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Note

One step conversion of perrhenate into an Re(IV) complex: synthesis and molecular structure of *trans*-[$ReCl_4(PMePh_2)_2$]

F. Ekkehardt Hahn *, Lutz Imhof, Thomas Lügger

Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany

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Abstract

KReO₄ reacts in a one-pot reaction with 4 mole of diphenylmethylphosphine and aqueous hydrochloric acid in boiling ethanol to yield *trans*-tetrachloro-bis(diphenylmethylphosphine) rhenium (1) in high yield. The almost quantitative, direct reduction of perrhenate to Re(IV) by PPh₂Me/HCl has been observed for the first time. Bright red 1 can be crystallized from chloroform/hexane to give bright red plates. Crystals of 1 are triclinic with a = 8.898(6), b = 9.543(4), c = 9.713(3) Å, $\alpha = 66.68(2), \beta = 88.54(4), \gamma = 63.10(3)^{\circ}, Z = 1$ and $D_{obs} = 1.83$ g cm⁻³. The structure was solved from 2327 diffraction data ($F_o^2 \ge 3\sigma(F_o^2)$) collected at 20(2)° and refined to R = 0.029 ($R_w = 0.039$).

Keywords: Perrhenate reduction; Rhenium(IV) complexes; Phosphine complexes; Chloride complexes; Crystal structures

1. Introduction

Rhenium tetrachloride fragments are useful precursors for the preparation of Re(IV) complexes. However, the existence of pure $ReCl_4$ remains in dispute and materials described to have the composition $ReCl_4$ are insoluble in most organic solvents [1]. To avoid these problems we investigated the synthesis of Re(IV) coordination compounds containing the $ReCl_4$ core.

Compared to Re(V) complexes containing the $Re(O)Cl_3$ core [2] and Re(III) complexes with the ReCl₃ moiety [3], less is known about Re(IV) complexes containing the $ReCl_{4}$ core and no simple, one-step synthetic procedure to such complexes starting with the most versatile rhenium precursor perrhenate has been published. The Re(IV) complexes cis- $[\operatorname{ReCl}_4(\operatorname{THF})_2]$ [4], cis- $[\operatorname{ReCl}_4(\operatorname{dme})]$ (dme = 1,2-dimethoxyethane) [5] and cis-[ReCl₄(dppe)] (dppe= bis(diphenylphosphino)ethane) [5] have been prepared from $ReCl_5$ or from Re(IV) acetylene complexes of the type $[\text{ReCl}_4(\text{RC}\equiv\text{CR})(\text{OPCl}_3)]$. The *cis*-geometry is not surprising for complexes with bidentate ligands, which form five-membered chelate rings upon complexation, while electronic reasons are assumed to be responsible for the *cis*geometry in cis-[ReCl₄(THF)₂] [4]. The oldest method for the preparation of complexes [ReCl₄L₂] (L₂=two monodentate phosphines or one bidentate diphosphine) is the oxidation of Re(III) complexes of the type *mer*-[ReCl₃L₃] or [Re₂Cl₆(L₂)₂] with chlorinated solvents [6–8] or chlorine [9]. While bidentate phosphines like dppe yield *cis*-[ReCl₄(dppe)] [6], *trans*-[ReCl₄(PR₃)₂] is the product if Re(III) complexes with monodentate phosphines PR₃ are oxidized [7,9,10].

In contrast to the preparation of Re(V) oxotrichloro and Re(III) trichloro complexes by reduction of perthenate with PR_3/HCl , the direct preparation of Re(IV) tetrachloro complexes from such reactions has not been reported. We have now found that KReO₄ reacts in ethanol with 4 equiv. of PMePh₂ and aqueous HCl to give directly the Re(IV) complex *trans*-[ReCl₄(PMePh₂)₂] (1). In this contribution we report on the preparation and molecular structure of 1.

2. Experimental

All solvents were freshly distilled prior to use. IR spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrometer. Elemental analyses were performed on a Vario EL elemental analyzer at the Institut für Anorganische und Analytische Chemie, Freie Universität Berlin. Mass spectra (EI) were recorded on a Finnigan MAT 112 instrument. KReO₄ and PMePh₂ were obtained from Aldrich and were used as obtained.

^{*} Corresponding author.

