SYNTHESIS AND METALLATION OF CHROMIUM ARENE CHELATE PHOSPHORUS-CONTAINING COMPLEXES WITH TRIMETHYLENE BRIDGES

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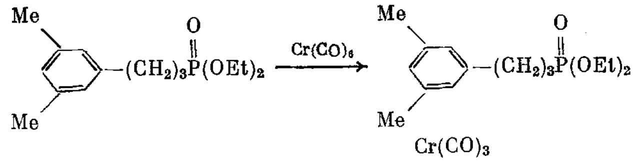
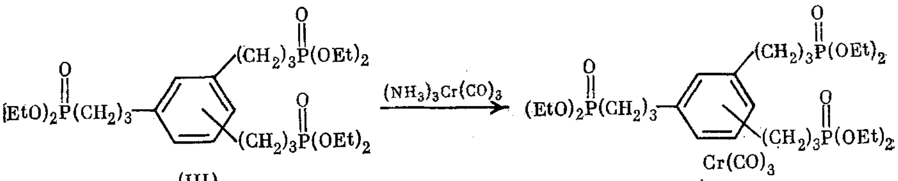
One of the possible approaches to the synthesis of new singly bridged phosphorus-containing chromium arene chelate complexes involves substitution at the coordinated phosphorus atom in known difluoro- and diphenylphosphite chelates [1]. However, the substitution products are isolated in only low yields and doubly and triply bridged complexes decompose upon the action of nucleophiles [2], apparently due to cleavage of the rings at the P—O bond. In order to prevent such cleavage, we undertook the synthesis of previously unreported chromium arene phosphine chelates with a C—P bond in the bridge.

The starting arenechromium tricarbonyl compounds containing pentavalent phosphorus not capable of forming strong complexes with zero-valent chromium in the ω-position of the side chain were synthesized by the reaction of the corresponding arenes with chromium hexacarbonyl or chromium triammine tricarbonyl

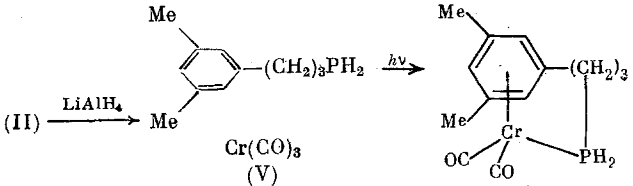


(I) (II)



(III) (IV)

The action of $LiAlH_4$ on complex (II) gives smooth reduction of the diethylphosphonate group to yield phosphine (V). UV irradiation of (V) leads to closure of the chelate ring with the formation of (VI).



(V) (VI)

Phosphonate (II) also gives diphenyl- and diethylphosphonite chelate complexes in 6% yield. The action of phosgene on complex (V) (obtained in situ from (II)) gives dichlorophosphine derivative (VII), which is converted by the action of phenol and triethylamine with subsequent UV irradiation to diphenylphosphonite chelate (VIIIa), IR spectrum (CH_2Cl_2): ν CO 1833, 1897 cm^{-1}, mass spectrum, m/z: 472 M^+, 416 $[M - 2CO]^+$. An analogous procedure with ethanol gave diethylphosphonite complex (VIIIb), IR spectrum (CH_2Cl_2): ν CO 1808, 1872 cm^{-1}, mass spectrum m/z: 376 M^+, 331 $[M - EtO]^+$, 320 $[M - 2CO]^+$. All the steps of this synthesis were carried out without the isolation of the intermediates with rigorous exlusion of air.

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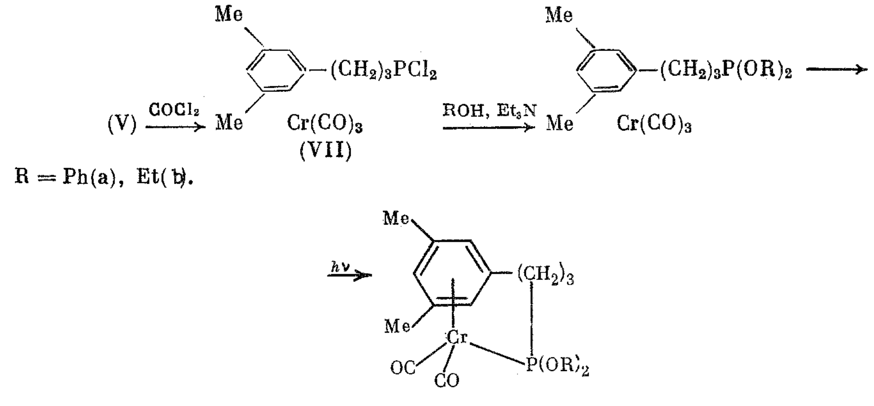
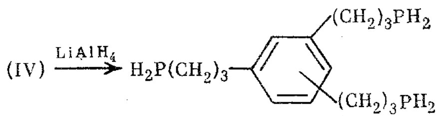


