Journal of Fluorine Chemistry, 52 (1991) 1–6

CARBONYL DIFLUORIDE: REACTIONS WITH METAL-PHOSPHINE COMPLEXES

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ABSTRACT

Nickel complexes of the composition $[Ni(L)_n]X_2$ [L = bis(diphenylphosphino)methane (dpm), 1,2-bis(diphenylphosphino)ethane (dpe) and 1,3-bis(diphenylphosphino)propane (dpp), X = Cl^-, Br^- and I^-, n = 1, 2] were allowed to react with carbonyl difluoride under homogeneous and heterogeneous conditions at ambient temperature or above. The dpm ligands of $[Ni(dpm)]X_2$ and $[Ni(dpm)_2]X_2$ were oxidatively fluorinated to the phosphorane but the complexes of the composition $[Ni(dpe)]X_2$ and $[Ni(dpp)]X_2$ did not react with carbonyl difluoride under any conditions tried. The 1:2 complexes $[Ni(dpe)_2]X_2$ and $[Ni(dpp)_2]X_2$ reacted with carbonyl difluoride at 25 °C in CH_2Cl_2 to form fluorinated phosphoranes and the 1:1 complexes $[Ni(dpe)]X_2$ and $[Ni(dpp)]X_2$, respectively. Carbonyl difluoride was found to react with the neutral complexes $[Ni(dpp)_2]$ and $[Ni(dpe)_2]$ to give the stoichiometric amounts of oxidatively fluorinated phosphoranes.

INTRODUCTION

Carbonyl difluoride (COF_2) is a versatile and nondestructive fluorine-transfer reagent as demonstrated by the ready introduction of fluorine into a variety of P-H, N-H or C-H containing compounds [1],[2]. Furthermore, metal oxides may be converted into metal fluorides [3] of high purity using COF_2. Christie *et al* [4] have shown that $FClO_3$ can be prepared by using

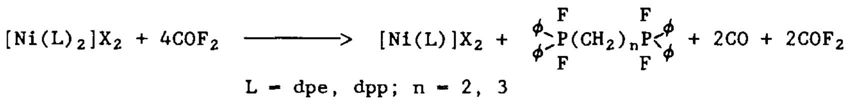
0022-1139/91/$3.50

COF_2 with alkali metal chlorates, $MClO_3$. While we have observed [1] that some phosphines are easily oxidatively fluorinated with COF_2, attempts to oxidatively fluorinate PF_3, PCl_3, and ϕPCl_2 with COF_2 failed. This was attributed to the high electronegativity of the atoms/groups bound to phosphorus. In this study we report the oxidative fluorination of phosphines via decomposition of a selected group of nickel phosphine complexes.

Since many transition metal complexes are used as catalysts in industrial processes, the recovery of metals from spent catalysts is an area of great interest. We have found that, in some cases, phosphines such as bis(diphenylphosphino)methane (dpm), 1,2-bis(diphenylphosphino)ethane (dpe) and 1,3-bis(diphenylphosphino)propane (dpp) are oxidatively fluorinated either at room temperature in solution or under heterogeneous conditions at higher temperatures when coordinated to nickel, and simultaneously removed from the coordination sphere. The nickel diphosphine complexes used in this study were prepared by known methods [5],[6] and were selected based on factors which were expected to affect their reactivity with carbonyl difluoride such as chelate ring size, charges on the complex cations and the anions, and the number of phosphine ligands present.

RESULTS AND DISCUSSION

Nickel complexes of the type $[Ni(L)_n]X_2$, where $n = 1, 2$; $X = Cl^-, Br^-, I^-$ and L = dpm, dpe, dpp were prepared. No reaction took place between the complexes $[Ni(dpe)]X_2$ or $[Ni(dpp)]X_2$ when they were reacted at room temperature for 12 to 24 h in CH_2Cl_2 with COF_2. Even at higher temperatures (up to 140 °C), these 1:1 dpe or dpp complexes did not react with COF_2. Reactivity was not changed by varying the anion present (Cl^-, Br^-, or I^-) under heterogenous reaction conditions (gas/solid). However, the 1:2 complexes, $[Ni(dpe)_2]X_2$ and $[Ni(dpp)_2]X_2$, did react under these conditions, but it was found that only a single phosphine ligand was fluorinated and displaced:



$$[Ni(L)_2]X_2 + 4COF_2 \longrightarrow [Ni(L)]X_2 + {}^{\phi}_{\phi}{>}\overset{F}{\underset{F}{P}}(CH_2)_n\overset{F}{\underset{F}{P}}{<}^{\phi}_{\phi} + 2CO + 2COF_2$$

L = dpe, dpp; n = 2, 3

The increased reactivity of the 1:2 complexes may be a result of the decreased effective electronegativity of the metal cation in these compounds. In addition, while no appreciable difference in reactivity was observed between the 1:2 dpe and dpp complexes (five- and six-membered chelate rings), the dpm (four-membered chelate ring) complex was much more labile, as evidenced by complete reaction with COF_2 at room temperature in CH_2Cl_2, even in the case of $[Ni(dpm)]X_2$ in contrast with $[NiL]X_2$ (L = dpe, dpp). In these cases, stoichiometric amounts of the oxidatively fluorinated phosphine (dpm) were recovered. Furthermore, the bromo and iodo complexes reacted more rapidly than the chloro complexes under heterogeneous conditions. Comparison of the reactivity of these complexes clearly shows that the chelate ring size plays a major role in the reaction. In all cases, the metal was isolated as the chloro, bromo or iodo salt depending on the anion present in the starting complex. Carbon monoxide was released in all reactions where COF_2 was found to react, and no evidence for the formation of $Ni(CO)_4$ was obtained.

