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Coupling of Two Phosphaalkynes via a Carbonyl Group in the Addition across a Rh=Rh Double Bond

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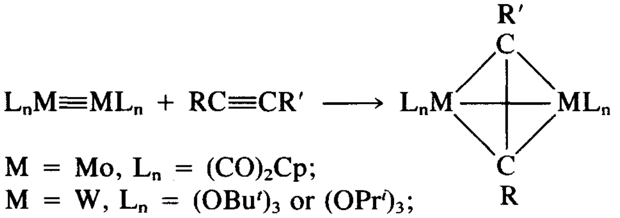
ABSTRACT

Phosphaalkynes, $RC{\equiv}P$ *(R = Bu^t, Adamantyl), add across the Rh=Rh double bond of* $[Rh_2Cp^*_2(CO)_2]$ *to give either* $[Rh_2Cp^*_2(\mu\text{-}CO)(COPCR)]$ *or* $[Rh_2Cp^*_2(CO)\{PCRC(O)CRP\}]$ *depending on the stoichiometry of the reaction (*$Cp^* = \eta^5\text{-}C_5Me_5$*). The structures of these complexes have been elucidated by NMR spectroscopy and by a single crystal X-ray study on* $[Rh_2Cp^*_2(CO)\{PCAdC(O)CPAd\}]$*. Small amounts of the 1,3-diphosphacyclobutadiene complexes* $[RhCp^*(P_2C_2R_2)]$ *and the trinuclear compound* $[Rh_3Cp^*_3(CO)_2]$ *are also formed in these reactions. The reactions of* $RC{\equiv}P$ *with* $[CoRhCp^*_2(CO)_2]$ *are also described.*††

INTRODUCTION

The chemistry involving the addition of alkynes across metal–metal multiple bonds has been extensively and systematically studied [1, 2]. Alkynes have been shown to add across metal–metal triple bonds to give tetrahedrane-type adducts [1, 2].



$M = Mo, L_n = (CO)_2Cp;$
$M = W, L_n = (OBu^t)_3$ or $(OPr^i)_3;$
$R = R' =$ alkyl or aryl

The isolobal principle first proposed by Hoffmann [3] and later extensively developed by Stone [4] has shown the following relationship:

$$RC \xleftrightarrow[\circ]{} P \xleftrightarrow[\circ]{} M(CO)_2Cp \quad (M = Cr, Mo, \text{ or } W)$$

This has led to a number of reactions involving additions of carbynes or P_4 across metal–metal triple bonds to afford a variety of novel complexes [5, 6].

Addition of alkynes across metal–metal double bonds has also been reported by Herrmann et al. [7] to afford dimetal–alkyne complexes. For example, $PhC{\equiv}CH$ adds across the Rh=Rh double bond of di(μ-carbonyl)-di(η^5-pentamethylcyclopentadienyl)dirhodium.

The close analogy between alkynes and phosphalkynes has led Nixon et al. [10, 12, 13] and Herrmann et al. [11] to carry out similar reactions of phosphaalkynes with dinuclear complexes containing metal–metal single and multiple bonds analogous to those outlined above.

They found that phosphaalkynes also add across the metal–metal multiple bonds to give tetrahedrane-type adducts, and analogous mixed metal phosphaalkyne complexes can be otained by similar routes if heterodinuclear metal–metal multiply-bonded complexes are used (see Scheme 1).

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This paper is dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

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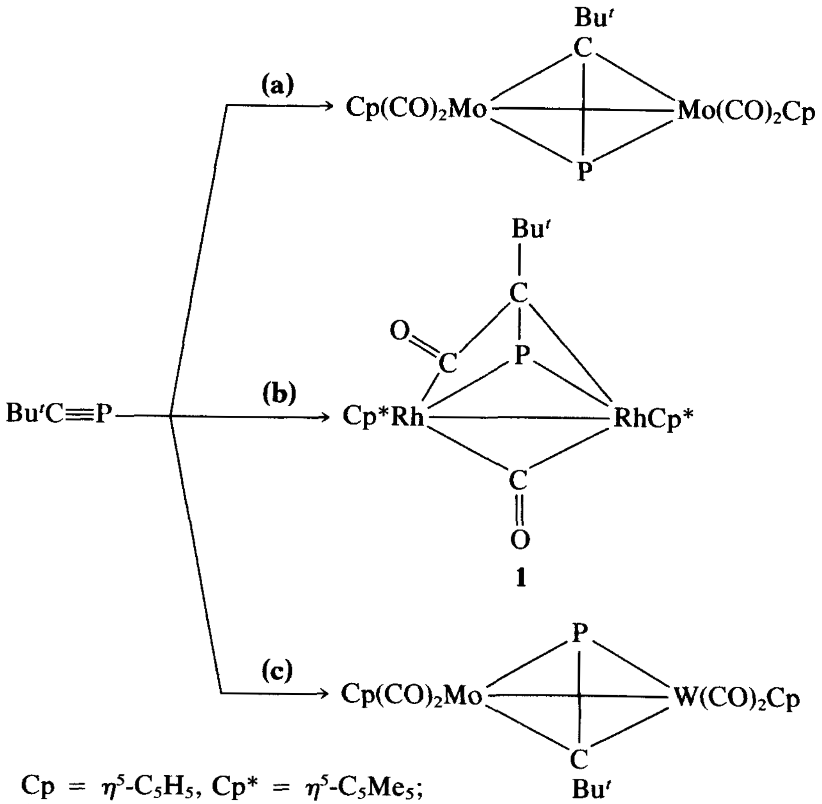


Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5;
(a) [$Mo_2Cp_2(CO)_4$](Mo≡Mo) [10, 11];
(b) [$Rh_2Cp_2^*(CO)_2$](Rh=Rh) [11];
(c) [$MoWCp_2(CO)_4$](Mo≡W) [12]

