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DOUBLE ACETYLENE INSERTION INTO A μ-METHYLENE COMPLEX OF IRON: FORMATION OF A μ-(DIVINYL)CARBENE COMPLEX OF IRON AFTER A DOUBLE HYDROGEN MIGRATION

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Summary

Acetylene reacts with $Fe_2[(\mu\text{-}CH_2)(CO)_8]$ to give, besides the known mono-insertion product $Fe_2\{[(\mu\text{-}CH)(\eta^2\text{-}CH{=}CH_2)](CO)_7\}$ and the linear di-insertion product $Fe_2\{[(\mu\text{-}CH)\text{-}(\eta^4\text{-}CH{=}CHCH{=}CH_2)][(CO)]_6\}$, the branched μ-divinyl carbene complex $Fe_2\{[(\mu\text{-}C)(\eta^2\text{-}CH{=}CH_2)_2][(CO)_6]\}$, the formation of which can be accounted for in terms of double hydrogen migration.

Introduction

One of the most interesting reactions of μ-alkylidene complexes of transition metal is the insertion of alkynes into the bridging carbene ligand [1–8]. Depending on the metal, but also on the reaction conditions, this reaction can lead either to new μ-alkylidine complexes, as a result of the mono- and the di-insertion reaction of the alkyne, or to conjugated linear polymers.

It has been shown by Pettit and coworkers [6], that $[(CO)_4Fe(\mu\text{-}CH_2)Fe(CO)_4]$ (**1**) reacts with alkynes to give mainly mono- and di-insertion linear products. In all cases, the formation of these new complexes can be explained by an insertion of the alkyne followed by the migration of a hydrogen originally bound to the methylene ligand in **1** (Scheme 1).

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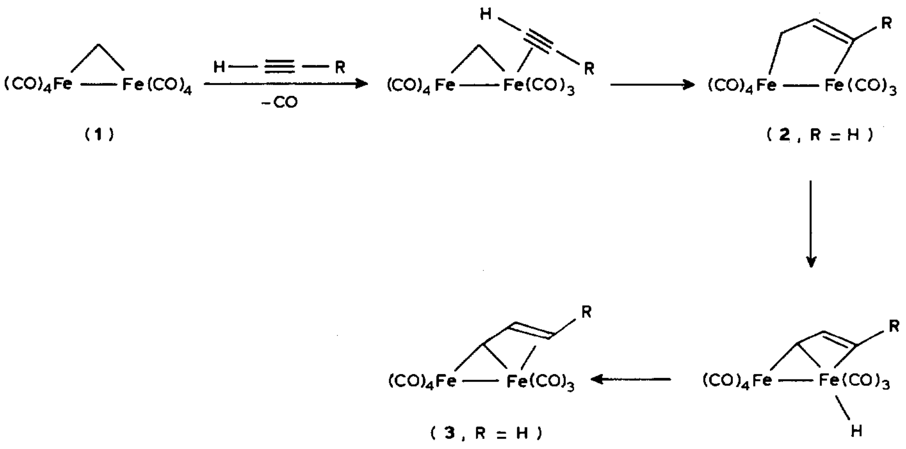


SCHEME 1

No such migrations were observed in the case of the μ-alkylidene complexes of tungsten [4].

Results and discussion

During the course of our study directed towards the systematic carbonylation of μ-alkylidene complexes of transition metals, we repeated the reaction of acetylene with **1**, and observed, besides the mono-insertion and the di-insertion products **3** and **5**, the formation of the unexpected branched di-insertion product **6**.

