Multiple Bonds between Main-Group Elements and Transition Metals. 130.[1] (Cyclopentadienyl)trioxorhenium(VII): Synthesis, Derivatives, and Properties[†]

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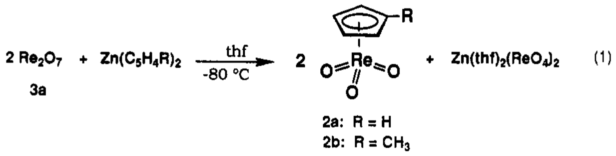
(η^5-Cyclopentadienyl)trioxorhenium(VII) and ring-substituted derivatives are conveniently synthesized from (trifluoroacetyl)perrhenate and substituted (cyclopentadienyl)tin compounds. As shown by cyclovoltammetry, peralkylated (cyclopentadienyl)tin derivatives undergo redox reactions with Re(VII) precursor compounds such as (trifluoroacetyl)trioxorhenium(VII). The reduction potentials of peralkylated $CpRe^{VII}$ systems differ significantly from those of the nonalkylated forms. Thermal stabilities of $CpReO_3$ derivatives increase with the number of methyl groups in the Cp ring, reflecting increasing Re–C bond strengths resulting from the electron density of the π-bonded ligands. Increasing π-donor capability of the Cp ligands with increasing substitution by alkyl groups is documented in the IR and ^{17}O NMR spectra. As shown by a single-crystal X-ray diffraction analysis of $(C_5H_5)ReO_3$, the Cp ligand is η^5-bonded to the metal. Crystal data: monoclinic $P2_1/m$, $a = 5.984(1)$ Å, $b = 9.179(1)$ Å, $c = 6.099(1)$ Å, $\beta = 116.30(1)°$, $R = 0.021$ for 559 reflections.

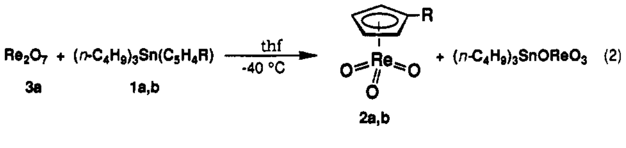
Introduction

Since the discovery of ferrocene in 1951/52 the cyclopentadienyl ligand has played a major role in the development of organometallic chemistry, where it has been classified as "ubiquitous".[2] However, the first instance of a cyclopentadienyl–metal–trioxide complex only was exemplified in 1984 with the isolation of $(C_5Me_5)ReO_3$.[3] Since then, numerous derivatives and reactions have been reported.[4] Interestingly enough, attempts to prepare the parent $(C_5H_5)ReO_3$ started as early as 1963.[5a] Many possible C_5H_5-transfer reagents (e.g. Mg, Cd, Hg) were used but remained unsuccessful, like the reactions of Re_2O_7 with $(C_5H_5)_4Sn$ or $(C_5H_5)Sn(t\text{-}C_4H_9)_3$.[5b,6] Following a method applied to the preparation of several other organorhenium(VII) oxides,[7,8] bis(cyclopentadienyl)zinc yielded $(C_5H_5)ReO_3$ under special synthetic conditions; *cf.* eq 1.[5b] The success of this method, however, depends on highly purified starting materials. We now report a simple preparation of $(C_5H_5)ReO_3$ which provides access to unlimited amounts of this little explored compound after a search which lasted as long as 30 years.[5a]



Results and Discussion

A. Synthesis. Treatment of dirhenium heptoxide (**3a**) with tin precursor compounds **1a,b** at −40 °C yields the known (cyclopentadienyl)trioxorhenium(VII) (**2a**)[5b] and (methylcyclopentadienyl)trioxorhenium(VII) (**2b**)[5b] in nearly quantitative yields (eq 2). Under the chosen reaction conditions, **2a,b** precipitate from solution as they form. The workup is easier than with the "zinc method" (eq 1), which requires complete removal of the solvent and



[†] Dedicated to Professor Helmut Werner on the occasion of his 60th birthday.

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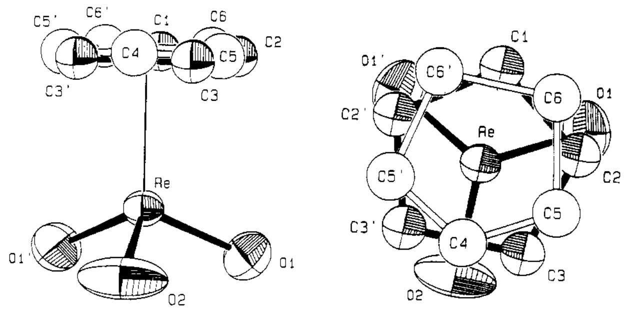
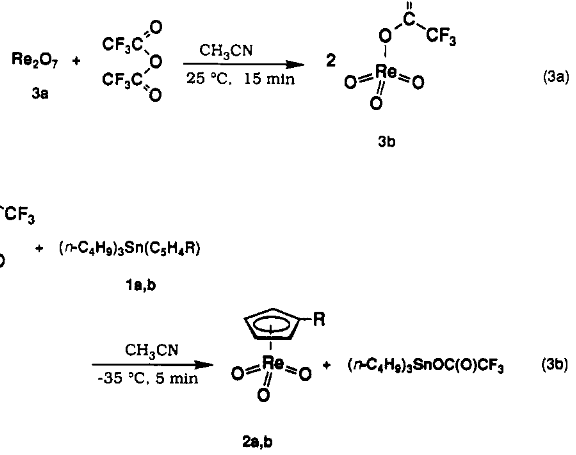


