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Ditertiary phosphine derivatives of the heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$

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Abstract

The heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**1**) reacted readily with a number of ditertiary phosphines under chemical activation with trimethylamine-*N*-oxide. The solid-state and solution structures of these derivatives have been examined. Six structural types have been characterized crystallographically, including one in which a phenyl group migrates from the ditertiary phosphine ligand to the metal framework. There are many more isomers present in solution, most of which are rapidly inter-converting via hydride migrations.

Keywords: Heterometallic; Ruthenium; Osmium; Ditertiary phosphines; Isomers

1. Introduction

Heteronuclear clusters containing group homologues are of interest as the different transition metals present in close proximity can display subtle synergistic effects, giving rise to novel chemistry. One such family is the tetrahedral clusters with the formulae $M'M_3(\mu\text{-}H)_2(CO)_{13}$, where M and M′ are group 8 elements. Currently, three members of this family are known, viz., $FeRu_3(\mu\text{-}H)_2(CO)_{13}$, $FeOs_3(\mu\text{-}H)_2(CO)_{13}$, and $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**1**). While the chemistry of $FeRu_3(\mu\text{-}H)_2(CO)_{13}$ and $FeOs_3(\mu\text{-}H)_2(CO)_{13}$ have been relatively well-investigated [1], the reactivity of **1** has been comparatively much less explored. It has been well-established that the chemistries of ruthenium and osmium are much more alike than they are to that of iron. We have recently reported a high-yield synthetic route to **1**, and have embarked on a series of investigations into its chemistry. The reactivity of **1** with group 15 ligands as well as various organic substrates has been described [2,3]. As part of our ongoing studies on the chemistry of **1** and its derivatives, we have examined the substitution chemistry of **1** with a number of representative ditertiary phosphines. We would like to report the results of this study here.

2. Results and discussion

The products from the reaction of **1** with a number of different ditertiary phosphines in the presence of 2 M equiv. of TMNO (trimethylamine-*N*-oxide) at ambient temperature are summarized in Scheme 1.

All these novel products have been characterized spectroscopically and analytically, and with the exception of **4f**, **8** and **9**, also by single-crystal X-ray crystallographic studies. The clusters will be grouped according to their structural types for the discussion that follows.

2.1. Ditertiary phosphine acting as an inter-cluster link

Clusters $[RuOs_3(\mu\text{-}H)_2(CO)_{10}(\mu\text{-}CO)_2]_2(\mu\text{-}L)$ (**2**) (L = dppe (**b**); dppp (**c**); dppb (**d**)) have the same general structure comprising two metal tetrahedra linked by a ditertiary phosphine ligand. The ORTEP plot showing the molecular structure of **2c**, which is representative, is given in Fig. 1. A common atomic numbering scheme, together with selected bond parameters for all three clusters are collected in Table 1.

