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SYNTHESIS OF DOUBLY AND TRIPLY BRIDGED CHROMIUM ARENE PHOSPHITE COMPLEXES

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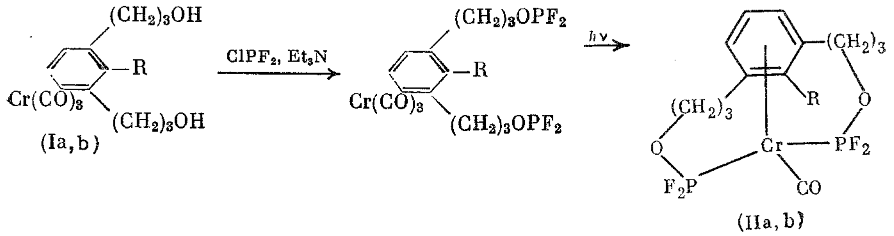
The nature of the organophosphorus group, presence of substituents in the arene and, in some cases, the bridge length are quite important in the synthesis of singly bridged chromium arene chelate complexes [1-3]. In our previous work [2, 4, 5], we showed that the nature of the substituents at the phosphorus atom is a determining factor in the synthesis of multiply bridged chelates.

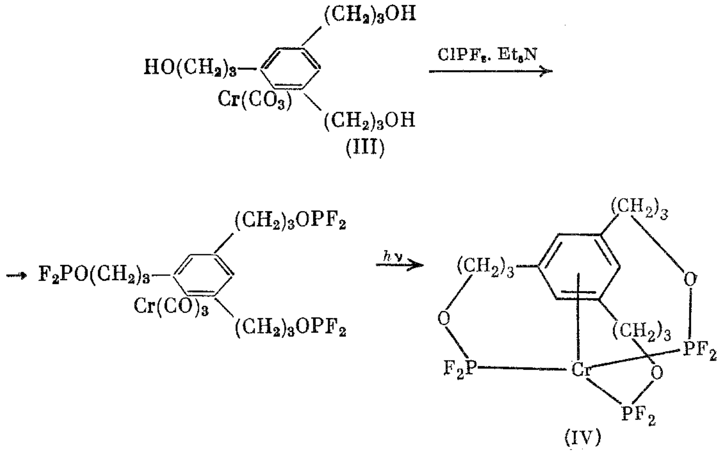
In order to study the effect of bridge length on the formation of multiply bridged compounds, we undertook the syntheses of doubly and triply bridged chromium arene chelate complexes with four-membered bridges, since previously synthesized compounds mostly contained three-membered rings, while doubly bridged chelates are not formed in the case of two-membered bridges [4]. The corresponding chelate compounds (IIa), (IIb) and (IV) are formed upon the UV irradiation of arenechromium tricarbonyl complexes with difluorophosphite groups in the ω position of the side chains



(Ia,b)

(IIa,b)

R=H (a), MeO (b)



(III)

(IV)

The yields of (IIa), (IIb) and (IV) are from 17 to 23%, i.e., about half that for their three-membered bridge analogs [2]. This difference may be attributed to the more rigid steric requirements in the formation of multiply bridged chelates.

An important factor in the formation of chelate complexes is the presence of substituents in the arene ring [3]. In the case of singly bridged compounds with o-methyl substituents, we showed that the yield of the chelate complex decreases upon the formation

