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THE CHEMISTRY AND CATALYTIC ACTIVITY OF NEW CATIONIC RUTHENIUM(II) COMPLEXES IN THE HYDROGENATION OF CYCLOHEXENE. CRYSTAL STRUCTURE OF $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2PCH_2CH_2AsPh_2)]ClO_4 \cdot n-C_5H_{12}$

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Abstract—Interaction of neutral ruthenium(II) complexes of the type $[RuHCl(CO)(PPh_3)(L\text{-}L')]$ [where L-L′ = $Ph_2PCH_2CH_2PPh_2$ (dppe), **1**; $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), **2**; $Ph_2PCH_2CH_2AsPh_2$ (arphos), **3**] with $AgClO_4$ in the presence of L″ [L″ = $P(OMe)_3$ or PMe_3] yielded the new cationic ruthenium(II) complexes $[RuH(CO)(PPh_3)(L'')(L\text{-}L')]ClO_4$ [where L-L′ = dppe, **4**; dppp, **5**; arphos, **6**; L″ = PMe_3, **4**; $P(OMe)_3$, **5** and **6**]. All the complexes have been characterized by both analytical and spectroscopic (IR and ^1H NMR) methods. The structure of a cationic complex **6**, $[RuH(CO)(PPh_3)(P(OMe)_3)(arphos)]ClO_4 \cdot n-C_5H_{12}$, has been confirmed by single-crystal X-ray diffraction. The Ru atom is octahedrally coordinated with CO, PPh_3 and arphos in the equatorial plane and H and $P(OMe)_3$ in the axial positions. In the hydrogenation of cyclohexene, some relations between structures and catalytic activities have been studied. The cationic complexes have shown lower catalytic activities than their neutral analogues.

The hydridocarbonyl ruthenium(II) phosphine complex, $RuHCl(CO)(PPh_3)_3$, has been found to catalyse many organic reactions such as isomerization, hydrogenation, hydroformylation, etc.[1–4] Its unambiguous stereochemistry was revealed by Sanchez-Delgado *et al.*[5] Interaction between $[MHCl(CO)(PPh_3)_3]$ (M = Ru or Os) and neutral ligands [L = $P(OR)Ph_2$, $P(OR)_2Ph$ or $P(OR)_3$, respectively; R = Me or Et] has resulted in the formation of $[RuHCl(CO)(L)(PPh_3)_2]$.[6] Recently, we have reported the preparation and catalytic activity of $[MHCl(CO)(PPh_3)(L\text{-}L')]$, where M = Ru or Os and L-L′ = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), *cis*-$Ph_2PCH{=}CHPPh_2$ (dppv), $Fe(\eta^5-C_5H_4PPh_2)_2$ (dppf), $Ph_2PCH_2CH_2AsPh_2$ (arphos) and $Ph_2AsCH_2CH_2AsPh_2$ (diarsine).[7–10] These ruthenium(II) complexes with bidentate chelate ligands are moderately stable and efficient catalyst precursors in the homogeneous reduction of C=O and C=C bonds of organic compounds.

To study this catalytic system further, we have synthesized the cationic ruthenium(II) analogues of $[RuHCl(CO)(PPh_3)(L\text{-}L')]$ (L-L′ = **1**, dppe; **2**, dppp; **3**, arphos) having a chelate ring. Other cationic analogues of $RuHCl(CO)(PPh_3)_3$ such as $[RuH(CO)(NCMe)_2(PPh_3)_2]ClO_4^{11}$ and $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4^{5}$ are known, although they do not contain a chelate ring.

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EXPERIMENTAL

Preparations and chemical reagents

Toluene, cyclohexene and n-heptane were fractionally distilled and stored over molecular sieves (4A). The preparations of all the complexes were necessarily performed in an oxygen-free environment. $RuCl_3 \cdot 3H_2O$, $AgClO_4$, PPh_3, $P(OMe)_3$, PMe_3, dppe and dppp ligands were purchased from Aldrich, arphos from Alfa Products, and used without further purification. All other chemicals and solvents were commercial reagent grade.

