strengthens the Os–carbonyl bond opposite the donor atom (Rh). This effect has been observed previously in related dative-bonded compounds.[25,38,52] The Rh–Os separation of 2.8744 (3) Å is typical of a single bond but is not a useful indication about the nature of this interaction, especially in the presence of the bridging alkyne. This Rh–Os bond is somewhat longer than that observed (2.758 (5) Å) in the related compound $[RhOsCl_2Br(\mu\text{-}CO)(dppm)_2]$,[53] which in our interpretation would have an Os→Rh donor–acceptor bond accompanied by semibridging carbonyl groups. The significant difference in these two Rh–Os distances no doubt results from the very different bridging ligands involved, with the alkyne group causing greater separation of the metals in the present case.

Summary

A series of low-valent, dppm-bridged complexes involving Rh and Os are readily obtained from $[RhOsH(CO)_3(dppm)_2]$. Carbonyl substitution in $[RhOs(CO)_4(dppm)_2]^+$ by the poorer π-acceptor but better σ-donor ^tBuNC ligand occurs on Os opposite the metal–metal bond, supporting our arguments that the Os–Rh bonds in these species are best regarded as donor–acceptor interactions. Carbonyl loss from the saturated Os center in the compounds $[RhOs(CO)_3(\mu\text{-}CO)(\mu\text{-}RC{\equiv}CR)(dppm)_2][BF_4]$ is accompanied by the unusual formation of a Rh→Os dative bond, regenerating coordinative saturation at Os. This may be viewed as an example of the neighboring-group effect, with Rh assisting in labilization of a carbonyl from Os. The presence of the coordinatively unsaturated Rh center in these compounds provides a route into chemistry involving the normally inert and coordinatively saturated Os center, and it is probable that substitution reactions occur by coordination at Rh, followed by facile rearrangement. This suggestion is supported by the reactions of $[RhOs(CO)_3(\mu\text{-}RC{\equiv}CR)(dppm)_2][BF_4]$ with a series of neutral and anionic ligands, in which the incoming ligands are clearly shown to be bound to the Rh center.

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Supplementary Material Available: Listings of anisotropic thermal parameters, positional and thermal parameters for the BF_4^- anion and CH_2Cl_2 molecules, additional bond lengths and angles, and hydrogen atom parameters for **12** and NMR data for **9–22** (11 pages); a listing of the observed and calculated structure factors for **12** (48 pages). Ordering information is given on any current masthead page.

Multiple Bonds between Main-Group Elements and Transition Metals. 77.[1] Condensation Reactions of Methyltrioxorhenium(VII) with Catechols and Aromatic Thiols

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The title compound methyltrioxorhenium(VII) reacts with catechols to yield complexes of the formula $CH_3Re(O)_2(1,2\text{-}O_2C_6R_4)$ ((**2**)) that are fully characterized as pyridine adducts **3**. Conducting these reactions in the presence of nucleophiles, e.g., halides, gives the hexacoordinate anions $[CH_3Re(O)_2(1,2\text{-}O_2C_6R_4)(X)]^-$ of compounds **4a–c** (X = Cl, Br, I) in high yields. Based upon spectroscopic data, the oxo ligands occupy cis positions and the halide ligand occupies trans positions with respect to the methyl group of these novel five-membered d^0 rhenacycles. The rhenium(V) species "CH_3ReO_2", prepared in situ from **1** by reduction with (polymer bound) triphenylphosphane, reacts with phenanthrenequinone in the presence of pyridine to give the neutral hexacoordinate complex $CH_3Re(O)_2(9,10\text{-}O_2C_{14}H_8)(NC_5H_5)$ (**5**), with the quinone ligand being present in the reduced form as catecholate while the rhenium is in the oxidation state VII. Reaction of **1** with thiophenol gives initially the rhenium(VII) complex $CH_3ReO(SC_6H_5)_4$ (**6**), which upon heating undergoes intramolecular elimination of diphenyl disulfide, $C_6H_5SSC_6H_5$, to give the dinuclear rhenium(V) complex $[CH_3ReO(\mu\text{-}SC_6H_5)(SC_6H_5)]_2$ (**7**; X-ray diffraction study). Condensation of **1** with benzene-1,2-dithiol gives the rhenium(VII) complex $CH_3ReO(1,2\text{-}S_2C_6H_4)_2$ (**8**).

Introduction

Alkyl- and arylrhenium oxides represent an interesting class of compounds.[3] They have useful catalytic applications, with olefin oxidation and olefin metathesis being typical, well-documented examples.[4] In these processes, especially, the title compound methyltrioxorhenium(VII) (**1**) acts as an effective catalyst. As part of our ongoing studies into the chemistry of this key compound, we recently reported on its condensation reactions with aromatic bidentate ligands of the type HO···X (X = N, NH_2, OH).[5] In the present account, we focus on condensation reactions with catechols; novel anionic rhenacycles are thus easily accessible. In addition, we report on condensation reac-

(1) For part 76 see: Herrmann, W. A.; Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E. *Z. Naturforsch.* **1990**, *45B*, 876.

