Structural Observation of Bis(diphenylphosphino)methane Reactivity at a Di-iron Centre: Crystal Structures of Isomeric [Fe₂(CO)₅(μ-CHCHCO){μ-P(Ph₂)CH₂PPh₂}], [Fe₂(CO)₆{μ-C(CH₂)P(Ph₂)CH₂PPh₂}], and [Fe₂(CO)₆{μ-C(CH₂Ph)P(Ph₂)CH₂PPh}]

Graeme Hogarth, Selby A. R. Knox, Brian R. Lloyd, Kirsty A. Macpherson, David A. V. Morton, and A. Guy Orpen

Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

X-Ray diffraction studies have elucidated the molecular rearrangements involved in the fluxionality of the complex [Fe₂(CO)₅(μ-CHCHCO){μ-P(Ph₂)CH₂PPh₂}] and in its isomerisation, *via* migration of one phosphorus of the bis(diphenylphosphino)methane ligand from iron to carbon, to give [Fe₂(CO)₆{μ-C(CH₂)P(Ph₂)CH₂PPh₂}], which in turn isomerises through phenyl migration from phosphorus to carbon, yielding [Fe₂(CO)₆{μ-C(CH₂Ph)P(Ph₂)CH₂PPh}].

Bis(diphenylphosphino)methane (dppm) has played a major role in the development of dinuclear transition metal chemistry.[1] In the preceding communication we described how its bridging of a di-iron centre allows the nature of the
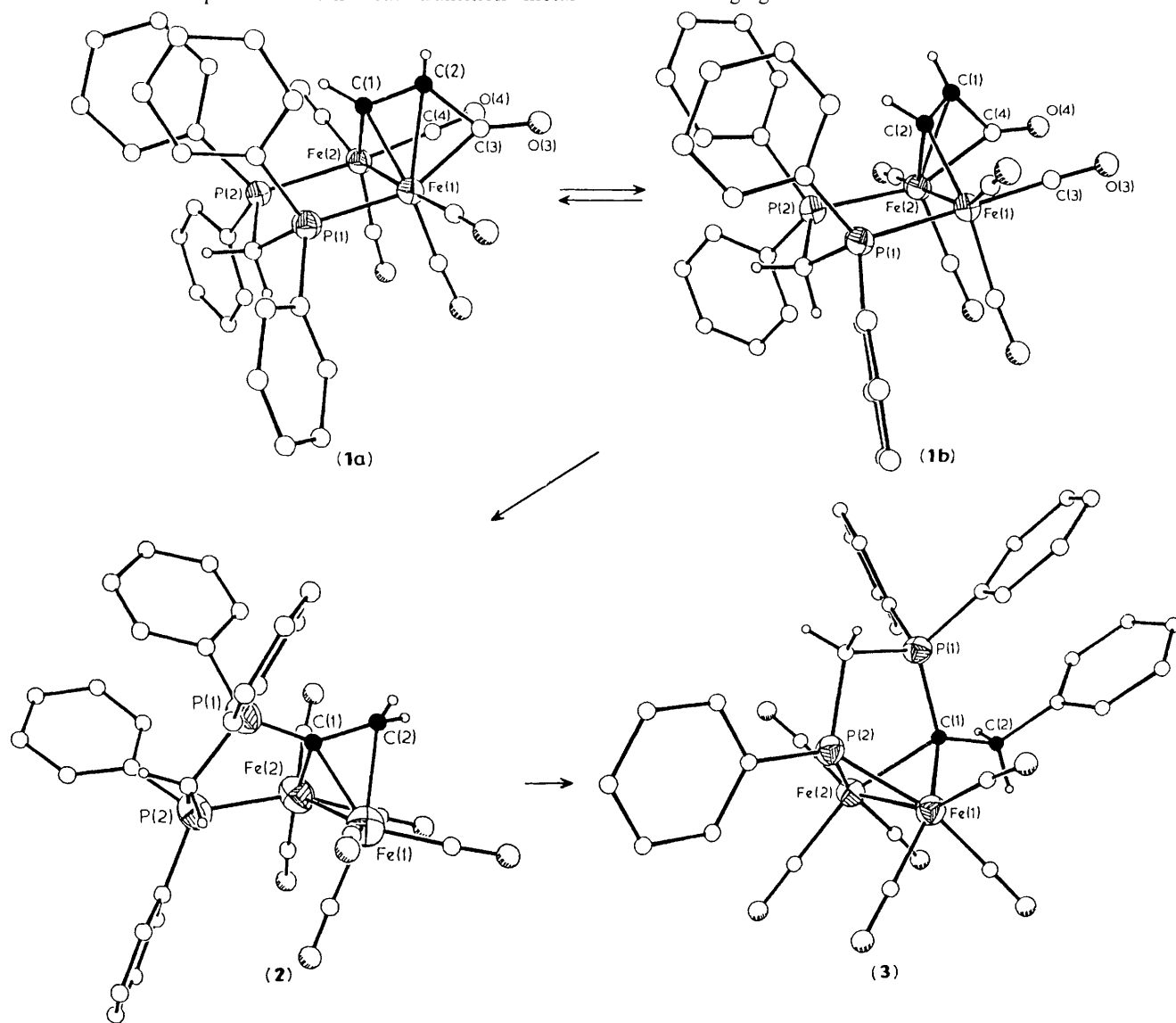