(VIIIa,b)

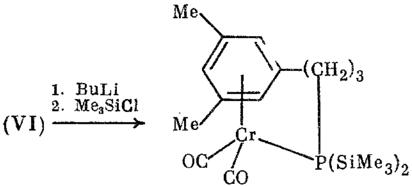
The action of $LiAlH_4$ on (IV) gives the quantitative reduction of all the diethylphosphonate groups to form triphosphine (IX).



(IX)

The ^{31}P NMR spectrum of the reaction mixture after the reduction has only signals for uncoordinated PH_2 groups (triplet at −139.7 ppm from H_3PO_4, j_{PH} = 189.2 Hz). The IR spectrum of the reaction mixture has CO group bands at 1875 and 1958 cm^{-1}. UV irradiation of (IX) before the disappearance of the CO group IR bands leads to decomposition. We may assume that the electron density on the chromium atom after closure of the first bridge (ν CO 1836, 1880 cm^{-1}) is so increased that oxidative addition of the PH_2 groups with subsequent decomposition of the products proceeds rather than substitution of the CO ligands. The IR spectrum of the reaction mixture in the CO group region during the irradiation shows the band at 1880 cm^{-1} for some time. The frequency of this band is considerably higher than expected for a monocarbonyl double-bridged compound with PH_2 ligands.

The reactivity of arene phosphine chelate complexes was studied in the case of (VI). The action of butyllithium on (VI) gives a lithium derivative due to metallation of the P–H bonds, which reacts smoothly with trimethylchlorosilane to give complex (X) in 62% yield.



(X)

Thus, chromium arene dicarbonyl chelates with a phosphorus–carbon bond in the bridge permit us to obtain products of substitution at the coordinated phosphorus atom by metallation in high yields.

EXPERIMENTAL

The chromium complexes were synthesized in an argon atmosphere using absolute solvents. The PMR spectra were carried out on Perkin-Elmer R-12 and Tesla BS-467A spectrometers at 60 MHz in acetone-d_6. The ^{31}P NMR spectra were taken on a Bruker HX-90 spectrometer at 36.43 MHz and Bruker WP-200SY spectrometer at 18.01 MHz relative to H_3PO_4 as the external standard. The IR spectra were taken on IKS-14A and IKS-29 spectrophotometers.

The diethyl ester of 3-(3,5-dimethylphenyl)propylphosphonic acid (I) was obtained from 3-(3,5-dimethylphenyl)propyl bromide [3] and triethyl phosphite. 1,3,5- and 1,2,4-Tris(3-diethylphosponopropyl)benzenes (III) were synthesized from a mixture of 1,3,5- and 1,2,4-tris(3-iodopropyl)benzenes (obtained by heating a mixture of the corresponding trichlorides [4] with anhydrous sodium iodide) and $(EtO)_2PONa$. (I) and (III) were characterized by their PMR spectra.

[η^6-3,5-Dimethyl-1(3-(diethylphosphonopropyl)benzene]chromium tricarbonyl (II) was obtained from 1.42 g (5 mmoles) (I) and 1.2 g (5.5 mmoles) $Cr(CO)_6$ according to Nicholls and Whiting [5]. The yield was 1.44 g (66%), mp 62-63°C. Found: C 52.19; H 5.90; Cr 12.36; P 7.30%. Calculated for $C_{18}H_{25}CrO_6P$: C 51.43; H 6.00; Cr 12.37; P 7.37%. IR spectrum (in heptane): ν CO 1899,1967 cm^{-1}. PMR spectrum: 1.27 t (6H, CH_3CH_2, J = 7 Hz), 1.93 m (4H, CH_2CH_2P), 2.24 s (6H, CH_3—Ar), 2.54 t (2H, CH_2—Ar, J = 7 Hz), 4.09 d. q (4H, $MeCH_2$, J_{HH} = J_{PH} = 7 Hz), 5.27 s (3H, H—Ar).

