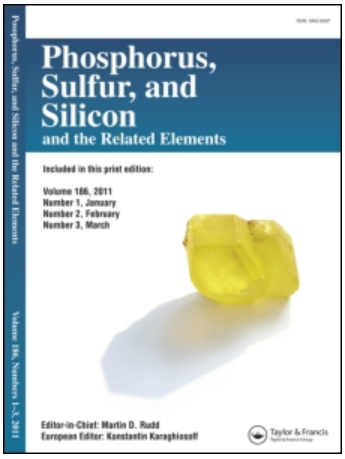

Phosphorus, Sulfur, and Silicon and the Related Elements

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Syntheses, Structures and Photoelectron Spectra of Phospha-Alkenes and Phospha-Alkynes and Their Transition Metal Complexes

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SYNTHESES, STRUCTURES AND PHOTOELECTRON SPECTRA OF PHOSPHA-ALKENES AND PHOSPHA-ALKYNES AND THEIR TRANSITION METAL COMPLEXES

J.C.T.R. BURCKETT ST. LAURENT, P.B. HITCHCOCK, M.A. KING, H.W. KROTO, M.F. MEIDINE, S.I. KLEIN, S.I. AL-RESAYES, R.J. SUFFOLK and J.F. NIXON
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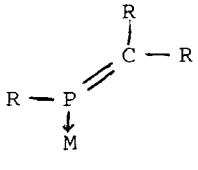
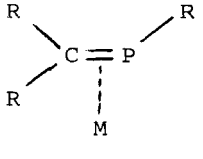
The chemistry of the novel phospha-alkenes $RP{=}CR'_2$, and phospha-alkynes, $RC{\equiv}P$, containing $2p_\pi$-$3p_\pi$ bonds is of current interest.[1,2] Recent molecular orbital calculations,[3,4] suggest that the highest occupied molecular orbital in $CH_2{=}PH$ is of the π-type with the phosphorus lone pair σ-orbital only slightly more stable while the π^* lumo orbital is relatively low lying. We now report He(I) photoelectron spectroscopic studies on a variety of $RC{\equiv}P$ molecules[5,6] which indicate that the homo is also of the π-type and the π-σ separation is much greater than that found in the analogous $RC{\equiv}N$ systems.

It might therefore be expected that phospha-alkenes are likely to act as both η^1- (phosphorus donors) and η^2- ($P{=}C$ π-donors) as in (a) and (b) below



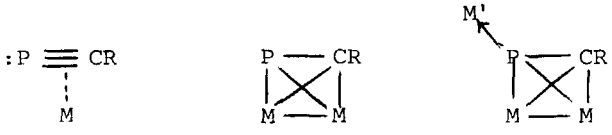
(a)



(b)

whereas in suitable transition metal complexes the phospha-alkynes might be envisaged to act as either 2e, 4e or 6e donors by making use of the $P{\equiv}C$ π-system and the lone pair on phosphorus (c) → (e). Recently we reported the first examples of complexes in which the

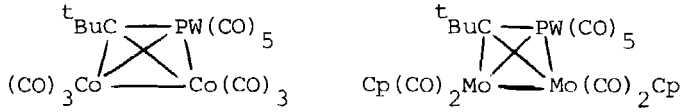
phospha-alkyne, $^{t}BuC{\equiv}P$ acts as a 2e donor in $[Pt(PPh_3)_2(P{\equiv}CBu^t)]$ as in (c) and as a 4e donor in $[Co_2(CO)_6(P{\equiv}CBu^t)]$ as in (d).[7]



(c) (d) (e)

We now describe the syntheses and first fully structurally characterised complexes in which the $^{t}BuC{\equiv}P$ acts as a 6e donor.

Treatment of $^{t}BuC{\equiv}P$ with $[Co_2(CO)_8]$ in toluene readily affords the deep red, light- and air-sensitive liquid complex $[Co_2(CO)_6(P{\equiv}CBu^t)]$ (I), which reacts with $[W(CO)_5THF]$ to give light- and air-stable, wine-red crystals of the complex $[Co_2(CO)_6(\mu\text{-}^{t}BuCP)W(CO)_5]$ (II). Similarly $^{t}BuC{\equiv}P$ reacts with $[(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ followed by $[W(CO)_5(THF)]$ to give $[\eta^5\text{-}(C_5H_5)_2Mo_2(CO)_4(\mu\text{-}^{t}BuCP)W(CO)_5]$ (III).



