Coupling of Two Phospha-alkyne Units *via* a Carbonyl Group, in the Addition across the Rh=Rh Double Bond of $[\mathrm{Rh_2(CO)_2(\eta^5\text{-}C_5Me_5)_2}]$, Crystal and Molecular Structure of the Complex $[\mathrm{Rh_2(CO)(\eta^5\text{-}C_5Me_5)_2\{PCRC(O)CRP\}}]$ (R = adamantyl)

Peter B. Hitchcock, Mohd Jamil Maah, and John F. Nixon*

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, U.K.

The novel ligating unit P=CRC(O)CR=P (R = adamantyl) has been obtained from two phospha-alkynes RC≡P on treatment with $[\mathrm{Rh_2(CO)_2(\eta^5\text{-}C_5Me_5)_2}]$.

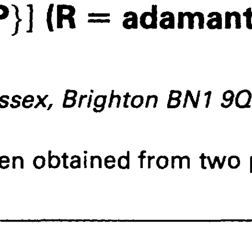
The close analogy between the co-ordination chemistry of alkynes and phospha-alkynes, RC≡P, is well illustrated by their behaviour towards metal–metal multiple bonds. Thus $\mathrm{Bu^tC{\equiv}P}$ adds readily across the Mo≡Mo triple bond in $[\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4}]$ and across the Rh=Rh double bond in $[\mathrm{Rh_2(CO)_2(\eta^5\text{-}C_5Me_5)_2}]$ giving the complexes (**1a**) (M = M′ = Mo)[1—4] and (**2a**) (M = M′ = Rh)[4] respectively.

We find that although $\mathrm{Bu^tC{\equiv}P}$ reacts analogously with the mixed metal complexes $[\mathrm{MoW(\eta^5\text{-}C_5H_5)_2(CO)_4}]$ and $[\mathrm{CoRh(\eta^5\text{-}C_5Me_5)_2(CO)_2}]$ to afford (**1b**) (M = Mo; M′ = W)[5] and (**2b**) (M = Co, M′ = Rh),[6] a different type of reaction also is observed when an excess of RC≡P (R = adamantyl) reacts with $[\mathrm{Rh_2(CO)_2(\eta^5\text{-}C_5Me_5)_2}]$.

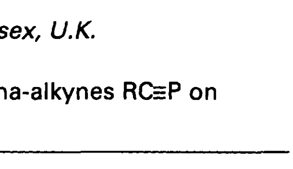
The novel product (**3**), the structure of which has been fully established by a single crystal *X*-ray study,[†] results from the coupling of two phospha-alkyne fragments *via* a carbonyl group originating from the starting dinuclear carbonyl complex to produce the new P=CRC(O)CR=P ligating unit. It is interesting to note the simple structural relationship of this unit with the complex $[\mathrm{W(\eta^5\text{-}C_5H_5)(CO)_2\{\mu\text{-}RCC(O)CR\}\text{-}W(\eta^5\text{-}C_5H_5)(CO)_2}]$ recently reported by Stone *et al.*[7] based on isolobal relationships $\mathrm{W(\eta^5\text{-}C_5H_5)(CO)_2} \underset{\circ}{\longleftrightarrow} \mathrm{P} \underset{\circ}{\longleftrightarrow} \mathrm{CR}$.

The structure of (**3**) (see Figure 1) indicates that one rhodium atom, Rh(1), is attached in an η^2-fashion to the P=C double bonds [d(P–C) 1.783(12) Å] while the other rhodium, Rh(2), (which also is ligated by a carbon monoxide ligand) is directly bonded to both phosphorus atoms [d(Rh–P) 2.357(4) Å].

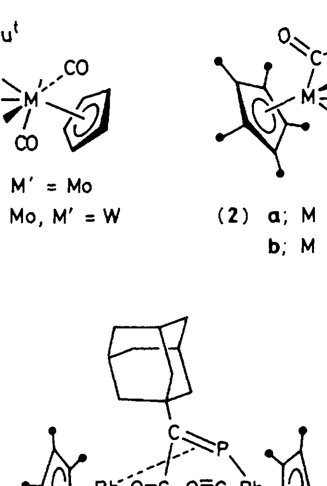
This is the first example of the interlinking of two phospha-alkyne ligands by a carbonyl group and the structure of (**3**) further underlines the similarity between alkynes and



(**1**) a; M = M′ = Mo
b; M = Mo, M′ = W



(**2**) a; M = M′ = Rh
b; M = Co, M′ = Rh



(**3**)

—• = Me

[†] *Crystal Data:* $\mathrm{C_{42}H_{60}O_2P_2Rh_2{\cdot}C_7H_8}$, $M = 956.9$, monoclinic, space group $P2_1/m$, $a = 9.636(5)$, $b = 22.295(7)$, $c = 11.480(5)$ Å, $\beta = 112.74(4)°$, $U = 2274.5$ Å^3, $Z = 2$, $D_c = 1.40$ g cm^{-3}. The structure was solved by heavy atom methods and refined to $R = 0.061$ using 2126 unique reflections with $|F^2| > \sigma|F^2|$ measured on an Enraf-Nonius CAD 4 diffractometer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

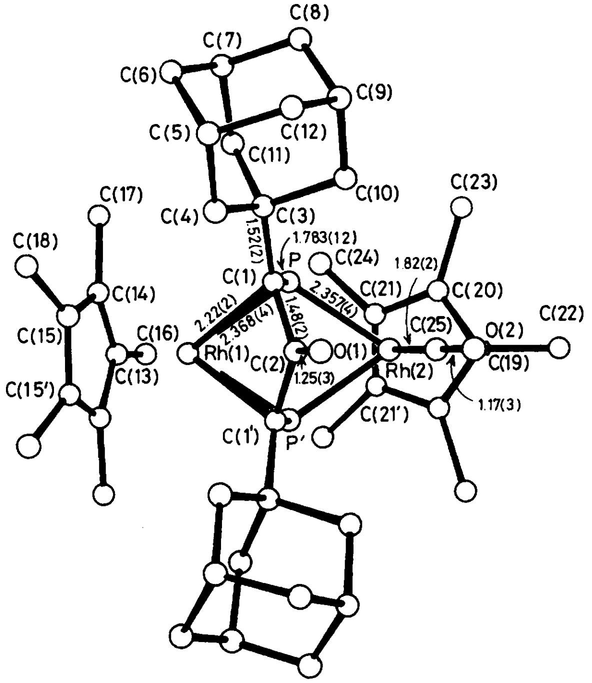


Figure 1. The molecular structure of $[Rh_2(CO)(\eta^5.C_5Me_5)_2\{PC\text{-}RC(O)CRP\}]$ (R = adamantyl) (**3**), with bond lengths in Å.

phospha-alkynes. Similar behaviour occurs for Bu^{t}CP, and these complexes are closely related to the rhodium complexes $[Rh_2(\eta^5\text{-}C_5H_5)_2(MeC_2Me)(CO)(CF_3C_2CF)_3]$[8] and $[Rh_2(\eta^5\text{-}C_5H_5)_2(RC_2R)_2(CO)]$ (R = CF_3 or Et),[9,10] and the iron compounds $[Fe_2(CO)_6(RC_2R(CO)]$ (R = Me or Ph)[11,12] and $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)\{C_4(CF_3)_4CO\}]$[13] which were derived from alkynes.

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