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MONO-, DI-, AND TRICYCLIC CHELATE CHROMIUM AREDIFLUOROPHOSPHITE COMPLEXES

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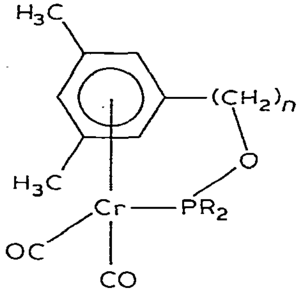
Summary

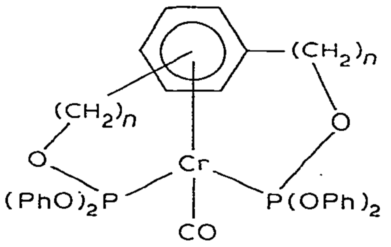
Difluorophosphites are shown to be able to replace all CO groups in arenetricarbonylchromium complexes under UV irradiation. New chromium chelates with polydentate arenedifluorophosphite ligands containing one, two, and three chelate cycles are reported. These are compared with analogous nonchelate phenyldifluorophosphite complexes. The structures of the complexes synthesized are proved by IR and ^{1}H, ^{19}F and ^{31}P NMR spectra and mass-spectrometry.

Introduction

Earlier we have synthesized chelate arene-containing chromium complexes of types I and II [1—3].



(I)



(II) $n \geq 2$

(R = Ph, OPh ; $n \geq 1$)

We have shown that with phosphinite ligands, displacement of one CO ligand only occurs to give I (R = Ph). Weaker electron donors of the phosphite series may replace two CO groups under UV irradiation to give complexes I and II. The reaction, however, terminates when disubstituted species are formed and can not be used to prepare three-bridged arene(tris-phosphite) complexes.

The problem of replacement of more than one CO ligand in arenetricarbonylchromium complexes has not been studied in detail. Several examples of the arene · $Cr(CO)L_2$ (L ≠ CO) complexes are known [4—6]. As for trisubstituted species, the replacement of all three CO ligands in benzenetricarbonylchromium with PF_3 with retention of the C_6H_6—Cr bond has been reported, but without any details [7]. Literature data and the results of our earlier investigations suggest that electronic effects by the substituting ligand L may play the determining role in the replacement of CO. With weaker electron donors than $—OP(OPh)_2$, the reaction may be expected to replace all three CO groups. That prompted us to test OPF_2 as terminal group for the preparation of three-bridged complexes. The mono-, bis-, and tris-β-oxyethylbenzenes have been used to synthesize mono-, di-, and tri-cyclic chelates.

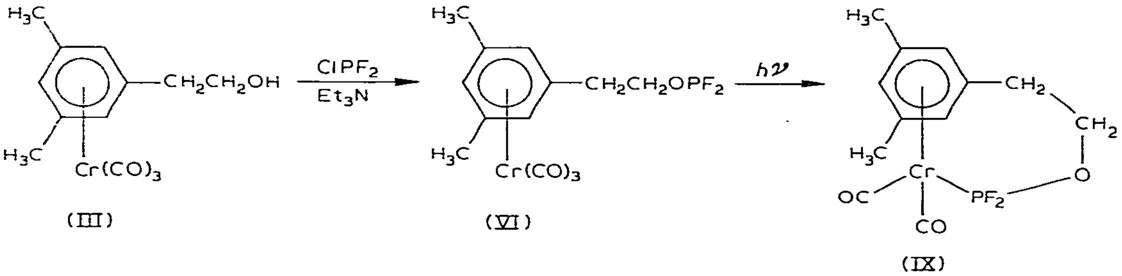
Results and discussion

Mono-, bis-, and tris-β-oxyethylbenzenechromium tricarbonyls III—V were prepared by the usual procedures. It was necessary to find a means for the introduction of the difluorophosphite group into the ω-positions of side chains of arene ligands coordinated to the $Cr(CO)_3$ moiety. By analogy to the methods used [1—3] to introduce phosphite and phosphinite functions, the reaction between alcohol OH groups and $ClPF_2$ in the presence of tertiary amines might be expected to give the desired products. This reaction has not been used in organophosphorus chemistry thus far. Moreover, the route to $ClPF_2$ via the substitution of F for Cl in PCl_3 under the action of SbF_3 is inconvenient because it leads to product mixtures whose separation requires low temperature fractionation [8]. Therefore we used the reaction between Et_2NPF_2 and PCl_3 described earlier [9]. It should be noted that $ClPF_2$ formed in that reaction was not identified in [9].

