Lorentz and polarization corrections were applied. Structure solution was by conventional heavy-atom (Patterson and difference Fourier) methods and refinement by blocked cascade full-matrix least-squares (with weights w set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics). All non-hydrogen atoms were assigned anisotropic displacement parameters, and all hydrogen atoms fixed isotropic displacement parameters. All non-hydrogen atoms were refined without positional constraints. All hydrogen atoms were constrained to idealized geometries (C-H 0.96 Å, H-C-H 109.5°) except for H(1) and H(2), which were refined without positional constraints. Residuals of convergence are listed in Table IV. All calculations were carried out with Nicolet proprietary software using complex scattering factors taken from ref 36.

Acknowledgment. C.J.S. wishes to thank Professor R. R. Schrock for some pertinent discussions.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters (4 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

(36) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Multiple Bonds between Transition Metals and Main-Group Elements. 74.[1] Five-Membered Rhenacycles through Condensation Reactions of Methyltrioxorhenium(VII) with Bidentate Ligands. X-ray Crystal Structures of 8-Oxyquinolinato and Catecholato Complexes

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Methyltrioxorhenium(VII), CH_3ReO_3 (**1**), undergoes condensation reactions with aromatic bidentate ligands of type HO···X (X = N, NH_2, OH) to yield products with strongly ligand-dependent structures. Mild conditions are characteristic of these condensation reactions. Thus, reactions of **1** with catechols 1,2-$(HO)_2C_6H_2RR'$-3,4 in the presence of pyridine give compounds **2a–c** of general formula $CH_3Re(O)_2$-(1,2-$O_2C_6H_2RR'$-3,4)(NC_5H_5) in high yields. The single-crystal X-ray diffraction study of the parent catecholato derivative **2a** (R = R′ = H) reveals an octahedral ligand sphere around the rhenium atom, with cis oxo ligands and the pyridine in trans position with respect to the methyl group. Treatment of **2a** with anhydrous hydrogen chloride yields the ionic complex **3a** of formula $[C_5H_5NH]^+[CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)Cl]^-$, resulting from nucleophilic replacement of the pyridine ligand by a chloride ion. Reaction of **1** with the heterobifunctional ligand 2-aminophenol yields the bis-substituted amidophenolato derivative CH_3Re-$(O)[1,2\text{-}O(HN)C_6H_4]_2$ (**4**). While the bis(thiophenolato) analogue of **4** could not be isolated, the pyridine adduct of the mono(amidothiophenolato) derivative $CH_3Re(O)_2[1,2\text{-}S(HN)C_6H_4](C_5H_5N)$ (**5**) is easily obtainable. Smooth reaction of **1** with 1 equiv of the chelating ligand 8-hydroxyquinoline results in the formation of the binuclear compound $(\mu\text{-}O)[CH_3Re(O)_2(8\text{-oxyquinolinato})]_2$ (**6**) in 90% yield. According to a single-crystal X-ray study, the centrosymmetric molecule consists of two corner-sharing distorted octahedra with a (linear) bridging oxo ligand. Most of the novel oxorhenium(VII) condensation products hydrolyze to the respective precursor compounds. The *aliphatic* analogues of this type of condensation products could not be isolated.

Introduction

High oxidation state organometallic chemistry has rapidly gained impetus in recent years. The general interest in this field stems partly from the potential of such complexes to promote facile transformations of organic compounds in a number of chemical processes. Many catalytic reactions such as olefin metathesis, polymerization, etc., have been known to involve high-valent organometallic species, and evidence is mounting that such intermediates are also important in other types of reactions such as metal oxide catalyzed olefin oxidation, hydroxylation, etc.[2,3] Biological systems featuring active sites with transition metals in medium-to-high oxidation states (Fe, Mo, etc.) also provide stimulus for work in this area.[4] At present, rhenium derives its importance mainly from the former field. However, a very promising new area related to bioinorganic chemistry is the synthesis of radiopharmaceuticals, based on the easily accessible isotopes ^{186}Re and

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(1) Part of this article was published as a preliminary communication: *J. Organomet. Chem.* **1989**, *369*, C1. Communication 73: Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Kiprof, P. *Organometallics*, in press.

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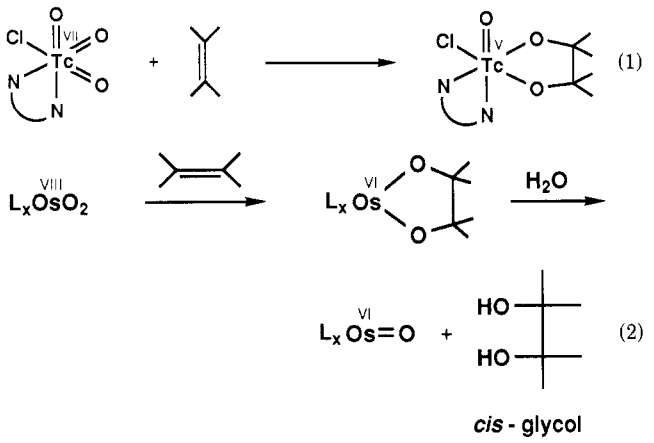
^{188}Re and designed by analogy to already existing radiodiagnostics of technetium.[5]

We have been investigating the catalytic activity of several organorhenium oxides in various oxidation processes (e.g., olefin epoxidation). To achieve a better understanding of the possible mechanisms, we have synthesized novel rhenacycles. Related technetium[6] and osmium[2] metallacycles, unlike their rhenium counterparts, can be made by direct reaction of the corresponding metal oxides and olefins according to eqs 1 and 2. The osmate



esters are the key intermediates in olefin hydroxylation: here, the last step is hydrolysis of the osmium(VI) species to yield 1,2-diols.

