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CHELATE ARENEBIS-PHOSPHITE CARBONYLCHROMIUM COMPLEXES

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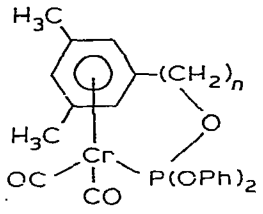
Summary

UV irradiation of arenetricarbonylchromium complexes containing —$OP(OR)_2$ phosphorus atoms in the δ- or ϵ-positions of two side chains causes complete displacement of two CO ligands to give two-bridge chelate arenebis-phosphite tricarbonylchromium complexes. With phosphorus in the γ-position, one-bridge chelate complexes only are formed. Intramolecular coordination of the second phosphorus atom does not occur because of steric hindrance. The reactions leading to the chelate complexes are compared with the similar reactions between mesitylenetricarbonylchromium and triphenylphosphite. The reactions terminate at the replacement of two groups under the conditions used in this work. The structures of the complexes isolated are proved by IR and ^1H and ^{31}P NMR spectra.

Introduction

Earlier, we have synthesized [1] chelate phosphitoalkylarene dicarbonylchromium complexes of type I by intramolecular coordination of the ω-phosphite



(I, n = 1,2,3)

group under UV irradiation of the corresponding arenetricarbonylchromium complexes. The purpose of this work is to study the formation of the second chelate cycle when one is already present in the molecule, and to compare the tendencies for the formation of two-bridge monocarbonyl compounds and non-chelate disubstituted arenechromium monocarbonyls.

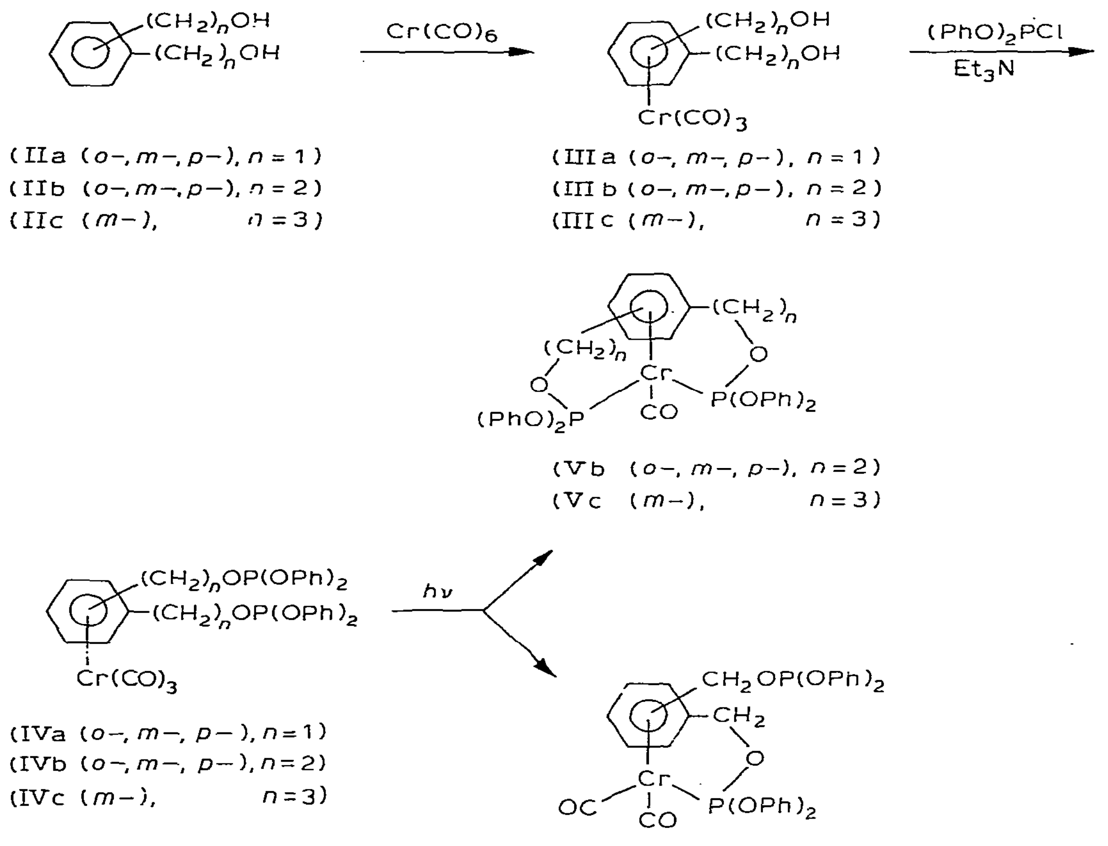
Only one carbonyl ligand in arenechromium tricarbonyls is known to enter easily into substitution reactions. Displacement of the second CO group is difficult to achieve, and only a few disubstituted species have been reported thus far [2—4]. This is mainly due to the use of ligands such as phosphines, amines, nitriles, olefins, etc. [5] which replace CO with a resulting increase in the electron density on the metal. Such substitution thus strengthens the bonds between the metal and the remaining CO groups. That this is the case follows from the lowering of $\nu(C{\equiv}O)$ IR frequencies and the shortening of M—CO bonds, e.g. on going from arenetricarbonylchromium (Cr—CO 1.842 Å [6]) to arenedicarbonylphosphinechromium complexes (Cr—CO 1.823 Å [7]). Phosphite ligands are weaker electron donors than phosphines and $(CH_3O)_3P$ and $(C_2H_5O)_3P$ ligands are noted for their ability to give disubstituted and monosubstituted products [2]. This led us to expect that the two-bridge chelate arenebisphosphite carbonylchromium complexes may be prepared, especially as the chelate effect should facilitate their formation.