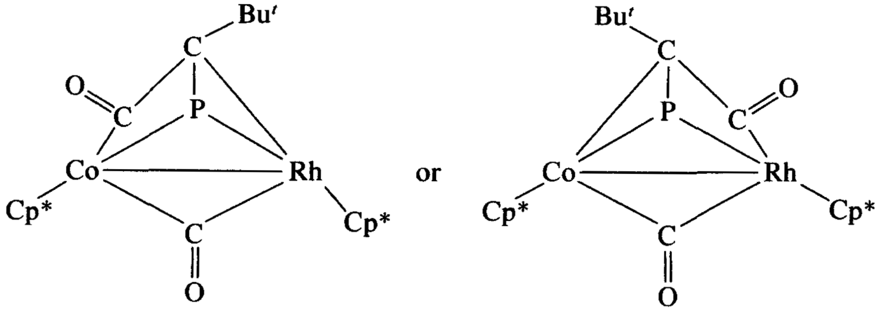
SCHEME 1

Study on the reactivities of some dirhodium–alkyne complexes of the type [$Rh_2Cp_2(CO)(RC≡CR)$] (R = CF_3, H, Ph) carried out by Dickson and coworkers [8, 9] has shown that these complexes can react further with alkynes to give a variety of products.

It was therefore of interest to investigate the reaction of phosphaalkynes with mixed metal complexes containing a M=M double bond, e.g. [$CoRhCp_2^*(CO)_2$](Co=Rh), and to reinvestigate the reactions of [$Rh_2Cp_2^*(CO)_2$](Rh=Rh) with an excess of phosphaalkyne.

RESULTS AND DISCUSSION

Treatment of [$CoRhCp_2^*(CO)_2$] [14] with Bu^{t}C≡P at room temperature readily afforded the red brown complex **2**. The formulation of **2** is based on its $^{31}P\{^1H\}$ and ^1H NMR spectra (Table 1), the former exhibiting a doublet with a small ^1J(RhP) coupling constant. There is a large phosphorus coordination shift (ca 434) upon coordination (δ(Bu^{t}CP) = −209), which was also observed in the dirhodium complex **1** [11] (see Table 1), suggesting that there is a metal–metal interaction between cobalt and rhodium at-



2a **2b**

FIGURE 1

TABLE 1 $^{31}P\{^1H\}$ and ^1H NMR and Infrared Spectroscopic Data of the Complexes 1–4 and 6

	$^{31}P\{^1H\}$ *NMR*		^1H *NMR*		*IR*
Complex	$\delta(P)^a$	$^1J(RhP)^b$	$\delta(C_5Me_5)^a$	$\delta(R)^a$	$\nu(CO)^c$
2	225.5(d)	24.4	1.63, 1.70	0.95	1788s, 1675m, br
3	193.4(t)	26.9	1.79, 1.89	1.30–1.60	1720s, 1608s
1	192.6(dd)	30, 27	1.78, 1.86	0.77	1795s, 1625br
1	189(t)	29	1.84, 1.92	0.83	1805s, 1680m, br
4	−107.9(dd)	46.5^d 22.4^e	1.79, 1.83	1.34–1.53	2059s, 1603br
6	−121.1(dd)	44.7^d 20.8^e	1.78, 1.95	1.28	2070br, 1610s

[a] Relative to trimethyl phosphite
[b] In Hz
[c] In cm^{-1}
[d] $^1J(Rh^2P)$
[e] $^1J(Rh^1P)$
[f] Ref. 11

oms as noted in the related phosphido-bridged complexes [15]. The small $^1J(RhP)$ coupling constant in **2** is comparable with that observed for **1**, suggesting a π-mode of coordination to the two metal centers.

Structures **2a** and **2b** are possible since the insertion of $Bu^tC{\equiv}P$ can be into the Rh–CO or Co–CO bond. As expected the ^1H NMR spectrum of **2** exhibits two different resonances for the C_5Me_5 protons, a broad singlet for the Co–C_5Me_5 protons and a doublet for the Rh–C_5Me_5 protons. The infrared spectrum shows two carbonyl stretching bands that correspond to the two bridging carbonyls. A $^{13}C\{^1H\}$ NMR study on the carbonyls of **2** would in principle be able to distinguish the two isomers since both carbonyls in **2b** would be coupled to the rhodium-103 nucleus in contrast to only one in **2a** (see Figure 1).

Treatment of $[Rh_2Cp^*_2(CO)_2]$ with an excess of $AdC{\equiv}P$ affords a deep red solution whose $^{31}P\{^1H\}$ NMR spectrum shows the presence of three different phosphorus-containing species, **3**, **4**, and **5**. A deep red complex, **3**, and a red-orange compound, **4**, were obtained by eluting this solution through an alumina column. The formulation of these complexes was established from their $^{31}P\{^1H\}$ and ^1H NMR spectra, (Table 1).

