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Oligophosphine Ligands.
XIII[*]. Halo and Hydro Complexes of Ruthenium(II) Containing the Novel Tripod Tetrakis(tertiary) Phosphine $P(CH_2CH_2CH_2PMe_2)_3$

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Abstract

The reaction of the ruthenium complexes $RuCl_2(PPh_3)_3$, $RuCl_2(PPh_3)_4$, $RuCl_2(PMe_3)_4$, $RuCl_2(Me_2SO)_4$, or $RuBr_2(PPh_3)_3$ with the tripod tetrakis(tertiary) phosphine $P(CH_2CH_2CH_2PMe_2)_3$ gave the compounds *cis*-$RuCl_2[P(CH_2CH_2CH_2PMe_2)_3]$ (**1**) and *cis*-$RuBr_2[P(CH_2CH_2CH_2PMe_2)_3]$ (**2**). The coordination geometry of **1** and **2** was derived from the ABX_2 type ^{31}P NMR patterns of the complexes, as well as from an X-ray structure determination for the chloride **1**. Crystals of **1** were found to be monoclinic, space group $P2_1/n$ ($Z = 4$), with $a = 942.0(3)$, $b = 1446.2(4)$, $c = 1680(1)$ pm, and $\beta = 104.99(4)°$. Anisotropic refinement of the structure converged at $R = 0.040$ and $R_w = 0.034$ (3318 data). Selected bond lengths are (in pm): Ru–P(CH$_2$–)Me$_2$ (*trans*-atom P), 235.8(1) and 239.3(1); Ru–P(CH$_2$–)Me$_2$ (*trans*-atom Cl), 227.9(1); Ru–P(CH$_2$–)$_3$, 225.3(1); Ru–Cl (*trans*-group P(CH$_2$–)$_3$), 252.1(1); and Ru–Cl (*trans*-group P(CH$_2$–)Me$_2$), 250.5(1). Reaction of **1** with $LiAlH_4$ yielded the hydro derivatives *cis*-$Ru(H)Cl[P(CH_2CH_2CH_2PMe_2)_3]$ (**3**) and *cis*-$RuH_2[P(CH_2CH_2CH_2PMe_2)_3]$ (**4**), which were characterized by IR and ^1H and ^{31}P NMR spectroscopy.

Introduction

Previous papers from this laboratory have reported the preparation of the novel tripod tetrakis(tertiary) phosphine $P(CH_2CH_2CH_2PMe_2)_3$ [1] as well as the synthesis, molecular structures and the spectroscopic properties of several halo, pseudohalo, and hydro complexes of iron(II) derived from them [2, 3]. This communication describes the related ruthenium compounds *cis*-$RuX_2[P(CH_2CH_2CH_2PMe_2)_3]$ ($X_2 = Cl_2$ (**1**), Br_2 (**2**), HCl (**3**), and H_2 (**4**)), the organometallic chemistry of which is under active investigation [4].

Experimental

General Procedures and Instrumentation

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to recommended methods and were distilled under nitrogen prior to use. IR spectra (KBr disks): Perkin Elmer 577. NMR spectra: Bruker WH 90 (36.44 MHz ^{31}P), Bruker WP 80 (80.13 MHz ^1H) and Bruker AM 360 (360.14 MHz ^1H). Chemical shifts are reported in ppm relative to external H_3PO_4 and TMS standards (downfield positive).

Preparation of Complexes

$RuCl_2[P(CH_2CH_2CH_2PMe_2)_3]$ (1)

The complex $RuCl_2(PPh_3)_3$ (2.13 g, 2.22 mmol) [5] was dissolved in 175 ml of toluene. 0.75 g (2.21 mmol) of the tetrakis(tertiary) phosphine [1] was added, and the solution was refluxed for 90 min, during which period it changed from dark brown to bright yellow. The formation of some oily deposits was also observed: these were removed by filtration, and the filtrate was evaporated to dryness *in vacuo* to give a semisolid yellow residue. This material solidified upon extraction with ether: it was collected on a Schlenk frit, thoroughly washed with ether, and dried *in vacuo*; yield: 0.70 g (62%) of yellow complex **1**.

This compound was also obtained starting from one of the complexes $RuCl_2(PPh_3)_4$ [5], $RuCl_2(PMe_3)_4$ [6], or $RuCl_2(MeSO)_4$[≠] [7]. Reaction conditions and working-up procedures were similar to those described above. Yields varied between 59 and 76%. *Anal.* Found: C, 35.03; H, 7.37; Cl, 13.43. Calcd. for $C_{15}H_{36}Cl_2P_4Ru$ (512.33): C, 35.17; H, 7.08; Cl, 13.84%.

