

Preliminary communication

Sequential H-migration reactions in the formation of
 $[\text{Os}_3(\mu_2\text{-H})(\mu_2\text{-PMe})(\text{CO})_{10}]$ and $[\text{Os}_3(\mu_2\text{-H})_2(\mu_3\text{-PMe})(\text{CO})_9]$ during the
reaction between the phosphinidene complex $[\text{W}(\text{PMe})(\text{CO})_5]$ and
 $[\text{Os}_3(\mu_2\text{-H})_2(\text{CO})_{10}]$

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Abstract

The transient phosphinidene complex $[\text{W}(\text{PMe})(\text{CO})_5]$ reacts with the unsaturated $[\text{Os}_3(\mu_2\text{-H})_2(\text{CO})_{10}]$ cluster to afford $[\text{Os}_3(\mu_2\text{-H})(\mu_2\text{-PMe})(\text{CO})_{10}]$ and subsequently $[\text{Os}_3(\mu_2\text{-H})_2(\mu_3\text{-PMe})(\text{CO})_9]$ via H-migration reactions involving both transfer from Os to P and from P to Os. © 1997 Elsevier Science S.A.

The chemistry of phosphinidenes (RP) which are analogous to the better-known carbenes has developed rapidly over the past decade [1]. Stable terminal phosphinidene complexes of the type $[\text{M}(\text{PR})(\text{L}_n)]$ are exemplified by $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PR})]$ and $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{PR})]$ (M = Mo, W; R = 2,4,6-Bu^t₃C₆H₂) [2–4] and more recently $[\text{Ta}(\text{PR})\text{N}_3\text{N}]$ (R = Ph, Cy, Bu^t; N₃N = (Me₃SiNCH₂CH₂)₃N) [5,6], which behave like Schrock-type carbenes.

Transient terminal phosphinidenes $[\text{M}(\text{PR})(\text{CO})_5]$ (M

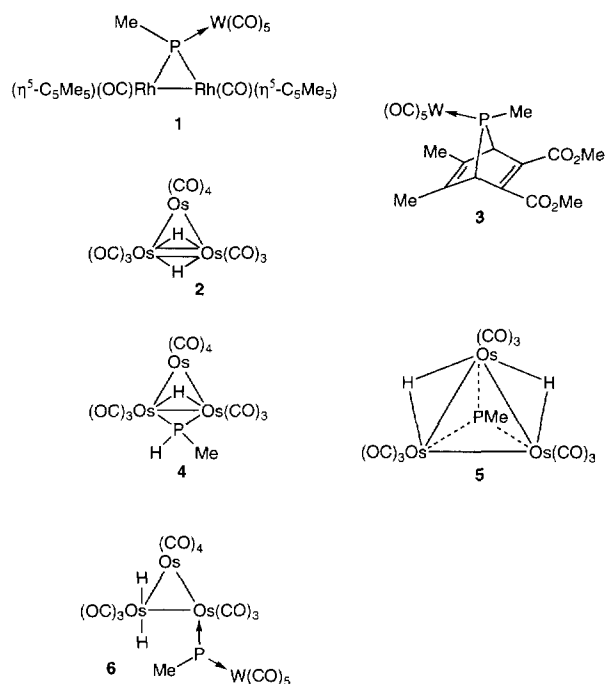
= Cr, Mo, W), which behave like Fischer-type carbenes, are generated from the corresponding 7-phosphanorbornadiene metal pentacarbonyl [7–9], readily insert into strained ring systems, and also undergo cycloaddition reactions with alkenes, alkynes, metal carbenes, and metal carbyne complexes [7–15].

Previously [16], we showed that $[\text{W}(\text{PMe})(\text{CO})_5]$ exhibits carbene-like behaviour in its ready addition across the Rh=Rh double bond of $[\text{Rh}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\eta\text{-CO})_2]$ to afford the three-membered ring, complex **1**. We have now extended this type of addition reaction to the unsaturated complex $[\text{Os}_3(\mu_2\text{-H})(\text{CO})_{10}]$ (**2**), which formally contains an Os=Os double bond, and have also observed interesting additional H-migration reactions. Thus treatment of equimolar amounts of **2** and the 7-phosphanorbornadiene complex **3** in benzene at 55 °C (in the presence of 10% CuCl catalyst) gave sequentially two products $[\text{Os}_3(\mu_2\text{-H})(\mu_2\text{-PMe})(\text{CO})_{10}]$ (**4**)

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and $[\text{Os}_3(\mu_2\text{-H})_2(\mu_3\text{-PMe})(\text{CO})_9]$ (**5**), both unambiguously established by ^{31}P and ^1H NMR spectroscopy.