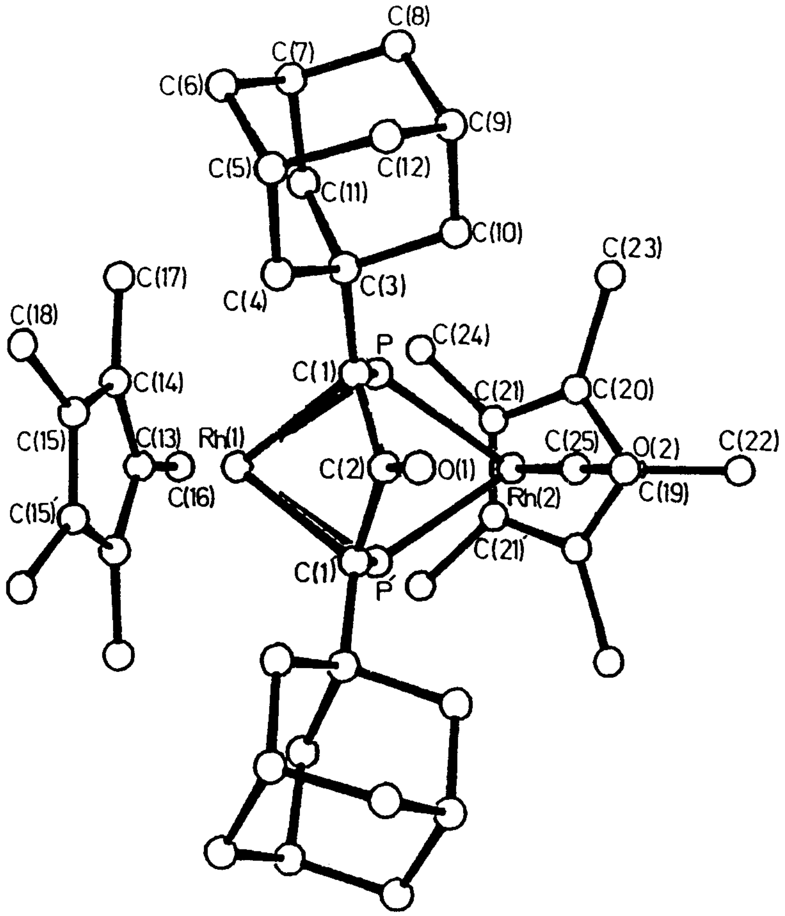
The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a triplet in the low field region. The ^1H NMR spectrum shows two different C_5Me_5 resonances and a broad multiplet for the adamantyl protons while the infrared spectrum indicates the presence of two bridging carbonyls. Interestingly the $^{31}P\{^1H\}$ NMR chemical shift of **3** lies in the same region as **1** and **2**, strongly suggesting that all three complexes have a similar structure. Thus $AdC{\equiv}P$ behaves analogously as $Bu^tC{\equiv}P$ and adds across the Rh=Rh double bond of $[Rh_2Cp^*_2(CO)_2]$.

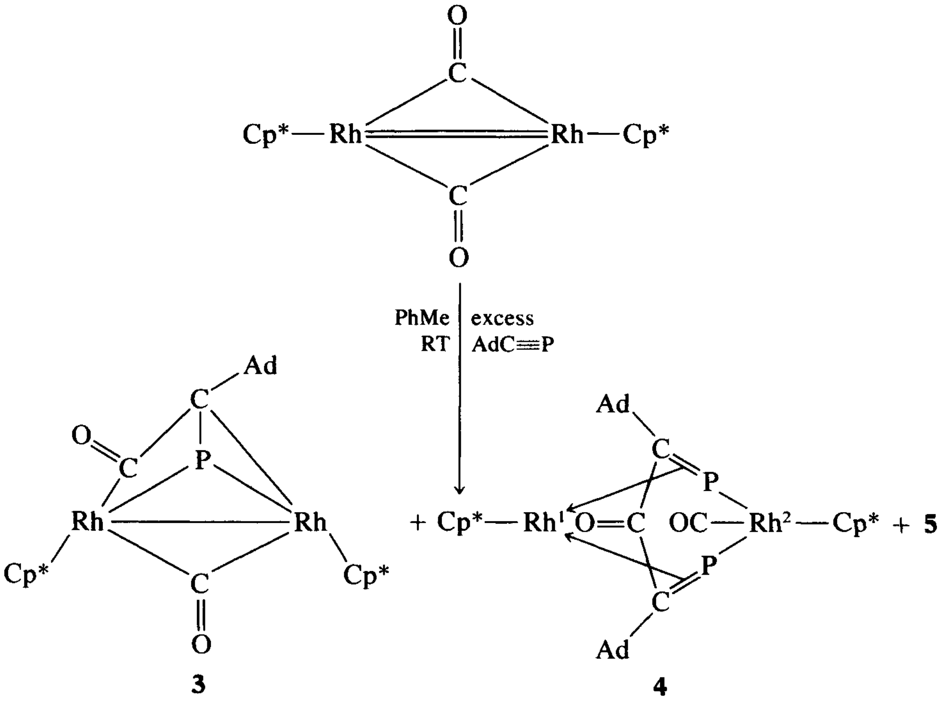
The ^1H NMR spectrum of **4** also exhibits two different signals for the protons of the two C_5Me_5 groups and resonances arising from the adamantyl group. Integration of the spectrum reveals that two moles of $AdC{\equiv}P$ have been consumed during the reaction. The infrared spectrum of **4** shows both ketonic and terminal carbonyl bands. The doublet of doublets pattern in the $^{31}P\{^1H\}$ NMR spectrum of **4** clearly indicates that the phosphorus atoms of the two phosphaalkyne units are bound in a different way to the two rhodium atoms. The small $^1J(RhP)$ coupling constants indicate that neither phosphorus atom is bonded to the rhodium via its lone pair of electrons since a larger value for $^1J(RhP)$ (>100 Hz) would be expected. A single crystal X-ray diffraction study confirms the above spectroscopic conclusions. Figure 2 reveals that the two $AdC{\equiv}P$ units have been coupled via a carbonyl group to provide a novel $P{=}CRC(O)CR{=}P$ (R = adamantyl) ligating unit. The reaction can be summarized as illustrated in Scheme 2.

The solid state structure of **4** shows that one rhodium atom, Rh(1), is attached in an η^2-fashion to each of the P=C double bonds while the other rhodium, Rh(2), is directly bonded to both phosphorus atoms. Both rhodium atoms satisfy the 18 electron rule if each phosphorus atom is considered to contribute one electron to Rh(2) and two electrons each from the two P=C double bonds to Rh(1).

