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MOLECULAR STRUCTURE OF THE CHELATE CHROMIUM COMPLEX WITH HEXADENTATE 1,3,5-$(F_2POCH_2CH_2)_3C_6H_3$ LIGAND

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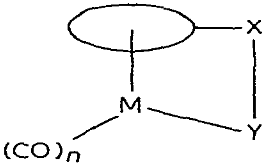
Summary

The new tri-bridged chromium complex 1,3,5-$(F_2POCH_2CH_2)_3C_6H_3Cr$ has been synthesized and its structure has been established by X-ray analysis.

Only recently has some work been published on the synthesis of new organometallic chelate compounds of the type I with a π-coordinated cyclic ligand [1].

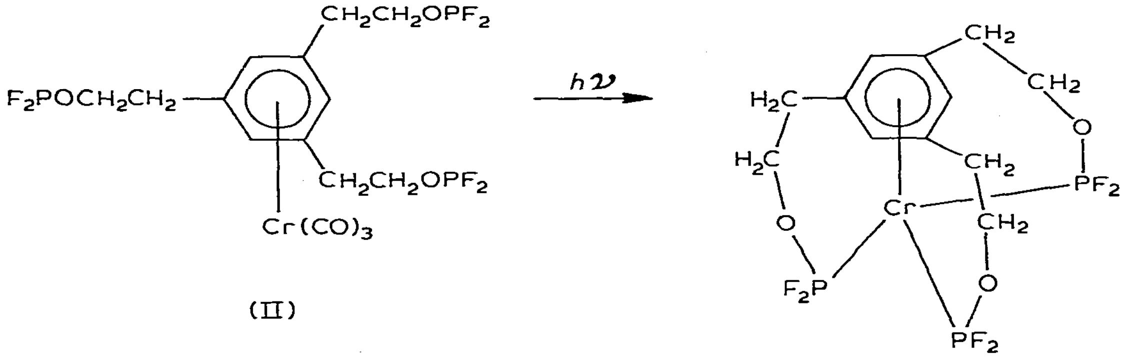


(I)

In our work [2], it was found that the optimal conditions for the formation of multi-bridged chelate chromium complexes involve a ligand containing a triatomic bridge X and a coordinating group Y, the electronic effect of which is similar to that of the CO group.

In this work, we have used arenetricarbonylchromium complex II, with Y = F_2PO in the β-position of the side chain, as precursor for the synthesis of tribridged complex III. It was found that under UV irradiation the complex II looses in turn all the CO ligands. This process is accompanied by the intramolecular coordination of chromium with the phosphorus atoms.

As a result we have prepared complex III in 50% yield. The chelate tribridged chromium complex III is the first example of a multi-bridged compound of this type. It is a light yellow crystalline compound, stable up to 350°C, which begins to sublimate at approximately 250°C. Complex III was characterized by elemental analysis, IR and mass spectra and its structure established



(II)

(III)

by X-ray analysis. Crystals of complex III suitable for the X-ray study were prepared by slow crystallization from 1,2-dichloroethane. Crystals of III are trigonal, a 9.346(2) Å, α 93.82(2)°, V 810.6(4)Å^3, M 466.2, $d_{\mathrm{cal.}}$ 1.92 g cm^{-3}, Z 2, space group $R3$, a molecule is situated in a special position of the triad axis. Intensities of 1768 reflections were measured with an automated Syntex P2$_1$ diffractometer (λMo-K_α, graphite monochromator, $\nu/2\nu$-scan, $2\nu_{\max}$ 60°). In structural calculations 1487 reflections with $I \geqslant 3\sigma$ were used without absorption corrections. The structure was solved by a standard heavy atom technique and refined by a least squares method in a full-matrix anisotropic approximation; hydrogen atoms with coordinates calculated from usual geometric considerations were included in the refinement with fixed positional and thermal parameters. Finally, R = 0.041 and R_w = 0.056 (for all 1768 measured reflections R = 0.049, R_w = 0.058). Atomic coordinates and temperature factors are given in Table 1, bond angles are listed in Table 2.