A more accurate knowledge of the marked differences in the catalytic behavior of rhenium and osmium oxides is expected to arise from a study of related rhenacyclic compounds, and the results should help to design further precursors of rhenium-containing catalysts. The present paper focuses on synthetic and structural aspects of these novel organorhenium(VII) oxo compounds which—with one exception—are representatives of the relatively small class of group VII d^0 *cis*-dioxo complexes (cf. ref 7).

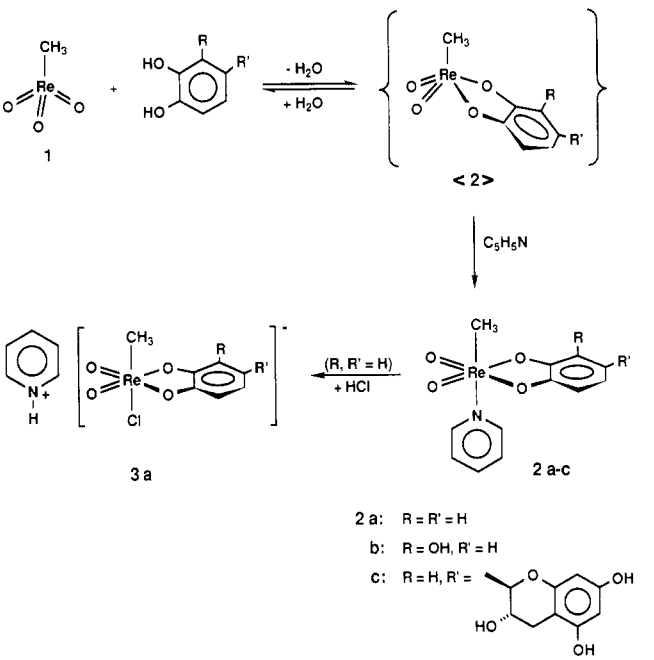
Results and Discussion

I. Synthetic and Spectroscopic Results: Condensation Reactions of Methyltrioxorhenium(VII). It was recently determined in our laboratory that the title complex **1**—unlike the congener osmium tetraoxide, OsO_4, and $TcO_3Cl(N\text{-}N)$ (N-N = phen, bpy; eq 1 and 2)—*does not react with olefins* under reasonably mild conditions.[8] Therefore, a different reaction pathway had to be found for the generation of the desired five-membered rhenacycles.

(1) Condensation with 1,2-Dihydroxybenzenes. Condensation reactions of the title compound **1** with diols appeared to be one of the alternative routes. Indeed, reaction of **1** with catechol (1,2-dihydroxybenzene) at room temperature yields a purple–violet solution containing a compound we assume is the condensation product **2a** of formula $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)$.

Attempted isolation of this complex in a pure state was unsuccessful. Addition of pyridine, however, resulted in an immediate color change to intense blue, and the dark-blue hexacoordinate pyridine adduct **2a** of formula $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)(NC_5H_5)$ was isolated in high yield.

Scheme I



Although this complex decomposes in the presence of a large excess of water, it is isolable from the reaction mixture when most of the water (as formed according to Scheme I) is removed azeotropically. The IR spectrum (KBr) of **2a** shows two strong absorptions of equal intensity in the ν(Re=O) region at 951 and 918 cm^{-1}, assigned to cis oxo groups. A single-crystal X-ray structure determination confirmed this assignment and showed the pyridine ligand to be trans to the methyl group as in most cases of the amine adducts $CH_3Re(O)_3{\cdot}(L)$.[9] The complex is thermally stable up to 112 °C and is chemically inert toward olefins and acetylenes. In this respect, note that reactions of **1** with catechol in the presence of olefins or acetylenes do not yield the expected complexes $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)(L)$ (L = olefin, acetylene). However, **2a** reacts with hydrogen chloride under anhydrous conditions with formation of an ionic rhenium(VII) complex that we formulate as $[C_5H_5NH]^+[CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)Cl]^-$, (**3a**); in this compound the pyridine ligand of **2a** has been replaced by a chloride ion (Scheme I).

In the presence of pyridine, reaction of **1** with pyrogallol (1,2,3-trihydroxybenzene) or (+)-catechine (3,3′,4′,5,7-pentahydroxyflavane) proceeds according to Scheme I, yielding the dark-blue products **2b** and **2c**, respectively. **2b** was isolated with a second molecule of pyridine, e.g., $CH_3Re(O)_2(1,2\text{-}O_2C_6H_3OH\text{-}3)(NC_5H_5){\cdot}(NC_5H_5)$. The ^1H NMR spectrum ($CDCl_3$, 25 °C) shows only *one* type of pyridine ligand in compound **2b**, which is compatible with a fast exchange of the two pyridine ligands on the NMR time scale. At −45 °C, two sets of the pyridine signals are observed. If the pyridine ligand attached to the rhenium is trans to the methyl group (as in the case of **2a**) and the hexacoordination is configurationally stable, then **2b** should occur as two enantiomers due to the asymmetric coordination of the pyrogallol ligand. Accordingly, compound **2c** as formed from **1** and (+)-catechine must be a mixture of the possible diastereomers since the molecule has two centers of chirality.