The structure of **4** as presented in Figure 3 illustrates clearly the modes of bonding between the phosphorus atoms of $AdC{\equiv}P$ and the two rhodium atoms. It also shows that **4** is in fact a novel metallodiphosphaalkene complex that coordinates in an η^4-fashion to the (Rh^1Cp^*) fragment. In recent years a number of metallophosphaalkenes of the type $L_nMP{=}CR_2$ (M = Fe, $L_n = Cp^*(CO)_2$, R = $SiMe_3$; M = Ni, $L_n = Cp^*(PPh_3)$, R = $SiMe_3$; M = Mo, W, $L_n = Cp(CO)_3$, R = $SiMe_3$) have been reported by Cowley, Niecke, Weber, and coworkers [16–19].

FIGURE 2 The Molecular Structure of **4**





SCHEME 2

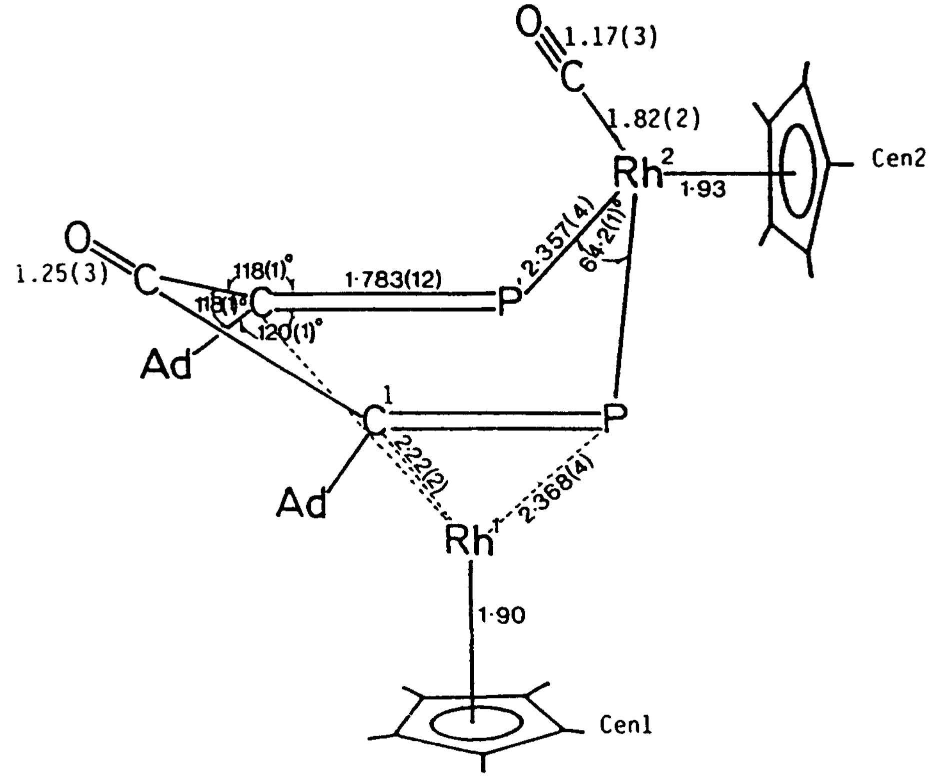


FIGURE 3 Structure of **4** (bond lengths in Å)

Very recently Nixon et al. [22] have synthesized platinum-substituted phosphaalkenes via Me_3SiCl elimination in reactions of $[Ad(Me_3SiO)C{=}P(SiMe_3)]$ (Ad = adamantyl) with $PtCl_2(PR_3)_2$ (R = Et or Pr^n).

Treatment of $Cp^*{-}P{=}C(SiMe_3)_2$ with transition metal complexes also afforded metallophosphaalkenes involving a migration of the pentamethylcyclopentadienyl ligand from phosphorus to the metal atom [17, 20, 21]. Complex **4** not only represents the first rhodium-substituted phosphaalkene but also the first reported metallodiphosphaalkene.

It is interesting to note that the values of $^1J(MP)$ (M = W, Pt, and Rh) coupling constants for metallophosphaalkenes are very small compared to the corresponding values for typical phosphine complexes. The low $^1J(MP)$ values can be attributed to the low s-character of the metal–phosphorus bond in the metallophosphaalkene compounds.

Complex **4** also represents the first example of interlinking of two phosphaalkyne ligands by a carbonyl group, and its structure further underlines the similarity between alkynes and phosphaalkynes (vide infra). The basic molecular structure of **4** consists of a PCRC(O)CRP (R = adamantyl) ligating unit bridging two [RhCp*] moieties. The arrangement of the atoms is symmetrical and the molecule has a plane of symmetry passing through the two rhodium atoms and the ketonic and terminal carbonyls.

The P–C bond distance (1.783(12) Å) in **4** (see Table 2) is longer than the P≡C triple bond distance found in free AdC≡P (1.54 Å) [23] and lies within the range normally observed for η^2-coordinated phosphaalkene complexes (1.74–1.83 Å) [24–30]. C(2) and Rh(2) lie above the P–*C(1)–C(1)′–P′* plane so that there is a boat conformation.

The Rh(2)–P–C(1) bond angle (114.3(6)°) lies within the range of M–P–C angles normally observed for metallophosphaalkenes (113.8–126.2°) [16, 17, 31, 32], and the lone pair of electrons at each phosphorus is not directly involved in bonding to the metal. The sum of the bond angles at C(1) is 360° within experimental error, indicating that as expected C(1) is sp^2-hybridized.

