

## CHEMISTRY OF MIXED TRANSITION-METAL COMPLEXES

### IV\*. PREPARATION OF TERTIARY PHOSPHINE DERIVATIVES OF CARBONYL- $\pi$ -CYCLOPENTADIENYLIRON- $\mu$ -DICARBONYL- $\pi$ -CYCLOPENTADIENYLNICKEL

KATSUTOSHI YASUFUKU and HIROSHI YAMAZAKI

*The Institute of Physical and Chemical Research, Wako-shi, Saitama 351 (Japan)*

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#### SUMMARY

$\pi$ -Cyclopentadienyl(L)iron- $\mu$ -dicarbonyl- $\pi$ -cyclopentadienylnickel (L = PPh<sub>3</sub>, PPh<sub>2</sub>CH<sub>3</sub>, PPh(CH<sub>3</sub>)<sub>2</sub>, P(CH<sub>3</sub>)<sub>3</sub> and P(OPh)<sub>3</sub>) compounds were prepared by the reaction of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Ni(L)X with NaFe(CO)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>. Insertion of SnCl<sub>2</sub> into the metal-metal bond of the analogous complex where L = CO was found to give new mixed transition metal complex,  $\pi$ -C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>FeSnCl<sub>2</sub>Ni(CO)- $\pi$ -C<sub>5</sub>H<sub>5</sub>.

#### INTRODUCTION

Although many mixed metal carbonyls with metal-metal bonds are now known<sup>1,2</sup>, few phosphine derivatives of such complexes have been reported to date, these are (Ph<sub>3</sub>P)<sub>2</sub>Ni[Co(CO)<sub>3</sub>PPh<sub>3</sub>]<sub>2</sub><sup>3</sup> and Fe<sub>2</sub>CoS(CO)<sub>9-n</sub>(PPh<sub>3</sub>)<sub>n</sub> (n = 1, 2)<sup>4</sup>.

In previous papers in this series<sup>5,6</sup>, we reported the preparation of some mixed transition-metal  $\mu$ -diphenylphosphido complexes. We now report the preparation of tertiary phosphine derivatives (II) of Tilney-Bassett's complex<sup>7</sup>, carbonyl- $\pi$ -cyclopentadienyliron- $\mu$ -dicarbonyl- $\pi$ -cyclopentadienylnickel (I).

#### RESULTS AND DISCUSSION

Reaction of C<sub>5</sub>H<sub>5</sub>Ni(PPh<sub>3</sub>)Cl with an equimolar amount of NaFe(CO)<sub>2</sub>-C<sub>5</sub>H<sub>5</sub> in THF solution afforded black-brown crystals of a product whose structure was established as triphenylphosphine- $\pi$ -cyclopentadienyliron- $\mu$ -dicarbonyl- $\pi$ -cyclopentadienylnickel (IIa), on the basis of analysis and mass, IR, and NMR spectra. The IR spectrum showed  $\nu$ (CO) bands at 1805 w and 1760 s cm<sup>-1</sup> indicating that two carbonyls are of the bridging type. The NMR spectrum showed signals of phenyl protons and of  $\pi$ -cyclopentadienyl protons at  $\tau$  4.91 (singlet, 5) and at  $\tau$  5.54 (doublet, 5). Protons of [C<sub>5</sub>H<sub>5</sub>Ni(CO)]<sub>2</sub> appear at  $\tau$  4.70 and those of [C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>]<sub>2</sub> at  $\tau$  5.22. From these values, the downfield signal is assigned to the protons of the cyclo-

\* For Part III, see ref. 13.

