Cationic complexes of Re with dppm (bis(diphenylphosphinomethane)). Crystal structure of [Re(dppm)$_3$]I·CH$_3$OH·CH$_2$Cl$_2$

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Abstract

The reaction of [ReO$_2$(PPh$_3$)$_2$I] with bis-diphenylphosphines (dpp) only produces complexes with general formula [ReO$_2$(dpp)$_2$]$^+$. However, when the ligand used in this work (bis(diphenylphosphinomethane) (dppm)) reacts with the same precursor an interesting Re(I) complex is also afforded. By changing the reaction conditions, *trans*-[Re^{V}O$_2$(dppm)$_2$]$^+$ and [Re^I(dppm)$_3$]I were obtained and characterized. The crystal structure of [Re(dppm)$_3$]I·CH$_3$OH·CH$_2$Cl$_2$ is given. In this compound, the P atoms are arranged in a strongly distorted octahedral coordination polyhedron around the rhenium center. This is the first case of a tris(dppm) complex ever reported. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In previous works [1,2], we have reported on the preparation and crystal structure of some *trans*-Re(V) dioxo complexes with didentate diphosphines, namely, [ReO$_2$(dppe)$_2$]I and [ReO$_2$(dppp)$_2$]PF$_6$ (dppe = 1,2-bis-(diphenylphosphinoethane) and dppp = 1,3-bis-(diphenylphosphinopropane)). They were obtained by reaction of [ReO$_2$(PPh$_3$)$_2$I] with the appropriate ligand. In both cases, the sole product was the dioxo compound, unchanged in the Re oxidation state. They are useful systems to study the influence of ring size on the coordination properties.

The next step in this study was to attempt the formation of a four-membered ring with this 5d-transition metal. This can be performed using dppm (bis-(diphenylphosphinomethane)) as chelating ligand. In

any case, the formation of a highly strained ring is expected. For this reason most dppm complexes show one or two phosphines connecting two metallic centers. Re$_2$Cl$_4$(μ-dppm)$_2$, Mo$_2$(dppm)$_2$X$_4$ (X = Cl$^-$, NCS$^-$) and Re$_2$Cl$_5$(dppm)$_2$ are good examples of this behavior [3–5]. As an alternative, dppm can participate in mixed ligand complexes, by bonding the two phosphorus atoms to the same central atom. This fact has been reported for some Re complexes in different oxidation states: *fac*-[Re^{V}OCl$_3$(dppm)], *mer*-[Re^{III}Cl$_3$(dppm)(PPh$_3$)], *fac*-[Re^{III}(NCH$_3$)Cl$_3$(dppm)], *trans*-[Re^{V}NCl$_2$-(dppm)(PPh$_3$)] and [Re^{V}NCl(dppm)$_2$]Cl [6]. It is interesting to note that the synthesis of these complexes involves the reduction of Re, presumably by the diphosphine. The identification of compounds such as [ReCl$_3$(dppm)(dppom)] and [ReCl$_4$(dppom)] (dppom = Ph$_2$PCH$_2$P(=O)Ph$_2$), in which dppm is partially oxidized to dppom, points in this direction [6,7]. The coordination of dppom seems to be a way to change the strained four-membered ring of dppm to a five-membered one.

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In any case, no tris(dppm)–Re complex has been reported up to now. The situation is not very different for other d-transition metals. No tris(dppm) complexes have been structurally elucidated. Only related compounds such as $\{[(Ph_2P)_2CH]_3V\}[Li(THF)_4](THF)_2$, in which dppm is deprotonated before coordination, have been reported [8].

In this work, we report on two new cationic complexes formed when $[Re^VO_2(PPh_3)_2I]$ reacts with dppm. During the development of procedures for the synthesis of *trans*-$[Re^VO_2(dppm)_2]^+$ by a substitution reaction, a novel cationic complex $[Re^I(dppm)_3]I$ was also obtained and characterized. This is the first time that a Re(I) complex has been prepared with dppm as the only didentate ligand. Dppm demonstrates the ability to act as didentate chelating ligand and its tendency to promote reductive reactions. The crystal structure of $[Re(dppm)_3]I \cdot CH_3OH \cdot CH_2Cl_2$ is the first case of a tris(dppm) complex ever reported.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and used as received. HPLC grade methanol and all other solvents (reagent grade) were used without further purification. Violet microcrystals of $[ReO_2(PPh_3)_2I]$ were obtained using the reported method [9] except for $NH_4[ReO_4]$, which was used in place of $H[ReO_4]$.

