Journal of Fluorine Chemistry, 11 (1978) 365–385

Received: September 12, 1977

FLUOROCARBON BRIDGED LIGANDS WITH DICYCLOHEXYLPHOSPHINO GROUPS. THEIR PREPARATION AND SOME METAL CARBONYL COMPLEXES AND A CRYSTAL STRUCTURE OF $[(C_6H_{11})_2PC=C(CF_2)_2]_2Mo(CO)_4$

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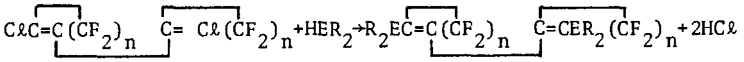
SUMMARY

$(C_6H_{11})_2PH$ reacts with $ClC=CCl(CF_2)_n$ and $[ClC=C(CF_2)_2]_2$ in DMF solution to give $XC=CY(CF_2)_n$ and $[XC=C(CF_2)_n]_2$ (X = Y = $(C_6H_{11})_2P$; X = $(C_6H_{11})_2P$, Y = Cl; n = 2,3). The di(tertiary phosphines) react with $M(CO)_6$ yielding $(P\text{-}P)M(CO)_4$ (M = Cr, Mo, W). The structure of one of these $[(C_6H_{11})_2PC=C(CF_2)_2]_2Mo(CO)_4$ was solved and refined to a final conventional R factor of 0.034. The unit cell contains two molecules and is triclinic with a = 13.532(7), b = 16.532(7), c = 9.856(4)Å, α = 117.06(2), β = 90.56(2), γ = 100.35(2)°. The molybdenum is in a irregular octahedral environment. The seven-membered chelate ring is considerably puckered and the Mo-P bonds are longer than usual.

INTRODUCTION

In a previous publication [1] we described the reactions of diphenylphosphine and dimethylarsine with certain 2,2'-dichloro(bicycloalken-1-yl) derivatives which proceed as indicated in equation 1 (E = As, R = CH_3, n = 2,3;



$$ClC=C(CF_2)_nC=CCl(CF_2)_n + HER_2 \rightarrow R_2EC=C(CF_2)_nC=CER_2(CF_2)_n + 2HCl \qquad (1)$$

$E = P$, $R = C_6H_5$, $n = 2$) although in the case $E = P$, $R = C_6H_5$, $n = 3$, only the monosubstituted derivative was obtained. This work was a natural extension of our earlier studies on the similar substitution reactions of 1,2-dihalopolyfluorocycloalkenes [2], equation 2. Here again some

$$\mathrm{ClC = CC\ell(CF_2)_n + HER_2 \rightarrow R_2EC = CER_2(CF_2)_n + 2HC\ell} \qquad (2)$$

monosubstituted products were obtained but usually these resulted from the lower temperature reactions of secondary arsines in the absence of solvent. The new di(tertiary phosphine) $[(C_6H_5)_2PC = C(CF_2)_2]_2$(XIII) proved to be very interesting in that it is photochromic. The solid is yellow in the dark and red in sunlight. The process is reversible although not yet understood. Since the bis(phosphine oxide) of XIII did not show this property it seemed that it was associated with the presence of lone pairs on the phosphorus and that the photochromism might be enhanced by replacing the phenyl groups in XIII by less electronegative cyclohexyl groups.

This study reports the synthesis and Group VI carbonyl complexes of such a compound, II, and the related compounds $(C_6H_{11})_2PC = CP(C_6H_{11})_2(CF_2)_n$ ($n = 2$, (I); $n = 3$ (III)).

RESULTS AND DISCUSSION

The reactions summarized in equation 2 have usually been carried out in the absence of solvent in a Carius tube and applying heat (or cooling) as the circumstances demanded. In a brief report Stockel [3] described the reaction between $(C_6H_{11})_2PH$ and 1,2-dichlorohexafluorocyclopentene in DMF solution which proceeds as indicated in equation 3. ($n = 3$, $R = C_6H_{11}$).

$$\mathrm{R_2PH + C\ell C = CC\ell(CF_2)_n \xrightarrow{DMF} R_2PC = CPR_2(CF_2)_n + R_2PC = CC\ell(CF_2)_n} \qquad (3)$$

The disubstituted derivative with $R = C_6H_5$ and $n = 3$ had been previously reported [4] as the only product from the reaction in the absence of solvent. However, Stockel [3] obtained only the monosubstituted compound ($R = C_6H_5$, $n = 3$) from the reaction in DMF. In the present investigation we have verified the DMF reaction for $R = C_6H_{11}$ and have isolated both the disubstituted (III) and monosubstituted products. The latter is a low melting solid (m.p. 26°), previously reported as a liquid [3], which undergoes some very interesting reactions with metal carbonyls [5]. The yield of the former is increased if higher phosphine/fluorocarbon ratios are used. We have also found that when dicyclohexylphosphine and 1,2-dichlorotetrafluorocyclobutene are mixed in DMF, both derivatives are obtained (eq. 3, n = 2, R = C_6H_{11}).

Diphenylphosphine reacts with 2,2'-dichlorooctafluoro-(bi-1-cyclobuten-1-yl) in ether solution giving the disubstituted product XIII (eq. 1, n = 2, R = C_6H_5) although only the monosubstituted compound is obtained when the bi-1-cyclopenten-1-yl derivative is used. We now find that DMF can be used as solvent for these reactions as well and under these conditions dicyclohexylphosphine yields the di(tertiary phosphine) II (eq. 1, n = 2, R = C_6H_{11}). This derivative is very similar to the photochromic compound XIII (R = C_6H_5) and was prepared for reason outlined in the Introduction. Like XIII, II is yellow in the dark but unfortunately the solid is also permanently yellow in sunlight. The solid state structure of XIII has the cisoid conformation [6]. Soulen _et al._ [7] have suggested that 2,2'-dichlorooctafluoro-(bi-1-cyclobuten-1-yl) has the transoid structure.

