

Unprecedented Rearrangement of Phosphino Alkynes $\text{Ph}_2\text{P}(\text{C}\equiv\text{CR})$ ($\text{R} = \text{Ph}, \text{Me}$) into Bridging Vinyl Phosphido Ligands $\text{PhP}(\text{CR}=\text{CPhH})$ during the Reaction with $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$

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The reaction of $\text{Ph}_2\text{P}(\text{C}\equiv\text{CR})$ ($\text{R} = \text{Ph}, \text{Me}$) with $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$ at 58 °C ($\text{R} = \text{Me}$) or 102 °C ($\text{R} = \text{Ph}$) leads to the formation of $[\text{PPh}_4][\text{Fe}_3(\text{CO})_9(\mu_3\text{-PhPCR}=\text{CPhH})]$, the X-ray crystal structure of which has been determined for $\text{R} = \text{Me}$.

The study of the reactivity of diphenyl phosphino alkynes $\text{Ph}_2\text{P}(\text{C}\equiv\text{CR})$ towards polynuclear complexes has been of interest in recent years and has led to interesting rearrangement reactions generally involving the breaking of the phosphorus alkynyl bond.^{1,2} Considering the great reactivity of $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$, (1), toward alkynes which we have recently reported,³ the reactivity of these ligands towards the cluster anion is of interest. Two types of reactivity are possible, *viz.* (i) complexation through the phosphorus lone pair and (ii) insertion of the carbon-carbon triple bond into the iron-hydrogen bond.

Preliminary results have shown that the reaction is complex and dependent on the nature of R. Here we report our observations where $\text{R} = \text{Me}$ and Ph showing an unexpected transformation of the $\text{Ph}_2\text{P}(\text{C}\equiv\text{CR})$ phosphine to the phosphido $\text{PhP}(\text{CR}=\text{CPhH})$ ligand.

Compound (1) reacts with an equimolecular quantity of $\text{Ph}_2\text{P}(\text{C}\equiv\text{CMe}_3)$ in refluxing acetone to give a dark red compound, $[\text{PPh}_4][\text{Fe}_3(\text{CO})_9(\text{PhPCMe}=\text{CPhH})]$, (2),[†] isol-

[†] The new complexes were characterized by elemental analyses and spectroscopic techniques: (2): $\nu(\text{CO})$ 2023 (m), 1967 (s), 1950 (sh), 1830 (w) cm^{-1} ; ^1H n.m.r. δ 7.99–7.56 (m, Ph), 5.38 (d, J_{PH} 18.8 Hz, H), 2.40 (d, J_{PH} 9.4 Hz, CH_3); $^{31}\text{P}\{^1\text{H}\}$ n.m.r. δ 28.4 (PPh₄) and 193.9 (from H_3PO_4 , 85% as external reference).

(3): $\nu(\text{CO})$ 2025 (m), 1970 (s), 1955 (s), 1800 (w); ^1H n.m.r. δ 8.05–7.30 (m, Ph), 5.12 (d, $J_{\text{PH}} = 17.9$ Hz, H); $^{31}\text{P}\{^1\text{H}\}$ n.m.r. δ 28.4 (PPh₄) and 195.2.