Figure 1. ORTEP drawing of $C_5H_5ReO_3$ (**2a**) (50% probability level, hydrogen atoms omitted for clarity). Symmetry-related atoms (x, $0.5 - y$, z) are primed. Left side: Side view. Right side: Top view of the molecule. Open circles define the "pseudo-eclipsed" position of the cyclopentadienyl ligand.

extraction of **2a**/**b** from the residue with dry toluene (approximately 800 mL of toluene for 1 g of **2a**).

The disadvantage of both methods, the waste of *ca.* 50% of the rhenium in the form of zinc perrhenate[7,9] or (tributylstannyl)perrhenate[8] is avoided by using chlorotrioxorhenium[9] or (trifluoroacetyl)trioxorhenium (**3b**) instead of Re_2O_7. **3b** is generated from **3a** and trifluoroacetic anhydride and can be used *in situ* for the reactions with organotin compounds.[8c,10] Since tetrahydrofuran (thf) might polymerize in the presence of **3b**, acetonitrile should be used as the solvent. **2a,b** are thus obtained in almost quantitative yields based on rhenium (eq 3). There



is no indication of a scale limitation for this reaction. The reaction proceeds within a few minutes at −40 °C. At room temperature, however, the solution becomes black, and only very little product can be isolated. As shown by X-ray and NMR data (part B and Experimental Section), the metal is pentacoordinated (η^5) by the cyclopentadienyl ring.

Table 1. Summary of Crystal Data and Details of Intensity Collection for Compound 2a

formula	$C_5H_5O_3Re$
fw	299.3
cryst syst	monoclinic
space group	$P2_1/m$ (No. 11)
a, Å	5.984(1)
b, Å	9.179(1)
c, Å	6.099(1)
β, deg	116.30(1)
V, Å^3	300.3
Z	2
D_{calc}, g cm^{-3}	3.310
λ(Mo Kα), Å	0.710 73
μ, cm^{-1}	204.3
range, deg	2.0–50.0
scan type	$\theta/2\theta$
no. of reflcns collctd	2092
no. of indpdt reflcns	559 (R_{merge} = 0.017)
no. of obsd reflcns	559 ($I > 0.01$)
no. of refined params	41
R^a	0.021
$R_w{}^b$	0.023
GOF^c	1.645

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

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) of Compound 2a^a

atom	x	y	z	B_{eq}	occ
Re	0.30156(4)	$^1/_4$	0.41138(4)	2.191(6)	1.00
O(1)	0.1358(6)	0.3949(5)	0.2484(6)	4.3(1)	1.00
O(2)	0.5659(8)	$^1/_4$	0.3693(9)	5.4(2)	1.00
C(1)	0.160(2)	$^1/_4$	0.713(2)	2.5(1)^c	0.60
C(2)	0.316(1)	0.376(1)	0.758(1)	$B_{C(1)}$	0.60
C(3)	0.562(1)	0.332(1)	0.826(1)	$B_{C(1)}$	0.60
C(4)^b	0.571(3)	$^1/_4$	0.843(3)	2.9(2)^c	0.40
C(5)^b	0.457(2)	0.364(2)	0.804(2)	$B_{C(4)}$	0.40
C(6)^b	0.202(2)	0.331(2)	0.735(2)	$B_{C(4)}$	0.40

^{a} B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ac(\cos\beta)\beta(1,3)]$. ^{b} Disorder of the Cp ring. ^{c} Atoms were refined isotropically.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a^a

Re–O(1)	1.693(4)	Re–C(3)	2.43(1)
Re–O(2)	1.711(4)	Re–C(4)	2.40(2)
Re–Cp	2.06	Re–C(5)	2.39(1)
Re–C(1)	2.34(1)	Re–C(6)	2.42(1)
Re–C(2)	2.38(1)		
O(1)–Re–O(1′)	103.5(3)	O(1)–Re–Cp	115.6
O(1)–Re–O(2)	104.6(2)	O(2)–Re–Cp	111.7

^{a} Cp denotes the center of cyclopentadienyl ligand C1, C2, C3, C3′, and C2′.