2.2. Physical measurements

IR spectra were recorded as KBr pellets on a Bomen MB FT-IR spectrophotometer. Proton NMR spectra were recorded at 200.133 MHz on a Bruker AC200 spectrometer. Peak positions in ppm are relative to TMS as external reference. $^{31}P\{^1H\}$ spectra were recorded on the same instruments operating at 81.015 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Elemental analysis was accomplished on a Carlo Erba model 1108 elemental analyzer. Fast Atom Bombardment spectra were obtained from a 3-nitrobenzylalcohol matrix using a Micromass–Autospec spectrometer.

2.3. HPLC analyses

Chromatograms were obtained with an HPLC system by Merck, equipped with a variable wavelength monitor and a PRP-X200 (10 μm) cation exchange column (4 × 250 mm). A 0.02 M solution of NaCl in methanol was used as mobile phase with 1.5 ml min^{-1} flow. Detection was accomplished at 255 nm.

2.4. Potentiometry measurements

The potentiometric titrations were carried out in mixed solvent dioxane–water (70:30 v/v) solutions at 25 °C and ionic strength $I = 0.1$ mol dm^{-3} in KCl. Experimental details can be found elsewhere [1]. The autodissociation constant of the solvent pK_w was 16.0, in good agreement with reported data [10]. Measurements were taken of dppm and the complex at the concentrations $C = 1.0$, 1.5 and 2.0 mmol dm^{-3}, between pH values of 1.7 and 7.0. The experimental potentiometric data were analyzed by means of the SUPERQUAD program [11].

2.5. Preparation of the complexes

2.5.1. $[ReO_2(dppm)_2]I$ (**1**)
$[ReO_2(PPh_3)_2I]$ (0.30 g, 0.345 mmol) and dppm (1.5 g, 3.90 mmol) were stirred in dichloromethane (20 ml) for 10 min at room temperature (r.t.). A yellow solution was obtained. It was evaporated to dryness under vacuum at a temperature not higher than 30°C. From this crude material, the complex was extracted with freshly distilled methanol (5 × 10 ml). The pale yellow solution was filtered (through paper) and the solvent was evaporated again under similar conditions. The yellow solid was washed with ether (4 × 5 ml); yield 65–70%. The solid can be recrystallized from methanol; yield 70%. IR spectrum (v, cm^{-1}): 3051 (s), 1483 (s), 1436 (vs), 1102 (s), 791 (s), 735 (vs), 725 (vs), 690 (vs), 504 (s), 477 (m), 279 (m), 247 (s). *Anal.* Calc. for $C_{50}H_{44}IO_2P_4Re$: C, 53.9; H, 4.0. Found: C, 53.8; H, 4.0%.

2.5.2. $[ReO_2(dppm)_2]PF_6$
Concentrated solutions of (**1**) showed the formation of a dark solid in CD_2Cl_2 while recording the NMR spectra. In spite of the color, IR spectrum of the solid proved to be essentially free dppm. Hexafluorophosphate salt was therefore prepared by adding a large excess of NH_4PF_6 to a methanolic solution of (**1**); yield: 40–50%. Selected NMR data (CD_2Cl_2, 293 K): ^1H NMR: 7.0–8.0 (m, 40H, C_6H_5), 5.41 ppm (t, $J_{P-H} = 5$ Hz, 4H, CH_2); $^{31}P\{^1H\}$: −45.9 ppm (s). *Anal.* Calc. for $C_{50}H_{44}F_6O_2P_5Re$: C, 53.1; H, 3.9. Found: C, 52.9; H, 4.1%.