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[≠] The yellow isomer, *i.e.* $RuCl_2[\underline{S}(O)Me_2]_3(\underline{O}SMe_2)$ [7], was used.

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$RuBr_2[P(CH_2CH_2CH_2PMe_2)_3]$ (2)

By analogy to compound **1** from $RuBr_2(PPh_3)_3$ (2.90 g, 2.77 mmol) [8] and 0.94 g (2.77 mmol) of the tetradentate in 250 ml of toluene; yield: 1.01 g (61%) of yellow complex **2**. *Anal.* Found: C, 31.42; H, 6.43; Br, 26.21. Calcd. for $C_{15}H_{36}Br_2P_4Ru$ (601.24): C, 29.97; H, 6.04; Br, 26.58%.

$Ru(H)Cl[P(CH_2CH_2CH_2PMe_2)_3]$ (3)

A mixture of **1** (0.62 g, 1.21 mmol) and $LiAlH_4$ (0.40 g, 10.54 mmol) in THF (80 ml) was stirred at room temperature for 60 h. The filtered solution was treated with ethanol (5 ml) and evaporated to dryness. The residue was extracted several times with small portions of a toluene/hexane mixture (1:4 v/v; 200 ml collectively). After filtration, the combined extract liquors were reduced to dryness, and the residual material was re-dissolved in hexane (5 × 20 ml). The solution was filtered and again taken to dryness to yield 0.19 g (33%) of greyish-white complex **3**. *Anal.* Found: C, 37.64; H, 7.86; Cl, 7.30; P, 25.00. Calcd. for $C_{15}H_{37}ClP_4Ru$ (477.88): C, 37.70; H, 7.80; Cl, 7.42; P, 25.93%.

$RuH_2[P(CH_2CH_2CH_2PMe_2)_3]$ (4)

To a solution of 1.68 g (3.28 mmol) of **1** in 80 ml of THF was added 0.48 g (12.64 mmol) of $LiAlH_4$. The mixture was stirred at room temperature for 65 h, filtered, and subsequently evaporated to dryness. The residual solid was extracted with several portions of a total of 100 ml of toluene, which were filtered and again reduced to dryness. The residue thus obtained was re-dissolved in toluene (3 × 15–20 ml), and the filtered colorless extract liquor was treated with 3 ml of ethanol. Removal of the solvent yielded a residue which was extracted several times with hexane (60 ml collectively). The resulting solution was filtered and evaporated to give 0.66 g (45%) of crude complex **4** as a white powder. For purification, this material was sublimed at 70 °C in the dynamic vacuum of a mercury diffusion pump to yield 0.50 g (34%) of the dihydride as white crystals. *Anal.* Found: C, 40.73; H, 8.91. Calcd. for $C_{15}H_{38}P_4Ru$ (443.43): C, 40.63; H, 8.64%.

X-ray Study*

Crystals of **1** suitable for X-ray work were grown from CH_2Cl_2/hexane. X-ray measurements were made at room temperature on a Syntex $P2_1$ diffractometer using Mo Kα radiation (λ = 71.069 pm). Details of data collection ($\theta/2\theta$ scan) and processing, and of programs used, have been described previously [9]. Absorption corrections were not applied.

Crystallographic data

$C_{15}H_{36}Cl_2P_4Ru$ (**1**): $M = 512.33$; monoclinic, space group $P2_1/n$; $a = 942.0(3)$, $b = 1446.2(4)$, $c = 1680(1)$ pm, $\beta = 104.99(4)°$; $V = 2210.4 \times 10^6$ pm^3, $Z = 4$, $D = 1.540$ g cm^{-3}, $\mu = 11.23$ cm^{-1}.

Structure solution and refinement

Out of the 3921 independent intensities collected within the range $2° \leqslant 2\theta \leqslant 50°$, 3318 gave structure factors with $|F_o| > 3\sigma(F_o)$, and only these were used in the subsequent analysis. The structure was solved by conventional Patterson and difference Fourier techniques. Anisotropic refinement resulted in convergence at $R = 0.040$ and $R_w = 0.034$ ($w = 1/\sigma^2(F_o)$; hydrogen atoms in idealized positions with allowance for isotropic vibrations; d(C–H), 96 pm). Final atomic positions are presented in Table I. Selected bond lengths and angles are contained in the legend to Fig. 1, which gives a perspective view of the molecule.

