115. *Cyclopentadienylnickel–Acetylene Complexes.*

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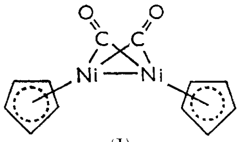
Acetylenes displace the two bridging carbonyl groups in dicyclopentadienyldinickel dicarbonyl and yield complexes of general formula $(C_5H_5Ni)_2,RC{\equiv}CR'$, from which the acetylene can be recovered unchanged. Diphenylbutadiyne has been used to prepare complexes in which nickel is bonded to one of the triple bonds, and cobalt or iron to the other.

IN a recent communication [1] it was suggested that dicyclopentadienyldinickel dicarbonyl (I), first prepared by Fischer and Palm,[2] is structurally in the same group as dicobalt octacarbonyl and the di-iron octacarbonyl anion. In each case it was suggested [1,3] that the bridging groups are not coplanar with the two metal atoms, but occupy two of the octahedral sites about each metal atom, whilst three others are occupied by terminal carbonyl groups, or in the case of (I) by a cyclopentadienyl group. The sixth position is unoccupied, and hence it should be readily attacked by a suitable substrate. This may provide an explanation of the catalytic activity of dicobalt octacarbonyl [4] and the di-iron octacarbonyl anion,[5] and for the ease with which both substances react with acetylenes.[6]

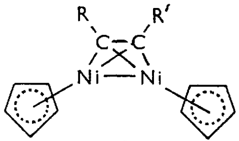
The above structural considerations indicated that (I) might show a similar reactivity and, as already reported in outline,[1] it does react with acetylenes giving compounds of

[1] Tilney-Bassett and Mills, *J. Amer. Chem. Soc.*, 1959, **81**, 4757.
[2] Fischer and Palm, *Chem. Ber.*, 1958, **91**, 1725.
[3] Mills and Robinson, *Proc. Chem. Soc.*, 1959, 156.
[4] Adkins and Kresk, *J. Amer. Chem. Soc.*, 1948, **70**, 383.
[5] Sternberg, Markby, and Wender, *J. Amer. Chem. Soc.*, 1956, **78**, 5704.
[6] Sternberg, Greenfield, Friedel, Wotiz, Markby, and Wender, *J. Amer. Chem. Soc.*, 1954, **76**, 1457; 1956, **78**, 120.

general formula $(C_5H_5Ni)_2,RC{\vdots}CR'$. The reaction is completed in refluxing toluene solution in 30—120 minutes for alkyl- or phenyl-substituted acetylenes. Diphenylacetylene gave an 88% yield of dicyclopentadienyldinickel–diphenylacetylene which was also prepared in a similar yield by refluxing dicyclopentadienylnickel, nickel carbonyl, and diphenylacetylene in benzene solution. The latter method is more convenient in this case, but leads to a less pure product from alkylacetylenes. Alkylacetylenes react cleanly with the carbonyl (I), but the yields of cyclopentadienylnickel–acetylene complexes were lower as purification was harder. In many cases cyclopentadienylnickel–acetylene complexes were not formed. Thus, acetylenedicarboxylic acid did not react with the carbonyl (I); and its dimethyl ester, although it did react, gave a small yield of tricyclopentadienyltrinickeldicarbonyl[2] rather than the expected acetylene complex. Reactions of di-iodoacetylene and of propargyl bromide did not yield an identifiable product. Acetylene itself gave only a very low yield of dicyclopentadienyldinickel–acetylene when bubbled through a refluxing solution of the carbonyl (I) in benzene; but this is probably due to the low concentration of acetylene in boiling benzene, as Dubeck has obtained this complex in 48% yield from dicyclopentadienenickel and acetylene under pressure.[7]



(I)



(II)

All the cyclopentadienylnickel–acetylene complexes so far prepared have an intense green colour in solution. Those derived from phenyl-substituted acetylenes form black crystals and are stable in air, but those from alkyl acetylenes are slowly oxidised. All the complexes are oxidised slowly by air in solution in non-polar solvents and rapidly in polar solvents such as ethanol or acetic acid. This oxidation can be used for the recovery of the acetylene, and high yields of diphenylacetylene were obtained from the dicyclopentadienyldinickel–diphenylacetylene complex. The complexes are also oxidised by mercuric chloride, which was reduced to mercurous chloride. Recovery of acetylenes after oxidation of the cyclopentadienylnickel–acetylene complex, and also the formation of bibenzyl when the diphenylacetylene complex is reduced with sodium and alcohol in liquid ammonia, show that the diphenylacetylene residue is attached only to nickel atoms and not to carbon. These facts, together with the formal analogy of the reactions of dicyclopentadienyldinickel dicarbonyl (I) and of dicobalt octacarbonyl with acetylenes, and Dubeck's report[7] that dicyclopentadienyldinickel–acetylene complex contains no unpaired electrons, support the structure (II) proposed in our preliminary communication.[1]

Treatment of dicobalt hexacarbonyl–acetylene complexes with carbon monoxide under pressure yields dicobalt nonacarbonyl–acetylene complexes[8] which contain a maleic anhydride nucleus.[3] Treatment of compound (II; R = R′ = Ph) with carbon monoxide at 110°/70 atm. did not yield an analogous complex, but resulted in the formation of diphenylacetylene and nickel carbonyl.

