

TRANSITION METAL CHEMISTRY II. SUBSTITUTION REACTIONS WITH TRIS(*p*-FLUOROPHENYL)PHOSPHINE IN CARBONYL COMPLEXES OF THE TRANSITION METALS

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SUMMARY

Substitution reactions between (*p*-FC₆H₄)₃P (L) and several transition metal carbonyl compounds are described. The new compounds L₃Fe(CO)₂, LCr(CO)₅, *trans*-L₂Cr(CO)₄, *trans*-L₂W(CO)₄, *cis*-L₂Mo(CO)₄, L₂Ni(CO)₂ and LNi(CO)₃ are characterized by melting point, C,H analysis results and IR absorption frequencies in the CO absorption region.

In a previous report¹ the synthesis of several tris(*p*-fluorophenyl)phosphine substituted carbonyls of Fe, Mo and W was described. In this article we want to report on reactions with (*p*-FC₆H₄)₃P (in the following text this compound will be named ligand L) yielding further substitution products of Fe(CO)₅ and of M(CO)₆ molecules (M=W, Cr, Mo) as well as on new substitution products obtained from Ni(CO)₄ with the same ligand.

TABLE I

TRIS(*p*-FLUOROPHENYL)PHOSPHINE TRANSITION-METAL CARBONYL COMPLEXES PREPARED

Compound	Analysis, found (calcd.) (%)		M.p. (°C)	IR CO absorption in nujol (cm ⁻¹)
	C	H		
[(<i>p</i> -FC ₆ H ₄) ₃ P] ₃ Fe(CO) ₂	66.01 (67.01)	3.72 (3.61)	102.8	1982, 1928
(<i>p</i> -FC ₆ H ₄) ₃ PCr(CO) ₅	53.54 (54.34)	2.34 (2.37)	122–125	2064, 1978, 1947
<i>trans</i> -[(<i>p</i> -FC ₆ H ₄) ₃ P] ₂ Cr(CO) ₄	59.02 (60.31)	2.97 (3.03)	185–189 dec.	1887
<i>trans</i> -[(<i>p</i> -FC ₆ H ₄) ₃ P] ₂ W(CO) ₄	51.23 (51.74)	2.57 (2.60)	215–219 dec.	1887
<i>cis</i> -[(<i>p</i> -FC ₆ H ₄) ₃ P] ₂ Mo(CO) ₄	56.21 (57.16)	2.99 (2.87)	188–190 dec.	2021, 1917, 1883, 1852
[(<i>p</i> -FC ₆ H ₄) ₃ P] ₂ Ni(CO) ₂	60.72 (61.08)	3.25 (3.23)	116–118	2005, 1948
(<i>p</i> -FC ₆ H ₄) ₃ PNi(CO) ₃	55.70 (54.95)	2.67 (2.63)	149–150 dec.	2002, 2067

The new products are listed in Table 1 and characterized by their melting point, results of C and H analysis and the IR absorption bands in the CO vibration region. The IR spectra were recorded with a Perkin-Elmer model 225 spectrometer on nujol mulls of the substances. All operations are made in a protective nitrogen atmosphere.

EXPERIMENTAL

(1). Preparation of $L_3Fe(CO)_2$

$C_7H_8Fe(CO)_2$ (0.104 mole), prepared according to the procedure elaborated by Manuel *et al.*², and L (0.104 mole) are dissolved in 150 ml 2,2,5-trimethylhexane which was previously deaerated by boiling in a nitrogen atmosphere for 2 h. The reaction mixture is heated to reflux temperature during 7 h and then cooled to -60° and filtered. A dark-coloured residue (A) and a redish brown filtrate (B) are obtained.

The filtrate (B) is evaporated and the resulting residue redissolved in a minimum quantity of $CHCl_3$. This solution is chromatographed on alumina. Elution with petroleum ether yields a yellow solution of $C_7H_8Fe(CO)_2$. The orange coloured band remaining on the column is then eluted with $CHCl_3$ and the eluate collected under a nitrogen blanket. After removal of $CHCl_3$ *in vacuo* and recrystallization of the residue from boiling petroleum ether 0.12 g of an orange-coloured substance are obtained, which was characterized as $L_3Fe(CO)_2$ (see Table 1).

The residue (A) is also subjected to chromatographic separation on an alumina column and petroleum ether used as the eluens. The eluate is evaporated *in vacuo* and the residue dissolved in a minimum amount of benzene. This solution is filtered and on adding twice its volume of petroleum ether and cooling to -12° 0.4 g of a yellow precipitate are obtained, which proved to be $L_2Fe(CO)_3$ ¹.

The brown band remaining on the column was extracted with $CHCl_3$ and after evaporation of the solvent and recrystallization another quantity of 0.17 g of the same compound was obtained.

