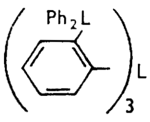
The Oxidation of Some Phosphine-substituted Chromium Carbonyls

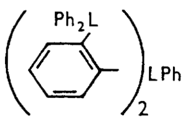
By **I. V. Howell** and **L. M. Venanzi**, Inorganic Chemistry Laboratory, University of Oxford

The potentially quadridentate ligand tris-(*o*-diphenylphosphinophenyl)phosphine (QP) reacts with chromium hexacarbonyl to give the complex $[Cr(CO)_3(QP)]$, in which QP acts as a terdentate ligand. This can be converted into the complex $[Cr(CO)_2(QP)]$ in which QP acts as a quadridentate ligand. Oxidation of the latter complex with mild halogenating agents gives the chromium(I) cation $[Cr(CO)_2(QP)]^+$ which is then further oxidised to the chromium(III) complexes $[CrX_3(QP)]$ (X = Cl, Br), where QP acts as a terdentate ligand, and $[CrI_2(QP)]I_3$, where QP acts as a quadridentate ligand. The ligand bis-(*o*-diphenylphosphinophenyl)phenylphosphine (TP) also reacts with chromium hexacarbonyl to give the complex $[Cr(CO)_3(TP)]$, but no complex could be isolated from its oxidation by mild halogenating agents. The preparation and properties of the complex $[Cr(CO)_3(TAS)]$ {TAS = bis-(*o*-diphenylarsinophenyl)phenylarsine} are also described.

THE oxidation by halogens of substituted Group VI carbonyl complexes containing bidentate nitrogen, phosphorus, arsenic, and sulphur ligands has been extensively studed.[1] This Paper reports the action of a number of oxidising agents on chromium carbonyl complexes with the ligands tris-(*o*-diphenylphosphinophenyl)phosphine, QP, and bis-(*o*-diphenylphosphinophenyl)phenylphosphine, TP.



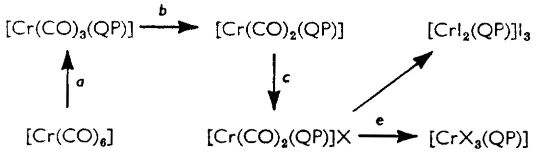
L = P ; QP
L = As; QAS



L = P ; TP
L = As ; TAS

The preparation of the QP-substituted carbonyls and their oxidation reactions are shown in the Scheme.

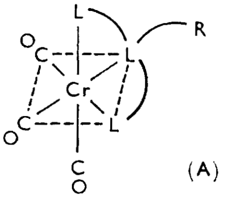
Scheme



[a] On refluxing with QP in Bu_2^nO for 3 hr. [b] On heating at 240°/0·1 mm. for *ca.* 15 hr. [c] On oxidation with $SbCl_5$, *N*-bromosuccinimide, Br_2, I_2, or $(NH_4)_2[Ce(NO_3)_6]$ (1 equiv.). [d] On addition of 4 equiv. of I_2. [e] On addition of an excess of $SbCl_5$, *N*-bromosuccinimide, or Br_2, or on refluxing with either $CHCl_3$ or $CHBr_3$.

Zingales and Ugo[2] obtained $[Cr(CO)_2(QAS)]$ by irradiation of $[Cr(CO)_3(QAS)]$. If this reaction is made to go to completion it is invariably accompanied by decomposition. A similar method can be used for the preparation of $[Cr(CO)_2(QP)]$ but the thermal process (see Experimental section) was found to be more satisfactory as the reaction could be taken to completion without decomposition of the product. The physical properties of $[Cr(CO)_3(QP)]$ and $[Cr(CO)_2(QP)]$ are similar to those of $[Cr(CO)_3(QAS)]$ and $[Cr(CO)_2(QAS)]$ described by Zingales and Ugo. The compound $[Cr(CO)_3(QP)]$ gives $[Cr(CO)_2(QP)]$ if exposed to sunlight. The complexes $[Cr(CO)_3(TP)]$ and $[Cr(CO)_3(TAS)]$ have similar properties to the above compounds. All these complexes are non-electrolytes in nitrobenzene. As the conductivity of these solutions increases with time the iodomethane test for the presence of uncoordinated donor atoms was inapplicable.

