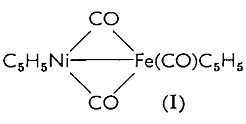
915. *Tricarbonylcyclopentadienyliron-cyclopentadienylnickel and Some New Cyclopentadienylnickel-irontricarbonyl–Acetylene Complexes.*

By J. F. Tilney-Bassett.

Dicyclopentadienylnickel reacts with pentacarbonyliron, yielding tricarbonylcyclopentadienyliron-cyclopentadienylnickel. Dicyclopentadienyldinickel–acetylene complexes react with iron carbonyl, yielding complexes $(C_5H_5Ni)_2RC{\equiv}CR'Fe(CO)_3$, $(C_5H_5Ni)_2RC{\equiv}CR'Fe_2(CO)_6$, and $(C_5H_5NiRC{\equiv}CR')_2Fe(CO)_3$.

This paper describes in detail the preparation and reactions of tricarbonylcyclopentadienyliron-cyclopentadienylnickel[1] and of some polynuclear cyclopentadienylnickel-tricarbonyliron–acetylene complexes. Reaction of dicyclopentadienylnickel with pentacarbonyliron yielded tricarbonylcyclopentadienylnickel-cyclopentadienyliron, together with dicarbonyldicyclopentadienyldinickel and tetracarbonyldicyclopentadienyldiiron, but dicyclopentadienyliron did not react with nickel carbonyl. Structure (I) is suggested for the first of these products.



(I)

The complex (I) forms diamagnetic chocolate-brown needles which decompose on exposure to air for a few minutes. Its reaction with iodine yielded one molecule of carbon monoxide per molecule and led to the isolation of iododicarbonylcyclopentadienyliron, proving the presence of the dicarbonylcyclopentadienyliron group. Reaction of compound (I) with diphenylacetylene did not result in the replacement of the bridging carbonyl groups to afford an acetylene-bridged iron–nickel compound, but instead resulted in disproportionation:[2,3]

$$2C_5H_5Ni(CO)_3FeC_5H_5 + 2I_2 \longrightarrow NiI_2 + CO + C_5H_5Fe(CO)_2I + ?$$

$$2C_5H_5Fe(CO)_3Ni(C_5H_5) + PhC{\equiv}CPh \longrightarrow (C_5H_5Fe)_2(CO)_4 + (C_5H_5Ni)_2PhC{\equiv}CPh$$

This reaction confirms the presence of the cyclopentadienylnickel group and indicates the structure (I). The presence of both bridging and terminal carbonyl groups is confirmed by strong infrared absorption bands at 1975 and 1806 cm.$^{-1}$ with a shoulder at 1836 cm.$^{-1}$.

During attempts to prepare a compound with an acetylene-bridged iron–nickel bond it was found that mixed iron–nickel–acetylene complexes were formed from dicyclopentadienyldinickel–acetylene complexes and iron carbonyls. Reaction of pentacarbonyliron

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[1] Cf. Tilney-Bassett, *Proc. Chem. Soc.*, 1960, 419.

[2] Tilney-Bassett and Mills, *J. Amer. Chem. Soc.*, 1959, **81**, 4757.

[3] Tilney-Bassett, *J.*, 1961, 577.

with dicyclopentadienyldiphenylacetylenedinickel, or more conveniently reaction of pentacarbonyliron with dicyclopentadienylnickel and diphenylacetylene, yielded two complexes:

$(C_5H_5Ni)_2PhC\equiv CPhFe(CO)_3$ (II) and $(C_5H_5Ni)_2PhC\equiv CPhFe_2(CO)_6$ (III)

Similarly dicyclopentadienylphenylacetylenedinickel reacts with tetracarbonyliron, yielding the related complexes:

$(C_5H_5Ni)_2PhC\equiv CHFe(CO)_3$ (IV) and $(C_5H_5Ni)_2PhC\equiv CHFe_2(CO)_6$ (V)

together with a third complex $(C_5H_5NiPhC\equiv CH)_2Fe(CO)_3$ (VI). These complexes are all diamagnetic solids that are stable in air and whose solutions decompose only very slowly in air. All the complexes gave infrared absorption bands corresponding to terminal carbonyl groups, as did the following two compounds:

$(C_5H_5Ni)_2PhC\equiv C{\cdot}C\equiv CPhFe(CO)_3$ (VII) and $(C_5H_5Ni)_2PhC\equiv C{\cdot}C\equiv CPhFe_2(CO)_6$ (VIII)

As previously reported[3] these are prepared from dicyclopentadienyldiphenylbutadiynedinickel and tetracarbonyliron and are probably related to complexes (II) and (IV) and to (III) and (V), respectively, rather than to the complexes $PhC\equiv CPhFe_2(CO)_6$ and $(PhC\equiv CPh)_2Fe_2(CO)_6$[4] as originally suggested.

Melting points and carbonyl infrared bands of these products and of a related cobalt complex are given in the Table.

Physical properties of organometallic compounds.

No.	Formula	M. p. (decomp.)	CO stretch (cm.$^{-1}$)				
(I)	$C_5H_5Fe(CO)_3Ni(C_5H_5)$	132°	1975	1836s	1806		
(II)	$(C_5H_5Ni)_2PhC\equiv CPhFe(CO)_3$	198—199	2043		1967		
(III)	$(C_5H_5Ni)_2PhC\equiv CPhFe_2(CO)_6$	180	2023	1980s	1961		
(IV)	$(C_5H_5Ni)_2PhC\equiv CHFe(CO)_3$	121 or 142—144	2037	1990s	1974		
(V)	$(C_5H_5Ni)_2PhC\equiv CHFe_2(CO)_6$	168	2050		1982		
(VI)	$(C_5H_5NiPhC\equiv CH)_2Fe(CO)_3$	142—144	2041		1974		
(VII)	$(C_5H_5Ni)_2PhC\equiv C{\cdot}C\equiv CPhFe(CO)_3$ [3]	160—161	2028	1987	1970		
(VIII)	$(C_5H_5Ni)_2PhC\equiv C{\cdot}C\equiv CPhFe_2(CO)_6$ [3]	156	2030	1988	1968		
(IX)	$Co_4(CO)_{10}PhC\equiv CPh$	175—180	2129	2095	2055	2008	1915

The diphenylacetylene complexes (II) and (III) were reduced to bibenzyl by sodium and alcohol in liquid ammonia, and when oxidised afforded diphenylacetylene. Pyrolysis of the di-iron complex (III) yielded the monoiron complex (II), together with one of the compounds $(C_5H_5Fe)_2(CO)_4$ and $(PhC\equiv CPh)_2Fe_2(CO)_6$[4] according to the conditions. Treatment of the monoiron complex (II) with iron carbonyl led mainly to the recovery of starting material, but small amounts of the di-iron complex (III) were formed.

The complex (VI) had a nuclear magnetic resonance spectrum which did not show peaks due to CH_2 or CH, but did show peaks consistent with the presence of C_6H_5, C_5H_5, and ethylenic hydrogen.

Since the compounds $(C_5H_5Ni)_2PhC\equiv CPh$ and $Co_2(CO)_6PhC\equiv CPh$ are structurally related[2,3] it seemed possible that they might undergo similar reactions with pentacarbonyliron. Treatment of the cobalt complex with pentacarbonyliron in refluxing toluene led very largely to recovery of the original cobalt complex, but gave also small yields of the red complex $PhC\equiv CPhFe_2(CO)_6$ first prepared by Hubel and Braye[4] and of a dark blue compound $Co_2(CO)_{10}PhC\equiv CPh$ (IX). The latter compound, which has been mentioned but not described by Hubel and Braye, has infrared absorption corresponding to terminal carbonyl groups.