Reaction of **1** with the catechol derivatives L-DOPA and (−)-3,4-dihydroxynorephedrine in the presence of pyridine

(5) Deutsch, E.; Libson, K.; Vanderheyden, J. L.; Ketring, A. R.; Maxon, H. R. *Nucl. Med. Biol.* **1986**, *13*, 465.
(6) Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981.
(7) Cai, S.; Hoffmann, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 313.
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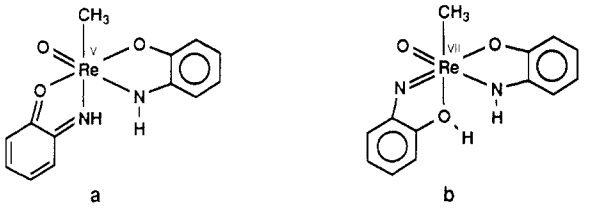
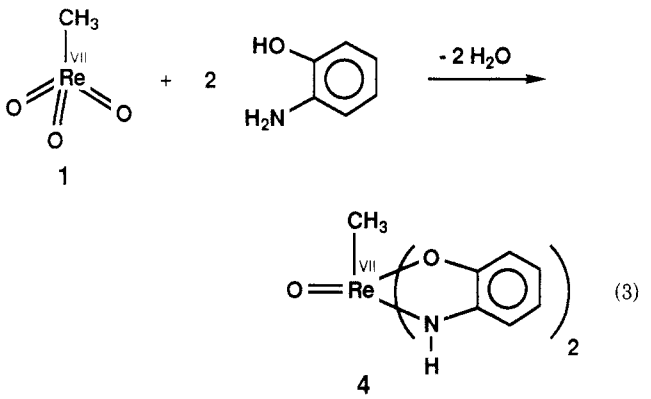


Figure 1.

yields dark blue solids that we believe are condensation products similar to compounds **2a–c**. However, low solubility of these derivatives in organic solvents has so far precluded full characterization.

(2) Condensation with 2-Aminophenol. The condensation reaction of **1** with the heterobifunctional ligand 2-aminophenol proceeds in a different way: The dark-red compound **4** of formula $CH_3Re(O)[1,2\text{-}O(HN)C_6H_4]_2$ is formed according to eq 3, even when a ligand-to-metal ratio as low as 1/1 is applied.



(3)

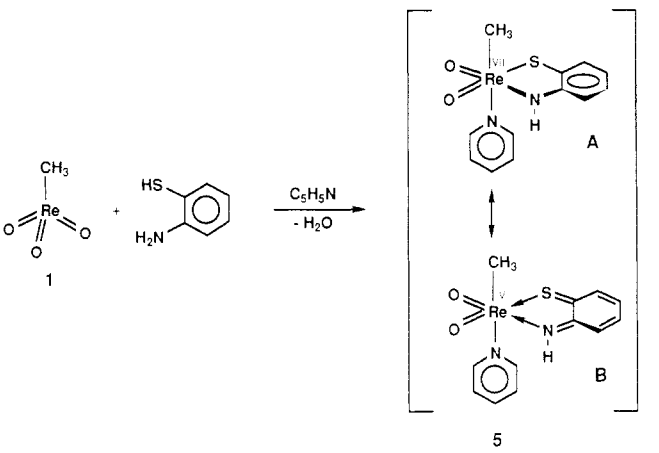
Although the solid-state structure of complex **4** remains unresolved because crystals suitable for an X-ray study could not be obtained, the symmetrical arrangement around the rhenium atom (e.g., oxo ligand trans to the methyl group) can be excluded on the basis of the available spectroscopic data. The IR spectrum shows *two* absorptions in the 3100–3400-cm^{-1} region, assigned to *two different amido (N–H) groups*. In the ^1H NMR spectrum of **4** *two* broad signals of the amido protons are clearly separated at δ = 7.9 and 11.3 (CD_2Cl_2). (The "acidity" of amido protons in high oxidation state rhenium amido complexes has been emphasized.[10]) The difference in chemical shift may be explained as a strong interaction between one of the amido protons and the oxo group (or the oxygen of the second phenolato ligand), e.g., an intra- or intermolecular hydrogen bridge. Other less likely alternatives may include a dimeric structure with terminal and bridging amidophenolato ligands, or perhaps a structure with one amidophenolato and one quinoimino ligand (Figure 1a), or a structure with one imidophenol ligand (Figure 1b). Unfortunatly, due to the low solubility of **4**, sufficient experimental data could not be obtained, which precluded further elucidation of the structure.

(3) Condensation with 2-Aminothiophenol. While treatment of CH_3ReO_3 (**1**) with 2 equiv of 2-aminothiophenol leads to an untractable mixture, reaction with *one* equiv of this compound in the presence of pyridine yields the red chelate complex **5** (Scheme II).

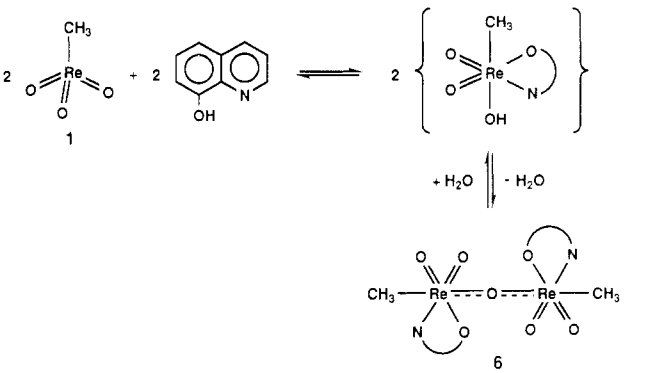
In the ^1H NMR spectrum of **5**, the amido proton at δ = 10.8 ($CDCl_3$) is again strongly deshielded. The fact that the ν(Re=O) vibrations of **5** occur at considerably lower

(10) Gardner, J. K.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1978**, *17*, 897.

Scheme II



Scheme III



frequencies than those of **2a** ($\Delta\nu$(Re=O) $\approx$ 45 cm^{-1}) might indicate the stronger electron-releasing properties of the amidothiophenolato ligand or perhaps a stronger contribution of the *o*-thioquinoimine resonance form **5B** (pentavalent rhenium) to the overall structure of this complex. The imidobenzenethiol form can be excluded in this case since according to the IR spectrum the hydrogen is attached to the nitrogen atom.