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2.1. Synthesis of trans- $[ReCl_4(PPh_2Me)_2](1)$

 $KReO_4$ (1.0 g, 3.46 mmol) and diphenylmethylphosphine (2.77 g, 13.84 mmol) were dissolved in a mixture of ethanol (55 ml) and aqueous HCl (10 ml, 24%). The reaction mixture was heated under reflux for 15 h. Within 30 min the colorless solution turned green. After another 4 h the solution had turned yellow and a red precipitate had formed. The reaction was complete (TLC control) after 15 h. The red precipitate was separated by filtration and washed with cold ethanol. It was analyzed as *trans*- $[ReCl_4(PPh_2Me)_2]$. The product can be recrystallized unchanged from chloroform/ hexane. Yield 2.14 g (85%) of bright red crystals. Anal. Calc. for $C_{26}H_{26}Cl_4P_2Re$ (M = 728.46): C, 42.87; H, 3.60. Found: C, 42.55; H, 3.55%. IR (KBr): v 3050 (Ar), 1434 (P–C), 324 (Re–Cl). MS (EI, 80 eV, *m*/*z*): 727 (*M*⁺, 0.11), 692 $(M^+ - \text{Cl}, 0.15), 657 (M^+ - 2\text{Cl}, 1.15), 492 (M^+ - \text{Cl} -$ PPh₂Me, 0.55), 200 (PPh₂Me, 100); correct isotope pattern for rhenium containing fragments.

2.2. Crystal structure analysis

Crystals of **1** were grown at room temperature from a chloroform/hexane solution and are air stable. A suitable specimen was selected in air and mounted at 20(2)°C on an Enraf-Nonius CAD-4 diffractometer. Search and autoindexing procedures gave a triclinic cell. Important crystal and data collection details are listed in Table 1. Diffraction data were

| Table 1 | | | | | |
|----------|---------|-----|------|------------|---------|
| Selected | crystal | and | data | collection | details |

| Crystal size (mm) | $0.30 \times 0.14 \times 0.12$ |
|---|------------------------------------|
| Formula | $C_{26}H_{26}Cl_4P_2Re$ |
| Formula weight (a.m.u.) | 728.46 |
| a (Å) | 8.898(6) |
| b (Å) | 9.543(4) |
| <i>c</i> (Å) | 9.713(3) |
| α (°) | 66.68(2) |
| β (°) | 88.54(4) |
| γ (°) | 63.10(3) |
| $V(Å^3)$ | 663.4(7) |
| Space group | <i>P</i> 1 (No. 2) |
| Ζ | 1 |
| $D_{\rm calc} ({\rm g}{\rm cm}^{-3})$ | 1.823 |
| $D_{\rm obs} ({\rm g}{\rm cm}^{-3})$ | 1.83 |
| μ (cm ⁻¹) | 51.81 |
| Radiation, λ (Å) | Μο Κα, 0.71073 |
| Data collection temperature (°C) | 20(2) |
| 2θ Range (°) | $2 \leq 2\theta \leq 50$ |
| hkl Range | $0 \le h \le 10, -9 \le k \le 10,$ |
| - | $-10 \le l \le 10$ |
| No. unique data | 2336 |
| No. observed data, $F_0^2 \ge 3\sigma(F_0^2)$ | 2327 |
| R ^a (%) | 2.89 |
| $R_{w}^{a}(\%)$ | 3.90 |
| GOF ^a | 1.077 |
| No. variables | 152 |
| | |

^a For definition of residuals see footnote 1.

Table 2 Positional parameters and isotropic equivalent thermal parameters for **1**^a