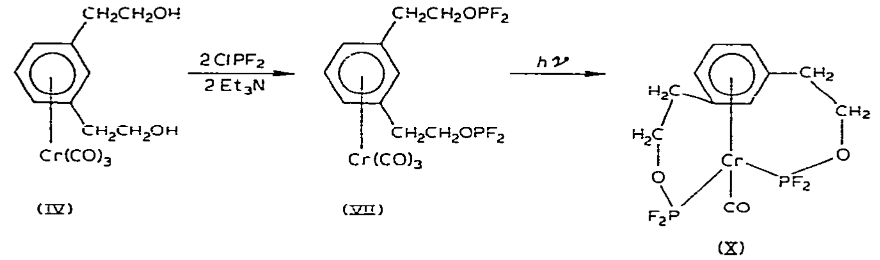
$$Et_2NPF_2 + PCl_3 \xrightarrow{T\ (°C)} Et_2NPCl_2 + ClPF_2$$

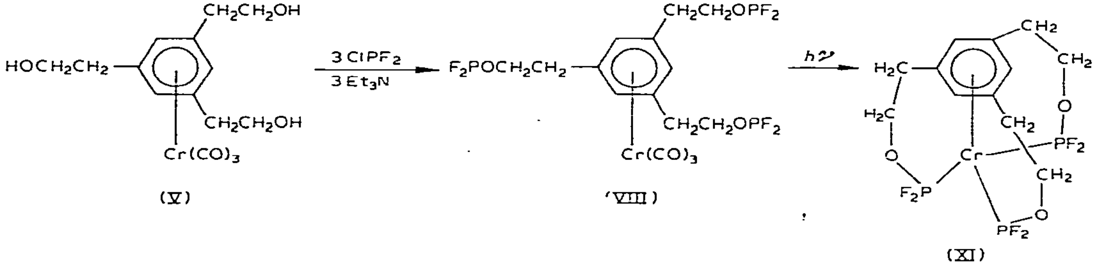
Gaseous $ClPF_2$ was used in reactions with ω-oxyethylsubstituted arene chromium tricarbonyls III—V in the presence of Et_3N (T —30 ÷ —50°C).

Difluorophosphites VI—VIII were obtained in high yields from these reactions.



At the higher temperatures, side reactions occur to an extent which decreases the yields. In order to identify difluorophosphites, compound VI was isolated and characterized by elemental analysis, IR and ^1H, ^{19}F, ^{31}P NMR spectra, and mass spectra (Table 1). The reaction of alcohols with $ClPF_2$ in the presence of Et_3N thus provides a new convenient route to difluorophosphites and may also be used with non-organometallic compounds.





Unlike its action on phosphite derivatives [3], UV irradiation of VI—VIII leads to the formation of not only one- and two-bridged chelates IX and X but also three-bridged derivative XI. The results obtained thus show that difluorophosphite groups may replace all of the CO ligands in arene chromium tricarbonyls to give chelate complexes.

For comparison, we studied the reaction between mesitylenetricarbonylchromium with phenyldifluorophosphite under UV irradiation. Replacement of all three carbonyl groups is also possible in that reaction, the process however terminates at the formation of a mixture containing XII—XIV which is

