numbers of phosphines to an electronic effect.

The length of the C(4a)–N(1b) bond between the two pyridine rings is 1.447 (11) Å which is not significantly different from the values of 1.459 (5)[28] and 1.471 (12) Å[29] reported for other *N*-phenylpyridinium ions. The remaining distances and angles in the ligand are all within the generally accepted values. The intermolecular distances less than 3.5 Å were calculated and no abnormally short contacts between the zwitterions were found.

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Registry No. (EtOPy-Py)$ZnCl_3$, 65982-74-3; 4-chloropyridine hydrochloride, 7379-35-3; $ZnCl_2$, 7646-85-7.

Supplementary Material Available: A listing of observed and calculated structure factors and a table of least-squares planes data (10 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322

Coordination Chemistry of Bidentate Difluorophosphines. 2. Complexes of 1,2-Bis(difluorophosphino)cyclohexane with Chromium(0), Molybdenum(0), and Tungsten(0)[1,2]

DARRELL L. GALLUP and JOSEPH G. MORSE*

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The reactions of 1,2-bis(difluorophosphino)cyclohexane with hexacarbonyls of Cr(0), Mo(0), and W(0) and with the norbornadiene tetracarbonyl compounds of Cr(0), Mo(0), and W(0) have been investigated. The hexacarbonyls react, either under photolytic or thermolytic conditions, to produce carbon monoxide and oily mixtures of products of the general formulation $(M(CO)_4P_2F_4C_6H_{10})_x$, where x varies apparently from 1 to 3. The higher values of x correspond to species involving bridging ligands. The dienetetracarbonyls react to produce chelates of the general formulation $M(CO)_4P_2F_4C_6H_{10}$. $Mo(CO)_4P_2F_4C_6H_{10}$ will react with more $P_2F_4C_6H_{10}$ to give $(Mo(CO)_2(P_2F_4C_6H_{10})_2)_x$. Analysis of the infrared spectra of these chelates indicates that the ligand fits into a sequence of π-acceptor strength as $PF_3 > PCl_3 \sim P_2F_4C_6H_{10} > RN(PF_2)_2 \gg Ph_2PCH_2CH_2PPh_2$. NMR, IR, and mass spectral data for the chelates are presented and discussed.

Introduction

Transition-metal complexes containing bidentate phosphine ligands or monodentate fluorophosphine ligands have been studied for many years.[3,4] A large number of phosphine-substituted derivatives of the group 6B metal carbonyls have been described[5] and attempts have been made to classify series of ligands according to π-acceptor ability.[6] For example, Nixon et al.[4] have developed such a series for fluorophosphine ligands. Until recently, bidentate fluorophosphine ligands containing carbon–hydrogen backbones have not been available.[7] The ligand, 1,2-bis(difluorophosphino)cyclohexane, is the first example of a bidentate ligand that contains fluorine atoms located on the phosphorus atoms which in turn are positioned across a hydrocarbon backbone. We have chosen this particular ligand for initial coordination studies due to the relative ease of its preparation and molecular rigidity.

The reaction of $Ni(CO)_4$ with 1,2-bis(difluorophosphine)cyclohexane, $P_2F_4C_6H_{10}$, which resulted in the preparation of the complex bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0) was reported by this laboratory.[2] Due to the stability of the complex and the relatively mild conditions required for the complete displacement of CO from $Ni(CO)_4$, in contrast to the conditions required for the displacement of PF_3, this ligand was assumed to exhibit strong π-acceptor and chelating character.

In a continuation of our study of the coordinating properties of bidentate fluorophosphines, we now describe analogous reactions of $P_2F_4C_6H_{10}$ with the group 6B metal carbonyls

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which resulted in the preparation and characterization of some new zerovalent complexes of the fluorophosphine ligand. In order to gain insight into the coordinating ability of the ligand as compared with other known phosphine ligands, we include a discussion of the Cotton–Kraihanzel[8] CO force constant parameters obtained from infrared spectral data and a discussion of coordination shift parameters from ^{19}F and ^{31}P NMR data.

Experimental Section

General Techniques. Due to the reactivities of the fluorophosphine ligand and the resultant complexes, all manipulations were carried out by use of standard high-vacuum techniques or under a dry nitrogen blanket. Infrared spectra were recorded on a Beckman IR-20A spectrometer in chloroform and hexane. Values reported are correct to ±3 cm^{-1}. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-6E spectrometer. ^{19}F and ^{1}H NMR spectra were obtained at 94.1 and 100.0 MHz, respectively, with a Varian Associates XL-100-12 instrument. ^{31}P NMR spectra were obtained at 40.5 MHz with a Varian Associates XLFT-100-15 instrument in the Fourier transform mode with proton noise decoupling and a deuterium lock. Benzene was used as the solvent and internal reference for the ^{1}H NMR spectra. External standards, CCl_3F and 85% H_3PO_4, were used for chemical shift measurements in the ^{19}F and ^{31}P NMR spectra. Molecular weights were obtained osmometrically in benzene with a Mechrolab vapor pressure osmometer, Model 301A. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. A Rayonet photochemical reactor (Southern N.E. Ultraviolet Co., Middleton, Conn.) containing RPR-3000 Å reactor lamps was used as the energy source for the photoreactions.