(2) (a) Alexander von Humboldt Fellow on leave from the Research Group for Petrochemistry of the Hungarian Academy of Sciences, Veszprem/Hungary. (b) Science and Engineering Research Council (U.K.) and NATO Postdoctoral Fellow (1988–1990).

(3) Reviews: (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297; *Angew. Chem.* **1988**, *100*, 1269. (b) Herrmann, W. A. *Comments Inorg. Chem.* **1988**, *7*, 73. (c) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165.

(4) Review: Herrmann, W. A. *J. Organomet. Chem.* **1990**, *382*, 1.

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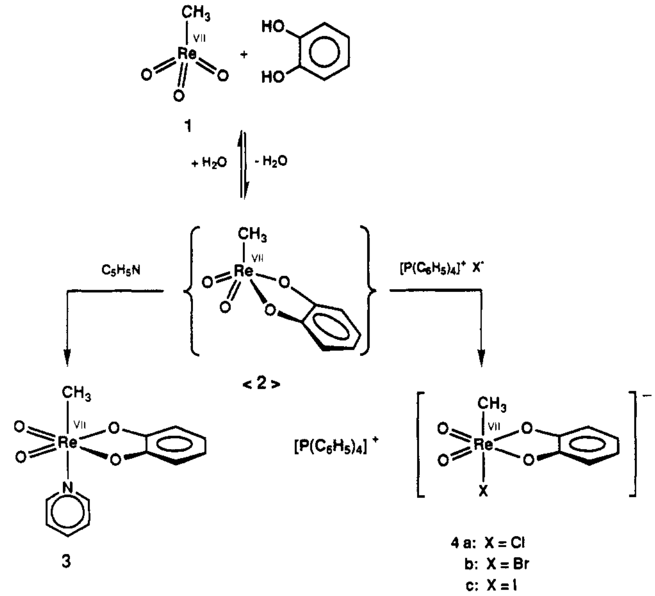
Scheme I



tions of 1 with *mono*- and *bi*dentate thiols.

Results and Discussion

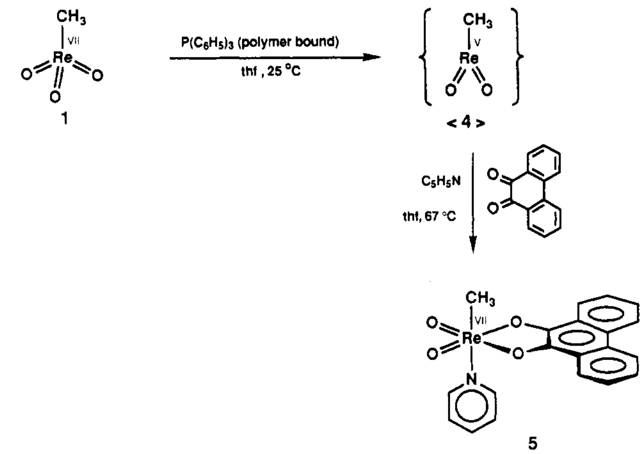
I. Condensation Reactions of Methyltrioxorhenium(VII) with Catechol in the Presence of Nucleophiles. A previous study has shown that methyltrioxorhenium(VII) (1) readily undergoes a condensation reaction with catechol to give a purple–violet intermediate (⟨2⟩), which forms a stable, crystallographically characterized adduct 3 with pyridine.[5] Although ⟨2⟩ cannot be isolated in a pure state, the spectroscopic and chemical data allow the formula $\{CH_3Re(O)_2(1,2\text{-}O_2C_6R_4)\}$ to be assigned. Wilkinson and co-workers have reported a trigonal-bipyramidal structure for $[CH_3ReO_2\{(HN)_2C_6H_4\}]$ obtained from the condensation reaction of 1 with *o*-phenylenediamine,[6] but no details of this structure are available as yet. The formation of the pyridine adduct and the Lewis acid of ⟨2⟩ prompted us to study the reactions of this species with other nucleophiles. Since ⟨2⟩ does not react with weak and soft nucleophiles such as alkenes and alkynes,[5] its reactivity with hard and strong ionic nucleophiles was investigated.

When the reaction of 1 with catechol is carried out in the presence of tetraphenylphosphonium halides, $[P(C_6H_5)_4]X$, the purple–violet color changed to intense blue for both the chloride and bromide and to green for the iodide (Scheme I). After azeotropic removal of the water formed in these reactions, the ionic rhenium(VII) complexes **4a–c** were isolated in good yields. The reaction with the fluoride $[(n\text{-}C_4H_9)_4N]F$ yields a blue, viscous oil, which could not be positively identified. (The ^1H NMR spectrum shows the catechol and butyl signals in the expected ratio; however, no rhenium-coordinated methyl group was observed, and the elemental analysis gave ambiguous results.)

