# Reversible Metal–Metal Bond Cleavage Accompanied by the Facile Reversible Addition of $H_2$ to a $Ru_3$ Cluster. Synthesis and X-ray Structures of $Ru_3(CO)_8(\mu\text{-}H)_2(\mu\text{-}t\text{-}Bu_2P)_2$ and $Ru_3(CO)_8(\mu\text{-}H)_2(H)_2(\mu\text{-}t\text{-}Bu_2P)_2$

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The reversible formation and cleavage of a metal–metal bond is a key reaction in dinuclear and cluster chemistry.[1] A few cases have been reported in which such a process is accompanied by the reversible addition of two electron donors such as CO or $PR_3$.[1] However, to our knowledge there have, so far, been no well characterized examples of the complete cleavage of a metal–metal bond accompanied by the reversible addition of $H_2$ under mild conditions. There are relatively few examples of the reversible addition of $H_2$ to a metal cluster[2] (see Note Added in Proof, ref 10), and in the cases where the products have been fully characterized, no cleavage of metal–metal bonds occurs.[2,3] We report here the first example of the facile, reversible addition of $H_2$ to a metal cluster which is accompanied by a clearly recognized reversible metal–metal bond cleavage.

Reaction of di-*tert*-butylphosphine ($t$-$Bu_2PH$) with $Ru_3(CO)_{12}$ in di-*n*-butylether (0.5 h) at 100 °C gives the purple bis-phosphido bridged trinuclear complex $Ru_3(CO)_8(\mu\text{-}H)_2(\mu\text{-}t\text{-}Bu_2P)_2$ (**1**) in 55% yield.[4] The diphenylphosphido analogue of **1** has been reported, and the two compounds have similar structures in the solid state[5] (see below). Spectroscopic data for **1** (IR, $^1H$, $^{31}P$, NMR) is in accord with the solid-state structure as determined by X-ray crystallography.[6] The IR spectrum contains only terminal $\nu_{CO}$ absorptions, while the $^1H$ NMR shows a triplet at $\delta$ −17.19 ($J_{P-H}$ = 19.5 Hz) assigned to two equivalent hydride ligands. A similar resonance is observed in the spectrum of $Ru_3(CO)_8(\mu\text{-}H)_2(\mu\text{-}Ph_2P)_2$, and the triplet pattern can be attributed to an AA′XX′ type of spectrum.[5] The $^{31}P\{^1H\}$ NMR spectrum of **1** is a singlet at $\delta$ 256.05 consistent with phosphido groups bridging metal–metal bonds.[7]

Purple hexane solutions of **1** rapidiy turn orange when exposed to $H_2$ (1 atm) at ambient temperature. From these solutions orange crystals of the 50-electron complex $Ru_3(CO)_8(\mu\text{-}H)_2(H)_2(\mu\text{-}t\text{-}Bu_2P)_2$ (**2**) may be isolated by crystallization from hexane under a hydrogen atmosphere. This compound is stable with respect to loss of $H_2$ in the solid state either under vacuum or a nitrogen atmosphere. However, when solutions of **2** are exposed to a nitrogen purge or vacuum, rapid loss of $H_2$ occurs, and the dihydride **1** is reformed. This cycle may be repeated many times, and the interconversion of **1** and **2** appears to be quantitative.

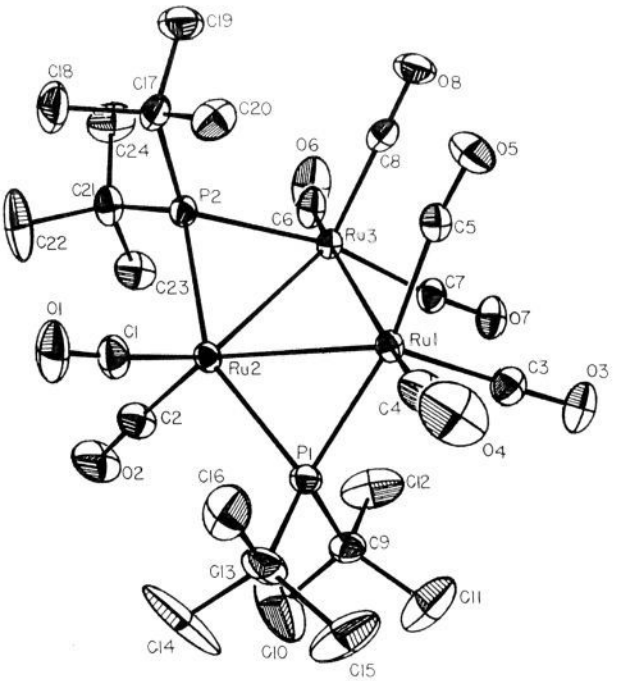
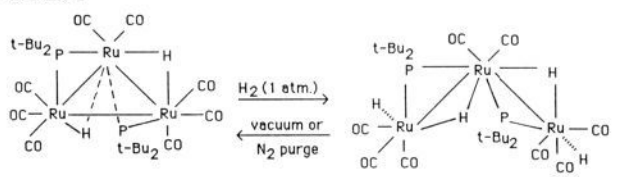



