

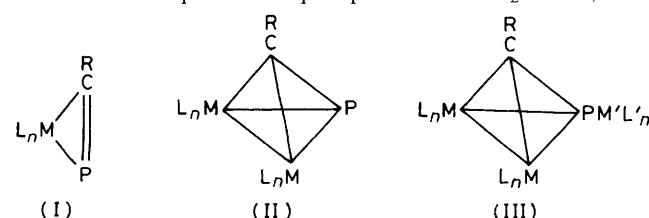
Synthesis of the First Example of a Metal Complex containing a Co-ordinated $\mu_3\text{-}(\eta^2\text{-L})$ Phospha-alkyne Ligand. Addition of an $\text{Fe}_2(\text{CO})_6$ Unit to the η^2 -Phospha-alkyne Complex $[\text{Pt}(\text{dppe})(\text{ButCP})]$: Crystal and Molecular Structure of $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{ButCP})]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)

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A new mode of co-ordination for a phospha-alkyne ligand has been established in the complex $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{ButCP})]$.

There is considerable current interest in the chemistry of compounds containing multiple bonds to second row elements.¹⁻³ Previously we have described syntheses and co-ordination complexes of phospha-alkenes $\text{R}_2\text{C}=\text{PR}'$, and



phospha-alkynes $\text{RC}\equiv\text{P}$, and established bonding types (I), (II), and (III) for the latter in which the phospha-alkyne acts as a 2e, 4e, and 6e donor respectively. {(I), $\text{M} = \text{Pt}$, $\text{L}_n = (\text{Ph}_3\text{P})_2$,⁴ $(\text{Ph}_2\text{C}=\text{Pmesityl})_2$,⁵ triphos $[(\text{PPh}_2\text{CH}_2)_3\text{CMe}]$,⁵ ($\text{R} = \text{But}^\ddagger$); (II), $\text{ML}_n = \text{Co}(\text{CO})_3$,⁴ $\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$,⁶ ($\text{R} = \text{But}^\ddagger$); (III), $\text{ML}_n = \text{Fe}(\text{CO})_3$,⁷ $\text{Cr}(\text{CO})_3$,⁸ $\text{V}(\text{CO})_3$,⁹ $\text{Nb}(\text{CO})_3$,¹⁰ $\text{Ta}(\text{CO})_3$,¹¹ $\text{W}(\text{CO})_3$,¹² $\text{Fe}(\text{CO})_5$,¹³ $\text{Cr}(\text{CO})_5$,¹⁴ $\text{V}(\text{CO})_5$,¹⁵ $\text{Nb}(\text{CO})_5$,¹⁶ $\text{Ta}(\text{CO})_5$,¹⁷ $\text{W}(\text{CO})_5$,¹⁸ $\text{Fe}(\text{CO})_6$,¹⁹ $\text{Cr}(\text{CO})_6$,²⁰ $\text{V}(\text{CO})_6$,²¹ $\text{Nb}(\text{CO})_6$,²² 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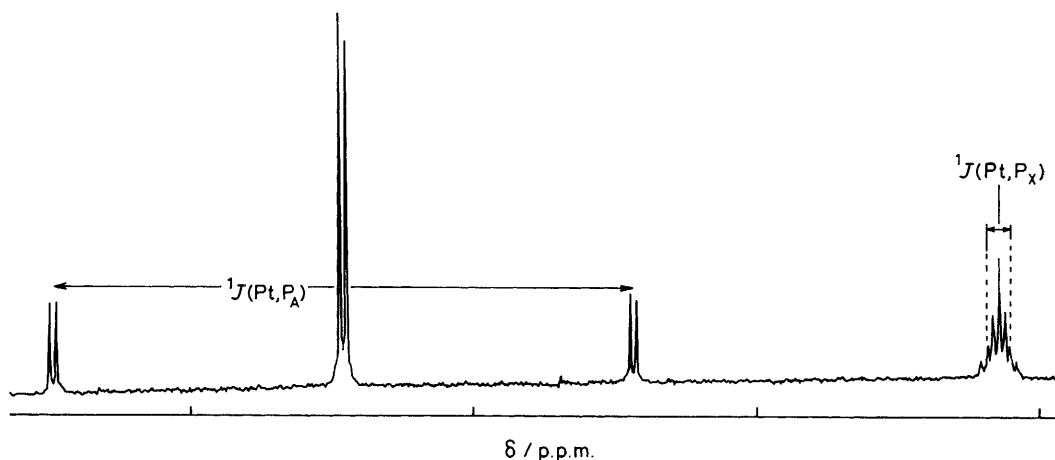


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ N.m.r. spectrum of $\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Bu}'\text{CP})$, (2).