4a–c show two strong absorptions in the IR spectra (KBr) around 945 and 910 cm^{-1}, typical of *cis*-dioxo groups. The shift of these bands to higher wavenumbers upon variation of the halides follows the Cl–Br–I order. A downfield shift of the methyl signal is observed in the ^1H NMR spectra in the same order, reflecting the nucleophilicity (basicity) and trans influence of the halides: Cl > Br > I. The Re–X bond strengths change in the opposite direction, with the Re–I bond of **4c** being so weak that this compound is not stable in donor solvents such as tetrahydrofuran (THF). Upon dissolution of **4c** in THF, the color changes to purple–violet and the phosphonium salt $[(C_6H_5)_4P]I$ precipitates as the solvent displaces the iodide ion.

(6) Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1990**, 315.

Scheme II



Condensation of 1 with catechol in the presence of the pseudohalides $[CN]^-$, $[SCN]^-$, $[RS]^-$, and $[OH]^-$ gives blue compounds that quickly decompose during workup. On the other hand, nucleophiles such as $[RCOO]^-$, $[RSO_3]^-$, and $[ReO_4]^-$ show no sign of coordination to ⟨**2**⟩.

Compounds **2**, **4a**, and **4b** represent useful precursors for alkylrhenium(VII) oxides of the type $CH_3ReO_2R_2$.[7]

II. Reduction of Quinones by Methyldioxorhenium(V). Reduction of the title complex 1 with triphenylphosphane is known to to give a rhenium(V) species, "CH_3ReO_2", which is stabilized by coordination of the triphenylphosphane oxide formed in this reaction.[1,8] Since alkyne complexes of the type CH_3ReO_2(alkyne) are easily accessible from this isolable intermediate, reactions with *o*-quinones are interesting to see if redox reactions occur.

When a mixture of 1, polymer-bound triphenylphosphane, 9,10-phenanthrenequinone, and pyridine is heated under reflux in THF, the color changes first to yellow, then to green, and gradually to intense blue. Upon workup, the novel blue, crystalline complex **5** is isolated in 76% yield (Scheme II).

Spectroscopic data for **5** indicate a structure analogous to that of the crystallographically characterized catechol derivative $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)(NC_5H_5)$,[4] e.g., the pyridine is trans to the methyl group, with the *cis*-dioxo and the phenanthrene-9,10-quinolato(*O,O*) ligand in the equatorial plane of the octahedron. In the ^{13}C NMR spectrum of **5**, the low-field resonance (assigned to the carbon atoms in 9- and 10-positions of the phenanthrene) appears at δ = 162 ppm. This is close to the signal observed in phenols and catechols for the carbon atoms to which the hydroxyl groups are attached[9] and contrasts to the range δ = 180–200 ppm found in quinones.[10] The IR spectrum of **5** does not show a band attributable to the characteristic ν(C=O) vibration. (The medium-intensity absorption at 1602 cm^{-1} is assigned to pyridine.) Complex

(7) Herrmann, W. A.; Romao, C. Unpublished results, 1990.

(8) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946; *Angew. Chem.* **1988**, *27*, 394.

(9) Bristow, S.; Enemark, J. H.; Garner, C. D.; Minelli, M.; Morris, G. A.; Ortega, R. B. *Inorg. Chem.* **1985**, *24*, 4070.

(10) E.g.: Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR Spectrocopy*; Georg Thieme Verlag: Stuttgart, 1984.

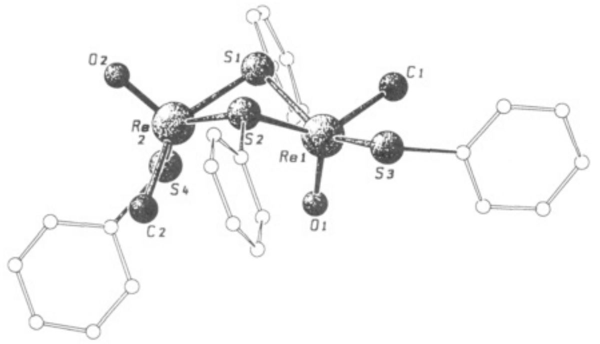
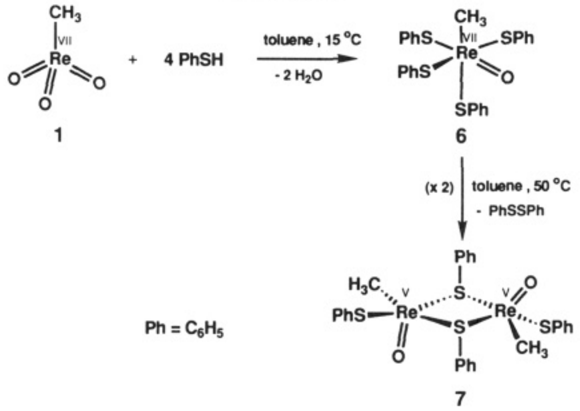


Figure 1. SCHAKAL[21] drawing of the dinuclear complex **7**. Important atoms are labeled and shaded. Hydrogen atoms are omitted for clarity reasons.