Results and discussion

In order to study the synthesis of two-bridge arenechromium monocarbonyls, we have prepared *ortho-*, *meta-*, and *para-*disubstituted diols II. These were used in reactions with $Cr(CO)_6$ to obtain the corresponding arenetricarbonylchromium complexes III. The latter were converted to arenechromium tricarbonyls IV containing ω-phosphitoalkyl groups on reaction with diphenylchlorophosphite in the presence of triethylamine.

UV irradiation of complexes IV containing sufficiently long bridges (3 and 4 units, $n = 2, 3$) in fact leads to consecutive elimination of two CO ligands accompanied by an intramolecular cyclization to give the two-bridge chelates V. The reaction goes irrespectively of the relative positions of the bridges (*ortho-*, *meta-*, or *para-*). With shorter bridges ($n = 1$, i.e., two-unit bridges), one chelate cycle is only formed under these conditions. The products VIa from the latter reaction may be isolated if desired, as has been done with VIa (*meta*) in this work. The second cycle can not be formed whatever the relative positions of the substituents in the ring. Prolonged irradiation only leads to complex decomposition. We explain such failures to prepare the two-bridge complexes with short bridges ($n = 1$) to arise from a considerable distortion of the molecule upon cyclization which strongly hinders the formation of the second cycle under the same conditions. The presence of distortions in complex I ($n = 1$) was proved by Yu.T. Struchkov and V.G. Andrianov by X-ray diffraction (to be published). Such steric hindrance does not occur with bridges of longer lengths ($n = 2, 3$).

It is of interest to note that irradiation of mesitylenetricarbonylchromium in the presence of excess triphenylphosphite also causes displacement of two CO ligands to give mesitylenebis-triphenylphosphite carbonylchromium (VII). The reaction however, can not be made to go to completion; three compounds are always present in the reaction mixture. We failed to isolate pure VII. The product was characterized by its IR and proton NMR spectra (Table 1) and ^{31}P



(IIa (*o*-, *m*-, *p*-), $n = 1$)
(IIb (*o*-, *m*-, *p*-), $n = 2$)
(IIc (*m*-), $n = 3$)

(IIIa (*o*-, *m*-, *p*-), $n = 1$)
(IIIb (*o*-, *m*-, *p*-), $n = 2$)
(IIIc (*m*-), $n = 3$)

(Vb (*o*-, *m*-, *p*-), $n = 2$)
(Vc (*m*-), $n = 3$)

(IVa (*o*-, *m*-, *p*-), $n = 1$)
(IVb (*o*-, *m*-, *p*-), $n = 2$)
(IVc (*m*-), $n = 3$)

(VIa (*o*-, *m*-, *p*-))

NMR spectrum (δ —190.4 ppm from external 85% H_3PO_4) in the presence of $(PhO)_3P$ and mesitylenedicarbonyltriphenylphosphitechromium (1,3,5-$(CH_3)_3$-$C_6H_3Cr(CO)_2P(OPh)_3$, δ ^{31}P —198.1 ppm; $(PhO)_3P$, δ ^{31}P —128.0 ppm from H_3PO_4).

Unlike with noncyclic systems, reactions leading to chelate products are strongly on the side of two-substituted species. Irradiation of complexes IVb (*o*-, *m*-, *p*-) and IVc (*m*-) results in complete conversion of the initial compounds to Vb (*o*-, *m*-, *p*-) and Vc (*m*-). The formation of monosubstituted intermediates was detected in the carbonyl stretching region of the IR spectra of the reaction mixtures. Reaction times increased in the order $t_{Vb} < t_{Vc} << t_{VII}$ which may be regarded as a manifestation of the chelate effect.

