Dimerisation of Ethyl *N*-α-Methylbenzyliminoacetate with Nonacarbonyldi-iron. Crystal and Molecular Structures of a Di-iron Carbonyl Intermediate and of the Dimerized Imine Di-iron Carbonyl Complex

By André De Cian and Raymond Weiss*
(*Institut de Chimie, Université Louis Pasteur, B.P.* 296/R8 67008 *Strasbourg, France*)

and Yves Chauvin,* Dominique Commereuc, and Didier Hugo
(*Institut Français du Pétrole,* 92502, *Rueil-Malmaison, France*)

Summary Ethyl *N*-α-methylbenzyliminoacetate, L, dimerizes with $[Fe_2(CO)_9]$, affording μ-[diethyl 2,3-bis-(α-methylbenzylamino)succinate]-hexacarbonyldi-iron-(*Fe–Fe*), $[Fe_2(CO)_6(L–L)]$; the *X*-ray crystal structures of this complex and of an intermediate complex $[Fe_2(CO)_6L]$ have been determined, the latter showing novel bridging of an –HC=N– group.

The *N*-α-methylbenzyliminoacetate $PhCH(Me)N{=}CHCO_2Et$ (L) is a valuable intermediate for the asymmetric synthesis of α-amino-acids.[1,2] We investigated in greater detail the reaction of (L) with $[Fe_2(CO)_9]$ and unexpectedly found that the imine ligand undergoes dimerisation. When a solution of (L) (2·7 mmol) and $[Fe_2(CO)_9]$ (2·6 mmol) in benzene (5 ml) was stirred overnight and then evaporated, several complexes were isolated by t.l.c. (silica gel, benzene as eluent). Subsequent crystallisation from pentane or benzene–pentane afforded two complexes with analytical data in accordance with the formulations $[Fe_2(CO)_6L]$ (**1**) and $[Fe_2(CO)_6L_2]$ (**2**).

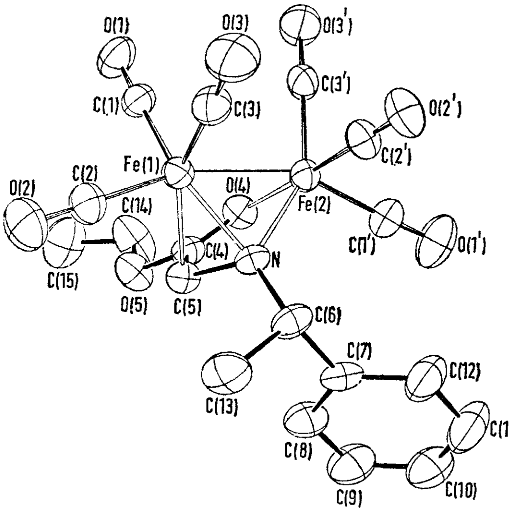


Figure 1. Complex (**1**): Fe(1)–Fe(2), 2·551(1); Fe(1)–N, 1·927(5); Fe(1)–C(5), 2·055(6); Fe(2)–O(4), 2·011(4); Fe(2)–N, 1·960(4); N–C(6), 1·481(8); N–C(5), 1·417(7); C(5)—C(4), 1·435(10); C(4)–O(4), 1·258(7); C(4)–O(5), 1·326(8) Å.

Single crystal *X*-ray diffraction studies established the molecular geometries in Figures 1 and 2 for complexes (**1**) and (**2**) respectively. *Crystal data:* Complex (**1**), $C_{18}H_{15}Fe_2NO_8$, $M = 485$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}164(5)$, $b = 10{\cdot}986(6)$, $c = 23{\cdot}780(8)$ Å, $\beta = 101{\cdot}78(10)°$, $U = 2085{\cdot}9$ Å^3, $D_m = 1{\cdot}52$, $D_c = 1{\cdot}54$ g cm^{-3}, $Z = 4$. The structure was solved with 2105 non-zero independent reflections recorded on a Picker FACS I diffractometer using Mo-K_α radiation; current $R = 0{\cdot}049$. Complex (**2**), $C_{30}H_{30}Fe_2N_2O_{10}$, $M = 690$, orthorhombic, space group *Pcca*, $a = 30{\cdot}699(8)$, $b = 14{\cdot}731(4)$, $c = 13{\cdot}768(4)$ Å, $U = 6226$ Å^3, $D_m = 1{\cdot}45$, $D_c = 1{\cdot}47$ g cm^{-3}, $Z = 8$. The intensities of 1100 non-zero independent reflections were recorded on a Philips PW1100 diffractometer using Cu-K_α radiation; current $R = 0{\cdot}083$.