Figure 1. Molecular structures of complexes (1) (two crystallographically independent molecules), (2), and (3), with phenyl group hydrogens omitted for clarity. The bridging CO in (2) is partially obscured by Fe(1). Selected bond lengths (Å): (1a) [(1b)], Fe(1)–Fe(2) 2.725(1) [2.709(1)], Fe(1)–P(1) 2.267(1) [2.277(1)], Fe(2)–P(2) 2.275(1) [2.270(1)], Fe(1)–C(1) 2.084(3) [2.084(3)], Fe(2)–C(1) 1.980(3) [1.977(3)], Fe(1)–C(2) 2.111(3) [2.109(3)], Fe(1)–C(3) 1.929(3) [1.921(3)], C(1)–C(2) 1.396(5) [1.392(5)], C(2)–C(3) 1.448(5) [1.443(5)]. (2), Fe(1)–Fe(2) 2.594(2), Fe(2)–P(2) 2.296(2), Fe(1)–C(1) 2.034(8), Fe(2)–C(1) 1.989(8), Fe(1)–C(2) 2.113(9), P(1)–C(1) 1.755(8), C(1)–C(2) 1.403(10). (3), Fe(1)–Fe(2) 2.544(1), Fe(1)–P(2) 2.202(1), Fe(2)–P(2) 2.206(1), Fe(1)–C(1) 2.092(2), Fe(2)–C(1) 2.093(2), P(1)–C(1) 1.790(2), C(1)–C(2) 1.562(3).

step-wise synthesis of tropone from ethyne and CO to be established.[2] Under these photochemical, *ambient* temperature conditions the dppm is an innocent spectator; however, at *elevated* temperature this important ligand takes part in an unprecedented sequence of rearrangements, involving both carbon–phosphorus bond-formation and bond-cleavage. Through a series of *X*-ray diffraction studies the intricacies of the molecular manoeuvres have been brought to light, revealing new reaction pathways and modes of co-ordination involving dppm.

The complex [Fe$_2$(CO)$_5$(μ-CHCHCO){μ-P(Ph$_2$)CH$_2$-PPh$_2$}] (**1**),[2] obtained by treatment of [Fe$_2$(CO)$_7$(μ-dppm)] with ethyne under u.v. irradiation, is fluxional in solution. Variable temperature ^{31}P and [1]H n.m.r. spectroscopy indicates that the molecule is static at room temperature, but on warming to 90 °C pair-wise averaging of the phosphorus and 'ethyne' proton environments is observed, consistent with the (**1a**) $\rightleftharpoons$ (**1b**) process depicted in Scheme 1. Such rapid breaking and re-forming of the carbon–carbon bond linking 'ethyne' and CO, exchanging ketonic and terminal CO between the two ends of the alkyne, has been suggested to occur for other complexes of this type.[3] However, an *X*-ray diffraction study on (**1**) has now provided an unusual insight into this process, in that the crystal was composed of a racemic mixture of the enantiomers (**1a**) and (**1b**) which are interconverting in solution.

The results of the structural study are presented in Figure 1 and in its caption.† On this basis, the transformation of (**1a**) to (**1b**) can be viewed as follows: cleavage of the C(2)–C(3) bond of (**1a**) generates the C(3)–O(3) terminal carbonyl of (**1b**) while, simultaneously, C(1) of (**1a**) links with the C(4) carbon to give the C(4)–O(4) ketonic carbonyl of (**1b**). As a result the CH groups exchange their environments, as required by the [1]H n.m.r. spectrum; an alternative process in which C(1) of (**1a**) remains fixed and C(2) oscillates between C(3) and C(4) would not do this.

