A Novel Route to Mixed Transition-Metal Complexes

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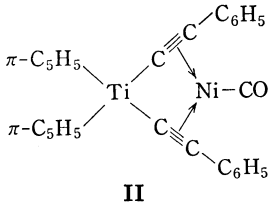
Preparation of complexes containing different transition metals has recently attracted much attention.[1,2] We report herewith on the preparation of mixed transition metal complexes in which metal atoms are joined by the alkynyl group.

Bis-π-cyclopentadienyl-bisphenylethynyltitanium (I)[3] reacted readily with nickel carbonyl in benzene at room temperature giving dark olive-green crystals (II) in good yield; mp 141—145°C (decomp.); NMR ($CDCl_3$, τ): 4.49 (s, C_5H_5) and 2.25—2.80 (m, C_6H_5); IR (KBr, ν, cm^{-1}): 1994 (vs, C≡O) and 1850 (C≡C coordinated). The data and the molecular weight (467.5 by vapor pressure osmometry and the molecular ion $[M]^+$ at *m/e* 466 followed by $[M-CO]^+$ at *m/e* 438 in the mass spectrum) suggest structure II.

$$(\pi\text{-}C_5H_5)_2Ti(C{\equiv}CC_6H_5)_2 + Ni(CO)_4 \longrightarrow$$

I

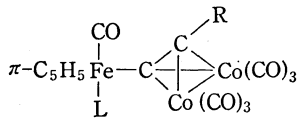


II

The propynyliron complex (IIIa)[4] reacted also readily with cobalt carbonyl giving black crystals

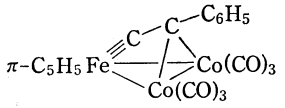
$$\pi\text{-}C_5H_5Fe(CO)(L)\text{-}C{\equiv}C\text{-}R + Co_2(CO)_8$$

IIIa-c



IVa-c

$-CO, L$



V

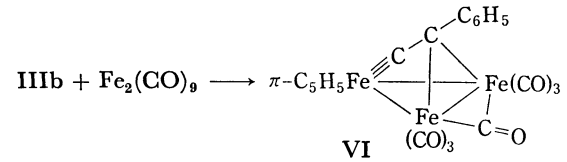
a (L: CO, R: CH_3)
b (L: CO, R: C_6H_5)
c (L: $PPhMe_2$, R: C_6H_5)

(IVa) in almost quantitative yield; mp 60—61°C; NMR: 5.01 (s, C_5H_5) and 7.32 (s, CH_3); IR (C_6H_{14}): 2065 (s), 2024 (vs), 1999 (s), and 1996 (sh) (terminal CO); Mass (*m/e*): 502 ($[M]^+$) and ions $[M-nCO]^+$ (n=1~8). The structure was assigned tentatively to IVa.

On the other hand, similar treatment of the phenylethynyliron complex (IIIb)[5] with the cobalt carbonyl afforded black crystals, $C_{19}H_{10}O_6FeCo_2$; mp 110—115°C (decomp.); Mass: 508 ($[M]^+$) and ions $[M-nCO]^+$ (n=1~6); IR: 2068 (s), 2026 (vs), 2000 (s), and 1986 (msh); NMR: 4.98 (s, C_5H_5) and 2.3—2.9 (m, C_6H_5). Structure V is postulated as a plausible one; unequivocal assignment being impossible with spectral data available at present. V might be formed *via* an intermediate IVb. Successful isolation of IVc, mp 91—94°C (decomp.), and its facile transformation into V support the above reaction sequence. Attempts to obtain a V analogue from IVa were not successful.

A similar triiron complex (VI), $C_{20}H_{10}O_7Fe_3$, mp 143—146°C, was obtained as brown crystals from the reaction of IIIb with iron nonacarbonyl in refluxing benzene; Mass: 530 ($[M]^+$) and ions $[M-nCO]^+$ (n=1~7); IR: 2053 (s), 2018 (vs), 2000 (s), 1996 (s), 1976 (s), and 1965 (s) (terminal CO) and 1870 (s, bridge CO).

$$IIIb + Fe_2(CO)_9 \longrightarrow$$

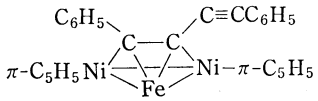


VI

Ethynylnickel complexes (VII) reacted also with the iron carbonyl giving mixed metal complexes. Reaction of VIIa with carbonyl gave the known olive-green crystalline compound VIII[6] and a new complex (IXa), mp 195—197°C, as brown crystals. Similarly, the carbomethoxy derivative (IXb), mp 202—204°C, was obtained from VIIb. Analysis of the mass and IR spectra support formula IX.

$$\pi\text{-}C_5H_5Ni(PPh_3)(C{\equiv}C\text{-}R) + Fe_2(CO)_9 \longrightarrow$$

VIIa, b



VIII

$+ \pi\text{-}C_5H_5NiFe(CO)_3\text{-}PPh_3(C_2R)$

IXa,b

a (R:C_6H_5) b(R:CO_2CH_3)

Thus, the transition metal acetylide complexes exhibit high reactivity toward metal carbonyls and provide a new type of mixed transition metal clusters.

1) M. C. Baird, "Progress in Inorganic Chemistry," Vol. 9, ed. by F. A. Cotton, Interscience Publishers, N. Y. (1968), p. 1.
2) K. Yasufuku and H. Yamazaki, *Kagaku no Ryoiki*, **25**, 1022 (1971).
3) J. H. Teuben and H. J. de Liefde Meijer, *J. Organometal. Chem.*, **17**, 87 (1969).
4) P. W. Jolly and R. Pettit, *ibid.*, **12**, 491 (1968).
5) M. L. H. Green and T. Mole, *ibid.*, **12**, 404 (1968).
6) J. F. Tilney-Bassett, *J. Chem. Soc.*, **1963**, 4784.
* Satisfactory microanalyses have been obtained for these compounds.