

NOTE

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

F. T. DELBEKE, G. P. VAN DER KELEN AND Z. EECKHAUT

Laboratory for General and Inorganic Chemistry B, University of Ghent (Belgium)

(Received December 14th, 1968)

In a recent review article by R. J. Angelici¹, the tris(*p*-fluorophenyl)phosphine was compared with other phosphines as to its nucleophilic ligand character in reactions with the halide complexes of Cr, Mo and W, $[M(CO)_5X]^-$, to form $[cis-M(CO)_4(L)X]^-$ and $M(CO)_5L$. In this article we want to report on the reactions between the pure carbonyl complexes of Fe, Mo and W, resulting in the formation of several new compounds.

EXPERIMENTAL

1. Substitution reaction with $Fe_3(CO)_{12}$. Preparation of $[(p-FC_6H_4)_3P]Fe(CO)_4$ and $[(p-FC_6H_4)_3P]_2Fe(CO)_3$

(a). In a first attempt, (*p*-FC₆H₄)₃P (0.013 mole) and Fe₃(CO)₁₂ (0.005 mole) are dissolved in 150 ml dry THF. The mixture is stirred while heating to 70° for 1 h. When the green colour has disappeared, the reaction mixture is cooled to room temperature and a brown deposit forms. This is filtered off and washed with dry THF. The filtrate and the washing liquid are vacuumdistilled; after removal of the solvent THF a residue is obtained which is now dissolved in 50 ml dry methanol. On subsequent cooling a yellow precipitate separates from this solution. This yellow deposit is filtered off, washed with several small portions of petroleum ether and purified by sublimation *in vacuo*. The sublimate is then recrystallized from benzene at -12°. The pure yellow substance thus obtained is $[(p-FC_6H_4)_3P]Fe(CO)_4$, m.p. 152-155° (with decompn.) (Found: C, 54.91; H, 2.55. C₂₂H₁₂F₃FeO₄P calcd.: C, 54.57; H, 2.99%). The IR spectrum shows three CO bands, thus suggesting also a mono-substituted ironcarbonyl.

The residue left in the sublimation vessel is then dissolved in benzene and precipitated on adding of petroleum ether and cooling. The yellow precipitate thus obtained proved to be $[(p-FC_6H_4)_3P]_2Fe(CO)_3$, with m.p. 235° (with decompn.). The IR spectrum, the mass spectrum and a carbon analysis all agree with this identification. (Found: C, 60.49. C₃₉H₂₄F₆FeO₃P₂ calcd.: C, 60.65%.)

(b). The yields obtained with the procedure outlined above are rather poor

when compared to those for $[(C_6H_5)_3P]Fe(CO)_4$ obtained by Clifford and Mukherjee², who used a much lower ratio of phosphine to carbonyl. Therefore, in a second synthesis, 0.03 mole of $Fe_3(CO)_{12}$ were brought into reaction with 0.057 mole of $(p-FC_6H_4)_3P$ in dry THF, at 76° . The heating was continued for 3 h. On removal of part of the THF by distillation a yellow crystalline deposit (3.2 g) was obtained, which was separated by filtration. The m.p., mass and IR spectrum show it to be the $[(p-FC_6H_4)_3P]Fe(CO)_4$.

On evaporation of the filtrate a new solid residue was obtained. This was extracted with alcohol. The alcohol was then evaporated and the residue purified by sublimation. The sublimation yielded another portion of 0.36 g of the $[(p-FC_6H_4)_3P]Fe(CO)_4$.

2. Substitution reaction with $Fe(CO)_5$. Preparation of $[(p-FC_6H_4)_3P]_2Fe(CO)_3$

A solution of 0.074 mole $Fe(CO)_5$ and 0.1 mole $(p-FC_6H_4)_3P$ in 150 ml freshly distilled cyclohexanol is refluxed for 1 h. A portion of 150 ml of petroleum ether is then added and the mixture cooled. A yellow precipitate is separated and purified by sublimation. Only one substance is obtained in the reaction, but with fairly good yield (1.4 g), namely the disubstitution product $[(p-FC_6H_4)_3P]_2Fe(CO)_3$ which was identified by the same methods as those mentioned above.

