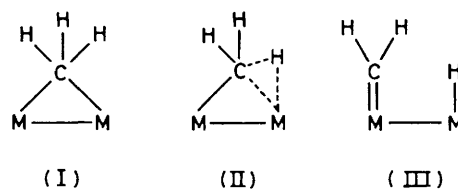


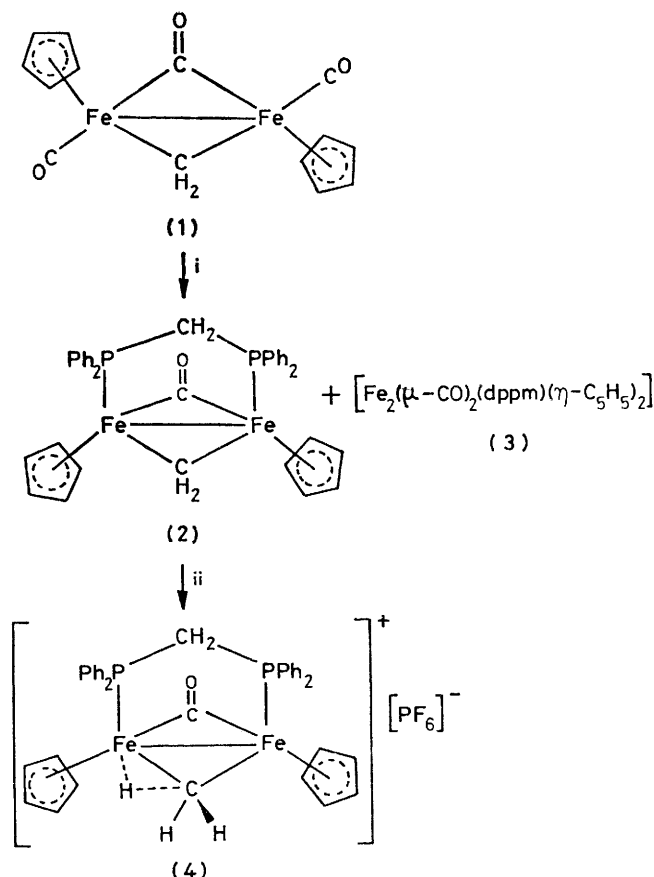
Synthesis and X-Ray Crystal Structure of $[\text{Fe}_2(\mu\text{-CH}_3)(\mu\text{-CO})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$: a Salt with a Bridging Methyl Group having a C - - H - - Fe Interaction

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Reaction of $[\text{Fe}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ with dppm (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) affords $[\text{Fe}_2(\mu\text{-CH}_2)(\mu\text{-CO})(\mu\text{-dppm})(\eta\text{-C}_5\text{H}_5)_2]$ which with HPF_6 yields $[\text{Fe}_2(\mu\text{-CH}_3)(\mu\text{-CO})(\mu\text{-dppm})(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$, a salt in which the CH_3 group is attached to one iron atom *via* a C-Fe σ bond with an η^2 C-H interaction with the other, as revealed by n.m.r. and single-crystal X-ray diffraction studies.

Symmetrically bridging methyl groups between two metal atoms, involving three-centre two-electron bonds, as in (I), are structurally well established, *e.g.* for Al_2Me_6 ¹ and for $[\text{Y}_2\text{Me}_2(\eta\text{-C}_5\text{H}_5)_4]$.² Of considerable interest, however, for homo- and hetero-geneous catalysis by transition metal compounds, is the bridged-methyl bonding mode (II), because it represents a possible pathway for hydrogen elimination from CH_3 groups at dimetal centres³ or the reverse process, the





Scheme 1. i, dppm in PhMe, ii, HPF₆ in (EtCO)₂O.

formation of such groups from methylene and hydrido-ligands (III).⁴ Evidence for the existence of a methyl group bridging as in (II) has been obtained⁵ from ¹H n.m.r. studies on the cluster compound [Os₃(μ-CH₃)(μ-H)(CO)₁₀] although in the crystalline state it exists⁶ exclusively as its methylene bridged tautomer [Os₃(μ-CH₂)(μ-H)₂(CO)₁₀].

