Multiple Bonds between Main-Group Elements and Transition Metals. 130.1
(Cyclopentadienyl)trioxorhenium(VII): Synthesis, Derivatives, and Properties

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(σ5-Cyclopentadienyl)trioxorhenium(VII) and ring-substituted derivatives are conveniently synthesized from (trifluoroacetyl)perrenate 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 CpReO3 systems differ significantly from those of the nonperalkylated forms. Thermal stabilities of CpReO3 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 σ-bonded ligands. Increasing π-donor capability of the Cp ligands with increasing substitution by alkyl groups is documented in the IR and 17O NMR spectra. As shown by a single-crystal X-ray diffraction analysis of (C5H5)ReO3, the Cp ligand is σ5-bonded to the metal. Crystal data: monoclinic ml/n, a = 5.984(1) Å, b = 9.178(1) Å, c = 6.099(1) Å, β = 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 (C5Me5)ReO3.3 Since then, numerous derivatives and reactions have been reported.4 Interestingly enough, attempts to prepare the parent (C5H5)ReO3 started as early as 1963.5a Many possible C5H5-transfer reagents (e.g. Mg, Cd, Hg) were used but remained unsuccessful, like the reactions of ReO3 with (C5H5)Sn or (C5H5)Sn(t-C4H9).5b,6 Following a method applied to the preparation of several other organorhenium(VII) oxides,7,8 bis(cyclopentadienyl)zinc yielded (C5H5)ReO3 under special synthetic conditions; cf. eq 1.5a The success of this method, however, depends on highly purified starting materials. We now report a simple preparation of (C5H5)ReO3 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

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[a] Dedicated to Professor Helmut Werner on the occasion of his 60th birthday.
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listed in Table 1, atomic coordinates are in Table 2, and selected bond lengths and angles are in Table 3. While ORTEP representation of the molecule is given in Figure 1b, the structural assignment was demonstrated for the crystalline phase of 2a by an X-ray diffraction study. An ORTEP representation of the molecule 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, 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 (2.39(3) Å) but longer as compared to those of the low-valent congeners (2.30 Å) and (2.32 Å) of (3c) (2.30 Å). This result is explained in terms of a “trans influence” resulting from the pronounced π-character of the oxo groups.

While (C₅Mes)ReO₃ (2c) and (C₅Me₅Et)ReO₃ (2d) do not react with donor ligands (e.g., quinuclidine), 2a reacts quickly under decomposition with liberation of cyclopentadiene (1H 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
are poorly soluble. In coordinating solvents (DMSO, pyridine, methanol) 2a,b decompose within seconds or minutes (decomposition in THF is much slower), and $\text{CpReO}_3$ is formed (shown by NMR, e.g. in methanol) as well as a dark precipitate. Elemental analyses show that this precipitate has a $\text{Re:O}$ ratio of $\approx 1:2.5$. This result is due to the different redox behavior of the tin precursors $\text{Sn(Re-Bu)}_4$. A detailed study of the photochemistry of $\text{2a-c}$ and other compounds $\text{R-ReO}_3$ 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 $\text{Sn(Re-Bu)}_4$ vs $\text{[C_5(CH_3)_5Sn(n-Bu)_5]}$. This reaction is unsuccessful for the preparation of $\text{Sn(n-Bu)_4}$, which is nearly inactive.13

B. NMR and IR Spectroscopy. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra (in solution) further corroborate the assumption that the cyclopentadienyl ligands of 2a,d are symmetrically $\pi$-bonded ($\pi^3$) to the metal over the investigated temperature range of $-100$ to $+100$ °C. The $^1\text{H}$ NMR spectra of 2a exhibit only one signal for the cyclopentadienyl protons (6.60 ppm, $d_9$-thf), and 2b has two signals for the Cp protons and one for the methyl group. An analogous pattern is seen in the $^{13}\text{C}$ NMR spectra. Remarkable shifts of the cyclopentadienyl signal positions indicate a strong influence of solvent donor capability according to the Gutmann donor numbers15 (Table 4a). These effects are in the same order as those observed for $\text{CH_3ReO}_3$ ("MTO").16 Weakly or non-

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### Table 4. $^1\text{H}$ NMR Data for ($\text{C}_2\text{H}_5\text{ReO}_3$ and $\text{CH}_3\text{ReO}_3$