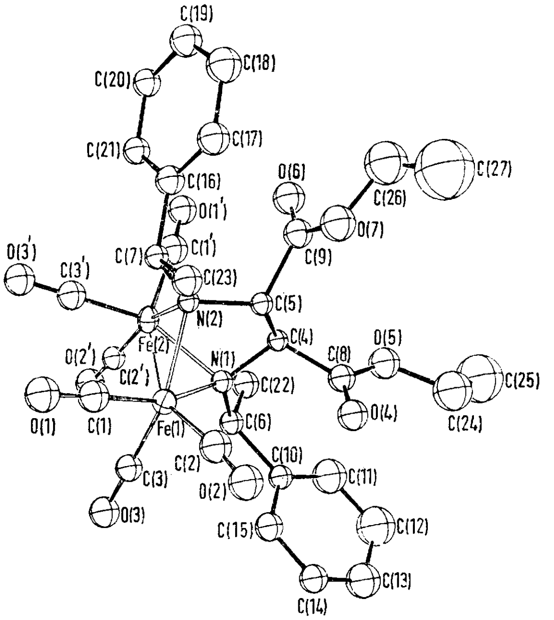
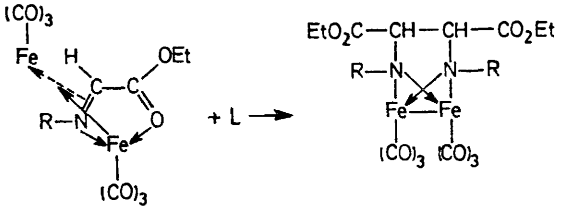


Figure 2. Complex (**2**): Fe(1)–Fe(2), 2·354(5); Fe(1)–N(1), 1·99(2); Fe(1)–N(2), 2·05(2); Fe(2)–N(1), 2·02(2); Fe(2)–N(2), 1·99(2); N(1)–C(6), 1·49(3); N(1)–C(4), 1·48(3); C(4)–C(5), 1·55(3); N(2)–C(5), 1·49(3); N(2)–C(7), 1·54(3) Å.

In (**1**), the metal atoms are not equivalent. One $Fe(CO)_3$ group is π-bonded to L through Fe(1) and the –N=CH– double bond whereas the other is σ-bonded through Fe(2) and two donor atoms of L, the nitrogen atom already involved in a π bond with Fe(1) and the ligand carbonyl oxygen atom O(4). The –N=CH– group thus acts as an unsymmetrical bridging group interacting with Fe(1) by a π bond and with Fe(2) by a σ bond. An analogous bridging mode has recently been found for a carbonyl group in $[Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2]$.[3] The iron–iron distance [2·551(1) Å] and electron counting indicate the presence of a formal Fe(2) → Fe(1) donor bond. The O(4), C(4), C(5), and O(5) atoms are approximately coplanar, with nitrogen 0·17 Å out of this plane. The Fe(2) atom is also removed from this plane by 0·30 Å but on the opposite side to nitrogen.

Dimerisation occurred between two molecules of L in (**2**) affording a 2,3-diaminosuccinic acid derivative to which are linked two iron carbonyl units forming a nitrogen-bridged binuclear carbonyl complex. C(6) and C(7) have the same absolute configuration (*S*,*S* Figure 2). A third complex giving similar analytical figures to those for (**2**) is obtained starting from racemic L, and we assume that in this complex C(6) and C(7) have the opposite absolute configuration (*R*,*S*).

On heating or irradiation, under CO, a benzene solution of (**1**) in the presence of an excess of L gave complex (**2**). Thus complex (**1**) is probably an intermediate in the dimerisation. In this way, the reactivity of L with iron carbonyls parallels that of ethyl acrylate,[4] the presence of the nitrogen atoms being responsible for the co-ordination of a second metal atom.



R = PhCHMe

(*Received*, 17*th December* 1975; *Com.* 1388.)

---

[1] J. C. Fiaud and H. Kagan, *Tetrahedron Letters*, 1970, 1813.

[2] J. Y. Chenard, D. Commereuc, and Y. Chauvin, *J.C.S. Chem. Comm.*, 1972, 750.

[3] R. Colton, C. J. Commons, and B. F. Hoskins, *J.C.S. Chem. Comm.*, 1975, 363.

[4] F. W. Grevels, D. Schulz, and E. Koerner von Gustorf, *Angew. Chem. Internat. Edn.*, 1974, **13**, 534.