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Multiple bonds between main group elements and transition metals, 154 methylrhenium(V) oxo complexes: derivatives of di(4-t-butylpyridine)dichloromethyloxorhenium(V) [1]

Wolfgang A. Herrmann *, Monika U. Rauch, Peter W. Roesky [2]

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Abstract

Di(4-t-butylpyridine)dichloromethyloxorhenium(V) (1) is obtained by reductive halogenation of methyltrioxorhenium(VII) in the presence of t-butylpyridine. A number of new methylrhenium(V) complexes can be synthesized by substitution of the halide and/or pyridine ligands, e.g. with chelating *N*- and *P*-bases or Schiff base ligands. The new rhenium complexes exhibit an asymmetric coordination of the ligands.

Keywords: Rhenium; Methylrhenium(V) oxo complexes; Schiff base ligands

1. Introduction

Rhenium(V) oxo halides like $(HBpz_3)ReOCl_2$ [2] [$HBpz_3$ = hydridotris(1-pyrazolyl)borato], $ReOCl_3 \cdot (PPh_3)_2$ [3] $ReO_2I \cdot (PPh_3)_2$ [4] and $(\eta^5\text{-}C_5Me_5)ReOCl_2$ [5] are potential precursors for Re^V and Re^{III} compounds. Particular interest in these complexes arises from the potential of ^{186}Re to serve as a nuclide in radiotherapy [6]. Since high-valent organorhenium oxides [7] and Schiff base complexes of manganese(III) [8] proved to be efficient catalysts for the oxidation of olefins, we became interested in the chemistry of mono-alkylated rhenium(V) complexes with bi- and tetradentate ligands. Until now such complexes have not been available from conventional starting materials. In this paper we present the synthesis and properties of $CH_3ReOCl_2 \cdot (t\text{-bupy})_2$ (1) (t-bupy = t-butylpyridine) as well as its reactivity towards potential donor ligands.

2. Results and discussion

2.1. Synthesis of $CH_3ReOCl_2 \cdot 2$(t-butylpyridine) (1)

The complex (t-bipy)CH_3ReOCl_2 (2) [t-bipy = 4,4′-di-t-butyl-2,2′-bipyridine] from (t-bipy)CH_3ReO_3 (Scheme 1) was described earlier [9,10]. An asymmetric ligand coordination (C_1-symmetry) is observed, with one of the bipyridine–nitrogen atoms trans to the Re=O moiety and the other trans to a chlorine atom. Considering the strong trans influence of an oxo ligand [11], it is evident that this coordination type is the preferred one.

In contrast, reaction of methyltrioxorhenium(VII) with 1 equiv. t-bupy yields penta-coordinated (t-bupy)CH_3ReO_3. The addition of a second t-bupy ligand was not observed [10b]. Thus **1** is not accessible in the same way as complex **2**. However, reductive halogenation of methyltrioxorhenium(VII) with trimethylsilylchloride/triphenylphosphine in the presence of 2 equiv. t-butylpyridine yields **1** as a pale-green solid (Scheme 1).

The ^1H NMR spectra of **1** exhibit only a single set of resonances for the pyridine ligands at room temperature and below (down to −60°C), showing a symmetrical coordination (contrary to **2**). Thus complex **1** is achiral (C_s-symmetry) and features a methyl group trans to the Re=O group. The spectra of **1** show also a strong

* Corresponding author.

[1] See Ref. [1].

[2] Present address: Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, II 60208-3113 (USA).

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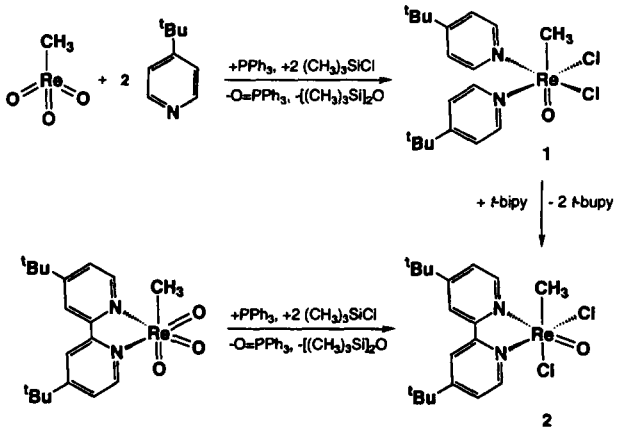