<table>
<thead>
<tr>
<th>$\delta$ (ppm)</th>
<th>$\text{C}_2\text{H}_5\text{ReO}_3$</th>
<th>$\text{CH}_3\text{ReO}_3$</th>
<th>$\delta$ (ppm)</th>
<th>$\text{C}_2\text{H}_5\text{ReO}_3$</th>
<th>$\text{CH}_3\text{ReO}_3$</th>
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<tr>
<td>$\text{CCL}_4$</td>
<td>7.15</td>
<td>2.72</td>
<td>$\text{CH}_3\text{OD}$</td>
<td>6.55</td>
<td>1.97</td>
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<tr>
<td>$\text{CD}_2\text{O}$</td>
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<td>b</td>
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<td>2.81</td>
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<td>$\text{C}_2$</td>
<td>7.00</td>
<td>2.86</td>
<td>$\text{d}_9\text{-ds}$</td>
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<td>1.67</td>
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<tr>
<td>$\text{CD}_2\text{Cl}_2$</td>
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<td>2.67</td>
<td>$\text{d}_9\text{-pyridine}$</td>
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<td>2.61*</td>
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<td>6.60</td>
<td>2.14*</td>
<td>$\text{C}_3$</td>
<td>5.70</td>
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<tr>
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<td>6.58</td>
<td>1.94*</td>
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#### (b) Temperature Dependence of Shifts ($d_9$-Toluene)

<table>
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<tr>
<th>temp. °C</th>
<th>$\delta$ (ppm)</th>
<th>$\text{C}_2\text{H}_5\text{ReO}_3$</th>
<th>$\text{CH}_3\text{ReO}_3$</th>
<th>$\delta$ (ppm)</th>
<th>$\text{C}_2\text{H}_5\text{ReO}_3$</th>
<th>$\text{CH}_3\text{ReO}_3$</th>
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<tr>
<td>100</td>
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<td>90</td>
<td>5.89</td>
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<td>5.42</td>
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<tr>
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<td>5.73</td>
<td>1.34</td>
<td></td>
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</tbody>
</table>

*Reference 16b. Decomposition.

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coordinating solvents (e.g. $\text{CCL}_4$, $\text{CD}_2\text{O}$, $\text{CD}_3\text{Cl}_2$, $\text{CD}_3\text{CN}$), the cyclopentadienyl signals are shifted further downfield than in typical $\sigma$-donor solvents (THF, $\text{CD}_2\text{CN}$). 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.16,17 This flexibility is lost in 2c,d due to the strong $\text{[C}_5\text{Me_5]}$-Re bond but regained in 2a,b due to much weaker ($\text{C}_5\text{H}_5$)-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 ($\text{17O}$ 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/$\text{C}_5\text{H}_5$, $\lambda_{max}$ = 222 nm; MTO/$\text{CH}_3\text{Cl}$, $\lambda_{max}$ = 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 $\text{17O}$ NMR signal. The (more electron-rich) peralkylated Cp ligands of 2c,d cause significant upfield shifts of the $\text{17O}$ 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 $\text{17O}$ 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 $\text{M(C_5H_5)}$ moieties,19 due to averaging by the
Table 5. $^{13}$C NMR Data of Selected Complexes of Type R-ReO$_3$.

<table>
<thead>
<tr>
<th>complex</th>
<th>$\delta$(ppm)</th>
<th>complex</th>
<th>$\delta$(ppm)</th>
</tr>
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<tr>
<td>[C$_5$(CH$_3$)$_2$(CH$_2$)ReO$_3$]</td>
<td>646</td>
<td>Ar-ReO$_3$</td>
<td>800$^a$</td>
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<tr>
<td>[C$_5$(CH$_3$)$_3$]ReO$_3$</td>
<td>647</td>
<td>Mes-ReO$_3$</td>
<td>811$^b$</td>
</tr>
<tr>
<td>[C$_5$H$_4$(CH$_2$)]ReO$_3$</td>
<td>674</td>
<td>CH$_3$ReO$_3$</td>
<td>829$^b$</td>
</tr>
<tr>
<td>(C$_5$H$_5$)ReO$_3$</td>
<td>691</td>
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</table>

$^a$ In CDCl$_3$ at normal spectrometer temperature. $^b$ Reference 7c. Ar = 2,6-dimethyl-4-(trimethylsiloxy)phenyl. Mes = mesityl.