(4) Condensation with 8-Hydroxyquinoline. Smooth reaction occurs between the title compound **1** and the chelating nucleophile 8-hydroxyquinoline. Yet another type of condensation reaction takes place: the violet, dinuclear, oxygen-bridged rhenium(VII) compound **6** with the unexpected formula $(\mu\text{-}O)[CH_3Re(O)_2(8\text{-}oxyquinolinato)]_2$ forms in 90% isolated yield (Scheme III).

Experimental evidence for a (plausible) hydroxy intermediate has not been found. Compound **6** shows two intense infrared absorptions at 968 and 937 cm^{-1} (KBr) typical of terminal oxo groups. A broad band observed at 700–712 cm^{-1} is tentatively assigned to the Re–O–Re stretching vibration, although this cannot be unequivocally identified due to strong absorptions of the aromatic rings in the 600–800-cm^{-1} spectral region.

A single-crystal X-ray structure determination of the dimer **6** revealed a distorted octahedral core geometry for each rhenium atom. The methyl groups are approximately trans to the bridging oxygen atom, which is the inversion center of the molecule. It is of interest that the Re–O–Re′ bonds have some doubled-bond character (vide infra).

All attempts to isolate and characterize the *aliphatic* derivatives of the above-mentioned condensation products have failed so far. One possible explanation for this failure might be that the related aliphatic ligands do not favor coplanar coordination (e.g., eclipsed conformation) to the rhenium atom (Figure 2, left). Staggered conformations

Figure 2. Possible effect of the oxygen lone pairs in the formation of condensation compounds as described in the text.

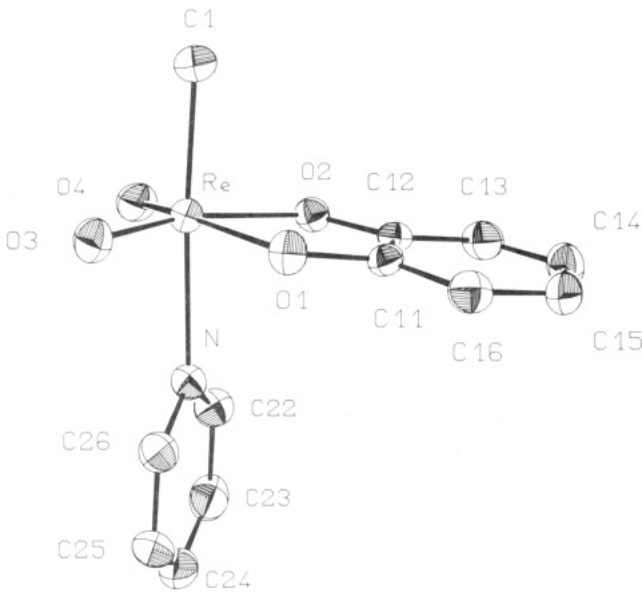


Figure 3. ORTEP drawing of a molecule of compound **2a** showing the atom-labeling scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

as in the known glycolato(*O,O*) complex (η^5-C_5Me_5)Re(O)(OCH_2CH_2O)[11] should rather dominate in these cases. This might imply that the lone pairs of the glycolato oxygen atoms point away from the rhenium (Figure 2, right) and, as a consequence, the overlap between the empty d orbitals of rhenium(VII) and the sp^3 oxygen lone pairs is smaller than in the case of coplanar coordination as in **2a**. Catecholates have been shown to be good π-donor ligands in high oxidation state transition-metal complexes.[12,13] However, the reaction between **1** and *cis*-3,5-cyclohexadiene-1,2-diol (which could form a planar, five-membered ReO_2C_2 cycle) in the presence of pyridine yields a light-blue solution, but repeated attempts to isolate a definite compound from this solution failed due to decomposition during the workup procedure. In addition to the thermodynamic reasoning, the weaker acidity of alcohols as compared to phenols may present a kinetic barrier if the first step of the condensation is protonation of an oxo group. In this respect, however, it has to be mentioned that reaction between **1** and the phenol derivative 2,2′-dihydroxy-1,1′-binaphthyl (which cannot be coplanar!) did *not* yield a condensation product analogous to compound **2a**. Obviously, there is need for more experimental data supporting the above hypothesis.

II. Structural Results. (1) The Catecholato(*O,O*) Complex 2a. Compound **2a** exhibits an octahedral core geometry around the rhenium(VII) center (Figure 3). The

Table I. Important Bond Distances and Angles of the Condensation Compounds 2a and 6

2a		6	
	Bond Distances (pm)		
Re–O1	199.5 (3)	Re–O1	187.1 (1)
Re–O2	201.1 (3)	Re–O2	169.8 (4)
Re–O3	170.7 (3)	Re–O3	168.5 (5)
Re–O4	171.1 (3)	Re–O4	201.7 (4)
Re–N	234.7 (4)	Re–N	227.0 (4)
Re–C	210.1 (5)	Re–C	215.1 (7)
	Bond Angles (deg)		
O1–Re–O2	75.4 (1)	O1–Re–O2	105.5 (2)
O2–Re–O3	162.2 (1)	O2–Re–O3	105.8 (2)
O3–Re–O4	108.2 (2)	O3–Re–O4	159.4 (2)
N–Re–C	175.5 (2)	N–Re–C	80.0 (2)
O1–Re–C	93.1 (2)	O1–Re–C	155.1 (2)
		N–Re–O1	77.6 (1)
		N–Re–O2	166.5 (2)
		N–Re–O4	74.1 (2)
		O2–Re–O4	93.0 (2)