We have previously established that the diphenylphosphino derivatives $(C_6H_5)_2P\overline{C = CP(C_6H_5)_2(C}F_2)_n$ (n = 2,3,4; f_{2n}fos) and XIII readily form chelate complexes of the form $(P\text{-}P)M(CO)_4$ (M = Cr, Mo, W) when reacted with the Group VI hexacarbonyls [1,8]. Similar compounds are obtained from the bis(dicyclohexylphosphino) derivatives I, II, and III (Tables 1 and 2). These have the expected spectroscopic properties such as mass spectra which show peaks corresponding to $[P\text{-}n(CO)]^+$ (n = 0-4). An unexpected feature is the extra ν(CO) band in the i.r. spectra of the chromium and tungsten derivatives of I; four bands are expected for compounds with C_{2v} symmetry [9]. Five bands have been observed in the spectra of $f_6fosM(CO)_4$ (M = Cr, Mo, W) yet the corresponding cyclobutene derivatives $f_4fosM(CO)_4$ have only four [8]. A rationalization was given for these observations in terms of the conformation of the cyclopentene bridging group. However, this is now unacceptable since as seen in Table 2 it is the cyclobutene derivative which is anomalous and not the cyclopentene.

The carbonyl stretching frequencies of the derivatives of I are slightly lower than those reported for the corresponding $f_n$fos complexes suggesting that the cyclohexyl groups make the new di(tertiary phosphines) better σ-donors (or worse π-acceptors). Similar conclusions can be reached

TABLE 1

Analytical Data for New Compounds

		Color	Melting Point (°C)	Analyses (%)			
				C		H	
				Calc.	Found	Calc.	Found
I	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2$	white	126	64.8	64.8	8.49	8.55
II	$[C_6H_{11})_2PC = CCF_2CF_2]_2$	yellow	174	59.8	59.8	6.85	6.99
III	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2CF_2$	yellow	176	61.3	61.1	7.75	7.50
IV	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2Cr(CO)_4$	yellow	221	56.3	56.6	6.50	6.64
V	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2Mo(CO)_4$	yellow	208	52.9	53.2	6.11	6.12
VI	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2W(CO)_4$	yellow	220	47.1	48.1	5.45	5.71
VII	$[(C_6H_{11})_2PC = CCF_2CF_2]_2Cr(CO)_4$	dark purple	175	53.6	53.4	5.46	5.54
VIII	$[(C_6H_{11})_2PC = CCF_2CF_2]_2Mo(CO)_4$	dark red	164	50.8	50.8	5.17	5.10
IX	$[(C_6H_{11})_2PC = CCF_2CF_2]_2W(CO)_4$	dark red	176	46.0	45.8	4.69	4.59
X	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2CF_2Cr(CO)_4$	orange	230	54.1	54.4	6.06	6.00
XI	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2CF_2Mo(CO)_4$	yellow	230	51.0	51.6	5.71	5.86
XII	$(C_6H_{11})_2PC = CP(C_6H_{11})_2CF_2CF_2CF_2W(CO)_4$	yellow-orange	220	45.8	45.5	5.13	4.93

TABLE 2

Preparative and Spectroscopic Data for New Complexes

Reactants	Conditions T(°C)	Time (h)	Product	Yield (%)	^{19}F n.m.r.[a]	ν(CO)[b]				
I + $Cr(CO)_6$	130	18	IV	70	108.0	2020(m)	1926(m)	1908(s)	1898(s)	1870(sh)
I + $Mo(CO)_6$	130	16	V	88	108.4	2030(m)	1932(s)	1910(s)	---	1880(sh)
I + $W(CO)_6$	150	144	VI	48	109.1	2020(m)	1925(m)	1910(s)	1900(s)	1870(sh)
II + $Cr(CO)_6$	150	24	VII	75	104.8 110.8	2030(s)	1935(s)	1920(s)	1910(s)	
II + $Mo(CO)_6$	120	6	VIII	80	105.8 112.4	2030(s)	1932(s)	1920(s)	1908(s)	
II + $W(CO)_6$	140	216	IX	22	106.0 111.5	2040(s)	1940(s)	1922(s)	1915(s)	
III + $Cr(CO)_6$	150	96	X	78	109.2(2) 128.2(1)	2003(s)	1920(m)	1890(s)		
III + $Mo(CO)_6$	120	20	XI[c]	44	109.2(2) 128.6(1)	2010(s)	1922(m)	1895(s)		
III + $W(CO)_6$	150	168	XII	41	109.5(2) 128.0(1)	2005(s)	1920(m)	1891(s)		

[a] The ^{1}H n.m.r. spectra of all complexes consists of a broad multiplet in the region 1.0 - 2.5

[b] Spectra run in cyclohexane except X, XI and XII for which the solvent was benzene.