The ^1H NMR spectrum of complex **4**, which is the first formed reaction product, exhibited the characteristic widely spaced doublet of quartets for the PH resonance (δ 6.15, $^1J_{\text{PH}} = 413$ Hz, $^3J_{\text{HH}} = 5.3$ Hz); a doublet of doublets for the MeP resonance (δ 1.81, $^2J_{\text{PH}} = 11.8$ Hz, $^3J_{\text{HH}} = 5.3$ Hz); and a doublet for the bridging hydride at -19.7 ppm ($^2J_{\text{PH}} = 16.0$ Hz). The ^{31}P NMR spectrum showed a resonance at -68.7 ppm consisting of the expected two doublets of quartets (see Fig. 1). When the reaction is extended, another complex (**5**) is formed, which exhibited a doublet in the ^1H NMR spectrum for the $\mu\text{-PMe}$ group (δ 2.9, $^2J_{\text{PH}} = 13.8$ Hz), and a doublet at -21.5 ppm for the two equivalent bridging hydride ligands ($^2J_{\text{PH}} = 10.3$ Hz). The ^{31}P NMR spectrum showed a triplet of quartets ($\delta_{\text{p}} =$

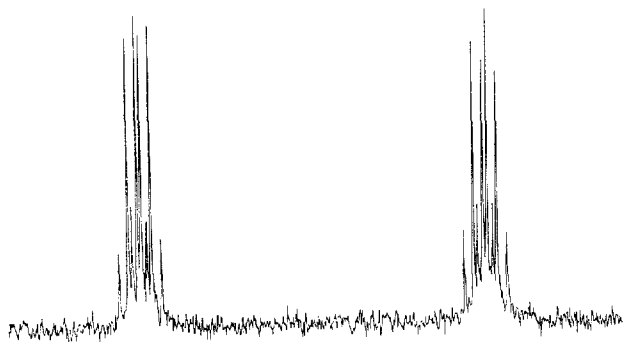


Fig. 1. ^{31}P NMR spectrum of compound **4**.

-105.3 ppm; $^2J_{\text{PH}} = 13.8$ Hz, $^2J_{\text{PH}} = 10.3$ Hz). All the NMR spectroscopic data for both **4** and **5** are in close agreement with those reported for several structurally related compounds described by Mays and coworkers [17] and Huttner and coworkers [18], who obtained both types of compounds from pyrolysis reactions of RPH_2 and osmium carbonyl clusters.

The mechanism of the reaction of the complexed phosphinidene $[\text{W}(\text{PMe})(\text{CO})_5]$ reaction with **2** presumably involves (i) migration of one of the H atoms from Os to P to afford **4**, and (ii) H atom migration back from phosphorus to the cluster system, the second step being accompanied by CO displacement to produce **5**. Previously, H-migration from bridging ligands to a cluster has been observed [19–21,23] and secondary phosphine substituted triosmium clusters of the type $[\text{Os}_3(\text{CO})_{11}(\text{PR}^1\text{R}^2\text{H})]$ are known to undergo deprotonation/protonation reaction sequences to form the phosphido bridged clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-PR}^1\text{R}^2)]$ ($\text{R}^1 = \text{R}^2 = \text{H}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$; $\text{R}^1, \text{R}^2 = \text{Ph}$) [22]. It seems likely that the initial step in the reaction sequence may involve **6** in which $[\text{W}(\text{PMe})(\text{CO})_5]$ acts as a $2e^-$ donor to the triosmium cluster **2**, as is well established in many reactions of **2** with other more conventional ligands, such as CNMe , CNPh , PPh_3 , etc. [23,24]. Careful monitoring of the early stages of the reaction of **2** and **3** by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed a new singlet ($\delta = 8.6$ ppm) which exhibits ^{183}W satellites ($^1J_{\text{PW}} = 239$ Hz) which can only be tentatively assigned to **6**, since it disappears rapidly as the reaction proceeds.

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