The Rh(2)–P bond distance (2.357(4) Å) is almost equivalent to the Rh(1)–P bond distance (2.368(4) Å) and similar P–Rh–P bond angles (P–Rh(1)–P 63.8(1)°; P–Rh(2)–P′ 64.2(1)°) are exhibited by both rhodium atoms. The Rh–P bond distances are within the range observed for phosphido-bridged rhodium complexes (2.244–2.418 Å) [33–36] and the molecular structure of **4** does resemble such complexes except for the presence of the P=C double bond. These Rh–P bond distances are longer than the observed Rh–P (phosphine) bond distances (2.18–2.33 Å) [37–41]. The longer bond distance can be attributed to the repulsion between the pentamethylcyclopentadienyl and the adamantyl groups. The Rh(1)–C(1) bond length lies within the range normally observed for Rh–C(alkene) bonds (2.098–2.254 Å) [40–42].

TABLE 2 Intramolecular Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

Bonds			
Rh(1)–P	2.368(4)	Rh(1)–C(1)	2.22(2)
Rh(1)–C(13)	2.20(2)	Rh(1)–C(14)	2.21(2)
Rh(1)–C(15)	2.293(15)	Rh(2)–P	2.357(4)
Rh(2)–C(19)	2.19(2)	Rh(2)–C(20)	2.25(2)
Rh(2)–C(21)	2.30(2)	Rh(2)–C(25)	1.82(2)
Rh(1)–Cen1	1.90	Rh(2)–Cen2	1.93
P–C(1)	1.783(12)	O(1)–C(2)	1.25(3)
O(2)–C(25)	1.17(3)	C(1)–C(2)	1.48(2)
C(1)–C(3)	1.52(2)	C(3)–C(4)	1.53(2)
C(3)–C(10)	1.55(2)	C(3)–C(11)	1.53(2)
C(4)–C(5)	1.49(2)	C(5)–C(6)	1.52(3)
C(5)–C(12)	1.55(3)	C(6)–C(7)	1.53(2)
C(7)–C(8)	1.52(3)	C(7)–C(11)	1.53(2)
C(8)–C(9)	1.47(3)	C(9)–C(10)	1.54(2)
C(9)–C(12)	1.50(2)	C(13)–C(14)	1.40(2)
C(13)–C(16)	1.51(3)	C(14)–C(15)	1.41(2)
C(14)–C(17)	1.50(3)	C(15)–C(18)	1.55(2)
C(19)–C(20)	1.36(3)	C(19)–C(22)	1.54(4)
C(20)–C(21)	1.37(3)	C(20)–C(23)	1.61(3)
C(21)–C(24)	1.50(4)	C(15)–C(15)[a]	1.37(2)
C(21)–C(21)[a]	1.41(3)	C(27)–C(30)[b]	1.43(4)
C(26)–C(27)	1.61(6)	C(26)–C(31)	1.12(4)
C(27)–C(28)	1.63(5)	C(28)–C(29)	1.08(4)
C(29)–C(30)	1.35(6)	C(30)–C(31)	1.17(5)

Angles			
P–Rh(1)–P[a]	63.8(1)	P–Rh(1)–Cen1[c]	130.7
P–Rh(1)–C(1)	45.6(3)	P–Rh(1)–C(1)[a]	83.1(4)
Cen1–Rh(1)–C(1)	144.0	C(1)–Rh(1)–C(1)[a]	66.4(6)
P–Rh(2)–P[a]	64.2(1)	P–Rh(2)–Cen2	124.3
P–Rh(2)–C(25)	95.2(6)	Cen2–Rh(2)–C(25)	132.1
Rh(1)–P–Rh(2)	116.0(2)	Rh(1)–P–C(1)	62.9(5)
Rh(2)–P–C(1)	114.3(6)	Rh(1)–C(1)–P	71.6(5)
Rh(1)–C(1)–C(2)	88(1)	Rh(1)–C(1)–C(3)	129(1)
P–C(1)–C(2)	118(1)	P–C(1)–C(3)	120(1)
C(2)–C(1)–C(3)	118(1)	C(14)–C(13)–C(16)	126(1)
O(1)–C(2)–C(1)	124(1)	C(1)–C(2)–C(1)[a]	111(2)
C(1)–C(3)–C(4)	113(1)	C(1)–C(3)–C(10)	107(1)
C(1)–C(3)–C(11)	113(1)	C(4)–C(3)–C(10)	108(1)
C(4)–C(3)–C(11)	108(1)	C(10)–C(3)–C(11)	107(1)
C(3)–C(4)–C(5)	112(1)	C(4)–C(5)–C(6)	111(1)
C(4)–C(5)–C(12)	107(1)	C(6)–C(5)–C(12)	111(2)
C(5)–C(6)–C(7)	108(1)	C(6)–C(7)–C(8)	109(2)
C(6)–C(7)–C(11)	111(1)	C(8)–C(7)–C(11)	108(2)
C(7)–C(8)–C(9)	112(2)	C(8)–C(9)–C(10)	110(2)
C(8)–C(9)–C(12)	110(2)	C(10)–C(9)–C(12)	109(1)
C(3)–C(10)–C(9)	109(1)	C(3)–C(11)–C(7)	111(1)
C(5)–C(12)–C(9)	109(2)	C(14)–C(13)–C(14)[a]	108(1)
C(13)–C(14)–C(15)	107(1)	C(13)–C(14)–C(17)	125(1)
C(15)–C(14)–C(17)	127(1)	C(14)–C(15)–C(15)[a]	108(1)
C(14)–C(15)–C(18)	127(2)	C(15)[a]–C(15)–C(18)	124(1)
C(20)–C(19)–C(20)[a]	108(2)	C(20)–C(19)–C(22)	126(1)
C(21)[a]–C(21)–C(24)	129(2)	C(19)–C(20)–C(21)	109(2)
C(19)–C(20)–C(23)	129(2)	C(21)–C(20)–C(23)	122(2)
C(20)–C(21)–C(21)[a]	107(2)	C(20)–C(21)–C(24)	124(2)
C(27)–C(26)–C(31)	121(4)	C(26)–C(27)–C(28)	102(2)
C(27)–C(28)–C(29)	120(4)	C(28)–C(29)–C(30)	126(4)
C(29)–C(30)–C(31)	122(3)	C(26)–C(31)–C(30)	128(5)
C(26)–C(27)–C(30)[b]	134(3)	C(28)–C(27)–C(30)[b]	124(3)

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[a] Symmetry elements: x, 0.5 − y, z

[b] Symmetry elements: −x, 1 − y, 1 − z

[c] Cen1 and Cen2 are the centroids of the cyclopentadienyl rings bonded to Rh(1) and Rh(2) respectively.

