Journal of Organometallic Chemistry, 369 (1989) C1–C5
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 9978PC

Preliminary communication

Multiple bonds between main group elements and transition metals

LXIX *. Condensation reactions of methyltrioxorhenium with 8-hydroxyquinoline and 2-hydroxyaniline: new rhenium(VII) chelate complexes

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(Received February 22nd, 1989)

Abstract

The title compound methyltrioxorhenium, (CH_3ReO_3, 1), reacts with 8-hydroxyquinoline at room temperature to give the dinuclear Re^{VII} complex $[CH_3Re(O)_2$(8-oxyquinoline)$]_2O$ (2) in 90% yield. A single crystal X-ray diffraction study has shown that 2 has a dimeric octahedral structure with a total of four terminal oxo ligands and one bridging oxygen atom. By contrast, the more complex condensation reaction of 1 with 2-hydroxyaniline gives the mononuclear Re^{VII} compound $CH_3Re(O)(2\text{-}OC_6H_4NH)_2$ (3) in 60% yield.

Methyltrioxorhenium (1) was first reported in 1979 [1] but owing to the difficulty of the preparation it only recently became possible to explore the chemistry of this compound when a simple effective synthesis was found [2]. In continuation of our work on organorhenium oxides [3], reactions of the title compound 1 with bases such as HO · · · N chelate ligands have been studied. Since the nucleophilic attack on CH_3ReO_3 by hydroxy (HO^-) and alkoxy (RO^-) groups results in cleavage of the carbon–rhenium bond [4], the use of nitrogen-containing bifunctional ligands (with which formation of a strong N→Re dative bond could be expected [3]) seemed more promising. The smooth reaction between the title compound 1 and

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* Preceding communication in this series: W.A. Herrmann, G. Weichselbaumer, and E. Herdtweck, J. Organomet. Chem., in press.

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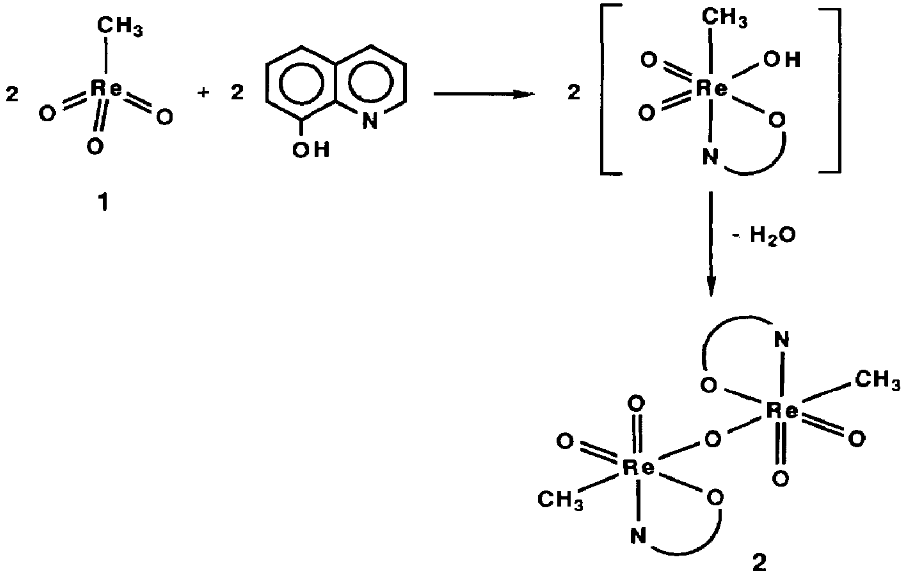

(1)

8-hydroxyquinoline at room temperature did, indeed, result in formation of the new rhenium(VII) *O*,*N*-chelate complex **2**, of formula (μ-O)[$CH_3Re(O)_2$(8-oxyquinoline)]$_2$, according to eq. 1.

Compound **2** shows two intense absorptions at 968 and 937 cm^{-1} in the infrared (KBr) spectrum, typical of terminal oxo groups. The proposed structure also involves a bridging oxo ligand, but the Re–O–Re vibration cannot be unequivocally identified owing to the strong absorptions of the aromatic rings in the 600–800 cm^{-1} region, although a broad band observed at 700 cm^{-1} may arise from the ν(Re–O–Re) vibration.

