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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.

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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 ^{1}H, and to 85% aqueous H_3PO_4 (external standard) for $^{31}P\{^{1}H\}$. 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%.

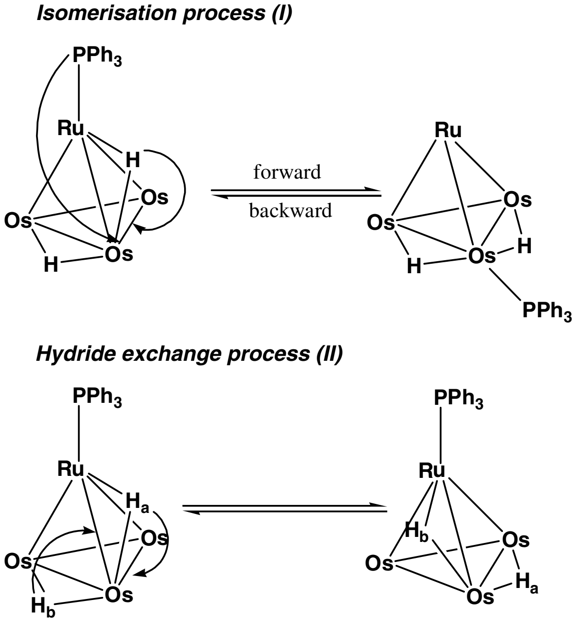
$RuOs_3(\mu\text{-}H)_2(CO)_{12}(SbPh_3)$ (**2c**) yield = 40%; ν_{CO}/cm^{-1} (hexane) 2093m, 2065s, 2055m, 2040vs, 2024m, 2010m, 1997mw, 1995mw. MS: 1362.6 (calculated for $M^+ = 1363.8$). Anal. Calcd for $C_{30}H_{17}O_{12}Os_3RuSb \cdot 1/2C_6H_{14}$: C, 28.19; H, 1.43. Found: C, 27.91; H, 1.47%.

$RuOs_3(\mu\text{-}H)_2(CO)_{11}(SbPh_3)_2$ (**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.

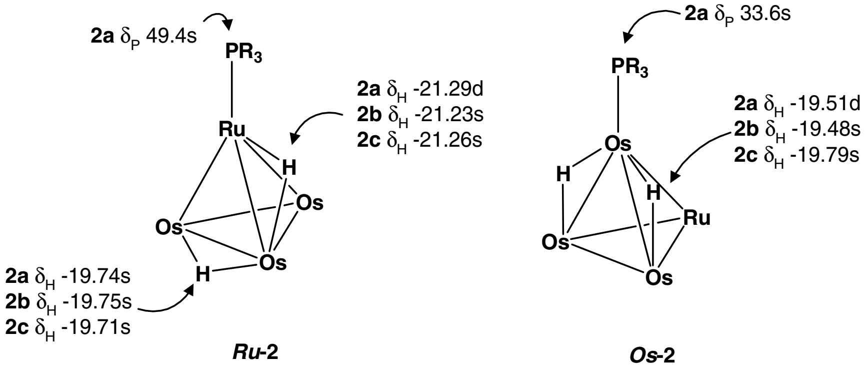


Fig. 1. Solution structures and tentative NMR assignments for the two major isomers of **2a**–**2c**.

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