**Figure 1.** ORTEP view of **1** showing the atom-numbering scheme. Key bond lengths (Å) and angles (deg) not in text are as follows: Ru(3)–P(2) 2.046 (1), Ru(2)–P(2) 2.362 (1), Ru(2)–P(1) 2.370 (1), Ru(1)–P(1) 2.414 (1); Ru(3)–P(2)–Ru(2) 75.03 (3), Ru(2)–P(1)–Ru(1) 75.11 (3). A complete listing is provided in the Supplementary Material.[9]

**Scheme I**




**1** **2**

There are several features of the structures which are of interest. The molecular geometry of **1** (Figure 1) consists of a closed 48-electron $Ru_3$ cluster in which two of the Ru–Ru bonds are bridged by $\mu$-$t$-$Bu_2P^-$ units (Ru(1)–Ru(2) = 2.918 (1) Å and Ru(2)–Ru(3) = 2.904 (1) Å). These groups lie above and below the $Ru_3$ plane. The unique Ru atom [Ru(2)] which is bonded to two phosphido groups also bears two cis CO units. The other Ru atoms each have three CO groups and are separated by a fairly long Ru–Ru bond of 3.046 (1) Å. Although the hydrides were not located in the X-ray structure of **1**, it is reasonable to assume that they occupy bridging sites across Ru(1)–Ru(2) and Ru(2)–Ru(3) and opposite to the $\mu$-$t$-$Bu_2P^-$ groups. Thus, the phosphido groups are roughly trans to each other [P(2)–Ru(2)–P(1) = 151.60 (5)°]. The coordination geometry of each metal is roughly octahedral if one ignores the metal–metal bonds for Ru(2) but includes the Ru(1)–Ru(3) interaction for Ru(1) and Ru(3).

Comparison of the X-ray structures of **1** and **2** indicates that the Ru(1)–Ru(3) bond is broken in the formation of **2**. The most striking feature of **2** (Figure 2) is the open $Ru_3$ framework. The Ru(1)–Ru(2)–Ru(3) angle in **1** [58.23 (1)°] is 106.91 (1)° in **2**, and the Ru(3)–Ru(1) distance in **2** is clearly nonbonding at 4.583 (1) Å. As for **1**, the hydride ligands in **2** could not be located in the X-ray structure. However, their locations may be inferred from the non-hydrogen atom framework, and we propose that there are two bridging and two terminal hydrides as shown in Scheme

(1) See, for example: Bruce, M. I.; Williams, M. L. *J. Organomet. Chem.* **1985**, *282*, C11. MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 1194. Richter, F.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1981**, *204*, C27. Vahrenkamp, H. *Organometallics* **1982**, *1*, 756.

(2) See, for example: Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometalics* **1982**, *1*, 1008. Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986**, *25*, 4618. Farrugia, L. J.; Green, M.; Hankey, D. R.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 310.

(3) The reversible addition of $H_2$ to $(Ph_3P)(CO)_4W(\mu\text{-}PPh_2)Ir(CO)_2(PPh_3)$ and $(Ph_3P)(CO)_3Fe(\mu\text{-}PPh_2)Ir(CO)_2(PPh_3)$ may lead to cleavage of the metal–metal in each case; however, no structural studies have been reported. Breen, M. J.; Schulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1983**, *3*, 782. Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 68.

(4) Full experimental details for **1** and **2** are given in the Supplementary Material.

(5) Patel, V. D.; Cherkas, A. A.; Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1985**, *4*, 1792. Field, J. S.; Haines, R. J.; Moore, M. H.; Smit, D. N.; Steer, L. M. *S. Afr. J. Chem.* **1984**, *3*, 36.