Since a dimeric corner-sharing octahedral structure may have several isomers with different positions of the ligands, an X-ray crystal structure determination of **2** was carried out. This study confirmed the dimeric distorted octahedral structure of **2**, with the methyl groups approximately *trans* to the bridging oxygen atom, which is at the inversion center of the molecule (Fig. 1). Full details of the structure of **2** will be published elsewhere *. The position of the methyl groups seems unusual as structurally characterized adducts of type $CH_3ReO_3 \cdot NR_3$ all contain the nitrogen ligand *trans* to the methyl group [3]. Electron-impact and field-desorption mass spectra both showed the presence of the $CH_3Re(O)_3$(oxyquinoline) fragment. However, no parent ion could be identified in these spectra, the compound presumably decomposing under the conditions used. Observation of fragments such as [$CH_3Re(O)$(oxyquinoline)$_2$]$^+$ and [$CH_3Re(O)_2$(oxyquinoline)$_2$]$^+$, which could be formed only by decomposition of a species such as **2** supports this view.

Preliminary results show that reactions of the title compound CH_3ReO_3 with other HO $\cdots$ N chelating ligands (containing the nitrogen as a heteroatom in the

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* *Crystal data.* $C_{20}H_{18}N_2O_7Re_2$. $M = 770.8$, monoclinic, $P2_1/c$, *a* 762.6(1), *b* 1641.1(2), *c* 881.3(1) pm, β 107.85(1)°, $Z = 2$, Mo-K_α radiation, μ 110.7 cm^{-1}, $R = 0.034$ for 2277 reflections with $I > 0.0$. Tables of atomic coordinates, bond lengths, and angles, and lists of observed and calculated structure factors are available from the Cambridge Crystallographic Data Centre.

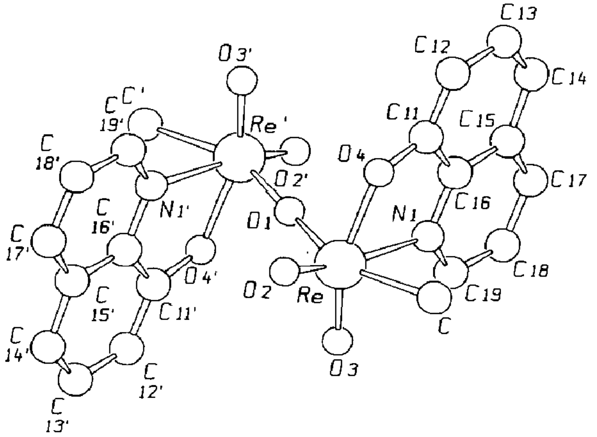
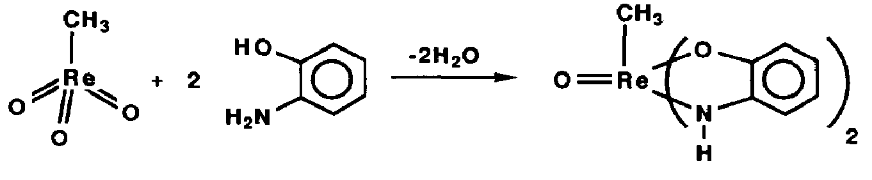


Fig. 1. Schakal drawing of the new Re^{VII} complex $(\mu\text{-}O)[CH_3Re(O)_2(8\text{-oxyquinoline})]_2$ (**2**) showing the atom labelling scheme. Hydrogen atoms are omitted for clarity. Important parameters: Re–N1 227.0(4), Re–O1 187.1(1), Re–O2 169.8(4), Re–O3 168.5(5), Re–O4 201.7(4), Re–C 215.1(7) pm; Re,O,Re′ 180(0), O1,Re,C 155.1(2), N1,Re,O1 77.6(1), N1,Re,O2 166.5(2), N1,Re,O4 74.1(2), O2,Re,O3 105.8(2), O2,Re,O4 93.0(2)°. The 8-oxyquinolinato rings including the rhenium atoms attached to them are strictly planar. Note the rather strong deviation from octahedral core geometry (e.g., the non-linearity of the moiety O1–Re–C).

aromatic ring, e.g. 8-hydroxyquinaldine) proceed in a similar way to the reaction depicted in eq. 1.

In contrast, reaction of CH_3ReO_3 with 2-hydroxyaniline yields the disubstituted, mononuclear product $CH_3Re(O)(2\text{-}HNC_6H_4O)_2$ (**3**), even when an equimolar ratio of the reactants is employed (eq. 2). This condensation reaction differs from the preceding one in that the hydrogen atoms of the amino group also react with the Re=O bonds, with formation of metal-attached amido groups.