Materials. All organic solvents were dried over Linde Molecular Sieves no. 3A and degassed before use. $P_2F_4C_6H_{10}$ was synthesized according to the published procedure.[7] Bicyclo[2.2.1]heptadienetetracarbonylmolybdenum(0) was purchased from Research Organic/Inorganic Chemical Corp., Sun Valley, Calif. The bicyclo[2.2.1]heptadienetetracarbonyl complexes of chromium[9,10] and tungsten[11] were prepared according to methods given in the literature. Hexacarbonylchromium(0) and -tungsten(0) were purchased from Strem Chemicals, Inc., Danvers, Mass., and hexacarbonylmolybdenum(0) was purchased from Ventron Corp., Beverly, Mass. All carbonyls were purified by high-vacuum sublimation immediately before use. Chromatography was performed on columns of Florisil (100–200 mesh) in hexane.

Reactions of Bicyclo[2.2.1]heptadienemetal Tetracarbonyls with $P_2F_4C_6H_{10}$. $P_2F_4C_6H_{10}$ was condensed onto a suspension of the appropriate bicyclo[2.2.1]heptadienemetal tetracarbonyl (freshly sublimed) in ca. 25 mL of solvent at −196 °C. After the particular reaction conditions were met, the product was recovered by cooling the solution to −36 °C and pumping off the solvent.

Preparation of *cis*-[1,2-Bis(difluorophosphino)cyclohexane]tetracarbonylchromium(0), [$Cr(CO)_4(P_2F_4C_6H_{10})$]. A solution (toluene) containing 0.302 g (1.38 mmol) of $P_2F_4C_6H_{10}$ and 0.256 g (1.16 mmol) of $C_7H_8Cr(CO)_4$ was refluxed several days under nitrogen with magnetic stirring. The resultant yellow-green oil was separated into tetracarbonyl reactant and a white solid by column chromatography. Recrystallization from hexane gave white crystals which sublimed at 55 °C, mp 77–79 °C (uncorrected), in 42% yield;[12] mol wt calcd 384, found 377.

Preparation of *cis*-[1,2-Bis(difluorophosphino)cyclohexane]tetracarbonylmolybdenum(0), [$Mo(CO)_4(P_2F_4C_6H_{10})$]. On warming a mixture of 0.211 g (0.958 mmol) of $P_2F_4C_6H_{10}$ and 0.268 g (0.893 mmol) of $C_7H_8Mo(CO)_4$ to room temperature and agitating, a colorless solution (pentane) resulted. White crystals were obtained which sublimed at 60 °C, mp 74–76 °C (uncorrected), in 60% yield. Anal. Calcd for $MoP_2F_4C_{10}H_{10}O_4$: C, 28.04; H, 2.34; P, 14.49; mol wt, 428. Found: C, 28.01; H, 2.34; P, 14.36; mol wt, 432.

Preparation of *cis*-[1,2-Bis(difluorophosphino)cyclohexane]tetracarbonyltungsten(0), [$W(CO)_4(P_2F_4C_6H_{10})$]. A solution (hexane) containing 0.263 g (1.20 mmol) of $P_2F_4C_6H_{10}$ and 0.329 g (1.00 mmol) of $C_7H_8W(CO)_4$ was refluxed under nitrogen with magnetic stirring for several hours, the yellow solution turning colorless after about 4 h. White crystals were obtained after sublimation at 60 °C, mp 76–78 °C (uncorrected), in 81% yield. Anal. Calcd for $WP_2F_4C_{10}H_{10}O_4$: C, 23.27; H, 1.96; P, 12.00; mol wt, 516. Found: C, 23.40; H, 2.02; P, 11.86; mol wt, 506.

Preparation of *cis*-Bis[1,2-bis(difluorophosphino)cyclohexane]dicarbonylmolybdenum(0), [$Mo(CO)_2(P_2F_4C_6H_{10})_2]_x$. A total of 0.083 g (0.38 mmol) of $P_2F_4C_6H_{10}$ was condensed onto a suspension of 0.155 g (0.362 mmol) of $Mo(CO)_4(P_2F_4C_6H_{10})$ in 25 mL of pentane at −196 °C. The mixture was photolyzed at 300 nm with stirring for 13 h. The solution was periodically removed from the photoreactor and cooled to −196 °C, and the evolved CO was measured and removed with pumping. The reaction appeared to be essentially complete within 10 h due to the absence of CO emerging from the solution. Recovery of 1.5 equiv of CO/equiv of $Mo(CO)_4(P_2F_4C_6H_{10})$ was made. The solvent was removed under vacuum and the colorless oil that remained was chromatographed giving unreacted $Mo(CO)_4(P_2F_4C_6H_{10})$ and a colorless oil identified by mass spectral, infrared, and NMR data as the dicarbonyl in about 45% yield; mol wt calcd 592, found 943.

Photoreactions of the Metal Hexacarbonyls with $P_2F_4C_6H_{10}$. $P_2F_4C_6H_{10}$ was condensed onto suspensions of the appropriate metal hexacarbonyl in ca. 30 mL of pentane at −196 °C. Upon warming to room temperature, the solution was photolyzed with magnetic stirring at 300 nm. The solution was periodically removed from the photoreactor and cooled to −196 °C, and all noncondensable material was measured and removed by a Toepler pump. When no more CO evolved, the solvent was removed with pumping at −36 °C. Attempts to obtain pure crystalline products from the residue by crystallization from a variety of solvents gave only viscous oils.

Photoreaction of $Cr(CO)_6$ with $P_2F_4C_6H_{10}$. The reactants, 0.180 g (0.82 mmol) of $P_2F_4C_6H_{10}$ and 0.160 g (0.73 mmol) of $Cr(CO)_6$, were photolyzed for 10 h. Recovery of 1.6 equiv of CO/equiv of $Cr(CO)_6$ was made. The orange oil decomposed rapidly;[13] mol wt calcd for $Cr(CO)_4(P_2F_4C_6H_{10})$ 384, found 949.