Bu' ; and (III) $\text{ML}_n = \text{Co}(\text{CO})_3$, $\text{M}'\text{L}'_n = \text{W}(\text{CO})_5$,⁶ $\text{ML}_n = \text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$, $\text{M}'\text{L}'_n = \text{W}(\text{CO})_5$,⁶ $\text{Os}_3(\text{CO})_{11}$, $\text{Ru}_3(\text{CO})_{11}$ ($\text{R} = \text{Bu}'$).⁷

We now report that treatment of the new colourless complex $\text{Pt}(\text{dppe})(\text{Bu}'\text{CP})$, (1) ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPPh}_2$) [made quantitatively from $\text{Pt}(\text{dppe})_2$ and $\text{Bu}'\text{CP}$] with $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ in toluene gives quantitatively the deep cherry red trimetallic complex $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Bu}'\text{CP})]$ (2).

The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of (1) shows the expected ABX pattern of lines $\delta = -93.6$ (P_A), -87.9 (P_B), -53.3 p.p.m. (P_X); ${}^1\text{J}(\text{Pt}, \text{P}_A) 3308$, ${}^1\text{J}(\text{Pt}, \text{P}_B) 2930$, ${}^1\text{J}(\text{Pt}, \text{P}_X) 166$, ${}^2\text{J}(\text{P}_A, \text{P}_B) 44$, ${}^2\text{J}(\text{P}_A, \text{P}_X) 27$, ${}^2\text{J}(\text{P}_B, \text{P}_X) 21$ Hz and the small magnitude of ${}^1\text{J}(\text{Pt}, \text{P}_X)$ (166 Hz) is indicative of the η^2 -phospha-alkyne bonding mode previously established crystallographically for type (I) bonding [$\text{M} = \text{Pt}$, $\text{L}_n = (\text{PPh}_3)_2$, $\text{R} = \text{Bu}'$].⁴ The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of (2) on the other hand (Figure 1) exhibits a simple A_2X pattern with platinum satellites $\delta = -76.9$ (P_A), -192.8 p.p.m. (P_X); ${}^1\text{J}(\text{Pt}, \text{P}_A) 3329$, ${}^1\text{J}(\text{Pt}, \text{P}_X) 128$, ${}^2\text{J}(\text{P}_A, \text{P}_X) 36$ Hz indicating that the molecule has a plane of symmetry. The low value of ${}^1\text{J}(\text{Pt}, \text{P}_X)$ (128 Hz) in (2) indicates that the phospha-alkyne is not bonded to platinum via its phosphorus lone pair.

A single crystal X-ray diffraction study[†] on (2) confirms the spectroscopic data and reveals that the phospha-alkyne $\text{RC}\equiv\text{P}$ fragment transversely bridges the $\text{Fe}-\text{Fe}$ bond so that the phosphorus atom is co-ordinated to the three metal atoms of the Fe_2Pt ring (Figure 2). This type of bonding is the first of its kind established for a phospha-alkyne ligand and is similar to the relatively rare examples known for alkynes $\text{RC}\equiv\text{CR}$ in the complexes $[\text{Ni}_4(\text{CO})_4\{\text{C}_2(\text{CF}_3)_2\}_3]$,⁸ $[\text{Ni}_4(\text{CNBu}')_4(\text{C}_2\text{Ph}_2)_3]$,⁹ $[\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)]$,¹⁰ and $[\text{W}_2\text{Fe}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)_2\{\text{C}_2(\text{C}_6\text{H}_4\text{-Me}_2)\}]$.¹¹

Interestingly the latter complex results from coupling of two RC fragments in the reaction of the carbyne complex $[\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)(\text{CC}_6\text{H}_4\text{Me})]$ with $\text{Fe}_2(\text{CO})_9$. On the other