(6) Details of the X-ray structures for **1** and **2** are given in the Supplementary Material.

(7) See, for example: Carty, A. J. *Adv. Chem. Ser.* **1982**, no *196*, 163, and references therein.

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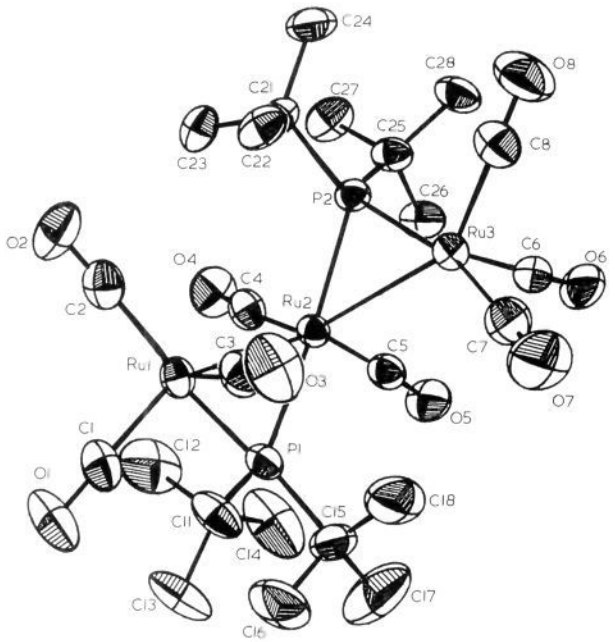


**Figure 2.** ORTEP view of **2** showing the atom-numbering scheme. Key bond lengths (Å) and angles (deg) not in text are as follows: Ru(1)–P(1) 2.378 (1), Ru(2)–P(1) 2.399 (1), Ru(2)–P(2) 2.401 (1), Ru(3)–P(2) 2.371 (1); Ru(1)–P(1)–Ru(2) 78.04 (3), Ru(2)–P(2)–Ru(3) 78.99 (3). A complete listing is provided in the Supplementary Material.[9]

I. Although the rupture of the Ru(1)–Ru(3) bond accompanied by the addition of $H_2$ might be expected to lead to a molecule in which the terminal hydrides point *toward* each other, the geometries of Ru(1) and Ru(3) indicate that the terminal hydrides are located at sites which arre pointing *away* from each other on the back side of the molecule. Thus the terminal hydride on Ru(1) is positioned trans to C(3) and that on Ru(3) is trans to C(8). One simple explanation for this is that on addition of $H_2$ to the molecule, the $\mu$-H atoms already present in **1** swing back and occupy the terminal positions. The incoming $H_2$ molecule then provides an H atom in each of the new $\mu$-H locations. In solution there is exchange of terminal and bridging hydrides, and so we have been unable to verify this suggestion by $D_2$ labeling experiments.

The $^{31}P\{^1H\}$ NMR spectrum for **2** is a singlet at +25 °C, while the $^1H$ NMR shows a second-order multiplet for the *t*-$Bu_2P$ protons. This signal consists of two sets of sharp outer lines ($\delta$ 1.50, 1.48 and $\delta$ 1.45, 1.44) which appear on either side of a broad inner peak at $\delta$ 1.47. At +40 °C all the peaks sharpen, and six lines can be observed at $\delta$ 1.66, 1.64, 1.63, 1.61, 1.60, and 1.59. At +25 °C, no signal to high field is observed. On cooling to −40 °C, two doublets are observed at $\delta$ −9.36 ($^2J_{P-H}$ = 18.0 Hz) and $\delta$ −9.62 ($^2J_{P-H}$ = 27.0 Hz), in addition to a broad singlet at $\delta$ −17.08 (relative areas 1:1:2). The resonances to high field are assigned to the terminal and bridging hydrides, respectively. The *t*-$Bu_2P$ protons now appear as a very broad triplet ($\delta$ 1.44, apparent $J_{P-H}$ = 10.0 Hz). Although the solid-state structure indicates chemically equivalent terminal hydrides, the low-temperature spectrum suggests that in solution they are slightly nonequivalent. On warming to −20 °C, the two doublets at $\delta$ −9.36 and $\delta$ −9.62 broaden into two broad peaks ($\delta$ −9.42, $\delta$ −9.64), and the singlet at $\delta$ −17.08 also broadens. Two broad resonances are observed at 0 °C ($\delta$ −9.67 and $\delta$ −17.08). At +60 °C, a single broad peak is observed at $\delta$ −13.30, and this splits into two broad peaks at +80 °C ($\delta$ −12.95, $\delta$ −13.63). Clearly, the hydrides are fluxional at elevated temperatures, and the rapid exchange process is frozen out at low temperature. The $T_1$ values for all of these high field signals, both at +60 °C and −40 °C, are ca. 250 ms indicating that they are due to conventional hydride ligands and ruling out the possibility of molecular hydrogen ($\eta^2$-$H_2$) species being present as dominant species.[8]

