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Multiple bonds between main-group elements and transition metals. 67. Synthesis of novel half-sandwich rhenium(V) complexes of mono- and bidentate sulfur-containing ligands: x-ray crystal structure of the xanthate-S,S complex (.eta.5-C5Me5)ReCl3(S2CO-c-C6H11)

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A-frames rearrange immediately to the alkyne-bridged species. These observations are consistent with the relative ease by which the monoanionic halide ligand can move to a terminal position relative to the dianionic sulfide group.

Comparison of the "Ir_2"–alkyne complexes to analogous "RhIr"–alkyne complexes suggests that the strength of the metal–alkyne bond is strongly influenced by the nature of the adjacent metal center. Such metal–metal cooperativity may be useful for "tailoring" the electronic environment at a metal center in order to enhance its catalytic activity. Oro and co-workers[40] have found, for example, that certain binuclear "RuRh" and "RuIr" complexes are more active than their mononuclear parent compounds in catalyzing the reduction of cyclohexene and that the "RuIr" complex is more active than the "RuRh" complex.

Although binuclear complexes that contain alkynes bound as cis-dimetalated olefins have been observed to give hydrogenated products upon reaction with H_2,[41] somewhat elevated temperatures appear necessary. In DPM-bridged complexes the bridging alkyne is quite stable and similar reactions have generally not been observed, whereas reaction of alkynes with hydride precursors is much more favorable.[41] This may be an indication that species containing terminal η^2-alkynes are more important in the hydrogenation of alkynes catalyzed by binuclear complexes. In that case, species of the type discussed herein may be useful since alkyne bridge formation is inhibited, and alkyne coordination is reversible, so that oxidative addition of H_2 can be more competitive, if such a route is favored.

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Supplementary Material Available: Tables of the anisotropic thermal parameters, distances and angles involving the phenyl and CH_2Cl_2 groups, and hydrogen atom parameters (4 pages); a listing of the observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

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Multiple Bonds between Main-Group Elements and Transition Metals. 67.[†] Synthesis of Novel Half-Sandwich Rhenium(V) Complexes of Mono- and Bidentate Sulfur-Containing Ligands: X-ray Crystal Structure of the Xanthate-*S*,*S* Complex (η^5-C_5Me_5)$ReCl_3$(S_2CO-c-C_6H_{11})

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The d^2 rhenium(V) complex (η^5-C_5Me_5)Re(O)Cl_2 (**1**) reacts with thiolates under ambient conditions to yield the *disubstituted* complexes **2** of composition (η^5-C_5Me_5)Re(O)$(SR^1)_2$ [R^1 = ethyl (**2a**), phenyl (**2c**), 2-pyridyl (**2d**)]. Bulkier ligands such as 2-methylpropane-2-thiolate give rise to formation of *monosubstituted complexes*, e.g., (η^5-C_5Me_5)Re(O)(Cl)(S-*t*-C_4H_9) (**3**) at room temperature, while disubstitution occurs in refluxing toluene with formation of compound **2b** (R^1 = *t*-C_4H_9). The reactions of (η^5-C_5Me_5)$ReCl_4$ (**4**) with sodium cyclohexylxanthate or with lithium *N*,*N*-diethyldithiocarbamate yield *monosubstituted* derivatives of formula (η^5-C_5Me_5)$ReCl_3$(S_2CR^2) (**5a**,**b**). A single-crystal X-ray diffraction study of the xanthate complex (η^5-C_5Me_5)$ReCl_3$(S_2CO-*c*-C_6H_{11}) (**5a**, R^2 = O-*c*-C_6H_{11}) shows an octahedral coordination sphere around the rhenium, with the sulfur atoms of the bidentate ligand being bonded to the metal atom in an equatorial and in an axial position.

Introduction

There has been continuing interest in the coordination chemistry of transition-metal complexes of sulfur-containing ligands because of the importance of such compounds in bioinorganic chemistry. In the case of rhenium, the interest stems partly from the use of the metastable isomer of its congener technetium (^{99m}Tc) in radiopharmaceuticals as well as from the properties of ^{186}Re and ^{188}Re, which isotopes may provide radiopharmaceuticals designed by analogy to existing Tc agents.[2,3] Although simple thiolato and sulfido rhenium complexes in high

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[†] Part 66, cf. ref 1.