The annexed structures are suggested for the compounds described in this paper. Each is consistent with the analysis and infrared spectrum and shows an inert-gas structure for the metal electrons which is consistent with the diamagnetism. The various structures suggested show similarities with many known compounds. Thus the tetrahedral arrangement of metal atoms suggested for complexes (III), (V), (VIII), and (IX) is also present in

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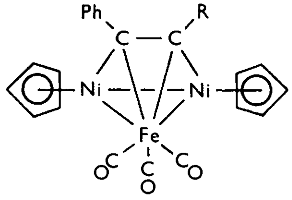
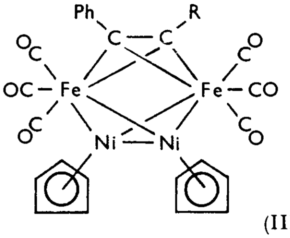
[4] Hubel and Braye, *J. Inorg. Nuclear Chem.*, 1959, **10**, 250.

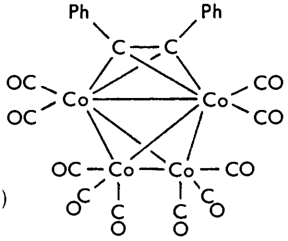
$Co_4(CO)_{12}$,[5] and the triangular arrangement in (II), (IV), and (VII) is similar to that in the complexes $RC[Co(CO)_3]_3$,[6] and the M–C bonding suggested for compounds (II), (IV), and (VII) may be considered as analogous to the Co–C bonding in the group (X) present in $RC[Co(CO)_3]_3$. A number of different structural types could be put forward for the complex (VI), and as with the other compounds *X*-ray crystallographic analysis would be required for complete proof of structure.



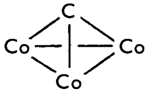
(II: R = Ph)
(IV: R = H)
(VII: R = –C≡CPh)



(III; R = Ph)
(V; R = H)
(VIII; R = –C≡CPh)



(IX)



(X)

EXPERIMENTAL

M. p.s of organometallic compounds were obtained in sealed evacuated tubes. Oxygen was determined by Oliver's method.[7] After acid oxidation of organic matter, nickel [8] and cobalt [9] were determined colorimetrically, and iron [10] volumetrically.

Tricarbonylcyclopentadienyliron-cyclopentadienylnickel (I).—Nickelocene (5 g.), pentacarbonyliron (10 c.c.), and benzene (100 c.c.) were stirred and refluxed under a stream of dry nitrogen for 8 hr. Most of the solvent was then removed and the residue dissolved in ligroin (b. p. 60—80°) and chromatographed on alumina. Unchanged nickelocene was eluted first, followed successively by a small amount of dicarbonyldicyclopentadienyldinickel, a brown compound, and tetracarbonyldicyclopentadienyldi-iron. The brown solution was collected and handled under nitrogen. The solvent was removed and the residue crystallised twice from ligroin (b. p. 40—60°), yielding chocolate-brown needles, m. p. 132° (decomp.), of tricarbonylcyclopentadienyliron-cyclopentadienylnickel (Found: C, 46·5; H, 3·7; Fe, 16·5; Ni, 18·0. Calc. for $C_{13}H_{10}FeNiO_3$: C, 47·5; H, 3·3; Fe, 17·0; Ni, 17·8%).

Reactions of Tricarbonylcyclopentadienyliron-cyclopentadienylnickel (I).—(*a*) The compound (0·127 g.) was treated under nitrogen with a solution of iodine (2 g.) in pyridine (20 c.c.) and yielded 8·6 c.c. (N.T.P.) (8·5%) of carbon monoxide (1 mol. = 8·5%).