(2)

1 **3**

The IR spectrum of **3** shows a strong band at 909 cm^{-1} (KBr) attributed to the Re=O vibration. In the region 3100–3400 cm^{-1}, however, two absorptions were found, indicating that the two amido protons are not equivalent. Correspondingly the ^1H NMR spectrum (CD_2Cl_2) of **3** shows two broad lines (each corresponding to 1H), at 7.88 and 11.33 ppm, which can be assigned to the amido protons. The chemical shift difference can be explained in terms of a strong interaction between one of the amido protons and an adjacent oxo ligand or the oxygen atom of the second phenolato ligand. (The "extreme acidity" of amido protons in high oxidation state inorganic rhenium complexes has been noted [5].) These condensation reactions seem not to be restricted to the title complex CH_3ReO_3. Thus, reaction of $(\eta^5\text{-}C_5Me_5)Re(O)Cl_2$ with a two molar proportion of 2-aminothiophenol yields the compound $(\eta^5\text{-}C_5Me_5)Re(2\text{-}HNC_6H_4S)_2$, which will be the subject of a forthcoming publication. Reactions of CH_3ReO_3 (**1**) with other chelating nucleophiles, as well as the structure of compound **3** are at present being studied.

Experimental

1. (μ-Oxo)bis[dioxo(8-oxyquinolato-N,O)methylrhenium(VII)] (2). 8-Hydroxyquinoline (58.0 mg 0.40 mmol) was added to a stirred toluene solution (10 ml) of 100.0 mg (0.40 mmol) CH_3ReO_3 (**1**); at 25 ° C. The solution became dark violet. As stirring was continued, a black precipitate formed. After 6 h the solution was concentrated in vacuo to ca. 5 ml, 8 ml of n-hexane were added, and the black precipitate was filtered off, washed with n-hexane, and dried in vacuo. Yield 139 mg (91%). M.p. 142°C. Elemental analysis: Found: C, 31.13; H, 2.34; N, 3.62; Re, 48.52; O, 13.93. $C_{20}H_{18}N_2O_7Re_2$ (770.76) calc.: C, 31.16; H, 2.35; N, 3.63; Re, 48.30; O, 14.50%.

Spectroscopic data. IR (KBr, cm^{-1}): 3060vw, 2915vw (ν(C–H)); 1577m, 1499s, 1468s, 1378s, 1325s, 1274m, 825s, 788s, 756s, 712s, 623s [C_9H_6NO]; 967s, 938s, 913w [ν(Re=O)]. ^1H NMR (CD_2Cl_2, 28 ° C, ppm): $\delta(CH_3)$ 1.39 [s, 6H], $\delta(C_9H_9NO)$ 6.98–8.65 [m, 18H]. EI-MS (70 eV): 506 ($[CH_3Re(O)(C_9H_6NO)_2]^+$, rel. int. 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%).

2. Oxo(methyl)bis(2-amidophenolato-N,O)rhenium(VII) (3). 2-Hydroxyaniline (87.3 mg, 0.8 mmol) and 2.0 g of anhydrous sodium sulfate were added to a solution of 100.0 mg (0.40 mmol) CH_3ReO_3 (**1**) in 40 ml of methylene chloride. The mixture was stirred under nitrogen for one day at 25 ° C and then 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 complex **3** containing 0.25 mol of solvent (CH_2Cl_2) per mol of **3**. This solid was filtered off and dried in vacuo. Yield 108 mg (60%). Elemental analysis: Found: C, 35.11; H, 3.01; N, 6.06; Re, 41.50; O, 10.82; Cl, 3.48. $C_{13}H_{13}N_2O_3 \cdot 0.25\ CH_2Cl_2$ (452.72) calc.: C, 35.15; H, 3.00; N, 6.19; Re, 41.13; O, 10.60; Cl, 3.91%.

Spectroscopic data. IR (KBr, cm^{-1}): 3356m, 3194m (ν(N–H)); 3071w, 2965w, 2923w (ν(C–H)); 1588m, 1476m, 1264m, 747m, 739s, 631m, 552s [HNC_6H_4O]; 909vs (ν(Re=O)). ^1H NMR (CD_2Cl_2, 28°C, ppm): $\delta(CH_3)$ 1.29 [s, 3H]; $\delta(HNC_6\mathit{H}_4O)$ 7.25–6.51 [m, 8H]; $\delta(N\mathit{H}_a)$ 7.9 [br, 1H]; $\delta(N\mathit{H}_b)$ 11.3 [br, 1H]. The N*H* signals disappear upon treatment of the solutions with D_2O. EI-MS (70 eV): 432 (M^+, rel. int. 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%).

Acknowledgment. One of us (J.T.) is grateful to the A. von Humboldt Foundation for the award of a Research Fellowship. We thank Dr. R.A. Paciello and Dr. A. Filippou for helpful discussions.

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