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Group 15 ligand migration in the heteronuclear clusters $RuOs_3(\mu\text{-}H)_2(CO)_{12}(EPh_3)$ (E = P, As, Sb)

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Abstract

The monosubstituted clusters $RuOs_3(\mu\text{-}H)_2(CO)_{12}(EPh_3)$ (where E = P, As, Sb) exhibit isomers in which the group 15 ligand is on an Os or an Ru vertex. Evidence is presented for hydride fluxionality and EPh_3 ligand migration. These processes have been examined by variable temperature NMR studies, and the kinetic parameters estimated.

Keywords: Heterometallic complexes; Ruthenium; Osmium; Group 15 ligand; Chemical exchange; Ligand migration

1. Introduction

Ligand migration involving triorganophosphine (PR_3) ligands has sometimes been invoked in the fluxional behaviour of organometallic compounds [1–3]. However, there are very few examples in the literature in which activation parameters and standard free energy values for PR_3 migration are available. To our knowledge, only two examples have been reported; these are: (i) a series of diruthenium dihydrido complexes, $[Cp^*Ru]_2(PR_3)(\mu\text{-}H)_2$ (R = Me, Et, *i*-Pr, Cy, Bz, OMe, OPh), in which the PR_3 ligand migrated between the two Ru centres (no new isomer was produced) [2], and (ii) the heterometallic clusters $PtRu_5(CO)_{16}(\mu_6\text{-}C)(PMe_2Ph)$ and $PtRu_5(CO)_{16}(\mu_6\text{-}C)(PMe_3)$, in which the phosphine ligand migrated between the Pt (major isomer) and the Ru (minor isomer) vertices of an octahedron, with a concomitant CO shift [3]. We have recently reported that the heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**1**) undergoes facile substitution with PPh_3 under trimethylamine N-oxide activation, to afford the mono- and disubstituted derivatives $RuOs_3(\mu\text{-}H)_2(CO)_{13-n}(PPh_3)_n$ ($n = 1$ (**2a**) or 2 (**3a**)). In solution, **2a** existed as a dynamic mixture of two isomers corresponding to substitution at either the unique ruthenium or an osmium vertex; the solid-state structures of both had been determined by single-crystal X-ray structural analyses and were also reported [4]. These isomers proved to be ideal for obtaining kinetic data on the phosphine ligand migration. Herein we report our studies on this migration process, as well as the analogous process in the related $AsPh_3$ and $SbPh_3$ derivatives.

2. Experimental

2.1. General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were purified, dried, distilled, and stored under nitrogen prior to use. Routine and variable temperature NMR spectra were acquired on a Bruker ACF300 NMR spectrometer. Selective decoupling experiments, spin-saturation transfer and 2D NMR spectra were acquired on a Bruker Avance DRX500 or Bruker AMX500 machine. EXSY spectra were recorded with a mixing time of 0.5 s unless otherwise stated. The solvent used was deuterated chloroform unless otherwise stated. Chemical shifts reported are referenced to that for the residual proton of the solvent for ^1H, and to 85% aqueous H_3PO_4 (external standard) for $^{31}P\{^1H\}$. Chemical exchange simulations were carried

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out with the GNMR program [5]. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in an *m*-nitrobenzyl alcohol matrix. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The preparation of cluster **1** appears in our earlier report [4]; all other reagents were from commercial sources and used as supplied.

The preparation of $RuOs_3(\mu\text{-}H)_2(CO)_{12}(PPh_3)$ (**2a**) and $RuOs_3(\mu\text{-}H)_2(CO)_{11}(PPh_3)_2$ (**3a**) have been previously described [4]. A similar procedure was employed in the preparation of the arsenic and stibine analogues from $AsPh_3$ and $SbPh_3$, respectively:

$RuOs_3(\mu\text{-}H)_2(CO)_{12}(AsPh_3)$ (**2b**) yield = 45%; ν_{CO}/cm^{-1} (hexane) 2093m, 2065s, 2055s, 2040vs, 2027s, 2010m, 1996mw, 1981w, 1970w, 1751mw. MS: 1316.7 (calculated for $M^+ = 1316.8$). Anal. Calcd for $C_{30}H_{17}AsO_{12}Os_3Ru$: C, 27.27; H, 1.29. Found: C, 27.36; H, 1.20%.

