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COORDINATION CHEMISTRY OF BIDENTATE DIFLUOROPHOSPHINES IV. COMPLEXES OF 1,2-BIS(DIFLUOROPHOSPHINO)ETHANE WITH NI(0) AND MO(0).

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SUMMARY

The ligand, 1,2-bis(difluorophosphino)ethane, ($PF_2C_2H_4PF_2$), reacts with $Ni(CO)_4$ in the gas phase and in solution to produce carbon monoxide and a polymer, $[Ni(PF_2C_2H_4PF_2)_2]_x$. $PF_2C_2H_4PF_2$ displaces norbornadiene from $(C_7H_8)Mo(CO)_4$ to yield the relatively air-stable complex, $Mo(CO)_4$-($PF_2C_2H_4PF_2$). Analysis of the infrared spectrum of the monomeric complex indicates that the ligand exhibits π-acceptor strength equal to $PF_2C_6H_{10}PF_2$.

INTRODUCTION

As a part of our study of the coordinating ability of polydentate fluorophosphine ligands [1-3], made available in this laboratory by the photoassisted addition of PF_2 radicals to carbon-carbon double bonds [4], we report here the initial investigation of the coordination chemistry of the ligand, 1,2-bis-(difluorophosphino)ethane with nickel(0) and molybdenum(0). This bidentate ligand is of particular interest since it is isostructural with the well-known ligand, 1,2-bis(diphenylphosphino)ethane (diphos).

Reactions of transition metal carbonyls with another bidentate difluorophosphine, 1,2-bis(difluorophosphino)cyclohexane, ($PF_2C_6H_{10}PF_2$) [1-3] has shown that this ligand exhibits strong π-back-bonding and chelating ability, stabilizes metal atoms in low oxidation states, and binds to metals in chelating and bridging modes, in spite of its stereochemically rigid carbon-hydrogen skeleton. Analogous reactions of transition metal carbonyls with $PF_2C_2H_4PF_2$ allow for comparison of two structurally different bidentate difluorophosphines with respect to coordination. The non-rigid carbon-hydrogen backbone of $PF_2C_2H_4PF_2$ is expected to render the ligand flexibility as a coordinating species, enhancing its bridging ability.

RESULTS

The Lewis base character of $PF_2C_2H_4PF_2$ has been demonstrated in reactions with diborane in which each PF_2 function has been shown to be an active basic site [5]. That $PF_2C_2H_4PF_2$ exhibits bifunctional character is verified by the displacement of CO from $Ni(CO)_4$ at room temperature in both the gas phase and in benzene solution to yield an air-stable, carbonyl-free brown solid.

This reaction product has been characterized by elemental analyses and infrared spectroscopy. C, H, and Ni analyses are in excellent agreement with the formula, $Ni(PF_2C_2H_4PF_2)_2$. The solid phase infrared spectrum consists of the following bands (cm^{-1}) with some tentative assignments as shown: 2950 m (νCH), 2908 m (νCH), 1170 s, 1075 m, and 785 vvs (νPF). Absorptions in the CO region of the spectrum were not observed. The solid is only slightly soluble in the polar solvents, $CHCl_3$, DMF, and DMSO. Because the analogous reaction of $C_6H_{10}(PF_2)_2$ with $Ni(CO)_4$ gave a monomer soluble in these solvents, it is assumed that this insolubility is a result of the polymeric nature of the compound. Due to the limited solubility of the compound, neither nmr spectra nor an osmometric molecular weight determination could be obtained. The low volatility of the complex even at temperatures as high as 400° precludes a mass spectrum.

That $PF_2C_2H_4PF_2$ can function in a chelating fashion is demonstrated by the facile displacement of the olefin from $(C_7H_8)Mo(CO)_4$ to yield the relatively air-stable, monomeric complex, $Mo(CO)_4(PF_2C_2H_4PF_2)$. Elemental analyses are in excellent agreement with the formula shown. The formulation as a coordination monomer was confirmed by vapor pressure osmometry. The solution (hexane) infrared spectrum in the CO region consists of four well-resolved bands expected for <u>cis</u>-$LM(CO)_4$ complexes, whose frequencies are presented in the Table. A strong PF stretching band was observed at 815 cm^{-1}. The mass spectrum of $Mo(CO)_4(PF_2C_2H_4PF_2)$ consists of a molecular ion peak at m/e 374 $[Mo(CO)_4(PF_2C_2H_4PF_2)^+]$. The successive stepwise loss of CO at -28 m/e intervals from the molecular ion is indicated by clusters of peaks (due to molybdenum isotopes). Ligand fragmentation peaks are present as expected and no peaks due to high mass ions above the molecular ion are observed.