Scheme III



5 is thus unequivocally formulated as a rhenium(VII) complex containing the quinone in the reduced dihydroxy (catecholato) form. The reaction of Scheme II is an *oxidative addition* of the quinone to methyldioxorhenium ($Re^V \rightarrow Re^{VII}$).

III. Condensation Reaction of Methyltrioxorhenium(VII) with Thiophenol. We have recently determined that the condensation reaction of $(\eta^5\text{-}C_5Me_5)ReO_3$ with thiophenol is accompanied by reduction of rhenium to the oxidation state +V.[11] The most obvious explanation was the bulkiness of the pentamethylcyclopentadienyl ligand, which induces reductive elimination of disulfides. A study of **1** in related reactions was necessary to gain some information on the stereoelectronic differences between the σ-methyl group in **1** and the π-aromatic ligand in $(\eta^5\text{-}C_5Me_5)ReO_3$.

Reaction of **1** with thiophenol gives initially the rhenium(VII) complex **6**, which then undergoes elimination of 1 equiv of diphenyl disulfide to give the dinuclear complex **7** according to Scheme III in 89% isolated yield.

Special care must be taken in the isolation of **6** as elimination of the disulfide occurs readily. Spectroscopic data for **6** indicate that the methyl ligand is cis to the oxo group, with the four thiophenol ligands occupying the other four corners of an octahedron. The ^1H NMR spectrum shows a complex set of signals for the aromatic protons which indicates that the aromatic rings are nonequivalent. (In the case where the oxo and methyl groups are trans, the aromatic rings would be equivalent, giving rise to a less complex ^1H NMR spectrum.)

The dinuclear complex **7** is formed by either heating the initial reaction mixture or by heating a sample of isolated **6** in toluene. Sincle crystals suitable for an X-ray structure determination were obtained from methylene chloride/hexane by slow diffusion.

The structure of **7** (Figure 1) is best described as two edge-sharing square-based pyramids with the oxygen atoms occupying the apical position of each pyramid. The two S atoms of the bridging thiolato ligands and the two Re atoms form a puckered four-membered ring with a butterfly angle of 122°. The two S atoms of the bridging thiolato groups (Table I) are separated by a distance of 286 pm, which is less than the sum of the *van der Waals* radii (360 pm) but significantly longer than the S–S bond in (monoclinic) elemental sulfur (204 pm).[12a] The Re–S bond lengths (average 228 pm) for the terminal thiolato groups correspond to the values found in other rhenium(V) complexes such as $(\eta^5\text{-}C_5Me_5)Re(3,4\text{-}S_2C_6H_3\text{-}1\text{-}CH_3)_2$ (average 233 pm)[11] and $Re(O)(SR)_4$ (average 232 pm).[12] The Re–S bond lengths for the bridging thiolato groups are longer (average 240 pm) than those for the terminal thiolato ligands. This difference compares well to the differences (ca. 10 pm) found in most transition-metal complexes containing thiolato ligands in both bridging and terminal modes.[13] The Re–O and the Re–C bond lengths are in the normal range for double and single bonds, respectively.[3]

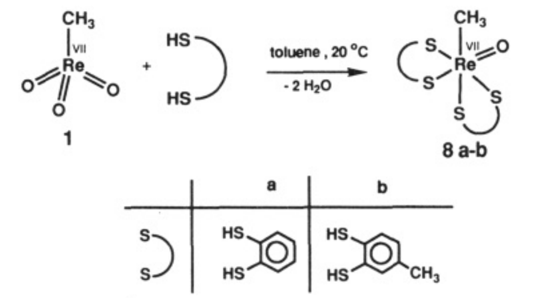
IV. Condensation of Methyltrioxorhenium(VII) with Benzene-1,2-dithiol and Toluene-3,4-dithiol. A condensation reaction is also observed when the title compound **1** is treated with benzene-1,2-dithiol. The rhenium(VII) complex **8** forms rapidly (Scheme IV). The ^1H NMR spectrum of **8** shows two nonequivalent aromatic rings indicative of a structure with the methyl ligand cis to the oxo group. The presence of only one methyl signal is further proof of the formation of only one isomer.

