Journal of Organometallic Chemistry, 256 (1983) 71–73
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

METAL COMPLEXES OF FLUOROPHOSPHINES

XII[*]. A NOVEL HETEROBIMETALLIC FLUOROPHOSPHINE METAL CARBONYL COMPLEX

R.B. KING and M. SHIMURA

Department of Chemistry, University of Georgia, Athens, Georgia 30602 (U.S.A.)

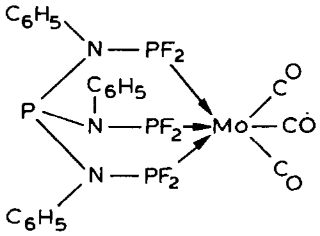
(Received July 1st, 1983)

Summary

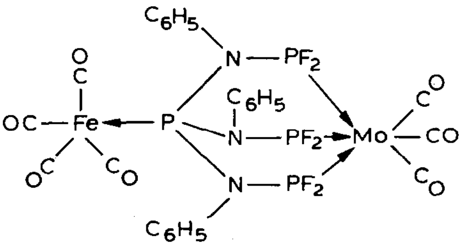
Reaction of $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ with excess $Fe_2(CO)_9$ in boiling diethyl ether results in complexation of the uncomplexed phosphorus atom to give the heterobimetallic complex $(OC)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3$.

Introduction

In 1981 we reported [2] the reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $C_6H_5N(PF_2)_2$ to give the novel bicyclol[2.2.2]octane-like cage complex $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (I). A characteristic feature of this complex is the presence of an uncomplexed trivalent phosphorus atom. Complexation of this phosphorus atom with transition metals provides a novel approach to the synthesis of heterobimetallic complexes. This note describes the first heterobimetallic complex of this type, namely, the mixed molybdenumiron carbonyl derivative $(CO)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3$ (II).



(I)



(II)

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[*] For part XI see ref. 1.

0022-328X/83/$03.00

Experimental

Preparation of $(OC)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3$

A mixture of 0.109 g (0.158 mmol) of $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ [2], 0.592 g (1.62 mmol) of $Fe_2(CO)_9$ [3], and 15 ml, of freshly redistilled dry diethyl ether was boiled under reflux under nitrogen for 2.5 h. The resulting deep green reaction mixture was filtered. Concentration of the filtrate and cooling in a $-10°C$ freezer resulted in the precipitation of green-black crystals of $Fe_3(CO)_{12}$ arising from the excess $Fe_2(CO)_9$ used for the reaction. These crystals of $Fe_3(CO)_{12}$ were removed by filtration. Removal of solvent from the filtrate at ~25°C/30 mmHg gave a green oil. This oil was treated with 1 ml of hexane. The resulting solution was cooled in a 0°C bath. The resulting crystals were filtered and washed with cold hexane to give 0.055 g (40% yield) of pale yellow $(OC)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3$, dec. 140°C without melting; infrared $\nu(CO)$ in CCl_4: 2072w, 2055s, 2006s, and 1966m cm^{-1}. The analytical sample was purified by recrystallization from diethyl ether.

Anal. Found: C, 34.1; H, 1.8; F, 13.0; Fe, 6.7; Mo, 11.5; N, 4.9; P, 14.3. Mol. wt., 869 in benzene. $C_{25}H_{15}F_6FeMoN_3O_7P_4$ cald.: C, 34.9; H, 1.8; F, 13.3; Fe, 6.5; Mo, 11.2; N, 4.9; P, 14.4%. Mol. wt., 859.

^{31}P NMR spectra

$P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (I) in CH_2Cl_2. δ 157.1 (triplet (J 1197 Hz) of multiplets) and δ 101.3 (unresolved singlet) downfield from external 85% H_3PO_4 corresponding to the three PF_2 groups and the central phosphorus atom, respectively.

