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Water-controlled reactions selectivity of the $ReOCl_3(OPPh_3)(SMe_2)$ synthon with a hydrophosphorane ligand

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ABSTRACT

The reaction of the hydrospirophosphorane $HP(OCMe_2CMe_2O)_2$ ligand or the five-membered cyclic hydrogen phosphonate $HP(O)(OCMe_2CMe_2O)$ ligand with the $ReOCl_3(OPPh_3)(SMe_2)$ precursor under controlled reaction conditions led to the isolation of dimeric oxo-rhenium(V) complexes containing $P(O)(OCMe_2CMe_2O)^-$ moieties, represented by $[ReOCl_2\{\mu\text{-}OP(OCMe_2CMe_2O)\}_3ReOCl(OPPh_3)]$ (**1**) and $[ReOCl_2(SMe_2)\{\mu\text{-}OP(OCMe_2CMe_2O)\}]_2$ (**2**). The chemical composition of these complexes was established by means of NMR, IR spectroscopic methods, and based on analytical data. The relative stereochemistry of **1** and **2** was unambiguously determined by single X-ray diffraction studies. The crystal structure of **1** comprises two crystallographically independent molecules in an asymmetric unit and co-crystallised molecules of both dichloromethane and acetonitrile. Two different six-coordinated monomeric subunits, $ReOCl_2$ and $ReOCl(OPPh_3)$, connected by three phosphonate bridges, build up the dinuclear complex **1**. It exhibits an uncommon feature, a *cis* disposition of the triphenylphosphine oxide molecule relative to the terminal Re=O bond. The crystal structure of **2** includes four molecules, in which two equivalent rhenium subunits $ReOCl_2(SMe_2)$ are linked by two $P(O)(OCMe_2CMe_2O)^-$ bridges.

1. Introduction

The chemistry of the diesters of H-phosphonic acid continues to attract much attention not only because they have numerous practical applications in agriculture, industry and medicine [1–4], but also because they extend the scope of transition metal chemistry with H-phosphonates as ligands [5–7]. The property that is unique to these compounds and frequently expressed in their names is the presence of a P–H bond. A vast majority of the compounds prefer the tetracoordinated form $HP(O)(OR)_2$ about a pentavalent phosphorus atom $\lambda^5\sigma^4$ to the tricoordinated form $(OH)P(OR)_2$ $\lambda^3\sigma^3$ (λ and σ indicate respectively the valency and coordination number of the P atom). Dialkyl phosphonates display a variety of complexation modes with metals. The proton bounded to the phosphorus may be retained or lost. Hence neutral or anionic forms can coordinate to the metal through the oxygen atom [8], the phosphorus atom [9–11], or both the phosphorus and the oxygen atoms in a bridging mode [12,13].

Literature data concerning the structures of rhenium complexes containing phosphonate moieties are rather scarce. Indeed, they are represented by only a few examples, and to our knowledge H-phosphonates exist in two coordination modes: with the phosphonate serving as a monodentate P-bonded ligand in the complexes $ReOCl(OMe)[P(O)(OMe)_2](PPh_3)_2$ [14] and $Re(\eta^5\text{-}C_5H_5)I(CO)_2[P(O)(OMe)_2]$ [15] and with a bidentate bridging O,P-bonded phosphonate found in $Re(CO)(bpy)(NO)[P(O)(OMe)_2]$ [16], $[ReOCl\{\mu\text{-}OP(OMe)_2\}(OCMe_2CMe_2O)POCMe_2CMe_2O]_2$ [17], and $[ReOCl\{\mu\text{-}OP(OCMe_2CMe_2O)\}(OCMe_2CMe_2O)POCMe_2CMe_2O]_2$ compounds. We [17] and others [14–16] have assumed that all the aforementioned compounds are generated from appropriate phosphites via a Michaelis–Arbuzov-like dealkylation process. Therefore, we were prompted to ask ourselves if there were only two possible coordination modes for phosphonate ligands incorporated in rhenium centres and which mode, bridging or monodentate, was favoured by the $HP(O)(OCMe_2CMe_2O)$ ligand.

In this paper we continue to explore the coordination chemistry of H-phosphonates and now report on the synthesis and crystal structure investigations of two dinuclear oxo-rhenium(V) complexes with $HP(O)(OCMe_2CMe_2O)$ deprotonated phosphonate: $[ReOCl_2\{\mu\text{-}OP(OCMe_2CMe_2O)\}_3ReOCl(OPPh_3)]$ (**1**) and $[ReOCl_2(SMe_2)\{\mu\text{-}OP(OCMe_2CMe_2O)\}]_2$ (**2**).