2.5.3. $[Re(dppm)_3]I$ (**2**)
A mixture of $[ReO_2(PPh_3)_2I]$ (0.30 g, 0.345 mmol) and dppm (0.7 g, 1.90 mmol) was refluxed in freshly distilled methanol (20 ml) for 3 h. A clear yellow solution was obtained, from which a yellow crystalline solid was separated after cooling to r.t. The solid was washed with ether (4 × 5 ml); yield 25–30%. Suitable yellow crystals for X-ray diffraction were obtained by slow evaporation of a methanol–dichloromethane solution. IR spectrum (v, cm^{-1}): 3050 (s), 1482 (s), 1433

(vs), 1310 (w), 1090 (s), 738 (vs), 726 (vs), 697 (vs), 513 (s), 485 (m), 408 (m). Selected NMR data (CD$_2$Cl$_2$, 293 K): ^{1}H NMR: 7.4–6.5 (m, 60H, C$_6$H$_5$), 5.51 ppm (s, broad, 6H, CH$_2$); ^{31}P{^{1}H}: − 50.3 ppm (s). *Anal.* Calc. for C$_{75}$H$_{66}$IP$_6$Re: C, 61.4; H, 4.5. Found: C, 61.6; H, 4.9%.

2.6. Crystallographic measurements and structure determinations

2.6.1. Crystal data

Colour: yellow. C$_{77}$H$_{72}$Cl$_2$IOP$_6$Re, $M = 1583.17$, orthorhombic, $a = 21.150(3)$, $b = 18.172(3)$, $c = 17.678(5)$ Å, $V = 6794(2)$ Å^3, space group $Pna2_1$, $Z = 4$, $D_{calc} = 1.548$ g cm^{-3}, μ(Mo Kα) = 2.509 mm^{-1}, $F(000) = 3176$, crystal size $0.36 \times 0.25 \times 0.22$ mm.

2.6.2. Structure determination

Data were collected at r.t. on a Rigaku AFC7S four-circle diffractometer [12] in the range $2.23 \le \theta \le 27.51°$, $-19 \le h \le 27$, $-7 \le k \le 23$, $-22 \le l \le 16$. A total of 8888 reflections were collected in the ω–2θ scan mode, of which 8825 were unique ($R_{int} = 1.64\%$) and 7381 ($I > 2\sigma(I)$) were used in the full-matrix least squares refinement with the SHELXL-97 program [13]. The structure was solved using the Patterson method with the SHELXS-97 program [14]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated geometrically suitable positions and refined riding on the corresponding atom, with isotropic thermal displacement parameter 1.2 times higher than the equivalent isotropic displacement parameter of the atoms bonded to them (1.5 times for the methanol solvent molecule). Final residuals were $R = 0.0312$ for a weighting scheme of $w^{-1} = (\sigma^2(F_o^2) + (0.0469P)^2 + 7.3285P)$ where $P = (F_o^2 + 2F_c^2)/3$. The goodness of fit (Goof) finished at 1.038. Mean final shift/esd was lower than 0.01. The maximum and minimum residual densities were 1.037 and −1.114 e Å^{-3}, respectively.

2.7. Calculations

Molecular mechanics calculations (MM) were performed using the MM + force field implemented in the HyperChem package version 5.0. Geometry optimizations were carried out using the Polak–Ribière (gradient conjugated) method with a convergence criterion of 0.01 kcal mol^{-1}.

3. Results and discussion

The reaction product of [Re^{V}O$_2$(PPh$_3$)$_2$I] with dppm is strongly affected by the reaction conditions. It has thus been possible to obtain Re complexes in different oxidation states. The composition of the solids, obtained by elemental analysis and confirmed by FABMS (see below), fitted with the formulae [Re^{V}O$_2$(dppm)$_2$]I (**1**) and [Re^I(dppm)$_3$]I (**2**). It is interesting to note that when preparation involves lower temperatures and larger dppm to Re molar ratios, the result is simply a substitution on the Re(V) core. But, if the reaction is carried out at a higher temperature and lower ligand to Re molar ratio, dppm is able to reduce the central atom and displace the two oxo groups, destroying the very stable [ReO$_2$]$^+$ core. The reduction of other Re precursors to yield stable dppm complexes has been previously reported [5,6], but this is the first time in which a Re(I) compound was obtained.