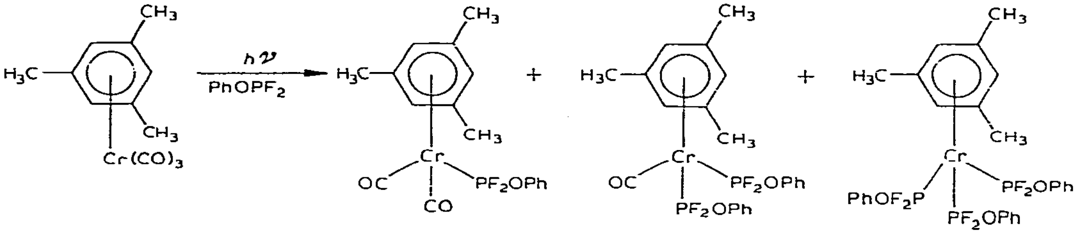
TABLE 1

YIELDS, M.P.'s, AND ANALYTICAL DATA

Compound	Yield (%)	M.p. (°C)	Analytical data (%) [a]		
			C	H	F
VI	80	79—80	44.23 (44.08)	3.93 (3.70)	10.56 (10.72)
IX	64	172—173	43.82 (44.18)	3.98 (4.02)	11.59 (11.65)
X	66	310—320 [b]	34.41 (34.57)	3.11 (3.17)	19.53 (19.88)
XI	50	350—360 [b]	31.18 (30.91)	3.51 (3.24)	24.07 (24.45)

[a] Calculated values are given in parentheses. [b] Decomposition point.

difficult to separate. Only after prolonged irradiation (2 to 3 days) is a mixture predominantly containing XIV formed, while complete conversion of VIII to the three-bridged XI takes 3 to 5 h. The difference may be explained by the chelate effect.



(XII) (XIII) (XIV)

Complexes VI, IX—XI were isolated as light yellow crystals, stable in air. Their solubilities decrease from VI through XI. Compounds VI, IX and X are soluble in most organic solvents, whereas XI is only slightly soluble and its NMR spectrum was obtained with its supersaturated solution in hexamethylphosphortriamide in which it is highly soluble at elevated temperatures.

Compounds VI, IX—XI were characterized by elemental analyses (Table 1), IR and ^{1}H, ^{19}F, ^{31}P NMR spectra and mass spectra, nonchelate complexes XII—XIV by IR and ^{1}H, ^{19}F NMR spectra and mass spectrometry. Two bands (A_1 and E) were observed in the region of carbonyl stretches in VI—VIII, IX, and XII also show two bands, and one band was present in the spectra of X and XIII, as in I and II described earlier [1—3]. Neither XI nor XIV show carbonyl bands. Comparison of the IR spectra of IX, X, and XII, XIII (Tables 2, 3) with the spectra of similar compounds containing diphenylphosphite ligands [1—3] shows that the latter generate higher negative charges on the metal than the ligands present in IX and X. Comparison of the donor—acceptor properties of the difluorophosphite and CO ligands from the IR spectra of the complexes indicates that CO is a weaker donor. Increase of ν(CO) in IX, X from its value in the nonchelate analogues XII and XIII may be explained by specific features of chelate systems of this type [1—3].

The structures of the products obtained were also proved by their NMR spectra. The proton NMR spectra contain coordinated arene proton signals at δ ca. 5 ppm. The replacement of one of the CO ligands with difluorophosphite shifts the arene proton signals to a higher field, similarly to what is observed with phosphite substituents [1]. This observation is consistent with the suggested higher donor ability of difluorophosphite ligands compared with CO (see the discussion of the IR data). The replacement of another CO group shifts the arene proton signals to a lower field from their position in monosubstituted derivatives IX and XII but not as low as in the spectra of arenetricarbonylchromium complexes. The replacement of the third CO ligand results in a still larger downfield shift; moreover, the arene protons in XI and XIV are deshielded compared with the corresponding tricarbonyls (Tables 2, 3). The discrepancy between the IR and proton NMR data may arise from the competitive action of electronic density variation effects and effects due to the magnetic anisotropy of distant molecular fragments, both of which influence arene ring proton