Physical measurements

^1H NMR spectra were recorded on Varian Gemini-300 (300 MHz) instruments. Chemical shifts are expressed in ppm relative to $SiMe_4$. IR spectra were measured with a MIDAC model 101025 FT-IR spectrometer in KBr discs. Elemental analyses were performed at Micro-Tech Analytical Laboratories, Skokie, Illinois, U.S.A. The analyses of the products of the catalytic reactions were carried out with a Hewlett Packard 5890 Series II gas chromatograph using the HP-5 (cross-linked 5% PhMe silicone; 25 m × 0.2 mm × 0.11 μm film thickness) column and internal standard (n-heptane) method. The chromatograph was connected to a HP3394A integrator.

Preparations of $[RuHCl(CO)(PPh_3)(L\text{-}L')]$ [where L-L′ = $Ph_2PCH_2CH_2PPh_2$ (dppe), **1**; $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), **2**; $Ph_2PCH_2CH_2AsPh_2$ (arphos), **3**]

Complexes **1**, **2** and **3** were prepared analogously by a previous method.[9,10]

Preparations of $[RuH(CO)(PPh_3)(PMe_3)(Ph_2PCH_2CH_2PPh_2)]ClO_4$ (**4**)

The compounds $[RuHCl(CO)(PPh_3)(dppe)]$ (**1**; 248 mg, 0.3 mmol), PMe_3 (23 mg, 0.3 mmol) and $AgClO_4$ (63 mg, 0.3 mmol) were vigorously stirred in CH_2Cl_2 (25 cm^3) at room temperature for 1 h, during which time AgCl was precipitated. After removal of AgCl by filtration the solution was evaporated in reduced pressure and the resultant residue was recrystallized from CH_2Cl_2/n-pentane to yield $[RuH(CO)(PPh_3)(PMe_3)(dppe)]ClO_4$ (**4**) as a grey powder. The resultant powder was filtered off in air and washed with n-pentane (30 cm^3) and dried *in vacuo* (195 mg, 67%). Found: C, 59.1; H, 5.0. $C_{48}H_{49}O_5ClP_4Ru$ requires: C, 59.6; H, 5.1%. IR (KBr disc, cm^{-1}): 1969 vs, 1622 w, 1485 m, 1435 s, 1190 m, 1094 vs, 747 s, 696 s, 623 m, 529 s. ^1H NMR (300 MHz, acetone-d_6, 25°C): δ −6.9 ppm (quintet).

Preparations of $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2PCH_2CH_2CH_2PPh_2)]ClO_4$ (**5**)

The compounds $[RuHCl(CO)(PPh_3)(dppp)]$ (**2**; 252 mg, 0.3 mmol), $P(OMe)_3$ (37 mg, 0.3 mmol) and $AgClO_4$ (63 mg, 0.3 mmol) were vigorously stirred in CH_2Cl_2 (25 cm^3) at room temperature for 1 h, during which time AgCl was precipitated. After removal of AgCl by filtration the solution was evaporated under reduced pressure and the resultant residue was recrystallized from CH_2Cl_2/n-pentane to yield $[RuH(CO)(PPh_3)(P(OMe)_3)(dppp)]ClO_4$ (**5**) as a white powder. The resultant powder was filtered off in air and washed with n-pentane (30 cm^3) and dried *in vacuo* (129 mg, 42%). Found: C, 56.9; H, 5.0. $C_{49}H_{51}O_8ClP_4Ru$ requires: C, 57.2; H, 5.0%. IR (KBr discs, cm^{-1}): 1983 vs, 1653 w, 1485 w, 1435 m, 1174 m, 1094 vs, 1028 s, 746 s, 698 s, 623 m, 513 s. ^1H NMR (300 MHz, $CDCl_3$ 25°C): δ −7.4 ppm (doublet of multiplet).