$RuOs_3(\mu\text{-}H)_2(CO)_{11}(AsPh_3)_2$ (**3b**) yield = 20%; ν_{CO}/cm^{-1} (hexane) 2077s, 2041vs, 2018s, 1996m, 1973mw. MS: 1595.7 (calculated for $M^+ = 1595.8$). Anal. Calcd for $C_{47}H_{32}As_2O_{11}Os_3Ru$: C, 35.18; H, 2.00. Found: C, 35.28; H, 1.88%.

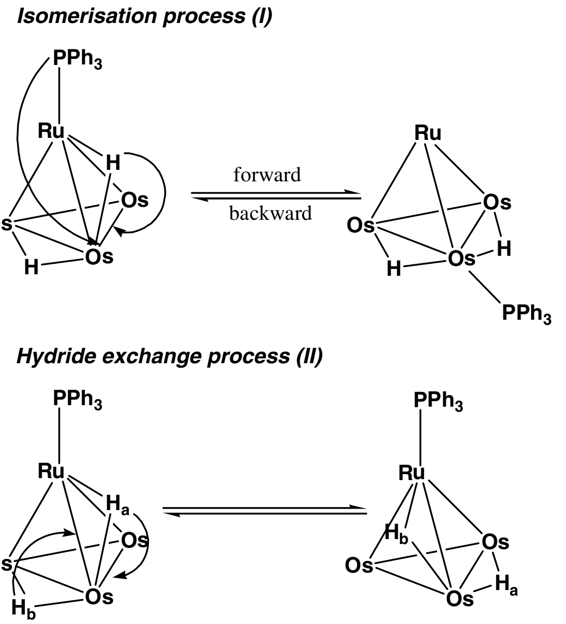
$RuOs_3(\mu\text{-}H)_2(CO)_{12}(SbPh_3)$ (**2c**) yield = 40%; ν_{CO}/cm^{-1} (hexane) 2093m, 2065s, 2055m, 2040vs, 2024m, 2010m, 1997mw, 1995mw. MS: 1362.6 (calculated for $M^+ = 1363.8$). Anal. Calcd for $C_{30}H_{17}O_{12}Os_3RuSb \cdot 1/2C_6H_{14}$: C, 28.19; H, 1.43. Found: C, 27.91; H, 1.47%.

$RuOs_3(\mu\text{-}H)_2(CO)_{11}(SbPh_3)_2$ (**3c**) yield = 18%; ν_{CO}/cm^{-1} (hexane) 2077s, 2041vs, 2018s, 2005mw, 1996mw, 1976mw, 1734mw, br. MS: 1687.8 (calculated for $M^+ = 1688.8$). Anal. Calcd for $C_{47}H_{32}As_2O_{11}Os_3Ru \cdot 1/4C_6H_{14}$: C, 34.08; H, 2.09. Found: C, 34.04; H, 2.04%.

3. Results and discussion

The $^{31}P\{^1H\}$ NMR spectrum of **2a** at 300 K showed two singlets at 33.6 and 49.4 ppm. The corresponding ^1H NMR spectrum consisted of three resonances: a well-resolved doublet at −19.37 ppm, and two broad signals at −19.66 and −21.24 ppm. At 253 K, these resolved into two doublets at −19.51 and −21.29 ppm, and a singlet at −19.74 ppm. With the aid of ^{31}P–^1H HMBC, these can be attributed to the presence of two isomers, present in a 1.0 : 0.23 ratio at 253 K, which presumably have the structures observed in the solid-state, viz., **Ru-2a** and **Os-2a**. Similar isomerism was also observed in the heavier group 15 analogues **2b** and **2c**; the major isomer was that with the group 15 ligand on the ruthenium vertex. The tentative NMR assignments for these isomers are given in Fig. 1.

On standing or at higher temperatures, the NMR spectra of **2a**–**c** also showed additional resonances, which were less obvious in **2a** and more so with **2b** and especially **2c**. These were presumably decomposition products. EXSY spectra showed that the hydrides in the two major isomers of **2a**–**c** underwent mutual exchange. Two exchange processes were discernible: an isomerisation (process I), for example, between **Ru-2a** and **Os-2a**, and a hydride exchange (process II) between the two non-equivalent hydrides in **Ru-2a**. The likely exchange processes are depicted in Scheme 1.



Scheme 1.