Another interesting feature of the molecular structure of **4** is the absence of a formal Rh–Rh bond indicating that the Rh=Rh double bond of $[Rh_2Cp^*_2(CO)_2]$ has been cleaved to accommodate the new PCRC(O)CRP ligating unit, leaving the other carbonyl bonded to one rhodium atom. This clearly differentiates the complex from other closely related rhodium complexes: $[Rh_2Cp_2(MeC_2Me)(CO)(CF_3C_2CF_3)]$ [43], $[Rh_2Cp_2(RC_2R)_2(CO)]$ [44, 45] (R = CF_3; Et), $[Rh_2Cp_2(CO)(HC_2Bu^t)(CF_3C_2CF_3)]$ [9] and the iron compounds $[Fe_2(CO)_6\{R_4C_4(CO)\}]$ [46, 47] (R = Me; Ph) and $[Fe_2Cp_2(CO)\{C_4(CF_3)_4CO\}]$ [48], all of which have formal metal–metal bonds.

The carbonyl group C(2)–O(2) that links the two AdCP units has a C–O bond distance of 1.25(3) Å, which is normal for a ketonic carbonyl group and is similar to carbonyl bond lengths found in many other structurally related organometallic compounds including the cyclopentadienone complex $[CoCp\{C_4(CF_3)_4CO\}]$ [49], the *p*-benzoquinone complex $[CoCp\{C_4(CH_3)_4(CO)_2\}]2H_2O$ [50], and the recently reported cyclopentadienone complex $[Rh_2Cp_2(CO)\{C_4(CF_3)_2HBu^tCO\}]$ [9].

The Rh to cyclopentadienyl plane distances are 1.90 and 1.93 Å for Rh(1) and Rh(2) respectively, which are shorter than found in the Rh–C_5Me_5 separations in $[CoRhCp^*_2(CO)_2]$ [14] and $[Rh_3(\mu\text{-}H)_2(\mu\text{-}CO)(\mu_3\text{-}CO)Cp^*_3]$ [51] (2.17–2.56 Å). The presence of the terminal carbonyl group on Rh(2) has little effect on the Rh(2)–C_5Me_5 separation compared to Rh(1)–C_5Me_5, and the C_5Me_5 planes are not parallel to each other but lie below the two rhodium and two phosphorus atoms and away from the adamantyl groups.

Reaction of $[Rh_2Cp^*_2(CO)_2]$ with an Excess of $Bu^tC{\equiv}P$

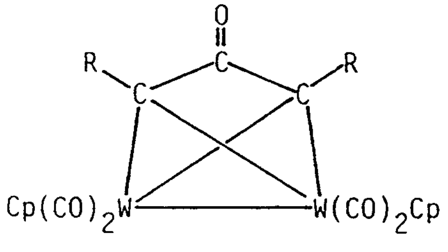
In an analogous way $[Rh_2Cp^*_2(CO_2]$ was treated with an excess of $Bu^tC{\equiv}P$ to afford a number of products. Two red orange products were identified as $[Rh_2Cp^*_2(CO)(Bu^tCPCO)]$, **1**, and $[Rh_2(CO)Cp^*_2\{PCBu^tC(O)Bu^tP\}]$, **6**, respectively, by their $^{31}P\{^1H\}$ and ^1H NMR spectra.

Complex **1** had been synthesized previously and characterized by Herrmann et al. [11] by the reaction of a 1 : 1 mixture of $[Rh_2Cp^*_2(CO)_2]$ and $Bu^tC{\equiv}P$ (see Scheme 1). The results on **1** obtained in this investigation are identical to Herrmann's and are summarized in Table 1. However, in addition we successfully recorded the $^{31}P\{^1H\}$ NMR spectrum of **1**, which was not previously reported, and exhibited a doublet of doublets, confirming the nonequivalence of the two rhodium atoms.

The $^{31}P\{^1H\}$ NMR spectrum of the new complex **6** corresponds to that of the adamantyl analogue **4**, exhibiting a doublet of doublets that indicates the nonequivalence of the two rhodium atoms. Further support for the structure comes from the ^1H NMR spectrum that shows two singlets (15H each) and a singlet (18H) that corresponds to the nonequivalent C_5Me_5 ligands and the equivalent *tert*-butyl groups respectively (see Table 1). The observation of two carbonyl stretching bands in the infrared spectrum indicates the presence of both ketonic and terminal carbonyls. Based on these spectroscopic results, the structure of **6** can be deduced to be similar to **4**.

Thus the reaction between the Rh=Rh double bond of $[Rh_2Cp^*_2(CO)_2]$ with an excess of phosphaalkyne not only gives the monophosphaalkyne complex reported by Herrmann et al. [11] but also affords a dirhodium complex containing the novel P=CRC(O)CR=P ligating unit. This is among the rare examples where a carbonyl group attacks the carbon instead of the phosphorus atom of the phosphaalkyne. Recently, Nixon et al. [52] reported a similar observation in complex $[Re_2(CO)_8Pt(dppe)\{Bu^tC(CO)P\}]$, where the carbon atom of the coordinated Bu^tCP is attacked by a carbon monoxide.