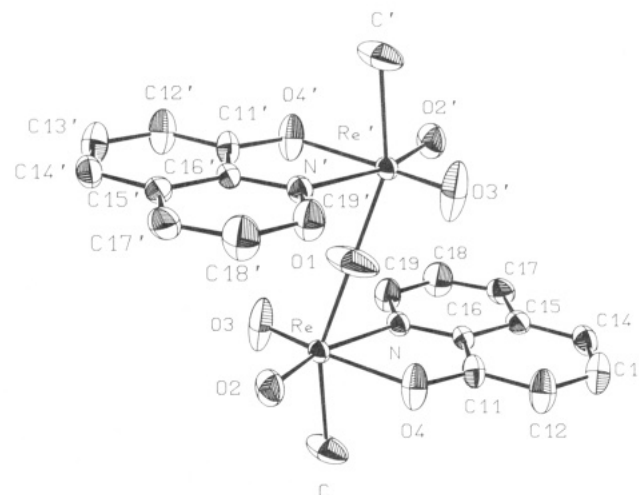


Figure 4. ORTEP drawing of a molecule of complex **6**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

chelating catecholate ligand is attached to the metal through two single-bonded oxygen atoms and is coplanar with the rhenium atom as well as with the cis oxo groups in the equatorial plane. The bonds between the rhenium and the oxygen atoms of the catecholate ligand are at the usual lengths for single bonds,[12] while the Re–O double bonds are slightly elongated compared to other oxorhenium(VII) compounds. This effect may result from the trans influence of the catecholato oxygen atoms O3 and O4 through a π-donor interaction. The pyridine molecule adopts an axial position trans to the methyl group. As in the case of the structurally characterized nitrogen base adducts of methyltrioxorhenium (type CH_3ReO_3·L) where the nitrogen donor is trans to the methyl group,[9] the Re–N distance is relatively long (234.7 (4) pm; Table I). The plane of the pyridine ligand is perpendicular to the plane defined by O_1–O_4,Re,C11–C16 (dihedral angle θ = 87.3°).

In the structural description of **2a** one may want to consider a rhenium(V) *o*-benzoquinone resonance form as a result of intramolecular oxidation of the catechol ligand. However, the comparison of the distances between the ring carbon atoms (e.g., C11–C16 139.5 (6) pm and C15–C16 139.2 (6) pm), as well as the Re–O (Re–O1 199.5 (3), Re–O2 201.1 (3) pm) and C–O bond lengths (C11–O1 135.4 (5) pm, C12–O2 133.1 (5) pm) show that the *o*-benzoquinone resonance form (pentavalent rhenium) does not significantly

(11) Herrmann, W. A.; Marz, D.; Herdtweck, E.; Schäfer, A.; Wagner, W.; Kneuper, H. J. *Angew. Chem.* **1987**, *89*, 462; *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 462.
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(13) Galeffi, B.; Postel, M.; Grand, A.; Rey, P. *Inorg. Chim. Acta* **1989**, *160*, 87.

contribute to the overall structure of **2a**. Important distances and angles of **2a** are summarized in Table I.

(2) The Oxyquinolinato(*O,N*) Complex 6. The structure of the centrosymmetric molecule **6** (Figure 4) is defined by two corner-sharing distorted octahedra connected by a bridging oxygen atom. Both the Re–O–Re′ angle (which is exactly 180°) and the Re–O–Re′ distances (187.1 (1) pm) indicate some π-bonding (double-bond contributions) between the bridging oxygen and the rhenium atoms. The octahedral arrangement around the rhenium centers is far from ideal because of the different steric and electronic properties of the various ligands. The nitrogen atom of the quinolinato ligand is in the trans position to the oxo ligand O2, and the Re–N distance (227.0 (4) pm) is considerably shorter as compared with **2a** and the nitrogen-base adducts of methyltrioxorhenium (CH_3ReO_3·L), where the nitrogen is trans to the methyl group (see Table I). This might be the result of the chelate effect and/or the influence of the highly electronegative oxo ligand (–I effect) in the *trans* position. In this respect note that in one of the isomers of CH_3ReO_3·$H_2NC_6H_5$, where the aniline ligand is trans to an oxo group, the Re–N distance is also significantly shorter than in the other isomer containing the aniline trans to the methyl group.[9] In compound **6** the methyl group is located trans to the bridging oxygen. This atom (O1) lies on the crystallographic inversion center of the unit cell and that of the molecule at [0,0,0]. The C–Re bond distance (215.1 (7) pm) is relatively long in comparison with that of **2a** (210.1 (5) pm), again indicative of the different trans influence of a bridging oxygen atom and of a pyridine ligand, respectively.

Conclusion

The Lewis acid methyltrioxorhenium(VII) (1) readily reacts with *vicinal* dihydroxybenzene derivatives and related *O,N* and *S,N* compounds to give *condensation products* that in certain cases require nitrogen bases for stabilization, preferably pyridine. The products—generally six-coordinate methylrhenium(VII) compounds—are susceptible to hydrolytic cleavage, under which conditions they normally form the starting compounds. This latter aspect could preclude the use of these type of ligands as auxiliary groups in catalytic applications of the title compound (e.g., olefin oxidation). On the other hand, the stability of the various condensation products depends on the particular ligand system. Thus, additional anchoring to the metal center, for example, via a pyridine-like moiety, should suffice to prevent hydrolytic "decomposition". These and related aspects are under continued investigation in our laboratory.

Experimental Section

General Data. All manipulations were carried out in an atmosphere of dry nitrogen using standard Schlenk techniques. The starting compound CH_3ReO_3 (1) was prepared according to the literature method.[14] ^1H NMR spectra were recorded at 25 °C, 400 MHz (JEOL JNM GX-400), EI mass spectra at 70 eV (Finnigan MAT 311-A). Elemental analyses were performed in the Microanalysis Laboratory of our institute. Mass spectra are based on the ^{187}Re isotope (*m/e* values).