The reaction of dicyclopentadienyldinickel dicarbonyl with diphenylbutadiyne yields two products, (III) and (IV), containing two and four nickel atoms per molecule, respectively, and corresponding to the reaction of, first, one and then the second triple bond.

(III) $(C_5H_5Ni)_2(PhC{\vdots}C{\cdot}C{\vdots}CPh)$ $(C_5H_5Ni)_4(PhC{\vdots}C{\cdot}C{\vdots}CPh)$ (IV)

The ease of recovery of acetylene from complexes (II) leads to the possibility that the formation of complexes of this type might be used for the protection of acetylenes.

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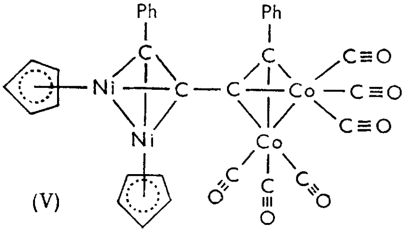
[7] Dubeck, *J. Amer. Chem. Soc.*, 1960, **82**, 502.

[8] Sternberg, Shukys, Donn, Markby, Friedel, and Wender, *J. Amer. Chem. Soc.*, 1959, **81**, 2339.

With this idea in mind some typical acetylenic reactions of the dinickel complex (III) were attempted in the hope that only the free triple bond would react. Hydration of the complex (III) failed owing to reduction of mercuric acetate to metallic mercury. Hydrogenation proceeded at room temperature and atmospheric pressure over either Raney nickel or 5% palladised charcoal, but it was impossible to stop hydrogenation sharply at any one stage, and absorption of two mols. of hydrogen gave mixtures of purely organic with organometallic products. The latter were not separated by chromatography on alumina. Reaction of neither phenyl azide nor benzenesulphonyl azide with the complex (III) leads to the expected triazole derivative. However, normal products were obtained by reaction with dicobalt octacarbonyl and with iron tetracarbonyl: the former yields black crystals, $C_{32}H_{20}Co_2Ni_2O_6$, that give dark brownish-green solutions. Infrared absorption at 2070 and 2047 cm.$^{-1}$ indicates terminal carbonyl groups, and the compound evidently has structure (V) in which one triple bond of the diyne has formed a complex with nickel and the other with cobalt. Iron tetracarbonyl in boiling ligroin yielded two products that were separated chromatographically. The first was a black solid which gave dark blue solutions in organic solvents. Infrared absorption at 2028 and 1970 cm.$^{-1}$ indicated the presence of terminal carbonyl groups and the analysis corresponded to the formula $(C_5H_5Ni)_2,PhC{:}C{\cdot}C{:}C{\cdot}Ph,Fe_2(CO)_6$. The second product was a black solid giving brown solutions in organic solvents, and its analyses corresponded to the structure $[(C_5H_5Ni)_2,PhC{:}C{\cdot}C{:}CPh]_2Fe_2(CO)_6$: it had infrared absorption bands due to carbonyl at 2030, 1988, and 1968 cm.$^{-1}$. Complexes $PhC{:}CPh,Fe_2(CO)_6$, and $(PhC{:}CPh)_2Fe_2(CO)_6$ have been prepared by Hubel and Braye,[9] and our two organo-iron-nickel complexes probably have analogous structures.



(V)

Experimental

M. p.s of organometallic compounds were obtained in sealed evacuated tubes. Oxygen was determined by Oliver's [10] method. After acid oxidation of organic matter, nickel [11] and cobalt [12] were determined colorimetrically, and iron [13] volumetrically.

Dicyclopentadienyldinickel Dicarbonyl.—This was prepared by an improvement on Fischer and Palm's procedure.[2] Dicyclopentadienenickel (24·5 g.), nickel carbonyl (45 c.c.), and benzene (250 c.c.) were stirred under reflux for 3½ hr. under nitrogen, on a water-bath at 80°. The solvent and excess of nickel carbonyl were removed, and the residue was extracted with boiling ether (400 c.c.). The filtered solution was concentrated and allowed to crystallise. Further crystals were obtained by concentrating the mother-liquors with the addition of low-boiling ligroin, giving black or dark red plates (29·1 g., 74%), m. p. 146—147° (Fischer and Palm reported m. p. 139°) (Found: C, 47·4; H, 3·4; O, 10·7. Calc. for $C_{12}H_{10}Ni_2O_2$: C, 47·5; H, 3·3; O, 10·5%).

