Carbon–Phosphorus Bond Cleavage and Carbon–Carbon Bond Formation at a Di-iron Centre: Formation of Ethyl Acrylate *via* Extrusion of Methylene from Bis(diphenylphosphino)methane

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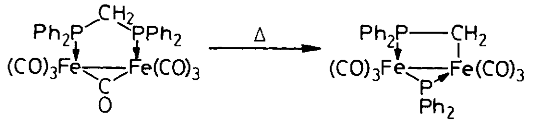
Treatment of [$Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)$] with ethyl diazoacetate under UV irradiation gives [$Fe_2(CO)_6(\mu\text{-}CHCO_2Et)(\mu\text{-}Ph_2PCH_2PPh_2)$], which on heating undergoes double P–CH_2 bond cleavage and C–C bond formation, forming $CH_2{=}CH(CO_2Et)$ and [$Fe_2(CO)_6(\mu\text{-}PPh_2)_2$].

It is now recognised that the ease of carbon–phosphorus bond cleavage at metal centres is dependent upon the hybridisation of carbon, following the order: P–C(sp) > P–C(sp^2) > P–C(sp^3).[1] Examples of P–C(sp^3) cleavage are rare, but recently we described how a single P–CH_2 bond of bis(diphenylphosphino)methane is broken upon thermolysis of [$Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)$] (**1**), to afford the μ-phosphidomethyl complex (**2**).[2] We now report that thermolysis of an analogous μ-alkylidene complex results in the unprecedented cleavage of both the P–CH_2 bonds of this important diphosphine ligand, and that the extruded CH_2 group combines with the alkylidene to release an alkene.



(**1**) (**2**)

The reaction of [$Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)$] (**1**) with an excess of ethyl diazoacetate in toluene under UV irradiation gives [$Fe_2(CO)_6(\mu\text{-}CHCO_2Et)(\mu\text{-}Ph_2PCH_2PPh_2)$] (**3**)† in 33% yield. The complex is stable at room temperature, but heating in toluene at reflux or in the solid state at 130 °C effects a rapid and apparently quantitative transformation to

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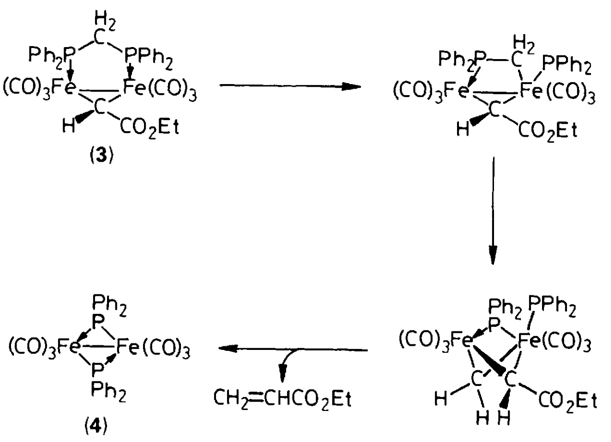
† Yellow crystalline (**3**) was identified by elemental analyses and by IR and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy. Selected data [IR in CH_2Cl_2, NMR in CD_2Cl_2, coupling constants (J) in Hz]: ν(CO) at 2048s, 2003s, 1981m, 1958m, 1944m, 1929sh, and 1605m cm^{-1}; ^1H NMR δ 5.82 (t, J_{HP} 19, 1H, μ-CH); ^{13}C NMR δ 109.8 (t, J_{CP} 12, μ-CH); ^{31}P NMR δ 61.6 p.p.m. (s).



Scheme 1

the known bis(μ-phosphido) species $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$ (**4**),[3] isolated in 65% yield after chromatography. The fate of the CH_2 and $CHCO_2Et$ groups was established by examining the nature of the organic products from the solid state thermolysis, when ethyl acrylate, CH_2=$CHCO_2Et$, was isolated in *ca.* 25% yield and identified by ^1H NMR spectroscopy and GLC.

The thermally-induced intramolecular linking of two alkylidene ligands at a dinuclear metal centre, to give an alkene, is a well-known process.[4] This strongly suggests that ethyl acrylate formation is preceded by the generation of an intermediate di-μ-alkylidene complex, derived from (**3**) by sequential oxidative-additions of P–C(sp^3) bonds. A possible pathway is shown in Scheme 1.

Attempts to generate other alkenes CH_2=CHR by heating the related μ-alkylidene complexes $[Fe_2(CO)_6(\mu\text{-}CHR)(\mu\text{-}Ph_2PCH_2PPh_2)]$ (R = H, Me, Et)[5] were unsuccessful. These complexes behave similarly to (**1**), undergoing a single P–CH_2 bond cleavage to give the μ-phosphidomethyl complex (**2**), *via* ejection of the alkylidene. It is likely that the retention of μ-$CHCO_2Et$ by (**3**), pending the second P–C(sp^3) bond cleavage, is due to the strong π-acceptor character of this alkylidene.

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References

1 P. E. Garrou, *Chem. Rev.*, 1985, **85**, 171.
2 N. M. Doherty, G. Hogarth, S. A. R. Knox, K. A. Macpherson, F. Melchior, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1986, 540.
3 B. E. Job, R. A. N. McLean, and D. T. Thompson, *J. Chem. Soc., Chem. Commun.*, 1966, 895.
4 R. E. Colborn, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, A. G. Orpen, J. E. Guerchais, and J. Roué, *J. Chem. Soc., Dalton Trans.*, 1989, 1799.
5 G. Hogarth and S. A. R. Knox, unpublished.