Preparations of $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2PCH_2CH_2AsPh_2)]ClO_4$ (**6**)

The compounds $[RuHCl(CO)(PPh_3)(arphos)]$ (**3**; 261 mg, 0.3 mmol), $P(OMe)_3$ (37 mg, 0.3 mmol) and $AgClO_4$ (63 mg, 0.3 mmol) were vigorously stirred in CH_2Cl_2 (25 cm^3) at room temperature for 12 h, during which time AgCl was precipitated. After removal of AgCl by filtration the solution was evaporated in reduced pressure and the resultant residue was recrystallized from CH_2Cl_2/ethyl ether to yield $[RuH(CO)(PPh_3)(P(OMe)_3)(arphos)]ClO_4$ (**6**) as a white powder. The resultant powder was filtered off in air and washed with ethyl ether (30 cm^3) and dried *in vacuo* (149 mg, 47%). Found: C, 53.9; H, 4.7. $C_{48}H_{49}O_8AsClP_3Ru$ requires: C, 54.4; H, 4.6%. IR (KBr discs, cm^{-1}): 1969 vs 1483 m, 1435 s, 1184 w, 1092 vs, 1030 s, 868 w, 747 s, 694 s, 623 m, 519 s. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ −7.7 ppm (doublet of quartets).

Structure determination of $[RuH(CO)(PPh_3)(P(OMe)_3)(arphos)]\ ClO_4 \cdot n\text{-}C_5H_{12}$, *crystal data, X-ray data collection and structural determination*

Crystals of $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2PCH_2CH_2AsPh_2)]ClO_4 \cdot n\text{-}C_5H_{12}$, (**6**) were grown by dissolving the compound in CH_2Cl_2 solution and layering of n-pentane in an NMR tube in air at ambient temperature. Colourless crystals were formed in the tube after several days. This complex crystallizes in the space group $P\bar{1}$ (No. 2) with cell parameters $a = 12.606(3)$, $b = 14.980(4)$, $c = 15.542(6)$ Å, $\alpha = 111.59(3)$, $\beta = 94.995(3)$, $\gamma = 102.98(2)^\circ$, $Z = 2$, $V = 2612.2(16)$ Å^3, $R = 0.056$ and $R_w = 0.066$ for the 3549 intensities with $F_o^2 > 3\sigma\,(F_o)^2$ and 603 variables.

A crystal (0.4 × 0.35 × 0.3 mm) sealed in a Lindemann capillary tube was mounted on an Enraf–Nonius CAD-4 diffractometer. X-ray data were collected using Mo-K_α radiation at room temperature. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The intensities of 3 standard reflections, recorded every 3 h of X-ray exposure, decayed by 50.7% on average by the end of the data collection. Crystal and refinement data are noted in Table 1.

The intensity data were corrected for Lorentz–polarization effects and crystal decay. Empirical absorption corrections were also applied (DIFABS). The structures were solved by a combination of Patterson and difference Fourier methods (SHELX86).[12] The hydride atom could not be located in the difference Fourier map. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. A disordered n-pentane molecule are found in the asymmetric unit and refined anisotropically. The positions of hydrogen atoms were idealized ($d_{\mathrm{C-H}} = 0.95$ Å) and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of attached atom. All the calculations except solving structures were carried out with the Enraf–Nonius MolEN program package. Bond lengths and bond angles are given in Table 2.

Hydrogenation reactions

Hydrogenation reactions were carried out analogously by a previous method using an autoclave.[9,13]

Table 1. Crystal and refinement data for complex **6**·n-C_5H_{12}

Formula	$C_{48}H_{49}O_8AsClP_3Ru \cdot C_5H_{12}$
fw	1130.44
Crystal system	Triclinic
Space group	$P\bar{1}$ (No.2)
a (Å)	12.606(3)
b (Å)	14.980(4)
c (Å)	15.542(6)
α (°)	111.59(3)
β (°)	94.995(3)
γ (°)	102.98(2)
V (Å^3)	2612.2(16)
Z	2
Temperature (°C)	23
d_{calc} (g/cm^3)	1.449
λ(Mo-K_α) (Å)	0.71073
Monochromator	Graphite
Linear absorption coefficient (cm^{-1})	11.22
Crystal dimensions (mm)	0.4 × 0.35 × 0.3
Crystal colour	colourless
Scan mode	ω
ω-scan width (°)	$0.85 + 0.35\tan\theta$
2θ range (°)	42
No. of data collected	5739
No. of unique data	5555
No. of data with $I > 3\sigma(I)$	3549
No. of parameters	603
R^a	0.056
$R_\omega(F)^b$	0.066

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

$^b R_\omega = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$; $\omega = 4F_o^2/\sigma^2(F_o^2)$; $\sigma(F_o^2) = [\sigma^2(I) + (pF_o^2)^2]^{1/2}$, $p = 0.04$.