| Atom | x | у | z | $B_{\rm eq}({\rm \AA}^2)$ |
|------|------------|-----------|------------|---------------------------|
| Re | 0.000 | 0.500 | 0.000 | 2.337(4) |
| Cl1 | 0.2195(1) | 0.2286(1) | 0.0507(1) | 3.82(2) |
| C12 | 0.1703(1) | 0.5311(1) | 0.1530(1) | 3.56(2) |
| Р | 0.1006(1) | 0.6432(1) | -0.2321(1) | 2.31(2) |
| C1 | -0.0727(6) | 0.7828(5) | -0.3960(5) | 3.4(1) |
| C2 | 0.1727(5) | 0.7893(4) | -0.2221(4) | 2.68(8) |
| C3 | 0.0654(6) | 0.9227(5) | -0.1834(5) | 3.7(1) |
| C4 | 0.1139(7) | 1.0396(5) | -0.1789(6) | 4.3(1) |
| C5 | 0.2706(7) | 1.0240(5) | -0.2106(6) | 4.3(1) |
| C6 | 0.3778(6) | 0.8943(6) | -0.2497(6) | 4.4(1) |
| C7 | 0.3301(5) | 0.7757(5) | -0.2549(5) | 3.5(1) |
| C8 | 0.2739(5) | 0.4898(4) | -0.2844(4) | 2.68(8) |
| C9 | 0.4289(6) | 0.3767(5) | -0.1828(5) | 3.4(1) |
| C10 | 0.5640(6) | 0.2602(6) | -0.2198(6) | 4.0(1) |
| C11 | 0.5454(6) | 0.2511(5) | -0.3551(6) | 4.2(1) |
| C12 | 0.3907(7) | 0.3621(5) | -0.4568(5) | 4.1(1) |
| C13 | 0.2555(5) | 0.4812(5) | -0.4213(5) | 3.22(9) |

^a Re resides on a special position (inversion center); $B_{eq} = 8/3\pi^2 - [\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j]$.

collected at 20(2)°C using ω -2 θ scans. Raw data were reduced to structure factors [11] (and their e.s.d.s) by correcting for scan speed, Lorentz and polarization effects. An empirical absorption correction was applied to the data. The space group was assumed to be P1. Solution by Patterson methods and refinement of the structure confirmed this choice. The positional parameters for all non-hydrogen atoms were refined by using first isotropic thermal parameters. A difference Fourier map calculated after refinement with anisotropic thermal parameters showed almost all hydrogen positions. However, hydrogen atoms were added to the structure model at calculated positions (d(C-H) = 0.95 Å) and are unrefined [12]. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the B_{eq} of the parent atom. All calculations were carried out with the MolEN package [13]¹. Atomic coordinates and equivalent isotropic thermal parameters for 1 are listed in Table 2.

3. Results and discussion

The reaction of phosphines and hydrochloric acid with perrhenate salts has been known for quite some time to yield complexes of types *mer*-[ReCl₃(PR₃)₃] [2] or *trans*-[ReOCl₃(PR₃)₂] [2,7,9] depending on the acidity of the solution and the phosphine used. In these reactions normally concentrated hydrochloric acid is used and the phosphines are added in excess and function as reducing agent and as ligands for the formed complexes. Under these conditions

¹ Definition of residuals: $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, $GOF = [\sum w||F_o| - |F_c||^2/(n_o - n_p)]^{1/2}$ with $n_o =$ number of structure factors and $n_p =$ number of parameters, $w = 1/[\sigma(F)]^2$.

triphenylphosphine will reduce perrhenate only to *trans*-[ReOCl₃(PR₃)₂] while dialkylarylphosphines reduce perrhenate [9] or Re(V)oxotrichloro complexes [7] to *mer*-[ReCl₃(PR₃)₃]. Rhenium(IV) complexes have not been isolated in these reactions. They can be obtained by reoxidation of *mer*-[ReCl₃(PPh₂R)₃] with chlorinated hydrocarbons [7] or chlorine [9]. This oxidation is strongly dependent on the phosphine coordinated to rhenium with the shortest reaction time (10 min) observed for P(nBu)₂Ph [7].

Since the reduction of Re(VII) to Re(V) or Re(III) as well as the oxidation of Re(III) to Re(IV) depends strongly on the phosphine present, we became interested in the possibility of stopping the reduction Re(VII) \rightarrow Re(V) \rightarrow Re(III) at the Re(IV) stage by an appropriate phosphine. Since triphenylphosphine can reduce Re(VII) only to Re(V) [7] and dialkyphenylphosphines reduce Re(VII) directly to Re(III) [9] we decided to investigate the reaction of perrhenate salts with the rarely used alkyldiphenylphosphines. For our investigations we chose diphenylmethylphosphine PMePh₂. It was hoped that the reducing power of this phosphine would lie between PPh₃ and P(alkyl)₂Ph, thus allowing the direct reduction of perrhenate to Re(IV) tetrachloro complexes without formation of Re(III) trichloro complexes.