[c] Also prepared from III+norbornadienetetracarbonylmolybdenum in refluxing C_6H_{12}(3.5 h).

regarding the properties of II and III. In addition, the high frequency bands, $A_1^{(2)}$, of the complexes of II are higher than those of the corresponding diphenylphosphino compound [1] yet those of the complexes of III are considerably lower. Since these frequencies involve trans carbonyl groups which are cis to the phosphine ligand, it is clear that the electronic effects of these ligands are not easily predictable. In this connection it should be noted that that the CO stretching frequencies of the complexes $f_n fosM(CO)_4$ are essentially independent of n. This is not the case for the cyclohexyl analogues.

The crystal structure of VIII was determined to see if the bulky cyclohexyl groups would have any large effect. (We have previously described the structure of $[(CH_3)_2AsC=C(CF_2)_n]_2Mo(CO)_4$ (n = 2,3) [1,10].) The crystal lattice of VIII contains discrete molecules and a perspective view of one is shown in Fig. 1.

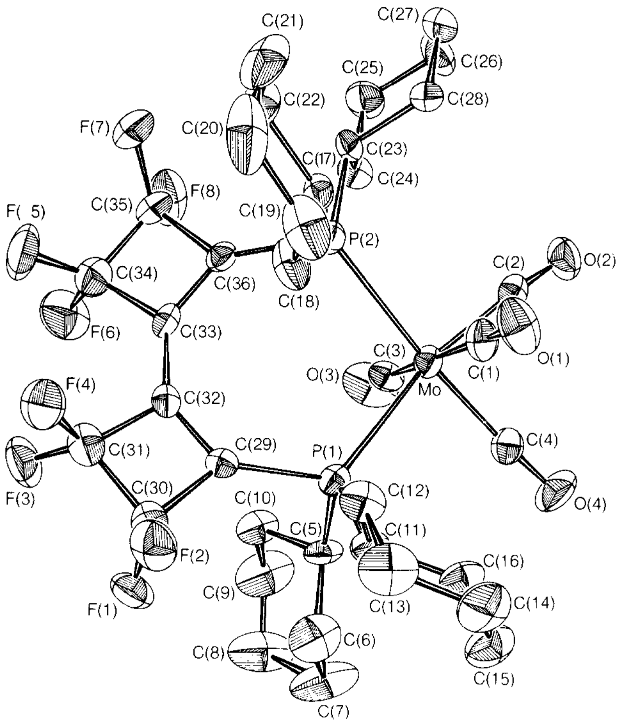


Figure 1. A perspective view of the molecular structure of VIII showing the numbering scheme employed in the Tables.

The molybdenum atom has an irregular octahedral environment comprising the two phosphorus atoms and the four carbonyl groups. The seven-membered chelate ring is considerably puckered.

The Mo-P bonds have lengths of 2.555(3) and 2.546(2)Å (Table 3) and are longer than those usually observed for Mo(O) derivatives of phosphines. For example in $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2Mo(CO)_4$ this distance is 2.505(5)Å [11] and in $((C_6H_5)_2PC_6H_4CH = CHCH_3)Mo(CO)_4$, 2.517(3)Å [12]. As expected the Mo-P distance seems to decrease as the oxidation state of the molybdenum increases; for example it is 2.477(5)Å in $[(C_2H_5)_3PMo(CO)_3P(CH_3)_2]_2$ [13] and 2.481(5)Å in $(C_5H_5)Mo(CO)_2P(C_6H_5)_3I$ [14]. The only comparable Mo-P distances are found in seven-coordinate complexes such as $[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Mo(CO)_3Br_2$ where the average distance is 2.559Å [15]. This comparison suggests that the elongation of the Mo-P bonds in VIII is the result of steric effects. The Mo-CO distances are not significantly different from each other and are similar to the values reported for other complexes [e.g. 11-15] as are the C-O distances.

The four cyclohexane rings are linked asymmetrically to the two phosphorus atoms and adopt the chair conformation. The C-C bond lengths are in the range 1.387-1.539Å. The C-P-C angles range from 99.7 to 104.9° and are considerably smaller than the tetrahedral value of 109.47°. This is invariably found in complexes of phosphines and it has been attributed to the fact that the P-Metal bond has more s-character than the others [14].

In the bridging group the cyclobutene rings are slightly distorted from planar (Table 4) and are joined by a short C(32)-C(33) bond of 1.451(12)Å. This "butadiene type" structure is found in the analogous complexes with dimethylarsino groups [1,10].

EXPERIMENTAL

All reactions were carried out either in conventional reaction flasks under a nitrogen atmosphere or in sealed evacuated Carius tubes.

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer and were calibrated using polystyrene; only selected bands are quoted. All nmr spectra were run using $CDCl_3$ solutions and a Varian T-60 instrument. Chemical shifts are given in ppm downfield from internal TMS (^1H) and upfield from internal $CFCl_3$ (^{19}F). Mass spectra were recorded using an AEI MS-9 spectrometer. Melting points were determined on a Gallenkamp

