Novel Reaction of Limonene(tricarbonyl)iron: Synthesis and Crystal Structure of $(\eta^4\text{-}C_{10}H_{16})\{C(OEt)C_6H_4Me\text{-}o\}Fe(CO)_2$ and $\{(\eta^3\text{-}C_{10}H_{16})C(OEt)Ar\}Fe(CO)_2$

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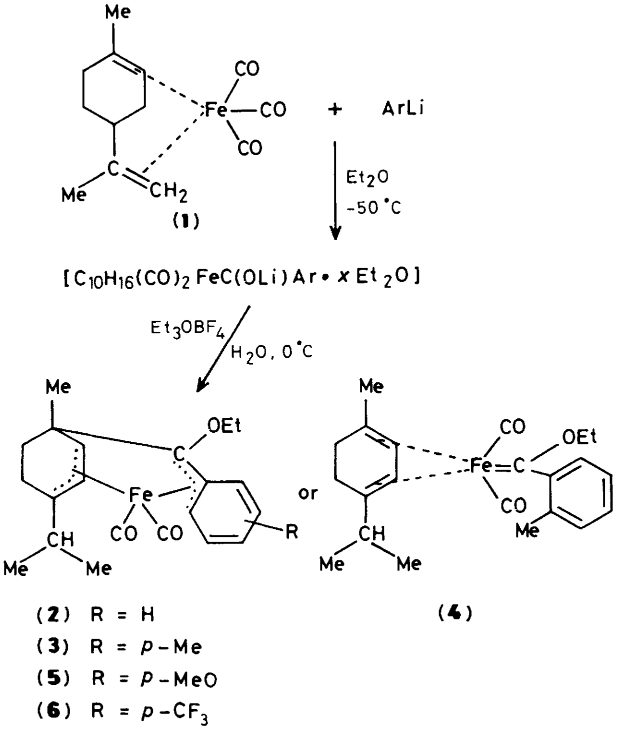
Reaction of limonene(tricarbonyl)iron (1) with aryl-lithium reagents gave intermediate acylmetallates, from which, by subsequent alkylation with Et_3OBF_4 in aqueous solution at 0 °C, the novel complexes $(\eta^4\text{-}C_{10}H_{16})\{C(OEt)C_6H_4\text{-}Me\text{-}o\}Fe(CO)_2$ (4) and $\{(\eta^3\text{-}C_{10}H_{16})C(OEt)Ar\}Fe(CO)_2$ (2), Ar = Ph; (3), Ar = $p\text{-}MeC_6H_4$; (5), Ar = $p\text{-}MeOC_6H_4$; and (6), Ar = $p\text{-}CF_3C_6H_4$ were obtained, the structures of (3) and (4) having been determined by *X*-ray crystallography.

In recent years, the syntheses and characterizations of a series of alkene-co-ordinating transition metal carbene complexes have been extensively studied in our laboratory. We found that polyalkene ligated carbonyliron compounds reacted with aryl-lithium reagents and the acylmetallates formed were subsequently alkylated with Et_3OBF_4 to give different types of products depending on the polyalkene.[1—6] We now report the novel reaction of limonene(tricarbonyl)iron (**1**), where the limonene is bonded to the $Fe(CO)_3$ moiety by both its non-conjugated double bonds, one being cyclic and the other acyclic, with aryl-lithium reagents at low temperature and subsequent alkylation with Et_3OBF_4. The reaction leads to substituted cyclohexa-1,3-diene iron carbene complexes and isomerized limonene(dicarbonyl)[ethoxy(aryl)carbene] iron complexes.

Limonene(tricarbonyl)iron (**1**) was treated with ArLi (Ar = Ph, *p*- and *o*-MeC_6H_4, *p*-$MeOC_6H_4$, and *p*-$CF_3C_6H_4$), at −50 to −40 °C and the acylmetallates formed were treated with Et_3OBF_4 in aqueous solution at 0 °C to give the orange–red, crystalline complex (**4**)† and the red complexes (**2**), (**3**), (**5**), and (**6**)† in moderate yields. On the basis of elemental analyses, spectral evidences, and *X*-ray crystallography, compound (**4**) is formulated as (1-methyl-4-isopropylcyclohexa-1,3-diene)dicarbonyl[ethoxy(*o*-tolyl)carbene]iron, the first example of a cyclodiene–iron–carbene complex isolated, and (**2**), (**3**), (**5**), and (**6**) are formulated as isomerized [ethoxy(aryl)carbenelimonene]dicarbonyliron complexes.

Complexes (**2**)—(**6**) are readily soluble in both polar and non-polar organic solvents. They are air-sensitive in solution, but relatively stable in the solid state. Complexes (**2**), (**3**), and (**6**) are rather sensitive to temperature, oxidative decomposition occurring on exposure to air at room temperature for a few hours. A possible mechanism for the formation of (**4**) and (**2**), (**3**), (**5**), and (**6**) involves a series of 1,3-shifts from a 1,5-diene to a 1,3-diene to afford (**4**), while a 1,4-addition of the carbene ligand to the six-membered ring afforded (**2**), (**3**), (**5**), and (**6**).