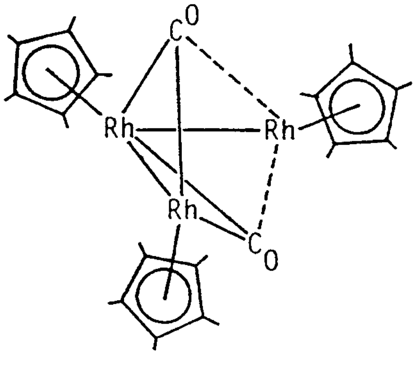
It is interesting to note the simple structural relationship of **4** and **6** with the complex $[WCp(CO)_2\{\mu\text{-}RCC(O)CR\}WCp(CO)_2]$ (R = C_6H_4Me-4) [53] reported by Stone et al. and based on the isolobal relationships $Cp(CO)_2W \underset{\circ}{\longleftrightarrow} P \underset{\circ}{\longleftrightarrow} CR$ viz:



R = C_6H_4Me-4

Identification of Other Products Obtained from the Reaction of $[Rh_2Cp^*_2(CO)_2]$ with $RC{\equiv}P$ (R = Ad or Bu^t)

A careful examination of the $^{31}P\{^1H\}$ NMR spectrum of the products of the reaction of $[Rh_2Cp^*_2(CO)_2]$ with an excess of $RC{\equiv}P$ (R = Bu^t, Ad) revealed a further product. Thus the reaction with $Bu^tC{\equiv}P$ exhibited a doublet ($\delta P = -100.0$, $^1J(RhP) = 29.8$ Hz) in addition to the signals for **1** and **6**. This resonance was identical to that for $[RhCp^*\{\eta^4\text{-}Bu^tCP)_2\}]$, **7**, previously reported by us [54]. After elution through an alumina column, another red-brown product, **8**, was isolated and identified as the trirhodium complex $[Rh_3Cp^*_3(CO)_2]$ by its characteristic ^1H NMR (δ-1.64, C_5Me_5) and infrared spectra ($\nu(CO)$: 1685 cm^{-1}). The synthesis of **8** has been reported by Stone et al. [14] from the reaction of $[RhCp^*(C_2H_4)_2]$ with $[Rh_2Cp^*_2(CO)_2]$.



8

A similar result is obtained in the reaction between $[Rh_2Cp^*_2(CO)_2]$ and an excess of AdC≡P, which exhibits a doublet ($\delta P = -102.1$, ${}^1J(RhP) = 29.3$ Hz) in the ${}^{31}P\{{}^1H\}$ NMR spectrum. By analogy with **7**, the product can be identified as $[RhCp^*\{\eta^4\text{-}(AdCP)_2\}]$, **5**, which has not been reported previously. The formation of **7** and **8** may result from a disproportionation of **6** or alternatively may be formed by separate reaction pathways.

EXPERIMENTAL

Reaction of $[CoRhCp^*_2(CO)_2]$ with Bu^{t}C≡P

A solution of $[CoRhCp^*_2(CO)_2]$ (52.9 mg, 0.11 mmol) in THF (3 mL) was treated with a solution of Bu^{t}C≡P (0.11 mg, 0.11 mmol) [55] in THF (2 mL) and the mixture immediately turned red brown. After 40 h at room temperature, removal of solvent in vacuo afforded a dark brown residue that was dissolved in toluene and eluted through an alumina column with toluene–ether (1:1) to give a red-brown solution. Removal of solvent gave red-brown crystals of μ-carbonyl-μ-[1-phospha-2-*tert*-butyl-3-oxo-propen-1,3-diyl-C^2(Co),C^3(Rh),P(Co,Rh)]-bis-η-(pentamethylcyclopentadienyl)-cobaltrhodium(Co-Rh), **2** (44 mg, 72%). Found: C, 58.23; H, 7.10; $C_{27}H_{39}PRhCo$ requires C, 58.28; H, 7.07%.

Reaction of $[Rh_2Cp^*_2(CO)_2]$ with an Excess of AdC≡P

To a solution of $[Rh_2Cp^*_2(CO)_2]$ (158 mg, 0.3 mmol) in toluene (5 mL) was added solid AdC≡P (108 mg, 0.60 mmol). The deep blue solution immediately turned deep red and was left to stir at room temperature for 24 h. The resulting red-brown solution was concentrated and eluted through an alumina column with toluene to afford deep red and red-orange solutions respectively. Removal of solvent in vacuo from the red solution afforded the red complex μ-carbonyl-μ-[1-phospha-2-adamantyl-3-oxo-prop-en-1,3-diyl-$C^2(Rh^1)$,$C^3(Rh^2)$,$P(Rh^1,Rh^2)$]-bis-η-(pentamethylcyclopentadienyl)dirhodium(Rh-Rh), **3** (97 mg, 53%). Found: C, 65.21; H, 7.42; $C_{33}H_{45}O_2PRh$ requires C, 65.23; H, 7.47%. Further concentration and leaving the red-orange solution standing at room temperature for several weeks gave red-orange crystals, 1-carbonyl-μ-[2,4-di-adamantyl-3-oxo-1,5-diphosphapenta-1,4-diene-1,5-diyl-$C^2(Rh^2)$,$C^4(Rh^2)$,$P^1(Rh^1,Rh^2)$,$P^5(Rh^1,Rh^2)$]-1,2-bis-η-(pentamethylcyclopentadienyl)dirhodium, **4** (25 mg, 9.4%). Found: C, 58.80; H, 6.42; $C_{44}H_{60}P_2Rh_2$ requires C, 59.41; H, 6.81%.