TABLE 3

Bond Lengths and Angles

(i) bond lengths (Å)^{a,b}

Mo-P(1)	2.555(3)	2.582(3)^{a}
Mo-P(2)	2.546(2)	2.579(2)^{a}
Mo-C(1)	2.004(6)	2.013(6)^{b}
Mo-C(2)	1.972(9)	1.977(9)^{b}
Mo-C(3)	2.055(7)	2.058(7)^{b}
Mo-C(4)	1.950(7)	1.957(7)^{b}
P(1)-C(5)	1.848(6)	
P(1)-C(11)	1.856(8)	
P(1)-C(29)	1.835(7)	
P(2)-C(17)	1.857(6)	
P(2)-C(23)	1.848(9)	
P(2)-C(36)	1.827(7)	
C(1)-O(1)	1.150(8)	
C(2)-O(2)	1.156(11)	
C(3)-O(3)	1.133(8)	
C(4)-O(4)	1.172(9)	
C(5)-C(6)	1.468(14)	
C(6)-C(7)	1.554(10)	
C(7)-C(8)	1.539(13)	
C(8)-C(9)	1.387(17)	
C(9)-C(10)	1.524(10)	
C(10)-C(5)	1.539(10)	
C(11)-C(12)	1.529(8)	
C(12)-C(13)	1.535(13)	
C(13)-C(14)	1.497(12)	
C(30)-F(1)	1.339(10)	1.368(9)^{b}
C(30)-F(2)	1.346(9)	1.373(9)^{b}
C(31)-F(3)	1.345(9)	1.373(9)^{b}
C(31)-F(4)	1.345(8)	1.371(7)^{b}
C(34)-F(5)	1.341(9)	1.379(10)^{b}

C(14)-C(15)	1.502(10)
C(15)-C(16)	1.533(13)
C(16)-C(11)	1.526(10)
C(17)-C(18)	1.515(13)
C(18)-C(19)	1.532(9)
C(19)-C(20)	1.502(13)
C(20)-C(21)	1.500(17)
C(21)-C(22)	1.534(10)
C(22)-C(17)	1.519(10)
C(23)-C(24)	1.534(8)
C(24)-C(25)	1.530(13)
C(25)-C(26)	1.519(12)
C(26)-C(27)	1.517(10)
C(27)-C(28)	1.513(14)
C(28)-C(23)	1.531(10)
C(29)-C(30)	1.522(14)
C(29)-C(32)	1.335(10)
C(30)-C(31)	1.529(12)
C(31)-C(32)	1.496(13)
C(32)-C(33)	1.451(12)
C(33)-C(34)	1.495(11)
C(34)-C(35)	1.524(17)
C(35)-C(36)	1.520(11)
C(36)-C(33)	1.359(12)

C(34)-F(6)	1.350(10)	1.392(8)[b]
C(35)-F(7)	1.337(10)	1.373(9)[b]
C(35)-F(8)	1.349(8)	1.389(10)[b]

[a] Each atom assumed to move independently after correction for thermal motion.

[b] The second atom is assumed to ride on the first.

(ii) bond angles (°)

P(1)-Mo-P(2)	98.7(1)	F(1)-C(30)-F(2)	106.3(8)
P(1)-Mo-C(1)	93.8(3)	F(1)-C(30)-C(29)	117.8(6)
P(1)-Mo-C(2)	168.2(2)	F(1)-C(30)-C(31)	114.3(6)
P(1)-Mo-C(3)	91.0(3)	F(2)-C(30)-C(29)	116.9(7)
P(1)-Mo-C(4)	86.2(3)	F(2)-C(30)-C(31)	114.6(6)
P(2)-Mo-C(1)	88.0(2)	C(29)-C(30)-C(31)	86.5(7)
P(2)-Mo-C(2)	93.1(2)	F(3)-C(31)-F(4)	106.2(6)
P(2)-Mo-C(3)	92.5(2)	F(3)-C(31)-C(30)	116.3(7)
P(2)-Mo-C(4)	175.0(3)	F(3)-C(31)-C(32)	116.9(7)
C(1)-Mo-C(2)	87.4(3)	F(4)-C(31)-C(30)	116.4(7)
C(1)-Mo-C(3)	175.1(4)	F(4)-C(31)-C(32)	114.5(7)
C(1)-Mo-C(4)	90.9(3)	C(30)-C(31)-C(32)	86.1(7)
C(2)-Mo-C(3)	87.7(3)	C(29)-C(32)-C(31)	95.1(7)
C(2)-Mo-C(4)	82.0(4)	C(29)-C(32)-C(33)	138.9(7)
C(3)-Mo-C(4)	88.2(3)	C(31)-C(32)-C(33)	126.0(6)
Mo-C(1)-O(1)	177.5(9)	C(32)-C(33)-C(34)	127.5(8)
Mo-C(2)-O(2)	174.3(6)	C(32)-C(33)-C(36)	138.0(6)
Mo-C(3)-O(3)	174.3(7)	C(34)-C(33)-C(36)	94.4(7)
Mo-C(4)-O(4)	174.3(9)	F(5)-C(34)-F(6)	107.0(7)
Mo-P(1)-C(5)	110.7(3)	F(5)-C(34)-C(33)	117.1(7)
Mo-P(1)-C(11)	117.4(3)	F(5)-C(34)-C(35)	114.7(7)
Mo-P(1)-C(29)	121.9(3)	F(6)-C(34)-C(33)	116.9(6)
Mo-P(2)-C(17)	116.4(2)	F(6)-C(34)-C(35)	113.7(8)
Mo-P(2)-C(23)	117.4(2)	C(33)-C(34)-C(35)	86.7(7)
Mo-P(2)-C(36)	115.6(2)	F(7)-C(35)-F(8)	105.6(8)
C(5)-P(1)-C(11)	104.9(3)	F(7)-C(35)-C(34)	116.0(8)