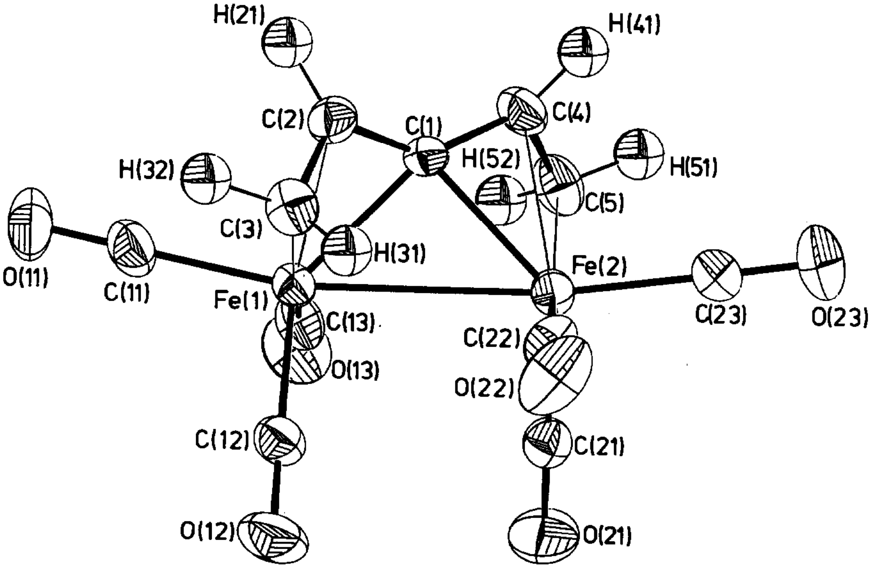
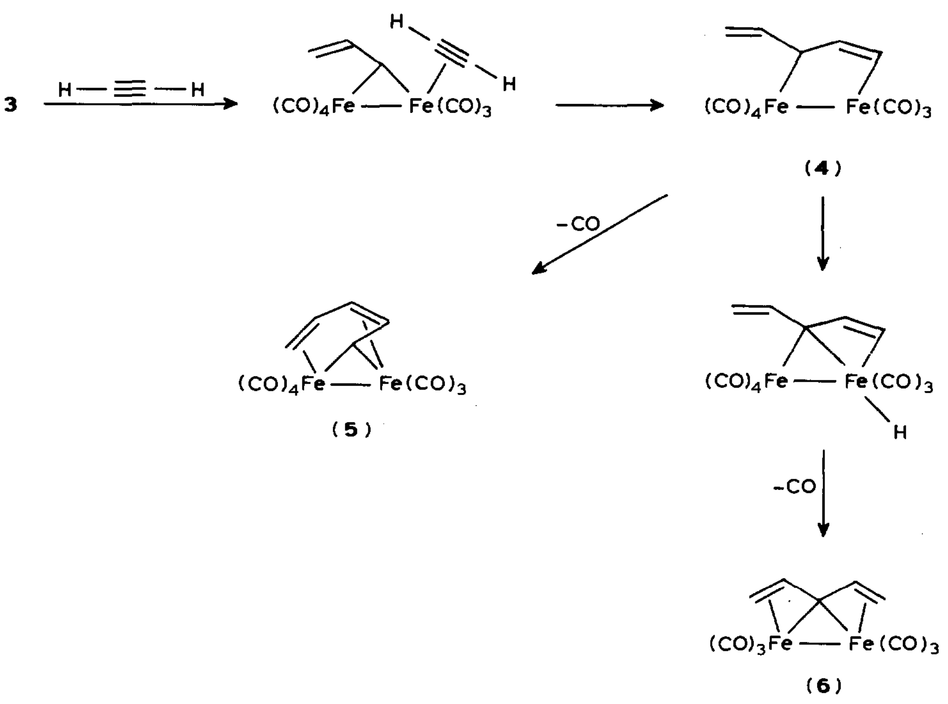


Fig. 1. ORTEP view of complex **6**.



SCHEME 2

The mass spectrum of **6** clearly shows that two molecules of acetylene had been inserted into **1**, but the ^{1}H NMR spectrum is very simple, showing only signals typical of a coordinated monosubstituted double bond, at 4.90 (dd, *J* 6.6 and 8.7 Hz), 2.14 (d, *J* 6.6 Hz) and 1.59 (d, *J* 8.7 Hz) ppm. Structure **6** was therefore assigned to this complex, and was confirmed by an X-ray analysis. An ORTEP view of complex **6** is shown in Fig. 1.

The structure of complex **6** shows that both hydrogens of the bridging methylene ligand migrated after the insertions. It thus appears that in the case of iron, in addition to the normal propagation reaction, hydrogen migrations can occur readily [1,6], probably via the coordinatively unsaturated intermediates **2** and **4** (Scheme 2).

The most interesting feature of complex **6**, besides the mechanism of its formation, lies in its geometry. Complex **6** can be compared to complex **7**, a dinuclear complex of allene which was described very recently [9]; the geometries around the two metal centers are quite similar, with values of the C(2)–C(1)–C(4) angle of 143.8° (146.8° in **6**), and Fe(2)–C(1)–Fe(1) of 88.3° (89.0° in **6**). Consequently complex **6** could also be regarded as a diferracycloallene.

(**6**)

(**7**)

Experimental

A solution of complex **1** (1 g, 2.85 mmol) in toluene (45 ml) was kept at 65°C and acetylene was bubbled through for 90 min, during which the solution gradually turned from yellow to red. The mixture was left at this temperature for a further 30 min then the solvent was evaporated under vacuum, and the residue taken up in light petroleum and chromatographed on silica gel. Elution with light petroleum first gave trace amounts of complex **3**, then complex **5** (335 mg, 34%), and finally gave complex **6**. (157 mg, 16%) as red crystals, which were recrystallized from hexane. M.p. 53°C. IR (hexane): 2090w, 2021s, 1995s, 1975m ν(CO). ^{1}H NMR ($CDCl_3$, 250 MHz): 4.90 (dd, J 6.6 and 8.7 Hz, 2H), 2.14 (d, J 6.6 Hz, 2H), 1.59 (d, J 8.7 Hz, 2H). $m/z = 346$ (M^+).