Preparations. $CH_3Re(O)_2(1,2\text{-}O_2C_6H_4)(NC_5H_5)$ (2a). To a toluene solution (16 mL) of 100.0 mg (0.4 mmol) of CH_3ReO_3 (1), 44.0 mg (0.4 mmoles) of 1,2-dihydroxybenzene was added. The color of the solution turned purple–violet. After 5 min of stirring, 33.8 μL (0.42 mmol) of pyridine was added. The purple–violet color turned immediately to intense deep blue. The stirring was continued for 1 h, and then the volume of the solution was reduced in vacuo to ca. 5–6 mL (H_2O evaporated). Addition of *n*-hexane (20 mL) and cooling to –30 °C yielded **2a** as a dark blue, analytically pure microcrystalline solid, which was filtered, washed with *n*-hexane, and dried in vacuo, yield 151 mg, 90%. Recrystallization from a toluene–CH_2Cl_2 mixture/*n*-hexane by slow diffusion gave single crystals suitable for X-ray study, mp 112 °C. Anal. Calcd for $C_{12}H_{12}NO_4Re$: C, 34.28; H, 2.88; N, 3.33; O, 15.22; Re, 44.29. Found: C, 34.43; H, 2.95; N, 3.30; O, 15.26; Re, 44.06. IR (cm^{-1}, KBr) 3104 vw, 3069 vw, 1603 m, 1569 m, 1448 m, 748 m, br, 697 m, 611 m, 548 m, [ν(Re=O)] 952 s, 918 s; ^1H NMR (CD_2Cl_2) δ 8.25 (d, 2 H, H-2,6[Py], J = 7.0 Hz), 7.81 (m, 1 H, H-4[Py]), 7.34 (m, 2 H, H-3,5[Py]), 6.99 (m, 2 H, H-3,6-[$O_2C_6H_4$]), 6.56 (m, 2 H, H-4,5[$O_2C_6H_4$]), 1.29 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 161.3, 147.0, 139.8, 126.1, 125.2, 116.6 (Ar C), 31.3 (CH_3); MS, *m/e* (rel intensity) 421 (M^+, 0.5), 342 ([M – NC_5H_5]$^+$, 30), 327 ([M – NC_5H_5 – CH_3]$^+$, 54), 79 ($NC_5H_5^+$, 100).

$CH_3Re(O)_2(1,2\text{-}O_2C_6H_3OH\text{-}3)(NC_5H_5)$·$NC_5H_5$ (2b). To a toluene solution (14 mL) of 100.0 mg (0.4 mmoles) of **1**, 50.44 mg (0.4 mmol) of 1,2,3-trihydroxybenzene and 80.5 μL (1.0 mmol) of pyridine were added. The deep blue solution was stirred for 1 h, then it was filtered, and the volume was reduced in vacuo to 6–7 mL. After addition of 15 mL of *n*-hexane and cooling to –30 °C, a dark precipitate formed overnight, which was filtered, washed with *n*-hexane, and dried in vacuo, yield 192 mg, 93%. Anal. Calcd for $C_{17}H_{17}N_2O_5Re$: C, 39.61; H, 3.32; N, 5.43; O, 15.52; Re, 36.12. Found: C, 39.72; H, 3.43; N, 5.28; O, 15.53; Re, 36.04. IR (cm^{-1}, KBr) 3067 w, 1605 m, 1580 s, 1488 m, 1451 m, 1290 s, 1220 m, 1046 m, 786 m, 736 m, 694 m, 633 m, [ν(Re=O)] 952 s, 918 s; ^1H NMR ($CDCl_3$, 25 °C) δ 8.65 (br sh, 1 H, $O_2C_6H_3OH$-3), 8.25 (br, 2 H, H-2,6[Py]), 7.74 (m, 1 H, H-4[Py]), 7.31 (m, 2 H, H-3,5[Py]), 6.60 (d, 1 H, $O_2C_6H_3OH$-3, J = 8.1 Hz), 6.36 (t, 1 H, H-5[$O_2C_6H_3OH$-3], J = 8.1 Hz), 6.22 (d, 1 H, $O_2C_6H_3OH$, J = 8.1 Hz), 1.27 (s, 3 H, CH_3), ($CDCl_3$, –45 °C) δ 8.80 (d, 2 H, H-2,6[Py], J = 4.0 Hz), 8.18 (d, 2 H, H-2,6[Py], J = 4.8 Hz), 7.8 (m, 2 H, H-4[Py]), 7.42 (m, 2 H, H-3,5[Py]), 7.31 (m, 2 H, H-3,5[Py]), 6.63 (d, 1 H, $O_2C_6H_3OH$, J = 8.2 Hz), 6.36 (t, 1 H, H-5[$O_2C_6H_3OH$], J = 8.2 Hz), 6.22 (d, 1 H, $O_2C_6H_3OH$, J = 8.2 Hz), 1.27 (s, 3 H, CH_3); MS, *m/e* (rel intensity) 358 ([M – $2NC_5H_5$]$^+$, 10), 342 ([M – $2NC_5H_5$ – CH_3]$^+$, 14), 79 ($NC_5H_5^+$, 100).