C(5)-P(1)-C(29)	99.7(3)	F(7)-C(35)-C(36)	115.0(8)
C(11)-P(1)-C(29)	99.8(3)	F(8)-C(35)-C(34)	115.5(6)
C(17)-P(2)-C(23)	104.3(3)	F(8)-C(35)-C(36)	117.5(7)
C(17)-P(2)-C(36)	100.6(3)	C(34)-C(35)-C(36)	87.0(7)
C(23)-P(2)-C(36)	100.0(3)	P(2)-C(36)-C(33)	132.6(6)
P(1)-C(29)-C(30)	133.5(6)	P(2)-C(36)-C(35)	135.2(7)
P(1)-C(29)-C(32)	133.9(7)	C(33)-C(36)-C(35)	91.9(6)
C(30)-C(29)-C(32)	92.3(6)	P(1)-C(5)-C(6)	120.2(5)
P(1)-C(5)-C(10)	113.2(5)	P(2)-C(17)-C(22)	117.8(5)
C(6)-C(5)-C(10)	108.1(6)	C(18)-C(17)-C(22)	109.2(6)
C(5)-C(6)-C(7)	110.9(8)	C(17)-C(18)-C(19)	109.8(7)
C(6)-C(7)-C(8)	108.3(7)	C(18)-C(19)-C(20)	109.9(7)
C(7)-C(8)-C(9)	112.0(8)	C(19)-C(20)-C(21)	113.0(8)
C(8)-C(9)-C(10)	113.7(9)	C(20)-C(21)-C(22)	112.9(7)
C(9)-C(10)-C(5)	110.7(6)	C(21)-C(22)-C(17)	110.3(7)
P(1)-C(11)-C(12)	113.9(5)	P(2)-C(23)-C(24)	111.2(5)
P(1)-C(11)-C(16)	112.5(5)	P(2)-C(23)-C(28)	111.8(5)
C(12)-C(11)-C(16)	109.3(5)	C(24)-C(23)-C(28)	110.2(6)
C(11)-C(12)-C(13)	109.9(6)	C(23)-C(24)-C(25)	110.5(6)
C(12)-C(13)-C(14)	111.8(8)	C(24)-C(25)-C(26)	109.7(6)
C(13)-C(14)-C(15)	111.8(6)	C(25)-C(26)-C(27)	112.0(8)
C(14)-C(15)-C(16)	111.1(7)	C(26)-C(27)-C(28)	112.9(7)
C(15)-C(16)-C(11)	110.8(7)	C(27)-C(28)-C(23)	111.5(6)
P(2)-C(17)-C(18)	112.7(5)		

apparatus and are uncorrected. Microanalyses were performed by Mr. Peter Borda of the Department of Chemistry, U.B.C.

The hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) and dicyclohexylphosphine were obtained from Strem Chemicals Incorporated. Fluorocarbons were purchased from PCR Incorporated. All were used without further purification.

Preparation of 1,2-Bis(dicyclohexylphosphino)hexafluorocyclopentene (III)

A 100 ml three necked flask fitted with nitrogen inlet, reflux condenser, stirrer, and rubber septum stopper was charged with 1,2-dichlorohexafluorocyclopentene-1 (1.22 g, 4.97 mmol) in 8 ml of dimethylformamide (DMF). The flask was cooled to 0° and dicyclohexylphosphine (1.96 g,

TABLE 4

Deviations of Atoms from Least-Square Planes
Planes through the carbon atoms of the two cyclobutene rings[a]

(i) $0.4456x + 0.5656y + 0.6939z - 1.2377 = 0$ $\chi^2 = 9.16$

atoms	deviations (Å)
C(29)	-0.012
C(30)	0.010
C(31)	-0.011
C(32)	0.012

(ii) $0.1490x + 0.3729y + 0.9158z - 3.6564 = 0$ $\chi^2 = 5.45$

atoms	deviations (Å)
C(33)	-0.009
C(34)	0.008
C(35)	-0.008
C(36)	0.009

[a] χ^2 is $\Sigma p^2/\sigma^2(p)$, where p is the deviation in Å of the atom normal to the plane.

9.9 mmol) was added using a syringe. After an hour the solution was warmed to 20°, left for 24 h (no precipitate formed), and refluxed for 2 h. On cooling to 20° a yellow solid appeared which was filtered off in a nitrogen atmosphere and dried under vacuum. The yellow filtrate was cooled to 5° and an oily solid separated which slowly crystallized into a pale yellow solid. (In other preparations the filtrates were added to water and the resulting suspension extracted with ether; the ether extracts were washed well with water, dried ($MgSO_4$), and removal of solvent gave the crystalline product.)

Recrystallization of the initial precipitate from hexane yielded 1.12 g (40%) of shiny yellow crystals which were identified as III, m.p. 184° (lit. 194-194.5° [3]). Mass spec. m/e 568 (P^+). i.r. (C_6H_{12}) 1175, 1120, 1068, 995 cm.$^{-1}$ ^{1}H nmr 0.9-2.36 (m, broad). ^{19}F nmr 107.7 (m, area 2), 134 (m, area 1).

The second solid was identified as 1-chloro-2-dicyclohexylphosphino hexafluorocyclopentene-1, m.p. 26°. Mass spec. m/e 406 (P^+). i.r. (C_6H_{12}) 1580 cm^{-1} (c=c). ^{1}H nmr 0.85-2.48 (m, broad). ^{19}F nmr 105.2 (m), 114 (m), 129.6 (m) all of equal area. Anal. Found: C, 50.2; H, 5.65. Calc. for $C_{17}H_{22}ClF_6P$: C, 50.2; H, 5.41%.

