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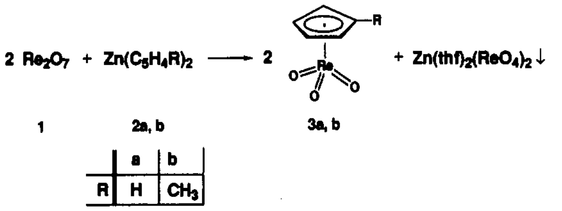
(η^5-Cyclopentadienyl)trioxorhenium[1]

Since the key compound trioxo(η^5-pentamethylcyclopentadienyl)rhenium, as the first example to demonstrate the compatibility of organic π-ligands with high oxidation state metals (e.g., Re^{VII}), was obtained in 1984,[2,3] numerous derivatives and reactions have been reported.[3,4] However, any attempt to apply the successful synthetic routes to the synthesis of the hitherto unknown parent compound *(η^5-cyclopentadienyl)trioxorhenium* remained unsuccessful. Moreover, no mononuclear compound of formula $(C_5H_5)MO_n$ has been reported in the literature up to the present.

It was argued that the Lewis acidity of unsubstituted $(\eta^5\text{-}C_5H_5)ReO_3$ at the metal would be so dominant that further reactions would occur or that the binding of the five-membered ligand is insufficient because of the missing methyl groups.[5] On the other hand, the existence of Lewis acid σ-alkyl and σ-aryl compounds of formula $R\text{–}ReO_3$ (e.g., R = CH_3, C_6H_5)[6] very much bring into question this tentative explanation, thus encouraging synthetic attempts. Here we report on the successful preparation of the title compound $C_5H_5ReO_3$ (**3a**) and its monomethylated derivative **3b**.

Oxidation of the carbonylrhenium(I) precursor compounds $(\eta^5\text{-}C_5H_4R)Re(CO)_3$ with various reasonable oxidizing reagents (e.g., oxygen/light,[2] hydrogen peroxide,[7a–c] dimanganese heptaoxide,[7d] and dimethyldioxirane[7e]) yielded intractable products. Reaction of ReO_3Cl with $Na[C_5H_5]$ does not yield **3a** either.[7] We therefore chose to introduce the cyclopentadienyl ligand into dirhenium heptaoxide (**1**), which, as a precursor compound, is more readily available anyway. However, cyclopentadienyl complexes of magnesium, cadmium, mercury, and tin did not react with **1** in the expected sense. The synthesis of title compound **3a** was finally achieved by treating an exactly 2-fold molar amount of dirhenium heptaoxide **1** with freshly prepared, sublimed bis(cyclopentadienyl)zinc (**2a,b**) in tetrahydrofuran, according to eq 1.[8,9]



(1)

Table I. Infrared and ^{17}O NMR Data for Organic Rhenium(VII) Oxides of Formula $RReO_3$

complex	solvent	ν(Re═O),[a] cm^{-1}	δ, ppm
$(\eta^5\text{-}C_5H_5)ReO_3$	CH_2Cl_2	933 m, 907 vs	691 ($CDCl_3$)
	KBr	925 m, 888 vs	
	Nujol	929 m, 885 vs	
$(\eta^5\text{-}C_5H_4Me)ReO_3$	CH_2Cl_2	930 m, 898 vs	674 ($CDCl_3$)
	KBr	925 m, 889 sh, 878 vs	
$(\eta^5\text{-}C_5Me_5)ReO_3$	C_6H_6	920 m, 890 s	646 ($CDCl_3$)[b]
	CS_2	922 s–vs, 892 vs	
	KBr	909 s–vs, 878 vs	
	CH_2Cl_2	918 m, 886 s	
CH_3ReO_3	C_6H_6	999 w, 966 vs	829 ($CDCl_3$)
	CS_2	1001 w, 965 vs	
	KBr	1005 w, 958 vs, br	
	CH_2Cl_2	1000 w, 966 vs	
$(\eta^1\text{-}C_6H_5)ReO_3$	KBr	986 m, 956 s	972 (pentane)
	CCl_4	988 m, 960 s	

[a] Abbreviations: Me = CH_3; vs = very strong, s = strong, m = medium, sh = shoulder, w = weak. [b] Kneuper, H. J.; Härter, P.; Herrmann, W. A. *J. Organomet. Chem.* **1988**, *340*, 353.

The components react even at −80 °C, with the insoluble zinc–perrhenate **4a** being formed as a colorless precipitate. After evaporation of the solvent in vacuo at 0 °C, the product was extracted into toluene, giving a yellow solution from which the title compound **3a** was crystallized at −30 °C as yellow needles. **3a** is stable at room temperature and up to 130–180 °C (slow decomposition) and is soluble in common organic solvents. The compound is not air-sensitive but undergoes slow decomposition upon exposure to light. **3a** can be sublimed in vacuo at ca. 50 °C/(10^{-4} Torr).