DISCUSSION

The ligand, $PF_2C_2H_4PF_2$, displaces CO easily from $Ni(CO)_4$ in both the gas phase and in solution. The mild conditions required for the complete displacement of the CO ligands are analogous to the $PF_2C_6H_{10}PF_2$ case [1] and illustrate the effective π-acceptor ability of $PF_2C_2H_4PF_2$. The insolubility of the resultant complex is good evidence of a polymeric species with an assumed high molecular weight. A polymer with the stoichiometry of two bidentate ligands per metal atom (as shown by elemental analyses) requires ligand bridging. Models show the non-rigid ligand can bridge two metal centers to give long chains or networks without inducing steric crowding. Evidence of ligand coordination is also verified by the shift of the P-F stretching band in the infrared spectrum. The coordinated ligand P-F stretch is observed at 785 cm^{-1} as compared to the free ligand P-F stretch at 793 cm^{-1} suggesting [6], as expected, a significant dπ-dπ bonding interaction between phosphorus and nickel.

Results of the displacement of norbornadiene from $(C_7H_8)Mo(CO)_4$ by $PF_2C_2H_4PF_2$ show that the ligand can function as an effective chelate. A monomeric complex is prepared (as verified by osmometric molar mass and mass spectral data) which demonstrates the ligand's ability to coordinate to metals in a chelating mode. The relative stability of the complex toward oxidation when exposed to air reflects the chelate effect.

That $PF_2C_2H_4PF_2$ is a strong π-acceptor ligand is demonstrated by analysis of the CO stretching bands in the infrared spectrum of $Mo(CO)_4(PF_2C_2H_4PF_2)$. The complex is expected to exhibit C_{2v} carbonyl symmetry which predicts the presence of four CO stretching bands labeled $2A_1 + B_1 + B_2$, which are infrared and Raman active. Bridging CO ligands are not observed in the region 1800-1600 cm^{-1}, but four distinct bands (CO terminal stretches) are observed between 2100 and 1950 cm^{-1}. (See Table) Examination of the CO stretching frequencies supports the assumption that $PF_2C_2H_4PF_2$ is a strong π-acceptor ligand. The frequencies obtained for $Mo(CO)_4(PF_2C_2H_4PF_2)$ compare closely with the corresponding frequencies obtained for the analogous complex of the strong π-acceptor bidentate difluorophosphine, $PF_2C_6H_{10}PF_2$ [2]. Representative values of the Cotton-Kraihanzel [7] CO force constants for the molybdenum tetracarbonyl complex are nearly equal to the force constants previously reported for $PF_2C_6H_{10}PF_2$ [2]. Comparison of the force constants and CO frequencies of molybdenum tetracarbonyl complexes of these ligands and PF_3 and $PPh_2C_2H_4PPh_2$ indicates that these bidentate difluorophosphines are strong π-acceptors; they exhibit π-acidity less than PF_3, but are substantially superior to diphos in this respect.

CONCLUSION

The results of the study of the coordination chemistry of $PF_2C_2H_4PF_2$

TABLE

CO frequencies and force constants for cis-$L_2Mo(CO)_4$ and cis-$LMo(Co)_4$ complexes

Compound	Frequencies, cm^{-1}				Force Constants, mdyne/Å [7]		
	A_1^2	A_1^1	B_1	B_2	k_1	k_2	k_i
$Mo(CO)_4(PF_2C_2H_4PF_2)$	2074	2005	1991	1973	16.30	16.30	0.29
$Mo(CO)_4(PF_2C_6H_{10}PF_2)^a$	2070	2003	1990	1971	16.27	16.28	0.28
$Mo(CO)_4(PF_3)_2^b$	2087	2014	2011	1990	16.59	16.53	0.27
$Mo(CO)_4(PPh_2C_2H_4PPh_2)^c$	2020	1919	1907	1881	14.64	15.41	0.36

a. Reference 2.
b. G. R. Dobson, I. W. Stolz, and R. K. Sheline, Adv. Inorg. Chem. Radiochem., 8, 1 (1966).
c. J. Chatt and H. R. Watson, J. Chem. Soc., London, 4980 (1961).

demonstrate that this ligand exhibits the characteristics anticipated: it binds to low valent metals very strongly, reflecting strong π-acidity which is similar to $PF_2C_6H_{10}PF_2$, and in both bridging and chelating fashions. The ligand is shown to function as a chelate only with special precaution. The tendency of the ligand to bridge metal centers is greater than $PF_2C_6H_{10}PF_2$ as anticipated (as shown by the polymeric product formation in the reaction with $Ni(CO)_4$) due to its non-rigid carbon-hydrogen skeleton.