Photoreaction of $Mo(CO)_6$ with $P_2F_4C_6H_{10}$. The reactants, 0.216 g (0.981 mmol) of $P_2F_4C_6H_{10}$ and 0.225 g (0.852 mmol) of $Mo(CO)_6$, were photolyzed for 12 h. Recovery of 1.8 equiv of CO/equiv of $Mo(CO)_6$ indicated nearly complete substitution of two CO ligands by $P_2F_4C_6H_{10}$. The white oil was chromatographed resulting in the appearance of four fractions. The first fraction was identified as unreacted hexacarbonyl (very low yield) and the remaining fractions as tetracarbonyl species. Anal. Calcd for $MoP_2F_4C_{10}H_{10}O_4$ (the three fractions combined): C, 28.04; H, 2.34; P, 14.49; mol wt, 428. Found: C, 28.20; H, 2.51; P, 14.30; mol wt, 968.

Photoreaction of $W(CO)_6$ with $P_2F_4C_6H_{10}$. A mixture of 0.218 g (0.991 mmol) of $P_2F_4C_6H_{10}$ and 0.266 g (0.756 mmol) of $W(CO)_6$ was photolyzed for 13 h. Recovery of 1.7 equiv of CO/equiv of $W(CO)_6$ suggested near completion of reaction. A viscous white oil was obtained. Anal. Calcd for $WP_2F_4C_{10}H_{10}O_4$: C, 23.27; H, 1.96; P, 12.00; mol wt, 516. Found: C, 23.50; H, 2.30; P, 11.87; mol wt, 1128.

Thermal Reactions of the Metal Hexacarbonyls with $P_2F_4C_6H_{10}$. The appropriate metal hexacarbonyl and $P_2F_4C_6H_{10}$ were heated in a sealed evacuated vessel in a sand bath. The CO liberated during the reaction was measured and removed by a Toepler pump, the solid being retained at −196 °C.

Thermal Reaction of $Cr(CO)_6$ with $P_2F_4C_6H_{10}$. A mixture of 0.163 g (0.741 mmol) of $P_2F_4C_6H_{10}$ and 0.172 g (0.782 mmol) of $Cr(CO)_6$ was heated for 9 h at 180 °C with the evolution of 1.5 equiv of CO/equiv of $Cr(CO)_6$. White, finely divided crystals were recrystallized twice from benzene. Anal. Calcd for $CrP_2F_4C_{10}H_{10}O_4$: C, 31.25; H, 2.62; P, 16.15; mol wt, 384. Found: C, 31.19; H, 2.80; P, 16.24; mol wt, 1563.

Thermal Reaction of $Mo(CO)_6$ with $P_2F_4C_6H_{10}$. The reactants, 0.200 g (0.91 mmol) of $P_2F_4C_6H_{10}$ and 0.238 g (0.902 mmol) of $Mo(CO)_6$, were heated for 3 h at 165 °C with the evolution of 1.4 equiv of CO/equiv of $Mo(CO)_6$. A brown oil was obtained which was not characterized further.

Thermal Reaction of $W(CO)_6$ with $P_2F_4C_6H_{10}$. The reactants, 0.133 g (0.605 mmol) of $P_2F_4C_6H_{10}$ and 0.280 g (0.796 mmol) of $W(CO)_6$, were heated for 7 h at 145 °C with the evolution of 1.2 equiv of CO/equiv of $W(CO)_6$. A yellow oil was obtained which was not characterized further.

Infrared Spectra. The following are frequencies in CO stretching region and PF stretching region in cm^{-1}. Photolysis products: Cr: 2076 (m), 2047 (m), 2003 (m), 1963 (vs, br); 801 (s). Mo: 2088 (m), 2064 (m), 2007 (m), 1998 (sh), 1974 (s), 1965 (sh); 825 (s), 811 (sh). W: 2081 (m), 2056 (m), 2006 (w), 1961 (vs, br); ~810 (s). Thermolysis products: Cr: 2085 (m), 2055 (m), 1990 (s, br), 1950 (s); 810 (s). Mo: 2090 (m), 2057 (m), 1996 (s), 1980 (sh), 1967 (s); 802 (s). W: 2080 (m), 2061 (m), 1980 (s), 1945 (s); no

Table I. Assignments, Mass Numbers, and Relative Intensities of Some Ions in the Mass Spectra of *cis*-$M(CO)_4(P_2F_4C_6H_{10})$

	M = Cr		M = Mo		M = W	
	Mass	Intensity	Mass	Intensity	Mass	Intensity
$LM(CO)_4^+$	384	11	428	94	516	51
$LM(CO)_3^+$	356	12	400	59	488	56
$LM(CO)_2^+$	328	15	372	35	460	70
$LM(CO)^+$	300	27	344	100	432	100
LM^+	272	100	316	53	404	19

data. Olefin displacement products: Cr: 2056 (s), 1994 (s), 1982 (s), 1960 (s), 823 (s). Mo: 2070 (s), 2003 (s), 1990 (s), 1971 (s); 825 (s). W: 2064 (m), 1995 (s), 1983 (s), 1968 (s); 825 (s). $Mo(CO)_2(P_2F_4C_6H_{10})_2$: 2007 (s), 1974 (s); 821 (s).