Table 2. Selected bond distance (Å) and angles (°) for complex **6**, $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2PCH_2CH_2AsPh_2)]ClO_4 \cdot n\text{-}C_5H_{12}$[a]

Ru—As	2.496(1)	P(2)—C(25)	1.84(2)
Ru—P(3)	2.386(3)	P(3)—C(43)	1.81(2)
As—C(11)	1.93(1)	O(3)—C(3)	1.39(3)
P(1)—O(3)	1.59(1)	Cl—O(5)	1.42(1)
P(2)—C(19)	1.84(2)	Cl—O(8)	1.39(1)
P(3)—C(37)	1.81(1)	Ru—P(2)	2.354(3)
O(2)—C(2)	1.41(3)	As—C(5)	1.91(2)
C(17)—C(18)	1.53(3)	P(1)—O(2)	1.581(8)
Cl—O(7)	1.44(2)	P(2)—C(18)	1.79(2)
Ru—P(1)	2.347(4)	P(3)—C(31)	1.80(2)
Ru—C(1)	1.38(1)	O(1)—C(1)	1.17(1)
As—C(17)	1.97(2)	O(4)—C(4)	1.24(3)
P(1)—O(4)	1.55(1)	Cl—O(6)	1.38(2)

As—Ru—P(1)	99.90(8)	As—Ru—P(2)	83.09(8)
As—Ru—P(3)	97.96(8)	As—Ru—C(1)	158.3(6)
P(1)—Ru—P(2)	92.2(1)	P(1)—Ru—P(3)	97.3(1)
P(1)—Ru—C(1)	100.0(6)	P(2)—Ru—P(3)	170.1(1)
P(2)—Ru—C(1)	87.6(5)	P(3)—Ru—C(1)	88.0(5)
Ru—As—C(5)	117.9(4)	Ru—As—C(11)	128.7(5)
Ru—As—C(17)	102.4(5)	C(5)—As—C(11)	101.6(6)
C(5)—As—C(17)	101.5(8)	C(11)—As—C(17)	100.2(7)
Ru—P(1)—O(2)	114.8(4)	Ru—P(1)—O(3)	108.8(4)
Ru—P(1)—O(4)	120.8(4)	O(2)—P(1)—O(3)	106.1(4)
O(2)—P(1)—O(4)	104.8(6)	O(3)—P(1)—O(4)	99.7(6)
Ru—P(2)—O(18)	111.1(6)	Ru—P(2)—O(19)	118.2(5)
Ru—P(2)—O(25)	116.6(5)	C(18)—P(2)—C(19)	106.6(8)
C(18)—P(2)—C(25)	102.1(8)	C(19)—P(2)—C(25)	100.5(7)
Ru—P(3)—O(31)	114.7(5)	Ru—P(3)—O(37)	119.4(5)
Ru—P(3)—O(43)	114.7(5)	C(31)—P(3)—C(37)	102.7(7)
C(31)—P(3)—C(43)	101.8(7)	C(37)—P(3)—C(43)	101.1(7)
P(1)—O(2)—C(2)	126.0(1)	P(1)—O(3)—C(3)	128.0(1)
P(1)—O(4)—C(4)	135.0(2)	Ru—C(1)—O(1)	174.0(2)
As—C(5)—C(6)	123.0(1)	As—C(5)—C(10)	118.0(1)
As—C(11)—C(12)	117.0(1)	As—C(11)—C(16)	122.0(1)
As—C(17)—C(18)	108.0(1)	P(2)—C(18)—C(17)	111.0(1)
P(2)—C(19)—C(20)	122.0(1)	P(2)—C(19)—C(24)	119.0(1)
P(2)—C(25)—C(26)	118.0(1)	P(2)—C(25)—C(30)	122.0(1)
P(3)—C(31)—C(32)	118.0(1)	P(3)—C(31)—C(36)	123.0(1)
P(3)—C(37)—C(38)	118.0(1)	P(3)—C(37)—C(42)	123.0(1)
P(3)—C(43)—C(44)	121.0(1)	P(3)—C(43)—C(48)	121.0(1)

[a] Atoms are labelled in accordance with Fig. 1. Numbers in parentheses are the estimated standard deviations in the least significant figure.