The structural assignment was demonstrated for the crystalline phase of **2a** by an X-ray diffraction study. An ORTEP representation of the molecule is given in Figure 1a, crystallographic and data collection parameters are listed in Table 1, atomic coordinates are in Table 2, and selected bond lengths and angles are in Table 3. While **2b** is ordered,[5b] the more symmetrical derivative **2a** shows a crystallographic mirror plane through O(2), Re, and C(1) and a cyclopentadienyl ligand which is disordered in two positions. We observe a preference of the "pseudo-staggered" configuration (occupation factor 0.60); see Figure 1b. The mean Re···C contacts of 2.39(1) and 2.41(1) Å, respectively, are in the same range as observed for **2b** [2.396(3) Å] but long as compared to those of the *low-valent* congeners (η^5-C_5H_5)Re(CO)$_3$ (2.28 Å)[5c] and (η^5-$C_5H_4SiMe_3$)Re(CO)$_3$ (2.30 Å).[5d] This result is explained in terms of a "trans influence" resulting from the pronounced π-donor character of the oxo groups.

While (C_5Me_5)ReO$_3$ (**2c**) and (C_5Me_4Et)ReO$_3$ (**2d**) do not react with donor ligands (e.g., quinuclidine), **2a** reacts quickly under decomposition with liberation of cyclopentadiene (^{1}H NMR). The much greater stability of **2c,d** against donor bases is attributed to the steric bulk and better π-donor properties of the peralkylated Cp ligands. **2c,d** are very soluble in most organic solvents, and **2a,b**

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(9) For an *in situ* preparation of $ClReO_3$, see ref 1.

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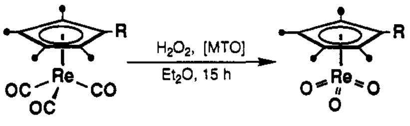
are poorly soluble. In coordinating solvents (DMSO, pyridine, methanol) **2a,b** decompose within seconds or minutes (decomposition in thf is much slower), and C_5H_6 is formed (shown by NMR, e.g. in methanol) as well as a dark precipitate. Elemental analyses show that this precipitate has a Re:O ratio of ≈1:3, and it contains very little amounts of C and H (<1%). This reactivity difference between **2a,b** and **2c,d** is expected on the basis of the theoretically predicted weaker Cp–Re bonds in the case of **2a,b**.[11] Electron-rich ligands (see above) add to the Lewis-acidic rhenium center and thus further weaken the Re–C_5H_5 bond. A detailed study of the photochemistry of **2a-c** and other compounds R–ReO_3 is in preparation.[12] It is remarkable that **2b** shows catalytic activity in olefin metathesis and aldehyde olefination, while **2c** is nearly inactive.[13]

Another difference between **2a,b** and **2c,d** is that the latter compounds cannot be synthesized by the "tin route". At first glance surprising, this result is due to the different redox behavior of the tin precursors **1a,b** *vs* $[C_5(CH_3)_5]Sn(n\text{-}Bu)_3$ (**1c**) $[C_5(CH_3)_4Et]Sn(n\text{-}Bu)_3$ (**1d**) (see section C). **2c,d** can only be prepared by oxidation of carbonyl precursors according to eq 4.[4b,14a] This particular route is unsuccessful for the preparation of **2a,b** as a result of oxidation of the Cp ligand.[5b,14b]



2c,d

(4)

•— = CH_3; R = CH_3 (**2c**), C_2H_5 (**2d**)

[MTO] = catalytic amounts of CH_3ReO_3

B. NMR and IR Spectroscopy. ^{1}H and ^{13}C NMR spectra (in solution) further corroborate the assumption that the cyclopentadienyl ligands of **2a-d** are symmetrically π-bonded (η^5) to the metal over the investigated temperature range of −100 to +100 °C. The ^{1}H NMR spectra of **2a** exhibit only one signal for the cyclopentadienyl protons (6.60 ppm, d_8-thf), and **2b** has two signals for the Cp protons and one for the methyl group. An analogous pattern is seen in the ^{13}C NMR spectra.

Table 4. ^{1}H NMR Data for $(C_5H_5)ReO_3$ and CH_3ReO_3

(a) Solvent Dependence of Shifts

	δ(^{1}H), ppm			δ(^{1}H), ppm	
solvent	$C_5H_5ReO_3$	CH_3ReO_3	solvent	$C_5H_5ReO_3$	CH_3ReO_3
CCl_4	7.15	2.72	d_7-dmf	6.55	1.97
$CD_3C(O)CD_3$	7.09	2.63[a]	D_2O	*b*	2.29
CD_3NO_2	7.03	2.81	CD_3OD	*b*	2.01[a]
CS_2	7.00	2.86	d_6-dmso	*b*	1.88
CD_2Cl_2	6.93	2.67	d_5-pyridine	*b*	1.67
$CDCl_3$	6.90	2.61[a]	d_8-toluene	5.73	1.34
d_8-thf	6.60	2.14[a]	C_6D_6	5.70	1.21[a]
CD_3CN	6.58	1.94[a]			

(b) Temperature Dependence of Shifts (d_8-Toluene)

temp, °C	δ(^{1}H), ppm		temp, °C	δ(^{1}H), ppm	
	$(C_5H_5)ReO_3$	CH_3ReO_3		$(C_5H_5)ReO_3$	CH_3ReO_3
100	5.91	1.55	0	5.65	1.21
90	5.89	1.53	−20	5.58	1.08
80	5.87	1.50	−40	5.50	0.99
60	5.82	1.45	−60	5.42	0.92
40	5.78	1.40	−80	5.34	0.82
20	5.73	1.34			

[a] Reference 16b. [b] Decomposition.