$(OC)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3$ (II) in $CDCl_3$. δ 177.2 (unresolved singlet) and δ 153.9 (triplet (J 1215 Hz) of quintets (J 21 Hz)) downfield from external 85% H_3PO_4 corresponding to the central phosphorus atom and the three PF_2 groups, respectively.

^{19}F NMR spectra

$P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (I) in $CDCl_3$. Doublet (J 1198 Hz) of triplets (J 22 Hz) of doublets (J 7 Hz) centered at 26.4 ppm, upfield from internal CCl_3F.

$(OC)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3$ (II) in $CDCl_3$. Doublet (J 1219 Hz) of doublets (J 11 Hz) centered at 20.5 ppm upfield from internal CCl_3F.

Results and discussion

The molybdenum complex $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (I) was found to react with $Fe_2(CO)_9$ under mild conditions according to the equation:

$$P[N(C_6H_5)PF_2]_3Mo(CO)_3 + Fe_2(CO)_9 \rightarrow$$
$$(OC)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3 + Fe(CO)_5$$

A large excess (~ 10/1 mole ratio) of $Fe_2(CO)_9$ to I was used in order to maximize the conversion of the relatively valuable I to II; however, the excess $Fe(CO)_4$ fragments so generated produced considerable quantities of dark green $Fe_3(CO)_{12}$ which had to be removed before isolation of the bimetallic product $(OC)_4Fe[N(C_6H_5)PF_2]_3Mo(CO)_3$ (II). The stoichiometry of II was indicated by a correct molecular weight determination in benzene and correct analyses for seven of its eight elements including both metals.

The complexation of the uncomplexed phosphorus atom in $P[N(C_6H_5)PF_2]_3$-$Mo(CO)_3$ (I) to an $Fe(CO)_4$ group in $(OC)_4FeP[N(C_6H_5)PF_2]_3Mo(CO)_3$ (II) is indicated most clearly by its ^{31}P NMR spectrum. The resonance at δ 101.3 assigned to the uncomplexed fluorine-free phosphorus atom in I moves downfield to δ 177.2 in II corresponding to a shift of 75.9 ppm upon coordination of the $Fe(CO)_4$ group. However, the resonance at δ 157.1 assigned to the Mo-complexed PF_2 groups in I moves only slightly upfield to δ 153.9 in accord with the relative remoteness of these phosphorus atoms to the coordinated $Fe(CO)_4$ group. The ^{19}F resonance in I also shifts slightly (5.9 ppm downfield) upon coordination of the $Fe(CO)_4$ group to form II.

The presence of both $Fe(CO)_4$ and $Mo(CO)_3$ groups in $(OC)_4FeP[N(C_6H_5)$-$PF_2]_3Mo(CO)_3$ (II) can be recognized by its infrared spectrum in the $\nu(CO)$ region. The A_1 and E modes in $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (I) at 2041 and 1988 cm^{-1}, respectively, shift to 2055 and 2006 cm^{-1} upon complexation of the $Fe(CO)_4$ group to form II. The two remaining $\nu(CO)$ frequencies at 2072w and 1966m correspond to two of the three $\nu(CO)$ frequencies expected [4] for axially substituted $LFe(CO)_4$ derivatives. These frequencies are ~ 7 cm^{-1} higher than those reported [4] for $(C_6H_5O)_3PFe(CO)_4$ suggesting that $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ as a ligand is a slightly stronger π-acceptor than triphenyl phosphite. Comparison of the $\nu(CO)$ frequencies in $(C_6H_5O)_3PFe(CO)_4$ and those of the $Fe(CO)_4$ group in II suggests that the third unobserved $\nu(CO)$ frequency of the $Fe(CO)_4$ group in II should appear as a relatively weak band around 2002 cm^{-1} where it would be obscured by the much stronger 2006 cm^{-1} $\nu(CO)$ frequency of the $Mo(CO)_3$ group in II.

Acknowledgment

We are indebted to the Petroleum Research Fund for partial support of this work under Grant PRF-12961-AC3.

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