Title Compound: A π-Complex. The C_5H_5 ligand shows a single sharp signal both in the ^1H and $^{13}C\{^1H\}$ NMR spectra, δ(H) = 6.60 ppm and δ(C) = 118.6 ppm, respectively (THF-d_8, 20 °C). This pattern does not change upon cooling the samples to −100 °C (THF-d_8), thus making σ-coordination highly unlikely. The

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(8) The preparation of **3b** is as follows. To a solution of Re_2O_7 (968 mg, 2 mmol) in THF (30 mL) at −80 °C was added dropwise a solution of $Zn(C_5H_5)_2$ (195 mg, 1 mmol)[9a] in THF (20 mL). The mixture was allowed to warm slowly to room temperature and then stirred for approximately 2 h until the color of the solution turns black. The mixture was *protected from light* during the time of the reaction. The resulting solution was evaporated to dryness in vacuo at 0 °C, and the residue was extracted once into *n*-pentane (20 mL) and then into toluene (5 × 40 mL) until the extracts become colorless. After the toluene fractions were cooled to −20 °C, yellow microcrystals formed. These were filtered and dried in vacuo to yield 270 mg (45%) of **3a**. The mother liquors were combined, concentrated to ca. 50 mL, and cooled to 30 °C to afford another crop of **3a** (60 mg). Total yield: 330 mg (56% on the basis of eq 1). IR KBr, cm^{-1}): 925 m, 888 vs [ν(Re═O)]; further bands, 854 m, 1017 w, 1430 w, 3102 m [ν(C—H)]. IR (Nujol, cm^{-1}): 929 m, 885 vs [ν(Re═O)]; further bands, 617 m, 857 sh, 1017 w, 1112 s, 1428 m, 3101 m [ν(C—H)]. IR (CH_2Cl_2, cm^{-1}): 933 m, 907 vs [ν(Re═O)]; further bands, 844 m, 1016 w, 1466 w, 2926 m, 3115 m [ν(C—H)]. ^1H NMR (20 °C, ppm): δ 5.70 (C_6D_6), 6.94 ($CDCl_3$), 6.93 (CD_2Cl_2), 6.60 (THF-d_8). ^1H NMR (−60 °C, ppm): δ 6.99 ($CDCl_3$). ^1H NMR (−100 °C, ppm): 6.76 (THF-d_8). $^{13}C\{^1H\}$ NMR (20 °C, ppm): δ 113.8 ($CDCl_3$), δ 114.2 (CD_2Cl_2), 118.6 (THF-d_8). $^{13}C\{^1H\}$ NMR (−100 °C, ppm): δ 118.2 (THF-d_8). ^{13}C NMR (20 °C, ppm): δ 114.1 (d quint, $^1J_{CH}$ = 181.6 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 6.4 Hz, CD_2Cl_2), 117.8 (d quint, $^1J_{CH}$ = 173 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 6.1 Hz, (THF-d_8). Elemental analyses (C, H, Re) confirm the composition $C_5H_5O_3Re$. EI-MS: m/z = 300 (parent ion, ^{187}Re). Slow decomposition with brown coloration upon prolonged heating in the temperature range 130–180 °C; no defined melting point. The preparation of $(CH_3C_5H_4)ReO_3$ (**2b**) from Re_2O_7 and $Zn(CH_3C_5H_4)_2$[9b] follows the above procedure. Yield: 50% on the basis of eq 1. IR (KBr, cm^{-1}) 925 m, 889 sh, 878 s [ν(Re═O)]; further bands, 838 w, 855 m, 1040 w, 1490 m, 2361 w, 3100 m [ν(C—H)]. IR (CH_2Cl_2, cm^{-1}): 930 m, 898 vs [ν(Re═O)]; further bands, 847 m, 875 w, 1034 w, 1520 m, 3110 m [ν(C—H)]. ^1H NMR (20 °C, ppm): δ 6.85 [AA′BB′, 2 H], 6.32 [AA′BB′, 2 H], 2.39 (s, 3 H, $CDCl_3$), 6.86 (2 H), 6.34 (t, 2 H), 2.37 (s, 3 H, CD_2Cl_2). $^{13}C\{^1H\}$ NMR (20 °C, ppm): δ 136.9 113.9, 106.9, 13.6 (CD_2Cl_2). ^{13}C NMR (20 °C, ppm): δ 136.9 (s), 113.9 (dm, $^1J_{CH}$ = 182.5 Hz), 106.9 (dm, $^1J_{CH}$ = 178 Hz), 13.6 (q, $^1J_{CH}$ = 130 Hz, CD_2Cl_2). Elemental analyses (C, H, Re) confirm the composition $C_6H_7O_3Re$. EI-MS: m/z = 314 (parent ion, ^{187}Re).