By contrast, reaction of **1** with toluene-3,4-dithiol gives a mixture of two configurational isomers (^1H NMR) where the oxo group is cis to the methyl ligand is one isomer and trans to the methyl ligand in the other isomer. (In this case, the situation is complicated by the possibility of more

Table I. Important Distances (pm) and Angles (deg) of the Thiolato Complex 7

Re1–S1	239.2 (3)	Re1–S2	238.2 (3)
Re1–S3	229.8 (2)	Re2–S1	240.1 (2)
Re2–S2	240.3 (2)	Re2–S4	226.2 (3)
Re1–O1	170.2 (6)	Re2–O2	169.2 (6)
Re1–C1	211.8 (9)	Re2–C2	220.5 (5)
S1–Re1–S2	73.79 (7)	S1–Re2–S2	73.24 (7)
S1–Re1–S3	145.84 (8)	S2–Re2–S4	140.4 (1)
Re1–S1–Re2	89.29 (7)	Re1–S2–Re2	89.50 (6)

Scheme IV



(12) (a) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984. (b) McDonell, A. C.; Hambley, T. W.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1983**, *36*, 253. (c) Blower, P. J.; Dilworth, J. R.; Hutchinson, J.; Nicholson, T.; Zubieta, J. *Inorg. Chem. Acta* **1984**, *90*, L27. (d) Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chem. Acta* **1989**, *156*, 27.

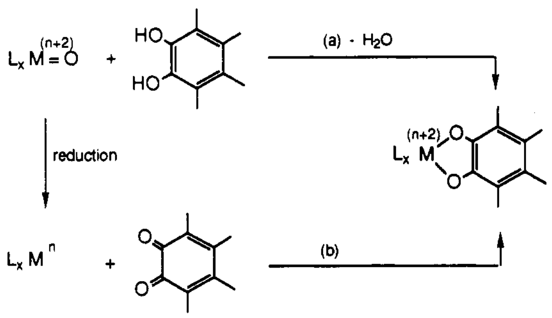
(13) Dance, I. A. *Polyhedron* **1986**, *5*, 1037.

(11) Takacs, J.; Kiprof, P.; Herrmann, W. A. *Polyhedron* **1990**, *9*, 2211.

isomers due to the asymmetric thiolato ligand.) Separation of the isomers has so far not proven possible, so the data given here are for the unresolved mixture.

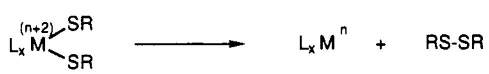
Conclusion

Methyltrioxorhenium(VII) readily undergoes condensation reactions with aromatic diols and thiols. The catecholato(*O,O*) complexes following eq 1a can also be synthesized by oxidative addition of the corresponding *o*-quinone to the organorhenium(V) species "CH_3ReO_2" according to the overall equation (1b).



(1)

Thiols normally entail multiple substitution (condensation), thus converting the title compound 1 into thiolato derivatives of type $CH_3ReO(SR)_4$ that eventually undergo reductive disulfide elimination represented by eq 2. Steric effects of the thiolate groups seem to govern this reaction.



(2)

Experimental Section

All manipulations were carried in a dry nitrogen atmosphere by using conventional Schlenk techniques. The title compound CH_3ReO_3 (1) was prepared according to the literature method.[14] Polymer-bound triphenylphosphane (3.06 mmol of phosphane/g) was obtained from Aldrich Chemical Co. and used as received. ^1H NMR spectra were recorded at 25 °C and 400 MHz (JEOL JNM GX-400). EI mass spectra were recorded at 70 eV (Finnigan MAT 311A) and are based on the ^{187}Re isotope (*m/e* values). Elemental analyses were carried out in the Microanalysis Laboratory of our institute.

1. Synthesis of $[(C_6H_5)_4P][CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)Cl]$ (4a). To a stirred solution of 1 (52.5 mg, 0.21 mmol) in CH_2Cl_2 (7 mL) and toluene (3 mL) were added catechol (22 mg, 0.20 mmol) and $[P(C_6H_5)_4]Cl$ (75 mg, 0.20 mmol). After 30 min, the blue solution was slowly evaporated to dryness in vacuo. The dark-blue residue was washed with toluene, extracted with CH_2Cl_2, filtered, and concentrated in vacuo to 1–2 mL. Addition of hexane gave a blue precipitate (sometimes oily, which crystallized later). The mother liquor was decanted and discarded. The precipitate was washed with hexane and dried in vacuo. Yield: 132 mg (92%). Anal. Calcd for $C_{31}H_{27}ClO_4PRe$: C, 51.98; H, 3.80; Re, 26.00. Found: C, 51.65; H, 3.71; Re, 25.76. IR (KBr, cm^{-1}): 3060 w, 2902 w, 1565 m, 1482 m, 1437 s, 1313 m, 1108 s, 996 m, 756 s, 723 s, 690 s, 607 m, 530 s; [ν(Re=O)] 943 s, 910 s. ^1H NMR (CD_2Cl_2, ppm): δ 0.99 (s, CH_3), 6.44 (m, 2 H, 4,5-[$O_2C_6H_4$]), 6.80 (m, 2 H, 3,6-[$O_2C_6H_4$]), 7.61 (m, 8 H, 2,6-[C_6H_5]), 7.75 (m, 8 H, 3,5-[C_6H_5]), 7.91 (m, 4 H, 4 [C_6H_5]).