At about 90 °C in solution the cleavage of the 'ethyne'–CO link in (**1**) becomes irreversible, and the complex rapidly and quantitatively isomerises to a second species (**2**), which in turn slowly converts to a third isomer (**3**). At 100 °C the latter is formed rapidly, but careful control of temperature permitted the isolation of the intermediate isomer. The new isomers were shown to be the zwitterions [Fe$_2$(CO)$_6${μ-C(CH$_2$)P-
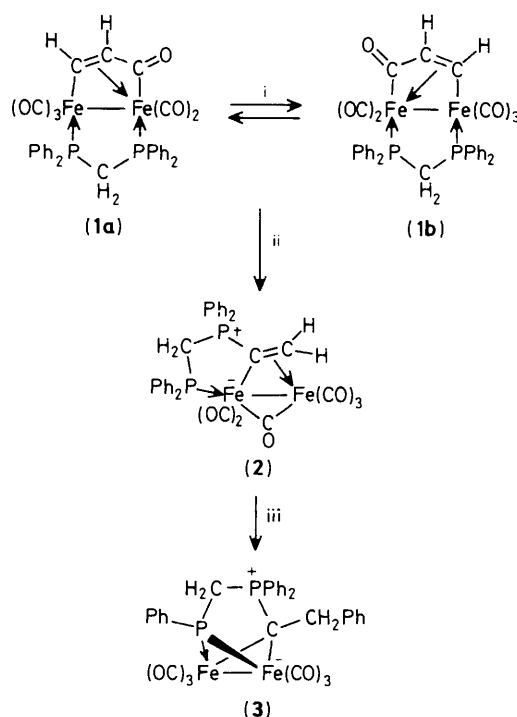
Scheme 1. *Conditions*: i, <90 °C; ii, 90 °C, fast; iii, 90 °C, slow.

(Ph$_2$)CH$_2$PPh$_2$}] (**2**)‡ and [Fe$_2$(CO)$_6${μ-C(CH$_2$Ph)P-(Ph$_2$)CH$_2$PPh}] (**3**)‡ by *X*-ray diffraction. The results of the structural studies are summarised in Figure 1 and in its caption.†

The views of the isomers (**1**), (**2**), and (**3**) given in Figure 1 are from a similar perspective and allow the structural changes to be readily appreciated. Thus, by comparing the structures of (**1a**) and (**2**), it can be seen that this transformation involves a pivoting of the dppm ligand about phosphorus P(2), permitting an internal nucleophilic attack of P(1) on carbon C(1), *i.e.* a 1,2-shift of P(1) from Fe(1) to C(1) occurs. This is associated with a 1,2-hydrogen shift from C(1) to C(2) and the cleavage of the C(2)–C(3) bond, creating a vinylidene unit and a terminal carbonyl. The resultant ligand can be considered to bind as a σ,η^2-μ-vinyl with an unusual α-carbon substituent. More significantly, the complex may be viewed as having dppm bridging a metal–carbon bond rather than, as normally observed,[1] a metal–metal bond.

The slightly higher energy transformation of (**2**) to (**3**) is similarly laid bare by reference to Figure 1. This reveals that a phenyl group of (**2**) migrates from terminal phosphorus P(2) to the vinylidene carbon C(2) at the other end of the chain,

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affording a benzyl group and releasing C(2) from co-ordination while P(2) enters a bridging site. The unusual ligand so created binds to the di-iron centre *via* both μ-phosphido and μ-alkylidene functionalities. A plausible pathway for this surprisingly efficient phenyl migration [(3) is isolated in 50% yield] would involve an oxidative addition of the P–Ph bond to Fe(1), followed by the formation of the C–Ph bond through reductive-elimination. The co-ordinative unsaturation on Fe(1) required for oxidative-addition could be readily achieved *via* the transfer of the μ-CO of (2) to a terminal site on Fe(2), with concomitant cleavage of the Fe–Fe bond. It is interesting to note that the conformational flexibility of the five-membered FeCPCFe ring in (2) will allow one phenyl group on P(2) into close proximity with Fe(1).

Studies with other organic derivatives of [Fe$_2$(CO)$_7$(μ-dppm)] reveal a similar situation; namely, that while at room temperature dppm is uninvolved in the organic chemistry occurring at the di-iron centre, at higher temperatures this ligand participates in an array of unique transformations. We shall report on these in due course.

References

1 R. J. Puddephat, *Chem. Soc. Rev.*, 1983, **12**, 99.
2 G. Hogarth, S. A. R. Knox, D. A. V. Morton, A. G. Orpen, and M. L. Turner, *J. Chem. Soc., Chem. Commun.*, preceding communication.
3 A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 1297.