Scheme 1.

down-field shift of the Re–CH_3 signal [$\delta(^1H) = 7.80$ ppm, $CDCl_3$] in contrast to the methyl-resonance of complex **2** [$\delta(^1H) = 5.44$ ppm, $CDCl_3$]. Although rhenium(V) oxo complexes are effectively closed-shell and diamagnetic, the deshielding can be induced by a local magnetic field generated by the d^2-rhenium electron pair associated with the Re=O multiple bond [12].

2.2. Exchange of the pyridine ligands

Reaction of **1** with chelating *N*- or *P*-donor ligands should effect an exchange of the pyridine ligands. Addition of 1 equiv. t-bipy affords complex **2** with liberation of t-butylpyridine (chelating effect). As described above, **2** features an asymmetric coordination of the bipyridine ligand so a conformational rearrangement must be part of the reaction ($C_s \rightarrow C_1$-symmetry).

The purple complex (dppe)CH_3ReOCl_2 (**3**) is obtained by reaction of **1** with 1,2-bis(diphenylphosphino)ethane (dppe) in toluene, with the four possible configurations being presented in Fig. 1. In the C_s-symmetric complex **3A** the methyl group is located trans to Re=O_{oxo}; both phosphorus donor atoms are in trans-position to one chlorine.

The structural types **3B–3D** exhibit an asymmetric coordination of the ligands, thus they are chiral (C_1-symmetry): in **3B** a chlorine atom and in **3C** and **3D** a phosphorus atom is located trans to the Re=O_{oxo} moiety. ^{31}P and ^1H NMR spectra are consistent with an asymmetric substitution pattern (^{31}P NMR: two separated signals for the dppe ligand, $\delta(^{31}P) = 15.3$ and 19.5 ppm, $^3J_{P,P} = 8.7$ Hz; ^1H NMR: multiplet for each (diastereotopic) proton). The symmetrical type **3A** can thus be excluded. Structures **3C** and **3D** seem unfavourable because of the strong trans influence of an oxo ligand. In fact, in rhenium oxo complexes a phosphine in trans-position to Re=O_{oxo} has never been observed with chloride present too. Therefore, structure **3B** is the most likely one. ^1H NMR spectra show the resonances of the Re–CH_3 protons [δ(Re–CH_3) = 4.35 ppm, $CDCl_3$] high-field shifted as compared with **1**. Compound **3** is the mono-methylated derivative of (dppe)$ReOCl_3$. A way to directly methylate this latter compound is not yet known.

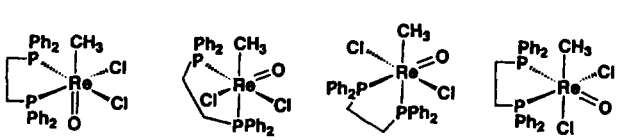
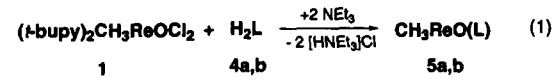
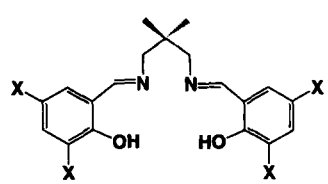


Fig. 1.

2.3. Reaction with tetradentate Schiff base ligands

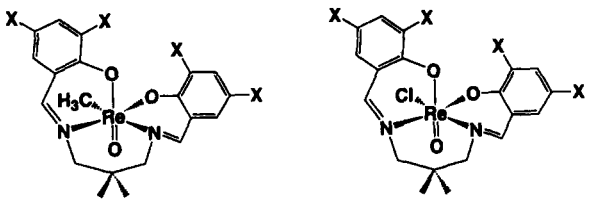
Complex **1** reacts with tetradentate Schiff bases like type-**4** bis(salicylidene)imine [sal_2en] ligands, while t-butylpyridine and HCl are released during this substitution reaction. The methylrhenium(V) sal_2en complexes **5a** and **5b** are thus available from the ligand precursors **4a** and **4b**. The reactions follow Eq. (1) when 1 equiv. H_2L is applied in the presence of triethylamine. Triethylamine serves as a base to deprotonate the phenolic hydroxy functions and to remove the 2 equiv. HCl.