Remarkable shifts of the cyclopentadienyl signal positions indicate a strong influence of solvent donor capability according to the Gutmann donor numbers[15] (Table 4a). These effects are in the same order as those observed for CH_3ReO_3 ("MTO").[16] In weakly or noncoordinating solvents (e.g. CCl_4, CS_2, $CDCl_3$, CD_2Cl_2), the cyclopentadienyl signals are shifted further downfield than in typical σ-donor solvents (thf, CD_3CN). The strongest donor solvents (DMSO, pyridine) lead to decomposition of **2a,b**. The signals of MTO show even stronger upfield shifts in DMSO and pyridine than in thf. The interaction of donor ligands with MTO is easily understandable given the electronic flexibility of the Re–O multiple-bond character which makes MTO a formally *18e* complex.[16a,17] This flexibility is lost in **2c,d** due to the strong $[C_5(Me_5)]$-Re bond but regained in **2a,b** due to much weaker (C_5H_5)-Re bond.[11] Hapticity changes may precede the observed Cp–Re bond cleavage.

From the solvents shown in Table IVa, toluene and benzene are clearly out of correlation with the aforementioned Gutmann numbers. Both **2a** and MTO show the strongest upfield shifts (^{1}H NMR) in toluene and benzene. We therefore postulate the formation of charge-transfer complexes between these aromatics (Ar) and the electron-deficient rhenium complexes. This effect is supported by the UV/vis spectra that differ significantly from aromatic to other solvents (e.g.: MTO/C_6H_6, λ_{max} = 282 nm; MTO/CH_2Cl_2, λ_{max} = 236 nm).[18] The effect is more pronounced as the temperature is lowered, where the molecules move with lower velocity (Table 4b).

The Re center of **2a** is the strongest Lewis acid. Therefore **2a** shows the most downfield-shifted ^{17}O NMR signal. The (more electron-rich) peralkylated Cp ligands of **2c,d** cause significant upfield shifts of the ^{17}O NMR resonance. The spectra (Table 5) clearly reflect the difference in the electron density at rhenium in **2a,b** *vs* **2c,d**. (Even **2a** and **2b** differ significantly in their ^{17}O NMR data.)

The solid-state NMR spectrum (CP, MAS) of polycrystalline **2a** shows a sharp peak with a half-width of 450 Hz at 116.6 ppm, which exhibits an axially symmetric chemical shift anisotropy (CSA) tensor (Figure 2a). The latter is consistent with those known for typical, symmetrical M(η^5-C_5H_5) moieties,[19a] due to averaging by the

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Table 5. ^{17}O NMR Data of Selected Complexes of Type R–ReO$_3$[a]

complex	$\delta(^{17}O)$, ppm	complex	$\delta(^{17}O)$, ppm
$[C_5(CH_3)_4(C_2H_5)]ReO_3$	646	$ArReO_3$[c]	800[b]
$[(C_5(CH_3)_5]ReO_3$	647	$MesReO_3$[d]	811[b]
$[C_5H_4(CH_3)]ReO_3$	674	CH_3ReO_3	829[b]
$(C_5H_5)ReO_3$	691		

[a] In $CDCl_3$ at normal spectrometer temperature. [b] Reference 7c. [c] Ar = 2,6-dimethyl-4-(trimethylsiloxy)phenyl. [d] Mes = mesityl.

Table 6. Infrared Data (ν(Re=O), KBr, cm^{-1}) of Compounds R–ReO$_3$

3 type	complex	$\nu_{sym}(ReO_3)$	$\nu_{as}(ReO_3)$
η^5	$[C_5(CH_3)_5]ReO_3$	909 st	878 sst
	$[C_5(CH_3)_4(C_2H_5)]ReO_3$	916 st	886 sst
	$[C_5H_4(CH_3)]ReO_3$	927 st	878 sst
	$(C_5H_5)ReO_3$	926 st	886 sst
η^1	$(C_6H_5)ReO_3$[a]	986 m	956 sst
	CH_3ReO_3[a]	1005 w	953 sst
	$C_2H_5ReO_3$[a,c]	996 m	961 sst

[a] Reference 7a,c. [b] Spectra taken at room temperature (approximately 25 °C). [c] Spectrum taken in CS_2.