We have also attempted to displace the last CO group in complexes of the type Vb in order to obtain three-bridge compounds. For that purpose, we have prepared complex IX from triol VIII and $Cr(CO)_6$ and converted it to X using a similar procedure to that applied for III. Irradiation of X only gave the two-bridge complex XI in which one phosphorus atom is not bonded to the metal. As the bridges in X are *meta* with respect to each other and have sufficient lengths (three-unit bridges), the failure to obtain the desired product should be explained by considerable increase in Cr—CO bond strength on the replacement of two CO ligands with phosphite electron donors. In fact, irradiation of com-

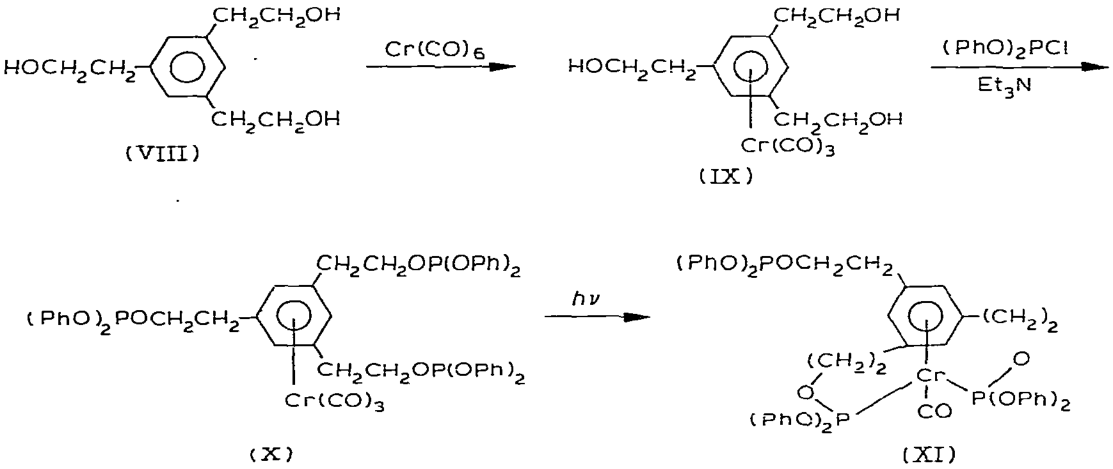
TABLE 1

SOME IR AND PROTON NMR DATA

Complex	$\nu(C\equiv O)$ (cm^{-1})	Chemical shifts δ_H (ppm) [a]					
		Ar—H	O—CH_2	Ar—CH_2	C—CH_2—C	O—H	O—C_6I
IIIa (*o*-)	1896 1973	5.48—5.98 m	4.46 d, 4.72 d J_{AB} = 13.3 Hz		—	4.60 b	—
IIIa (*m*-)	1891 1970	5.50—5.90 m	4.54 br		—	4.70 b	—
IIIa (*p*-)	1891 1969	5.74 s	4.48 s		—	4.55 b	—
IIIb (*o*-)	1887 1966	5.43—5.90 m	3.88 t *J* = 6.4 Hz	2.23—3.23 m	—	4.23 b	—
IIIb (*m*-)	1887 1965	5.30—6.00 m	3.81 t *J* = 6.1 Hz	2.61 t *J* = 6.1 Hz	—	4.10 b	—
IIIb (*p*-)	1887 1966	5.70 s	3.84 t *J* = 6.1 Hz	2.58 t *J* = 6.1 Hz	—	4.02 b	—
IIIc (*m*-)	1886 1964	5.25—6.03 m	3.79 t *J* = 6.1 Hz	2.57 t *J* = 6.1 Hz	1.53—2.23 m	3.90 b	—
IX	1883 1962	5.53 s	3.88 t *J* = 6.2 Hz	2.67 t *J* = 6.2 Hz	—	4.05 b	—
Vb (*o*-)	1846	3.68—4.97 m		2.30 t	—	—	7.32m
Vb (*m*-)	1854	3.73—4.73 m		2.25 t *J* = 5.1 Hz	—	—	7.33 r 7.42 r
Vb (*p*-)	1857	3.78—4.58 m		2.35 t	—	—	7.37 r
Vc (*m*-)	1838	3.98—4.93 m		2.70	1.95		7.18 r
XI	1850	4.39	3.72—4.27 m 4.07 t *J* = 6 Hz	2.22 1.99 t *J* = 6 Hz	—	—	7.18 r
VII	1839	4.00 t *J* = 2.2 Hz	—	1.77 [b]	—	—	7.28 r

[a] The spectra of complexes III, IX were obtained in $(CD_3)_2CO$, the spectra of V, VII, XI in $CDCl_3$. Notation: s singlet, d doublet, t triplet, m multiplet, br broad peak. [b] Ar—CH_3.

plexes containing still stronger electron donors, phosphinite groups —$OPPh_2$,



yields one-bridge chelates as it has been shown for the phosphinite analogue of IVb (*m*-).