(*b*) The complex (0·55 g.) in chloroform (10 c.c.) was treated with a solution of iodine (0·85 g.) in chloroform (30 c.c.) and set aside for 30 min. Most of the chloroform was then removed and the residue crystallised from ligroin (b. p. 60—80°), yielding black crystals of

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[5] Corradini, *J. Chem. Phys.*, 1959, **31**, 1676.
[6] Kruerke and Hubel, *Chem. and Ind.*, 1960, 1264. Dent, Duncanson, Guy, Reed, and Shaw, *Proc. Chem. Soc.*, 1961, 169.
[7] Oliver, *Analyst*, 1955, **80**, 593.
[8] B.D.H. Book of Organic Reagents, B.D.H., London, p. 44.
[9] Young, " Industrial Inorganic Analysis," Chapman & Hall, London, 1953, p. 79.
[10] Kolthoff and Belcher, " Volumetric Analysis," Interscience Publ., Inc., New York, 1957, Vol. III, p. 623.

iododicarbonylcyclopentadienyliron, m. p. 117—119° (decomp.), identical with a sample obtained from tetracarbonyldicyclopentadienyldi-iron and iodine.

(*c*) The complex (0·14 g.) and tolan (0·04 g.) were refluxed in toluene (20 c.c.) for 20 min. The solvent was then removed and the residue chromatographed on alumina. Dicyclopentadienyldiphenylacetylenedinickel, m. p. and mixed m. p. 150° [2,3] (0·07 g., 74%), was eluted first, followed by tetracarbonyldicyclopentadienyldi-iron, m. p. and mixed m. p. 198° (0·04 g., 49%).

Preparation of Mixed Iron–Nickel–Diphenylacetylene Complexes.—Dicyclopentadienylnickel (5·6 g.), diphenylacetylene (5·6 g.), and pentacarbonyliron (12 c.c.) in benzene (150 c.c.) were refluxed under nitrogen for 22 hr. The solvent was then removed and the residue chromatographed on alumina. Elution with ligroin (b. p. 60—80°) yielded dicyclopentadienylnickel (1·7 g.), followed by unchanged diphenylacetylene and then by a blue layer which on evaporation and crystallisation from ligroin (b. p. 40—60°) yielded *dicyclopentadienyldinickel-di-iron-hexacarbonyl-diphenylacetylene* (III) (0·905 g.) as permanganate-coloured needles, m. p. 180° (decomp.) (Found: C, 51·4; H, 3·2; O, 13·0; Ni, 16·6; Fe, 16·2. $C_{30}H_{20}Fe_2Ni_2O_6$ requires C, 51·1; H, 2·9; O, 13·6; Ni, 16·6; Fe, 15·8%). Further elution with ligroin yielded a small amount of dicyclopentadienyldiphenylacetylenedinickel,[2,3] m. p. and mixed m. p. 150°, followed by a small amount of a yellow complex, m. p. 203—205°, which had properties identical with those described by Hubel and Braye [4] for the complex $(PhC{\equiv}CPh)_2Fe_2(CO)_6$ (Found: C, 63·7; H, 3·5; O, 15·5. Calc. for $C_{34}H_{20}Fe_2O_6$: C, 64·2; H, 3·2; O, 15·1%). This was followed in the chromatography by a brown solution which on evaporation and crystallisation from ligroin (b. p. 60—80°) yielded black needles of *dicyclopentadienyldinickel-tricarbonyliron-diphenylacetylene* (II) (2·12 g.), m. p. 198—199° (Found: C, 57·2; H, 3·8; Ni, 20·7; Fe, 10·2. $C_{27}H_{20}FeNi_2O_3$ requires C, 57·3; H, 3·6; Ni, 20·8; Fe, 9·9%). Further elution yielded tetracarbonyldicyclopentadienyldi-iron (2·02 g.), m. p. and mixed m. p. 198°.

Reactions of Dicyclopentadienyldinickel-irontricarbonyl-diphenylacetylene (II).—*Reduction.* Reduction of the complex (1·0 g.) with sodium and alcohol in liquid ammonia yielded bibenzyl (0·143 g.), m. p. and mixed m. p. 52°.

Oxidation. Air oxidised the complex (II) in chloroform–ethanol solution containing some hydrochloric acid, yielding diphenylacetylene, m. p. and mixed m. p. 60°.

With iron carbonyls. Reaction of the complex (II) with pentacarbonyliron or dodecacarbonyltri-iron gave only small yields of the di-iron complex (III), and the complex (II) was largely recovered unchanged.