Preparation of 1,2-bis(dicyclohexylphosphino)tetrafluorocyclobutene-1 (I)

As described above for the preparation of III, 1,2-dichlorotetrafluorocyclobutene-1 (0.97 g, 4.79 mmol) in DMF (15 ml) was treated with dicyclohexylphosphine (1.95 g, 9.85 mmol) in DMF (5 ml). The solution was warmed to 20° and left for 24 h. The white solid which precipitated was filtered off in a nitrogen atmosphere, dried under vacuum, and recrystallized from hexane to give 1.5 g (60%) of I. Mass spec. m/e 518 (P^+). i.r. (C_6H_{12}) 1310 (s), 1228 (m), 1142 (s), 1105 (s) cm^{-1} (C-F). ^{1}H nmr 0.85-2.20 (m, broad). ^{19}F nmr 106.4 (m). Anal. Table 1.

The filtrate which was pale yellow was extracted with ether, washed and dried as above, to yield a colorless oily liquid which was identified as 1-chloro-2-dicyclohexylphosphinotetrafluorocyclobutene-1. Mass spec. m/e 356 (P^+). i.r. (C_6H_{12}) 1569 cm^{-1} (c=c). ^{1}H nmr 0.9-2.48 (m, broad). ^{19}F nmr 108.4 (m) and 114.8 (m) of equal area. Anal. Found: C, 54.4; H, 6.42. Calc. for $C_{16}H_{22}ClF_4P$: C, 53.9; H, 6.22%.

Preparation of 2,2'-bis(dicyclohexylphosphino)octafluoro(bi-1-cyclobuten-1-yl)(II)

In the usual way 2,2'-dichlorooctafluoro-(bi-1-cyclobuten-1-yl) (7) (0.56 g, 1.76 mmol) in DMF (10 ml) was reacted with dicyclohexylphosphine (0.7 g, 3.52 mmol) in DMF (5 ml). The mixture was left for 24 h at 20°. The yellow precipitate was filtered off, dried, and recrystallized from hexane to give 0.74 g (65%) of II. Mass spec. m/e 642 (P^+). i.r. (C_6H_{12}) 1310, 1225, 1124 cm^{-1} (C-F). ^{1}H nmr 0.97-2.23 (m, broad). ^{19}F nmr 105.8 (m) and 109.4 (m) of equal area.

Preparation of the Metal Carbonyl Complexes

A general method of preparation of the new complexes is given below. The details applying to specific complexes are listed in Table 2.

A 1:1 mole ratio of ligand to hexacarbonyl in ~8 ml of benzene was heated in a Carius tube at the indicated temperature for 12-216 h. At the end of the reaction period the tube was opened and the solvent removed. The solid residue was then chromatographed on a Florosil column and the colored bands were isolated. The solvent was then removed at reduced pressure to give the crude complex. All solids except X and XI (which were recrystallized from benzene) and XII (from dichloromethane) were recrystallized from hexane.

Determinate of the Crystal Structure of VIII

A crystal of dimension 0.20 x 0.20 x 0.17 mm was mounted with its a axis parallel to the axis of the goniometer head, and was used for all diffraction work. Weissenberg and precession photographs taken with CuKα ($\lambda = 1.54184$Å) radiation indicated that the crystals were triclinic. Preliminary cell dimensions were measured from these photographs, and were then refined by a least-squares fit to the 2θ's of twelve computer centered reflections ($2\theta > 22°$) measured using monochromated MoKα_1 ($\lambda = 0.70926$Å) radiation, on a Picker FACS-1 computer controlled diffractometer.

Intensities were collected over the range $0.5° \leq 2\theta \leq 35°$ by the θ-2θ scan technique. Each reflection was scanned with a base width of 1.2° (extended for the splitting of α_1 and α_2) at a speed of 2° min.$^{-1}$, and twenty second background measurements were taken at each of the scan limits. In total 2459 reflections were collected of which 437 were coded unobserved ($I \leq 2.3\sigma(I)$. where σ(I) is the standard deviation).

Intensities were corrected for background and Lorentz-polarization effects, but not for the absorption. Crystal data are summarized as follows: $C_{36}H_{44}F_8O_4P_2Mo$, fw = 850.619, Triclinic, a = 13.532(7)Å, b = 16.532(7)Å, c = 9.856(4)Å, α = 117.06(2)°, β = 90.56(2)°, γ = 100.35(2)°, V = 1920.9Å^3, Z = 2, d(calc) = 1.470 g cm^{-3}, d(obs) = 1.40 g cm^3 (flotation in CCl_4/C_6H_5Br) u(MoKα) = 5.01 cm^{-1}, Space group P$\bar{1}$.

The structure was solved using the heavy atom method and was refined by full-matrix least-squares techniques. Refinement of the positional parameters for the molybdenum and two phosphorus atom yielded an R value ($R = \Sigma(|Fobs| - |Fcalc|)/\Sigma|Fobs|$) of 0.38, and a Fourier synthesis phased by these atoms revealed the positions of all fluorine, oxygen and most carbon atoms, and thus confirmed that the space group is $P\bar{1}$. The positions of the other non-hydrogen atoms were determined from subsequent electron-density difference syntheses. With hydrogen atoms not included, the refinement of the positional and isotropic thermal parameters of all non-hydrogen atoms gave R = 0.087.

At this stage the 44 hydrogen atoms were then included in the structure-factor calculations at computed positions assuming C-H = 0.96Å and B = 6.0Å^2, and weights ($= 1/(\sigma F)^2$) were given in terms of $\sigma F = \sigma(I)/(Lp)(2Fo)$. The refinement converged at R = 0.049 when only the molybdenum, phosphorus, and the terminal fluorine and oxygen atoms were assigned anisotropic temperature factors, and at R = 0.034 when all non-hydrogen atoms were refined anisotropically.