Table 7. Electrochemical Data (Bu = *n*-C$_4$H$_9$)

compd	$E_{1/2(red)}$, mV[c]	$E_{1/2(ox)}$, mV[c]
$(C_5H_5)SnBu_3$ (**1a**)[a]		777
$(C_5H_4CH_3)SnBu_3$ (**1b**)[a]		845
$[C_5(CH_3)_5]SnBu_3$ (**1c**)[a]		393
$[C_5(CH_3)_4Et]SnBu_3$ (**1d**)[a]		500
Re_2O_7 (**3a**)[a]	303, –965	
$(CF_3COO)ReO_3$ (**3b**)[a]	305, –700	
$(CCl_3COO)ReO_3$ (**3c**)[a]	300, –960	
$(CH_3COO)ReO_3$ (**3d**)[a]	211, –1290	
$(C_5H_5)ReO_3$ (**2a**)[b]	–920	
$(C_5H_4CH_3)ReO_3$ (**2b**)[b]	–900	
$[C_5(CH_3)_5]ReO_3$ (**2c**)[b]	–1450	1980
$[C_5(CH_3)_4Et]ReO_3$ (**2d**)[b]	–1600	2040

[a] In acetonitrile. [b] In CH_2Cl_2. [c] Vs Ag/AgCl.

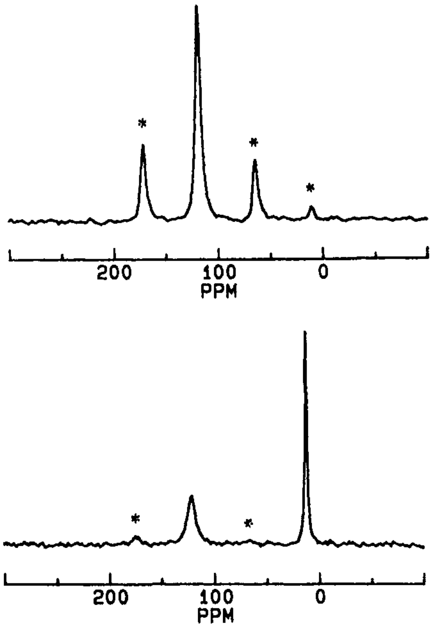


Figure 2. (a) Top: ^{13}C CP/MAS NMR spectrum of $(C_5H_5)ReO_3$ at 75.5 MHz. Asterisks denote spinning sidebands. (b) Bottom: ^{13}C CP/MAS NMR spectrum of $(C_5Me_5)ReO_3$ at 75.5 MHz. Asterisks denote spinning sidebands of the quarternary carbon signal (121.0 ppm). Methyl carbon signal: 11.8 ppm.

fast reorientation process.[19b] The absence of any quadrupolar coupling[19c] to the $^{185/187}Re$ nuclei ($I = {}^5/_2$), even in the case of the σ-bonded methyl carbon atom of CH_3ReO_3, should be mentioned.

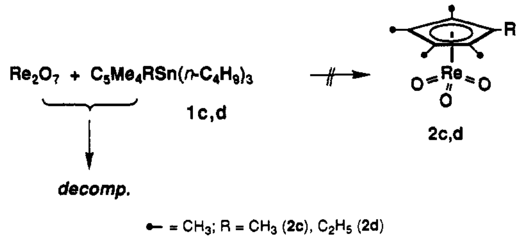
The ^{13}C CP/MAS spectrum of **2c** (Figure 2b) with its two signals is also consistent with pentahapticity of the Cp* ligand. The narrow line at 11.8 ppm with a half-width of 220 Hz originates from the CH_3 groups, undergoing a fast reorientational process with a 3-fold jump mechanism.[19d] The broader resonance at 121.0 ppm is due to the ring carbon nuclei. The larger half-width (740 Hz) as compared with **2a** could stem from a higher activation barrier of reorientation of the alkylated Cp ring. This effect is well-known for alkylated arene rings π-bonded to metal atoms.[19e]

The *IR spectra* allow the following statement regarding the ReO bonds: As shown by the ν_{sym}(ReO) band positions, the ReO bond strength increases in the order $(C_5Me_5)ReO_3 < (C_5H_4CH_3)ReO_3 < (C_5H_5)ReO_3 < CH_3ReO_3$; *cf.* Table 6 and ref 16a.

C. Electrochemistry. An electrochemical study uncovered unexpectedly strong effects of methyl (alkyl) substitution of C_5H_5 ligands and explains the failure to synthesize **2c** by the "tin route" (eq 3): The tin compounds **1a-d** show an irreversible oxidation wave in acetonitrile but no reduction wave above –2000 mV. Table 7 lists the electrochemical data as measured by cyclic voltammetry using a glassy-carbon electrode in acetonitrile or CH_2Cl_2 (0.1 M $[Bu_4N][PF_6]$).

The potential of $(C_5H_4CH_3)Sn(n\text{-}Bu)_3$ (**1b**) is by 68 mV higher than that of $(C_5H_5)Sn(n\text{-}Bu)_3$ (**1a**). One single methyl group thus stabilizes the electronic system of the Cp ring at the tin atom. The inductive effect of one methyl group is not sufficient to decrease the $E_{1/2}$(ox) value. The same tendency is observed for the peralkylated compounds **1c,d**. According to the positive inductive influence of five alkyl groups, the $E_{1/2}$(ox) values for **1c,d** are shifted by about –400 mV *vs* that for **1a**. However, the oxidation potential of **1d** is considerably higher compared with permethylated **1c**. This gives evidence for a strong influence of steric hindrance and/or asymmetry upon the redox potential, which for **1b,d** outweighs the opposite inductive effect of additional alkyl groups. It seems, though, that asymmetry increases resistance against oxidation (cf. Table 7).