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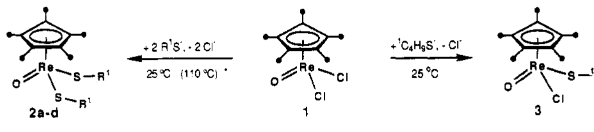
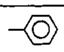
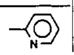
Scheme I



	2a	2b *	2c	2d
R^1	C_2H_5	$^tC_4H_9$		

oxidation states are no longer rare,[4-8] half-sandwich rhenium derivatives of these ligands are much less common, with the first examples having been prepared only recently.[9,10] This present work reports the synthesis and characterization of some new pentamethylcyclopentadienyl rhenium(V) thiolate compounds, as well as the preparation and the X-ray crystal structure of the xanthate complex (η^5-C_5Me_5)$ReCl_3(S_2CO$-*c*-C_6H_{11}).

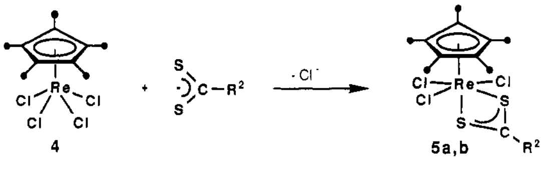
Results and Discussion

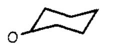
A. Synthetic and Spectroscopic Part. Addition of the sodium salts of sterically less demanding thiolates, such as those derived from mercaptoethane, thiophenol, and 2-mercaptopyridine, to a solution of (η^5-C_5Me_5)Re(O)Cl_2 (**1**) in toluene at room temperature results in a smooth reaction yielding complexes **2a,c,d** of general formula (η^5-C_5Me_5)Re(O)$(SR^1)_2$ (Scheme I). The synthesis also works when the thiolate is generated in situ from the corresponding thiol upon addition of excess triethylamine. When bulkier ligands such as the 2-methylpropane-2-thiolate (generated in situ from *tert*-butylmercaptan and triethylamine) are used *at room temperature*, the monosubstituted compound (η^5-C_5Me_5)Re(O)Cl(S-*t*-C_4H_9) (**3**) is formed, even when a more than 2-fold excess of the thiolate is employed. The disubstituted compound **2b** is only formed when the lithium salt Li[*t*-C_4H_9S] is used and the reaction is carried out in *refluxing toluene* for several hours (Scheme I). Compound **3** can, of course, be converted to the disubstituted product **2b** under analogous severe reaction conditions.

The thiolate complexes **2a–d** and **3** are stable both thermally and toward air. Although thiolate ligands have a tendency to form bridges between unsaturated metal centers,[11] tetrahedral mononuclear structures similar to that of the analogous vanadium(V) compound (η^5-C_5Me_5)V(O)$(SC_6H_5)_2$[10] are proposed for the 16e species **2a–d** and **3**. With the assumption that the pentamethylcyclopentadienyl ligand occupies one vertex of the tetrahedron in compound **3**, the rhenium atom has four different substituents, and therefore **3** must be chiral, occurring as a mixture of the two possible enantiomers.

Because of the replacement of the chlorides by thiolate ligands, more electron density is present at the metal atom; this, in effect, decreases the rhenium–oxygen bond order. Consequently, a shift to lower energy in the infrared ν(Re=O) vibration of **2a–d** as compared to compound **1** is observed: $\Delta\nu$(Re=O) = 40 cm^{-1}, **2a**; 28 cm^{-1}, **2b**; 36 cm^{-1}, **2c**; 24 cm^{-1}, **2d**. In accordance with the results obtained for other compounds of type (η^5-C_5Me_5)Re(O)X_2,[12] the change of the resonance position in the ^{17}O NMR spectrum of complexes **2c,d** as compared to **1** gives futher support to this statement: the signal for complex **1** ($\delta(O)$ = 854 ppm relative to H_2O, external standard) moved to higher field ($\delta(O)$ = 821 ppm, **2c**; 832 ppm, **2d**), demonstrating the higher electron density that remains at the terminal oxygen ligand in the thiolate derivatives. The shift of the C_5Me_5 proton NMR signal to *higher* field also reflects this phenomenon: $\Delta\delta(CH_3)$ = 0.20 ppm, **2a**; 0.25 ppm, **2b**; 0.59 ppm, **2c**; 0.68 ppm, **2d**.