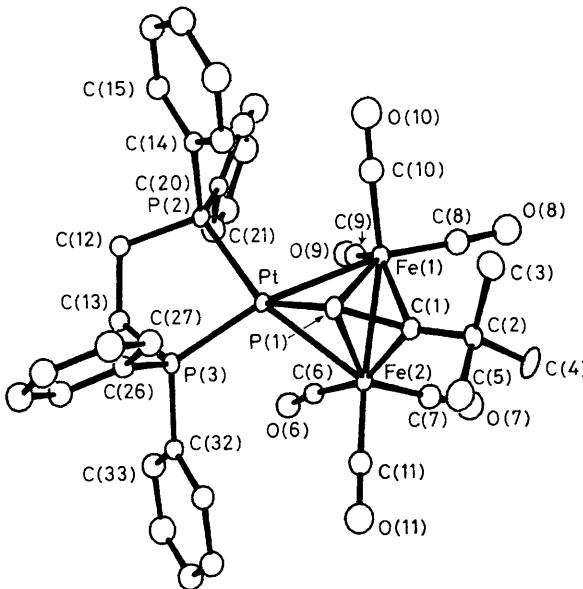


Figure 2. Molecular structure of $\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Bu}'\text{CP})$, (2). Selected bond lengths (\AA) and bond angles ($^\circ$) of interest are: $\text{Pt}-\text{Fe}(1) 2.671(1)$, $\text{Pt}-\text{Fe}(2) 2.669(1)$, $\text{Pt}-\text{P}(1) 2.343(2)$, $\text{Pt}-\text{P}(2) 2.263(2)$, $\text{Pt}-\text{P}(3) 2.270(2)$, $\text{Fe}(1)-\text{Fe}(2) 2.518(1)$, $\text{Fe}(1)-\text{P}(1) 2.343(2)$, $\text{Fe}(2)-\text{P}(1) 2.446(2)$, $\text{Fe}(1)-\text{C}(1) 2.080(6)$, $\text{Fe}(2)-\text{C}(1) 1.974(6)$, $\text{P}(1)-\text{C}(1) 1.703(6)$, $\text{Pt}-\text{P}(1)-\text{C}(1) 113.6(2)$, $\text{P}(1)-\text{C}(1)-\text{C}(2) 128.1(5)$, $\text{Fe}(1)-\text{P}(1)-\text{Fe}(2) 63.40(5)$.

hand Stone *et al.*¹² found that the analogous reaction of the carbyne complex $[\text{Pt}(\text{PR}_3)_2\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)(\text{CC}_6\text{H}_4\text{Me})]$ in tetrahydrofuran with $\text{Fe}_2(\text{CO})_9$ {in which the carbyne $[\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)(\text{CC}_6\text{H}_4\text{Me})]$ fragment is isolobal^{13,14} with $\text{RC}\equiv\text{P}$ } gave products involving only one iron atom.

Further structural features of interest in complex (2) are (a) the lengthening of the P-C bond of the co-ordinated phospha-alkyne from 1.54 \AA in the free ligand to 1.70 \AA which is more typical for a $\text{C}\equiv\text{P}$ double bond,² (b) the preference for the phosphorus atom rather than the CBu' group as the μ_3 bonding moiety, and (c) the Pt-P bond length [$2.343(2)$ \AA] is only slightly longer than the Pt-P bonds to the dppe ligand even though the phosphorus lone pair appears not to participate significantly in Pt-phospha-alkyne bonding.

The $\text{RC}\leftarrow\text{C}\rightarrow\text{P}\leftarrow\text{O}\rightarrow\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ isolobal relationship however suggests that it should be possible to synthesise many

[†] Crystal data for (2): $\text{C}_{37}\text{H}_{33}\text{Fe}_2\text{O}_6\text{P}_3\text{Pt}$, monoclinic, space group $P2_1/c$, $a = 13.238(1)$, $b = 11.295(2)$, $c = 25.642(2)$ \AA , $\beta = 100.72(1)^\circ$, $Z = 4$. The structure was solved by heavy atom methods and refined to $R = 0.040$ by least squares using 3954 reflections with $I > \sigma(I)$ measured on a CAD4 diffractometer with $\text{Mo-K}\alpha$ radiation. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

metal phospha-alkyne complexes analogous to the extensive series of carbyne-metal derivatives developed by Stone and coworkers.¹⁴

Further types of co-ordination modes for phospha-alkyne ligands in metal complexes will be the subject of future publications.

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