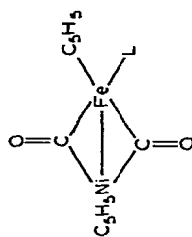


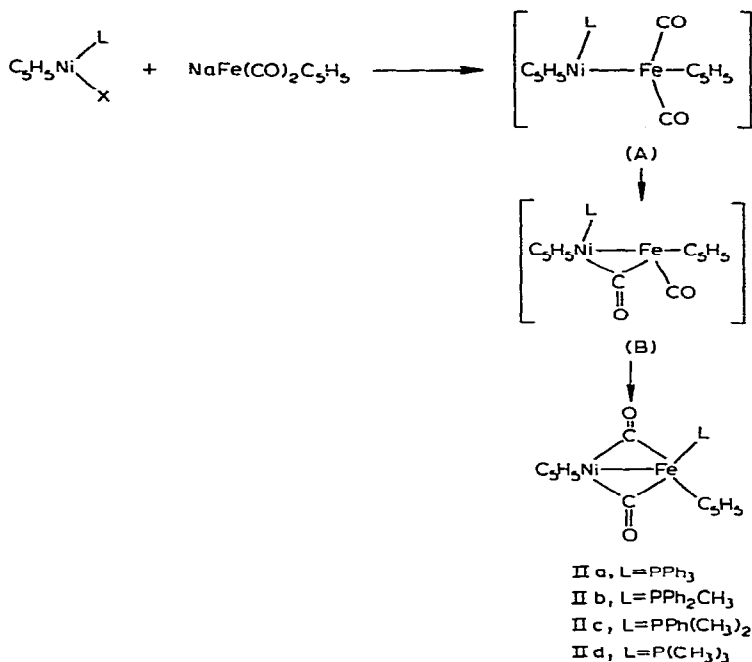
TABLE I

L	M.p. (°C)	Analyses, found (calcd.) (%)			M <sup>+</sup> (m/e)	NMR <sup>a</sup> (τ)	ν(CO) <sup>a</sup> (cm <sup>-1</sup> )
		C	H	Fe			
I	~130 (dec.)	46.70 (47.49)	2.93 (3.07)	16.3 (17.0)	328	4.69 s, 5.08 s	2000 s, 1809 s
IIa	140-150 (dec.)	64.06 (64.00)	4.65 (4.48)	9.4 (9.9)	562	4.91 s, 5.54 d (1.2 Hz)	1805 w, 1760 s
IIb	174-175	59.43 (59.93)	4.51 (4.62)	10.7 (11.1)	500	4.90 s, 5.51 d (1.8 Hz)	1802 w, 1750 s
IIc	140-150 (dec.)	55.03 (54.74)	4.96 (4.82)		438	4.79 s, 5.68 d (1.8 Hz)	1800 w, 1753 s
IIId	~170 (dec.)	47.69 (47.82)	4.95 (5.10)		376	4.72 s, 5.45 d (1.8 Hz)	1800 w, 1753 s
IIe						4.84 <sup>f</sup> , 5.75 <sup>f</sup>	1820 w, 1768 s

<sup>a</sup> Measured in CDCl<sub>3</sub>; s, singlet; d, doublet. <sup>b</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solutions. <sup>c</sup> A little broad signal.

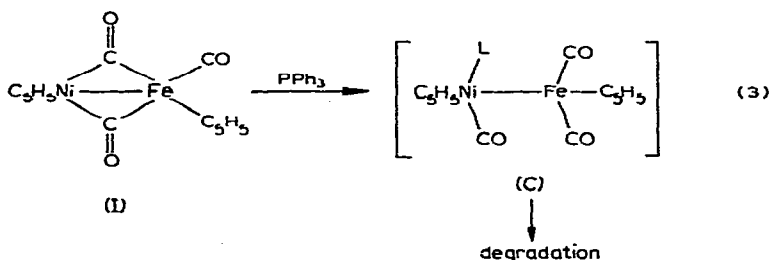
pentadienyl group attached to the nickel and the upfield signal to the protons of the one attached to the iron.

Similarly, the tertiary phosphine derivatives IIb, IIc and IId were obtained from the respective nickel halide and  $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ .



In this preparation it is possible that (A) might be formed initially. The migration of the phosphine ligand from Ni to Fe would then take place smoothly through a second transition-state structure (B) with CO bridging groups. A similar transition-state structure was proposed by Ellgen<sup>8</sup> for the reaction of  $[\text{C}_5\text{H}_5\text{Ni}(\text{CO})]_2$  with  $\text{PR}_3$ .

An attempt to obtain IIa by direct substitution of I with  $\text{PPh}_3$  was unsuccessful. The only products were  $(\text{C}_5\text{H}_5)_2\text{Ni}$ ,  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  and  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ . This suggests that an intermediate (C) might be formed in this case before the metal-metal bond fission to the degradation products occurs. The extra CO group coordinated to Ni, compared with (A), may cause the migration of L to be prevented in structure (C).



