{-}E_2C_6H_4)_2$. The arylimido group is much less reactive than the oxo ligand. The reaction of $HSCH_2CH_2SH$ with $CH_3Re(NAr)_3$ did not occur under the same experimental conditions.

Chelating Effect. No observable interaction occurs between **2** and any of the amines, alcohols, or thiols; under the same conditions, however, 1,2-diamines, diols, and dithiols react readily with **2**. The chelating effect is crucial to the formation of the condensation products. Herrmann and co-workers have shown that **1**, as a Lewis acid, interacts with many monodentate ligands to form a trigonal-bipyramidal structure with three oxygen atoms on the equatorial plane.[2] Coordination of two monodentate ligands to **1** is rare. Bidentate ligands, such as 2,2′-bipyridine and its derivatives, are stable six-coordinate species with octahedral structures that have been well characterized. Interestingly, ethylenediamine and **1** form a six-coordinate adduct instead of a five-coordinate condensation product. Coordination is likely faster than condensation and it yields an adduct with an extremely low solubility. Aniline derivatives also form the simple adducts with **1**. Again, owing to the chelating effect, phenylenediamine forms condensation products with both **1** and **2**.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-7405-Eng-82.

Supporting Information Available: X-ray crystallographic tables and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Except for pinanediols. Also, Herrmann has isolated $CH_3ReO_2(OCX_2CX_2O)$ ($X = CH_3, CF_3$), see refs 11 and 12.