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Preliminary communication

REDUCTION OF AN ACETYLIDE C≡CR TO AN IMINOETHYL GROUP $CH_2C(R)=NR'$ IN A BINUCLEAR IRON COMPLEX VIA HYDROGEN MIGRATION FROM NITROGEN TO CARBON: X-RAY STRUCTURE OF $Fe_2(CO)_6\{CH_2C(Ph)NMe\}(PPh_2)$

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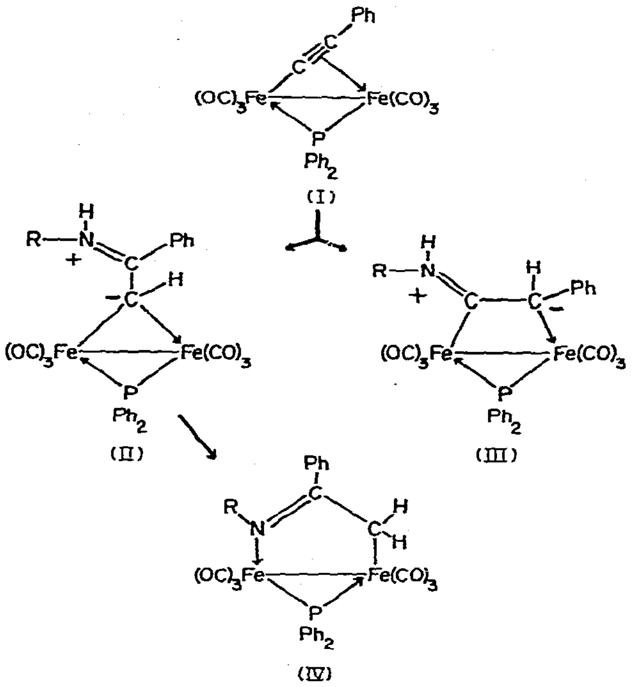
Summary

Primary amines RNH_2 effect reduction of the triple bond of the binuclear σ—π-acetylide $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ affording novel iminoethyl complexes $Fe_2(CO)_6\{CH_2C(Ph)NR\}(PPh_2)$ via hydrogen migration from nitrogen to carbon. An X-ray analysis of the iminoalkyl derivative $Fe_2(CO)_6\{CH_2C(Ph)NMe\}(PPh_2)$ shows the reduced ligand bonded as a bridging C(1*e*)—N(2*e*) donor.

Hydrogen transfer from ligand to metal and vice versa as well as intraligand hydrogen transfer with or without the intermediacy of metal hydrides are key processes in the activation and isomerisation of organic molecules by transition metal carbonyls [1]. Considerable attention has focused on the ability of certain polynuclear metal carbonyls, particularly $Os_3(CO)_{12}$ [2] and $Os_3(CO)_{10}H_2$ [3] but also recently $[Fe_3(CO)_{11}H]^-$ [4] to facilitate hydrogen migrations and hence catalyse the reduction, isomerisation and elaboration of substrate molecules. We have previously reported the facile addition of secondary and primary amines across the triple bond of binuclear σ—π acetylides such as I, generating organometallic zwitterions [5]. Further work has now shown that a second hydrogen transfer from nitrogen to carbon can occur yielding bridging (*C*,*N*), 2-phenyl-2-iminoalkyl ligands as in IV. The net effect of the reaction between $MeNH_2$ or $EtNH_2$ and I is the reduction of the triple bond of I to a carbon—carbon single bond. To our knowledge bridging iminoalkyl ligands of the type shown to be present in IV by single crystal X-ray analysis, are unprecedented in organoiron chemistry although structurally related groups CHRC(OR)=O have been postulated in model intermediates $HOs_3(CO)_{10}\{CH(R)COOR\}$ for hydrogen transfer in $H_2Os_3(CO)_{10}$ catalysed hydrogenations [6].