Positive fast atom bombardment mass spectroscopy of Pt(II) and Pd(II) dppm complexes has been previously discussed [15]. Re complexes follow a similar fragmentation pathway. The most prominent peaks of (**1**) were present at $m/z = 988$ [M$^+$ + H] and 603 [M$^+$ + H − dppm]. For (**2**), signals were found at 1335 [M$^+$ − 2H$_2$], 956 [M$^+$ + H − dppm], 877 [M$^+$ − H − dppm − Ph] and 755 [M$^+$ − H − dppm − Ph − PhP=CH$_2$].

The IR spectrum of [Re^{V}O$_2$(dppm)$_2$]I showed a very strong absorption at 791 cm^{-1} characteristic of the linear [O=Re=O]$^+$ core. This vibration was in the expected range (775–836 cm^{-1}) for the asymmetric [ReO$_2$]$^+$ stretching [16]. The characteristic IR absorption of the [O=Re=O]$^+$ core is not present in (**2**), showing the complete substitution of the oxo ligands. In addition, it was also possible to observe in the IR spectra the characteristic vibrations of dppm. In particular, the scissoring of CH$_2$ groups (around 1483 cm^{-1}) and the P–CH$_2$ deformation band (around 1435 cm^{-1}) are present in the complexes (see Section 2). This is consistent with the presence of dppm in the compounds and rules out the possibility that it could be deprotonated in the complex (as, for example, in {[(Ph$_2$P)$_2$-CH]$_3$V}[Li(THF)$_4$](THF)$_2$ [8]).

Selected bond distances and angles for [Re(dppm)$_3$]I·CH$_3$OH·CH$_2$Cl$_2$ are given in Table 1. Tables of coordinates, anisotropic temperature factors, hydrogen atom coordinates and a full listing of geometric data are available as supplementary data.

Fig. 1 illustrates the geometry and atom-numbering scheme. The structure consists of monomeric units of [Re(dppm)$_3$]$^+$, iodide as counterion and dichloromethane and disordered methanol as cocrystallization solvent molecules. The coordination polyhedron around Re(I) ion can be described as a distorted octahedron. The bond lengths for Re–P range from 2.400(2) to 2.467(2) Å and the P–Re–P angles for P atoms belonging to the same ligand from 68.01(6) to 69.08(6)°. No evidence for charge delocalization suggesting the presence of dppm as anion can be obtained from the structural results. On the contrary, the

Re–Pi–C–Pj torsion angles range from 17.1(3) to 20.3(3)°, for Re1–P3–C2–P4 and Re1–P5–C3–P6, respectively, clearly indicating non-planarity of the ligand skeleton (Pi and Pj belonging to the same dppm lig-

Table 1
Selected bond lengths (Å) and angles (°) for [Re(dppm)$_3$]I·CH$_3$OH·CH$_2$Cl$_2$