Because of the limitations of the least-squares program, not all parameters could be varied in each refinement cycle. The parameters for the heavy atoms were refined together with the parameters of alternate groups of non-hydrogen atoms.

Atomic scattering factors for non-hydrogen atoms and anomalous dispersion corrections $\Delta f'$ and $\Delta f''$, for the molybdenum and phosphorus atoms were taken from the International Tables for X-ray Crystallography, Vol. IV, (1974), while the scattering factor for hydrogen atoms was taken from a Table of Stewart, Davidson, and Simpson [16].

The final atomic coordinates and thermal parameters with estimated standard deviation are listed in Tables 5 and 6. A perspective view of the molecule and the atom labelling is shown in Figure 1. Bond lengths and bond angles are listed in Table 3.

A copy of the table of calculated and observed structure factors can be obtained, if requested, from the authors.

TABLE 5

Fractional Atomic Coordinates[a]

Atom	x	y	z
Mo	-16826(5)	23862(4)	21105(7)
P(1)	-17663(14)	13339(12)	33820(20)
P(2)	-27383(14)	34998(13)	38452(21)
F(1)	-2928(3)	84(3)	5380(5)
F(2)	-1917(3)	1297(3)	7083(5)
F(3)	-4482(3)	927(3)	6347(5)
F(4)	-3468(3)	2167(3)	7985(4)
F(5)	-5252(3)	2791(4)	6750(5)
F(6)	-5772(3)	1657(3)	4492(6)
F(7)	-5020(3)	3974(3)	5569(5)
F(8)	-5546(3)	2839(3)	3339(5)
O(1)	265(4)	3797(4)	4201(6)
O(2)	-1284(4)	3339(3)	6(6)
O(3)	-3555(4)	1040(4)	-329(6)
O(4)	-365(4)	1159(4)	-227(6)
C(1)	-453(5)	3280(5)	3468(8)
C(2)	-1464(5)	3018(5)	824(8)
C(3)	-2921(6)	1522(5)	598(8)
C(4)	-843(5)	1606(5)	705(8)
C(5)	-2266(5)	110(4)	1973(8)
C(6)	-1890(6)	-637(6)	2093(10)
C(7)	-2242(7)	-1576(5)	620(11)
C(8)	-3404(7)	-1802(6)	400(13)
C(9)	-3794(7)	-1094(6)	352(12)

Fractional Atomic Coordinates[a]

Atom	x	y	z
C(10)	-3427(5)	-152(5)	1747(8)
C(11)	-565(5)	1325(4)	4295(8)
C(12)	-162(5)	2208(5)	5789(8)
C(13)	781(6)	2101(5)	6520(9)
C(14)	1586(6)	1882(6)	5454(10)
C(15)	1203(6)	1037(6)	3952(10)
C(16)	261(5)	1138(5)	3214(8)
C(17)	-2100(5)	4405(4)	5746(7)
C(18)	-1643(5)	4003(5)	6650(8)
C(19)	-898(6)	4773(6)	7980(9)
C(20)	-1436(7)	5508(7)	9017(9)
C(21)	-1998(7)	5881(6)	8182(10)
C(22)	-2689(6)	5113(5)	6776(9)
C(23)	-3334(5)	4146(4)	3071(7)
C(24)	-3935(5)	3489(5)	1506(8)
C(25)	-4468(5)	4029(5)	922(9)
C(26)	-3694(6)	4770(6)	787(10)
C(27)	-3043(5)	5415(5)	2287(9)
C(28)	-2555(5)	4901(5)	2952(8)
C(29)	-2585(5)	1434(4)	4900(7)
C(30)	-2689(6)	1011(6)	5991(9)
C(31)	-3583(6)	1487(5)	6532(9)
C(32)	-3387(5)	1819(4)	5359(7)
C(33)	-3984(5)	2351(4)	4987(7)
C(34)	-5053(6)	2429(6)	5288(10)

Fractional Atomic Coordinates[a]

Atom	x	y	z
C(35)	-4928(6)	3105(6)	4617(10)
C(36)	-3848(5)	2969(4)	4418(7)
H(51)[b]	-206	-7	103
H(61)	-117	-48	224
H(62)	-214	-69	296
H(71)	-198	-153	-25
H(72)	-200	-206	73
H(81)	-363	-236	-54
H(82)	-365	-190	124
H(91)	-360	-105	-55
H(92)	-452	-126	28
H(101)	-368	31	160
H(102)	-367	-17	264
H(111)	-71	82	454
H(121)	-67	232	648
H(122)	1	273	558
H(131)	104	267	743
H(132)	59	161	679
H(141)	214	177	592
H(142)	182	240	526
H(151)	103	50	413
H(152)	172	95	327
H(161)	44	165	298
H(162)	1	58	229
H(171)	-155	475	551

Fractional Atomic Coordinates[a]

Atom	x	y	z
H(181)	-217	373	705
H(182)	-129	354	599
H(191)	-37	504	758
H(192)	-61	451	855
H(201)	-95	601	978
H(202)	-191	525	950
H(211)	-240	628	887
H(212)	-152	624	785
H(221)	-296	538	621
H(222)	-323	481	711
H(231)	-380	444	377
H(241)	-348	319	79
H(242)	-443	303	160
H(251)	-483	361	-6
H(252)	-493	432	163
H(261)	-404	513	49
H(262)	-326	447	2
H(271)	-346	577	302
H(272)	-252	582	212
H(281)	-223	533	396
H(282)	-206	462	230

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[a] Mo and P atoms X10^5, the other non-hydrogen atoms X10^4, hydrogen atoms X10^3.