2. Experimental

2.1. General procedures

Chemicals and deuterated solvents were purchased from Aldrich and Fluka and used as received. All reactions were performed under a nitrogen atmosphere, using conventional Schlenk techniques unless specified otherwise. Solvents were carefully dried and deoxygenated by standard methods [18]. The ligand precursor

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$HP(OCMe_2CMe_2O)_2$ 2,2,3,3,7,7,8,8-octamethyl-1,4,6,9-tetraoxa-5λ^5 phosphaspiro[4,4]nonane, abbreviated as HP∼O [19], and the ligand $HP(O)(OCMe_2CMe_2O)$ [20] 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide were prepared according to the literature methods; *trans*-$ReOCl_3(OPPh_3)(SMe_2)$ [21] was obtained as described previously.

IR and FIR measurements were performed in KBr pellets either with a Nicolet FTIR Impact 400 or in Nujol with a Bruker IFS 113V. ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded at ambient temperature on a Bruker Avance III (300 and 600 MHz for ^1H NMR). The chemical shifts δ are given in ppm relative to the TMS (^1H, ^{13}C) and H_3PO_4 (^{31}P) using deuterated solvents as lock and reference (^1H), respectively. Coupling constants are in Hz. 2D ^1H–^{31}P, ^1H–^{13}C ^{31}P–^{31}P- hetero- and homonuclear correlation spectra were acquired and processed with a standard Bruker program. Elemental analyses were performed on a Vario EL III by the Laboratory of Elemental Analyses in our Department.

2.2. Crystal structure determinations

The data collected on a KM4CCD diffractometer were corrected for Lorentz and polarisation effects. Data reduction was carried out using the Oxford diffraction (Poland) programs. The structures were solved by the Patterson method using SHELXS-97 and refined by the full-matrix least-squares method on F^2 using SHELXL software [22]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were set in calculated positions and refined using the riding model with a common fixed isotropic thermal parameter.

2.3. Synthesis of the complexes

2.3.1. $[ReOCl_2\{\mu\text{-}OP(OCMe_2CMe_2O)\}_3ReOCl(OPPh_3)]$ (1)

2.3.1.1. Method (a). $HP(OCMe_2CMe_2O)_2$ (0,16 g, 0.60 mmol) was added to a light-green suspension of *trans*-$ReOCl_3(OPPh_3)(SMe_2)$ (0.13 g, 0.20 mmol) in moist toluene[1] (10 cm^3). The reaction mixture was refluxed for 9 h until the starting compound reacted and a dark-green solid was afforded. The crude product was filtered off, washed with diethyl ether, and dried *in vacuo* (0.10 g, 80%). Single crystals suitable for X-ray analysis were obtained by re-crystallisation from an acetonitrile/dichloromethane/ethyl ether solution.

2.3.1.2. Method (b). To a dry toluene (10 cm^3) suspension of *trans*-$ReOCl_3(OPPh_3)(SMe_2)$ (0.13 g, 0.2 mmol) was added $HP(O)(OCMe_2CMe_2O)$ (0.10 g, 0.6 mmol). The suspension was heated and stirred for 6 h, and it changed colour from light to dark green. The crude product was filtered off, washed with diethyl ether, and dried *in vacuo* (0.09 g, 70%).

Anal. Calc. for $C_{36}H_{51}Cl_3O_{12}P_4Re_2$ C, 33.81; H, 3.99; Cl, 8.33. Found: C, 33.47; H, 4.01; Cl, 8.47%;

FT-IR ν_{max}(KBr)/cm^{-1}: 538m δ(P═O), 954vs, 994vs ν(Re═O), 923vs, 1068vs ν(C–O–P), 1136vs ν(P═O), ν_{max} (nujol)/cm^{-1} 298s, 319s, 338s, (Re–Cl), 189w, 225m, 237m (Re–P).

^1H NMR (CD_2Cl_2): δ 0.87, 1.04, 1.30, 1.38 (s's, 12, CH_3)[a], 1.22, 1.25, 1.50, 1.57 (s's, 12, CH_3)[b], 1.23, 1.26, 1.30 (s's, 12, CH_3)[c] 7.64 (td, 2H; $^3J_{HH}$ = 7.80, $^3J_{HH}$ = 3.46 *m*–$OPPh_3$), 7.75 (td, 1H; $^3J_{HH}$ = 3.78, $^4J_{HH}$ = 1.52 *p*–$OPPh_3$), 7.94 (m, 2H; $^3J_{PH}$ = 13.11, $^3J_{HH}$ = 8.19, $^4J_{HH}$ = 1.08 *o*–$OPPh_3$).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 43.8 (d, $^3J_{PP}$ = 23.4, $POCCH_3$), 47.2 (d, $^3J_{PP}$ = 23.6, $OPPh_3$), 81.6 (d, $^2J_{PP}$ = 47.2, $POCCH_3$), 86.7 (d, $^2J_{PP}$ = 47.0, $POCCH_3$).