|	
Re(1)–P(1)	2.3999(19)
Re(1)–P(2)	2.4203(17)
Re(1)–P(3)	2.4232(17)
Re(1)–P(4)	2.4577(18)
Re(1)–P(5)	2.4585(17)
Re(1)–P(6)	2.4670(17)
P(1)–C(1)	1.831(7)
P(2)–C(1)	1.843(7)
P(3)–C(2)	1.847(7)
P(4)–C(2)	1.843(7)
P(5)–C(3)	1.850(7)
P(6)–C(3)	1.829(7)
P(1)–Re(1)–P(2)	68.88(6)
P(1)–Re(1)–P(3)	96.75(6)
P(2)–Re(1)–P(3)	93.95(6)
P(1)–Re(1)–P(4)	153.59(6)
P(2)–Re(1)–P(4)	89.35(6)
P(3)–Re(1)–P(4)	69.08(6)
P(1)–Re(1)–P(5)	96.04(6)
P(2)–Re(1)–P(5)	161.43(6)
P(3)–Re(1)–P(5)	98.70(6)
P(4)–Re(1)–P(5)	107.82(6)
P(1)–Re(1)–P(6)	95.25(6)
P(2)–Re(1)–P(6)	101.61(6)
P(3)–Re(1)–P(6)	162.99(6)
P(4)–Re(1)–P(6)	103.96(6)
P(5)–Re(1)–P(6)	68.01(6)
P(1)–C(1)–P(2)	95.8(3)
P(4)–C(2)–P(3)	97.2(3)
P(6)–C(3)–P(5)	97.0(3)
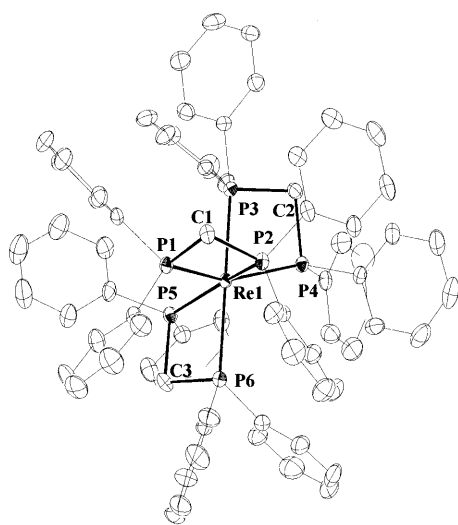
Fig. 1. ORTEP view [17] of the complex (2) with displacement ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity.

and). In a previously reported vanadium analogue ({[(Ph$_2$P)$_2$CH]$_3$V}[Li(THF)$_4$](THF)$_2$ [8]) two deprotonated dppm ligands exhibited very low torsion angles, 0.3° for V1–P4–C38–P3 and 1.7° for V1–P3–C83–P6, and only the third one corresponded to neutral dppm, with the torsion angle V1–P2–C13–P1, 14.8°.

In spite of the distorted geometry of (2), the Re–P bonds present the usual lengths and fall within the range of values observed in other phosphine-containing Re complexes. Moreover, distance seems to be independent of the Re oxidation state [3].

As far as we know, this is the first structure of a tris(dppm) complex ever reported. Steric strain involved in the geometry of three four-membered rings supports the unusual appearance of these complexes. In order to know how strained the ligand in the complex is, we performed molecular mechanics calculations on the dppm. The optimized structure of dppm shows a P–C–P angle of 110.6°, not far from 106.2(3)° reported for the crystalline structure at −40°C [18]. As a second step, we optimized the structure of the ligand fixing the P–C–P angle (up to 60°) but allowing the rearrangement of the rest of the molecule. Fig. 2 shows the increase in the total energy at different P–C–P angles. As can be seen, the adjustment of the angle to 95° (the angle found in the structure of (2)) represents an increase of only 30% in the total energy of the molecule. This small angle does not seem to involve a large strain in the ligand, resulting in a very stable complex. The soft–soft interaction between the P atoms and the Re(I) center seems to be strong enough to compensate the strain of the three ligands.

The solid state structure found for the complexes is sustained in solution. The positive overall charge of the complexes in solution was checked by HPLC. Chromatograms in a cation exchange column show a characteristic peak at 3.9 (1) and 5.6 (2) min.

The ^{1}H and ^{31}P NMR spectra of the compounds agree with octahedral coordination. ^{31}P signals are very sharp, suggesting the diamagnetic character of the complexes. In particular the ^{31}P spectrum of (1) indicates that the two oxygens atoms are in *trans* position. Another remarkable result is the proton integration of the signals. Once more, the presence of two methylenic protons per ligand molecule is confirmed in solution.