RESULTS AND DISCUSSION

In the case of halide-bearing metal complexes, halide abstraction method is a very useful way of preparing their cationic analogues.[14] Strictly speaking, this halide abstraction results in the cationic complex salts with non-coordinating anions, e.g. ClO_4^-, BF_4^-, PF_6^-, BPh_4^-, etc., although sometimes they can weakly coordinate to the metal centre.[15] We have synthesized three new cationic ruthenium(II) complexes containing a bidentate chelate ligand and a neutral ligand L″ [L″ = $P(OMe)_3$ or PMe_3] via the substitution of the chloride ligand by a neutral ligand L″ in the presence of $AgClO_4$ in CH_2Cl_2 at room temperature. The transformations observed in this work are summarized in eq (1) and the spectroscopic data are shown in Table 3.

For all cationic complexes there is an increase in the ν(CO) stretching frequency with respect to those for their corresponding starting compounds. They are all up to 1960 cm^{-1}, as shown in Table 3; in fact,

Table 3. Spectroscopic data

	^1H NMR (ppm, $SiMe_4$)		IR (cm^{-1})^a		
Complex	δ(Ru—H)	^2J(P—H) (Hz)	ν(CO)	ν(ClO)	ν(OClO)
1^b	-5.8(dq)	115.0, 16.8, 16.9	1931	—	—
	-15.5(dt)	25.5, 17.3, 17.3			
2^c	-6.1(m), -14.9(m)	—	1927	—	—
3^b	-7.0(dd)	20.7, 15.9	1935	—	—
4^d	-6.9(quint)	19.3	1969	1094	623
5^b	-7.4(dm)	130	1983	1094	623
6^b	-7.7(dq)	129.0, 19.2, 17.2	1969	1092	623

^{a} KBr discs.
^{b} In $CDCl_3$.
^{c} In toluene-d_8.
^{d} In acetone-d_6.

the increase in $v(C\equiv O)$ on going to the cationic complexes almost certainly arises because there is an overall reduction of electron density on the Ru centre (because it is cationic) and hence less back-bonding to the CO.

The substitution of the chloride ligand with $AgClO_4$ and a neutral ligand L″ [L″ = $P(OMe)_3$ or PMe_3], in the ruthenium(II) complexes of the type $RuHCl(CO)(PPh_3)(L\text{-}L')$ can give $[RuH(CO)(PPh_3)(L'')(L\text{-}L')]ClO_4$, as shown in eq. (1), with the incoming ligand L″ *cis* or *trans* position relative to the hydride ligand.

$$RuHCl(CO)(PPh_3)(L\text{-}L') \xrightarrow[AgClO_4]{L''}$$

(1–3)

$$[RuH(CO)(PPh_3)(L'')(L\text{-}L')]ClO_4 + AgCl\downarrow$$

(4–6)

L-L″ = dppe(**1** and **4**), dppp (**2** and **5**), arphos (**3** and **6**)

$$L'' = PMe_3\,(\mathbf{4}), P(OMe)_3\ (\mathbf{5}\ \text{and}\ \mathbf{6}) \qquad (1)$$

^1H NMR spectra of complex **4**, which contains PMe_3 (more basic alkylphosphine than alkylphosphites), has shown quintet hydride signals (integral ratio = 1 : 4 : 6 : 4 : 1) at δ *ca* -6.9 ppm in acetone-d_6 with ^2J(H—*cis*-P) = 19.3 Hz. Therefore, all phosphine ligands are located in the *cis*-position to the hydride ligand. In the case of complex **5**, $[RuH(CO)(PPh_3)(P(OMe)_3)(dppp)]ClO_4$, the hydride signals in the ^1H NMR spectra were poorly resolved at *ca* -7.4 ppm [^2J(H—*trans*-P) $\simeq$ 130 Hz], respectively. There is good evidence from the IR spectroscopic data, however, that for all the cationic complexes there is an increase in the ν(CO) stretching frequency with respect to those for their starting compounds. They are all up to 1960 cm^{-1}, as shown in Table 3 which is indicative of the *trans* position of the carbonyl ligand being occupied by a good π-bonding ligand such as an incoming L″ or phosphorus or arsenic atom of the chelate ligand instead of the chloride ligand, which was abstracted in the course of substitution[16] and also indicative of the cationic metal centre discussed previously but for complex **4**.