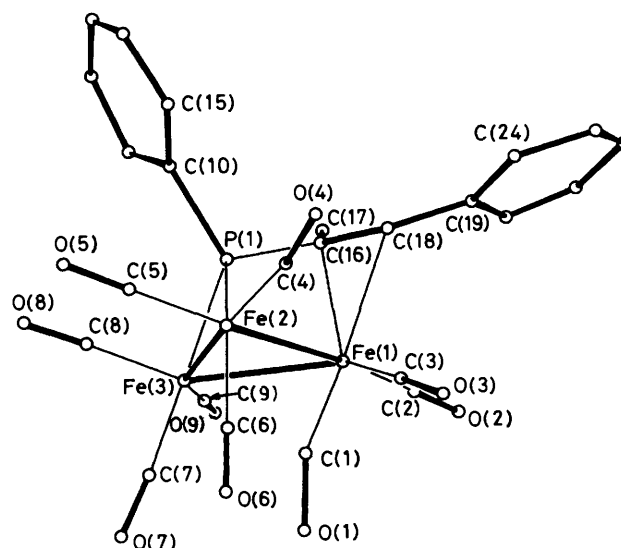


Figure 1. Structure of the anion $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-PhPCMe}=\text{CPhH})]^-$. Selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.678(4), Fe(1)–Fe(3) 2.730(5), Fe(2)–Fe(3) 2.636(4), Fe(2)–P(1) 2.151(6), Fe(3)–P(1) 2.183(6), P(1)–C(16) 1.76(2), C(16)–C(17) 1.53(3), C(16)–C(18) 1.40(3), Fe(2)–P(1)–Fe(3) 74.9(2), C(10)–P(1)–C(16) 105.4(9), P(1)–C(16)–C(18) 116(1), P(1)–C(16)–C(17) 119(1), C(16)–C(18)–C(19) 129(2).

ated in 30% yield after crystallisation. The molecular structure of (2) was determined by X-ray diffraction.† The structure consists of a triangle of iron atoms, each iron being bonded to three CO ligands. All FeCO angles except Fe(1)–C(1)–O(1) are close to 180° and C(1)–O(1) is in a semi-bridging position between Fe(1) and Fe(3) [Fe(1)–C(1)–O(1) = 156(2)°].

The most salient feature of the structure is the presence of the PhP(CMe=CPhH) phosphido ligand. This ligand bridges the Fe(2)–Fe(3) bond through the phosphorus atom P(1) in a nearly symmetrical fashion, a common situation for this type of bridge,^{1,4} while the CMe=CPhH vinyl group is π bonded to Fe(1).

The Fe(1)–C(18) bond length is slightly longer than that of the Fe(1)–C(16), which is in the normal range for a Fe–C π -bond,⁵ and might be a consequence of steric strain. The C(16)–C(18) bond distance has a value in the normal range for a π -bonded carbon–carbon double bond.

The formation of the PhP(CMe=CPhH) ligand from Ph₂P(C \equiv CMe) implies that P–(C \equiv CMe) bond breaking has occurred with the formation of a P–CMe bond, followed by migration of hydrogen from iron and a phenyl group from phosphorus on to the other carbon of the alkynyl group.

† Crystal data for C₄₈H₃₄O₉P₂Fe₃, *M* = 983.5, triclinic, space group P $\bar{1}$, *a* = 11.140(6), *b* = 12.033(8), *c* = 16.998(3) Å, α = 90.99(3), β = 92.73(4), γ = 97.84(5)°, *U* = 2254(2) Å³, *Z* = 2, *D_c* = 1.40 g/cm⁻³, Mo-*K α* radiation (λ = 0.71069 Å), *R* = 0.11 for 3081 observed data with *I* > 3 σ (*I*) and 2 < θ < 27. Intensities were collected by $\omega/2\theta$ scan mode using graphite monochromatized Mo-*K α* radiation (Enraf-Nonius CAD4 diffractometer). The structure was solved by heavy atom methods (Patterson, Fourier) and refined by least-squares. All the H atoms were included in fixed idealized position.

Atomic co-ordinates, bond lengths, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

This constitutes a further example of the migration of phenyl group from phosphorus to a carbon atom, the literature containing several examples of this type of reaction,^{6,7} and evidence that this reaction is metal-assisted.⁸ In the case of Ph₂P(C \equiv CPh) we have also observed the same type of reaction but this occurs at higher temperature (102 °C) and gives the [PPh₄]{Fe₃(CO)₉[PhP(CPh=CPhH)]}, (3)† complex in 25% yield as the unique product of the reaction.

The mechanism of this unusual reaction is under study.

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