The reaction of gaseous $MeNH_2$ or $EtNH_2$ (1 equiv) in benzene with I at 20°C for 30 min readily forms II (R = Me, R' = H; ν(CO) C_6H_{14}, 2038(sh), 2035m,



2002s, 1959s, 1954(sh), 1915w cm^{-1}; $\delta(^{31}P)$, 85% H_3PO_4, +153.7 ppm: R = Et, R′ = H, ν(CO) C_6H_{12}, 2038(sh), 2035m, 2002s, 1959s, 1954(sh), 1915 cm^{-1}; $\delta(^{31}P)$ + 153.8 ppm) in ~45% yield together with III (R = Me, R′ = H, ν(CO) C_6H_{12} 2052s, 2014s, 1984m, 1966m, 1950m cm^{-1}; $\delta(^{31}P)$ + 183.1 ppm): R = Et, R′ = H, ν(CO) C_6H_{12} 2052s, 2014s, 1984m, 1966m, 1950m cm^{-1}, $\delta(^{31}P)$ + 183.1 ppm (40%). Compounds II and III are separable via column chromatography on Florisil (eluant 1/1 benzene/petroleum ether) when III is eluted first. On slow elution, II gradually converted to a new complex IV (R = Me, R′ = H, yellow crystals, m.p. 161°C ν(CO) C_6H_{12}, 2057s, 2010s, 1989s, 1960m, 1948m cm^{-1}; $\delta(^{31}P)$ + 197.8 ppm; R = Et, R′ = H, yellow crystals, m.p. 154°C ν(CO) C_6H_{12}, 2058s, 2010s, 1989s, 1960m, 1948m cm^{-1}, $\delta(^{31}P)$ 198.5 ppm). The transformation II→IV is catalysed by Florisil, 90% conversions being achieved when pure II is shaken with Florisil in benzene for 2 h. The structure of IV (R = Me, R′ = H) was revealed by X-ray analysis. Crystal Data: $Fe_2PO_6NC_{36}H_{29}$, mol. wt. 714.30, monoclinic space group $P2_1/c$, a 9.067(2), b 23.178(4), c 16.527(5) Å, β 90.53(2)°, $Z = 4$, ρ_c 1.366, ρ_m 1.37 g cm^{-3}, μ(Mo-K_α) 9.5 cm^{-1}. Intensity data were collected on a GE-XRD6 diffractometer with Mo-K_α radiation. From 3240 measured reflections, 2251 had $I \geqslant 3\sigma(I)$ and were used in the solution and refinement of the structure. Standard heavy atom methods of solution were used and least squares refinement with all non-hydrogen atoms anisotropic has given an R value of 0.041. All hydrogen atoms except those of the molecules of solvent were located. An ORTEP II plot is shown (Fig. 1). Atomic positions have been deposited as Tables S1 and S2. Structure factors are also available as supplementary data*. Selected bond lengths and angles are given in Table 1. The two iron atoms (Fe(1)—Fe(2) 2.707(1) Å) are bridged by a phosphido group (Fe(1)—P—Fe(2) 75.6(0)°) and by the bridging bidentate, 2-phenyl-2-*N*-methyliminoethyl with the methylene group bound to Fe(1) and the nitrogen atom to Fe(2). The entire five-membered ring Fe(1)—Fe(2)—N—

TABLE 1

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $Fe_2(CO)_6\{CH_2C(Ph)NMe\}PPh_2 \cdot 1.5\ C_6H_6$

Bond lengths			
Fe(1)—Fe(2)	2.707(1)	P—C(21)	1.824(6)
Fe(1)—P	2.194(2)	C(1)—O(1)	1.146(9)
Fe(1)—C(1)	1.790(7)	C(2)—O(2)	1.163(7)
Fe(1)—C(2)	1.780(6)	C(3)—O(3)	1.142(9)
Fe(1)—C(3)	1.801(7)	C(4)—O(4)	1.144(8)
Fe(1)—C(7)	2.106(7)	C(5)—O(5)	1.158(8)
Fe(2)—P	2.222(2)	C(6)—O(6)	1.140(9)
Fe(2)—C(4)	1.801(6)	C(7)—C(8)	1.485(8)
Fe(2)—C(5)	1.767(7)	C(8)—C(31)	1.502(8)
Fe(2)—C(6)	1.816(7)	C(8)—N	1.298(7)
Fe(2)—N	2.029(5)	N—C(9)	1.507(8)
P—C(11)	1.835(7)		