TABLE I. Atomic Positions with e.s.d.s

Atom	*x/a*	*y/b*	*z/c*
Ru	0.56830(4)	0.30462(2)	0.28586(2)
Cl(1)	0.41408(14)	0.18130(9)	0.20037(8)
Cl(2)	0.79239(13)	0.20246(9)	0.31191(8)
P(1)	0.62271(15)	0.34017(9)	0.15775(8)
P(2)	0.71668(15)	0.41087(9)	0.36723(8)
P(3)	0.49205(15)	0.23244(9)	0.39374(8)
P(4)	0.36506(14)	0.39347(9)	0.25968(8)
C(11)	0.7616(9)	0.4196(6)	0.1413(4)
C(12)	0.6758(9)	0.2387(4)	0.1074(4)
C(13)	0.4646(7)	0.3813(5)	0.0763(4)
C(14)	0.3907(8)	0.4661(4)	0.1037(4)
C(15)	0.2867(7)	0.4362(5)	0.1535(3)
C(21)	0.8509(7)	0.4761(4)	0.3269(4)
C(22)	0.8449(8)	0.3676(5)	0.4613(4)
C(23)	0.6302(7)	0.5062(4)	0.4060(4)
C(24)	0.5077(7)	0.5539(4)	0.3393(4)
C(25)	0.3652(6)	0.4974(4)	0.3213(4)
C(31)	0.5253(8)	0.2792(4)	0.4989(3)
C(32)	0.5624(7)	0.1154(3)	0.4145(4)
C(33)	0.2948(6)	0.2100(4)	0.3723(4)
C(34)	0.1977(7)	0.2951(5)	0.3544(4)
C(35)	0.1942(6)	0.3399(5)	0.2709(4)

Results and Discussion

The strategy of synthesis applied for the preparation of the $P(CH_2CH_2CH_2PMe_2)_3$ derivatives **1** and **2** involves the displacement of the unidentate ligands

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*Further crystallographic information including the calculated coordinates of the hydrogen atoms, tables of thermal parameters and F_o/F_c listings are available from the Fachinformationszentrum Energie, Physik, Mathematik GmbH (cooperating with the Cambridge Crystallographic Data Centre), D-7514 Eggenstein-Leopoldshafen 2 (F.R.G.). Any request should be accompanied by the registration number CSD-51381, as well as by the full literature citation for this communication.

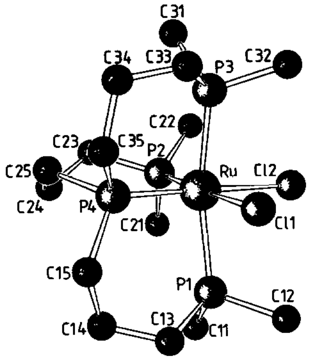

Fig. 1. The structure of $RuCl_2[P(CH_2CH_2CH_2PMe_2)_3]$ (1). Important bond lengths (pm) and angles (°) are: Cl1–Ru, 250.5(1); Cl2–Ru, 252.1(1); P1–Ru, 239.3(1); P2–Ru, 227.9(1); P3–Ru, 235.8(1); P4–Ru, 225.3(1). Cl2–Ru–Cl1, 91.0; P1–Ru–Cl1, 82.2; P1–Ru–Cl2, 85.3; P2–Ru–Cl1, 177.0; P2–Ru–Cl2, 86.3; P2–Ru–P1, 98.8; P3–Ru–Cl1, 83.0; P3–Ru–Cl2, 90.9; P3–Ru–P1, 164.7; P3–Ru–P2, 95.7; P4–Ru–Cl1, 87.5; P4–Ru–Cl2, 178.5; P4–Ru–P1, 94.1; P4–Ru–P2, 95.2; P4–Ru–P3, 89.4 (the e.s.d.s of the angles are less than 0.1°).

from $RuX_2(PPh_3)_3$ (X = Cl, Br), $RuCl_2(PR_3)_4$ (R = Me, Ph), or $RuCl_2(Me_2SO)_4$ by the chelate phosphine. Similar methods have previously been utilized by Khan and Mohiuddin [10] and by de Gil and coworkers [11], who prepared and characterized some complexes of ruthenium(II) containing the linear tetradentate $[Ph_2PCH_2CH_2P(Ph)CH_2-]_2$.

Different from $RuCl_2\{[Ph_2PCH_2CH_2P(Ph)CH_2-]_2\}$ which, as a solid, adopts a *trans*-octahedral structure [11] but behaves as a 1:1 electrolyte in dimethyl acetamide [10], the complexes **1** and **2** are hexacoordinate both in the solid state and in solution. This is confirmed by their lack of electrolytic conductivity, by their ^{31}P NMR spectra, and by an X-ray structure determination for the chloride **1**.