In Table 1, analyses, molecular weights, IR and the NMR spectral data for complexes (I) and (II) are collected.

Mass spectra of the complexes showed molecular ions  $[M]^+$  followed by ions  $[M-2CO]^+$  but no ions corresponding to  $[M-CO]^+$ . A metastable peak at  $m/e$  272.3 was exhibited in the spectrum of IIc which shows that direct loss of two carbonyls takes place in one step. The most abundant ions in these spectra were  $[(C_5H_5)_2FeNi]^+$   $m/e$  244 for IIa, IIc and I,  $[(C_5H_5)_2FeNiC_6H_5]^+$   $m/e$  321 for IIb and  $[(C_5H_5)_2FeNiCH_3]^+$   $m/e$  259 for IIc, respectively.

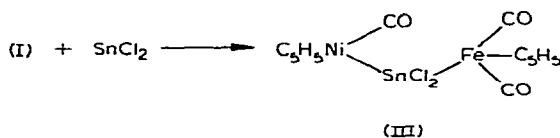
Complexes II are less stable than complex I, both in solution and in the crystalline state when exposed to air. On treatment of  $C_5H_5Ni[P(OPh)_3]I$  with  $NaFe(CO)_2C_5H_5$ , the complex IIe was obtained as an inseparable mixture with  $[C_5H_5Fe(CO)_2]_2$ . The IR and the NMR spectra showed bands for  $\nu(CO)$  and signals for  $\pi-C_5H_5$  protons of IIe and of the contaminant, which was present in varying ratios. The bands and the signals for IIe are shown in Table 1.

TABLE 2

Compound	Color	M.p. (°C)	NMR <sup>a</sup> ( $\tau$ ) $\pi-C_5H_5$	$\nu(CO)^b$ ( $cm^{-1}$ )
$[C_5H_5Ni(CO)]SnCl_2[Fe(CO)_2C_5H_5]$ (III)	brown	110–120 (dec.)	4.47, 4.95	2032 s, 2010 s, 1972 s
$[C_5H_5Fe(CO)_2]_2SnCl_2^{12}$	yellow	166–168	4.98	2026 vs, 1999 s, 1972 s 1965 (sh)
$[C_5H_5Ni(CO)]_2SnCl_2^8$	dark green	>90 (dec.)	4.45	2086 w, 2043 s, 2019 s

<sup>a</sup> Measured in  $CDCl_3$ . <sup>b</sup> Measured in  $CH_2Cl_2$  solution.

It was found that treatment of I with excess  $SnCl_2$  in THF for 6 hours at  $40^\circ$ , followed by column chromatography, gave III as brown crystals, the NMR spectrum and  $\nu(CO)$  bands of which are shown in Table 2. Insertion of  $MX_2$  ( $M = Ge, Sn$ ;  $X = Cl, Br, I$ ) into metal-metal bonds is already known<sup>9</sup> but the formation of III is the first reported example of  $SnCl_2$  insertion into a mixed metal-metal bond.



II was also found to react with  $SnCl_2$  to give a pink-red solution, but neither insertion products nor other isolable products were obtained. Reactions of IIa with  $I_2$  and with  $PhC\equiv CPh$  were also carried out.  $C_5H_5Fe(CO)_2I$  and  $[C_5H_5Fe(CO)_2-PPh_3]I$  were isolated in yields of 20 and 16% respectively from the former reaction and  $(C_5H_5Ni)_2PhC\equiv CPh$ ,  $[C_5H_5Fe(CO)_2]_2$  and  $Ni(CO)_2(PPh_3)_2$  were isolated in yields of 21, 35 and 4% respectively from the latter reaction.

Reactions of the nickel halide with  $NaMn(CO)_5$ ,  $NaCo(CO)_4$  and  $NaMo(CO)_3C_5H_5$  were also attempted, but no mixed metal complexes were obtained in these cases.