Attempts were made to determine if $Ni(CO)_4$ was obtained when $[Ni(dpe)_2]$ and $[Ni(dpp)_2]$ were used, i.e. nickel(0) is present. Both these complexes were allowed to react with COF_2 in CH_2Cl_2 at 25 °C or in a stainless steel vessel at ~100°C as follows:

$$\underset{L\ =\ \text{dpe, dpp}}{[Ni(L)_2]} + 4COF_2 \xrightarrow[\text{II. stainless steel, 100 °C}]{\text{I. 25 °C, } CH_2Cl_2} [Ni(CO)_4] + F_4L$$

Reactions occurred under both sets of conditions with complete destruction of the complex and oxidative fluorination of the ligand. No noncondensible gas (CO) was isolated and the formation of $Ni(CO)_4$ could not be confirmed although the IR spectra showed the bands due to CO stretch. Although complexes $[Ni(dpp)_2]$ and $[Ni(dpe)_2]$ have a different chelate ring size, they showed similar reactivity towards COF_2 in contrast to the charged complexes with the same ligands.

These observations show that phosphine ligands coordinated to the transition metal ion, Ni^{+2}, can be oxidatively fluorinated and the metal halides are recovered. Thus, the recovery of metals as simple salts is possible without difficulties. Further studies with other transition metal complexes are underway.

EXPERIMENTAL

General Procedure

A conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge was used for manipulation of gases and volatile liquids. Reactions carried out at 25 °C were accomplished in 50 mL round-bottomed flasks equipped with Teflon stopcocks. ^1H, ^{19}F and ^{31}P NMR spectra were recorded on a JEOL FX 90Q FT NMR spectrometer with $(CH_3)_4Si$, CCl_3F or H_3PO_4 as external references, respectively. In all cases, samples were prepared in deuterated chloroform. Infrared spectra were obtained on a Perkin-Elmer 599B spectrometer by using a 10 cm cell-fitted with KBr windows for gases, KBr disks for liquids and KBr pellets for solids. Mass spectra were recorded on a VG HS 7070 mass spectrometer.

Materials

Bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, and 1,3-bis(diphenylphosphino)propane were purchased from Strem Chemicals Inc. and used as such. Carbonyl difluoride (COF_2) was used without purification (PCR Inc.). The complexes were prepared by reported methods [5],[6]. Dichloromethane was stored over molecular sieves (4Å).

CAUTION: Carbonyl fluoride is highly poisonous and quickly hydrolyses when it comes in contact with moisture. It must be transferred by using vacuum line techniques and manipulated in an efficient hood.

Reactions of Nickel-Phosphine Complexes with COF_2

Method-1. To a dry 100 mL Pyrex round-bottomed flask, equipped with a Kontes Teflon stopcock, 2-3 mmol of complex was added under an inert atmosphere and dissolved in 10 mL of dry CH_2Cl_2. The flask was cooled at -196 °C and was evacuated. The stoichiometric amount of COF_2 was transferred to the flask by using vacuum line techniques. The vessel was allowed to warm to room temperature and then was stirred for 12 - 14 hrs. It was filtered and the solvent was removed under vacuum. The solid left after filtration was washed twice with 50 mL CH_2Cl_2 and dried under vacuum. The solid was characterized [7],[8].

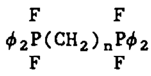
Method-2. The nickel complex (2-3 mmol) was placed in a 75 mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve and the cylinder was cooled to -196 °C. It was then evacuated and a slight excess over the stoichiometric amount of COF_2 required was transferred using vacuum line techniques. The cylinder was allowed to warm to room temperature and was heated at 60°/100 °C for 12 hrs. or 24 hrs. The volatile materials were examined for CO and unreacted COF_2 via infrared spectra. They were removed under vacuum and the contents of the cylinder were dissolved in dry CH_2Cl_2 and filtered. The filtrate was concentrated to dryness. The residue was washed with dry 50 mL CH_2Cl_2, dried under vacuum, and the fluorinated phosphoranes were characterized.

Representative reactions which were carried out are listed in Table 1.

TABLE 1

Reactants	Temp.°C	Time-hrs./Solvent*	Products**
$[Ni(dpm)_2]X_2$‡	25	12, CH_2Cl_2	NiX_2, CO, A
$[Ni(dpe)_2]X_2$	25 50 140	24, CH_2Cl_2 12 12	$[Ni(dpe)]X_2$, CO, B
$[Ni(dpe)]X_2$	25 140	24, CH_2Cl_2 24	No Reaction
$[Ni(dpp)_2]X_2$	25 50 140	24, CH_2Cl_2 12 12	$[Ni(dpp)]X_2$, C
$[Ni(dpp)]X_2$	25 140	24, CH_2Cl_2 24	No Reaction
$[Ni(dpe)_2]$	25	24, CH_2Cl_2	NiF_2, B
$[Ni(dpp)_2]$	25	24, CH_2Cl_2	NiF_2, C

* If no solvent, reaction carried out in stainless steel vessel.

** 
$\phi_2\overset{F}{\underset{F}{P}}(CH_2)_n\overset{F}{\underset{F}{P}}\phi_2$; A, n = 1; B, n = 2; C, n = 3.

‡ X = Cl, Br, I.

ACKNOWLEDGEMENTS

We would like to thank the National Science Foundation (Grant CHE-8703790) and the Air Force Office of Scientific Research (Grant 87-0067) for support of this research. One of the authors (O. D. G.) thanks the University of Rajasthan (India) for the opportunity to do research at the University of Idaho.

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