X-Ray studies

Preliminary unit cell dimensions and symmetry information were derived from precession photographs; the selected crystal was then set up on a Nonius CAD4 automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained from least-squares refinements of the setting angles of 25 well centered reflections ($24 < 2\theta < 28$).

TABLE 1

CRYSTAL DATA

Empirical formula	$C_{11}H_6O_6Fe_2$
Formula wt.	345.86
Crystal system	monoclinic
Space grop	$P2_1/c$
a (Å)	9.378(2)
b (Å)	9.390(2)
c (Å)	15.441(2)
β (°)	106.91(2)
V (Å^3)	1300.9(8)
Z	4
Crystal size (mm)	0.3×0.2×0.18
D_{calc} (g cm^{-3})	1.77
μ(Mo-K_α) (cm^{-1})	23.03
Diffractometer	Nonius CAD4
Temp (°C)	20
Radiation	Mo-K_α (λ 0.71069 Å, graphite)
Scan range (°)	$1.5 + 0.345\mathrm{tg}\phi$
2ϕ range (°)	3–50
Scan speed v (° s^{-1})	$0.02 < v < 0.09$
Scan type	θ–2θ
Standard reflectns	2, measured every hour (2 6 3, 6 −3 −5)
Reflectns collected	2667 (hkl, $-hkl$)
Reflectns merged	1566 ($I > 2\sigma(I)$)
Degrees of freedom	1376
$R = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	0.0334
$R_w = \{\Sigma w(\|F_0\| - \|F_0\|)^2/\Sigma w F_0{}^2\}^{1/2}$	0.0403
Final shift/e.s.d's	0.06

TABLE 2

FRACTIONAL ATOMIC COORDINATES (with e.s.d.s in parentheses)

Atom	x	y	z
Fe(1)	0.06671(8)	0.19482(9)	0.37921(5)
Fe(2)	0.34725(9)	0.2995(1)	0.38763(5)
C(1)	0.1710(6)	0.2389(6)	0.2870(4)
C(2)	0.0236(7)	0.2820(7)	0.2503(4)
C(3)	−0.0376(8)	0.3745(7)	0.3020(5)
C(4)	0.2965(7)	0.1888(8)	0.2652(4)
C(5)	0.4001(8)	0.1067(8)	0.3299(5)
C(11)	−0.1107(8)	0.1051(8)	0.3526(5)
O(11)	−0.2201(6)	0.464(7)	0.3355(4)
C(12)	0.0644(7)	0.2810(7)	0.4829(4)
O(12)	0.0642(6)	0.3396(6)	0.5482(3)
C(13)	0.1558(7)	0.0311(8)	0.4243(5)
O(13)	0.2052(6)	−0.0736(6)	0.4553(4)
C(21)	0.4160(7)	0.2400(7)	0.5040(5)
O(21)	0.4577(6)	0.2057(6)	0.5768(3)
C(22)	0.2860(7)	0.4764(8)	0.4040(4)
O(22)	0.2557(6)	0.5887(6)	0.4163(4)
C(23)	0.5171(8)	0.3747(9)	0.3762(4)
O(23)	0.6246(6)	0.4195(7)	0.3683(4)
H(21)	−0.036(6)	0.233(6)	0.197(4)
H(31)	0.007(6)	0.462(7)	0.326(4)
H(32)	−0.153(6)	0.376(6)	0.276(4)
H(41)	0.330(6)	0.237(6)	0.221(4)
H(51)	0.498(6)	0.092(6)	0.313(4)
H(52)	0.374(7)	0.031(7)	0.351(4)

Crystal data and data collection parameters are listed in Table 1. Intensities of two standard reflections were monitored every hour; they showed no change during data collection. Corrections were made for Lorentz and polarization effects. Psi scan curves showed significant intensity variations; absorption correction was then made by an empirical procedure [10].

Computations were performed by using the CRYSTALS system [11] adapted for a VAX 11/725. Atomic scattering factors for neutral Fe, C, O and H were taken from ref. 12; anomalous dispersion for Fe atoms was taken into account.