Scheme II



	5a	5b
R^2		$N(C_2H_5)_2$

An attempt was made to create a formally 18e compound with one S,N-chelate by employing 2-mercaptopyridine instead of the thiophenol ligand; however, no definite support for such bonding was observed in the spectroscopic data of compound **2d**. (Using the ligand 2-aminothiophenol, the 16e compound of formula (η^5-C_5Me_5)Re(2-$SC_6H_4NH)_2$—with five-membered S,N-chelate rings—formed in a complex condensation reaction, which will be the topic of a forthcoming publication.)

Both the clean reaction of **1** with thiolates and the considerable thermal stability of compounds **2a–d** and **3** prompted us to investigate the reaction of **1** and the related Re(V) compound (η^5-C_5Me_5)$ReCl_4$ (**4**) with chelating sulfur-containing ligands such as xanthate and dithiocarbamate. **1** and **4** are formally 16e species. Upon replacement of one chlorine atom by a xanthate or dithiocarbamate ligand, the resulting complexes could achieve an 18e count. This reasoning accounts to the latter substituents, provided they bind to the rhenium atom through both sulfur atoms. While the reaction of **1** with xanthates as well as dithiocarbamates gave only intractable mixtures, treatment of **4** with sodium cyclohexylxanthate or with lithium *N,N*-diethyldithiocarbamate afforded compounds **5a** and **5b**, respectively (Scheme II). Compounds **5a** and **5b** are air-stable and thermally stable up to ≈155 °C (**5a**) and ≈188 °C (**5b**). In most cases xanthates and dithiocarbamates bind to transition metals as bidentate ligands,[13] with only few exceptions of monodentate coordination being known (for rhenium see ref 14 and 15). In the case

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Table I. Crystallographic Data of Trichloro(cyclohexylxanthato-*S*,*S*)(η^5-pentamethylcyclopentadienyl)rhenium(V) (5a)

(a) Crystal Parameters	
empirical formula	$C_{17}H_{26}Cl_3OReS_2$
fw	603.1
cryst color	dark brown truncated octahedra
cryst dimens, mm	0.50 × 0.35 × 0.40
radiatn	Mo Kα (λ = 71.073 pm)
temp, °C	23 ± 1
space group	*Pbca* (No. 61)
a, pm	1704.78 (10)
b, pm	1203.2 (1)
c, pm	2083.7 (2)
V, pm^3	4274 × 10^6
Z	8
ρ(calcd), g·cm^{-3}	1.874
μ(Mo Kα), cm^{-1}	63.3
(b) Data Collection	
diffractometer	CAD4 Enraf-Nonius
monochromator	graphite, incident beem
scan type	ω scan
scan time, s	maximum 60
scan width, deg	(1.25 + 0.30 tan θ) ± 25% for correctns
max 2θ, deg	50
no. of reflcns measd	7975 (*h*, 0/20; *k*, ±14; l, 0/24)
no. of indep reflcns	3462
correctns	Lorentz–polarization, empirical absorption (0.8404–0.9964)
std reflectns	3 every 3600 s intensity check, 3 every 200 orientation check
(c) Refinement	
solution	Patterson method
hydrogen atoms	not found, calcd, included but not refined
refinement	full matrix least squares
minimization functn	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting scheme	$1/\sigma(F_o)^2$
anomalous dispersion	all non-hydrogen atoms
no. of reflcns included (NO)	2973 [$I \geq 1.0\sigma(I)$]
no. of params refined (NV)	217
R	0.038[a]
R_w	0.028[b]
goodness of fit	1.608[c]
shift/err	0.00