Figure 2. (a) Top: $^{13}$C CP/MAS NMR spectrum of (C$_5$H$_5$)ReO$_3$ at 75.5 MHz. Asterisks denote spinning sidebands. (b) Bottom: $^{13}$C CP/MAS NMR spectrum of (C$_5$Me$_5$)ReO$_3$ at 75.5 MHz. Asterisks denote spinning sidebands of the quaternary carbon signal (121.0 ppm). Methyl carbon signal: 11.8 ppm.

fast reorientation process.$^{19b}$ The absence of any quadrupolar coupling$^{18c}$ to the $^{185}/^{187}$Re nuclei ($I = 5/2$), even in the case of the $\sigma$-bonded methyl carbon atom of CH$_3$ReO$_3$, 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.$^{18d}$ 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 $\pi$-bonded to metal atoms.$^{19c}$

The IR spectra allow the following statement regarding the ReO bonds: As shown by the $\nu_{sym}$(ReO) band positions, the ReO bond strength increases in the order (C$_5$Me$_5$)ReO$_3$ < (C$_5$H$_4$CH$_2$)ReO$_3$ < (C$_5$H$_5$)ReO$_3$ < CH$_3$ReO$_3$; cf. Table 6 and ref 16a.

C. Electrochemistry. An electrochemical study un-covered unexpectedly strong effects of methyl (alkyl) substitution of C$_5$H$_5$ 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$_2$Cl$_2$ (0.1 M [Bu$_4$N][PF$_6$]).

The potential of (C$_5$H$_5$CH$_2$Sn(n-Bu)$_3$ (1b) is by $68$ mV higher than that of (C$_5$H$_5$)Sn(n-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(V$^II$O$_3$)$_4$] $^+$ 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$_3$COO)ReO$_3$) = 305 mV) are close enough to make a redox reaction possible.
Re-Cp bond cleavage.

and its fragments show up in the second decomposition material (Figure 4; see also ref 20). That the organic ligand by C- and H-containing fragments of predecomposed reduction of the Re03 fragment because of oxygen uptake are now experimentally confirmed.

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–Re03 and R–Sn–Bu3 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)SnBu3 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 CpReO3, at much higher oxidation potentials. In addition, redox reactions occurring with (R–Cp)SnBu3 can hamper the synthesis of (R–Cp)ReO3.

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 σ-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 σ-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 (C5Me5)ReO3 over (C5H5)ReO3 are now experimentally confirmed.

The second decomposition steps occur around 350 °C. Mainly extrusion of H2O and CO2 is observed, suggesting reduction of the ReO3 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.

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 17O NMR). The large-scale synthesis of (C5H5)ReO3 now opens the way toward detailed studies of its chemistry, which is expected to be quite different from what is known about (C5Me5)ReO3 and CH3ReO3.


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 Spectrometer 1650 FTIR and Nicolet FT-5DX spectrometer. The 1H, 13C, and 19F NMR spectra were recorded at 399.78, 100.5, and 51.21 MHz, respectively, on a FT-JEOL GX 400 instrument and a JEOL JNM-GX 270 instrument. The 19F NMR spectra were externally referenced to D2O. All NMR solvents were "freeze-pump-thaw"-degassed and stored over molecular sieves (4 Å; CH2CN, 9 Å) before use. The solid-state 13C NMR spectra were recorded at room temperature (298 K) on a Bruker MSL 300 NMR spectrometer, using a 7-mm double-bore MAS probehead and ZrO2 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 13C 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, which also served for the optimization of the Hartmann-Hahn condition. Elemental analyses were performed in the Microanalytical Laboratory of this institute. Mass spectra were obtained with Finnigan MAT 311 and a MAT 90 spectrometers.

Electrochemical measurements were performed on a PAR 173/274 potentiostat (EG&G) with a specially developed CV software program. Cyclic voltammery was performed by using a three-electrode configuration. 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 Series 1650 FTIR and Nicolet FT-5DX spectrometer by a capillary interface heated to 280 °C. Each sample was heated in a dynamic He atmosphere (purity ≥99.999%).

Spectroscopic and Analytical Data. C5H6ReO3 (2a). IR (KBr, cm–1): ν = 3079 st, 3089 m, 2986 w, 1487 st, 1450 m, 1398 w, 1370 st, 1344 w, 1282 w, 1243 w, 1231 w, 1076 m, 1051 m, 1098 st, 927 s, 888 sh, 878 sst, 856 m, 729 m, 631 m, 610 m, 584 m, 387 m, 352 m, 181 m. EI–MS (70 eV) (m/z (%)): 514 (10) [M+19F], 456 (100) [M – ReO3]2+.

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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 of a stereo cell plot (8 pages). Ordering Information is given on any current masthead page.

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