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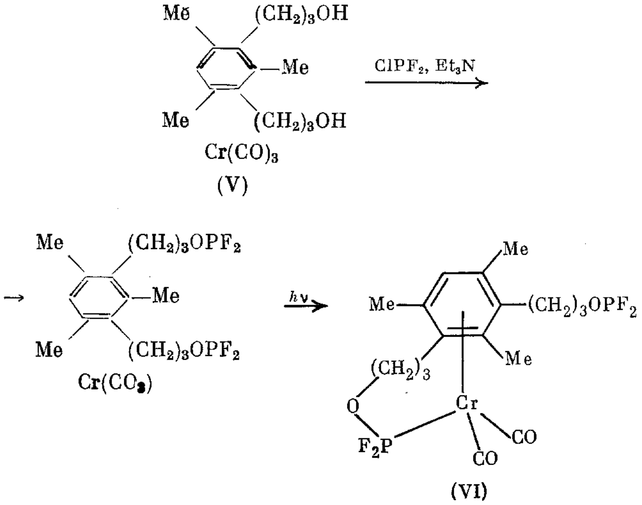
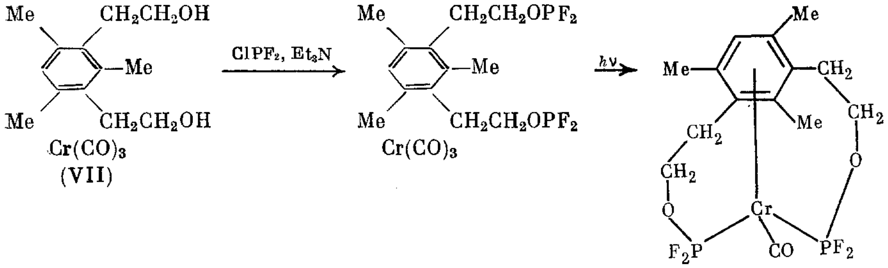
of an eight membered chelate ring (five-membered bridge) due to steric hindrance [3]. We found that in the case of doubly bridged chelates, such steric hindrance completely prevents the formation of even seven-membered chelate rings. Thus, the reaction upon the UV irradiation of (V) stops at the stage of dicarbonyl complex (VI) (ν CO 1851, 1907 cm^{-1} in $CHCl_3$) and an increase in the irradiation time does not lead to closure of the second bridge.



(V)

(VI)

On the other hand, the analogous compound with shorter bridges upon IR irradiation gives monocarbonyl complex (VIII) in 20% yield.



(VII)

(VIII)

In this case, the formation of six-membered chelate rings is favorable not only due to the chelate effect but also as a consequence of the significant reduction in steric hindrance as seen by an examination of the molecular models.

EXPERIMENTAL

The synthesis of the chromium complexes was carried out in an argon atmosphere using absolute solvents. The PMR spectra were taken on a Perkin-Elmer R-12 spectrometer at 60 MHz in acetone-d_6. The ^{31}P NMR spectra were taken on a Bruker HX-90 spectrometer at 36.43 MHz relative to external H_3PO_4. The IR spectra were taken on IKS-14A and IKS-29 spectrophotometers and the mass spectra were taken on a Finnigan-4500 mass spectrometer.

Samples of 1,3-bis(3-hydroxypropyl)benzene, 1,3,5-tris(3-hydroxypropyl)benzene and 1,3,5-trimethyl-2,4-bis(3-hydroxypropyl)benzene were obtained by the consecutive effect of $SOCl_2$ in pyridine, NaCN in ethanol–water, KOH in water, ethanol in benzene and $LiAlH_4$ in ether on 1,3-bis(2-hydroxyethyl)benzene [6], 1,3,5-tris(2-hydroxyethyl)benzene [7] and 1,3,5-trimethyl-2,4-bis(2-hydroxyethyl)benzene, respectively. The latter was obtained by the consecutive reactions of 1,3,5-trimethyl-2,4-bis(chloromethyl)benzene [8] with KCN, KOH/H_2O, ethanol, and $LiAlH_4$. 2-Methoxy-1,3-bis(3-hydroxypropyl)benzene was synthesized by the hydroborylation of 2,6-diallylanisole (obtained from 2,6-diallylphenol [9] and MeI in the presence of anhydrous K_2CO_3) by the action of $(Me_2CHCMe_2)_2BH$ [10].