Steric hindrance due to the presence of bulky phenoxy groups at P in XI seems to be of little importance since no three-bridge product is formed with OC_2H_5 either.

The compounds isolated are light-yellow substances stable in storage. Their compositions and structures were proved by elemental analyses, IR, proton NMR, and, for Vb (*o*-, *m*-, *p*-), Vc (*m*-), VIn (*m*-), XI, ^{31}P NMR spectra.

Complexes III, IV, IX show two bands in the carbonyl stretching region $A_1 + E$, which is consistent with C_{3v} local symmetry of the metal carbonyl moiety. Compound VIb gives two bands similar to those observed in I [1], and the spectra of V, VII, and IX each contain one band corresponding to the stretching vibrations of the CO ligand bonded to the metal. Substitution of phosphite ligands for CO results in successive lowering of $\nu(C{\equiv}O)$ frequencies because of the higher electron donor power of phosphite groups compared to CO. As in complexes I, an increase of the bridge length in Vb (*m*-) and Vc (*m*-) lowers $\nu(C{\equiv}O)$ from 1854 to 1838 cm^{-1}, probably because of the decrease in steric strain. The observed frequency lowering ($\Delta\nu = 16\ cm^{-1}$) is larger than that characteristic on one-bridge systems where $\Delta\nu$ is equal to ca. 6—7 cm^{-1}. Steric strain variations may also be responsible for the small frequency differences between complexes Vb (*o*-, *m*-, *p*-) differing in the relative positions of bridges on the ring (Table 1).

The NMR spectra are also consistent with the suggested structures. Complexes IIIa (*o*-), IIIb (*o*-) with $-(CH_2)_nOH$ groups positioned *ortho*- with respect to each other provide an interesting example of diastereotopism of α-methylene protons in organometallics. Although the compounds have symmetry planes the methylene groups contain diastereotopic protons that may be anichronous because the CH_2 carbon atoms lie off the symmetry plane [8,9]. The α-CH_2 protons are anisochronous in the proton NMR spectra (in Va, $\Delta\delta$ 0.26 ppm, $J_{AB} = 13.3$ Hz). In *meta*-substituted species IIIa (*m*-), IIIb (*m*-), IIIc (*m*-), the methylene protons are also diastereotopic but the effect is far less pronounced in the latter case, and the protons are practically isochronous. The same may be said of β- and γ-methylene protons in *ortho*- and *meta*-substituents. In the *para*-substituted IIIa (*p*-) and IIIb (*p*-), the methylene protons are enantiotopic and should therefore be isochronous as it is in fact observed.

Comparison of the proton NMR spectra of complexes Vb (*o*-, *m*-, *p*-), Vc (*m*-) and XI on the one hand and one-bridge compounds I on the other shows that arene proton shielding increases on going to the disubstituted derivatives. The arene proton signals, however, shift to the region where they overlap with the signals from CH_2OP to produce complex multiplets. The $\Delta\delta = \delta_{mono} - \delta_{di}$ difference may therefore only be estimated for the nonchelate complex VII where it is equal to 0.3 ppm. The arene protons in VII give a triplet owing to spin—spin couplings with two phosphorus nuclei. The methylene signals are broadened markedly because of the nonequivalence of the two methylene protons. Unlike in tricarbonyl complexes, these protons are diastereotopic not only in Vb (*o*-, *m*-), Vc (*m*-), XI, but also in *para*-substituted Vb (*p*-). Proton anisochronism gives rise to additional couplings and increases signal multiplicities in the proton NMR spectra. On the contrary, the α-methylene protons of the side chain containing a free phosphite terminus in XI are enantiotopic and give rise to a well-defined triplet.

The ^{31}P NMR spectra of complexes VIa (*m*-) and XI contain two signals each at —129.4 and —129.5 (non bonded phosphite) and —230.0 and —210.8 ppm (bonded phosphite), respectively, with peak area ratios consistent with the suggested structures (1/1 for VIa (*m*-) and 1/2 for XI). The ^{31}P chemical shifts are similar to those observed in I and Vb (*o*-, *m*-, *p*-).

Experimental

Synthesis and isolation of the complexes were carried out under an argon atmosphere.