4a (X = H)
4b (X = Cl)

Earlier work [1] showed that rhenium(V) sal_2en complexes of formula ClReO(L) (**6**) with type-**4** ligands have an asymmetric configuration. The two sal_2en units are perpendicular to each other with the phenolate oxygen atom being trans to the Re=O moiety. These results underline the preferred binding of a relatively hard phenoxy donor ligand trans to Re=O_{oxo}. The same type of structure is anticipated for the methylated derivatives $CH_3ReO(L)$ (**5a, 5b**): ^1H NMR data exhibit double sets of resonances due to the asymmetric coordination of the



5a (X = H)
5b (X = Cl)

6a (X = H)
6b (X = Cl)

ligand (all protons in a different chemical environment). This feature is in accord with the IR data: two well-separated stretching bands are observed for the imino double bonds [ν(CH=N) = 1628 and 1592 cm^{-1} (**5a**; ν(CH=N) = 1628 and 1601 cm^{-1} (**5b**)]. The ν(Re=O) bands at 964 and 970 cm^{-1} respectively fall in the typical range for Schiff base Re^{V} complexes [13]. The ^{1}H NMR resonances of the Re–CH_3 protons [δ(Re–CH_3) = 3.96 ppm (**6a**); 4.38 ppm (**6b**); $CDCl_3$] are in the same range as in complex **3** [δ(Re–CH_3) = 4.35 ppm, $CDCl_3$]. **5a** and **5b** are the first methylated examples of Schiff base rhenium(V) complexes. Catalytic epoxidation studies using different oxidizing agents are in progress.

3. Conclusion

A simple, efficient route for the preparation of new methylrhenium(V) complexes has been developed. Apart from *N,N*- and *P,P*-chelate derivatives, methylrhenium-(V) sal_2en complexes of type $CH_3ReO(L)$ are formed with tetradentate bis(salicylidene)imine ligands. They all have asymmetric structures of C_1-symmetry, so a structural rearrangement has occurred during the ligand replacement.

4. Experimental details

4.1. General procedures

All reactions were performed with standard Schlenck techniques in oxygen-free nitrogen atmosphere. Solvents were dried by standard methods and distilled under N_2. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer, the ^{1}H, ^{13}C, and ^{31}P NMR spectra at 399.80, 100.54 and 161.85 MHz respectively were recorded on a FT Jeol GX 400 instrument. Elemental analyses were performed in the microanalytical laboratory of our institute (M. Barth). Mass spectra were obtained with Finnigan MAT 311A and MAT 90 spectrometers. 2-Hydroxybenzaldehyde, 3,5-dichloro-2-hydroxybenzaldehyde, 2,2′-dimethylpropyldiamine, triphenylphosphine, and trimethylchlorosilane were used as received from Aldrich. Bis(salicylidene)-imine ligands (**4a, 4b**) were prepared by mixing the substituted benzaldehydes and amines in a 2:1 stoichiometric ratio, and recovering the Schiff base ligands as yellow solids by filtration. Methyltrioxorhenium was prepared as described in the literature [7b,14].