The *X*-ray structure of (**3**) (Figure 1)‡ shows that the double bond of the limonene ring of (**1**) has led to C(26) forming a new bond with the 'carbene' carbon atom C(1) and leaving the other three carbon atoms, C(21), C(22), and C(23), of the limonene ligand forming an allyl-type ligand bonded to the iron atom in an η^3 side-on mode. Of the other ligands

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† Satisfactory elemental analyses were obtained for (**2**)—(**6**); (**4**): m.p. 38 °C (decomp.); ν_{CO} (CH_2Cl_2) 1955vs and 1901vs cm^{-1}; (cyclohexane) 1974sh, 1960vs, 1930sh, and 1915vs cm^{-1}; ^1H n.m.r. $\delta(CD_3COCD_3)$ 7.24, 7.16 (m, 4H, C_6H_4Me), 5.12 (d, 1H, $C_{10}H_{16}$), 5.00 (d, 1H, $C_{10}H_{16}$), 4.71 (q, 2H, OCH_2Me), 2.68 (m, 1H, $C_{10}H_{16}$), 2.14 (s, 3H, $C_6H_4CH_3$), 2.08 (m, 2H, $C_{10}H_{16}$), 1.88—1.68 (m, 2H, $C_{10}H_{16}$), 1.55 (t, 3H, OCH_2CH_3), 1.40 (s, 3H, $C_{10}H_{16}$), and 1.10—1.01 (dd, 6H, $C_{10}H_{16}$); *m/z* 396 (M^+).

(**2**): m.p. 79—80 °C (decomp.); ν_{CO} (CH_2Cl_2) 1968vs and 1903vs cm^{-1}; (cyclohexane) 1986vs and 1933vs cm^{-1}; ^1H n.m.r. δ (CD_3COCD_3) 7.82 (m, 1H, C_6H_5), 7.43 (m, 1H, C_6H_5), 7.21 (m, 2H, C_6H_5), 6.17 (d, 1H, $C_{10}H_{16}$), 5.25 (d, 1H, $C_{10}H_{16}$), 3.97 (q, 1H, OCH_2Me), 3.84 (q, 1H, OCH_2Me), 2.60—2.42 (m, 1H, $C_{10}H_{16}$), 1.95—1.84 (m, 2H, $C_{10}H_{16}$), 1.72—1.63 (m, 2H, $C_{10}H_{16}$), 1.40 (t, 3H, OCH_2CH_3), 1.20—1.13 (dd, 6H, $C_{10}H_{16}$), and 0.83 (s, 3H, $C_{10}H_{16}$); *m/z* 382 (M^+).

(**3**): m.p. 79—81 °C (decomp.); (**5**): red oil; (**6**): m.p. 82 °C (decomp.); i.r. and n.m.r. data comparable with data for (**2**).

‡ *Crystal data* for (**3**): $M = 396.31$, monoclinic, space group $P2_1/c$, $a = 14.188(3)$, $b = 9.157(2)$, $c = 16.269(3)$ Å, $\beta = 106.22(2)°$, $U = 2029.5(8)$ Å^3, $Z = 4$, $D_c = 1.30$ g/cm^3. Of 2476 unique reflections collected ($3° \leqslant 2\theta \leqslant 42°$), 1728 with $F_o \geqslant 3\sigma(F_o)$ were used to solve the structure by the Patterson method; refinement by block-diagonal matrix least-squares led to the final discrepancy indices $R = 0.0318$ and $R_w = 0.0306$.

(**4**): $M = 396.31$, monoclinic, space group $P2_1/a$, $a = 7.795(5)$, $b = 26.677(13)$, $c = 9.989(5)$ Å, $\beta = 93.19(4)°$, $U = 2074.0(17)$ Å^3, $Z = 4$, $D_c = 1.27$ g/cm^3. Of 2986 independent reflections collected ($3° \leqslant 2\theta \leqslant 50°$) 1755 with $F_o \geqslant 3\sigma(F_o)$ were used in the solution (Patterson) and refinement (block-diagonal least-squares) of the structure to yield the final discrepancy indices $R = 0.0847$ and $R_w = 0.0616$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