Reactions of Dicyclopentadienyldinickel-hexacarbonyldi-iron-diphenylacetylene (III).—*Reduction.* Reduction of this complex with sodium and alcohol in liquid ammonia yielded bibenzyl, m. p. and mixed m. p. 52°.

Oxidation. An alcoholic solution of ferric chloride was run into a boiling alcoholic solution of the complex (III) until the colour was destroyed. The solution was filtered and the solvent removed, leaving a residue which yielded diphenylacetylene, m. p. and mixed m. p. 60° (from ligroin).

Pyrolysis. The complex (III) slowly sublimed at 130°/0·02 mm., but at 180°/0·01 mm. yielded a black sublimate which was chromatographed on alumina, yielding the monoiron complex (II), m. p. 198—199°, and $(PhC{\equiv}CPh)_2Fe_2(CO)_6$. When sublimed at 155°/15 mm. the complex (III) yielded a sublimate of tetracarbonyldicyclopentadienyldi-iron, m. p. and mixed m. p. 198°, and a residue which when chromatographed on alumina gave the complex (II).

Preparation of Iron–Nickel–Phenylacetylene Complexes.—Dicyclopentadienylphenylacetylenedinickel (4·0 g.) and tetracarbonyliron (4·0 g.) in benzene (100 c.c.) were refluxed under nitrogen for 2 hr. The solvent was then removed and the residue chromatographed on alumina. Elution with ligroin (b. p. 40—60°) yielded *dicyclopentadienyldinickel-hexacarbonyldi-iron-phenylacetylene* (V) which crystallised from its blue solution in ligroin as black crystals (0·11 g.), m. p. 168° (decomp.) (Found: C, 46·0; H, 2·9; Ni, 18·8; Fe, 17·7. $C_{24}H_{16}Fe_2Ni_2O_6$ requires C, 45·8; H, 2·7; Ni, 18·6; Fe, 17·7%). Further elution with ligroin afforded *dicyclopentadienyldinickel-tricarbonyliron-phenylacetylene* (IV) which crystallised from ligroin as black crystals (1·1 g.), m. p. 121° or, when finely powdered, at 142—144° (decomp.) (Found: C, 51·0; H, 3·2; Ni, 23·7. $C_{21}H_{16}FeNi_2O_3$ requires C, 51·5; H, 3·3; Ni, 24·0%). Further elution with ligroin gave *bis(cyclopentadienylnickel-phenylacetylene)-tricarbonyliron* (VI) as black rhombs, m. p. 142—144° (decomp.) [from ligroin (b. p. 40—60°)] (Found: C, 59·5; H, 3·7; Ni, 19·6; Fe, 9·4. $C_{29}H_{22}FeNi_2O_3$ requires C, 58·9; H, 3·7; Ni, 19·6; Fe, 9·4%). Further elution gave tetracarbonyldicyclopentadienyldi-iron, m. p. and mixed m. p. 198°.

Reaction of Hexacarbonyldiphenylacetylenedicobalt with Pentacarbonyliron.—Hexacarbonyldiphenylacetylenedicobalt (3·8 g.), pentacarbonyliron (10 c.c.), and toluene (100 c.c.) were heated for 2 days under nitrogen on a boiling-water bath. The solvent was then removed and the residue chromatographed. Elution with ligroin gave unchanged complex, followed by a small amount of *decacarbonyldiphenylacetylenetetracobalt* (IX) which formed black crystals, decomp. 175—180°, from a blue solution in ligroin (Found: C, 41·2; H, 1·7; Co, 34·4. $C_{24}H_{10}Co_4O_{10}$ requires C, 41·9; H, 1·4; Co, 34·0%). Further elution with ligroin gave a small amount of a complex which crystallised as red cubes, m. p. 150°, from ethanol and has properties identical with those described by Hubel and Braye[4] for $Fe_2(CO)_6PhC{\equiv}CPh$ (Found: C, 52·6; H, 2·4. Calc. for $C_{20}H_{10}Fe_2O_6$: C, 52·4; H, 2·2%).

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