^{13}C NMR (CD_2Cl_2): 23.45, 23.50, 23.55, 23.62, 23.67, 23.89, 24.06, 24.27, 24.53, 24.73, 24.97, 25.05 (s's, CH_3), 87.94 (d, $^2J_{PC}$ = 5.40, CCH_3), 88.52 (d, $^2J_{PC}$ = 4.21, CCH_3), 88.92 (d, $^2J_{PC}$ = 5.11, CCH_3), 89.08 (d, $^2J_{PC}$ = 4.26, CCH_3), 90.06 (d, $^2J_{PC}$ = 3.93, CCH_3), 90.41 (d, $^2J_{PC}$ = 3.44, CCH_3), 127.85 (d, $^1J_{PC}$ = 109.90, C_{ipso}–$OPPh_3$), 129.37 (d, $^2J_{PC}$ = 13.32, C_m–$OPPh_3$), 133.54 (d, $^3J_{PC}$ = 11.75, C_o–$OPPh_3$), 134.05 (d, $^4J_{PC}$ = 2.94, C_p–$OPPh_3$).

The letters [a, b, c] define methyl groups bound to three different phosphorus cycles ascertained by 2D ^1H–^{31}P heteronuclear correlation NMR experiments.

2.3.2. $[ReOCl_2(SMe_2)\{\mu\text{-}OP(OCMe_2CMe_2O)\}]_2$ (2)

The synthesis of complex **2** might be performed according to the method (a) or (b) already described for complex **1**.

The crude product obtained upon the syntheses was filtered off, washed with diethyl ether, and dissolved in acetone in order to remove **1**. The remaining blue solid was washed with ethyl ether and dried *in vacuo* (0.015 g, 15% calculate for method b). Single crystals suitable for X-ray analysis were obtained by re-crystallisation from dichloromethane/ethyl ether solution.

Anal. Calc. for $C_{16}H_{36}Cl_4O_8P_2Re_2S_2$: C, 19.28; H, 3.64; Cl, 14.23. Found: C, 19.62; H, 3.48 Cl, 14.12%.

FT-IR ν_{max}(KBr)/cm^{-1} 620s ν(C–S), 917vs, 956vs, 986vs, 994vs, 1075vs, ν(Re═O) and ν(C–O–P); ν_{max} (nujol)/cm^{-1} 175s, 212w, 235m, 286s, 304s, 388s ν(Re–Cl), ν(Re–P) and ν(Re–S).

^1H NMR (CD_2Cl_2), δ 1.05, 1.08, 1.40, 1.43 (s, 24, CCH_3), 3.08 (s, 12, SCH_3).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 65.7s.

3. Results and discussion

3.1. Synthesis of the complexes

We endeavoured to synthesise the complex $[ReOCl_2\{\mu\text{-}OP(OCMe_2CMe_2O)\}_3ReOCl(OPPh_3)]$ (**1**) in two ways (Chart 1): through prolonged reaction of *trans*-$ReOCl_3(OPPh_3)(SMe_2)$ with a hydrospirophosphorane $HP(OCMe_2CMe_2O)_2$ precursor in wet toluene and through reaction with the 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide ligand $HP(O)(OCMe_2CMe_2O)$ in dry toluene. Both routes were followed at an elevated temperature (110 °C) with the substitution of the dimethyl sulfide ligand. It seems that in the first method (a) water plays a crucial role. Presumably three phosphonate bridges are formed during the hydrolysis reaction of the hydrospirophosphorane ligand HP∼O with the participation of H_2O contaminated toluene. The absence of water causes monomeric *trans*-$ReOCl_2[(OCMe_2CMe_2O)POCMe_2CMe_2O](OPPh_3)$ [23] to appear in the system instead of **1**. Although the hydrogen phosphonate ligand $HP(O)(OCMe_2CMe_2O)$ is more resistant to hydrolysis than hydrospirophosphorane HP∼O, the synthesis (method b) carried out in the presence of water admitted to the system generates only an intractable oily mixture. The substitution of labile *trans*-$ReOCl_3(OPPh_3)(SMe_2)$ with the $P(O)(OCMe_2CMe_2O)^-$ moiety in a non-polar solvent leads to the formation of **1** as the main product, as well as the formation of a by-product in the form of a dinuclear complex of the type $[ReOCl_2(SMe_2)\{\mu\text{-}OP(OCMe_2CMe_2O)\}]_2$ **2,** which involves two phosphonate bridges P,O^- and, unexpectedly, two molecules of dimethyl sulfide. There are several examples in the literature illustrating much higher lability of SMe_2 in substitution reaction than $OPPh_3$ or even chlorides in the commonly used *trans*-$ReOCl_3(OPPh_3)(SMe_2)$ precursor [24–26]. In this context, **2** seems to be an unusual example of an oxo-rhenium(V) complex with a labile thioether ligand still coordinated to the rhenium centre.

All the obtained compounds are stable in the solid state as well as in solution. Only complex **1** is soluble in dichloromethane, ace-

[1] The toluene which was used was not dried and taken from the bottle; or the water, an equivalent molar amount to $HP(OCMe_2CMe_2O)_2$ quantity was deliberately added to the system.