Electrochemical data (acetonitrile) show that the $[Re^{VII}O_3]^+$ starting compounds **3a-d** can oxidize Cp^*SnBu_3. The failure to synthesize Cp^*ReO_3 according to eq 5 is thus explained. The relevant $E_{1/2}$ values ($E_{1/2}$[ox, Cp^*SnBu_3] = 393 mV; $E_{1/2}$[red, $(CF_3COO)ReO_3$] = 305 mV) are close enough to make a redox reaction possible.



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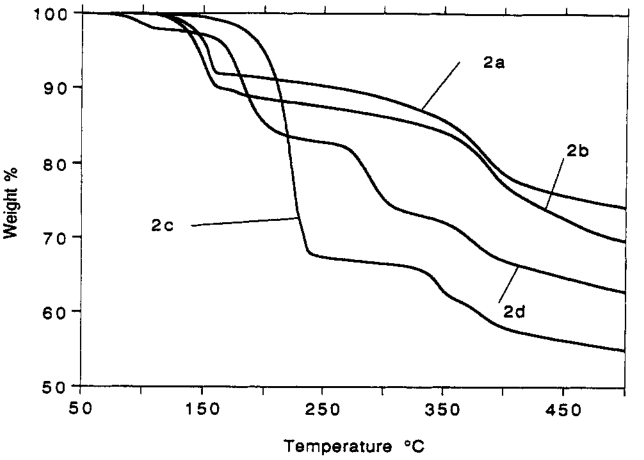

Figure 3. TG curves of $(C_5H_5)ReO_3$ (**2a**), $(C_5H_4CH_3)ReO_3$ (**2b**), $[C_5(CH_3)_5]ReO_3$ (**2c**), and $[C_5(CH_3)_4(C_2H_5)]ReO_3$ (**2d**). See text.

$(C_5Me_4Et)ReO_3$ cannot be obtained by the tin route either, although the potential would allow such a reaction. High solubility of starting material and product, even at −40 °C, could entail consecutive reactions such as redox decomposition processes.

Surprisingly, the considerable steric effects in the organotin series **1a-d** are not paralleled in the *reduction* of **2a-d**. The peralkylated compounds show high resistance against reduction (strong inductive effects of the alkyl groups). The *oxidation* chemistry of $R-ReO_3$ and $R-SnBu_3$ follows the same characteristics. For the less-substituted Cp derivatives **2a,b** no oxidation is seen. The two peralkylated compounds **2c,d** exhibit high oxidation potentials at 1980 and 2040 mV, respectively. The oxidation waves for **2a,b** are expected at values beyond the limits of experiment (oxidation of solvent).

In conclusion the oxidation potentials of compounds $(R-Cp)SnBu_3$ do not depend only on the number of substituents and their inductive effects but also on symmetry. This trend is also observed for the derivatives of $CpReO_3$, at much higher oxidation potentials. In addition, redox reactions occurring with $(R-Cp)SnBu_3$ can hamper the synthesis of $(R-Cp)ReO_3$.

D. Thermogravimetry/Mass Spectrometry. A comparison of the TG curves of **2a-d** (Figure 3) shows increasing decomposition "onsets" with improved donor capability of the π-ligand (**2a**, 134.2 °C; **2b**, 144.7 °C; **2c**, 207.8 °C; **2d**, 166.0 °C). The total weight loss is more than expected for the mere loss of the π-ligand, suggesting extrusion of Re-containing fragments (not detected by MS due to technical limitations regarding the TG/MS coupling system). The weight loss related to the first step is decreased due to the sublimation of evolved organic ligand onto the colder parts of the stirrup. In the first decomposition step, the organic ligand, its fragments, and even its dimer are detected by mass spectrometry (*cf.* Figure 4). The above decomposition temperatures thus refer to *Re–Cp bond cleavage*. Theoretical predictions of the higher thermal stability of $(C_5Me_5)ReO_3$ over $(C_5H_5)ReO_3$[11] are now experimentally confirmed.

The second decomposition steps occur around 350 °C. Mainly extrusion of H_2O and CO_2 is observed, suggesting reduction of the ReO_3 fragment because of oxygen uptake by C- and H-containing fragments of predecomposed material (Figure 4; see also ref 20). That the organic ligand and its fragments show up in the second decomposition step again (with little intensity), may originate from a "memory effect" caused by the warming of the stirrup and evaporation of previously condensed ligand.