The infrared spectra of compounds $[Cr(CO)_3(Ligand)]$ (Ligand = TP, TAS, QP, and QAS) in chloroform show one sharp band at *ca.* 1940 $cm.^{-1}$ and a broader band with a maximum at *ca.* 1855 $cm.^{-1}$ with a shoulder at *ca.* 1845 $cm.^{-1}$ attributable to C–O stretching vibrations. For complexes *cis*-$[Cr(CO)_3(L')_3]$ (L′ = unidentate ligand) (C_{3v} symmetry) one would expect two carbonyl stretches ($A_1 + E$ modes[1]) and for complexes *trans*-$[Cr(CO)_3(L')_3]$ (C_{2v} symmetry) three ($2A_1 + B_1$ modes). As the splitting of the E mode on reduction of symmetry from C_{3v} to C_{2v} is often quite small and as our complexes, if they have the *cis* structure (A), have C_s symmetry ($2A' + A''$ modes[1]) because of structure of the multidentate ligand, it is not possible to assign their geometry on the basis of their C–O stretches.



R = Ph or *o*-$Ph_2L\cdot C_6H_5$
L = P or As

(A)

The oxidants indicated in the Scheme on $[Cr(CO)_2(QP)]$ give $[Cr(CO)_2(QP)]^+$ which was isolated as the $[SbCl_6]^-$ salt (from the $SbCl_5$ oxidation) and as the $[BPh_4]^-$ salt (from the I_2 oxidation). Spectral measurements show that the same complex cation is produced by the other oxidants. For the oxidation of $[Cr(CO)_2(QP)]$ with iodine, spectrophotometry and conductometry show that the $[Cr(CO)_2(QP)]I$ first formed gives $[Cr(CO)_2(QP)]I_3$ on further addition of iodine. The chromium(I) complexes decompose fairly rapidly in air, with loss of carbon monoxide, both in the solid state (followed magnetically) and in solution (followed spectrophotometrically). The C–O stretching frequencies in $[Cr(CO)_2(QP)]^+$ occur at about 70 $cm.^{-1}$ higher than those of $[Cr(CO)_2(QP)]$ (see Table) as would be expected for an increase in oxidation state.

Further oxidation of the chromium(I) complexes gives complexes $[CrX_3(QP)]$ (X = Cl and Br), except for $[Cr(CO)_2(QP)]I_3$ which gives $[CrI_2(QP)]I_3$. Attempts to produce salts of this cation with other anions, *e.g.*,

---

[1] G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Adv. in Inorg. Chem. and Radiochem.*, 1966, **8**, 1, and references therein.

[2] F. Zingales and R. Ugo, *Istituto Lombardo di Scienze e Lettere, Rendiconti* [*A*], 1962, **96**, 763 (*Chem. Abs.*, 1963, **58**, 13,414h).

$[BPh_4]^-$ or ClO_4^-, or attempts to reduce I_3^- to I^- with sulphur dioxide, led to decomposition.

As the reaction[3] of CrX_3 with QP and the oxidation of $[Cr(CO)_2(QP)]$ with reagents leading to the formation of chloro- and bromo-complexes give compounds of the type $[CrX_3(QP)]$ in which the organic ligand is acting as terdentate, while the direct reaction of CrI_3 and QP does not give a complex of the above type, and from oxidation experiments one obtains the complex cation $[CrI_2(QP)]^+$, we conclude that the relative affinity of chromium(III) for phosphorus and the halide ligands in our complexes is $Cl > Br > P > I$.