$CH_3Re(O)_2$[(+)-3′,4′-*O,O*-3,5,7-trihydroxyflavanato]-(NC_5H_5) (2c). To a THF solution (12 mL) of 105 mg (0.42 mmol) of 1, 116 mg (0.4 mmol) of 3,3′,4′,5,7-pentahydroxyflavane ((+)-catechine) and 32.2 μL (0.4 mmol) of pyridine were added. The deep-blue solution was stirred for 1 h, and then it was filtered and concentrated to 4–5 mL. Addition of *n*-hexene (≈15 mL) yielded the crude product as a fine precipitate, which was separated. This precipitate was taken up in THF, and upon addition of *n*-hexane, **2c** precipitated as a dark-blue solid containing 1.5 equiv of THF per molecule, yield 235 mg, 83%. Anal. Calcd for $C_{21}H_{20}NO_8Re$·1.5THF (708.73): C, 45.75; H, 4.54; N, 1.97; O, 21.45; Re, 26.27. Found: C, 45.70; H, 4.43; N, 1.88; O, 21.77; Re, 26.26. IR (cm^{-1}, KBr) 3380 m, 3066 w, 2981 w, 1629 s, 1608 m, 1449 m, 1146 s, 1044 m, 816 w, 789 w, 762 w, 698 w, 633 m, [ν(Re=O)] 949 s, 918 s; ^1H NMR (acetone-d_6) δ 8.34–7.52 (m, 5 H, NC_5H_5), 7.08–6.68 (m, 5 H, Ar H of catechine), 6.02 and 5.86 (s, 2 H, 5,7-*H*O), 4.84 (d, 1 H, ^3J = 7.9 Hz, 2-H[catechine]), 3.96 (m, 1 H, 3-H[catechine]), 3.78 (br, 1 H, 3-*H*O), 3.61 (m, 6 H, THF), 2.94 (m, 1 H, 4-H[catechine]), 2.52 (m, 1 H, 4-H[catechine]), 1.77 (m, 6 H, THF), 1.14 (s, 3 H, CH_3).

$[C_5H_5NH]^+[CH_3Re(O)_2(O_2C_6H_4)Cl]^-$ (3). To a toluene solution (6 mL) of 91.2 mg (0.2 mmol) of **2a**, 0.2 mmol of anhydrous hydrogen chloride (200 μL of 1.0 M Et_2O solution) was added under stirring. A blue solid precipitated, which was separated after addition of 4 mL of *n*-hexane by filtration and dried in vacuo, yield 87 mg, 95%. Anal. Calcd for $C_{12}H_{13}ClNO_4Re$: C, 31.55; H, 2.87; N, 3.07; Cl, 7.76; Re, 40.75. Found: C, 31.87; H, 2.81; N, 3.07; Cl, 8.10; Re, 40.39. IR (cm^{-1}, KBr) 3228 w, 3165 w, 3066 w, 2960 w, 1567 m, 1484 m, 1322 m, 743 s, 675 s, 610 m, 545 m, [ν(Re=O)] 946 s, 918 s, [Re–Cl] 370 m, 335 m; ^1H NMR (CD_2Cl_2) δ 8.87 (br, 2 H, 2,6H[Py]), 8.55 (br, 1 H, 4H[Py]), 8.03 (br, 2 H, 3,5-H[Py]), 6.89 (br, 2 H, 3,6-H[$O_2C_6H_4$]), 6.57 (br, 2 H, 4,5-H-[$O_2C_6H_4$]), 1.31 (s, 3 H, CH_3).

(14) (a) Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem.* **1988**, *100*, 420; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394. (b) Improved, scaled up procedure: Herrmann, W. A.; Kuchler, J. G.; Herdtweck, E.; Kiprof, P.; Weichselbaumer, G. *J. Organomet. Chem.* **1989**, *372*, 351.

Table II. Crystallographic Parameters of 2a and 6

	2a	6
empirical formula	$C_{12}H_{12}NO_4Re$	$C_{20}H_{18}N_2O_7Re_2$
MW	420.43	770.78
cryst color and habit	dark blue blocks	dark violet blocks
cryst dimens, mm	0.20 × 0.25 × 0.60	0.20 × 0.30 × 0.60
T, °C	−50 ± 3	−50 ± 3
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, pm	1025.0 (1)	762.6 (1)
b, pm	1533.6 (2)	1641.1 (2)
c, pm	833.1 (2)	881.3 (1)
β, deg	99.23 (1)	107.85 (1)
V, pm^3	1293 × 10^6	1050 × 10^6
Z	4	2
ρ(calcd), g·cm^{-3}	2.09	2.44
μ(Mo Kα), cm^{-1}	90.02	110.7
abs corr	empirical	empirical
	Data Collection	
scan type	ω scan	ω scan
scan speed, deg·min^{-1}	0.7–29.3	0.8–29.3
scan width, deg	0.8	0.9
max 2θ, deg	52	54
measd reflns	2830	2527
unique data	2540	2277
unique data used	2537, $I > 0.0$	2277, $I > 0.0$
	Refinement	
hydrogen atoms	11 found but not refined	all found and refined
refined parameters	211	178
R^a	0.026	0.034
$R_w{}^b$	0.027	0.032
final residues, e/Å^3	+0.66	+1.84, close to Re

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

$CH_3Re(O)[1,2\text{-}O(HN)C_6H_4]_2$ (4). To a methylene chloride solution (40 mL) of 100 mg (0.4 mmol) of **1**, 87.3 mg (0.8 mmol) of 2-hydroxyaniline and 2.0 g of anhydrous sodium sulfate were added. The reaction mixture was stirred under nitrogen for 1 day at 25 °C. Then it was filtered, and the Na_2SO_4 was washed with CH_2Cl_2 (2 × 10 mL). The combined CH_2Cl_2 fractions were concentrated in vacuo to 5 mL. Addition of *n*-hexane (20 mL) and cooling to −30 °C yielded a dark brown precipitate of the complex **3** containing 0.25 mol of solvent (CH_2Cl_2) per mole of **3**. This product was filtered and dried in vacuo, yield 108 mg, 60%. Anal. Calcd for $C_{13}H_{13}N_2O_3{\cdot}0.25CH_2Cl_2$: C, 35.15; H, 3.00; N, 6.19; Re, 41.13; O, 10.60; Cl, 3.91. Found: C, 35.11; H, 3.01; N, 6.06; Re, 41.50; O, 10.82; Cl, 3.48. IR (cm^{-1}, KBr) 3071 w, 2965 w, 2923 w, 1588 m, 1476 m, 1264 m, 747 m, 739 s, 631 m, 552 s, [ν(N–H)] 3356 m, 3194 m, [ν(Re=O)] 909 br s; ^{1}H NMR (CD_2Cl_2) δ 1.29 (s, 3 H, CH_3), 7.25–6.51 (8 m, 8 H, HNC_6H_4O), 7.9 (br, 1 H, [NH_a]), 11.3 (br, 1 H, [NH_b]) [the N*H* signals disappear upon treatment of the solution with D_2O]; MS, m/e (rel intensity) 432 (M^+, 10), 417 ([M − CH_3]$^+$, 23), 341 ([M − HNC_6H_4]$^+$, 35), 326 ([M − HNC_6H_4O]$^+$, 100), 311 ([M − CH_3 − HNC_6H_4O]$^+$, 18).