Reaction of [Fe₂(μ-CH₂)(μ-CO)(CO)₂(η-C₅H₅)₂] (1)⁷ with dppm in toluene under u.v. irradiation (45 h), followed by refluxing (90 min) gave complex (2)[†] (36%) and the known⁸ compound (3) (5%) (Scheme 1). Protonation of (2) with an excess of HPF₆ in propionic anhydride gave a black crystalline salt (4) [m.p. 195 °C (decomp.), ν_{CO} (CH₂Cl₂) 1764 s cm⁻¹]. The n.m.r. data[‡] for this compound, including the observation that a ¹³C n.m.r. spectrum (non-¹H decoupled) gave a quartet signal [*J*(CH) 114 Hz] for the μ-CH₃ group, are in accord with either a symmetrical CH₃ bridge as in (I) or a structure of type (II) undergoing dynamic behaviour. The spectra were unchanged from 25 to -80 °C. A single crystal X-ray dif-

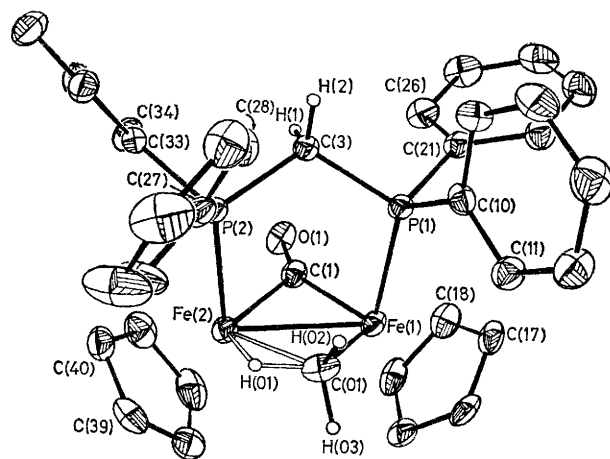


Figure 1. Molecular structure of [Fe₂(μ-CH₃)(μ-CO)(μ-dppm)(η-C₅H₅)₂]⁺ (first molecule shown) with cyclopentadienyl and phenyl hydrogen atoms omitted for clarity. Important geometrical parameters for first molecule [second molecule] are: Fe(1)-C(01) 2.008(4) [2.043(3)], Fe(2)-C(01) 2.108(3) [2.118(3)], Fe(2)-H(01) 1.64(4) [1.78(3)], Fe(1)-Fe(2) 2.544(1) [2.538(1)], C(01)-H(01) 1.06(4) [0.83(4)], Fe(1)-P(1) 2.210(ave.), Fe(2)-P(2) 2.231(ave.), Fe(1)-C(1) 1.882(ave.), Fe(2)-C(1) 1.963 Å (ave.); ∠ Fe(1)-C(01)-Fe(2) 76.3(1) [75.1(1)], Fe(2)-H(01)-C(01) 101(3) [103(3)]°.

fraction study was carried out on (4) in order to establish the molecular structure in the solid state.

Crystal data: C₃₇H₃₅F₆Fe₂OP₃, *M* = 814.3, triclinic, space group *P* $\bar{1}$, *a* = 16.335(4), *b* = 12.053(4), *c* = 18.287(6) Å, α = 81.75(3), β = 75.63(3), γ = 84.52(3)°, *U* = 3 444.9(17) Å³, *Z* = 4, *F*(000) = 1 664, *D*_c = 1.570 g cm⁻³, μ(Mo-Kα) = 10.4 cm⁻¹, Mo-Kα X-radiation, λ = 0.710 69 Å. †

The structure was solved by heavy atom (direct and Fourier) methods and refined using blocked cascade full-matrix least-squares. For 8 795 unique, absorption corrected, observed data [*I* > 2σ(*I*)], measured at 200 K on a Nicolet *P3m* diffractometer in the range 4 ≤ 2θ ≤ 50°, the current residual *R* is 0.030. All hydrogen atoms were located from difference Fourier syntheses; methyl and methylene hydrogens were refined without positional constraints, and cyclopentadienyl and phenyl hydrogens constrained to idealised geometries.