(II) (III)

Single crystal X-ray structure determinations on (II) and (III) have been carried out and the molecular parameters will be discussed in relation to other complexes of this structural type, *e.g.* $[(Co(CO)_3)_2E_2]$ (E = P,As) and $[(Mo(C_5H_5)(CO)_2)As_2]$. Of particular interest is the establishment of the side-on coordination of the phospha-alkyne to the Co_2 or Mo_2 system and the attachment of the $W(CO)_5$ unit *via* the phosphorus lone pair. The C-P bond length is much longer than that found for the free phospha-alkyne but interestingly is closer to that expected for a phospha-alkene than for a formal P-C single bond.

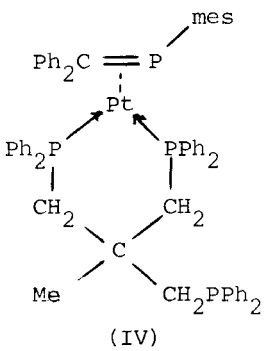
The volatility of $[Co_2(CO)_6{}^{t}BuCP]$, (I) offers a unique opportunity to compare its He(I) photo-electron spectrum with both that of the free phospha-alkyne and the alkyne complexes $[Co_2(CO)_6(RCCR)]$. The ready interconversion of the dinuclear

complex $[Pt(PPh_3)_2(PC^tBu)]$ to the dinuclear complex $[(Pt(PPh_3)_2)_2PC^tBu]$ will also be described.

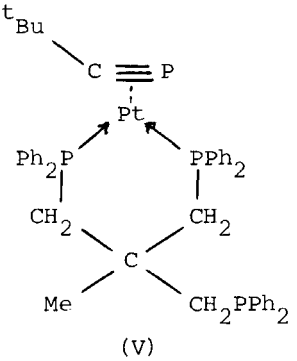
Previously we and others established the type (a) η^1-bonding for the phospha-alkene P(mesityl)=CPh_2 in single crystal X-ray studies on *cis*-$PtCl_2(PEt_3)$(P(mesityl)=CPh_2),[8] $Cr(CO)_5$-(P(mesityl)=CPh_2)[9] and $Pt(PPh_3)_2$P(mesityl)=CPh_2)[10]. The latter complex showed a solution nmr spectrum also supporting the possible existence of an η^2-isomer.

We now describe[11] the synthesis of an η^2-phospha-alkene complex Pt(triphos)(P(mesityl)=CPh_2) (IV) (two isomers) (triphos = $(PPh_2CH_2)_3CMe$) formed unexpectedly in the displacement reaction of PPh_3 from $Pt(PPh_3)$(triphos). The η^2-phospha-alkyne complex Pt(triphos)($P{\equiv}C^tBu$), (V) is formed in a similar way. ^{31}P and ^{195}Pt nmr spectra will be presented and discussed.

The η^2-mode of coordination of both (IV) and (V) is unambiguously established by the unusually small values of $^1J_{Pt-P}$ for the coordinated phospha-alkene and phospha-alkyne which reflect the large s-character of the phosphorus lone pair



(IV)

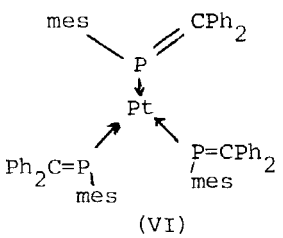


(V)

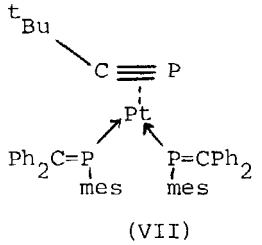
of the phospha-alkene and phospha-alkyne which is directed away from the metal atom. A similar effect was noted by us in the η^2-$Pt(PPh_3)_2(P{\equiv}C^tBu)$ complex.

In contrast to the above, treatment of $Pt(cod)_2$, (cod = 1,5-cyclooctadiene), with P(mesityl)=CPh_2 gave the η^1-complex $Pt(P(mesityl)=CPh_2)_3$ (VI), likewise when a 2:1 mixture of

P(mesityl)=CPh_2 and ^tBuCP was reacted with $Pt(cod)_2$ the product is $Pt(P(mesityl)=CPh_2)_2(P\equiv C^tBu)$ (VII) which is an interesting example of a complex containing only ligated phospha-alkenes (η^1-) and a phospha-alkyne (η^2-). Clearly a delicate balance of factors can result in either η^1- or η^2-coordination of the phospha-alkene.



(VI)



(VII)

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