TABLE 2

IR, ^1H, ^{19}F, ^{31}P NMR SPECTRA OF VI, IX—XI

Complex	$\nu(C\equiv O)$ [a] (cm^{-1})	^1H, ppm from TMS [b]				^{19}F [b] ppm from external CF_3COOH	^{31}P [c] ppm from external H_3PO_4
		CH_3	CH_2-arene	CH_2-O	H-arene		
VI	1881 1961 (1905 1972)	2,22	2,71 t [e] $J(CH_2—CH_2)$ 6.2 Hz	4.27 dt J(P—H) 5.9 Hz	4.95	27,1 d ^1J(P—F) 1298	112,9 t ^1J(P—F) 1290
IX	1873 1930 (1896 1944)	2.20	2,53 t $J(CH_2—CH_2)$ 4.4 Hz	4,17 dt J(P—H) 17.2 Hz	4,72 (*o*-) 5,07 (*p*-)	72,5 d ^1J(P—F) 1206	217,0 t ^1J(P—F) 1208
X	1889 (1916)		2,50	3.85—4,45 m	4,50—5,22	72,6 [d] ^1J(1P—F) 1212 ^1J(2P—F) 1197	217,1 ^1J(P—F) 1206
XI	—		in the region 2.0—3,0 [d]	4,22	5,32	80,6 [d] ^1J(P—F) 1210	217,2 [d] ^1J(P—F) 1181

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[a] In $CHCl_3$ (in parentheses, in heptane). [b] In $CDCl_3$. [c] In CH_2Cl_2. [d] In HMPT. [e] d, doublet; t, triplet; m, multiplet; dt, doublet of triplets.

TABLE 3

IR, ^{1}H, ^{19}F NMR SPECTRA OF NONCHELATE COMPLEXES XII—XIV

Complex	ν(CO) [a] (cm^{-1})	^{1}H (δ, ppm) [b]			^{19}F [b, c] (δ, ppm)
		CH$_3$	H-arene	Ph	
MesCr(CO)$_3$	1891 1962	2.22	4.97		
XII	1867 1923	2.06	4.65 d J(P—H) 2.4 Hz	7.13	67.8 ^1J(P—F) 1222
XIII	1874	2.13	4.78 t J(P—H) 2.4 Hz	7.13	73.0 ^1J(P—F) ≈ 1222
XIV		2.18	5.22 q J(P—H) 2.4 Hz	7.18	74.8 ^1J(P—F) ≈ 1221

[a] In CHCl$_3$. [b] In CDCl$_3$. [c] δ(PhOPF$_2$) 31.3 ppm, ^1J(P—F) 1326 Hz.

chemical shift values. Consecutive substitution of CO ligands by difluorophosphite may contribute to the latter as well as to the former. The arene proton signals in the spectra of XII—XIV are split because of spin—spin coupling with the ^{31}P nuclei of coordinated phosphorus atoms. The signal multiplicities unambiguously indicate the number of phosphorus-containing ligands attached to the metal. Thus, the proton NMR spectra of XII, XIII, and XIV contain doublet, triplet, and quartet arene proton signals, respectively, which is indicative of the presence of 1, 2, and 3 difluorophosphite ligands at the metal atom, respectively. The spin—spin coupling constant $J(^{31}\text{P}—^1\text{H})$ value in these compounds is equal to 2.4 Hz which is near the value reported for phosphite and phosphinite chromium complexes [1—3].

In order to substantiate the complex structures and to determine more spectral information we have also studied the ^{19}F NMR spectra of compounds VI, IX—XIV and the ^{31}P NMR spectra of compounds VI, IX—XI. The corresponding NMR parameters are listed in Tables 2 and 3. The ^{19}F and ^{31}P NMR chemical shifts in complex VI in which phosphorus is not bonded to the metal are in the spectral region typical for difluorophosphites [10]. Coordination bonding of the phosphite groups strongly shifts the signals to the lower field, e.g. shifting of the ^{31}P signals in IX—XI ($\Delta\delta_{(\text{P})}$) amounts to ca. 104 ppm which is far larger than that observed for nonchelate chromium complexes $(\text{RPF}_2)_n\text{Cr(CO)}_{6-n}$ ($\Delta\delta$ ~60—70 ppm [10]) and even for related chelate arenediphenylphosphite complexes ($\Delta\delta$ ca. 80 ppm [3]). It should also be noted that the ^{31}P NMR chemical shifts in the complexes are practically independent of the number of difluorophosphite ligands attached to the metal.

Coordination bonding-induced shifts of ^{19}F NMR signals in chelate complexes IX—XI ($\Delta\delta_{(\text{F})}$ 45—54 ppm) also exceed those observed in their nonchelate counterparts XII—XIV ($\Delta\delta$ 34—44 ppm). Their values increase with the number of coordinated difluorophosphite ligands. A small decrease of the ^1J(PF) values provides yet further evidence of the coordination bonding [10].