Oxidation of $[Cr(CO)_3(TP)]$ by antimony pentachloride or by chloroform gives a solution with a visible and ultraviolet spectrum identical with that of $[CrCl_3(TP)]$ and oxidation with *N*-bromosuccinimide or bromoform gives solutions containing $[CrBr_3(TP)]$ as indicated by spectral evidence. No species with intermediate oxidation states could be isolated. Their transient formation is, however, indicated by: (1) the slow addition of a chloroform solution of antimony pentachloride to a solution of $[Cr(CO)_3(TP)]$ in the same solvent gave a red solution showing C–O stretching vibrations at 2040, 1975, and 1905 cm.$^{-1}$ in addition to those of the starting material at 1930, 1860, and 1820 cm.$^{-1}$. However, further oxidation of this new species to chromium(III) occurred before all the chromium(0) complex had been oxidised; (2) the addition of iodine to a solution of $[Cr(CO)_3(TP)]$ in toluene at −70° gave a solution showing the gradual disappearance of the original carbonyl bands and the appearance of new bands at 2045, 1985, and 1910 cm.$^{-1}$ suggesting that the complex produced is similar to that obtained in the other oxidation experiment. Also in this case no characterisable compound could be isolated.

Physical properties of chromium complexes

	Compound	Decomp. pt.[a]	$\mu_{eff.}$[b] (B.M.)	CO stretches (cm.$^{-1}$)	$10^3\nu_{max.}$ ($\varepsilon_{max.}$) (cm.$^{-1}$) (cm.^{2} mole^{-1})
I	$[Cr(CO)_3(TP)]$	290—300°	Diamag.[c]	1940, 1860, 1845[d]	32·0 (sh.)[e]
II	$[Cr(CO)_3(QP)],\frac{1}{2}EtOH$	*ca.* 240	Diamag.[c]	1940, 1860, 1850[d]	30·0 (sh.)[e]
III	$[Cr(CO)_2(QP)]$	330—340	Diamag.[c]	1860, 1805[d]	27·0 (8·3)[e]
IV	$[Cr(CO)_2(QP)][BPh_4]$	[f]	2·2[g]	1950, 1845[h]	21·2, 16·2[i]
V	$[Cr(CO)_2(QP)][SbCl_6]$	[f]	2·2[g]	1945, 1840[h]	21·2, 16·2[i]
VI	$[CrI_2(QP)]I_3$	200—210	3·8	—	34·0 (69·0), 27·4 (38·0), 16·0 (0·4)[e]
VII	$[Cr(CO)_3(TAS)]$	265—275	Diamag.[c]	1940, 1855, 1845[d]	32·0 (sh.), 28·0 (sh.)[e]

[a] In an evacuated tube. [b] At room temperature. [c] These compounds show χ_m (corr.) values between 120 and 290 × 10^{-6} e.m.u. [d] In chloroform solution. [e] In dichloromethane solution. [f] Gradual decomposition. [g] Extrapolated to zero time (see Experimental section). [h] In Nujol mulls. [i] Solid reflection spectra in potassium chloride. The band at 16,200 cm.$^{-1}$ is due to chromium(III) species produced by further oxidation.

Oxidation[4] of *cis*-$[Cr(CO)_2(diars)_2]$ [diars = *o*-phenylenebis(dimethylarsine)] and of several triarsine complexes gives heptaco-ordinate complexes of chromium(II).[5] No chromium(I) intermediate appears to have been isolated. The difference in behaviour between the oxidations of the above complexes and of $[Cr(CO)_2(QP)]$ may be due to steric effects caused by the bulkiness of the organic ligand which may prevent the formation of heptaco-ordinate species. The relative stability of chromium(I) in a near-octahedral environment is indicated by the ease of formation of species such as $[Cr(C_6H_6)_2]^+$.[6]

It is surprising that trigonal bipyramidal complexes such as $[CrX(QP)]^+$ could not be isolated in view of the expected favourable crystal-field stabilisation energy and of the recent preparation of the complex $[CrBr\{N(CH_2CH_2NMe_2)_3\}]Br$.[7] If such intermediates are formed they must react further very rapidly as no evidence for their existence was observed.

EXPERIMENTAL

The phosphorus[8] and arsenic[9] ligands and the complexes[2] $[Cr(CO)_3(QAS)]$ and $[Cr(CO)_2(QAS)]$ were prepared as described elsewhere.