2. Synthesis of $[(C_6H_5)_4P][CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)Br]$ (4b). To a stirred solution of 1 (52.5 mg, 0.21 mmol) in THF (5 mL) and CH_2Cl_2 (5 mL) were added catechol (22 mg, 0.20 mmol) and $[(C_6H_5)_4P]Br$ (84 mg, 0.20 mmol). After 30 min, the blue solution was evaporated to dryness in vacuo. The residue was washed with toluene and then dissolved in a minimum amount of THF/CH_2Cl_2 (4/1) and filtered. The filtrate was concentrated in vacuo. Addition of hexane yielded a dark-blue precipitate, which was separated. Recrystallization from CH_2Cl_2/hexane by slow diffusion at −30 °C gave analytically pure 4b. Yield: 138 mg (91%). Anal. Calcd for $C_{31}H_{27}BrO_4PRe$: C, 48.95; H, 3.58; Br, 10.50; Re, 24.48. Found: C, 49.01; H, 3.59; Br, 10.40; Re, 24.32. IR (KBr, cm^{-1}): 3058 w, 1565 w, 1481 w, 1437 s, 1313 m, 1108 s, 996 m, 756 s, 722 s, 690 s, 608 m, 529 s, 409 m; [ν(Re=O)] 945 s, 911 s. ^1H NMR (CD_2Cl_2, ppm): δ 1.12 (s, 3 H, CH_3), 6.47 (m, 2 H, 4,5-[$O_2C_6H_4$]), 6.83 (m, 2 H, 3,6-[$O_2C_6H_4$]), 7.63 (m, 8 H, 2,6-[C_6H_5]), 7.75 (m, 8 H, 3,5-[C_6H_5]), 7.92 (m, 4 H, 4-[C_6H_5]).

3. Synthesis of $[(C_6H_5)_4P][CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)I]\cdot{}^1/_2(CH_3C_6H_5)\cdot{}^1/_2(CH_3NO_2)$ (4c). To a stirred solution of 1 (55 mg, 0.22 mmol) in nitromethane (8 mL) toluene (2 mL) were added catechol (22 mg, 0.20 mmol) and $[P(C_6H_5)_4]I$ (93 mg, 0.20 mmol). After 30 min, the deep-green solution was slowly evaporated to dryness in vacuo. The residue was washed with toluene; then it was dissolved in nitromethane and filtered. After concentration of the solution to ca. 1 mL, toluene (10–15 mL) and hexane (1–2 mL) were added. Dark-green crystals of 4c precipitated. After the solvent was decanted, the crystals were washed with hexane and dried in vacuo. The compound crystallized with a half mole of toluene and nitromethane per molecule. Yield: 164 mg (93%). Anal. Calcd for $C_{31}H_{27}IO_4PRe\cdot{}^1/_2(CH_3C_6H_5)\cdot{}^1/_2(CH_3NO_2)$: C, 47.54; H, 3.70; N, 0.79. Found: C, 48.07; H, 3.90; N, 0.70. IR (KBr, cm^{-1}): 3055 w, 2906 w, 1566 m, 1482 m, 1437 s, 1312 m, 1267 m, 1196 w, 1107 s, 996 m, 753 s, 722 s, 689 s, 608 m, 526 s; [ν(Re=O)] 949 s, 916 s. ^1H NMR (CD_2Cl_2, ppm): δ 1.31 (s, 3 H, CH_3), 2.33 (s, 1.5 H, $CH_3C_6H_5$), 4.31 (s, 1.5 H, CH_3NO_2), 6.51 (m, 2 H, 4,5-[$O_2C_6H_4$]), 6.86 (m, 2 H, 3,6-[$O_2C_6H_4$]), 7.21 (m, 2.5 H, $CH_3C_6H_5$), 7.63 (m, 8 H, 2,6-[C_6H_5]), 7.76 (m, 8 H, 3,5-[C_6H_5]), 7.92 (m, 4 H, 4-C_6H_5).