Results and Discussion

Reactions with Dienemetal Tetracarbonyls. Because direct reaction between bidentate fluorophosphine ligands and the metal hexacarbonyls can produce any one of a number of substitution products or a mixture, syntheses of the monomeric tetracarbonyl complexes were carried out by reactions involving the displacement of the olefin from norbornadiene metal tetracarbonyls (reaction 1). The use of olefin displacement

$$cis\text{-}C_7H_8M(CO)_4 + L \rightarrow C_7H_8 + cis\text{-}LM(CO)_4 \qquad (1)$$
$$L = P_2F_4C_6H_{10}$$

reactions has found wide application in recent years as a means of obtaining specific substitution products and isomers.[4,14] In general, these reactions can be carried out under rather mild conditions and their progress can be followed by the loss of the intense color of the olefin complex and the appearance of the colorless fluorophosphine complex. All of the monomeric metal complexes prepared as a result of these reactions are white, relatively air-stable crystalline solids. The tungsten complex appears to be most easily oxidized, the white solid turning blue after being exposed to air for several days. All of the complexes are oxidized rapidly in the presence of solvent.

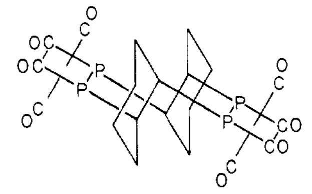
An important feature of the data obtained on the complexes prepared by olefin displacement is the molecular weights (see Experimental Section). These molecular weights, in contrast to those obtained for the products of photolysis and thermolysis, are in good agreement with monomeric formulations. Further evidence confirming the existence of monomeric complexes is found in the mass spectra. Assignments for the peaks in the mass spectra for the monomeric tetracarbonyl complexes of Cr, Mo, and W are given in Table I. In each case, prominent peaks arise at −28 *m/e* intervals indicating a successive stepwise removal of CO groups from the parent ion. Isotope peaks due to the metals and fragmentation peaks due to the ligand were in each case present as expected. No peaks of higher mass than the parent peak were observed.

Reaction with $Mo(CO)_4L$. A few phosphine-substituted dicarbonyl complexes have been prepared containing either monodentate or bidentate ligands.[3,12] In the cases of the bidentate ligands, the dicarbonyl product is often prepared by allowing the phosphine-substituted tetracarbonyl complex to react with excess ligand under rather vigorous conditions. We have attempted such a reaction scheme by photolyzing the monomeric molybdenum tetracarbonyl complex with $P_2F_4C_6H_{10}$ in solution. A colorless oil was obtained which was identified as $Mo(CO)_2(P_2F_4C_6H_{10})_2$. The mass spectrum of *cis*-$Mo(CO)_2(P_2F_4C_6H_{10})_2$ gives the following peaks (assignments and intensities of peaks are included in brackets): 592 [$Mo(CO)_2(P_2F_4C_6H_{10})_2^+$, 33], 564 [$Mo(CO)(P_2F_4C_6H_{10})_2^+$, 24], and 536 [$Mo(P_2F_4C_6H_{10})_2^+$, 100]. No higher *m/e* peaks were seen in the mass spectrum, although a high solution molecular weight was obtained for the complex which suggests that some dimeric product is present. Attempts to obtain the dicarbonyl complex and the complex, $Mo(P_2F_4C_6H_{10})_3$, by the photoreaction of $P_2F_4C_6H_{10}$ and $Mo(CO)_6$ in mole ratios as great as 4:1 have not been successful in contrast to the photoreaction of excess $CH_3N(PF_2)_2$ and $Mo(CO)_6$ giving the carbonyl-free complex, $Mo[CH_3N(PF_2)_2]_3$, that has recently been reported.[15]

Reactions with Metal Carbonyls. Many photochemical reactions of the metal carbonyls have been studied in solution and derivatives of the carbonyls have been prepared by irradiation in the presence of a great many coordinating agents.[16] Thus, the direct photoreactions of $P_2F_4C_6H_{10}$ with the metal carbonyls were attempted. The products obtained from these photoreactions are air and water sensitive. The products appear to be most sensitive to oxidation in the presence of solvent and, for this reason, were handled under inert atmospheres.

The oils that were produced in the photoreactions appear to be mixtures of products. The oil obtained from the photoreaction of $Mo(CO)_6$ and $P_2F_4C_6H_{10}$, which gave an elemental analysis in reasonably good agreement with that calculated for $[Mo(CO)_4(P_2F_4C_6H_{10})]_x$, consisted of at least three components as shown by column chromatography. The first fraction that was collected contained a trace of unreacted $Mo(CO)_6$. The second fraction gave an identical infrared spectrum with that of the monomeric complex, gave a parent peak in the mass spectrum at *m/e* 428 corresponding to $Mo(CO)_4(P_2F_4C_6H_{10})^+$, and showed successive losses of four CO ligands. The infrared spectrum of the third fraction appeared to be identical in the CO stretching region with that obtained for the nonseparated product. The mass spectrum gave a parent peak at *m/e* 428 with no higher *m/e* peaks observed. Fraction four gave an infrared spectrum nearly identical with that reported for the monomeric product, gave a parent peak in the mass spectrum at *m/e* 428 with no higher *m/e* peaks, and gave an osmometric molecular weight of 836 which corresponds to a dimer. We interpret the absence of higher *m/e* peaks in the mass spectrum to be due to fragmentation of the polymeric species in such a way as to produce only the apparent spectrum of the monomer.