The IR spectra, in chloroform solutions, were obtained on an IKS-14A spectrophotometer, the proton NMR spectra on Perkin—Elmer R-20 (60 MHz) and R-32 (90 MHz) instruments. The $^{31}P-\{^1H\}$ spectra were recorded on a Bruker HX-90 (36.43 MHz) spectrometer (solutions in CH_2Cl_2).

Ortho-, *meta*-, and *para*-bis(oxymethyl)benzenes IIa (*o*-, *m*-, *p*-) [10] and bis-(β-oxyethyl)benzenes IIb (*o*-, *m*-, *p*-) were obtained by reduction of the corresponding isomeric phthalates and phenylenediacetates [11] with $LiAlH_4$. *Meta*-bis(γ-oxypropyl)benzene IIc was made by reaction of malonic ester with *m*-xylylene dibromide [12] followed by reduction of the dibasic acid ester with

TABLE 2

YIELDS, M.P.'s AND ANALYTICAL DATA

Complex	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)			
			C	H	Cr	P
IIIa (*o*-)	72	134—135	48.29	3.65	18.72	—
			(48.18)	(3.68)	(18.96)	
IIIa (*m*-)	76	114—115	48.43	3.64	18.68	—
			(48.18)	(3.68)	(18.96)	
IIIa (*p*-)	70	85—87	48.48	3.74	18.62	—
			(48.18)	(3.68)	(18.96)	
IIIb (*o*-)	78	80—82	51.78	4.70	17.04	—
			(51.66)	(4.67)	(17.20)	
IIIb (*m*-)	68	76—77	51.79	4.73	17.01	—
			(51.66)	(4.67)	(17.20)	
IIIb (*p*-)	71	106—108	51.85	4.76	16.94	—
			(51.66)	(4.67)	(17.20)	
IIIc (*m*-)	65	87—89	54.72	5.53	15.51	—
			(54.54)	(5.49)	(15.74)	
IX	64	140—141	52.02	5.35	14.99	—
			(52.02)	(5.24)	(15.02)	
VIa (*m*-)	28	oil	60.35	4.38	7.72	9.00
			(60.18)	(4.16)	(7.66)	(9.13)
Vb (*o*-)	38	183—185	61.75	5.04	7.71	9.19
			(61.95)	(4.75)	(7.66)	(9.13)
Vb (*m*-)	40	161—162	61.66	5.03	7.70	9.14
			(61.95)	(4.75)	(7.66)	(9.13)
Vb (*p*-)	33	108—110	62.00	5.00	7.80	9.30
			(61.95)	(4.75)	(7.66)	(9.13)
Vc (*m*-)	25	150—152	62.97	5.34	7.24	9.01
			(62.80)	(5.27)	(7.35)	(8.76)
XI	74	44—45	62.76	4.98	5.46	9.80
			(62.69)	(4.83)	(5.54)	(9.90)

$LiAlH_4$ in ether. Symmetric tris-(β-oxyethyl)benzene VIII was prepared as recommended in ref. 13.

Synthesis of arenetricarbonylchromium complexes IIIa, b, c and IX

An aromatic polyol (10 mmol) and $Cr(CO)_6$ (11 mmol) were refluxed in 50 ml diglyme and 20 ml octane until sublimation of $Cr(CO)_6$ ceased (this was periodically returned into the reaction mixture). The solution was then cooled, filtered, evaporated under vacuum, and the residue was recrystallized from toluene/heptane, Yields, m.p.'s, and analytical data are listed in Table 2, the IR and proton NMR data in Table 1.

Synthesis of two-bridge chelates Vb, c and XI

Complexes IIIa, b, c or IX (1 mmol) were dissolved in minimal quantities of tetrahydrofuran, diluted with 30 ml absolute diethyl ether. Triethylamine (2.1 mmol) was added to the solution and then, with stirring, diphenylchlorophosphite (2 mmol) in 10 ml ether. The mixture was stirred for 1 h, triethylamine hydrochloride was filtered off, the solution was evaporated, and the residue was extracted with 50 ml ether. The extract was filtered, evaporated, and the light-yellow oil-wise residue was dissolved in 100 ml absolute benzene and irradiated with a 1000 W PRK-7 mercury arc lamp until the complete consumption of the arenetricarbonylchromium and arenedicarbonylchromium complexes (4—7 h) (monitored by IR spectra). The reaction mixture was evaporated to dryness, the residue was dissolved in 7 ml CH_2Cl_2 and diluted with 15 ml ether. The solution was filtered, diluted with 70 ml petroleum ether, and kept at solid CO_2 temperature for 2 days. The precipitate was separated by filtration and dried.

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