(2). Preparation of $LCr(CO)_5$

L (0.036 mole) and $Cr(CO)_6$ (0.035 mole) are dissolved in 150 ml of diglyme and refluxed for 4 h. The reaction mixture is then cooled, filtered and the solvens evaporated *in vacuo*. Threefold recrystallization from a mixture of chloroform/ethanol yields 8.34 g pale-yellow crystals which proved to be $LCr(CO)_5$.

(3). Preparation of *trans*- $L_2Cr(CO)_4$

For this synthesis a specially designed reaction tube, preventing the sublimation of the chromium hexacarbonyl at the end is used. $Cr(CO)_6$ (0.01 mole) and L (0.03 mole) are placed into it, and heated for 4 h at $170-200^\circ$ in a nitrogen atmosphere. The contents of the tube are subsequently extracted with benzene, the solution is filtered and then evaporated *in vacuo*. The residue is treated with several small portions of ether to remove unreacted phosphine, filtered and again dissolved in a minimum amount of benzene. On adding twice the volume of C_2H_5OH and cooling to -12° a yellow precipitate is obtained which was freed from $Cr(CO)_6$ contaminant by sublimation. The sublimation residue is nearly pure *trans*- $L_2Cr(CO)_4$, with characteristics as reported in Table 1. In the IR spectrum a weak band at 2016 cm^{-1} is

observed and this is probably due to the *cis*-isomer. This impurity could be removed using the separation method of Grim³. A total amount of 0.25 g of pure *trans*-L₂Cr(CO)₄ was obtained.

Tentative preparations of *cis*-L₂Cr(CO)₄ and of L₃Cr(CO)₃ starting from C₇H₈Cr(CO)₄ and from C₇H₈Cr(CO)₃ along published procedures^{4,5} always resulted in the *trans*-L₂Cr(CO)₄.

(4). *Preparation of trans-L₂W(CO)₄*

This compound is obtained using the same method as for the chromium derivative from 0.01 mole of W(CO)₆ and 0.03 mole of L. However, the residue, obtained after the ether extraction, is now dissolved in acetone, followed by precipitation with ethyl alcohol, cooling to -12° and removal of unreacted W(CO)₆ by sublimation. *trans* L₂W(CO)₄ is yellow; a yield of 0.57 g was obtained.

(5). *Preparation of cis-L₂Mo(CO)₄*

A solution of 0.0017 mole C₇H₈Mo(CO)₄⁶ and of 0.0075 mole L in 20 ml benzene is stirred for 1½ h under nitrogen. A yellow precipitate gradually forms. This is filtered off, and washed with small portions of ether. A total amount of 0.78 g of the pure compound was isolated.

(6). *Preparation of L₂Ni(CO)₂*

The method elaborated by Rose and Statham⁷ was used for the synthesis of this complex. In a three-necked flask equipped with a nitrogen inlet, reflux condenser and pressure-equalized dropping funnel, is placed a solution of 0.05 mole L in 20 ml of dry and oxygen-free ether. This solution is heated to reflux temperature and meanwhile a solution of 0.0246 mole Ni(CO)₄, in the same solvent, is added carefully and dropwise. The reaction mixture is then heated for another hour to reflux temperature and then cooled to -30°. The yellow precipitate formed is filtered off and washed several times with ether; the yield was 4.78 g.

The IR spectrum of L₂Ni(CO)₂ shows two CO absorptions respectively at 2005 and 1948 cm⁻¹. The latter band however shows slight splitting so that the number of CO bands actually present becomes questionable. Meriwether and Fiene⁸ have found only two CO bands for [(C₆H₅)₃P]₂Ni(CO)₂.

Therefore a laser Raman spectrum of the solid substance was taken; only two peaks were observed (2004, 1947 cm⁻¹), thus removing any doubts about the number of CO bands. When, however, the laser Raman spectrum of a hexane solution is taken a new peak appears at 2071 cm⁻¹. The intensity of this peak increases as a function of time and the intensity of the 1947 cm⁻¹ peak decreases simultaneously. A Raman spectrum of a saturated solution of CO in hexane shows a peak at about 2070 cm⁻¹. We therefore think that on irradiation of carbonyl compounds (in CHCl₃, C₆H₆, cyclo-C₆H₁₂) with He/Nc laser light slight decomposition occurs locally, setting free some CO. Our experience has shown that this decomposition is not restricted to nickel carbonyls only but instead seems a property of many other carbonyl compounds.

(7). *Preparation of LNi(CO)₃*

The procedure of Meriwether⁸ whereby Ni(CO)₄ is reacted with a phosphine

in boiling super-dry alcohol always yielded a mixture of $\text{LNi}(\text{CO})_3$ and $\text{L}_2\text{Ni}(\text{CO})_2$. We therefore preferred Bigorgne's method⁹. $\text{Ni}(\text{CO})_4$ (0.023 mole) is added dropwise at room temperature to a solution of 0.025 moles of L in dry ether. After completion of the addition the mixture is stirred for 2 h at room temperature. Evaporation of the ether solvent yielded a green residue which was washed several times with small portions of ether and 1.1 g of $\text{LNi}(\text{CO})_3$ was obtained.

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