The most unexpected results obtained during the characterization of the photolytically generated products were the molecular weight data. These results indicate the presence of mixtures of polymeric species (dimers or trimers). The observation of high molecular weight fractions is somewhat surprising, since the ligand should favor chelating as opposed to bridging behavior. The ligand appears to be highly sterically crowded in models of bridged tetracarbonyl structures (I) relative to monomeric structures (II) as a result of the bulkiness of the cyclohexane ring.[17] This implies that the product selection may be kinetically controlled under the reaction conditions. The first photolytic dissociation (reaction 2) may be sufficiently more facile than reaction 3 to make the initial bridge formation much more favorable than monomer formation. That is, the most probable reaction of $(CO)_5M(PF_2C_6H_{10}PF_2)$ may be the reaction with a second $M(CO)_5$ molecule. This suggested two experimental approaches to test the hypothesis, neither of which has, so far,



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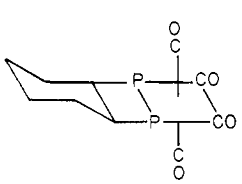

II

$$M(CO)_6 \rightleftarrows M(CO)_5 + CO \qquad (2)$$

$$(CO)_5M(PF_2C_6H_{10}PF_2) \rightleftarrows (CO)_4M(PF_2C_6H_{10}PF_2) + CO \qquad (3)$$

Table II. CO Frequencies and Force Constants for *cis*-$L_2M(CO)_4$ and *cis*-$LM(CO)_4$ Complexes

	Frequencies, cm^{-1}				Force constants, mdyn/A[8]		
Compound	A_1^2	A_1^1	B_1	B_2	k_1	k_2	k_i
$Cr(CO)_4(P_2F_4C_6H_{10})$	2056	1994	1982	1960	16.14	16.07	0.28
$Cr(CO)_4$diphos[a]	2009	1914	1899	1877	14.49	15.32	0.36
$Mo(CO)_4(P_2F_4C_6H_{10})$	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
$Mo(CO)_4(PCl_3)_2$[b]	2072	2004	1994	1986	16.30	16.44	0.27
$Mo(CO)_4(CCl_3PF_2)_2$[c]	2079	2015	2010	1990	16.56	16.51	0.26
$Mo(CO)_4(R_2NPF_2)_2$[c]	2055	1974	1950	1942	15.97	15.87	0.32
$Mo(CO)_4[RN(PF_2)_2]$[d]	2066	1991	1973	1963	16.03	16.18	0.31
$Mo(CO)_4$diphos[a]	2020	1919	1907	1881	14.64	15.41	0.36
$W(CO)_4(P_2F_4C_6H_{10})$	2064	1995	1983	1968	16.16	16.20	0.28
$W(CO)_4$diphos[a]	2016	1912	1901	1876	14.58	15.32	0.32

[a] Reference 18. [b] Reference 5. [c] Reference 4. [d] Reference 21.

produced unequivocal results. Carrying out the reaction at high dilution should favor monomer production. No detectable difference in product was observed over a fourfold concentration range. More dilute solutions than ~0.01 M proved impractical with respect to retrieval of sufficient material for analysis. Second, thermolysis, rather than photolysis, should favor chelation over bridged species if, in fact, the chelate is the thermodynamically favored form. Chatt and Watson[18] have shown that thermolysis reactions of the hexacarbonyls and bidentate phosphine ligands produce monomeric tetracarbonyl derivatives. Direct thermal reactions were, therefore, attempted as a means of preparing monomeric substitution products. The thermolysis reactions of the ligand with the hexacarbonyls led again to high molecular weight species, although in the case of chromium a crystalline material was obtained in contrast to the previously encountered oils. The precise nature of the bonding, mechanism of reaction, and structures of these high molecular weight products remains to be explored in detail.

Infrared Spectra. Complexes of the type *cis*-$L_2M(CO)_4$ exhibit C_{2v} carbonyl symmetry which predicts the presence of four CO stretching frequencies, 2 A_1 + B_1 + B_2, which are infrared and Raman active. The CO stretching frequencies for the complexes synthesized by photolysis are not highly resolved, appear to result from a mixture, and are not completely comparable with the frequencies given for the well-defined monomeric complexes (see infrared data). For this reason, the frequencies so reported have not been labeled according to symmetry modes. Bridging CO ligands have been excluded due to the absence of CO bridging frequencies in the infrared spectra. Noteworthy is the fact that several of the frequencies correspond to those given for the monomeric complexes obtained by the olefin displacement reactions.

Table II shows the CO stretching frequencies obtained from the solution infrared spectra of the complexes obtained by olefin displacement, along with the frequencies of similar complexes for comparative purposes. Examination of the CO stretching frequencies in the table supports the assumption that $P_2F_4C_6H_{10}$ is a good π-acceptor ligand. The frequencies for the $P_2F_4C_6H_{10}$ complexes compare favorably with those for the complexes of the better π acceptors as assessed by others.[19] This assessment has been based largely on the assumption that CO stretching frequencies higher than those in the unsubstituted carbonyls imply a greater contribution of the triply bonded resonance form, M–C≡O, further implying that the substituted ligand competes favorably with CO in accepting electron density from the metal. Lower CO stretching frequencies imply the reverse to be true.

Table III. Force Constants and CO Frequencies for *cis*-$L_4Mo(CO)_2$ and *cis*-$L_2M(CO)_2$ Complexes

	Frequencies, cm^{-1}		Force constants, mdyn/Å[8]	
Compound	A_1	B_1	k	k_i
$Mo(CO)_2(P_2F_4C_6H_{10})_2$	2007	1974	16.00	0.27
$Mo(CO)_2(PF_3)_4$[a]	2048	2010	16.59	0.29
$Mo(CO)_2(diphos)_2$[b]	1852	1786	13.36	0.48

[a] Reference 5. [b] Reference 18.