The configuration of the molecule with bond lengths is shown in Fig. 1 projected down the triad axis of symmetry. As in other complexes of the type (η^6-arene)CrL$_3$ (L = ligand coordinated by its lone electron pair) the Cr atom coordination is octahedral. The ideal C_{3v} symmetry of the CrP$_3$ fragment is preserved and the P—Cr—P bond angles 91.93(2)° are close to the ideal value, 90°. The relative orientation of the benzene ring and the CrP$_3$ moiety approaches an eclipsed conformation similar to that found in the structure of (2,5-Me$_2$C$_6$H$_3$-CH$_2$OCH$_2$CH=CH$_2$)Cr(CO)$_2$ (IV) [1b], where a chelate ring is formed by the bridge of the same length as in III. However, the molecule of 3,5-Me$_2$C$_6$H$_3$CH$_2$-OP(OPh)$_2$Cr(CO)$_2$ (V) [1e] has an intermediate conformation (between eclipsed and staggered) which is caused by a considerable rigidity of a chelate ring due to the smaller bridge length.

Thus, chelate systems in III and IV are more flexible and mobile than that in V, and this is reflected in torsional angle values. While in the bridges —CH$_2$—CH$_2$—O— of III and —CH$_2$—O—CH$_2$— of IV these angles are equal to 65.6 and −70.8 (III), 66.1 and −98.5 (IV), in V the torsional angle around the —CH$_2$—O— is diminished to 23.2°.

The benzene ring in III is planar (within ±0.001 Å), whereas in IV this cycle is slightly deformed towards a boat-like conformation with out-of-plane dis-

TABLE 1

ATOMIC COORDINATES ($X10^5$ FOR Cr AND P, $X10^4$ FOR THE REST) AND PARAMETERS OF TEMPERATURE FACTORS ($X10^2$) [a]

Atom	x	y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	22686(3)	22686(3)	22686(3)	169(1)	169(1)	169(1)	3(1)	3(1)	3(1)
P	19987(6)	45281(5)	26702(6)	297(2)	195(2)	358(2)	14(1)	21(2)	3(2)
F(1)	2667(2)	5420(2)	4063(2)	735(11)	306(6)	497(8)	8(6)	−73(7)	−159(6)
F(2)	2651(2)	5637(2)	1642(2)	595(9)	284(6)	638(9)	17(6)	135(7)	185(6)
O	450(2)	5136(2)	2605(3)	353(8)	270(7)	990(16)	112(6)	111(9)	3(8)
C(1)	221(2)	996(2)	2252(3)	253(8)	287(8)	347(9)	−90(6)	28(6)	−15(7)
C(2)	45(2)	2097(2)	1332(3)	191(7)	336(9)	337(9)	−1(6)	−49(6)	−15(7)
C(3)	−1112(3)	3145(4)	1516(4)	233(9)	489(13)	705(18)	112(8)	−29(9)	20(12)
C(4)	−792(3)	4205(3)	2795(4)	287(10)	435(12)	763(19)	117(9)	135(11)	−28(12)

[a] Temperature factor: $T = exp[-1/4(B_{11}h^2a^{x^2} + \dots 2B_{23}klb^xc^x)]$.

TABLE 2

BOND ANGLES ω (°)

Angle	ω	Angle	ω
P—Cr—P'	91.93(2)	C(2)—C(1)—C(2')	121.1(2)
Cr—P—F(1)	122.58(7)	C(1)—C(2)—C(1')	118.9(2)
Cr—P—F(2)	119.64(7)	C(1)—C(2)—C(3)	121.5(2)
Cr—P—O	121.44(9)	C(1')—C(2)—C(3)	119.6(2)
F(1)—P—F(2)	93.1(1)	C(2)—C(3)—C(4)	113.2(2)
F(1)—P—O	98.6(1)	C(3)—C(4)—O	110.6(3)
F(2)—P—O	94.8(1)	C(4)—O—P	120.0(2)
Ar[a]—Cr—P	123.9(2)		

[a] Centre of the arene ligand.

placements of the carbon atoms bearing Me groups by 0.030 and 0.040 Å away from the metal atom.

At the same time, in III and IV the methylenic carbons linked to the arene ring are displaced from its plane towards the Cr atom by 0.039 and 0.030 Å, respectively, and in V, due to the smaller bridge length, this displacement is considerably larger, 0.27 Å. Benzene ring bonds in III are of equal length, averaging 1.408(3) Å, usual for η^6-arene complexes. The distances of the type C(2)—C(3) to exocyclic carbon atoms is equal to 1.517(4) Å, i.e. are close to the standard ordinary C(sp^2)—C(sp^3) bond length, 1.51 Å [3].