It has been demonstrated that Re(V) dioxo complexes with didentate diphosphines, [ReO$_2$(dppe)$_2$]$^+$ and [ReO$_2$(dppp)$_2$]$^+$ can be protonated in dioxane–water (70:30 v/v) [1] according to:

$$[ReO_2(phosphine)_2]^+ + 2H^+$$

$$\leftrightarrows [Re(OH)_2(phosphine)_2]^{3+}$$
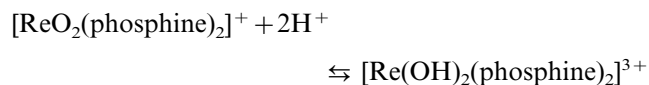
The titrations of [ReO$_2$(dppm)$_2$]$^+$ performed under the same conditions, show no protonation of the complex. The lower basicity of the oxo groups could be
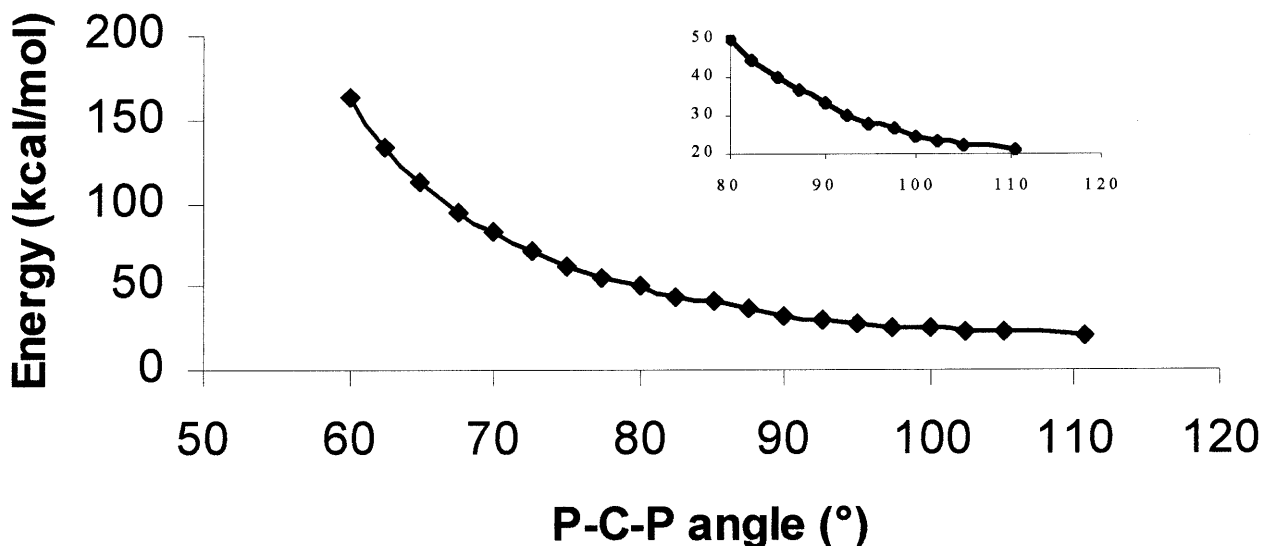
Fig. 2. Total energy of the dppm molecule as a function of the P–C–P angle, obtained by molecular mechanics calculations.

originated either in a short Re–O distance, which diminishes the availability of the lone pair of electrons of the oxygen atoms, or in the steric hindrance of the complex. IR stretching band at 791 cm^{-1} is almost at the same energy than those for $[ReO_2(dppe)_2]I$ and $[ReO_2(dppp)_2]I$ [1]. So, Re–O bond strength seems to be similar. This fact makes more probable the second argument.

For the free ligand, a simultaneous protonation of both phosphine groups is detected with $\log \beta_{12} = 3.04 \pm 0.06$ ($\chi^2 = 10.5$; $\sigma(E) = 3.50$). This value is in line with those for similar diphosphines [1].

4. Conclusions

In spite of many existing examples of complexes with dppm (including several transition metals), no reports could be found that include a tris(dppm) structure. Both the formation of a four-membered ring and the reductive character of the ligand seem to be the reason for this fact. All results reported in this work provide evidence of the formation of a tris(dppm) complex. The reasons why this unexpected compound is obtained seem to be the reductive character of the ligand, which promotes the reduction of the metallic atom, as well as the soft character of the Re(I) center. These results open up the study of a new aspect of the dppm characteristics in coordination chemistry.

5. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 133405 for compound **2**. Copies of

this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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