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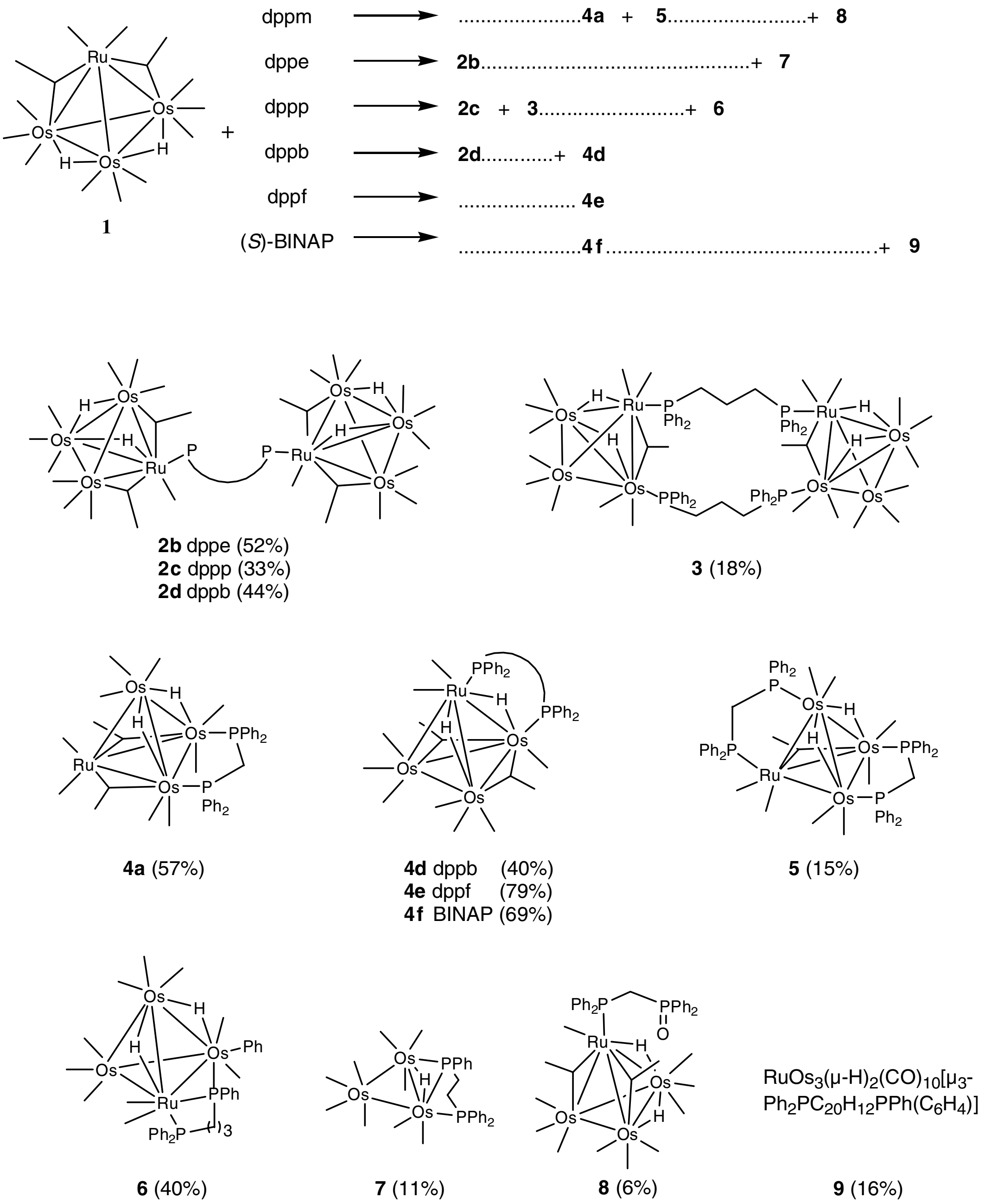

Scheme 1.

A comparison of the structural parameters indicates that they are similar to one another as well as to the monosubstituted ER_3 derivatives of **1** [2d]; this includes the relative dispositions of the hydrides and bridging carbonyls. As previously observed, there appears to be an electronic preference for substitution at an Ru vertex. Similarly, without exception, both hydrides in each metal tetrahedron share a common vertex. All the structures also exhibit bridging carbonyls, due to the greater electron density imparted to the cluster core by the strong σ donating phosphine ligand; bridging carbonyls are better π-acceptors than terminal CO ligands [4]. The crystals of **2b** and **2d** exhibited disorder of the metal framework. This disorder was equivalent to the presence of two isomers in a 1:1 and 4:1 ratio for **2b** and **2d**, respectively; the latter is similar to that observed for the PPh_3 derivative [2a]. For **2b**, this is in agreement with the observation of isomers in solution. The proposed solution state structures and tentative NMR assignments (phosphorus and hydride resonances) for **2b–d** have been made as shown in Fig. 2.

Besides **2c**, the reaction of **1** with dppp also yielded $[RuOs_3(\mu\text{-}H)_2(CO)_{10}(\mu\text{-}CO)]_2(\mu\text{-}dppp)_2$ (**3**). A molecular plot of **3** is shown in Fig. 3, together with selected bond parameters. There was disorder of the metal framework, with ruthenium occupancies refined to 0.5:0.5 for M(1) and M(2), as well as for M(5) and M(6), respectively. In **3**, two tetrahedral metal cores are linked by the ditertiary phosphine ligand, resulting in a cyclic arrangement. The