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

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Re	0.09419 (1)	0.21349 (2)	0.18646 (1)	2.552 (4)
Cl1	0.1540 (2)	0.3078 (2)	0.27543 (9)	7.33 (6)
Cl2	0.22864 (9)	0.1724 (2)	0.15558 (9)	5.38 (4)
Cl3	−0.0125 (1)	0.3424 (2)	0.2007 (1)	7.14 (5)
S1	0.0688 (1)	0.2230 (2)	0.07053 (8)	4.61 (4)
S2	0.1450 (1)	0.3899 (2)	0.14004 (8)	3.60 (4)
O1	0.1239 (3)	0.3999 (5)	0.0128 (2)	6.3 (1)
C1	0.1143 (4)	0.3478 (7)	0.0684 (3)	4.9 (2)
C2	0.1635 (4)	0.5084 (6)	0.0120 (3)	4.5 (2)
C3	0.1036 (4)	0.5973 (8)	0.0002 (4)	6.5 (2)
C4	0.1436 (5)	0.7101 (7)	−0.0110 (5)	7.8 (2)
C5	0.2019 (5)	0.6992 (8)	−0.0650 (4)	6.7 (2)
C6	0.2600 (6)	0.6155 (9)	−0.0502 (4)	8.3 (3)
C7	0.2226 (5)	0.5042 (9)	−0.0387 (4)	7.5 (2)
C11	−0.0172 (3)	0.1068 (6)	0.2265 (3)	4.1 (2)
C12	0.0113 (4)	0.0590 (6)	0.1662 (3)	3.8 (2)
C13	0.0888 (4)	0.0260 (6)	0.1776 (3)	3.5 (1)
C14	0.1118 (3)	0.0546 (6)	0.2423 (3)	3.4 (1)
C15	0.0438 (4)	0.1074 (6)	0.2677 (3)	3.9 (1)
C21	−0.1030 (4)	0.1348 (8)	0.2345 (5)	7.4 (2)
C22	−0.0380 (4)	0.0287 (9)	0.1075 (4)	7.1 (2)
C23	0.1360 (5)	−0.0492 (8)	0.1299 (4)	6.5 (2)
C24	0.1842 (4)	0.0158 (8)	0.2736 (3)	5.5 (2)
C25	0.0345 (6)	0.1418 (8)	0.3389 (4)	7.6 (2)
Cp*	0.0480	0.0710	0.2160	

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Hydrogens were all calculated and therefore omitted from this list.

Table III. Selected Bond Distances (pm) and Bond Angles (deg) of 5a[a]

Re–Cl1	240.0 (2)	Cl1–Re–Cl2	84.28 (8)
Re–Cl2	243.1 (1)	Cl1–Re–Cl3	85.48 (9)
Re–Cl3	240.9 (2)		
Re–S1	245.7 (2)	S1–Re–S2	68.86 (5)
Re–S2	248.8 (2)		
Re–Cp*	198.4	Cl1–Re–Cp*	109.7
		Cl2–Re–Cp*	106.3
		Cl3–Re–Cp*	102.6
		S1–Re–Cp*	106.0
		S2–Re–Cp*	174.7
S1–C1	169.1 (7)	S1–C1–S2	113.1 (4)
S2–C1	166.1 (6)		

[a] Cp* denotes the center of the pentamethylcyclpentadienyl ligand.

of the half-sandwich compounds **5a,b** the monodentate coordination cannot be excluded, since the metal coordination sphere is very crowded. Unfortunately, the binding mode of the xanthate and dithiocarbamate ligands could not be elucidated unequivocally by IR and NMR measurements; therefore, the structure of the cyclohexylxanthate complex **5a** was determined by a single-crystal X-ray diffraction study. The results revealed a chelating coordination mode via the *two sulfur atoms*, one of which is in an axial and the other which is in an equatorial position of the octahedral framework.

B. Crystallographic Results. Trichloro(cyclohexylxanthato-*S*,*S*)(η^5-pentamethylcyclopentadienyl)rhenium(V) (**5a**) crystallizes from CH_2Cl_2/*n*-hexane in the orthorhombic space group *Pbca* (Table I). The structure was determined at room temperature. Atomic coordinates are listed in Table II; bond lengths and bond angles are compiled in Table III.