The structure of one of the two crystallographically independent cations is shown in Figure 1; the second molecule is similar. The μ-CH₃ group is markedly asymmetric, with an evidently strong interaction between Fe(2) and H(01). The geometry of the three-centre C(01)-H(01)-Fe(2) linkage would appear to be intermediate between those observed in the neutron diffraction analyses of [Fe{P(OMe)₃}₃(C₈H₁₈)⁺]⁹ and [Fe₂(μ-H)(μ-CH)(CO)₁₂].¹⁰ The cation of (4) is the first asymmetrically bridging μ-CH₃ ligand of this type to be structurally characterised. The orientation of the methyl ligand is clearly defined in both molecules, the bridging hydrogen atom lying close to the plane defined by Fe(1), Fe(2), and C(01); such an orientation corresponds to effective protonation of one of the Fe-C(methylene) bonds in the parent complex (2), and, as occurs for complexes containing μ-hydrido-ligands, the bridged bond Fe(2)-C(01) is lengthened by ca. 0.08 Å with respect to Fe(1)-C(01). The remaining geometrical features are as expected, with bond lengths to Fe(2) in general marginally longer than the corresponding ones to Fe(1), indicating some localisation of the positive charge on Fe(2).

[†] ν_{CO} (tetrahydrofuran) 1 688 s cm⁻¹; n.m.r.: ¹H δ ([²H₂]toluene), 10.3 [d, 1 H, μ-CH₃, *J*(HH) 3.3 Hz], 7.2 (m, 20 H, Ph), 6.1 [t of d, 1 H, μ-CH₂, *J*(HH) 3.3, *J*(PH) 17.6 Hz], 4.3 (s, 10 H, C₅H₅), and 1.5 (m, 2 H, CH₂ of dppm); ³¹P {¹H}, δ (in [²H₂]chloroform, to high frequency of extn. H₃PO₄), 88.7 p.p.m.; ¹³C {¹H} (in [²H₂]chloroform), δ 304 (μ-CO), 142-128 (Ph), 34.2 (C₅H₅), and 26.6 p.p.m. [CH₂ of dppm, *J*(PC) 18 Hz].

[‡] N.m.r.: ¹H, δ ([²H₂]dichloromethane), 7.5-7.3 (m, 20 H, Ph), 4.8 (s, 10 H, C₅H₅), 2.0 (m, 2 H, CH₂ of dppm), and -2.9 (s, 3 H, Me); ³¹P {¹H} (-80 °C, in [²H₂]dichloromethane-CH₂Cl₂, to high frequency of extn. H₃PO₄), δ 72.8 (dppm) and -144.8 [sept, PF₆⁻, *J*(PF) 710 Hz]; ¹³C {¹H}, δ (in [²H₂]dichloromethane-CH₂Cl₂), 275 (μ-CO), 138-127 (Ph), 86.2 (C₅H₅), 25.4 (t, CH₂ of dppm, *J*(PC) 21 Hz), and 17.8 p.p.m. (br, Me).

[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Complex (2) was dissolved in $\text{CF}_3\text{CO}_2[{}^2\text{H}]$, and the ${}^1\text{H}$ n.m.r. spectrum of the solution measured (25 °C, in $[{}^2\text{H}_2]$ dichloromethane). Resonances observed at $\delta -2.90$ and -3.47 were assigned to CH_3 and CH_2D groups, respectively, the former being of low intensity. Moreover, the signal for the CH_2D group had a large temperature dependence changing by 0.25 p.p.m. to $\delta -3.72$ at -70 °C, whereas the CH_3 resonance changed by only $\delta 0.02$. The ${}^2\text{H}$ n.m.r. spectrum (25 °C) of the deuteriated form of (4) revealed a corresponding shift to lower field for the CH_2D group ($\delta -1.88$). The large chemical shift difference (0.57 p.p.m.) between the ${}^1\text{H}$ resonances for the CH_3 and CH_2D groups, and the temperature dependence of the signal for the latter follow a similar pattern to that observed⁵ for the ' $\text{Os}_3(\text{CO})_{10}\text{CH}_2\text{D}_2$ ' system, which was interpreted as evidence for a CH_2 - -H- -Os interaction (II). Hence with (4), the deuteration and X-ray diffraction studies provide conclusive evidence for methyl-bridge bonding of type (II) in solution and in the solid state.

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