3. Substitution reaction with $Mo(CO)_6$. Preparation of $[(p-FC_6H_4)_3P]Mo(CO)_5$ and $[(p-FC_6H_4)_3P]_2Mo(CO)_4$

(a). $[(p-FC_6H_4)_3P]Mo(CO)_5$. A mixture of 0.092 mole $Mo(CO)_6$ and 0.08 mole of $(p-FC_6H_4)_3P$ in 250 ml of freshly distilled diglyme is heated to reflux temperature for 4 h. Some hexacarbonyl which sublimes eventually into the reflux cooler is scraped down again into the reaction vessel, with a glass rod. The mixture is then cooled to room temperature and filtered. The solid residue is discarded and the filtrate is evaporated *in vacuo*, leaving a yellow-greenish residue in the flask. This is recrystallized five times from a mixture of ethanol and chloroform and 13.3 g of $[(p-FC_6H_4)_3P]Mo(CO)_5$ are obtained. M.p. 168° . (Found: C, 50.55. $C_{23}H_{12}F_3MoO_5P$ calcd.: C, 50.02%.)

(b). $[(p-FC_6H_4)_3P]_2Mo(CO)_4$. $(p-FC_6H_4)_3P$ (0.015 mole) and $Mo(CO)_6$ (0.009 mole) are heated in a glass tube to $170-180^\circ$ for 4 h. After cooling, the contents are washed out with benzene and the solvent evaporated. The mixture thus obtained is then extracted with several small portions of ether. The insoluble residue is filtered off and again dissolved in benzene. Methanol is now added to the benzene solution and on cooling to -15° 1.3 g of yellow-white crystals separate out, which were proved to be $[(p-FC_6H_4)_3P]_2Mo(CO)_4$; m.p. 176° (with decompn.). The observation of only one CO band in the IR spectrum at 1897 cm^{-1} is accepted as evidence for a *trans*-configuration in this complex³.

4. Substitution reaction with $W(CO)_6$. Preparation of $[(p-FC_6H_4)_3P]W(CO)_5$

0.08 mole of $(p-FC_6H_4)_3P$ and 0.092 mole of $W(CO)_6$ were heated to reflux temperature for 3 h in freshly distilled and oxygen free diglyme. The next steps of the separation are analogous to those mentioned for $[(p-FC_6H_4)_3P]Mo(CO)_5$. After three recrystallizations 11.8 g of $[(p-FC_6H_4)_3P]W(CO)_5$ (m.p. 215° with decompn.) are obtained.

REMARKS

All the reactions were done in an atmosphere of pure dry nitrogen. The IR spectra were recorded on a P.E. model 225 spectrometer; nujol mulls were used. The mass spectra were recorded on an M.S. 9 instrument of A.E.I. in the Organic Chemistry Laboratory of the University of Ghent. The authors thank Prof. VAN DE WALLE for his cooperation in this respect. The elemental analyses were done under the supervision of Dr. VAN POUCKE of this laboratory to whom we express our sincere gratitude. The tris(*p*-fluorophenyl)phosphine was prepared by a procedure elaborated by lic. DE KETELAERE of this laboratory⁴.

REFERENCES

- 1 R. J. ANGELICI, *Organometal. Chem. Rev.*, 3 (1968) 173-226.
- 2 A. F. CLIFFORD AND A. K. MUKHERJEE, *Inorg. Chem.*, 2 (1963) 151.
- 3 W. HIEBER AND J. PETERHANS, *Z. Naturforsch., B*, 14 (1959) 462.
- 4 R. DE KETELAERE, lic. thesis 1966, University of Ghent.

J. Organometal. Chem., 16 (1969) 512-514