The synthesis of arenechromium tricarbonyl complexes was carried out by heating 2 mmoles of the corresponding arene with 2.3 mmoles $Cr(CO)_6$ in diglyme–octane at reflux. The structures were supported by IR and PMR spectral data. The yield for [η-1,3-bis(3-hydroxypropyl)benzene]tricarbonylchromium (I) was 85%, mp 86-87°C. Found: C 54.52; H 5.49; Cr 15.40%. Calculated for $C_{15}H_{18}CrO_5$: C 54.55; H 5.49; Cr 15.74%. IR spectrum (ether): CO 1894, 1958 cm^{-1}. PMR spectrum: 1.63-2.05 m (4H, $CH_2CH_2CH_2$), 2.32-2.68 m (4H, CH_2-Ar), 3.65 t (J = 6 Hz), 3.80 s (6H, CH_2OH), 5.25-5.82 m (4H, H–Ar).

Doubly bridged complexes (IIa), (IIb) and (VIII) were obtained from 1 mmole arenechromium tricarbonyl complex according to our previous procedure [2]. The products were subjected to chromatography on a silica gel plate using 3:1 ether—hexane as eluant and recrystallized from chloroform—hexane as eluent and recrystallized from chloroform—hexane.

[η^6-1,3-Bis(3-difluorophosphinoxypropyl)benzene-P,P']carbonylchromium (IIa) was obtained in 17% yield, mp 168-170°C (dec.). Found: C 38.84; H 4.17; Cr 12.41; P 14.22%. Calculated for $C_{13}H_{16}CrF_4O_3P_2$: C 38.06; H 3.93; Cr 12.68; P 15.10%. IR spectrum (in chloroform): ν CO 1878 cm^{-1}. Mass spectrum, m/z: 410 M$^+$, 382 [M — CO]$^+$.

[η^6-2-Methoxy-1,3-bis(3-difluorophosphinoxypropyl)benzene-P,P']carbonylchromium (IIb) was obtained in 18% yield, mp 185-186°C (dec.). Found: C 38.12; H 4.01; Cr 11.50; P 13.05%. Calculated for $C_{14}H_{18}CrF_4O_4P_2$: C 38.20; H 4.12; Cr 11.81; P 14.07%. IR spectrum ($CHCl_3$): ν CO 1865 cm^{-1}. PMR spectrum: 1.91-2.38 m (4H, $CH_2CH_2CH_2$), 2.56-3.23 m (4H, CH_2-Ar), 3.65 s (3H, CH_3O), 4.02-4.74 m (4H, CH_2O), 5.5 m (3H, H-Ar). Mass spectrum, m/z: 440 M$^+$, 412 [M — CO]$^+$.

[η^6-1,3,5-Trimethyl-2,4-bis(2-difluorophosphinoxyethyl)benzene-P,P']carbonylchromium (VIII) was obtained in 20% yield. Found: C 40.13; H 4.77; Cr 11.97%. Calculated for $C_{14}H_{17}CrF_4O_3P_2$: C 39.73; H 4.05; Cr 12.29%. IR spectrum (in $CHCl_3$): ν CO 1870 cm^{-1}.

[η^6-1,3,5-Tris(3-difluorophosphinoxypropyl)benzene-P,P',P"]chromium (IV) was obtained analogously from 0.39 g (1 mmole) complex (III). The product was subjected to chromatography on a silica gel column using $CHCl_3$ as eluant and recrystallized from chloroform—ether. The yield was 0.13 g, dec. >320°C. Found: C 35.70; H 4.22; Cr 10.14%. Calculated for $C_{15}H_{21}CrF_6O_3P_3$: C 35.45; H 4.16; Cr 10.23%. ^{31}P NMR spectrum (in hexamethylphosphorotriamide): 217.3 t, J_{PF} = 1166 Hz. Mass spectrum, m/z 508 M$^+$.

CONCLUSIONS

1. Previously unknown doubly- and triply-bridged chromium arene phosphite complexes with four-membered rings were synthesized.

2. An increase in the bridge length and the introduction of substituents into the arene lead to a decrease in the yield of multiply bridged chromium arene phosphite chelates.

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