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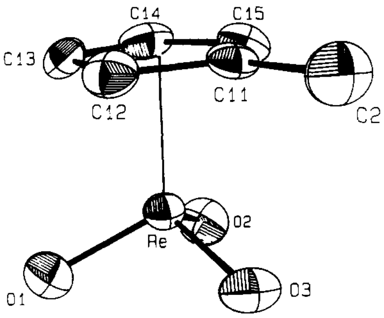

Figure 1. ORTEP representation of the crystal and molecular structure of (η^5-methylcyclopentadienyl)trioxorhenium(VII) (**3b**), without hydrogen atoms. Thermal ellipsoids are drawn to 50% probability. Selected bond distances (pm) and angles (deg): Re–O1 = 173.1 (3), Re–O2 = 171.8 (3), Re–O3 = 171.1 (3), Re–C = 236.0 (3)–245.9 (3); O1–Re–O2 = 105.7 (1), O2–Re–O3 = 104.5 (1), Cp–Re–O1 = 114.4 (1) (Cp = center of $C_5H_4CH_3$ ligand).

^{1}H NMR pattern of **3b** (see below) rules out both rigid and dynamic σ-coordination. Infrared spectra of **3a** and **3b** support the presence of aromatic π-ligands (Table I). In accord with the structural assignment of π-complexation, the ^{17}O NMR and IR data for the *ReO* moiety are much closer to those of (η^5-C_5Me_5)ReO_3 than to those of the σ-alkyl series R-ReO_3 (Table I).

It can be seen that methylation of the ring ligand C_5H_5 leads to lower *ReO* bond strength (lower stretching frequencies) due to the *+I* effect of methyl groups.

(η^5-Methylcyclopentadienyl)trioxorhenium (3b) was synthesized in the same way from **1** and **2b**, according to eq 1. Spectra and physical properties of this compound are similar.

The above structural assignment was demonstrated for the crystalline phase by an X-ray diffraction study (Figure 1).[10] While **3a** is disordered, the less symmetrical methyl derivative **3b** shows an almost undistorted π-coordination of the C_5 ring ligand, with relatively *long* Re···C bonds of 236.0 (3) –245.9 (3) pm as compared to those of the *low-valent* congeners (η^5-C_5H_5)Re(CO)$_3$ (228 pm, average)[11] and (η^5-$C_5H_4SiMe_3$)Re(CO)$_3$ (230 pm, average).[11b] This result is due to the pronounced π-donator capability (trans influence) of metal-attached oxo groups.

The analogous imido complexes (C_5H_5)Re(=NR)$_3$ and (C_5Me_5)Re(=NR)$_3$ have escaped isolation inspite of the extraordinarily high thermal stability of the σ-allyl complex (η^1-C_3H_5)Re(=NR)$_3$ (R = -C_6H_3-2,5-(CH_3)$_2$).[12] It was suggested that π-coordination of the C_5H_5 ligand at tris(imido)rhenium fragments is not favored.[12]

Compound **3a** is the first example within the series (C_5H_5)MX_3, with X representing oxo or imido groups =O or =NR, respectively. A recent failure to access such compounds happened to Wilkinson et al., who, in unspecified yields, obtained a strangely composed oxygen-containing compound by treatment of ClRe(=NR)$_3$ with Na[C_5H_5].[13] In light of our results, there is no doubt that imido complexes (C_5H_5)Re(=NR)$_3$ will become accessible by appropriate synthetic routes, even if the C_5H_5 ligand may be σ-bonded.

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Supplementary Material Available: Tables of anisotropic temperature factors and hydrogen atom coordinates for **3b**, complete lists of atomic coordinates, bond distances, and bond angles, and a unit cell diagram (7 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for **3b** ($ReC_6H_7O_3$): yellow columns, 0.1 × 0.02 × 0.03 mm; M_r = 313.3; space group $P2_1/c$ (No. 14); a = 6.000 (1) Å; b = 10.724 (1) Å; c = 10.644 (1) Å, β = 91.99 (1)°; V = 684 (1) Å^3; Z = 4; d_{calc} = 3.04 g cm^{-3}; Enraf-Nonius CAD4-instrument; 295 K; Cu Kα (λ = 1.541 84 Å); scan method, $\omega/2\theta$; data collection range, $1° < \theta < 65°$; total number of data measured, 1356 (81 systematic absences and 147 reflections with negative intensity were eliminated, the number of unique data being 1128); total number of data used 1118 (10 peaks were removed due to bad agreement); solution by heavy atom methods (Patterson and Fourier) with full-matrix least-squares refinement to convergence (number of refined parameters 92); extinction corrected, $\epsilon = 3.78 \times 10^{-6}$; R = 0.031; R_w = 0.030; GOF = 3.87; from final difference Fourier maps, a residual electron density of +1.2 and −2.2 e/Å^3, respectively (87 and 93 pm from Re).

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Anorganisch-chemisches Institut der
Technischen Universität München
Lichtenbergstrasse 4
D-8046 Garching, Germany

Wolfgang A. Herrmann*
Marc Taillefer
Claude de Méric de Bellefon
Joachim Behm

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