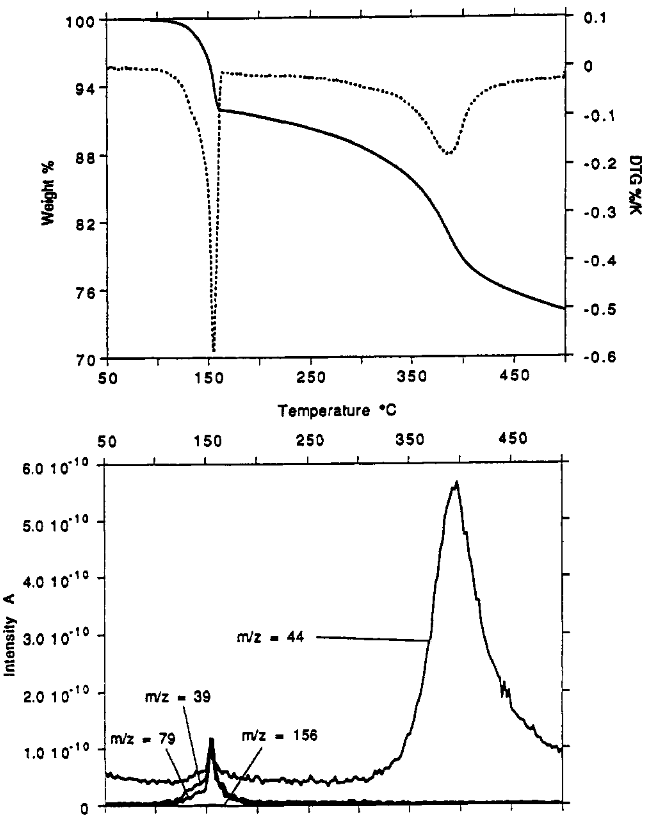

Figure 4. TG and DTG curves and selected intensities of $(C_5H_4CH_3)ReO_3$ (**2b**) (*m/z* = 44 (CO_2), 79 (methylcyclopentadiene), 156 (dimethylfulvalene)).

Conclusions

(Cyclopentadienyl)trioxorhenium(VII) and substituted derivatives are conveniently accessible in good yields via (trifluoroacetyl)trioxorhenium(VII) and (cyclopentadienyl)tin reagents. Methyl substitution of the Cp ligand stabilizes the resulting Re(VII) compounds (TG data), enhances the solubility in all common organic solvents, and lowers the ReO bond order (IR and ^{17}O NMR). The large-scale synthesis of $(C_5H_5)ReO_3$ now opens the way toward detailed studies of its chemistry, which is expected to be quite different from what is known about $(C_5Me_5)ReO_3$ and CH_3ReO_3.[4,8,14a,21]

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Experimental Section

All reactions were performed in Schlenk flasks under oxygen and dry nitrogen. Solvents were dried and distilled under nitrogen with the standard methods. Infrared spectra were recorded on a Perkin-Elmer Series 1650 FTIR and Nicolet FT-5DX spectrometer. The ^{1}H, ^{13}C, and ^{17}O NMR spectra were recorded at 399.78, 100.5, and 54.21 MHz, respectively, on a FT-JEOL GX 400 instrument and a JEOL JNM-GX 270 instrument. The ^{17}O NMR spectra were externally referenced to D_2O. All NMR solvents were "freeze–pump–thaw"-degassed and stored over molecular sieves (4 Å; CH_3CN, 3 Å) before use. The solid-state ^{13}C NMR spectra were recorded at room temperature (298 K) on a Bruker MSL 300 NMR spectrometer, using a 7-mm double bearing MAS probehead and ZrO_2 rotors. A spinning speed of 4000 Hz was applied. About 1000 transients with cross polarization (CP) gave spectra with satisfactory signal to noise ratio. The contact time was 5 ms, the ^{13}C 90° pulse length 4 μs, and the pulse repetition time 4 s. Chemical shifts are reported on the scale with respect to δ(TMS) = 0 and were referenced to the second, external standard adamantane,[19f] which also served for the optimization of the Hartman–Hahn condition. Elemental analyses were performed in the Microanalytical Laboratory of this institute. Mass spectra were obtained with Finnigan MAT 311 A and a MAT 90 spectrometers.

Electrochemical measurements were performed on a PAR 173/276 potentiostat (EG&G) with a specially developed CV software programm.[22] Cyclic voltammetry was performed by using a three-electrode configuration.[23] Background CV spectra of the blank electrolyte solution were always recorded. Potentials are reported *vs* aqueous Ag/AgCl/3 M KCl and were standardized against ferrocene. TG–MS data were obtained by a Perkin-Elmer TGA 7 thermobalance coupled with a Balzers QMG 420 mass spectrometer by a capillary interface heated to 280 °C. Each 1–6-mg sample was heated in a dynamic He atmosphere (purity 5.0, flow 45 sccm) using a 50–500 °C temperature program at a rate of 10 K/min. $(C_5H_5)Sn(n\text{-}C_4H_9)_3$, $(C_5H_4CH_3)Sn(n\text{-}C_4H_9)_3$, $(C_5Me_5)Sn(n\text{-}C_4H_9)_3$, and $(C_5Me_4Et)Sn(n\text{-}C_4H_9)_3$ were prepared according to literature methods;[24] the preparation of **2c,d** was carried out according to ref 14a.

