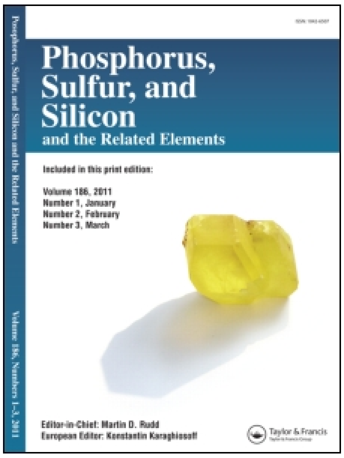

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Böttcher, Hans-Christian , Graf, Marion and Wagner, Christoph(2001) 'Synthesis and Characterization of Electron-Rich Phosphido-Bridged Clusters', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 185 — 188

To link to this Article: DOI: 10.1080/10426500108546620

URL: http://dx.doi.org/10.1080/10426500108546620

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 185-188

Synthesis and Characterization of Electron-Rich Phosphido-Bridged Clusters

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The reaction of $[Ru_3(CO)_{12}]$ with $[Ir(Bu^t_2PH)_3Cl]$ (**1**) in refluxing toluene leads to $[Ru_3Ir(CO)_8(\mu_3\text{-}H)(\mu\text{-}Cl)_2(\mu\text{-}PBu^t_2)_2(Bu^t_2PH)]$ (**4**). The molecular structure in the solid reveals **4** as species containing a butterfly metal framework, Electron counting exhibits **4** with 64 cluster valence electrons as an electron-rich cluster. The reaction of $[\{Cu(Bu^t_2PH)Cl\}_4]$ (**5**) with $[Ru_3(CO)_{12}]$ in refluxing toluene yields as main product the electron-rich 50e-cluster $[Ru_3(CO)_6(\mu\text{-}Cl)_3(\mu\text{-}PBu^t_2)(Bu^t_2PH)]$ (**6**).Furthermore, thermolysis of $[Ru_3(CO)_{12}]$ with Cy_2PH in toluene leads to $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PCy_2)_3]$ (**7**). **7** reacts with carbon monoxide under pressure yielding the 52e-complex $[Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}PCy_2)_3]$ (**8**). The preliminary X-ray crystal structure investigation reveals **8** as species with three metal-metal bonds and therefore as an electron-rich cluster.

Keywords: ruthenium; iridium; electron-rich; cluster

INTRODUCTION

Heteronuclear metal clusters are of current interest in view of their site-selective reactivity and synergetic effects in catalytic reactions.[1] Recently we reported the synthesis and the molecular structures of the clusters $[Ru_3Ir(CO)_7(\mu\text{-}H)_2(\mu_3\text{-}Cl)(\mu\text{-}PBu^t_2)_2(Bu^t_2PH)]$ and $[Ru_3Rh(CO)_7(\mu_3\text{-}$

H)(μ-Cl)$_2$(μ-PBu$^t_2$)$_2$(Bu$^t_2$PH)] with butterfly configured tetrametal cores.[2] Now we found a synthesis for the novel electron-rich 64e-cluster [Ru$_3$Ir(CO)$_8$(μ$_3$-H)(μ-Cl)$_2$(μ-PBu$^t_2$)$_2$(PBu$^t_2$H)] with closed tetrametal framework. The presence of two or more phosphido bridging ligands in metal clusters is often a recurring feature of formally electron-rich species as described by Carty and coworkers.[3] We summarize here some recent results in the chemistry of electron-rich clusters from our laboratory which were described in detail elsewhere.[4]