[b] H(51) - H(282) were given a B of 6.0$\mathring{A}^2$.

TABLE 6

Thermal Vibration Parameters[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	362(5)	379(5)	353(4)	65(3)	84(3)	132(3)
P(1)	369(13)	353(13)	387(13)	60(11)	27(11)	116(11)
P(2)	405(14)	374(13)	398(13)	65(11)	104(11)	149(11)
F(1)	114(4)	51(3)	85(3)	17(3)	25 (3)	43(3)
F(2)	80(3)	107(4)	67(3)	19(3)	2(3)	54(3)
F(3)	70(3)	95(4)	103(4)	1(3)	25(3)	68(3)
F(4)	123(4)	86(3)	45(3)	33(3)	23(3)	28(3)
F(5)	89(4)	153(5)	96(4)	61(3)	62(3)	77(4)
F(6)	48(3)	93(4)	160(5)	-10(3)	4(3)	72(4)
F(7)	83(4)	76(3)	130(4)	44(3)	60(3)	47(3)
F(8)	46(3)	146(5)	105(4)	13(3)	4(3)	80(4)
O(1)	53(4)	102(5)	94(5)	-27(4)	-16(4)	56(4)
O(2)	87(4)	78(4)	63(4)	12(3)	24(3)	44(4)
O(3)	89(5)	78(5)	87(5)	-15(4)	-49(4)	31(4)
O(4)	94(5)	98(5)	78(5)	53(4)	45(4)	31(4)
C(1)	36(6)	60(6)	56(6)	1(5)	6(5)	29(5)
C(2)	45(5)	52(6)	45(6)	11(4)	10(4)	15(5)
C(3)	61(7)	51(6)	58(6)	19(5)	7(5)	37(5)
C(4)	54(6)	57(6)	43(6)	9(5)	7(5)	20(5)
C(5)	46(6)	29(5)	77(6)	10(5)	-5(5)	18(5)
C(6)	69(7)	74(7)	103(8)	-6(6)	-13(6)	22(7)
C(7)	115(10)	31(6)	121(9)	24(6)	-40(7)	-31(6)
C(8)	72(9)	53(8)	215(12)	-21(6)	-63(8)	44(8)
C(9)	68(8)	66(8)	160(10)	-10(7)	-29(7)	12(8)
C(10)	37(6)	36(6)	79(6)	-3(4)	-12(5)	9(5)
C(11)	40(5)	34(5)	52(5)	4(4)	-3(5)	13(5)
C(12)	57(6)	48(6)	57(6)	0(5)	-13(5)	19(5)
C(13)	72(7)	68(7)	74(7)	2(6)	-29(6)	19(5)
C(14)	47(7)	101(8)	104(8)	13(6)	-14(7)	49(7)
C(15)	52(7)	78(7)	101(8)	19(6)	1(6)	34(7)
C(16)	49(6)	54(6)	66(6)	16(5)	-8(5)	18(5)
C(17)	54(5)	36(5)	32(5)	0(4)	13(4)	6(4)
C(18)	62(6)	64(6)	39(5)	-14(5)	-2(5)	24(5)

Thermal Vibration Parameters[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(19)	88(7)	93(7)	45(6)	-18(7)	-12(6)	32(6)
C(20)	89(9)	113(10)	55(8)	-45(8)	14(7)	4(7)
C(21)	94(9)	53(7)	83(9)	0(6)	39(7)	-22(7)
C(22)	73(6)	56(6)	59(6)	5(6)	19(6)	-4(5)
C(23)	40(5)	30(5)	49(6)	0(4)	14(4)	18(4)
C(24)	47(5)	47(5)	49(6)	5(5)	-3(5)	21(5)
C(25)	59(6)	70(6)	77(6)	21(5)	7(5)	45(5)
C(26)	68(7)	84(7)	105(8)	13(6)	16(6)	76(7)
C(27)	61(6)	49(6)	86(7)	16(5)	19(5)	35(6)
C(28)	57(6)	41(5)	59(6)	14(5)	12(4)	21(5)
C(29)	40(6)	37(5)	38(5)	8(5)	3(5)	18(5)
C(30)	56(7)	51(8)	51(7)	7(6)	7(6)	24(6)
C(31)	66(8)	47(7)	42(8)	-2(7)	8(6)	15(7)
C(32)	36(6)	32(5)	30(6)	-1(5)	3(5)	10(5)
C(33)	31(7)	42(6)	37(6)	6(5)	9(5)	7(5)
C(34)	57(9)	70(8)	73(8)	21(7)	18(7)	41(7)
C(35)	55(8)	56(8)	66(7)	28(6)	22(6)	25(7)
C(36)	40(7)	32(6)	37(5)	11(5)	12(4)	8(5)

[a] The thermal parameters are anisotropic Uij values in the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}\ell^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*h\ell+2U_{23}b^*c^*k\ell)]$$

The values for molybdenum and phosphorus atoms are $\mathring{A}^2 \times 10^4$ while for others $\mathring{A}^2 \times 10^3$.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the National Research Council of Canada. One of us (M.W.) wishes to thank the Canadian Commonwealth Scholarship and Fellowship plan for assistance.

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