(1) Typical Preparation of (η^5-Cyclopentadienyl)trioxorhenium (2a) and (η^5-Methylcyclopentadienyl)trioxorhenium (2b). A magnetically stirred suspension of Re_2O_7 (9.69 g, 20 mmol) in 60 mL of acetonitrile is treated with 4.90 g of perfluoroacetic anhydride (20.60 mmol) at room temperature. After 10 min the reaction mixture becomes clear and pale yellow. The solution containing (trifluoroacetyl)perrhenate is cooled down to −35 °C. A 40-mmol amount of **1a** (or **1b**) is then added. The mixture turns brown while a yellow solid precipitates after a few seconds.

After being stirred for an additional 5 min, the supernatant solution is filtered. The remaining powder is brought to room temperature and washed with portions of 5 mL of acetone until the washings are yellow. Then the precipitate is washed twice with Et_2O or *n*-pentane and dried in an oil-pump vacuum. Yield: 9.61 g (80%) of **2a**; 10.85 g (86%) of **2b**.

Spectroscopic and Analytical Data. $C_5H_5ReO_3$ (2a). IR (KBr, cm^{-1}): ν = 3100 st, 1429 st, 1262 w, 1094 w, 1080 w, 1017 st, 926 st, 886 sst, 871 sh, 855 st, 835 sh, 589 m, 385 m, 355 m, 195 m. EI-MS (70 eV) (*m/z* (%)): 300 (37) [M^+, ^{187}Re], 65 (100) $[M - ReO_3]^+$. CI-MS (isobutene as CI gas) (*m/z* (%)): 301 (100) [$M + H^+$, ^{187}Re]. ^{1}H NMR ($CDCl_3$, 25 °C, ppm): δ = 6.90. ^{13}C NMR ($CDCl_3$, 25 °C, ppm): 114.0. ^{17}O NMR ($CDCl_3$, 20 °C, ppm): 691. Anal. Calcd for $C_5H_5ReO_3$ (299.29): C, 20.07; H, 1.68; Re, 62.21; O, 16.04. Found: C, 20.15; H, 1.77; Re, 62.51; O, 15.66.

$C_6H_7ReO_3$ (2b). IR (KBr, cm^{-1}): ν = 3079 st, 3089 m, 3078 m, 2960 w, 1487 st, 1450 m, 1398 w, 1370 st, 1344 w, 1262 w, 1243 w, 1231 m, 1076 m, 1051 m, 1038 st, 927 st, 888 sh, 878 sst, 856 st, 839 m, 631 m, 610 m, 584 m, 387 m, 352 m, 181 m. EI-MS (70 eV) (*m/z* (%)): 314 (10) [M^+, ^{187}Re], 78 (100) $[M - ReO_3]^+$. CI-MS (isobutene as CI gas) (*m/z* (%)): 315 (100) [$M + H^+$, ^{187}Re]. ^{1}H NMR ($CDCl_3$, 25 °C, ppm): δ = 6.91 (A,A′B,B′, 2H), 6.32 (A,A′B,B′, 2H), 2.39 (s, 3H): ^{13}C NMR ($CDCl_3$, 25 °C, ppm) 136.90, 114.2, 106.6, 13.60. ^{17}O NMR (20 °C, $CDCl_3$, ppm): 677. Anal. Calcd for $C_6H_7ReO_3$ (313.32): C, 23.00; H, 2.25; Re, 59.43; O, 15.32. Found: C, 22.87; H, 2.20; Re, 59.57; O, 15.54.

(2) Crystal Structure Determination. Tiny, yellow crystals of **2a** were grown by standard cooling techniques at −30 °C from a toluene solution. A suitable crystal for X-ray diffraction (0.09 × 0.04 × 0.13 mm) was mounted on a glass fiber capillary. Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation at 25 °C. Final cell constants were obtained by least-squares refinement of 25 automatically centered high-angle reflections (39.8° < 2θ < 45.6°). During data collection [range, $1.0° \leq \theta \leq 25.0°$; ($\pm h, \pm k, \pm l$); width, $(0.70 + 0.20 \tan \theta)°$ ± 25%; time, 120 s] no decay was observed. The intensity data were corrected for Lorentz and polarization effects and for adsorption (numerical; 6 faces; $T_{min/max}$ = 0.1385/0.3734). After the merging of data, all unique reflections were used in the refinements. The structure was solved by Patterson methods and subsequent full-matrix least-squares techniques and difference Fourier map calculations. The cyclopentadienyl ligand is disordered in two positions. Only one common isotropic displacement parameter was refined for the carbon atoms. All other atoms were refined with anisotropic displacement parameters. A strong extinction parameter was included (ϵ = 0.4164 × 10^{-5}). Hydrogen atoms were calculated in ideal positions but were not refined. The refinements stopped at shift/error < 0.001, and final difference Fourier maps showed no significant features. Crystallographic data are summarized in Table 1. All calculations were performed on a MicroVAX 3100 computer with the STRUX-IV system[25a] including the programs ORTEP,[25b] PLATON,[25c] PLUTON,[25c] SCHAKAL,[25d] and SDP.[25e]

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Supplementary Material Available: Complete tables of crystal data and refinement details, atomic positional and thermal parameters, and bond lengths and angles and a stereo cell plot (8 pages). Ordering information is given on any current masthead page.

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