RESULTS AND DISCUSSION

The reaction of [Ru$_3$(CO)$_{12}$] with [Ir(Bu$^t_2$PH)$_3$Cl] (**1**) (molar ratio 1:1) in toluene yields [Ru$_3$Ir(CO)$_7$(μ-H)$_2$(μ$_3$-Cl)(μ-PBu$^t_2$)$_2$(Bu$^t_2$PH)] (**2**) and [Ru$_3$(CO)$_8$(μ-H)$_2$(μ-PBu^t)(Bu$^t_2$PH)] (**3**).[2a] The same reaction carried out in a molar ratio of 1:2 leads to the electron-rich 64e-cluster [Ru$_3$Ir(CO)$_8$(μ$_3$-H)(μ-Cl)$_2$(μ-PBu$^t_2$)$_2$(PBu$^t_2$H)] (**4**).[4c] The Ru$_3$Ir core of **4** can be considered as a closed tetrametal framework. However the hinge bond Ru(1)-Ru(2) is considerably elongated and the two Ru-Ir bonds are also expanded (Fig. 1). The ^{31}P{^{1}H} NMR spectrum of **4** consists of a doublet at δ 267.2 (μ-PBu$^t_2$) and a corresponding triplet at δ 45.7 (Bu$^t_2$PH, $^3J_{PP}$ = 15.5 Hz). These data indicate two chemically equivalent phosphorus nuclei of two phosphido bridges across metal-metal bonds which couple with a phosphorus nucleus of a phosphine ligand. The comparison of the ^{31}P chemical shifts of the phosphido bridges of **2** and **4** shows that these ligands resonate for **4** at higher field (**2**: δ 318.2). That is a further indication exhibiting **4** as an electron-rich cluster. (These upfield shifts correlate with increased Ru-P-Ru angles and therefore with an elongation of the Ru-Ru bonds bridged by the phosphido groups.) The hydrido ligand of 4 could not be located directly during the X-ray analysis (omitted in Fig. 1), however its ^1H NMR spectrum exhibits a corresponding resonance in the metal hydride region at δ -13.77 (t, $^2J_{PP}$ = 15.5 Hz, 1H). According to the splitting pattern of the phosphorus nuclei in the $^{31}P\{^1H\}$ NMR spectrum and the lack of a second coupling in the hydride resonance a capping position (μ_3) of the hydrido ligand on the Ru_2Ir triangle is assumed.

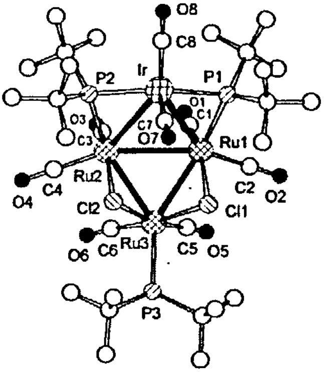

FIGURE 1 Molecular structure of 4. Selected bond distances (Å): Ru(1)-Ru(3), 2.9305(5); Ru(1)-Ru(2), 3.1176(7); Ru(2)-Ru(3), 2.9246(5); Ru(1)-Ir, 2.9882(4); Ru(2)-Ir, 3.0309(4).

The reaction of $[Ru_3(CO)_{12}]$ with $[\{Cu(Bu^t_2PH)Cl\}_4]$ in refluxing toluene yields as main product the electron-rich 50e-cluster $[Ru_3(CO)_6(\mu\text{-}Cl)_3(\mu\text{-}PBu^t_2)(Bu^t_2PH)]$ (6).[4a] Compound 6 consists of a closed Ru_3 core in which each Ru-Ru edge is supported by a chloro ligand. Two Ru-Ru bonds are elongated [Ru(1)-Ru(2), 2.997(2); Ru(1)-Ru(3), 3.016(2) vs. Ru(2)-Ru(3), 2.835(2) Å]. The thermolysis of $[Ru_3(CO)_{12}]$ with an excess of Cy_2PH leads to $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PCy_2)_3]$ (7) as main product.

7 reacts with CO under pressure yielding the novel complex $[Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}PCy_2)_3]$ (**8**).[4b] Because of unsufficient crystal qualities up to now only a preliminary crystal structure analysis exists. However the found metal-metal distances confirm **8** as 52e-cluster with three expanded Ru-Ru bonds.

Acknowledgements

We thank the Kultusministerium des Landes Sachsen-Anhalt and the Fonds der Chemischen Industrie for financial support and the Degussa AG for a generous loan of $RuCl_3x3H_2O$ and $IrCl_3x3H_2O$.

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