4. Synthesis of $CH_3Re(O)_2(9,10\text{-}O_2C_{14}H_8)(NC_5H_5)$ (5). To a stirred solution of 1 (75 mg, 0.30 mmol) in THF (15 mL) were added polymer-bound triphenylphosphane (0.30 mol), 9,10-phenanthrenequinone (62.4 mg, 0.30 mmol), and pyridine (32 μL, 0.40 mmol). The mixture was heated at reflux for 2 h and then cooled to 25 °C. Pyridine (32 μL, 0.40 mmol) and CH_2Cl_2 (15 mL) were added, and the mixture was stirred for 30 min. The blue solution was then filtered, and the solids were washed with CH_2Cl_2 (2 × 10 mL). The combined filtrates were evaporated to dryness in vacuo, and the residue was redissolved in a small amount of CH_2Cl_2. Addition of hexane precipitated the product as shining dark-blue crystals. After the solvent was decanted, the crystals were washed with hexane and dried in vacuo. Recrystallization from CH_2Cl_2/hexane gave analytically pure 5a. Yield: 118 mg (76%). Anal. Calcd for $C_{20}H_{16}NO_4Re$: C, 46.14; H, 3.10; N, 2.69. Found: C, 45.71; H, 3.14; N, 2.59. IR (KBr, cm^{-1}): 3070 w, 1602 m, 1560 w, 1507 w, 1446 m, 1413 m, 1320 m, 1213 m, 1066 m, 1040 m, 1011 m, 754 s, 720 m, 692 m, 631 m, 561 w, 542 m, 514 w, 438 w, [ν(Re=O)] 953 sh, 942 s, 905 s. ^1H NMR (CD_2Cl_2, ppm): δ 0.63 (s, 3 H, CH_3), 7.20–8.60 (7 m, 13 H). ^{13}C NMR ($CDCl_3$, ppm): δ 162.1, 147.2, 139.3, 131.0, 130.6, 127.2, 125.6, 125.1, 123.0, 121.0 (aromatic carbons); 30.4 (CH_3). EI-MS (*m/e*, rel intensity %): 442 ([M − NC_5H_5]$^+$, 1.5), 427 ([M − NC_5H_5 − CH_3]$^+$, 1.5), 79 (NC_5H_5, 100). FD-MS (*m/e*, rel intensity, %): 442 ([M − NC_5H_5]$^+$, 100).

5. Synthesis of $CH_3Re(O)(SC_6H_5)_4$ (6). To a stirred solution of 1 (90 mg, 0.36 mmol) in toluene (15 mL) was added thiophenol (238 mg, 222 μL, 2.16 mL). The reaction mixture was stirred at 15 °C for 6 h and then concentrated to ca. 5 mL. (*Note*: Heating must be avoided when the sample is concentrated!) Hexane (20 mL) was added, and the product precipitated as a microcrystalline, brown solid. Yield: 219 mg (93%). Anal. Calcd for $C_{25}H_{23}OReS_4$: C, 45.93; H, 3.48; O, 2.45; S, 19.6. Found: C, 46.16; H, 3.52; O, 2.48; S, 19.7. IR (KBr, cm^{-1}) 3060 w, 2924 w, 1580 m, 1474 m, 1438 m, 1070 w, 1023 w, 992 s, 738 vs, 688 s. ^1H NMR (CD_2Cl_2, ppm): δ 7.20–7.61 (m, 20 H, 4C_6H_5, 2.85 (s, 3 H, CH_3).

6. Synthesis of $(CH_3)_2Re_2(O)_2(SC_6H_5)_4$ (7). To a stirred solution of 1 (124 mg, 0.50 mmol) in toluene (15 mL) was added thiophenol (330 mg, 306 μL, 3.00 mmol). The reaction mixture was heated at 40–50 °C for 6 h and then concentrated in vacuo to ca. 5 mL. Hexane (20 mL) was added and a fine brown powder precipitated. Recrystallization from CH_2Cl_2/hexane by slow diffusion gave crystals suitable for X-ray study. Yield: 193 mg (89%). mp: 168–171 °C (dec). Anal. Calcd for $C_{26}H_{26}O_2Re_2S_4$: C, 35.84; H, 3.01; O, 3.67; Re, 42.75; S, 14.72. Found: C, 35.99; H, 3.10; O, 3.76; Re, 42.26; S, 14.51. IR (KBr, cm^{-1}): 3057 w, 2920

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Table II. Crystallographic Data, Parameters of the Data Collection, and Structure Refinement for the Dinuclear Thiolato Complex 7

(a) Crystal Parameters	
empirical formula	$C_{26}H_{26}O_2Re_2S_4$
fw	871.1
cryst color and shape	red–brown plate
radiation	Cu Kα (λ = 154.18 pm)
temp, °C	23 ± 1
space group	$P2_1/c$ (No. 14)
a, pm	992.6 (1)
b, pm	1855.7 (1)
c, pm	1613.2 (2)
β, deg	107.54 (<1)
V, pm^3	2832 × 10^6
Z	4
ρ(calcd), g·cm^{-3}	2.042
μ(Cu Kα), cm^{-1}	187.4
(b) Data Collection	
diffractometer	CAD4 Enraf-Nonius
monochromator	graphite, incident beam
scan type	$\omega/2\theta$ scan
scan time, s	max 90
scan width, deg	(1.20 + 0.25 tan θ) ± 25% for corrections
max 2θ, deg	130
no. of reflns measd	5283 (−11/0,0/21,−18/18)
no. of indep reflns used	3684 ($I > 3.0\sigma$)
corrections	Lorentz–polarization, [F_c(corr) = $F_c/(1 + \epsilon F_c^2$LP)]
std reflns	3 every 3600 s of intensity check; 3 every 200 orientation check

w, 1514 w, 1469 m, 1436 m, 1067 w, 1024 m, 990 vs, 743 s, 689 s, 527 w, 488 m, 440 w. ^{1}H NMR (CD_2Cl_2, ppm): δ 7.34 (m, 4 H, C_6H_5), 7.42 (m, 8 H, C_6H_5), 7.59 (m, 8 H, C_6H_5), 2.84 (s, 6 H, 2CH_3).

