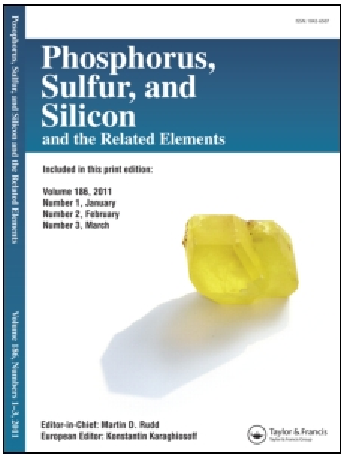

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Use of Phospha-Alkynes RC=P in Organometallic Chemistry

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USE OF PHOSPHA-ALKYNES RC≡P IN ORGANOMETALLIC CHEMISTRY

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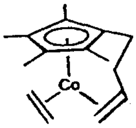
Abstract Novel reactions of phospha-alkynes are described.

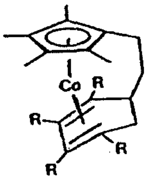
Phospha-alkynes, RC≡P, are proving to be important building blocks in inorganic and organometallic chemistry. A variety of ligating modes are exhibited by RC≡P towards transition metal centres but, interestingly, the preferred bonding interaction is with the P≡C triple bond, rather than *via* the phosphorus lone-pair electrons. Previously,[1,2] we have shown that η^1-phospha-alkyne complexes of Mo(O) and Fe(II) can be synthesised in certain compounds, in which linear molecules can approach the metal centre by virtue of the constraints imposed by the attendant diphosphane ligands.

We report here an analogous Re(I) system $[ReCl(dppe)_2Bu^tCP]$ (A), which readily undergoes addition of water across the P≡C triple bond, to afford $[ReCl(dppe)_2Bu^tCH_2PO]$ (B), which is a rare example of a complex containing a coordinated phosphinidene oxide $RCH_2P{=}O$ (R = Bu^t), whose stucture has been confirmed by a single crystal *X*-ray structure revealing a trigonal planar P atom and a P=O bond length of 1.499(3) Å.[3]

We also wish to describe some further developments in the metal-induced cyclodimerisation of phospha-alkynes to 1,3-diphosphacyclobutadiene metal complexes (see paper by P. Binger *et al.* for detailed background). Recently, J. Okuda[4] showed that the cobalt complex (C), shown below, undergoes a [2+2+2]



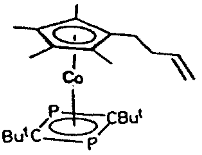
(C)



(D)

cycloaddition reaction with an activated alkyne to give the η^4-cyclohexadiene complex (D).

In contrast, when an analogous reaction is carried out using $Bu^tC{\equiv}P$, the pendant double bond is displaced from the metal centre and the 1,3-diphosphacyclobutadiene complex (E) is formed exclusively.[5]



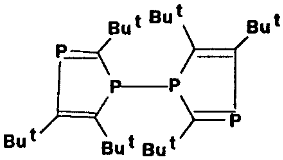
(E)

Continuing our investigations on $P_3C_2R_2$ and $P_2C_3R_3$ anions and cage molecules derived from their interactions, we discovered the surprising facile syntheses of P_3C_2RR' and $P_2C_3R_2R'$ anions ($R = Bu^t$ and/or Pr^i), merely by treatment of a mixture of the $Bu^tC{\equiv}P$ and $Pr^iC{\equiv}P$ phospha-alkynes with Na/Hg at room temperature. The corresponding green pentaphosphaferrocenes $[Fe(\eta^5\text{-}P_3C_2RR')(\eta^5\text{-}P_2C_3R_2R')]$ (characterised in a mixture by the observation of parent ions in the mass spectrum) are readily formed by reacting the mixture of anions with $FeCl_2$.[6]

