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Preparation of Tricarbonyliron-μ-Carbonyl-μ-Diphenylphosphido-π-Cyclopentadienylnickel[*1]

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Since hexacarbonyl-π-cyclopentadienylmolybdenum-π-cyclopentadienyltungsten was reported by Abel,[1] many efforts have been made for the preparation of mixed transition-metal complexes with metal-metal bond.[2] The complexes were mostly mixed metal carbonyls in which metals are bonded only with a metal-metal bond. Tricarbonyl-π-cyclopentadienyliron-π-cyclopentadienylnickel[3] and monocarbonyl-π-cyclopentadienyliron-μ-dicarbonyl-tricarbonylcobalt[4] belong to a few complexes which consist of a metal-metal bond and

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[*1] Paper I in a series of " Chemistry of Mixed Transition-Metal Complexes."

[1] E. W. Abel, Apar Singh and G. Wilkinson, *J. Chem. Soc.*, **1960**, 1321.

[2] N. S. Vyazankin, C. A. Razuvaev and O. A. Kruglaya, *Organometal. Chem. Rev.*, **A3**, 323 (1968).

[3] J. F. Tilney-Bassett, *J. Chem. Soc.*, **1963**, 4784.

[4] J. K. Joshi and P. L. Pauson, *Z. Naturforsch.*, ***B*, 17**, 565 (1962).

bridged carbonyls. Recently, Thompson[5] reported the synthesis of a new class of heterodinuclear transition-metal complexes joined by a metal-metal bond and a single phosphorus bridge by the reaction of tetracarbonyldiphenylphosphineiron with π-allyltricarbonylmanganese, -cobalt and π-allylpalladium chloride dimer.

In the present paper, we wish to report the preparation of a new mixed transition-metal complex consisting of iron and nickel which are bonded with a metal-metal bond, and with a bridged phosphido and a bridged carbonyl groups.

Experimental and Results

π-Cyclopentadienyltriphenylphosphinenickel chloride (1 g)[6] and 0.8 g of tetracarbonyldiphenylphosphineiron (I)[7] were allowed to react with excess diethylamine in methylene chloride at room temperature for two days. The reaction mixture was concentrated and subjected to chromatography on alumina with hexane-methylene chloride mixture as an eluent. Concentration of the brown eluate gave 0.41 g of brown cyrstals, mp[*2] 150—152°C, (Yield 45%. Found: C, 52.93; 3.30%. Calcd for $C_{21}H_{15}O_4PFeNi$: C, 52.90; H, 3.17%) The X-ray emission spectrum[*3] indicated bands corresponding to NiKα at 51°34′, to FeKα at 61°08′ and PKα at 54°54′.

The same product was obtained in 25% yield by a similar treatment from π-cyclopentadienylcarbonylnickel iodide (prepared by method of Schropp[8]) and I in benzene with excess diethylamine at 0°C for four hours and at room temperature for two days.

π-$C_5H_5Ni(PPh_3)Cl$
or
π-$C_5H_5Ni(CO)I + HPh_2PFe(CO)_4 \rightarrow C_{21}H_{15}O_4PFeNi$
or (I)
$(\pi$-$C_5H_5)_2Ni$

IR spectrum of the product showed the presence of terminal carbonyls and a bridged carbonyl both in KBr disk and in solutions as shown in Table 1. NMR spectrum (in $CDCl_3$) indicated signals of phenyl protons at 2.2—2.8τ and of cyclopentadienyl protons at 4.58τ. In mass spectrum,[*4] the molecular peak consisting of ^{58}Ni and ^{56}Fe (which are the most abundant isotopic combination) appeared at m/e 476 (Calcd Mol Wt, 476) followed by peaks corresponding to successive loss of carbonyls as shown in Table 2. The peak at m/e 364 ($C_5H_5NiPPh_2Fe^+$) was the most abundant.

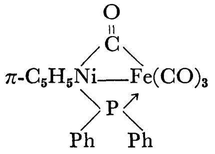
TABLE 1. IR SPECTRUM OF II IN THE ν_{CO} REGION

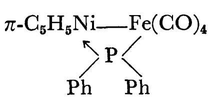
Solvent	ν_{CO} cm^{-1}				
	terminal CO				bridged CO
KBr	2025	2018 s	1977 s	1956 s	1814 s
Hexane	2035 s	1990 s	1978 s		1840 s
CH_2Cl_2	2030 s	1985 s	1970 s		1820 s
CS_2	2032 s	1986 s	1972 s		1830 s
THF	2030 s	1965 s	broad		1825 s

TABLE 2. MASS SPECTRUM OF II
(only peaks consisting of ^{58}Ni and ^{56}Fe)

Fragment	m/e	Relative intensity
M^+	476	24
$(M-2CO)^+$	420	22
$(M-3CO)^+$	392	11
$(M-4CO)^+$	364	100
$(M-4CO-C_6H_6)^+$	286	22
$(M-4CO-C_6H_6-H_2)^+$	284	20

These spectral data suggest structure II for the present complex. It had been noted that the infrared spectra of octacarbonyldicobalt[9] and dicarbonyl-π-cyclopentadienyliron dimer[10] are markedly dependent on solvent in the ν_{CO} region and the structure in solution differs from that in crystalline state. Although the other structure III seems to be plausible as seen in the complexes obtained by Thompson,[5] the IR spectra in various solvents indicated no serious transformation in the ν_{CO} region showing the absence of any contribution of structure III even in solution.


(II)


(III)

II was also obtained in 35% yield by the reaction of I with nickelocene in tetrahydrofuran at room temperature for a week. The reaction did not occur in benzene or in methylene chloride solutions. In contrast to the high reactivity of the π-allyl complexes of cobalt, manganese and palladium with I,[5] π-allyl-π-cyclopentadienylnickel was much less reactive and gave II only in a low yield (<2%).

II is very stable in air, especially in solid state and is soluble in most organic solvents.

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[5] B. C. Benson, R. Jackson, K. K. Joshi and D. T. Thompson, *Chem. Commun.*, **1968**, 1506.

[6] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida and N. Hagihara, *J. Organometal. Chem.*, **6**, 86 (1966).

[7] J. G. Smith and D. T. Thompson, *J. Chem. Soc.*, *A*, **1967**, 1694.

[*2] Measured on hot-stage apparatus.

[*3] Measured by JEOL Primary X-ray Analyzer Type JPX-3 with KAP.

[8] W. K. Schropp, *J. Inorg. Nucl. Chem.*, **24**, 1690 (1962).

[*4] Measured by JEOL Mass Spectrometer Type JPS-1S at 75eV.

[9] K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).

[10] F. A. Cotton, H. Stammreich and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9**, 3 (1959).