With the assumption that the η^5-C_5Me_5 ligand occupies one coordination site, the structure of **5a** can be described as a distorted octahedron (Figure 1). Due to the steric bulk of the pentamethylcyclopentadienyl ligand in the axial position as well as to the strain in the four-membered ring formed by the rhenium atom and the xanthate ligand, all angles differ from the ideal value of 90°. The chlorine atoms and the equatorial sulfur atom are pushed out of the equatorial plane closer toward the axial sulfur atom. Thus the Cp*–Re–X angles (Cp* indicates the center of the aromatic π-ligand) are greater than 90°: Cp*–Re–Cl = 109.72 (5)°, 106.30 (5)°, and 102.62 (4)°; Cp*–Re–S_{eq} = 105.98 (4)°. Consequently the angles between the equatorial substituents also differ from 90°: Cl–Re–Cl = 84.28 (8)° and 85.48 (9)°; Cl–Re–S_{eq} = 75.08 (6)° and 87.59 (7)°. The value of the Cp*–Re–S_{ax} angle is smaller than 180°; Cp*–Re–S2 = 174.66 (4)°. The S1–Re–S2 angle (68.86) (5)°) as well as the rhenium–sulfur distances (Re–S_{eq} = 245.7 (2) pm and Re–S_{ax} = 248.8 (2) pm) are in the range of what has been found in rhenium complexes containing the structurally related *N*,*N*-dialkyldithiocarbamate ligands.[13,17,18] **5a** has a similar structure as the adduct (η^5-C_5Me_5)$ReCl_4(PMe_3)$[19] and represents a sterically

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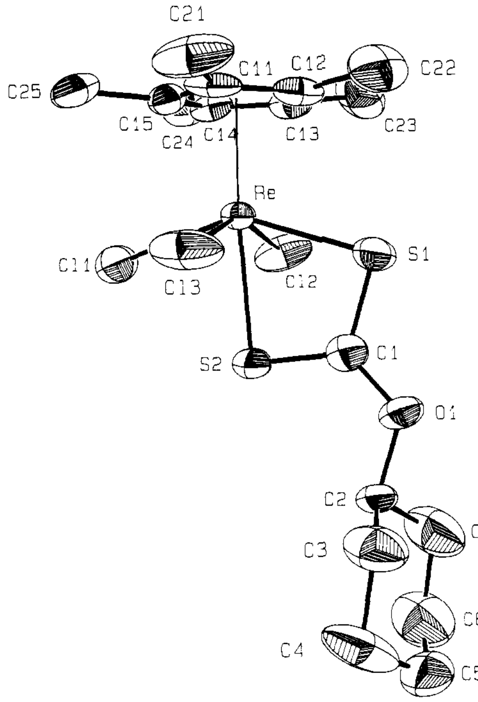

Figure 1. ORTEP drawing of **5a** showing the atom-labeling scheme at probability levels of 50%. Hydrogen atoms are omitted for clarity.

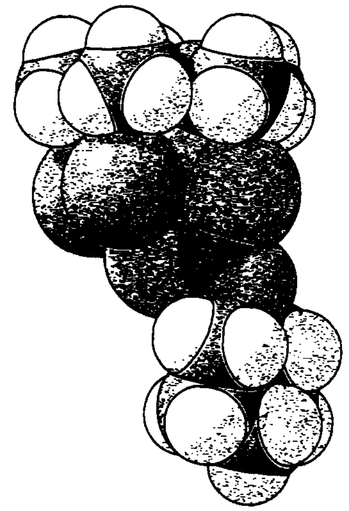

Figure 2. SCHAKAL drawing of **5a** showing the space-filling model.

crowded system (Figure 2). Both the 18e configuration of **5a** and the steric crowding explain the stability of this compound against hydrolysis, which is in striking contrast to the 16e species **4** (d^2 Re).

Experimental Section

All reactions were carried out under nitrogen using Schlenk tube techniques. The starting compounds $(\eta^5\text{-}C_5Me_5)Re(O)Cl_2$ (**1**) as well as $(\eta^5\text{-}C_5Me_5)ReCl_4$ (**4**) were prepared according to literature methods.[16] Other chemicals were used as purchased. ^1H NMR (400 MHz) spectra were recorded at 25 °C, JEOL JNM GX-400; mass spectra were recorded 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 and ^{37}Cl isotopes (*m*/*e* values).

(1) Oxo(η^5-pentamethylcyclopentadienyl)bis(alkane/arenethiolato)rhenium(V) (2a–d). 2a. $Li[SC_2H_5]$ (29 mg, 0.42 mmol) was added to a toluene solution (12 mL) of 81.6 mg (0.2 mmol) **1**. The mixture was stirred at room temperature for 6 h. The initial green color changed to red-brown. After 6 h the solvent was pumped off, and the residue was extracted with *n*-hexane (two times, 15-mL each). After filtration the volume was reduced in vacuo; cooling to −30 °C yielded red-brown crystals of **2a**: yield 66 mg (72%); mp 61 °C. Anal. Found (calcd for $C_{14}H_{25}OReS_2$) (459.66): C, 36.30 (36.58); H, 5.64 (5.48); S, 13.88 (13.95); Re 40.96 (40.50).