Table IV. ^{31}P and ^{19}F NMR Data for $M(CO)_4L$ and $M(CO)_2L_2$ Complexes,[a] $L = P_2F_4C_6H_{10}$

Compound	δ_P(complex),[b] ppm	$\Delta\delta_P$,[c] ppm	J_{FP},[d] Hz	ϕ_F (complex),[e] ppm	$\Delta\phi_F$,[f] ppm
$Cr(CO)_4L$[g]	+288.8	+54.7	1180	−63.6	+17.7
$Mo(CO)_4L$[h]	+264.9	+30.8	1170	−64.7	+16.6
$W(CO)_4L$[g]	+238.8 +230.8	+4.7 −3.3	1160	−66.1	+15.2
$Cr(CO)_4L$[i]	+287.1	+53.0	1158	−64.7	+16.6
$Mo(CO)_4L$[i]	+263.1	+29.0	1156	−65.4	+15.9
$W(CO)_4L$[i]	+236.7	+2.6	1141	−66.1	+15.2
$Mo(CO)_2L_2$[g]	+274.7 +271.2	+40.6 +37.1	1155	−61.9	+19.4

[a] Sign convention for chemical shifts: + = downfield. [b] Because of second-order splitting patterns in the spectra, the chemical shifts and J_{FP} values were measured from the centroids of the signals. [c] δ_P(ligand) = +234.1 ppm. [d] J_{FP}(ligand) = 1218 Hz. [e] Shifts reported for the dominant doublet. [f] ϕ_F(ligand) = −81.3 ppm. [g] Photolysis product. [h] Thermolysis product. [i] Olefin displacement product.

A quantitative estimate of this effect can be made by the method of Cotton and Kraihanzel who derived "nonrigorous" secular equations through which sets of force constants for the series of metal carbonyl derivatives may be obtained.[6] Although absolute values for these force constants have no significance and thus cannot be compared to force constants for molecules of different structural type, they are claimed to give internally consistent results for a particular series of derivatives.

Representative values of Cotton–Kraihanzel force constants for the series of complexes are included in Table II. From the arguments of Cotton and Kraihanzel, it follows that as the π-acceptor character of the competing, substituted ligand is increased, the magnitude of the carbonyl stretching frequencies and the force constants k_1 and k_2 should increase and k_i, the CO–CO interaction force constant, decrease. The complexes of $P_2F_4C_6H_{10}$ exhibit comparable CO force constants to those of the complexes of PF_3, PCl_3, CCl_3PF_2, and $RN(PF_2)_2$. These considerations allow the ligand, $P_2F_4C_6H_{10}$, to be placed in the following order of decreasing π-acceptor ability: $CF_3PF_2 > (CF_3)_2PF > CCl_3PF_2 > PCl_3 \sim P_2F_4C_6H_{10} > RN(PF_2)_2 > R_2NPF_2 \gg PPh_3 >$ diphos. The CO frequencies and force constants for the $P_2F_4C_6H_{10}$ complexes are notably much higher than the corresponding diphos complexes. In our series of tetracarbonyls, the CO frequencies decrease in the order Mo > W > Cr, an observation previously noted by Chatt and Watson.[18]

cis-$L_4M(CO)_2$ complexes also have C_{2v} carbonyl symmetry, the two carbonyl stretching vibrations being distributed among the symmetry classes of the point group as A_1 + B_1, which are infrared and Raman active. Table III presents the CO stretching frequencies obtained from the solution infrared spectrum of the dicarbonyl complex we prepared. Included in the table are the calculated values of the Cotton–Kraihanzel force constants. (CO stretching frequencies and C–K force constants for other dicarbonyl complexes are included for comparison.) As was previously observed for the tetracarbonyl complexes, the π-acceptor ability of $P_2F_4C_6H_{10}$ in the dicarbonyl complex is slightly less than the π-acceptor ability of PF_3 but much greater than the ligand, diphos.

NMR Spectra. The general feature of the 40.5-MHz phosphorus-31 NMR spectra for the complexes is a triplet with a large P–F coupling constant resulting from the two fluorine nuclei adjacent to the phosphorus atom. The chemical shift and coupling constant data are summarized in Table IV. The coordination shifts (δ_P(complex) − δ_P(ligand)) calculated for the complexes, are all downfield and are in good agreement with chemical shift data reported for complexes of the strong π-acceptor fluorophosphine ligands.[20,21] The coordination shifts decrease in the order Cr > Mo > W, in agreement with the common observation that the coordination shift is largest for the first-row metal in any particular group.[22] These low-field coordination shifts have been attributed to ring strain in five-membered chelate rings.[23] The coordination shifts have been used to distinguish between chelate complexes and bridged complexes, the latter occurring at slightly higher field.[23] Inspection of the ^{31}P NMR spectra of reaction mixtures has been used to determine the relative amounts of chelate product vs. other products (such as bridged binuclear species)[24] and should be a useful method for identifying possible bridged products in the high molecular weight mixtures obtained in this study. Differences in coordination shifts of bridged vs. chelated complexes have been reported to be as great as 10 ppm. For the tungsten complex prepared photolytically, two triplets have been observed, whose coordination shifts are +4.7 and −3.3 ppm, a difference of 8 ppm. The higher field triplet is about two-thirds as intense as the lower field triplet. We interpret the lower field triplet as arising from a chelate species in the product mixture, the higher field triplet being attributed to a bridged species. A similar observation is made for the photolysis product of the chromium hexacarbonyl reaction in that a weak intensity triplet is seen 5.9 ppm upfield from the triplet reported in Table IV. The spectra of the monomeric complexes all contain only one triplet indicating purity of sample.