The NMR spectra of compounds X, XI, XIII and XIV are far more complex. These are difficult to interpret without theoretical calculations. Nevertheless, taking into consideration the similarity of the ^{31}P NMR spectrum of XI and

^{19}F NMR spectra of XI and XIV to the corresponding spectra of (PhOPF$_2$)$_3$-Mo(CO)$_3$ [11] for which the theoretical analysis of the $[AX_2]_3$ spectra has been made on the assumption $|J_{AX}| \gg |J_{AA'}| \gg |J_{AX'}| \gg |J_{XX'}| = 0$, we have estimated the ^1J(PF) values for X, XI, XIII, and XIV (see Tables 2, 3).

Following [12], we have estimated the ^2J(P—P′) constant values for XI and XIV (116 and 130 Hz, respectively) and found them to be far larger then those for (RPF$_2$)$_2$Cr(CO)$_4$ where ^2J(P—P′) do not exceed 80 Hz [10].

The difference in the ^{19}F NMR spectra of disubstituted complexes X and XIII is more apparent (see Fig. 1).

The NMR patterns observed and the differences between them depend on the stereochemistry of the complexes. In both X and XIII, the fluorine atoms attached to the same phosphorus atom are diastereotopic and hence magnetically nonequivalent, although to different extents. The presence of bridges hinders free rotation about the Cr—P bonds in X but not in XIII. Nonequivalence of fluorine atoms should therefore give rise to stronger effects in the spectrum of X. In fact, Fig. 1 shows that the larger difference between ^{19}F chemical shifts (Δδ 5.8 ppm) in X makes its spectrum the simpler one: this

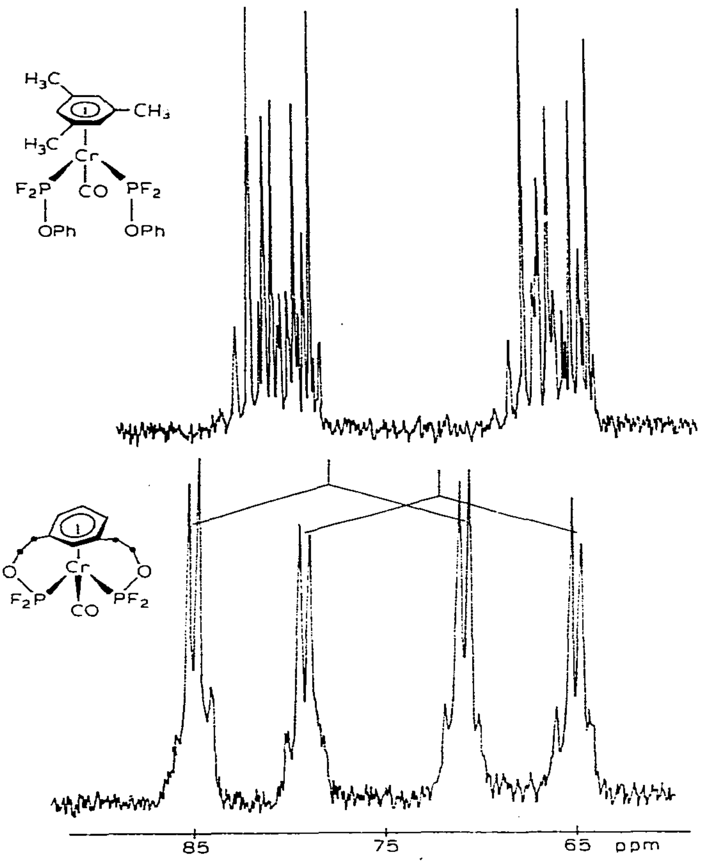

Fig. 1. ^{19}F NMR spectra of arene(bis-difluorophosphite)carbonylchromium complexes X (the lower spectrum) and XIII (the upper spectrum).

may be described in terms of the $AA'MM'XX'$ spin system (A, A' are the ^{31}P nuclei, M, M' and X, X' are the ^{19}F nuclei). Compound XIII shows a far more complex spectrum because of the small difference between ^{19}F chemical shifts which may, seemingly, be described as $AA'XX'YY'$ spectrum (X, X' and Y, Y' are fluorine nuclei). The theoretical analysis of the spectra of complexes of this type is under way in this laboratory.