7. Synthesis of $CH_3Re(O)(1,2\text{-}S_2C_6H_4)_2$ (8a). To a stirred solution of 1 (260 mg, 1.04 mmol) in toluene (15 mL) was added benzene-1,2-dithiol (196 mg, 240 μL, 2.08 mmol). The mixture was stirred for 1 h; then the toluene was concentrated to ca. 3 mL, and hexane (15 mL) was added. Slow diffussion at −30 °C gave dark-brown crystals. Yield: 418 mg (81%). mp: 194–197 °C (dec). Anal. Calcd for $C_{13}H_{11}OReS_4$: C, 31.37; H, 2.23. Found: C, 31.58; H, 2.41. IR (KBr, cm^{-1}): 3040 w, 2959 w, 2923 m, 2853 w, 1442 m, 1425 m, 1248 m, 1100 m, 956 vs, 749 s. ^{1}H NMR (CD_2Cl_2, ppm): δ 7.96 (d, 1 H), 7.93 (d, 2 H), 7.86 (d, 1 H), 7.41 (t, 1 H), 7.26 (t, 1 H), 7.19 (t, 1 H), 7.14 (t, 1 H), 3.31 (s, 3 H, CH_3). EI-MS (m/e rel intensity, %) 498 ([M]$^+$, 6), 483 ([M − CH_3]$^+$, 5), 375 ([M − CH_3 − C_6H_4S]$^+$, 1.5), 343 ([M − CH_3 − $C_6H_4S_2$]$^+$, 1).

8. Synthesis of $CH_3Re(O)(1,2\text{-}S_2C_6H_3\text{-}4\text{-}CH_3)_2$ (8b). To a stirred solution of 1 (195 mg, 0.78 mmol) in toluene (15 mL) was added toluene-3,4-dithiol (390 mg, 331 μL, 2.50 mmol). After 15 min, the brown solution was quickly concentrated in vacuo and hexane was added. The brown precipitate was filtered, washed with a small amount of hexane, and dried in vacuo. Yield: 296 mg (74%). Anal. Calcd for $C_{15}H_{15}OReS_4$: C, 34.27; H, 2.88. Found: C, 34.66; H. 3.14. IR (KBr, cm^{-1}): 2916 w, 1580 m, 1458 s, 1255 m, 806 s, 548 m; [ν(Re═O)] 959 s. ^{1}H NMR (CD_2Cl_2; ppm): 2.42, 2.45 (2 s, 6 H, [$S_2C_6H_3CH_3$]), 3.26, 3.29 (2 s, 3 H, CH_3), 6.95–7.82 (m, 6 H, [$S_2C_6H_3CH_3$]). EI-MS (m/e, rel intensity, %): 526 ([M]$^+$, 98); 511 ([M − CH_3]$^+$, 100); 357 ([M − CH_3 − $S_2C_6H_3CH_3$]$^+$, 10).

9. X-ray Diffraction Study of Bis[methyloxo(μ-benzenethiolato)(benzenethiolato)rhenium(V)] (7). A single crystal of 7 crystallized from CH_2Cl_2/hexane at −30 °C was used for diffraction data collection. Data were collected at room temperature on a CAD-4 (Enraf-Nonius) with graphite-monochromated Cu Kα radiation (λ = 154.18 pm). Parameters of data collection are summarized in Table II. Lattice constants were obtained by a least-squares fit of 25 reflections in the range 37.1° ≤ 2θ ≤ 58.8°.[15] Intensities of three standard reflections for decomposition and three orientation control reflections were measured every 60 min and every 200 reflections, respectively, during data collection. No decay or disorientation was observed. Correction for Lorentz and polarization effects was applied. An empirical absorption correction was applied (μ = 187.4 cm^{-1}). The structure was solved by Patterson methods (SHELX-86)[16] and refined by subsequent least-squares and difference Fourier techniques.[17] Hydrogen atoms were included in the structure factor calculation but not refined. Scattering factors were taken from ref 18 including anomalous scattering.[19]

All non-hydrogen atoms except C2 and O2 were refined with anisotropic displacement parameters. The refinement yielded final R values of R = 0.064 and R_w = 0.063 considering all observed reflections ($I \geq 3.0$). Final difference Fourier maps demonstrated high electron density peaks with a maximum of 2.61 e/Å^3 (82 pm from Re2) and a minumum of −3.32 e/Å^3 (95 pm from Re1). All computation were carried out on VAX 11/730 and VAX 8200 computing systems using the Program System STRUX.[20]

Due to difficulties encountered during the structure determination (atoms C2 and O2 could only be refined with isotropic displacement parameters and high residual electron density), only certain aspects of the structure can be discussed. On the other hand, the structural refinement converged with relatively low values for R and R_w (0.064 and 0.063, respectively).[22]

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(22) Further details of the structure can be obtained from the authors (P.K.) on request.