[η^6-Tris(3-diethylphosphonopropyl)benzene]chromium tricarbonyl (IV) was obtained from 1 g (1.64 mmole) (III) and 0.76 g (4.06 mmoles) $(NH_3)_2Cr(CO)_3$ according to Rausch et al. [6]. The yield was 1.01 g (82%). IR spectrum (in $CHCl_3$): ν CO 1882, 1961 cm^{-1}. PMR spectrum: 1.29 t (18H, CH_3CH_2, J = 6 Hz), 1.58-2.18 m (12H, CH_2CH_2P), 2.33 t (6H, CH_2—Ar, J = 6 Hz), 4.02 d. q (12H, $MeCH_2$), J_{HH} = J_{PH} = 6.5 Hz), 5.33 s, 5.20-5.60 m (3H, H—Ar).

[η^6-3,5-Dimethyl-1-(3-phosphinopropyl)benzene-P]chromium Dicarbonyl (VI). A solution of 0.84 g (2 mmoles) (II) in a mixture of 1 ml THF and 10 ml ether was added with stirring to a suspension of 0.2 g (5.4 mmoles) $LiAlH_4$ in 50 ml ether and heated at reflux for 1 h. Then, water was added at —10°C. The organic layer was dried over Na_2SO_4. The filtrate was evaporated. The residue was dissolved in 100 ml benzene and irradiated with UV light using a PRK-7 lamp for 105 min. After evaporation of the benzene, the residue was subjected to chromatography on a silica gel column using 10:1 petroleum ether—ether as eluent to give 0.34 g (59%) (VI). Found: C 54.36; H 5.91; Cr 17.86%. Calculated for $C_{13}H_{17}CrO_2P$: C 54.17; H 5.94; Cr 18.04%. IR spectrum (heptane): ν CO 1857, 1903 cm^{-1}. ^{31}P NMR spectrum (in CH_2Cl_2): 15.9 J_{PH} = 316, J_{PCH} = 12 Hz.

{η^6-3,5-Dimethyl-1-[3-bis(trimethylsilyl)phosphinopropyl]benzene-P}chromium Dicarbonyl (X). A solution of 0.2 g (0.7 mmole) (VI) in 20 ml ether was added to a solution of 2.9 ml (0.007 eq.) of C_4H_9Li in 5 ml ether at —78°C and stirred for 2 h at —78°C. Then, a solution of 0.88 ml (0.76 g, 7.1 mmoles) Me_3SiCl in 5 ml ether was added and left overnight at —78°C. The solution was evaporated and the residue was extracted with pentane. The extract was evaporated to give 0.25 g (83%) (X). Recrystallization from pentane at —78°C gave 0.14 g (47%) (X). IR spectrum (in heptane): ν CO 1830, 1878 cm^{-1}. PMR spectrum: 0.28 d (18 h, CH_3Si, J_{PH} = 4.5 Hz), 1.11-1.45 m (4H, CH_2CH_2P), 2.08 s (6H, CH_3—Ar), 2.25 t (2H, CH_2—Ar, J = 6 Hz), 4.31-4.47 d (3H, H—Ar, J_{PH} = 2.5 Hz). Found: Cr 11.31; P 6.56%. Calculated for $C_{19}H_{33}CrO_2PSi_2$: Cr 12.02; P 7.16%.

CONCLUSION

1. A method has been developed for the synthesis of previously unreported singly bridged chromium arene phosphine chelate complexes not containing an argon atom in the bridge.

2. The arenechromium tricarbonyl complexes with PH_2 groups in the ω-position of the side chains are incapable of forming a triply bridged chelate by the substitution of carbonyl ligands.

LITERATURE CITED

1. V. V. Krivykh, M. V. Tolstaya, and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1900 (1981).
2. V. V. Krivykh, M. V. Tolstaya, and M. I. Rybinskaya, in: Abstracts of the Second All-Union Conference on Organometallic Chemistry [in Russian], Gorki (1982).
3. V. V. Krivykh, Dissertation, Moscow (1978), p. 147.
4. A. J. Hubert, J. Chem. Soc., C, 6 (1967).
5. B. Nicholls and M. C. Whiting, J. Chem. Soc., 551 (1959).
6. M. D. Rausch, G. A. Moser, E. J. Zaiko, and A. L. Lipman, Jr., J. Organomet. Chem., 23, 185 (1970).