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Preliminary Communication

First example of the cycloaddition of a terminal phosphinidene across the Rh=Rh bond of $[Rh_2(\eta^5\text{-}C_5Me_5)_2\{\mu\text{-}(CO)_2\}]$. Crystal structure of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{MePW(CO)_5\}]$

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Abstract

The transient phosphinidene complex $[MeP{=}W(CO)_5]$ undergoes a cycloaddition to the Rh=Rh double bond in $[Rh_2(\eta^5\text{-}C_5Me_5)_2\{\mu\text{-}(CO)_2\}]$ to afford $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{MePW(CO)_5\}]$, which has been structurally characterised, thereby completing a series of reactions involving isolobal C=C, C=M, and M=M compounds.

There is considerable current interest in the chemistry and ligating ability of compounds of phosphorus having low coordination numbers [1].

Phosphinidenes RP are highly reactive species, whose identity has been deduced by complexation and/or isolation of products from trapping reactions [2–6]. The transient formation of terminal phosphinidene metal complexes was first proposed by Huttner [7], and subsequently stable species typified by $[M(\eta^5\text{-}C_5H_5)_2PR]$ (M = Mo. W) [8] and $[W(\eta^5\text{-}C_5Me_5)_2PNHR]$ [9] ($R = 2,4,6\text{-}{}^tBu_3C_6H_2$) have been reported.

Mathey *et al.* [10–12] have previously shown that 7-phosphanorbornadiene complexes are precursors of transient phosphinidene complexes of the type [RP=M] ($M = [Cr(CO)_5]$, $[Mo(CO)_5]$, $[W(CO)_5]$) which readily insert into C-H, N-H, O-H strained N-C and O-C bonds and metal-carbon bonds [13–17].

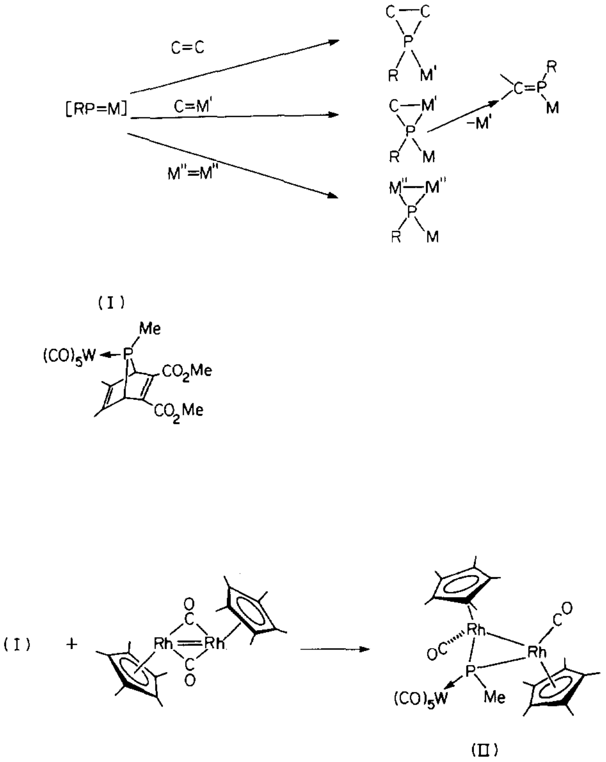
Terminal phosphinidenes also undergo [1 + 2] cycloadditions with alkenes with retention of configuration indicating that they are singlet species [18], and with transition metal carbene complexes they can give transient four-electron σ-, π-phospha-alkene metal complexes [19,20], which lose their π-bonded metal to form η^1-phospha-alkene complexes (see Scheme 1).

In view of the known isolobal relationships [21,22]:

$$RP \underset{\circ}{\longleftrightarrow} CH_2 \underset{\circ}{\longleftrightarrow} Rh(CO)(\eta^5\text{-}C_5Me_5)$$

we decided to investigate the reaction of the phosphinidene complex $[MePW(CO)_5]$ with $[Rh_2(\eta^5\text{-}C_5Me_5)_2\{\mu\text{-}(CO)_2\}]$, which formally contains a Rh=Rh double bond, in order to see if we could complete a series of related cycloaddition reactions spanning organic, organometallic and inorganic chemistry (see Scheme 1).

Treatment of an equimolar amount of the pentacarbonyl(tungsten)-Me-7-phosphanorbornadiene complex (I) with $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}(CO)_2)]$ in benzene at 55–60°C, in the presence of CuCl as catalyst, gave red



Scheme 1.

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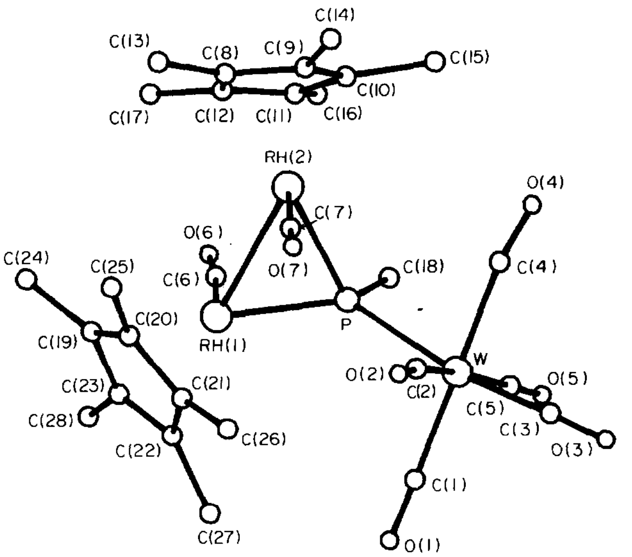

Fig. 1.

crystals (*ca.* 50%) of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{MePW(CO)_5\}]$ (**II**). (νCO) 2072, 2017, 2054, 1967, 1910, 1877 cm^{-1}) whose FAB mass spectrum contained the parent ion at m/e 902 and peaks corresponding to $M^+ - CO$, $M^+ - 2CO$, and $M^+ - 5CO$. The $^{31}\{^1H\}$ NMR spectra of **II** consisted of a 1-2-1 triplet (δ(P) 195.6 ppm. ^1J(PRh) 75.8 Hz), each line exhibiting ^{183}W satellites (^1J(PW) 194 Hz).

The molecular structure of **II**, which was confirmed by a single crystal X-ray diffraction study (Fig. 1), shows that only terminal carbonyl ligands are attached to the two Rh atoms, as in the structurally related μ-methylene complex $[Rh_2(\eta^5\text{-}C_5H_5)_2\mu\text{-}CH_2(CO)_2]$ (**III**) [23,24]. The Rh–Rh bond in **II** (2.721(1) Å) is slightly longer than that in **III** (2.665(1) Å), and the Rh(1)–P–Rh(2) angle (71.4°) in **II** is narrower than the corresponding Rh(1)–C–Rh(2) angle (81.7°) in **III**.

Although the two terminal CO's attached to the rhodium atoms lie on opposite sides of the rings in both **II** and **III**, the disposition of the two cyclopentadienyl rings is different in the two complexes no doubt reflecting the presence of the $[W(CO)_5]$ fragment attached to the bridging PR group in **II**.

The synthesis of **II** further underlines the usefulness of the isolobal principle as the basis for a strategy in synthetic chemistry, thereby linking apparently unrelated aspects of organic, organometallic, and inorganic chemistry.

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