TABLE 3 Fractional Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses

	x	*y*	*z*
Rh(1)	294(2)	2500	1798(1)
Rh(2)	−1738(2)	2500	−1976(1)
P	−756(4)	1938(2)	−93(4)
O(1)	3313(13)	2500	480(14)
O(2)	1081(22)	2500	−2483(20)
C(1)	1245(14)	1954(7)	664(13)
C(2)	2047(21)	2500	536(19)
C(3)	2131(14)	1370(7)	1010(14)
C(4)	3646(14)	1436(7)	2125(13)
C(5)	4526(16)	865(9)	2415(16)
C(6)	3658(18)	367(9)	2749(17)
C(7)	2176(17)	279(8)	1619(19)
C(8)	2512(20)	114(8)	468(21)
C(9)	3367(19)	587(8)	147(17)
C(10)	2450(16)	1171(8)	−159(14)
C(11)	1257(16)	861(7)	1314(17)
C(12)	4840(18)	696(8)	1233(19)
C(13)	−1456(22)	2500	2587(19)
C(14)	−559(14)	1993(8)	3042(13)
C(15)	891(15)	2193(8)	3841(13)
C(16)	−3102(24)	2500	1730(23)
C(17)	−1136(18)	1362(9)	2879(19)
C(18)	2200(19)	1800(10)	4719(16)
C(19)	−3385(26)	2500	−3928(20)
C(20)	−3716(18)	2007(8)	−3384(17)
C(21)	−4167(17)	2185(9)	−2440(15)
C(22)	−2970(36)	2500	−5093(24)
C(23)	−3672(28)	1313(12)	−3747(29)
C(24)	−4652(23)	1761(13)	−1649(22)
C(25)	1(21)	2500	−2254(21)
C(26)[a]	607(34)	5276(16)	4291(30)
C(27)[a]	563(38)	4868(19)	5437(34)
C(28)[a]	−1218(30)	4890(14)	5205(26)
C(29)[a]	−2013(41)	5116(20)	4383(37)
C(30)	−1680(26)	5429(14)	3522(24)
C(31)[a]	−450(42)	5455(20)	3554(37)

[a] Occupancy 0.5.

Reaction of $[Rh_2Cp^*_2(CO)_2]$ with an Excess of Bu^{t}C≡P

In a similar fashion, a solution of $[Rh_2Cp^*_2(CO)_2]$ (50 mg, 0.95 mmol) in toluene was treated with a solution of Bu^{t}C≡P (200 mg, 2 mmol) in toluene (5 mL) to give a red-brown solution. The solvent was removed under reduced pressure leaving a dark brown residue that was dissolved in toluene and eluted through an alumina column with toluene to give red brown, red, and red-orange solutions consecutively. Removal of solvent in vacuo respectively afforded red-brown, red, and red-orange crystals. Red-brown crystals, $[Rh_3Cp^*_3(\mu_3\text{-}CO)_2]$, **8** (168 mg, 23%); infrared spectrum ($CDCl_3$), $\nu(CO)$: 1685 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.64(s,C_5Me_5). Red crystals μ-carbonyl-μ-[1-phospha-2-*tert*-butyl-3-oxo-prop-en-1,3-diyl-$C^2(Rh^1)$,$C^3(Rh^2)$,$P(Rh^1,Rh^2)$]-bis-η-(pentamethylcyclopentadienyl)dirhodium(Rh-Rh), **1** (319 mg, 56%). Found: C, 51.10; H, 6.16; $C_{27}H_{39}PRh_2O_2$ requires C, 51.28; H, 6.22%. Red-orange crystals, 1-carbonyl-μ-[2,4-di-*tert*-butyl-3-oxo-1,5-diphosphapenta-1,4-dien-1,5-diyl-$C^2(Rh^2)$,$C^4(Rh^2)$,$P^1(Rh^1,Rh^2)$,$P^5(Rh^1,Rh^2)$]-1,2-bis-η-(pentamethylcyclopentadienyl)dirhodium, **6** (52 mg, 7.2%). Found: C, 52.41; H, 6.21; $C_{32}H_{48}O_2P_2Rh_2$ requires C, 54.47; H, 6.61%.

X-ray Structural Analysis of $[Rh_2Cp^*_2(CO)\{PCAdC(O)CAdP\}]$ (**4**)

Crystal Data. $C_{44}H_{60}O_2P_2Rh_2 \cdot C_7H_8$, $M = 956.9$, 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}. Monochromated MoKα radiation, $\lambda = 0.71069$ Å, $\mu = 8.2$ cm^{-1}.

Data Collection and Processing. Crystal size ca 0.30 × 0.18 × 0.08 mm, CAD4 diffractometer, $\theta - 2\theta$ mode. $\Delta\theta = (0.8 + 0.35 \tan\theta)°$, maximum scan time 1 minute. A total of 3242 reflections measured for $2 < \theta < 22°$, $+h \pm k \pm l$, 2126 unique reflections with $|F^2| > \sigma(F^2)$ used in the refinement, $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/\text{Lp}$. No crystal decay and no absorption correction.

Structure Solution and Refinement. The structure was initially solved by routine heavy atom methods in space group $P2_1$ and was later changed to $P2_1/m$ with a mirror plane through the Rh complex and with a molecule of toluene disordered about an inversion center. Refinement was by full matrix least squares with the nonhydrogen atoms of the Rh complex anisotropic and the C atoms of the toluene isotropic. H atoms for the adamantyl groups were held fixed at calculated positions with B_{iso} of 6.0 Å^2; all other H atoms were omitted. Final residuals were R = 0.061, R′ = 0.082 with a weighting scheme of $w = 1/\sigma^2(F)$. A final difference map was featureless. Programs were from Enraf-Nonius SDP-Plus package (see also Table 3).

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of thermal parameters, hydrogen atom positions and structure factors are available from the authors.

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