The mass spectra provide unambiguous evidence of the monomeric structures of the compounds isolated. All spectra contain molecular ions P^+ possessing high intensities in the chelate complexes IX—XI, especially in the three-bridged compound XI.

Further fragmentations involve the competitive processes of the elimination of CO and F, similar to those occurring in complexes of the type $(CO)_nMPX_3$ where X = F, Cl, Br [13]. With nonchelate complexes XII, XIII, the loss of F is the major path, whereas chelate complexes IX, X loose CO more readily than F, though the ions $P - CO^+$ and $P - 2\ CO^+$ are also quite intense in their spectra.

The mass spectra of the complexes studied will be discussed in more detail later.

Experimental

Synthesis and isolation of the complexes studied were carried out under an argon atmosphere. The IR spectra were recorded on an IKS-14A spectrophotometer, the ^1H and ^{19}F NMR spectra on a Perkin—Elmer R 32 instrument operated at 90 and 84.68 MHz, respectively, the ^{31}P—^1H NMR spectrum on a Bruker HX-90 instrument operated at 36.43 MHz.

The tricarbonylchromium complexes of arene-containing alcohols have been described earlier [1—3]. Phenyldifluorophosphite was prepared according to [14] and diethylaminodifluorophosphite according to [15].

Synthesis of (3,5-dimethylphenylethyl)difluorophosphitetricarbonylchromium

PCl_3 (0.5 ml) and Et_2NPF_2 (0.5 ml) were placed in a two-neck flask equipped with an argon inlet and a condenser cooled with solid CO_2. The mixture was warmed up gradually to 80°C and the gaseous $ClPF_2$ formed was bubbled together with argon through an ether solution of 3,5-dimethylphenylethanoltricarbonylchromium (0.28 g, 1 mmol) and Et_3N (0.2 ml) cooled to —30 to —50°C with stirring. After 30 min, the reaction mixture was allowed to warm up to 0°C. The precipitate formed was filtered off, the filtrate was evaporated to dryness, and the residue was recrystallized from hexane.

Synthesis of 3,5-dimethylphenylethyldifluorophosphitedicarbonylchromium

$ClPF_2$ made from 0.5 ml PCl_3 and 0.5 ml Et_2NPF_2 was mixed with argon and bubbled through a solution of 3,5-dimethylphenylethanoltricarbonylchromium complex (0.28 g) and Et_3N (0.2 ml) in 30 ml absolute ether at —30 to —50°C. After the completion of the reaction, the reaction mixture was filtered and evaporated, and the residue was dissolved in 100 ml absolute benzene. The benzene solution was filtered and irradiated with a 1000 W PRK-7 mercury-vapour arc lamp until the arenetricarbonylchromium complex disappeared (1.5 h).

The reaction mixture was filtered, evaporated to dryness, the residue was dissolved in 5 ml CH_2Cl_2 and the solution was diluted with 10 ml petroleum ether and allowed to stay in solid CO_2 for several h. The crystals formed were isolated by filtration, washed with petroleum ether, and dried.

Synthesis of two-bridged arene[bis(difluorophosphite)]carbonylchromium

$ClPF_2$ from 1 ml PCl_3 and 1 ml Et_2NPF_2 was bubbled through a solution of *meta*-bis(oxyethyl)benzenetricarbonylchromium (0.3 g) and Et_3N (0.4 ml) in 50 ml ether cooled to —50°C. The benzene solution obtained (100 ml) was irradiated until the chromium tricarbonyl and dicarbonyl complexes disappeared (3 h). The product was frozen out from CH_2Cl_2/petroleum ether by cooling with solid CO_2.

Synthesis of three-bridged arene[tris(difluorophosphite)]chromium

$ClPF_2$ from 1.5 ml PCl_3 and 1.5 ml Et_2NPF_2 was bubbled through a solution of tris(β-oxyethyl)benzenetricarbonylchromium (0.35 g) and Et_3N (0.6 ml) in 10 ml THF and 40 ml ether at —50°C. The solution obtained was irradiated until the IR bands in the carbonyl region disappeared (4 h). The solution was filtered and evaporated to dryness. The crystals formed were washed with ether and acetone and dried.

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