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**Supplementary Material Available:** Experimental details of the synthesis and X-ray crystallography of **1** and **2** and tables of bond lengths, angles, positional parameters, and thermal parameters (17 pages); tables of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

(8) See, for example: Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. Wasserman, J. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. Crabtree, R. H.; Lavin, M.; Bennevoit, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032 and references therein.

(9) See paragraph at the end of the paper regarding Supplementary Material.

(10) **Note Added in Proof**: For a recent example of the reversible addition of $H_2$ to a $Ru_3$ phosphido cluster giving a phosphine ($R_2PH$) unit, see: Lugan, N.; Lavigne, G.; Bonnet, J.-J.; Réau, R.; Neibecker, D.; Tratchenko, I. *J. Am. Chem. Soc.* **1988**, *110*, 5369.

## Biosynthesis of Marine Lipids. 19.[1] Dealkylation of the Sterol Side Chain in Sponges

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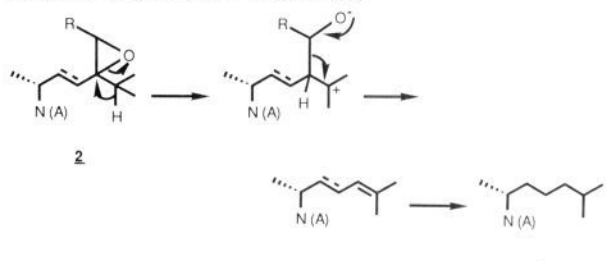
Recently, we have shown[2] unequivocally that some, but not all, sponges are capable of de novo synthesis of unusual as well as conventional sterols. We now report the first documentation that cholesterol (**1**) can be produced in sponges by dealkylation of 24(28)-unsaturated precursors, that the reaction proceeds through the same epoxide intermediate **2** operative in insects,[3] and most strikingly, that this dealkylation can occur in sponges that are capable of de novo sterol biosynthesis and side-chain alkylation. Therefore, Goad's comment[4] that "it would certainly be an extraordinary situation if animals of the same phylum have evolved the enzyme systems required for both C-24 alkylation and C-24 dealkylation reactions" seems to apply to a real situation.

Sterols, notably cholesterol (**1**), are required by insects, even though arthropods are incapable of de novo sterol biosynthesis. Clark and Bloch,[5] and later many other investigators,[6] have shown that insects are capable of dealkylating C-24 substituted plant sterols obtained from the diet by a mechanism that has been summarized by Ikekawa[3a] and Svoboda.[3b] Its key feature is the intermediacy of a 24,28-epoxide (**2**).




**2** **1**

(1) For part 18, see: Malik, S.; Stoilov, I. L.; Djerassi, C. *Tetrahedron Lett.*, in press.

(2) Kerr, R. G.; Stoilov, I. L.; Thompson, J. E.; Djerassi, C. *Tetrahedron*, submitted for publication.

(3) (a) Ikekawa, N. In *Sterols and Bile Acids*; Danielsson, H., Sjövall, J., Eds.; Elsevier: Amsterdam, 1985; pp 199–230. (b) Svoboda, J. A. In *Isopentenoids in Plants*; Nes, W. D., Fuller, G., Tsai, L., Eds.; Marcel Dekker: New York, 1984; pp 367–388.

(4) Goad, L. J. *Pure Appl. Chem.* **1981**, *51*, 837–852.

(5) Clark, A. J.; Bloch, K. *J. Biol. Chem.* **1959**, *234*, 2589–2594.

(6) For leading references, see: Thompson, M. J.; Kaplanis, J. N.; Robbins, W. E.; Svoboda, J. A. *Adv. Lipid Res.* **1973**, *11*, 219–265.

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