In the ^{31}P NMR spectrum of the monomeric tungsten complex, two symmetrically positioned "satellite" lines arising from further spin coupling of the phosphorus nuclei with the ^{183}W nucleus are observable. A value of 375 Hz for the coupling constant, J_{WP}, is obtained, a value much larger in magnitude than those reported for other bidentate phosphine carbonyl complexes,[21,24,25] attributable to the highly electronegative fluorine atoms located on the phosphorus nuclei of the ligand.[26]

The first reported examples of spin–spin coupling of $^{95,97}Mo$ to ^{31}P in some pentacarbonylmolybdenum phosphine complexes appeared recently.[27] We also observe six weak peaks of equal intensity symmetrically distributed about the center peak of the ^{31}P triplet in $Mo(CO)_4(F_2PC_6H_{10}PF_2)$ which arises from coupling between the ^{31}P nucleus and either ^{95}Mo ($I = {}^5/_2$, 15.72% abundance) or ^{97}Mo ($I = {}^5/_2$, 9.46% abundance) or both. Comparable peaks are barely discernible above the noise about the two outside peaks of the ^{31}P triplet but cannot be assigned with confidence. The coupling constant, $^1J_{MoP}$, was found to be 215 ± 5 Hz for the six peaks observed. This value is substantially smaller than that reported for $Mo(CO)_5PF_3$ to be 284 ± 2 Hz. This smaller coupling constant is consistent with the observations that ring strain in chelates frequently is associated with smaller coupling constants than are observed in complexes with similar, monodentate ligands[24] and that lower electronegativity of the substituents on phosphorus leads to smaller coupling constants.[27]

Only a few phosphorus-31 chemical shifts have been reported for dicarbonyl complexes. Mathieu et al.[28] obtained two phosphorus signals of equal intensity due to nonequivalent positions of the phosphorus atoms in the octahedral complexes *cis*-$Mo(CO)_2[P(CH_3)_3]_4$ and *cis*-$Mo(CO_2)[P(OCH)_3]_4$. It was suggested that the chemical shifts for phosphorus atoms trans to a CO group occur at higher fields than the chemical shifts for phosphorus atoms trans to another phosphorus atom. The complex *cis*-$Mo(CO)_2[P_2F_4C_6H_{10}]_2$ exhibits two triplets in the ^{31}P NMR spectra of nearly equal intensity consistent with this argument. The coordination shifts are downfield from the coordination shift obtained for the tetracarbonyl analogue, although there appears to be no major trend in the coordination shifts of various substitution products of the same metal.[25]

The ^{19}F NMR spectra of the complexes give a large doublet and two small doublets like those previously for the Ni–$P_2F_4C_6H_{10}$ complex.[2] The doublets were attributed to the presence of coordinated trans and cis difluorophosphino groups in the ligand. The ^{19}F NMR spectra of the complexes exhibit a downfield coordination shift and a decrease in the P–F coupling constant from that of the free unbound ligand, consistent with trends reported for similar fluorophosphine–metal complexes.[20,21] The doublets observed in the spectra are a result of the spin coupling of the fluorine nuclei with the phosphorus nucleus. Table IV represents the data obtained from the spectra, including the fluorine coordination shifts, $\Delta\phi_F$ (ϕ_F(complex) − ϕ_F(ligand)).

The 100.1-MHz proton NMR spectra of the complexes give complex multiplets (identical spectra are seen for both the polymeric and monomeric products). In the spectrum of each complex, the multiplet is centered near δ 2.0 with benzene as the internal reference (free ligand, δ 1.97 broad multiplet).

Because most of these spectra exhibit second-order character, their complete analysis requires extensive study. Results of these analyses will be the subject of a future publication.

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Registry No. $C_7H_8Cr(CO)_4$, 12146-36-0; $C_7H_8Mo(CO)_4$, 12146-37-1; $C_7H_8W(CO)_4$, 12129-25-8; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Cr(CO)_4(P_2F_4C_6H_{10})$, 65890-21-3; $Mo(CO)_4(P_2F_4C_6H_{10})$, 65890-20-2; $W(CO)_4(P_2F_4C_6H_{10})$, 65890-19-9; *cis*-$Mo(CO)_2(P_2F_4C_6H_{10})_2$, 65890-18-8.

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Contribution from the Research Institute of Materials, University of Nijmegen,
Toernooiveld, Nijmegen, The Netherlands

Mössbauer Investigation and Novel Synthesis of Gold Cluster Compounds

F. A. VOLLENBROEK,* P. C. P. BOUTEN, J. M. TROOSTER, J. P. VAN DEN BERG, and J. J. BOUR

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Mössbauer spectra of $Au_{11}(PAr_3)_7X_3$ (Ar = C_6H_5, p-ClC_6H_4; X = SCN, I, CN) show different gold sites while an interpretation with five different gold sites (according to crystal structure) is possible. The peripheral gold atoms in the cluster are best described as linearly coordinated. A new way for the synthesis of these clusters was found; the evaporation of metallic gold into a solution of $Au(PAr_3)X$ and PAr_3 in ethanol resulted in a yield of 70% of the desired clusters.

Introduction

Reactions of $Au(PAr_3)X$ compounds with $NaBH_4$ produce $Au_{11}(PAr_3)_7X_3$ cluster compounds.[1] The yields of these reactions have not been reported but we found them to be low. A new technique described in this article for the preparation of these cluster compounds gives substantially higher yields.