Dicyclopentadienyldinickel–Acetylene Complexes.—General method. Dicyclopentadienyldinickel dicarbonyl (I) was refluxed under nitrogen with 10—50% excess of the acetylene in

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

[10] Oliver, *Analyst*, 1955, **80**, 593.

[11] " The B.D.H. Book of Organic Reagents," B.D.H., London, p. 44.

[12] Young, " Industrial Inorganic Analysis," Chapman and Hall, London, 1953, p. 79.

[13] Kolthoff and Belcher, " Volumetric Analysis," Interscience Publ. Inc., New York, 1957, Vol. III, p. 623.

toluene for ½—2 hr. The solvent was then evaporated and the excess of acetylene removed at the pump on a steam-bath. The residue was chromatographed on alumina, and the green fraction recrystallised or sublimed, or, if liquid, rechromatographed. This method was employed in the following cases:

(1) Hex-1-yne (4·0 c.c.) and the carbonyl (I) (4 g.) yielded *dicyclopentadienyldinickel–hex*-1-*yne* (1·51 g., 35%), m. p. 46·5—47° (Found: C, 58·4; H, 5·8. $C_{16}H_{20}Ni_2$ requires C, 58·3; H, 6·1%).

(2) Hex-3-yne (1·0 c.c.) and the carbonyl (I) (1·0 g.) yielded *dicyclopentadienyldinickel–hex*-3-*yne* as a dark green oil (Found: C, 58·4; H, 6·3%).

(3) Phenylacetylene (3 c.c.) and the complex (I) (1·52 g.) yielded dicyclopentadienyldinickel–phenylacetylene (1·21 g., 69%) as black needles, m. p. 132—133° (Found: C, 62·1; H, 4·8. Calc. for $C_{18}H_{16}Ni_2$: C, 61·8; H, 4·6%).

(4) Diphenylacetylene (1·03 g.) and the carbonyl (I) (0·60 g.) yielded dicyclopentadienyldinickel–diphenylacetylene as black crystals, m. p. 149—150° (1·28 g., 88%) (Found: C, 68·0; H, 5·2%; *M*, 409. Calc. for $C_{24}H_{20}Ni_2$: C, 67·7; H, 4·7%; *M*, 426).

In the following cases variations of the general method were employed:

(1) Acetylene was bubbled through a refluxing solution of the carbonyl (I) in benzene and gave a very small yield of dicyclopentadienyldinickel–acetylene as dark green crystals, m. p. 143—144° (Found: C, 52·9; H, 4·6. Calc. for $C_{12}H_{12}Ni_2$: C, 52·7; H, 4·8%).

(2) But-2-yne (1·5 c.c.), the carbonyl (I) (4·0 g.), and benzene (50 c.c.) were heated in 2 hr. to 130°, in a sealed tube in an atmosphere of carbon dioxide. This yielded a green oil which sublimed at 100°/0·01 mm., yielding black crystals of *dicyclopentadienyldinickel–but*-2-*yne* (1·95 g., 49%) that on resublimation had m. p. 55° (Found: C, 55·8; H, 5·5. $C_{14}H_{16}Ni_2$ requires C, 55·7; H, 5·4%).

(3) Diphenylbutadiyne (10·1 g., 2·16 mol.), the carbonyl (I) (7·0 g., 1·0 mol.), and benzene (250 c.c.) were refluxed under nitrogen for 6 hr. The mixture, on cooling, was filtered from needles of *tetracyclopentadienyltetranickel–diphenylbutadiyne* (IV), and the filtrate was evaporated. The residue was extracted with boiling ether (150 + 50 c.c.) which left most of the tetranickel complex behind. This together with the first portion was recrystallised from chloroform–ligroin (b. p. 60—80°), yielding black needles (3·2 g.), m. p. 296—297° (Found: C, 62·0; H, 4·6. $C_{36}H_{30}Ni_4$ requires C, 62·0; H, 4·3%). The ether extract was evaporated and the residue chromatographed on alumina. Elution with ligroin (b. p. 40—60°) gave, first, diphenylbutadiyne, then *dicyclopentadienyldinickel–diphenylbutadiyne* that recrystallised from ether–ligroin as black crystals (3·3 g.), m. p. 121° (Found: C, 69·2; H, 4·7. $C_{26}H_{20}Ni_2$ requires C, 69·4; H, 4·5%).