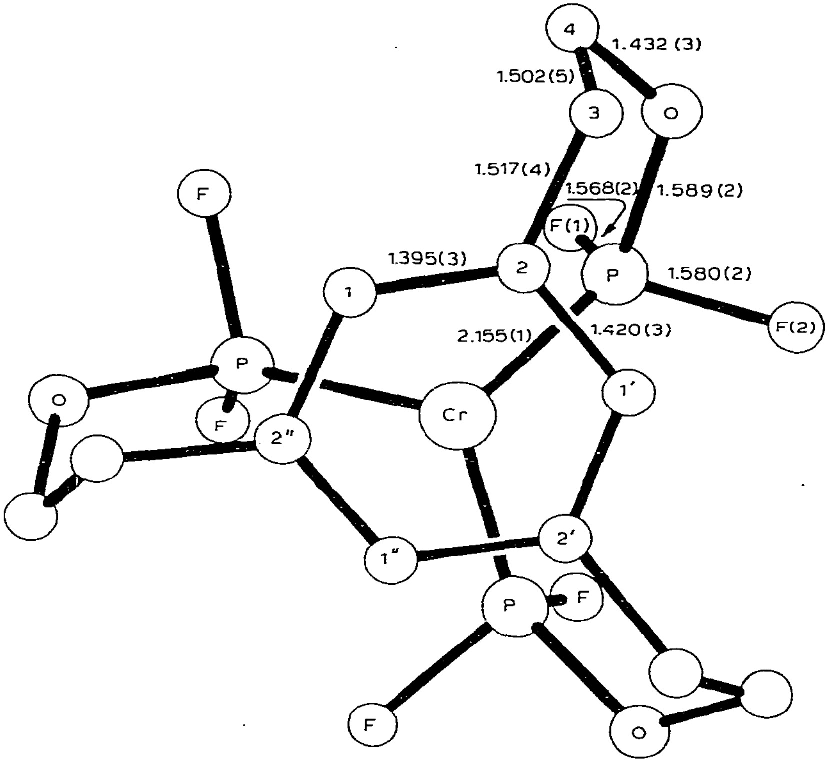


Fig. 1. Projection of atoms onto the benzene ring plane. H atoms omitted for clarity.

The average Cr—C(arene) distance is 2.188(2) Å, close to 2.202 Å in V and 2.198 Å in (η^6-PhCOOMe)Cr(CO)$_2$PPh$_3$ [4], although it is slightly shorter than the value usual for arene complexes in general, probably due to a tightening action of three bridges. Moreover, the difference in individual Cr—C values is notably smaller than in the less symmetric molecules of IV and V.

An interesting feature of the structure of III is the unusually short Cr—P length, 2.155(1) Å, which is considerably contracted in comparison not only with the sum 2.56 Å of single bonded covalent radii (Cr 1.46 Å [5] and P 1.10 Å [6]), but also with values found in other Cr complexes with phosphite ligands (2.201 Å in V, 2.252 Å in *trans*-Cr(CO)$_4$[P(OPh)$_3$]$_2$ (VI) [7] and 2.309 Å in Cr(CO)$_5$P(OPh)$_3$ (VII) [8]). This bond shortening reflects a considerable dative interaction $d_\pi(\text{Cr}) \rightarrow d_\pi(\text{P})$ which is favoured by the presence of strongly electron-accepting substituents (F and O) at the P atom. Furthermore, a general tendency for metal atom bond lengths to contract by formation of chelate systems is revealed in this case.

The P atom has a distorted tetrahedral coordination with an appreciable inequality of bond angles Cr—P—F (av. 121.11(7)°) and Cr—P—O (121.44(9)°) on the one hand, and F—P—F (93.1(1)°) and F—P—O (av. 96.7(1)°) on the other. A similar distortion of the P atom tetrahedral coordination is characteristic in general for transition metal complexes with phosphine, phosphite and similar ligands. Thus, in the structures V, VI and VII bond angles Cr—P—O are equal to 119.0, 117.8 and 117.1° and O—P—O angles are diminished to 98.6, 100.0 and 100.8°, respectively. The P—O and O—C bond lengths 1.589(2) and 1.432(3) Å are not exceptional and comparable with those in structures V, VI and VII (P—O, 1.637, 1.603 and 1.604 Å; O—C, 1.41, 1.399 and 1.403 Å), respectively. The average P—F distance, 1.574(2) Å, is very close to the corresponding bond length in a free trifluorophosphine (1.569 Å [9]) but is somewhat longer than values in a series of transition metal complexes with this ligand: 1.561 Å in Ni(PF$_3$)$_4$ [10,11], 1.557 Å in Mo(CO)$_5$PF$_3$ [12] and 1.546 Å in Pt(PF$_3$)$_4$ [10].

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