Spectroscopic data: IR (cm^{-1}, KBr) 2958 m, 2921 m, 2864 w [ν(C–H)], 916 vs [ν(Re=O)]. ^1H NMR ($CDCl_3$) $\delta(C_5Me_5)$ 2.00 (s, 15 H), $\delta(CH_AH_B)$ 3.15 [dq, 2 H, $^2J(H,H) = 12.8$ Hz, $^3J(H,H) = 7.3$ Hz], $\delta(CH_AH_B)$ 3.23 (dq, 2 H), $\delta(CH_3)$ 1.39 (t, 6 H, $^3J(H,H) = 7.3$ Hz); EI-MS (70 eV) 460 ($[M]^+$, rel int 50%), 369 ($[M - C_2H_5SH - C_2H_5]^+$, 100%).

2b. $Li[S\text{-}t\text{-}C_4H_6]$ (42.3 mg, 0.44 mmol) was added to a toluene solution (12 mL) of 81.6 mg (0.2 mmol) of **1**. The reaction mixture was refluxed for 6 h. After 6 h the solvent was pumped off and the residue was extracted with *n*-hexane (two times, 15 mL). After filtration of the *n*-hexane extract, the solvent was removed in vacuo, yielding a greenish-brown viscous oil, which turned to a waxy solid after several days; yield 74 mg (72%). Anal. Found (calcd for $C_{18}H_{33}OReS_2$) (515.76) C, 41.53 (41.90); H, 6.38 (6.44); Re, 36.37 (36.10); S, 12.05 (12.40).

Spectroscopic data: IR (cm^{-1}, KBr) 2958 m, 2915 m, 2855 m [ν(C–H)]; 928 vs [ν(Re=O)]; ^1H NMR ($CDCl_3$) $\delta(C_5Me_5)$ 1.98 (s, 15 H), $\delta(CH_3)$ 1.62 (s, 18 H); EI-MS (70 eV) 516 ($[M]^+$, rel int 13%), 370 ($[M - C_4H_9S - C_4H_9]^+$, 82%); 57 ($[C_4H_9]^+$, 100%).

2c. Sodium thiophenolate (50 mg, 0.38 mmol) was added to a toluene solution (10 mL) of 81.6 mg (0.2 mmol) of **1**. As the stirring was continued, the color of the reaction mixture turned to brown. After 2 h the solution was filtered on silylated silica (Merck No. 7719, 70–230 mesh). Concentration of the filtrate in vacuo, addition of *n*-hexane, and cooling this solution to −30 °C yielded yellowish brown crystals: yield 95 mg (85%); mp 248 °C. Anal. Found (calcd for $C_{22}H_{25}OReS_2$) (555.77): C, 47.21 (47.55); H, 4.66 (4.53); O, 2.91 (2.88); Re, 33.59 (33.50), S, 11.27 (11.54).

Spectroscopic data: IR (cm^{-1}, KBr) 2962 m, 2915 m, 2862 m, 1381 s [$\nu(C_5Me_5)$], 1577 s, 1465 s [$\nu(C_6H_5)$], 923 vs [ν(Re=O)]; ^1H NMR ($CDCl_3$) $\delta(C_5Me_5)$ 1.64 (s, 15 H), $\delta(C_6H_5)$ 7.15–7.72 (m, 10 H); ^{17}O NMR (54.2 MHz, CD_2Cl_2, vs. H_2O external) δ(O) 821 (s); EI-MS (70 eV) 556 ($[M]^+$, rel int 80%), 447 ($[M - SC_6H_5]^+$, 62%); 370 ($[M - SC_6H_5 - C_6H_5]^+$, 100%), 135 ($[C_{10}H_{15}]^+$, 48%).

2d. At −78 °C 80 mg (0.6 mmol) of sodium 2-mercaptopyridine was added to a toluene solution (20 mL) of 122.4 mg (0.3 mmol) of **1**. When the solution was warmed to room temperature, the color changed to greenish brown. Stirring at ambient temperature was continued for 1 hour. The solution was then transferred to a chromatography column charged with silylated silica (Merck No. 7719, 70–230 mesh). Elution with CH_2Cl_2 produced a yellow band. Evaporation of the solvent in vacuo yielded 120 mg (74%) of **2d**. Anal. Found (calcd for $C_{20}H_{23}N_2OReS_2$) (557.74): C, 42.92 (43.07); H, 4.29 (4.16); N, 4.78 (5.02); S, 11.01 (11.50).