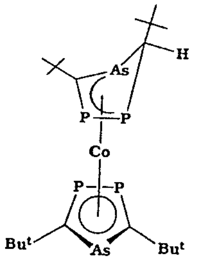
Our earlier attempts to synthesise Ru analogues of the sandwich compounds $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$ and $[Fe(\eta^5\text{-}P_2C_3Bu^t{}_3)\text{-}(\eta^5\text{-}P_3C_2Bu^t{}_2)]$ using $RuCl_3$ failed. However, we now find that when $[RuCl_2(PPh_3)_3]$ is treated with a mixture of the $P_3C_2Bu^t{}_2$ and $P_2C_3Bu^t{}_3$ anionic rings, both $[Ru(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$ (F) and $[Ru(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}P_2C_3Bu^t{}_3)]$ (G) complexes are obtained. They have been fully characterised by ^{31}P NMR and mass spectroscopy and, in the case of (F), by a single crystal *X*-ray structure determination. The complete loss of PPh_3 from the metal in these reactions is unexpected and presumably reflects the high stability of the sandwich complexes.^{5}

Two different reactions occur when $[RuCl_2(COD)]n$ (COD = 1,5-cyclo-octadiene) is treated with a mixture of the $P_3C_2Bu^t{}_2$ and $P_2C_3Bu^t{}_3$ anionic rings, depending on the reaction temperature. At ambient temperature, the product is the mixed ring sandwich complex $[Ru(\eta^5\text{-}P_2C_3Bu^t{}_3)(\eta^5\text{-}C_8H_{11})]$ (H). But at -30^o, two $P_2C_3Bu^t{}_3$ rings undergo oxidative coupling to give the compound $P_4C_6Bu^t{}_6$ (J). The latter is isoelectronic with both the cage $P_5C_5Bu^t{}_5$^{7} and the two $P_6C_4Bu^t{}_4$ cage isomers independently reported by Regitz and Zenneck at this meeting (see papers in this issue of the Journal). The mass spectra of (J) exhibits the parent ion; the ^{31}P NMR spectra shows two triplets, (δ_pA + 303; δ_pX = 24.4 ppm); and the ^1H NMR spectra reveals three types of Bu^t groups. Originally, we considered several cage structures, but the δ_pA value is characteristic of the presence of a P=C double bond. A single crystal *X*-ray diffraction study has subsequently established the novel structure shown below as a remarkable diphospholyl (J).^{5}

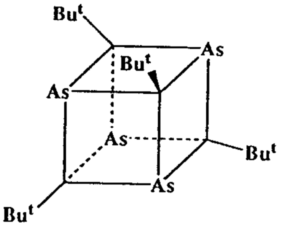
The new 4-arsa-1,2-diphosphacyclopentadienyl anion, $AsP_2C_2Bu^t{}_2{}^-$, which has been synthesised from Bu^tCP and $LiAs(SiMe_3)_2$ reacts with (i) $CoCl_2$ in dimethoxyethane to give the red $[Co(\eta^5\text{-}AsP_2C_2Bu^t{}_2H)$ (K), (ii) $[Mn(CO)_5Br]$ to give the orange $[Mn(CO)_3(\eta^5\text{-}AsP_2C_2Bu^t{}_2)]$ (L), and (iii) $[RuCl_2(PPh_3)_3]$



(J)



(K)



(N)

to give the yellow $[Ru(\eta^5\text{-}AsP_2C_2Bu^t{}_2)_2]$ (M), which have all been characterised by ^{31}P NMR and/or mass spectra. Complex (K) is thus closely related to the fully structurally characterised analogous hexa-phosphorus complex $Co[\eta^5\text{-}(P_3C_2Bu^t{}_2)(\eta^4\text{-}P_3C_2Bu^t{}_2H)]$.[8]

The orange $[Mn(CO)_3(\eta^5\text{-}AsP_2C_2Bu^t)]$ complex, (L), exhibits a singlet at δ_p = 109.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum and peaks in the mass spectra at m/z 413, 356, and 330 corresponding to the parent ion M^+, $M^+\text{-}2CO$, $M^+\text{-}3CO$, respectively. The yellow sandwich complex $[Ru(\eta^5\text{-}AsP_2C_2Bu^t{}_2)_2]$, (M), exhibits peaks at m/e 652 (parent ion).

Attempts to extend this reaction to the $PAs_2C_2Bu^t{}_2$ ring system, led to the novel $[As_4C_4Bu^t{}_4]$ cage system (N) and its $Fe(CO)_4$ adduct (P), whose molecular structures have been confirmed by single crystal X-ray studies.[9] Full spectroscopic and structural details will be published separately elsewhere. The $As_4C_4Bu^t{}_4$ compound is the arsenic analogue of the well-known tetraphosphacubane, previously reported by Regitz *et al.*[10]

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