EXPERIMENTAL

Due to the reactivities of the fluorophosphine ligand and the resultant complexes, all manipulations were carried out using standard high-vacuum techniques or under a dry nitrogen blanket [8]. Infrared spectra were recorded on a Beckman IR-20A spectrometer in hexane or mulls (Nujol and Halo-carbon 25-5S Grease). Values reported are correct to ± 3 cm^{-1} (polystyrene reference). Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-6E spectrometer. Molecular weights were obtained osmometrically in benzene with a Mechrolab Vapor Pressure Osmometer Model 301A. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

All organic solvents were dried over Linde Molecular Sieves no. 3A and degassed before use. $PF_2C_6H_{10}PF_2$ was prepared according to the published procedure [4,5]. Bicyclo[2.2.1]heptadienetetracarbonylmolybdenum(0) was purchased from Research Organic/Inorganic Chemical Corp., Sun Valley, California. Tetracarbonylnickel(0) was purchased from Strem Chemicals, Inc., Danvers, Massachusetts.

Preparation of Bis[1,2-bis(difluorophosphino)ethane]nickel(0), $[Ni(PF_2C_2H_4PF_2)_2]_x$. In a typical reaction, 2.29 mmol of $PF_2C_2H_4PF_2$ were condensed at -196° into a 200 mL reaction vessel connected via a stopcock to a 500 mL reaction vessel in which 0.76 mmol of $Ni(CO)_4$ were condensed. The reactants were allowed to warm to room temperature (both reactants were completely vaporized) and the connecting stopcock opened. White clouds formed in the larger vessel over a period of 20 minutes. A colorless oil condensed onto the walls of the vessel, the oil solidifying upon standing overnight. The CO that was liberated during reaction was removed while holding the solid at -196°. Anal. Calcd for $NiP_4F_8C_4H_8$: Ni, 15.03; C, 12.30; H, 2.05. Found: Ni, 14.08; C, 12.95; H, 2.15.

0.47 mmol of $Ni(CO)_4$ and 1.39 mmol of $PF_2C_2H_4PF_2$ were condensed into a 50 mL Pyrex vessel containing ca. 20 mL of dry, air-free benzene at -196°. The mixture was allowed to warm to room temperature and was shaken over a period of 13 hours. Liberated CO was removed while holding the mixture at -196°. Recovery of 3.36 equivalents/equivalent of $Ni(CO)_4$ was made. Removal of the solvent and unreacted starting materials under reduced pressure resulted in a light brown solid, which was identified as $[Ni(PF_2C_2H_4PF_2)_2]_x$ upon comparison of physical properties and the solid phase infrared spectrum of the solid obtained from the gas phase reaction.

Preparation of cis-[1,2-Bis(difluorophosphino)ethane]tetracarbonylmolybdenum(0), $[Mo(CO)_4(PF_2C_2H_4PF_2)]$. 0.160 g (0.533 mmol) of freshly sublimed $(C_7H_8)Mo(CO)_4$ were allowed to react for 12 hours at 50° with 0.48 mmol of $PF_2C_2H_4PF_2$ in ca. 25 mL of dry, air-free hexane. The solvent and displaced norbornadiene were removed under vacuum and the white solid that remained was chromatographed on a Florisil column. Elution with hexane resulted in the separation of a colorless band from a yellow band (unreacted $(C_7H_8)Mo(CO)_4$). Removal of the hexane from the colorless fraction under reduced pressure gave white crystals, m.p. 48-50° (uncorrected) in 26% yield. Anal. Calcd. for $MoP_2F_4C_6H_4O_4$: C, 19.25; H, 1.07; P, 16.58; MW, 374. Found: C, 19.46; H, 1.20; P, 16.22; MW, 371.

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