Bond angles			
Fe(2)—Fe(1)—P	52.7(0)	C(5)—Fe(2)—C(6)	90.4(3)
Fe(2)—Fe(1)—C(1)	155.8(2)	C(5)—Fe(2)—N	175.4(2)
Fe(2)—Fe(1)—C(2)	97.3(2)	C(6)—Fe(2)—N	88.6(2)
Fe(2)—Fe(1)—C(3)	94.5(2)	Fe(1)—P—Fe(2)	75.6(0)
Fe(2)—Fe(1)—C(7)	84.7(1)	Fe(1)—P—C(11)	118.6(2)
P—Fe(1)—C(1)	105.3(2)	Fe(1)—P—C(21)	124.5(1)
P—Fe(1)—C(2)	92.5(2)	Fe(2)—P—C(11)	121.7(2)
P—Fe(1)—C(3)	147.2(2)	Fe(2)—P—C(21)	117.9(1)
P—Fe(1)—C(7)	89.0(2)	C(11)—P—C(21)	99.6(2)
C(1)—Fe(1)—C(2)	93.0(2)		
C(1)—Fe(1)—C(3)	106.6(3)	Fe(1)—C(1)—O(1)	175.8(2)
C(1)—Fe(1)—C(7)	85.3(2)	Fe(1)—C(2)—O(2)	177.6(2)
C(2)—Fe(1)—C(3)	93.4(3)	Fe(1)—C(3)—O(3)	178.9(2)
C(2)—Fe(1)—C(7)	178.0(2)	Fe(2)—C(4)—O(4)	175.4(2)
C(3)—Fe(1)—C(7)	86.1(2)	Fe(2)—C(5)—O(5)	177.1(2)
Fe(1)—Fe(2)—P	51.7(0)	Fe(2)—C(6)—O(6)	177.4(2)
Fe(1)—Fe(2)—C(4)	154.7(2)	Fe(1)—C(7)—C(8)	120.3(2)
Fe(1)—Fe(2)—C(5)	87.9(2)	C(7)—C(8)—C(31)	114.8(3)
Fe(1)—Fe(2)—C(6)	98.6(2)	C(7)—C(8)—N	122.3(3)
Fe(1)—Fe(2)—N	87.8(1)	C(31)—C(8)—N	122.8(2)
P—Fe(2)—C(4)	103.0(2)	Fe(2)—N—C(8)	124.7(2)
P—Fe(2)—C(5)	90.9(2)	Fe(2)—N—C(9)	115.9(2)
P—Fe(2)—C(6)	150.2(2)	C(8)—N—C(9)	119.4(3)
P—Fe(2)—N	87.8(1)	P—C(11)—C(12)	121.0(2)
C(4)—Fe(2)—C(5)	91.3(2)	P—C(11)—C(16)	120.0(3)
C(4)—Fe(2)—C(6)	106.8(2)	P—C(21)—C(22)	120.4(2)
C(4)—Fe(2)—N	93.3(2)	P—C(21)—C(26)	122.1(3)

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*A list of calculated and observed structure factors, thermal parameters and an analysis of variance have been deposited as NAPS Document No. 3540 (16 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513 Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $5 for photocopies or $3 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