4.2. Syntheses

4.2.1. Di-(4-t-butylpyridine)dichloromethyloxorhenium-(V) (1)

Methyltrioxorhenium(VII) (1.0 g, 4 mmol) was dissolved in 30 ml dichloromethane. 4-t-Butylpyridine (1.08 g, 8 mmol) was added at room temperature. Trimethylchlorosilane (0.87 g, 8 mmol) and triphenylphosphine (1.0 g, 4 mmol) were added at once to the yellow reaction mixture. The resulting blue mixture was heated for 3 h under reflux while the color turned to turquoise. The solution was concentrated to ca. 10 mL and the product precipitated on the addition of diethylether. The pale green product was collected by filtration, washed with diethylether and dried in vacuo. Yield 1.45 g (65%). Anal. Found: C, 41.56; H, 5.22; N, 4.75; O, 3.40; Re, 31.45. $C_{19}H_{29}Cl_2N_2ORe(\cdot 0.25(C_2H_5)_2O)$. Calc.: C, 41.62; H, 5.50; N, 4.85; O, 3.47; Re, 32.26. Spectra — IR (KBr, ν[cm^{-1}]): 979 s (ν[Re=O]); ^{1}H NMR ($CDCl_3$, 399.80 MHz, 25°C, ppm): 1.35 ($(CH_3)_3C$, s, 18H), 7.63 (t-bupy H-3, dd, $^{3}J_{H,H}$ = 6.73 Hz, 4H), 7.80 ($ReCH_3$, s, 3H), 8.58 (t-bupy H-4, dd, $^{3}J_{H,H}$ = 6.11 Hz, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.51 MHz, 25°C, ppm): 15.2 ($ReCH_3$), 30.8 ($(CH_3)_3C$), 34.6 ($(CH_3)_3C$), 121.0 (t-bupy C-3), 157.0 (t-bupy C-4), 168.1 (t-bupy C-2); CI-MS (70 eV): m/z = 559 ($[M]^+$, 27%), 523 ($[M]^+$–Cl, 10%).

4.2.2. (4,4′-Di-t-butyl-2,2′-bipyridine)dichloromethyloxorhenium(V) (2)

Di-(4-t-butylpyridine)dichloromethyloxorhenium(V) (**1**) (195 mg, 0.35 mmol) was dissolved in 10 ml of toluene. 4,4′-Di-t-butyl-2,2′-bipyridine (94 mg, 0.35 mmol) was added and the reaction mixture was heated for 1 h under reflux while the color turned to brownish purple. The solvent was evaporated and the green product was washed with pentane and dried in vacuo. Yield 180 mg (92%). For experimental data see Refs. [9,10].

4.2.3. 1,2-Bis(diphenylphosphinoethane)dichloromethyloxorhenium(V) (3)

Di-(4-t-butylpyridine)dichloromethyloxorhenium(V) (**1**) (195 mg, 0.35 mmol) was dissolved in 10 ml of toluene. 1,2-Bis(diphenylphosphino)ethane (139 mg, 0.35 mg) was added and the reaction mixture was heated under reflux for 1 h while the color changed from green to purple. The solvent was evaporated and the resulting purple residue was washed with pentane and dried in vacuo. Yield 220 mg (92%). Anal. Found: C, 49.47; H, 4.19; Cl, 9.93; O, 2.30. $C_{27}H_{27}Cl_2OP_2Re$ ($\cdot$0.5 toluene). Calc.: C, 49.21; H, 4.17; Cl, 9.88; O, 2.23; P, 8.64. Spectra — IR (KBr, ν[cm^{-1}]): 992 s ν(Re=O). ^{1}H NMR ($CDCl_3$, 399.80 MHz, 25°C, ppm): 2.60–2.76 (P–CH_2, m, 2H), 3.33–3.41 (P′–$C'H_2$, m, 1H), 3.60–3.68 (P′–$C'H_2$, m, 1H), 4.35 (Re–CH_3, d, $^{3}J_{H,P}$ = 4.3 Hz, 3H), 7.22–7.94 (phenyl–H, m, 20H); $^{13}C\{1H\}$ NMR ($CDCl_3$, 100.51 MHz, 25°C, ppm): 25.57 ($ReCH_3$, d), 29.46 (P–CH_2, dd, $^{1}J_{C,P}$ = 36.8 Hz, $^{2}J_{C,P}$ = 4.6 Hz), 33.24 (P′–$C'H_2$, dd, $^{1}J_{C,P}$ = 40.4 Hz, $^{2}J_{C,P}$ = 7.4 Hz), 128.21–133.41 (phenyl–C, m); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.85 MHz, 25°C, ppm): 15.2 (d, $^{3}J_{P,P}$ = 8.7 Hz), 19.5 (d); CI-MS (70 eV): m/z = 631 ($[M]^+$, 100%).