In the cation of **6**, the resonance signals for the hydridic hydrogen shows a clearly resolved doublet of quartets at δ *ca* -7.7 ppm, with ^2J(H—*trans*-P) = 129.0 Hz, ^2J(H—*cis*-P) = 19.2 and 17.2 Hz, corresponding to the coupling with one *trans*-phosphorus atom and two inequivalent *cis*-phosphorus atoms, which is in agreement with the solid-state structure of **6**.

The crystal structure of complex **6**, $[RuH(CO)(PPh_3)(P(OPMe)_3)(arphos)]ClO_4 \cdot n\text{-}C_5H_{12}$ has been confirmed by single-crystal X-ray diffraction. The overall geometry of the solvated complex **6** is shown in Fig. 1, along with the labelling scheme used for the atoms. Interatomic distances and angles are listed in the Table 2. The geometry of the coordination sphere is best described as a six-coordinate distorted octahedron in which the ruthenium atom is coordinated with CO, PPh_3 and arphos in the equatorial plane; H and $P(OMe)_3$ in the axial positions. The interatomic distance of 1.83(1) Å involving Ru—C(1) is expected and agrees well with those observed in other mononuclear hydridocarbonyl Ru^{II} complexes reported previously.[17] The geometry of the coordinated phosphorus or arsenic ligands is similar to that observed in other Ru complexes. The arphos ligand bonded to Ru atom in an usual bidentate manner with δ conformation. The bond from Ru to P(3) [2.386(3) Å] is long compared with those of

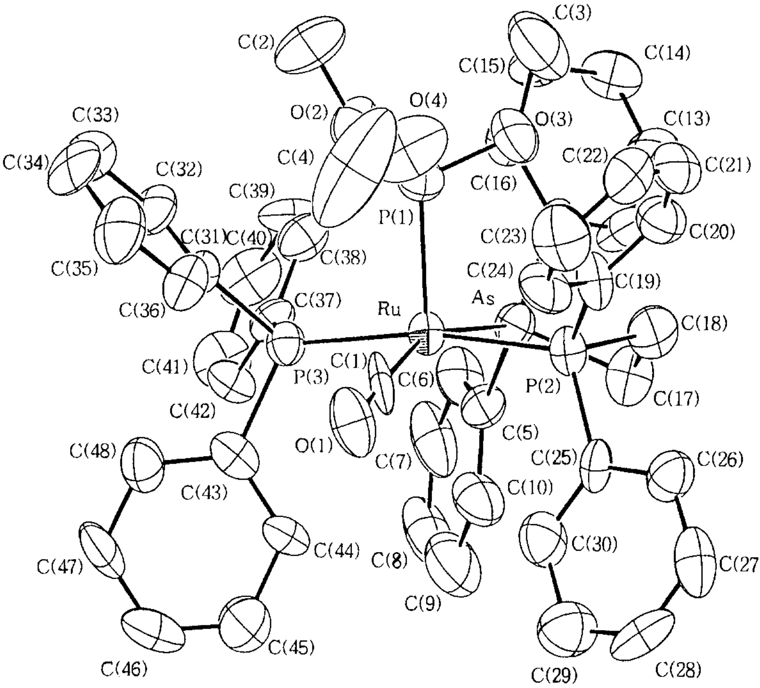

Fig. 1. View of a $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2CH_2AsPh_2)]ClO_4 \cdot n\text{-}C_5H_{12}$ molecule with atom numbering. The ClO_4^- and $n\text{-}C_5H_{12}$ are omitted for clarity. The metal bonded H atom was not deleted and is not shown here.