On the basis of their phosphorus-31 spectra (which are of AMX_2 type), both **1** and **2** have been assigned *cis*-octahedral coordination geometry. The parameters collected in Table II were extracted from the resonance patterns. In agreement with the empirical assignments given by Venanzi [12] for the ^{31}P NMR spectrum of *cis*-$RuCl_2[P(o\text{-}C_6H_4PPh_2)_3]$ and by ourselves [3] for that of *cis*-$FeCl_2[P(CH_2CH_2CH_2PMe_2)_3]$, the resonance due to P_A was attributed to the nucleus of the bridging $P(CH_2-)_3$ moiety.

Cis-octahedral hexacoordination similar to that found for $RuBr_2[As(o\text{-}C_6H_4AsPh_2)_3]$ [13] is also evident from the results of the X-ray diffraction study performed on **1** (Fig. 1). Due to the flexibility of the trimethylene connecting chains of the $P(CH_2CH_2CH_2PMe_2)_3$ ligand, the chelates of **1** are much less constrained than are those of $RuCl_2\{[Ph_2PCH_2CH_2P(Ph)CH_2-]_2\}$ [11]. In the latter complex, the $-CH_2CH_2-$ linkages of the tetraligate phosphine permit P–Ru–P chelate bite angles of 81.9, 83.3 and 84.3° only, whilst in **1** the phosphorus–metal–phosphorus bond angles within the six-membered rings vary between 89.4 and 95.2°. As a consequence of the pronounced *trans*-bond weakening effect exerted by P donor ligands, the ruthenium-to-chloride distances of the *cis* configurated complex **1**, 250.5(1) and 252.1(1) pm, are considerably longer than those of 241.7(4) and 246.3(4) pm observed for the $[Ph_2PCH_2CH_2P(Ph)CH_2-]_2$ derived dichlororuthenium(II) complex which, as mentioned above, contains a *trans*-Cl–Ru–Cl unit [11].

TABLE II. ^{31}P NMR data[a]

	1	2	3	4	
$\delta(P_A)$	22.0	20.5	32.6	4.1	
$\delta(P_M)$	17.4	16.4	−11.2	0.8	
$\delta(P_X)$	−9.3	−14.8	−1.3	5.0	
$^2J(P_AP_M)$	39	36	27	28	Hz
$^2J(P_AP_X)$	39	36	40	32	Hz
$^2J(P_MP_X)$	30	30	22	25	Hz

[a] *cf.* Experimental; 1 in EtOH, 2 in CH_2Cl_2, 3 and 4 in toluene; $P_A = P(CH_2-)_3$, $P_M = P(CH_2-)Me_2$ (*trans*-atom Cl, Br, or H), $P_X = P(CH_2-)Me_2$ (*trans*-atom P) [3, 12]; mutual assignment of P_A and P_M for complex 3 uncertain (see text).

Depending upon the working-up method (*cf.* Experimental), either the hydrochloride $Ru(H)Cl[P(CH_2CH_2CH_2PMe_2)_3]$ (**3**) or the dihydride $RuH_2[P(CH_2CH_2CH_2PMe_2)_3]$ (**4**) was isolated from the reaction of **1** with $LiAlH_4$ in THF. The IR spectrum of complex **3** shows a strong hydride stretch at 1809 cm^{-1}, and the symmetric and asymmetric $\nu(RuH_2)$ vibrations of **4** give rise to equally strong absorptions occurring at 1808 and 1736 cm^{-1}. Similar to the ^{31}P NMR spectra of **1** and **2**, the $^{31}P\{^1H\}$ patterns observed for the *cis*-configurated complexes **3** and **4** present examples of AMX_2 spin systems (Table II). The ^1H NMR spectrum of the dihydride **4**, collected in C_6D_6, contained two RuH multiplets centered at $\delta = -8.20$ and $\delta = -9.45$. We were not able to apply ^{31}P decoupling techniques and thus could not extract any reliable $^1H-^{31}P$ or $^1H-^1H$ coupling constant from these $ABXYZ_2$ resonance patterns. The proton spectrum of the hydrochloride **3**, obtained in acetone-d_6, showed the RuH resonance at $\delta = -8.04$ as a doublet of quartets with *trans*-$^2J(PH) = 123.2$ and *cis*-$^2J(PH) = 28.1$ Hz. It was not possible to deduce the position of the hydride ligand of **3**, *trans* to the bridging $\mathit{P}(CH_2-)_3$ nucleus or *trans* to one of the PMe_2 substituents, from the ^1H and ^{31}P NMR spectra of this compound.

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