4.2.4. General procedure for $CH_3ReO(L)$; methyl[N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-diaminopropyl]oxorhenium(V) (5a), methyl[N,N'-bis(3,5-dichlorosalicylidene)-2,2'-dimethyl-1,3-diaminopropyl]oxorhenium(V) (5b)

Di-(4-t-butylpyridine)dichloromethyloxorhenium(V) (**1**) (279 mg, 0.5 mmol) was dissolved in 20 ml of dichloromethane and 0.5 mmol of the Schiff base ligands **4a** and **4b** were added at once. Triethylamine (0.1 g, 1 mmol) was added dropwise to the reaction mixture while the color turned brown. The mixture was stirred for 24 h and the green solution was concentrated to a small volume. The resulting green precipitate was collected by filtration and washed with ether and pentane. Impurities of the byproduct $NEt_3 \cdot HCl$ were removed by sublimation (100°C, oil pump vacuo). Yield 65–70%.

5a: Anal. Found: C, 45.97; H, 4.47; N, 5.18. $C_{20}H_{23}N_2O_3Re$. Calc.: C, 45.70; H, 4.41; N, 5.33. Spectra — IR (KBr, ν[cm^{-1}]): 964.3 s ν(Re=O), 1261.8 vs, 1286.2 vs ν(C–O), 1628.0 vs, 1592.0 vs ν(CH=N); ^{1}H NMR ($CDCl_3$, 399.80 MHz, 25°C, ppm): 3.96 (Re–CH_3, s, 3H), 6.70 (H-5', d, $^3J_{H\text{-}5',H\text{-}4'} = 8.5$ Hz, 1H), 6.78, 6.83 (H-3, H-3', 2 · m, 2 · 1H), 6.97 (H-4', m, 1H), 7.17 (H-5, dd, $^3J_{H\text{-}5,H\text{-}4} = 7.8$ Hz, $^4J_{H5-H3} = 1.7$ Hz, 1H), 7.37 (H-2', d, $^3J_{H\text{-}2',H\text{-}3'} = 8.0$ Hz, 1H), 7.52 (H-4, m, 1H), 7.44, 8.08 (H-7, H-7', 2 · s, 2 · 1H); CI-MS (70 eV): $m/z = 526.1$ ([M]$^+$, 97%), 511.1 (M–CH_3)$^+$, 100%).

5b: Anal. Found: C, 35.95; H, 2.96; Cl, 21.27; N, 4.12; O, 7.44; Re, 28.63. $C_{20}H_{19}Cl_4N_2O_3Re$. Calc.: C, 36.21; H, 2.89; Cl, 21.38; N, 4.22; O, 7.24; Re, 28.07. Spectra — IR (KBr, ν[cm^{-1}]): 964.5 s ν(Re=O), 1285.4 vs ν(C–O), 1600.7 vs, 1627.5 vs ν(CH=N); ^{1}H NMR ($CDCl_3$, 399.80 MHz, 25°C, ppm): 0.78, 0.84 (H-10, H-10', 2 · s, 2 · 1H), 3.72, 3.94 (H-8'a, H-8'b, 2 · d, $^2J_{H8'a,H8'b} = 13.5$ Hz, 2 · 1H), 4.32, 4.63 (H-8a, H-8b, 2 · d, $^2J_{H8a,H8b} = 11.3$ Hz, 2 · 1H), 4.38 (Re–CH_3, s, 3H), 6.97 (H-3', d, $^4J_{H\text{-}3',H\text{-}5'} = 2.5$ Hz, 1H), 7.00 (H-5', d, 1H), 7.07 (H-5, d, $^4J_{H\text{-}5,H\text{-}3} = 3.0$ Hz, 1H), 7.55 (H-3, d, 1H), 7.19, 7.66 (H-7, H-7', 2 · s, 2 · 1H); CI-MS (70 eV): $m/z = 664.9$ ([M]$^+$, 37.6%), 648.9 (M–CH_3)$^+$, 26.5%).

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