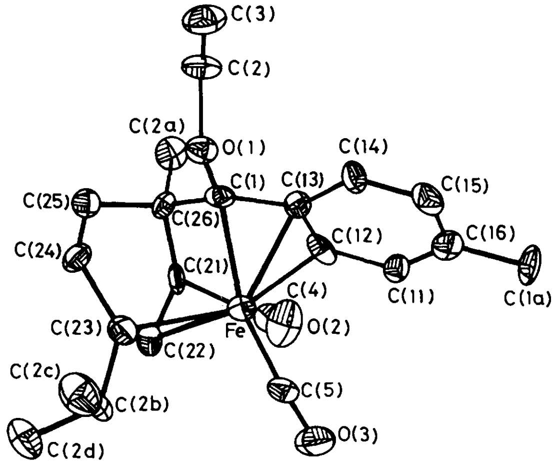

Figure 1. Molecular structure and labelling diagram for (**3**). Fe–C(12), 2.277(4); Fe–C(13), 2.138(4); Fe–C(1), 2.075(4); Fe–C(4), 1.773(4); Fe–C(5), 1.781(4); Fe–C(21), 2.139(4); Fe–C(22), 2.081(3); Fe–C(23), 2.205(4); C(1)–O(1), 1.406(4); C(1)–C(13), 1.439(5); C(12)–C(13), 1.412(6); C(13)–C(14), 1.436(5); C(14)–C(15), 1.343(6); C(15)–C(16), 1.413(6); C(16)–C(11), 1.352(5); C(11)–C(12), 1.427(6); C(21)–C(22), 1.385(6); C(22)–C(23), 1.402(6); C(23)–C(24), 1.519(7); C(26)–C(21), 1.522(6) Å; ∠C(13)–C(1)–C(26), 124.8(3); O(1)–C(1)–C(13), 114.3(3); O(1)–C(1)–C(26), 117.6(3)°.

bonded to Fe, each of the two CO ligands contributes two electrons. C(1), C(12), and C(13) form the second group orbital by using their three p_z orbitals to co-ordinate with the Fe atom and provide three electrons to satisfy the 18-electron rule.

The molecular structure of (**4**) is shown in Figure 2.‡ The carbene carbon atom C(1) forms three bonds with Fe, O(1), and C(11) by using its sp^2 hybridized orbitals and provides a pair of electrons to form a co-ordinated π bond with Fe. Each of the two CO ligands provides two electrons. The carbon atoms C(21), C(22), C(23), and C(24) of the limonene ligand form a group orbital by using their four p_z orbitals to interact with the orbitals of Fe atom in an η^4 side-on mode, and provide four electrons to satisfy the 18-electron rule.

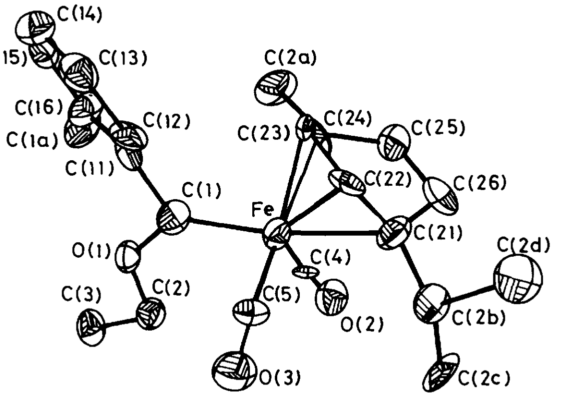

Figure 2. Molecular structure and labelling diagram for (**4**). Fe–C(1), 1.915(15); Fe–C(4), 1.771(14); Fe–C(5), 1.729(15); Fe–C(21), 2.152(13); Fe–C(22), 2.029(15); Fe–C(23), 2.058(15); Fe–C(24), 2.152(14); C(1)–O(1), 1.324(17); C(1)–C(11), 1.515(21); C(21)–C(22), 1.406(20); C(22)–C(23), 1.403(21); C(23)–C(24), 1.374(23); C(24)–C(25), 1.554(20); C(25)–C(26), 1.526(23); C(21)–C(26), 1.531(21) Å; ∠Fe–C(1)–O(1), 130.5(11); Fe–C(1)–C(11), 123.9(10); O(1)–C(1)–C(11), 105.3(11)°.

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References

1 J.-B. Chen, G.-X. Lei, W.-H. Xu, X.-L. Jin, M.-C. Shao, and Y.-Q. Tan, *J. Organomet. Chem.*, 1985, **286**, 55.

T.-L. Wang,J.-B. Chen, W.-H. Xu, S.-W. Zhang, Z.-H. Pan, and Y.-Q. Tang, *Acta Chim. Sin.*, 1987, **1**, 85.

3 J.-B. Chen, G.-X. Lei, W.-H. Xu, Z.-H. Pan, S.-W. Zhang, Z.-Y. Zhang, X.-L. Jin, M.-C. Shao, and Y.-Q. Tang, *Organometallics*, 1987, **6**, 2461.

4 J.-B. Chen, G.-X. Lei, Z.-H. Pan, S.-W. Zhang, and Y.-Q. Tang, *J. Chem. Soc., Chem. Commun.*, 1987, 1273.

5 J.-B. Chen, G.-X. Lei, Z.-Y. Zhang, and Y.-Q. Tang, *Acta Chim. Sin.*, 1987, **45**, 418.

6 J.-B. Chen, G.-X. Lei, M.-C. Shao, X.-J. Xu, and Z.-Y. Zhang, *Angew. Chem.*, to be published.