## EXPERIMENTAL

All manipulations were carried out under an atmosphere of nitrogen. Infrared spectra were recorded on a Perkin-Elmer model 521 spectrometer and NMR spectra were recorded on a Nippon Denshi model C-60 instrument. Mass spectra were recorded on a Nippon Denshi model 1S instrument at 75 eV. Compounds  $C_5H_5Ni(PR_3)X$  were prepared from the reaction of  $(C_5H_5)_2Ni$  with  $(R_3P)_2NiX_2$  in THF<sup>10</sup>. I was prepared in 80% yield by the method of Tilney-Bassett (reaction of  $(C_5H_5)_2Ni$  with  $Fe(CO)_5$ )<sup>7</sup>. I was also formed in 30% yield from the reaction of  $C_5H_5Ni(CO)I$  with  $Fe(CO)_5$  when the reaction temperature was kept below  $-30^\circ$ .

*Preparation of IIa.*  $C_5H_5Ni(PPh_3)Cl$  (1.07 g, 2.5 mmole) was allowed to react with  $NaFe(CO)_2C_5H_5$  prepared from 0.46 g (1.3 mmole) of  $[C_5H_5Fe(CO)_2]_2$  and Hg-Na in THF at room temperature. After stirring for two days, the solvent was evaporated and the residue was extracted with a minimum volume of benzene followed by chromatography on a silica gel column. A trace of a red-pink band, eluted with hexane, was discarded. A brown band was eluted with hexane-benzene mixture (1/2), and with benzene a small amount of a red-purple band was eluted (from which 0.08 g of  $[C_5H_5Fe(CO)_2]_2$  was recovered). The brown solution was concentrated, and addition of hexane gave black-brown crystals in 40% yield.

IIb, IIc and IId were prepared similarly from  $C_5H_5Ni(L)Br$  in 15, 50 and 30% yields, respectively.

*Reaction of I with  $PPh_3$ .* I (0.33 g) and 0.27 g of  $PPh_3$  were stirred in 20 ml of benzene for 24 h at room temperature. After evaporation of the mixture, the residue was chromatographed on a silica gel column.  $(C_5H_5)_2Ni$  (0.04 g) was first eluted with hexane, followed by a yellow band from which 0.15 g of  $(Ph_3P)_2Ni(CO)_2$  was obtained. From the third red-brown band, eluted with benzene, 0.11 g of  $[C_5H_5Fe(CO)_2]_2$  was obtained.

*Reaction of IIa with  $I_2$ .* A solution of 0.17 g of  $I_2$  in 20 ml of  $CH_2Cl_2$  was added slowly to a solution of 0.38 g of IIa in 10 ml of  $CH_2Cl_2$  and stirred for 3 h at room temperature. After concentration, the mixture was chromatographed on a silica gel column. The first brown band, eluted with a hexane- $CH_2Cl_2$  mixture of 1/1 gave 0.04 g of  $C_5H_5Fe(CO)_2I$ . A trace of green band was then eluted with a 1/2 mixture; this may be  $C_5H_5Fe(CO)PPh_3I$ <sup>11</sup>. From a yellow band, eluted with  $CH_2Cl_2$ -acetone mixture 1/1, 0.006 g of  $[C_5H_5Fe(CO)_2PPh_3]I$ <sup>11</sup> was obtained.

*Reaction of IIa with  $PhC\equiv CPh$ .* IIa (0.14 g) and 0.04 g of  $PhC\equiv CPh$  were refluxed in 20 ml of toluene for 1 h. After concentration, the mixture was chromatographed on an alumina column.  $(C_5H_5Ni)_2PhC\equiv CPh$  (0.016 g), 0.01 g of  $(Ph_3P)_2Ni(CO)_2$  and 0.015 g of  $[C_5H_5Fe(CO)_2]_2$  were obtained from a green band, a yellow band, and a red-brown band eluted with 4/1, 2/1 and 1/1 hexane- $CH_2Cl_2$  mixtures respectively.

*Preparation of III.* I (0.3 g) and 0.5 g of anhydrous  $SnCl_2$  were stirred for 2 days at  $40^\circ$  in THF. The solution changed from dark brown to light brown. The reaction mixture was evaporated to dryness and the residue, dissolved in a minimum volume of  $CH_2Cl_2$ , was chromatographed on a silica gel column using hexane- $CH_2Cl_2$  mixture (1/1) as an eluent. Concentration of the brown band gave brown crystals in 60% yield. (Found: C, 30.40; H, 1.70; Cl, 13.67; Fe, 10.0.  $C_{13}H_{10}Cl_2FeNiO_3Sn$  calcd.: C, 30.12; H, 1.95; Cl, 13.68; Fe, 10.6%.)

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