New Type Acetylene Compexes with Mixed Transition Metals

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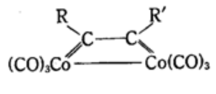
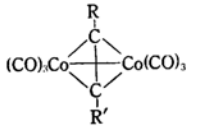
At an early stage of acetylene complex chemistry, an assumed structure (I) was proposed for the complexes $RC_2R'Co_2(CO)_6$ by Sternberg *et al.*[1] Afterwards, X-ray diffraction study[2] verified that the structure is II which has been recognized as a general structure of the coordinated acetylenes in the acetylene complexes.



(I)

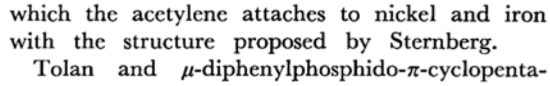


(II)

In this communication, we wish to report the preparation of new type acetylene complexes in which the acetylene attaches to nickel and iron with the structure proposed by Sternberg.

Tolan and μ-diphenylphosphido-π-cyclopentadienyltetracarbonylironnickel(III)[3] were heated for six hours under reflux in benzene. After evaporation of the solvent, the residue was subjected to chromatography on alumina with hexane-methylene chloride mixture as an eluant. Concentration of the eluate gave air-stable brown crystals (IVa). (Yield 85%, mp 215—220°C (with decomp). Found: C, 65.02; H, 4.19%. Calcd for $C_{34}H_{25}O_3PFeNi$: C, 65.13; H, 4.00%.)

IR spectrum (KBr disk) showed bands of terminal carbonyls at 2010, 1960, and 1948 cm^{-1} (ν_{CO}). NMR spectrum (in $CDCl_3$) indicated phenyl protons at 2.0—3.2 τ and π-cyclopentadienyl protons at 4.93 τ. Mass spectrum showed a parent peak at *m/e* 626 corresponding to the formula $C_{34}H_{25}O_3P^{56}Fe^{58}Ni$. Peaks due to the successive loss of three carbonyl groups and tolan were also found at *m/e* 598, 570, 542, and 364.



(III) (IV)

a : R, R′=Ph
b : R, R′=CO_2CH_3
c : R=Ph, R′=CO_2CH_3
d : R=Ph, R′=CH_3

Following similar procedures, the complexes of dimethyl acetylenedicarboxylate (IVb), methyl phenylacetylenecarboxylate (IVc), and methylphenylacetylene (IVd) were obtained, in which IVc and IVd consist of two isomers respectively.

IVb: Yield 37%, mp 128—133°C. NMR: 1.9—2.9 τ (C_6H_5), 4.82 τ (C_5H_5), 6.11 τ (one CH_3), and 6.43 τ (another CH_3). M(*m/e*) 590.

IVc$_1$: (formerly eluted isomer): Yield 36%, mp 178—179°C. NMR: 1.9—2.9 τ (C_6H_5), 4.84 τ (C_5H_5), and 6.60 τ (CH_3). M(*m/e*) 608.

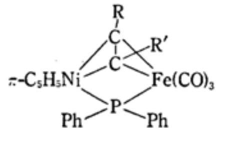
IVc$_2$: (lately eluted isomer): Yield 24%, mp 159—161°C. NMR: 2.0—3.0 τ (C_6H_5), 4.93 τ (C_5H_5), and 6.14 τ (CH_3). M(*m/e*) 608.

IVd$_1$: Yield 20%, brown oil. NMR: 2.1—3.0 τ (C_6H_5), 5.02 τ (C_5H_5), and 6.88 τ (CH_3, doublet, $J_{P-M=C-CH}=4.8$ cps). M(*m/e*) 565.

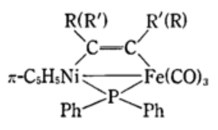
IVd$_2$: Yield 21%, mp 169—170°C. NMR: 2.1—2.9 τ (C_6H_5), 4.95 τ (C_5H_5), and 8.46 τ (CH_3, doublet, $J_{P-M=C-CH}=13.2$ cps). M(*m/e*) 565.

We suggest structure IV for these complexes. A relatively large coupling constant of CH_3 in IVd$_1$ and in IVd$_2$ with ^{31}P nucleus seems to give effective support.

Presence of dissimilar methyl groups in IVb and the presence of isomers in IVc and in IVd eliminate structure V. Another probable structure VI might be excluded from the absence of $\nu_{C=C}$ band in the IR spectra, and from steric consideration.



(V)



(VI)

The complexes are new compounds for the following reasons: (1) They are the first complexes in which acetylene coordinates on two different transition metals, and (2) they are considered to coordinate on metals with the dicarbene structure. The configurations of the isomers have not been determined as yet. Detailed study of these complexes is now in progress.

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[1] H. W. Sternberg, H. Greenfield, R. A. Fiedel, J. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954).

[2] W. G. Sly, *ibid.*, **81**, 18 (1959).

[3] III was obtained in the reaction of $HPh_2PFe(CO)_4$ with $(C_5H_5)_2Ni$, which was an extention of the method by Benson *et al.* (*Chem. Commun.*, **1968**, 1506).