Spectroscopic data: IR (cm^{-1}, KBr) 2985 m, 2916 m, 1412 s [$\nu(C_5Me_5)$], 3036 s, 1567 s, 1447 s, 731 s, 717 m [(C_5H_4N)], 935 s, 890 m [ν(Re=O)]; ^1H NMR ($CDCl_3$) $\delta(C_5Me_5)$ 1.54 (s, 15 H), $\delta(C_5H_4N)$ 6.48–8.38 (m, 8 H); ^{17}O NMR (54.2 MHz, $CD_2Cl_2/CDCl_3$, ppm vs. H_2O external) δ(O) 832 (s); EI-MS (70 eV) 558 ($[M]^+$, rel int 5%), 542 ($[M - O]^+$, 42%), 448 ($[M - SC_5H_4N]^+$, 75%), 423 ($[M - C_{10}H_{15}]^+$, 100%).

(2) Chlorooxo(η^5-pentamethylcyclopentadienyl)(2-methylpropane-2-thiolato)rhenium(V) (3). To a stirred toluene solution (10 mL) of 81.6 mg (0.2 mmol) of **1** were added 24 μL (0.21 mmol) of *tert*-butylmercaptan (Aldrich) and 29 μL (0.21 mmol) of dry triethylamine. The stirring was continued for 6 h, and then the solvent was removed in vacuo. The residue was extracted with *n*-hexane (two times, 10-mL each). The combined *n*-hexane extracts were first filtered and then concentrated in vacuo to a small volume. Cooling to −78 °C yielded olive-green crystals of **3**: yield 77 mg (83%); mp 115.5 °C. Anal. Found (calcd for $C_{14}H_{24}ClOReS$) (462.04): C, 36.71 (36.40); H, 5.4 (5.24); Cl 7.70 (7.67); Re, 40.73 (40.30); S, 7.13 (6.94).

Spectroscopic data: IR (cm^{-1}, KBr) 2957 m, 2917 m [ν(C–H)], 1475 m, 1454 m, 1379 m, 1358 m [ν(C–C)], 923 s [ν(Re–O)]; ^1H NMR ($CDCl_3$) $\delta(C_5Me_5)$ 2.02 (s, 15 H), $\delta(C_4H_9)$ 1.72 (s, 9 H); EI-MS

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[19] Herrmann, W. A.; Voss, E.; Küsthardt, U.; Herdtweck, E. *J. Organomet. Chem.* **1985**, *294*, C37.

(70 eV) 464 ($[M]^+$, rel int 5%), 370 ($[M - Cl - C_4H_9]^+$, 100%).

(3) Trichloro(cyclohexylxanthato-*S*,*S*)(η^5-pentamethylcyclopentadienyl)rhenium(V) (5a). Sodium cyclohexylxanthate (83.2 mg, 0.42 mmol) was added to a solution of 185.2 mg (0.4 mmol) of **4** in 18 mL of CH_2Cl_2. As the solution was stirred at room temperature, the color changed from purple to brown, and a white precipitate formed. After 8 h the solvent was removed in vacuo. The residue was then extracted with a mixture of 15 mL of CH_2Cl_2 and 5 mL of *n*-hexane. The solution was filtered, and the filtrate was evaporated to dryness. The product was taken up in a small amount of CH_2Cl_2. Upon addition of *n*-hexane and cooling to −30 °C brown crystals formed overnight. Yield: 208 mg (86%). Crystals suitable for an X-ray diffraction study were prepared from CH_2Cl_2 and *n*-hexane at −30 °C by slow diffusion method; mp 155 °C. Anal. Found (calcd for $C_{17}H_{26}Cl_3OReS_2$) (603.03): C, 33.87 (33.85); H, 4.34 (4.34); Cl, 17.46 (17.64); Re, 31.07 (30.88); S, 10.37 (10.63).

Spectroscopic data: IR (cm^{-1}, KBr) 2939 m, 2858 w [ν(C–H)], 1289 s [ν(C–O)], 295 m [ν(Re–Cl)]; ^1H NMR ($CDCl_3$) $\delta(C_5Me_5)$ 2.03 (s, 15 H), $\delta(OCH)$ 5.27 (m, 1 H), $\delta(C_6H_{10})$ 1.3–1.8 (m, 10 H).