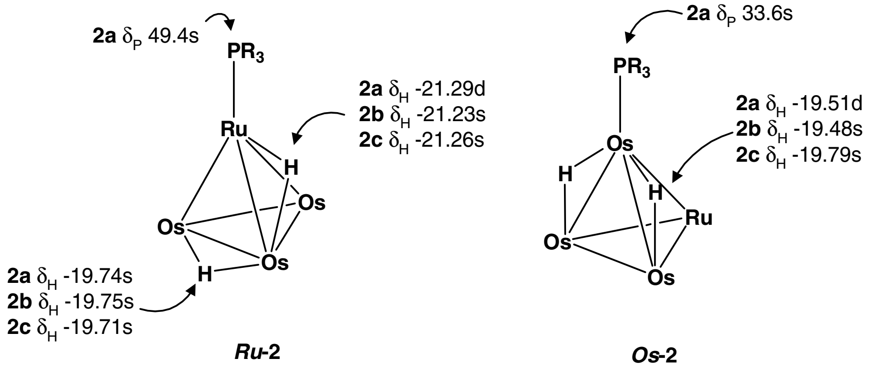


Fig. 1. Solution structures and tentative NMR assignments for the two major isomers of **2a**–**2c**.

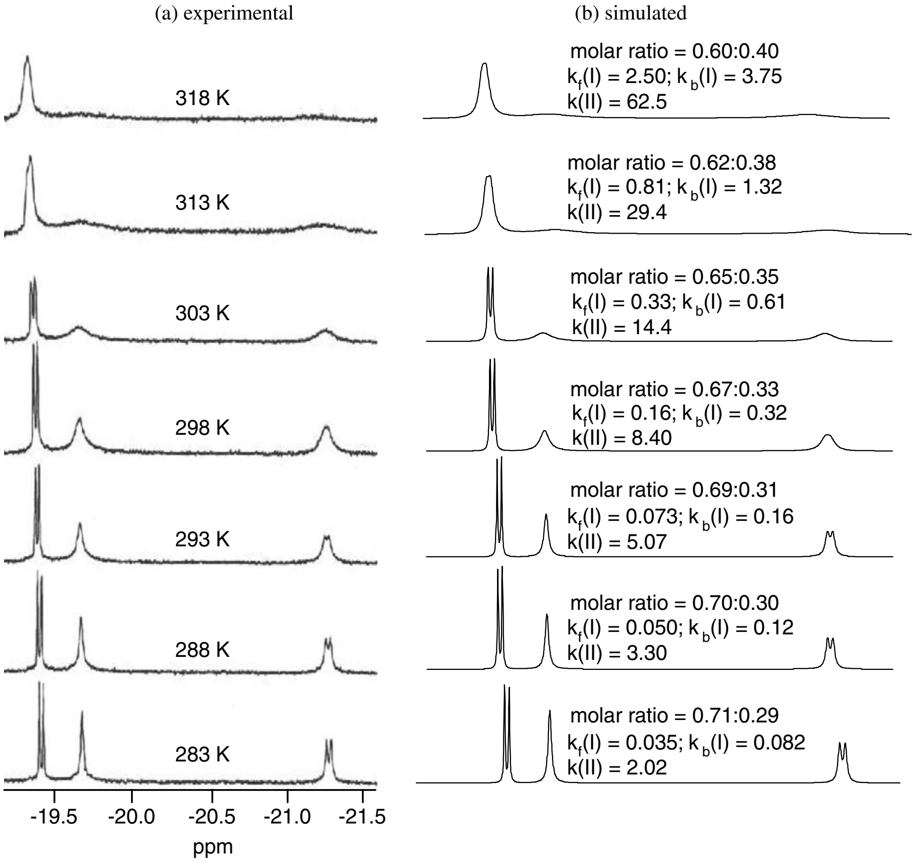


Fig. 2. Experimental (left) and simulated (right) variable temperature ^{1}H NMR spectra of **2a** obtained in $CDCl_3$ from 283 to 313 K. Molar ratio refers to **Ru-2a**:**Os-2a**; k_f(I) and k_b(I) are the simulated rate constants (s mol^{-1} m^3) for the forward and backward isomerisation process (I), respectively; k(II) refers to the simulated rate constant (s mol^{-1} m^3) for the hydride exchange process (II).