Preparation of Dicyclopentadienyldinickel–Diphenylacetylene from Dicyclopentadienylnickelocene.—Dicyclopentadienylnickel (2·89 g.), diphenylacetylene (2·7 g.), nickel carbonyl (6·0 c.c.), and benzene (70 c.c.) were refluxed for 6 hr. under nitrogen. The benzene and excess of nickel carbonyl were removed and the residue was recrystallised from ether–ligroin, yielding black crystals of dicyclopentadienyldinickel–diphenylacetylene (5·55 g., 85%).

Reactions of Cyclopentadienylnickel–Acetylene Complexes.—*Oxidation.* A rapid stream of air was bubbled through a solution of dicyclopentadienyldinickel–diphenylacetylene (0·40 g.) and hydrochloric acid (1 c.c.) in ether (20 c.c.) and ethanol (25 c.c.), until, after 5 min., the colour was destroyed. Water was added and the ether layer separated and evaporated, yielding impure diphenylacetylene (0·177 g., 100%) which was recrystallised and had m. p. and mixed m. p. 60°. A solution of tetracyclopentadienyltetranickel–diphenylbutadiyne in chloroform–ethanol gave a 100% yield of diphenylbutadiyne by similar treatment.

Carbon monoxide. A solution of dicyclopentadienyldinickel–diphenylacetylene (10·4 g.) in benzene (400 c.c.) was heated in an autoclave at 110° with 70 atm. of carbon monoxide for 11 hr. On cooling, the solution was pale brown and evaporation gave a pale oil which yielded diphenylacetylene on chromatography. The colourless benzene distillate readily gave a nickel mirror, and reacted vigorously with nitric acid, giving nickel nitrate, and evidently contained most of the nickel as nickel carbonyl.

Reduction. Dicyclopentadienyldinickel–diphenylacetylene (0·50 g.) was reduced with sodium (2 g.) and ethanol (4 c.c.) in liquid ammonia (100 c.c.) in the normal way and gave bibenzyl (0·19 g., 89%), m. p. and mixed m. p. 51—52°.

Dicyclopentadienyldinickel–diphenylacetylene did not react when refluxed for 15 hr. with triphenylphosphine in toluene, or for 18 hr. with pyridine in benzene. This is in contrast with dicyclopentadienyldinickel dicarbonyl which gave a 54% yield of tricyclopentadienyltrinickel dicarbonyl[2] when left at room temperature with pyridine in ether for 10 days.

Reaction of dicyclopentadienyldinickel–diphenylbutadiyne with cobalt carbonyl. Cobalt carbonyl (1·6 g.) and dicyclopentadienyldinickel–diphenylbutadiyne (1·0 g.) were refluxed under nitrogen in ether (45 c.c.) for 1 hr. The solvent was removed and the residue crystallised from ether–ligroin yielding black *dicyclopentadienyldinickel–diphenylbutadiyne–dicobalt hexacarbonyl,* m. p. 156—158° (decomp.) (Found: C, 52·3; H, 2·7; O, 13·7; Ni, 16·5; Co, 16·1, $C_{32}H_{20}Co_2Ni_2O_6$ requires C, 52·2; H, 2·7; O, 13·1; Ni, 15·95; Co, 16·0%).

Reaction of dicyclopentadienyldinickel–diphenylbutadiyne with iron tetracarbonyl. The dinickel complex (2·0 g., 3 mol.), iron tetracarbonyl (0·76 g., 1 mol.), and ligroin (100 c.c.; b. p. 80—100°) were refluxed under nitrogen for 3 hr. The solvent was removed and the residue chromatographed on neutralised alumina. Elution with ligroin gave a blue solution which on evaporation gave a black solid (0·12 g.), m. p. 156° (from ligroin). The infrared spectrum and analysis corresponded to a structure $(C_5H_5Ni)_2,PhC{:}C{\cdot}C{:}CPh,Fe_2(CO)_6$ (Found: C, 53·1; H, 3·1; O, 12·4; Ni, 16·1; Fe, 15·9. $C_{32}H_{20}Fe_2Ni_2O_6$ requires C, 52·7; H 2·8; O, 13·2; Ni, 16·1; Fe, 15·3%). Further elution with ligroin yielded a brown gum (0·86 g.) which on crystallisation from ligroin yielded black crystals, m. p. 160—161°. The analysis corresponds best to a structure $[(C_5H_5Ni)_2,PhC{:}C{\cdot}C{:}CPh]_2Fe_2(CO)_6$ (Found: C, 59·2; H, 3·6; O, 8·6; Ni, 20·4; Fe, 10·2. $C_{58}H_{40}Fe_2Ni_4O_6$ requires C, 59·1; H, 3·4; O, 8·1; Ni, 19·9; Fe, 9·5%).

The author thanks Dr. O. S. Mills for suggesting the work and the University of Sheffield for an Imperial Chemical Industries Research Fellowship. He also thanks the Mond Nickel Co. for gifts of nickel and cobalt carbonyls.

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[*Received, May* 30*th*, 1960.]