(4) Trichloro(*N*,*N*-diethyldithiocarbamato-*S*,*S*)(η^5-pentamethylcyclopentadienyl)rhenium(V) (5b). Lithium *N*,*N*-diethyldithiocarbamate (32.5 mg, 0.21 mmol) was added to a solution of 92.6 mg (0.2 mmol) of **4** in 12 mL of CH_2Cl_2. The color of the solution turned to yellowish brown. After the solution was stirred for 12 h, the solvent was pumped off. The residue was extracted with CH_2Cl_2/*n*-hexane (1/1 mixture). After filtration the volume of the solution was reduced in vacuo. Addition of *n*-hexane and cooling to −78 °C yielded a light brown microcrystalline solid: yield 88 mg (77%); mp 188 °C dec. Anal. Found (calcd for $C_{17}H_{25}Cl_3NReS_2$) (576.04): C, 31.60 (31.27); H, 4.50 (4.37); N, 2.37 (2.43); Re, 32.07 (32.32); S, 10.80 (11.11).

Spectroscopic data: IR (KBr, cm^{-1}) 2974 w, 2930 w [ν(C–H)], 1521 s [ν(C=N)]; ^1H NMR ($CDCl_3$) $\delta(C_5Me_5)$ 1.98 (s, 15 H), $\delta(C^aH_3–C^aH_2)$ 1.32 [t, 3 H, $^3J(H,H) = 7.3$ Hz], $\delta(C^bH_3–C^bH_2)$ 1.29 [t, 3 H, $^3J(H,H) = 7.3$ Hz], $\delta(C^aH_3–C^aH_2)$ 3.70 [q, 2 H, $^3J(H,H) = 6.7$ Hz], $\delta(C^bH_3–C^bH_2)$ 3.60 [q, 2 H, $^3J(H,H) = 6.7$ Hz].

(5) Crystal Structure Determination. Crystal data together with details of the X-ray diffraction experiment are reported in Table I. **5a** crystallizes in the orthorhombic space group *Pbca* (No. 61; systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$). Cell constants were obtained from least-squares refinement by using a set of 74 reflections in the range $31.9° \leq 2\theta \leq 48.3°$; orientation matrix by using a set of 25 reflections. During data collection only slight decay (4%) was observed; thus, no decay correction was applied. The reflection data was corrected for Lorentz–polarization and absorption (empirical absorption correction; four reflections with χ values greater than 80°). The rhenium atom was determined from a Patterson function. All remaining non-hydrogen atoms were located by successive least-squares refinements and difference Fourier maps. Hydrogen atoms were not found; their ideal positions were added to the calculations but not refined. Refinements converged with the unweighted and weighted agreement factors $R = 0.038$ and $R_w = 0.028$, respectively. Final difference fourier maps yielded a residual electron density of +0.67 and −0.64 e/Å^3 respectively. All calculations were performed on a VAX 8200 and VAX 11/730 in the program system STRUX-II[20] with the programs SDP,[21] ORTEP,[22] SCHAKAL,[23] and PARAM.[24] Scattering factors were taken from ref 25 and anomalous dipersion parameters from ref 26.

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Registry No. 1, 104349-81-7; **2a**, 122471-07-2; **2b**, 122471-11-8; **2c**, 122471-12-9; **2d**, 122471-13-0; **3**, 122471-08-3; **4**, 104349-79-3; **5a**, 122471-09-4; **5b**, 122471-10-7; Li[SC_2H_5], 30383-01-8; Li[S-*t*-C_4H_9], 16203-42-2; sodium thiophenolate, 930-69-8; sodium 2-mercaptopyridine, 13327-62-3; *tert*-butylmercaptan, 75-66-1; sodium cyclohexylxanthate, 42977-02-6; lithium *N*,*N*-diethyldithiocarbamate, 32831-18-8.

Supplementary Material Available: A table of crystal data in German and tables of atomic coordinates, least-squares planes, root-mean-square amplitudes, anisotropic displacement parameters, and bond lengths and angles (19 pages); a listing of F_o/F_c values (19 pages). Ordering information is given on any current masthead page.

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