$CH_3Re(O)_2[1,2\text{-}S(HN)C_6H_4](NC_5H_5)$ (5). To a toluene solution (10 mL) of 100 mg (0.4 mmol) of **1**, 40 μL (0.5 mmol) of pyridine was added. Stirring was continued for 5 min, and then 44 μL (0.4 mmol) 2-aminothiophenol was added to the pale-yellow solution. The color turned red, and a small amount of a fine-yellow precipitate formed, which was filtered off after a few minutes. The filtrate was concentrated in vacuo to ca. 5 mL. Upon addition of *n*-hexane a dark-red solid separated, which was collected by filtration and dried in vacuo. The product was recrystallized from toluene/*n*-hexane, yield 142 mg, 82%. Anal. Calcd for $C_{12}H_{13}N_2O_2ReS$: C, 33.09; H, 3.01; N, 6.43; O, 7.35; Re, 42.75; S, 7.36. Found: C, 32.97; H, 3.12; N, 6.40; O, 7.41; Re, 42.43; S, 7.67. IR (cm^{-1}, KBr) 3066 w, 2982 w, 1601 m, 1446 m, 1216 w, 1069 w, 858 m, 750 m, 691 m, 626 m, [ν(N–H)] 3184 m, [ν(Re=O)] 910 s, 870 s; ^{1}H NMR ($CDCl_3$) δ 1.34 [s, 3 H, CH_3], 6.68 (m, 1 H, HNC_6H_4S), 7.00 (m, 1 H, NHC_6H_4S), 7.11 (m, 1 H, HNC_6H_4S), 7.59 (d, 1 H, HNC_6H_4S), 7.23 (m, 2 H, H-3,5[Py]), 7.66 (m, 1 H, H-4[Py]), 8.25 [m, 2 H, H-2,6[Py]), 10.83 (br, 1 H, HNC_6H_4S).

(μ-O)[$CH_3Re(O)_2$(8-oxyquinolinato-*O*,*N*)]$_2$ (6). To a toluene solution (10 mL) of 100 mg (0.40 mmol) of **1**, 58.0 mg (0.40 mmol) of 8-hydroxyquinoline was added at 25 °C under stirring. The color of the solution turned to dark-violet. As the stirring was continued, a black precipitate formed. After 6 h, the solution was concentrated in vacuo to ca. 5 mL, and 8 mL of *n*-hexane was added. Then the black precipitate was filtered, washed with *n*-hexane, and dried in vacuo, yield 139 mg, 91%, mp 142 °C. Single crystals of **6** suitable for X-ray diffraction study were obtained from CH_2Cl_2/*n*-hexane by slow diffusion. Anal. Calcd for $C_{20}H_{18}N_2O_7Re_2$ (770.76): C, 31.16; H, 2.35; N, 3.63; Re, 48.30; O, 14.50. Found: C, 31.13; H, 2.34; N, 3.62; Re, 48.52; O, 13.93. IR (cm^{-1}, KBr) 3060 vw, 2915 vw, 1577 m, 1499 s, 1468 s, 1378 s, 1325 s, 1274 m, 825 s, 788 s, 756 s, 712 s, 623 s, [ν(Re=O)] 967 s, 938 s, 913 w. ^{1}H NMR (CD_2Cl_2) δ 1.39 (s, 6 H, CH_3), 6.98–8.65 (m, 12 H, C_9H_9NO); EI MS, m/e (rel intensity) 506 ([$CH_3Re(O)(C_9H_6NO)_2$]$^+$, 1), 491 ([$Re(O)(C_9H_6NO)_2$]$^+$, 3), 394 ([$CH_3Re(O)_3(C_9H_6NO)$]$^+$, 3), 378 ([$CH_3Re(O)_2(C_9H_6NO)$]$^+$, 20), 363 ([$Re(O)_2(C_9H_6NO)$]$^+$, 15), 348 ([$CH_3Re(C_9H_6NO)$]$^+$, 16), 250 ([$CH_3Re(O)_3$]$^+$, 40), 220 ([$Re(O)_2H$]$^+$, 100), 145 ([C_9H_7NO]$^+$, 50); FD MS 522 ([$CH_3Re(O)_2(C_9H_6NO)_2$]$^+$, 42), 506 ([$CH_3Re(O)(C_9H_6NO)_2$]$^+$, 100), 145 ([C_9H_7NO)]$^+$, 18).

X-ray Diffraction Studies. All data were collected on an automatic four-circle diffractometer (Syntex $P2_1$). Lorentz polarization correction was applied. In both cases empirical absorption correction was also applied (nine reflections). The structures were solved by the heavy-atom method (SHELX-86) and refined by subsequent least-squares and difference Fourier techniques (SHELX-76).[15] Hydrogen atoms could all be located for **6** and all except one for **2a** in final difference Fourier maps. All hydrogen atoms of **6** were refined with individual isotropic displacement parameters. Details of the structure determination are summarized in Table II.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and least-squares plane calculation (15 pages); lists of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

(15) For further details on X-ray diffraction studies, the reader is referred to preceeding communications of this series (full papers)[1,9,14] and literature quoted therein.