The isomerisation process (I) required movement of the EPh_3 ligand between the ruthenium and an osmium vertex. The ^{31}P EXSY spectrum of **2a** at 300 K, and a spin saturation transfer experiment, also supported the presence of such an exchange; no exchange crosspeak between the cluster and added free PPh_3 was observed, however, suggesting that the ligand migration was nondissociative. We have also carried out variable temperature ^{1}H NMR studies on **2a**–**c**, as well as a variable temperature ^{31}P NMR study on **2a**. These spectra have been simulated to obtain rate constants with which kinetic parameters for the exchange processes have been estimated from an Eyring plot. The experimental and simulated ^{1}H NMR spectra for **2a** is shown in Fig. 2, and the kinetic and thermodynamic parameters obtained from the Eyring plots for **2a**–**2c** are given in Table 1, together with those reported earlier for

Table 1
Kinetic parameters obtained from simulations of the variable temperature NMR experiments

Cluster	Ligand	Forward reaction (**Ru-2** → **Os-2**)		Backward reaction (**Os-2** → **Ru-2**)	
		$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
Isomerisation process (I)					
2a	PPh_3	21.1(15)	9(5)	18.5(14)	2(5)
2a[a]	PPh_3	15.7(9)	−7(3)	13.2(8)	−15(3)
2b	$AsPh_3$	13(5)	−21(17)	10(5)	−29(16)
2c	$SbPh_3$	8.8(12)	−34(4)	5.4(11)	−41(4)
$[Cp^*Ru]_2(PR_3)(\mu\text{-}H)_2$	PR_3	6.2 to 15.7[2]	−3.5 to −16.3[2]		
$PtRu_5(CO)_{16}(\mu_6\text{-}C)(PMe_2Ph)$	PMe_2Ph	15.1(3)[3]	−7.7(9)[3]		
$PtRu_5(CO)_{16}(\mu_6\text{-}C)(PMe_3)$	PMe_3	14.0(1)[3]	−10.7(4)[3]		

Cluster	Ligand	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
Hydride exchange process (II)			
2a	PPh_3	16.4(7)	1(2)
2b	$AsPh_3$	14.1(7)	−6(3)
2c	$SbPh_3$	11.6(4)	−12.9(12)

[a] From ^{31}P{^{1}H} VT NMR.

the diruthenium dihydrido complexes $[Cp^{*}Ru]_2(PR_3)(\mu\text{-}H)_2$ (R = Me, Et, *i*-Pr, Cy, Bz, OMe, OPh), and the heterometallic clusters $PtRu_5(CO)_{16}(\mu_6\text{-}C)(PMe_2Ph)$ and $PtRu_5(CO)_{16}(\mu_6\text{-}C)(PMe_3)$. In the simulations, we have allowed for the variation of the molar ratio of the two isomers with temperature. This allowed us to obtain a plot of $\ln K$ against $1/T$, and hence ΔG^{ϕ}, from the simulated molar ratio which was used as a check against the values obtained from the Eyring plots.

The similarity in the values of the kinetic parameters obtained from both the $^{31}P\{^1H\}$ and ^1H VT spectra for **2a** suggests that the movement of the PPh_3 and hydride ligands are concerted. As may be expected, the activation enthalpy decreases from **2a** to **2c**, consistent with the trend in the metal–pnictogen bond strength: M–P > M–As > M–Sb. The marginally higher $\Delta H^{\neq}$ for the isomerisation process in **2a** compared to those for these other clusters may be attributed to the concomitant hydride shifts. On the other hand, the $\Delta S^{\neq}$ values are close to zero or negative; in the previously reported systems, the negative $\Delta S^{\neq}$ values had been attributed to relatively symmetrical transition states, and μ-PR_3 intermediates were suggested; a similar situation probably applies here.

4. Concluding remarks

We have thus shown that there is both hydride and group 15 ligand migration in the monosubstituted clusters $RuOs_3(\mu\text{-}H)_2(CO)_{12}(EPh_3)$ (where E = P, As, Sb). The group 15 ligand migration is reversible and the rates, and hence the associated kinetic parameters, have also been estimated via variable temperature ^1H and ^{31}P NMR experiments and simulations. This study is also the first in which phosphine migration has been studied by variable temperature ^{31}P NMR measurements. The kinetic parameters determined are comparable to the few other phosphine migrations that have been reported, and are consistent with a nondissociative mechanism.

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Appendix A. Supplementary data

$^{31}P\{^1H\}$ EXSY, experimental and simulated variable temperature $^{31}P\{^1H\}$ NMR spectra of **2a**, and experimental and simulated variable temperature ^1H NMR spectra of **2b** and **2c**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.007.

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