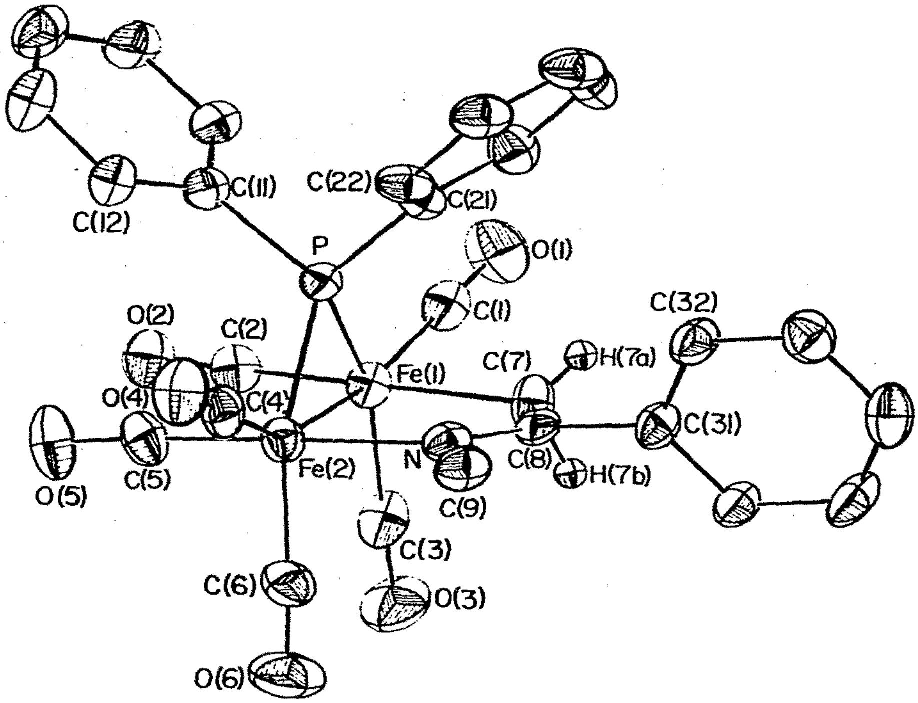

Fig. 1. An ORTEP II view of the molecular structure of $Fe_2(CO)_6(CH_2C(Ph)NMe)(PPh_2)$ showing the atomic numbering. Ellipsoids represent 30% probability except for those of hydrogen atoms which are arbitrarily drawn.

C(8)—C(7) is planar. To our knowledge there are no other examples of binuclear iron carbonyl complexes where a direct Fe—C(sp^3) linkage is present although acyl derivatives $Na[Fe_2(CO)_5(C(OR))(PPh_2)_2]\cdot 2THF$ (R = Me, Ph) have recently been characterised [7]. The Fe(1)—C(7)(sp^3) bond length of 2.106(7) Å can however be compared with the Fe—C(propyl) distance of 2.20(2) Å in the mononuclear anion $[Fe(CO)_4(C_3H_7)]^-$ [8]. The C(7)—C(8) (1.485(8) Å) and C(8)—N(1.298(7) Å) bond lengths are consistent with C—C single and C=N double bonds, respectively, between these atoms.

The conversion II→IV appears to require a heterogeneous, surface active catalyst since we have been unable to accomplish the specific synthesis of IV homogeneously from II under either acidic or basic conditions. Compounds IV are air stable in the solid state and in contrast to the structurally related osmium derivatives $HOs_3(CO)_{10}\{CHRC(OR')=O\}$ [6] they do not decompose extensively in solution presumably owing to the lack of a suitable mechanism for reductive elimination. However treatment with protic acids HX (X = Cl, Br, I, CH_3COO) results in rapid elimination of $CH_3(Ph)C=NMe$, and the generation of halo- or carboxylato-bridged binuclear complexes $Fe_2(CO)_6(PPh_2)(X)$ [9]. A hydrido species $[HFe_2(CO)_6(CH_2C(Ph)NMe)(PPh_2)]^+ X^-$, the presumed intermediate in these reactions has been spectroscopically identified but not yet isolated.

Acknowledgements

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