Ru—P(1)[2.347(4) Å] and Ru—P(2) [2.354(3) Å]. The lengthening might be due to restrictions imposed by the bulky PPh_3 ligand. However, the Ru—P and Ru—As [2.496(1) Å] bond lengths lie within the sum of the relevant van der Waals radii of Ru^{II}, phosphorus ($1.33+1.1 = 2.43$ Å) and the arsenic atom ($1.33+1.21 = 2.54$ Å), respectively.[18] The As—Ru—C(1) [158.3(6)°], P(2)—Ru—P(3) [170.1(1)°], As—Ru—P(1) [99.90(8)°] and P(1)—Ru—C(1) [100.0(6)°] angles are considerably distorted from the ideal octahedral geometry in order to minimize the steric congestion arising from the meridional arrangements of three bulky ligands, PPh_3 and arphos. Further distortion from the octahedral structure is caused by the small size of the hydride ligand, although its position cannot be obtained. The ClO_4^- ion maintains a T_d symmetry as in Table 2. Other bond distances and angles are normal.

The catalytic activities of these complexes have been examined in the hydrogenation of cyclohexene to cyclohexane. Rate constants (k_{obs}) have been obtained from the slopes of the ln[cyclohexene] versus time lines, and the experimental data are shown in Table 4. There has been no detectable side reaction in the hydrogenation of cyclohexene (mass balances were over 95%). Their activities decreases in the order **2** > **5** > **1** > **4** > **3** > **6** for the cyclohexene reduction. In summary, the cationic complexes have shown lower catalytic activities than their neutral pairs.

As shown in our proposed mechanism for *trans*-isomers,[7–10] the first step in the catalytic cycle might be the dissociation of *trans*-positioned ligand relative to the hydride ligand to produce a vacant site for the substrate accommodation. This step might also have a great role in the catalytic activities of the complexes $[RuHCl(CO)(PPh_3)(L\text{-}L')]$ (L-L′ = dppm, dppe, dppp, dppv and dppf). This equilibrium between 18-electron and 16-electron species may also be an important process for the catalytic system in this work. Compared with neutral complexes (**2** and **3**), the cationic analogues (**5** and **6**), possessing a small *trans*-positioned $P(OMe)_3$ ligand to the hydride ligand, may show a low dissociation ability of the *trans*-positioned ligand according to the previous mechanism.[9]

The lower catalytic activity of cationic complexes (**4**, **5** and **6**) may be explained in terms of the previously proposed mechanism. Cation **5** has a higher catalytic activity than complexes **1** and **3**, which contain the relatively bulkier *trans*-positioned —PPh_2 or —$AsPh_2$ moiety of the chelate ligands (dppe or arphos) than $P(OMe)_3$. This can be explained by means of the combined effect of fluxionality and basicity of the dppp ligand, as mentioned earlier.[9] Complex **5** dissociates *trans*-positioned $P(OMe)_3$ relatively more slowly than complexes **1**

Table 4. Hydrogenation of cyclohexene by Ru complexes[a]

Complex	$k_{obs} \times 10^3$ (min^{-1})[b]	Rel. Act[c]
1, $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$	22.28 ± 0.11[d]	—
2, $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$	73.49 ± 0.22[d]	—
3, $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)$	4.76 ± 0.04[d]	—
4, $[RuH(CO)(PPh_3)(PMe_3)(Ph_2PCH_2CH_2PPh_2)]ClO_4$	5.15 ± 0.02	0.23
5, $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2PCH_2CH_2CH_2PPh_2)]ClO_4$	27.51 ± 0.29	0.37
6, $[RuH(CO)(PPh_3)(P(OMe)_3)(Ph_2PCH_2CH_2AsPh_2)]ClO_4$	1.22 ± 0.03	0.26

[a] In toluene, 150°C, 20 atm. H_2 [cyclohexene] = 20 mmol, [catalyst] = 2.0×10^{-2} mmol.

[b] k_{obs} in $-d[\text{cyclohexene}]/dt = k_{obs}[\text{cyclohexene}]$.

[c] k_{obs}/k_{obs} for a corresponding neutral complex $RuHCl(CO)(PPh_3)(L\text{-}L')$, L-L′ = dppe, dppp, arphos.

[d] From refs 9 and 10.

and **3**, but it can give an additional vacant site very easily to accommodate a molecular hydrogen, via oxidative addition due to the more fluxional behaviour of the dppp ligand (six-membered chelate ring) than the dppe and arphos ligands (five-membered chelate rings). However small the concentration of five-coordinate species with the dissociated *trans*-positioned ligand, its high reactivity overrides the concentration effect.

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