The reaction of KReO₄ with exactly 4 equiv. of PMePh₂ and aqueous HCl (24%) in ethanol yields the bright red Re(IV) complex **1** (Scheme 1). The reaction can be followed optically. The initially colorless reaction solution turns yellow–green within 30 min, indicating the formation of *trans*-[ReOCl₃(PMePh₂)₂] [2]. After heating for another 4 h a red precipitate begins to form. The reaction is completed after 15 h. The red precipitate was isolated and characterized as **1**.

The direct formation of an Re(IV) complex like **1** by reduction of perthenate has not been observed previously. We attribute the formation of **1** to (i) the use of diphenylmethylphosphine as reducing agent and (ii) the use of only 4 equiv. phosphine in the reduction reaction.

Alkyldiphenylphosphines have rarely been used for the reduction of perrhenate or Re(V)oxo complexes. The only example we found in the literature was the reduction of *trans*-[ReOCl₃(PPh₃)₂] to *mer*-[ReCl₃(PPh₂Me)₃] with a large excess of phosphine, which proceeded in exceptionally low yield compared to the same reaction carried out with dialkylphenylphosphines [7]. We take this as an indication for the weaker reducing power of PMePh₂ compared to dialkyl-



Scheme 1. Preparation of complex 1 from KReO₄.

phenylphosphines. In accordance with our observation, diphenylmethylphosphine is not well suited for the reduction of Re(V)oxotrichloro complexes to Re(III)trichloro complexes.

The reduction of perrhenate or Re(V) oxotrichloro complexes with phosphines to Re(III) normally requires an excess of phosphine (1:6 for $\text{Re}(\text{VII}) \rightarrow \text{Re}(\text{III})$ [9], 1:4.8 for $\text{ReO}(V) \rightarrow \text{Re}(\text{III})$ [7]). In contrast to this we used only 4 equiv. of diphenylmethylphosphine for the $\text{Re}(\text{VII}) \rightarrow$ Re(IV) reduction. Since 2 equiv. of phosphine are used for coordination in **1**, only 2 equiv. are available for the threeelectron reduction. This constitutes a much smaller excess than in the previously described reductions.

We believe that the choice of diphenylmethylphosphine as the reducing agent and its almost stoichiometric use are responsible for the unusual, direct conversion of perrhenate to **1**. This appears to be another example of the significant effect of small changes in a phosphine ligand upon the reactivity.

The molecular structure of **1** was established by X-ray crystallography (Fig. 1). The molecule resides on an inversion center. Only small deviations from a perfectly octahedral geometry were observed in **1**. The Re–Cl and Re–P distances (Table 3) fall in the range observed previously for $[\text{Re}(\text{IV})\text{Cl}_4\text{L}_2]$ complexes (L₂ = two monodentate phosphines [5,6] or one bidentate phosphine [10]).



Fig. 1. Molecular structure of **1** with the crystallographical numbering scheme. Atom Re resides on an inversion center; starred atoms represent transformed coordinates of the type (-x, -y, -z).

Table 3 Selected bond distances (Å) and angles (°) in **1**

| Re | Cl1 | 2.2863(11) | Cl1 | Re | C12 | 89.61(4) |
|----|-----|------------|-----|----|-----|------------|
| Re | Cl2 | 2.3382(11) | C11 | Re | Р | 92.66(4) |
| Re | Р | 2.5133(10) | Cl2 | Re | Р | 90.42(4) |
| Р | C1 | 1.810(5) | Re | Р | C1 | 110.8(2) |
| Р | C2 | 1.812(4) | Re | Р | C2 | 116.00(14) |
| Р | C8 | 1.813(4) | Re | Р | C8 | 113.48(14) |
| | | | C1 | Р | C2 | 102.9(2) |
| | | | C1 | Р | C8 | 106.9(2) |
| | | | C2 | Р | C8 | 105.9(2) |
| | | | | | | |

A full list of data collection and refinement details, tables of positional parameters for all atoms, all bond distances and angles, anisotropic temperature factors, as well as calculated and observed structure factor amplitudes have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, D-76433 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-59293, the names of the authors and the journal citation.

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