Preliminary results of the crystal-structure determinations of $Au_{11}[P(C_6H_5)_3]_7(SCN)_3$ and $Au_{11}[P(p\text{-}ClC_6H_4)_3]_7I_3$ and the complete crystal structure of $Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$ have been reported.[2-4] In the latter compound (see Figure 1) a central gold atom is surrounded by ten peripheral gold atoms at distances varying from 2.60 to 2.71 Å. The distances between the peripheral gold atoms are in the range of 2.84–3.19 Å (mean 2.98 Å) and their interactions are therefore considered to have bonding character.[1,4]

X-ray photon electron spectra (XPS) reported by Battistoni et al.[5] seemed to implicate a large electron delocalization over the gold atoms, because only one absorption corresponding with the Au(4f) ionization energy was observed.

However, a molecular orbital calculation performed by Mingos[6] indicated large differences in the atomic charge of the various gold atoms within a $Au_{11}{}^{3+}$ cluster. The same calculation also led to the conclusion that, apart from the radial interactions between the peripheral atoms and the atom at the center of the polyhedron, the somewhat weaker metal–metal bonds on the periphery of the polyhedron make an important contribution to the cluster stability. We have taken Mössbauer spectra of several Au_{11} cluster compounds to gain more insight in the bonding of the gold atoms.

Experimental Section

The gold cluster compounds were prepared by the $NaBH_4$ method described in the literature[7] and by means of a metal evaporation technique. For the evaporation experiments a rotary apparatus introduced by Timms[8] was used. Gold metal was evaporated from a resistively heated tungsten boat into an ethanol film of −100 °C containing $Au(PAr_3)X$ and PAr_3. The ratio of the reactants was $Au{:}Au(PAr_3)X{:}PAr_3 = 8{:}3{:}4$. The pressure in the continuously pumped 1-L flask of the rotary apparatus could be kept at about 10^{-2} Torr. After completion of the metal evaporation, the solvent was removed in vacuo. Subsequently, the residue was crystallized from methylene chloride–ethanol. Some of the products were identified through comparison of their cell dimensions with those reported in the literature but in most cases the infrared spectrum, elemental analysis, and the color of the product were used for identification.

The Mössbauer spectra were recorded at 4.2 K with an apparatus described earlier.[9,10] The integrating counting technique was used.[11] From each measurement two spectra, which were analyzed independently, were obtained due to the application of a triangular variation of the velocity. The spectrum of $Au_{11}[P(C_6H_5)_3]_7(CN)_3$ was also measured at 25 K, but apart from a sharp decrease of intensity no significant change in the spectrum was observed.

Results

Preparation of Gold Clusters. The yields obtained with the metal evaporation technique were much higher than those obtained with the $NaBH_4$ method (e.g., 60–70% vs. 10–20%, respectively, for $Au_{11}(PPh_3)_7(SCN)_3$ (Ph = C_6H_5)).

Apart from the preparation route described above, $Au_{11}(PPh_3)_7(SCN)_3$ could also be prepared through evaporation of gold into an ethanolic solution of KSCN and PPh_3. From the latter reaction $Au(PPh_3)_2SCN$ could be isolated as a by-product, obviously as a result from the oxidation of Au in the solution of PPh_3 and KSCN in ethanol. $Au(O_2)$, recently reported by McIntosh,[12] might be an intermediate in this oxidation reaction. Formation of this intermediate is possible because of the air flow through the system. Subsequent reaction of $Au(PPh_3)_2SCN$ with Au leads to $Au_{11}(PPh_3)_7(SCN)_3$. The earlier described cluster compounds $Au_9(PPh_3)_8(PF_6)_3$ and $Au_9[P(p\text{-}MeC_6H_4)_3]_8(PF_6)_3$[13] could also be prepared by the evaporation technique via the reaction of $Au(PAr_3)_2NO_3$ and PAr_3 with gold in ethanol ($Au(PAr_3)_2NO_3{:}PAr_3{:}Au = 3{:}2{:}6$). Addition of NH_4PF_6 results in the precipitation of the Au_9-cluster compounds with a 60% yield. Mössbauer spectra of these compounds will be reported later.

Mössbauer Spectra. The Mössbauer spectra of $Au_{11}(PAr_3)_7X_3$ with Ar = p-ClC_6H_4 and X = SCN, I, and CN are given in Figure 2. Practically the same spectra were obtained for the corresponding PPh_3 compounds. In the crystal structures of the Au_{11} clusters five different gold sites can be distinguished[2-4] (see Figure 1). Each site can give rise to one quadrupole pair of Mössbauer absorption lines. To reduce the number of parameters we made the following assumptions:

(a) To account for saturation broadening the line width of all absorptions is taken as 2.00 mm/s which is slightly more than the natural line width (1.86 mm/s).

(b) For each of the peripheral gold atoms at sites 2, 3, 4, and 5 (see Figure 1), the intensities were assumed to be equal whereas the intensity for the central gold atom is allowed to be different. This is reasonable as the Mössbauer absorption intensity is proportional to $\exp(-\langle x^2\rangle_T)$, where $\langle x^2\rangle_T$ is the mean-squared vibration amplitude at temperature T.

(c) Because of the almost spherical environment of the central gold atom we assume that the quadrupole splitting of this atom is zero.

The number of parameters is thus reduced to eleven: nine line-position parameters and two intensities. This number can be further reduced assuming that variation of X ligands at site 4 has a negligible influence upon the other gold sites. Thus,