The positions of Fe atoms were determined by Harker vector analysis of a three-dimensional Patterson map. All remaining non-hydrogen atoms were found from successive electron density maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a difference electron density map; their atomic coordinates were refined with a fixed overall isotropic thermal parameter ($U = 0.05$). The criteria for a satisfactory completed analysis were the ratio of the parameter shifts to standard deviations (Table 1), and no significant features in the final difference map.

Copies of the observed structure amplitudes and structure factors calculated from the final atomic parameters, and anisotropic thermal parameters are available.

TABLE 3

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) (with e.s.d.'s in parentheses)

Fe(1)-Fe(2)	2.776(1)		
Fe(1)-C(1)	1.992(5)	C(2)-C(3)	1.410(9)
Fe(1)-C(2)	2.080(6)	C(4)-C(5)	1.40(1)
Fe(1)-C(3)	2.133(6)	C(11)-O(11)	1.127(7)
Fe(1)-C(11)	1.802(7)	C(12)-O(12)	1.150(7)
Fe(1)-C(12)	1.800(6)	C(13)-O(13)	1.132(8)
Fe(1)-C(13)	1.791(7)	C(21)-O(21)	1.124(7)
Fe(2)-C(1)	1.994(5)	C(22)-O(22)	1.123(8)
Fe(2)-C(4)	2.087(6)	C(23)-O(23)	1.132(8)
Fe(2)-C(5)	2.138(7)	C(2)-H(21)	0.96(5)
Fe(2)-C(21)	1.812(7)	C(3)-H(31)	0.95(6)
Fe(2)-C(22)	1.800(7)	C(3)-H(32)	1.04(6)
Fe(2)-C(23)	1.797(7)	C(4)-H(41)	0.95(6)
C(1)-C(2)	1.393(8)	C(5)-H(51)	1.03(6)
C(1)-C(4)	1.396(8)	C(5)-H(52)	0.84(6)
C(11)-Fe(1)-C(1)	123.1(3)	Fe(2)-C(1)-Fe(1)	88.3(2)
C(11)-Fe(1)-C(2)	93.2(3)	C(2)-C(1)-Fe(1)	73.5(3)
C(11)-Fe(1)-C(3)	90.0(3)	C(2)-C(1)-Fe(2)	137.2(5)
C(12)-Fe(1)-C(1)	132.7(3)	C(4)-C(1)-Fe(1)	136.5(5)
C(12)-Fe(1)-C(2)	128.7(3)	C(4)-C(1)-Fe(2)	73.6(4)
C(12)-Fe(1)-C(3)	91.1(3)	C(4)-C(1)-C(2)	143.8(6)
C(12)-Fe(1)-C(11)	99.4(3)	C(3)-C(2)-C(1)	117.9(6)
C(13)-Fe(1)-C(1)	100.7(3)	C(5)-C(4)-C(1)	118.1(6)
C(13)-Fe(1)-C(2)	130.4(3)	O(11)-C(11)-Fe(1)	178.5(7)
C(13)-Fe(1)-C(3)	169.4(3)	O(12)-C(12)-Fe(1)	178.0(6)
C(13)-Fe(1)-C(11)	89.0(3)	O(13)-C(13)-Fe(1)	175.7(6)
C(13)-Fe(1)-C(12)	99.5(3)	O(21)-C(21)-Fe(2)	178.5(6)
C(21)-Fe(2)-C(1)	131.3(3)	O(22)-C(22)-Fe(2)	176.2(6)
C(21)-Fe(2)-C(4)	131.8(3)	O(23)-C(23)-Fe(2)	178.6(8)
C(21)-Fe(2)-C(5)	95.4(3)	H(21)-C(2)-C(1)	117.7(34)
C(22)-Fe(2)-C(1)	98.4(3)	H(21)-C(2)-C(3)	123.2(34)
C(22)-Fe(2)-C(4)	126.1(3)	H(31)-C(3)-C(2)	123.5(36)
C(22)-Fe(2)-C(5)	164.2(3)	H(32)-C(3)-C(2)	110.0(31)
C(22)-Fe(2)-C(21)	100.4(3)	H(32)-C(3)-H(31)	115.3(48)
C(23)-Fe(2)-C(1)	126.4(3)	H(41)-C(4)-C(1)	119.3(35)
C(23)-Fe(2)-C(4)	94.7(3)	H(41)-C(4)-C(5)	118.3(34)
C(23)-Fe(2)-C(5)	88.4(3)	H(51)-C(5)-C(4)	112.1(31)
C(23)-Fe(2)-C(21)	98.5(3)	H(52)-C(5)-C(4)	121.3(43)
C(23)-Fe(2)-C(22)	88.8(3)	H(52)-C(5)-H(51)	111.1(53)

Atomic coordinates are listed in Table 2, and bond lengths and bond angles in Table 3.

Acknowledgements

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