*Tricarbonylbis-(*o*-diphenylphosphinophenyl)phenylphosphinechromium*(0).—Resublimed chromium hexacarbonyl (0·15 g.) and TP (0·38 g.) in dry di-n-butyl ether (50 ml.) were refluxed under dry nitrogen for 3 hr. The solvent was removed by rotary evaporation, and the residue extracted into benzene. The product was recrystallised from hot benzene–heptane (1 : 2). Drying at 200° *in vacuo* was necessary to remove all the solvent from the *crystals*; yield 0·40 g. (Found: C, 70·1; H, 4·2; Cr, 6·8; P, 11·95. $C_{45}H_{33}CrO_3P_3$ requires C, 70·5; H, 4·3; Cr, 6·8; P, 12·1%).

*Tricarbonyltris-(*o*-diphenylphosphinophenyl)phosphinechromium*(0) *Hemi-ethanol*.—Resublimed chromium hexacarbonyl (0·14 g.) and QP (0·41 g.) in dry di-n-butyl ether (50 ml.) were refluxed under dry nitrogen for 2 hr. The solvent was then removed by rotary evaporation and the residue extracted with dichloromethane. The *product* was obtained after addition of ethanol, and dried *in vacuo* at room temperature; yield 0·40 g. (Found: C, 71·4; H, 4·6; Cr, 5·35; P, 12·75. $C_{58}H_{45}CrO_{3\cdot5}P_4$ requires C, 71·7; H, 4·7; Cr, 5·35; P, 12·75%).

*Dicarbonyltris-(*o*-diphenylphosphinophenyl)phosphinechromium*(0).—Complex (II) (0·50 g.) was heated at 240°/0·1 mm. for 12 hr., and the *product* recrystallised from dichloromethane–ethanol (1 : 4), and dried *in vacuo* at 130°; yield 0·42 g. (Found: C, 72·7; H, 4·75; Cr, 5·55;

---

[3] I. V. Howell, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc.* (*A*), 1967, 395.

[4] J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 3009.

[5] C. D. Cook, R. S. Nyholm, and R. S. Tobe, *J. Chem. Soc.*, 1965, 4194; R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *ibid.*, p. 6570.

[6] G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, 1959, **1**, 1.

[7] M. Ciampolini, *Chem. Comm.*, 1966, **2**, 47.

[8] B. Chiswell and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 417.

[9] T. E. W. Howell, S. A. J. Pratt, and L. M. Venanzi, *J. Chem. Soc.*, 1961, 3167.

P, 13·3. $C_{56}H_{42}CrO_2P_4$ requires C, 72·9; H, 4·6; Cr, 5·6; P, 13·4%). The complex appears to exist in two crystalline forms: one has infrared carbonyl absorption bands at 1870, 1816, and 1806 cm.$^{-1}$ (yellow form), and the other at 1859 and 1792 cm.$^{-1}$ (red form). Recrystallisation seems to affect the proportions by random amounts. In solution, only two bands at 1860 and 1805 cm.$^{-1}$ are observed.

Dicarbonyltris-(o-*diphenylphosphinophenyl*)*phosphine-chromium*(I) *Tetraphenylboron.*—Complex (III) (0·16 g.) in chloroform (10 ml.) was treated with iodine (0·022 g.) in ethanol (10 ml.) during 10 min. with vigorous stirring under dry nitrogen at room temperature. No gas was evolved. The yellow solution was treated with sodium tetraphenylboron (0·07 g.) in ethanol (20 ml.) with stirring, and the precipitate filtered off, washed with ethanol, and dried at the pump; yield 0·07 g. (Found: Cr, 4·0; P, 9·8. $C_{80}H_{62}BCrO_2P_4$ requires Cr, 4·2; P, 10·0%); $\mu_{eff} = 2·6$, 2·9, and 3·5 B.M. after $1\frac{1}{4}$, $2\frac{1}{2}$, and 48 hr., respectively.

Dicarbonyltris-(o-*diphenylphosphinophenyl*)*phosphine-chromium*(I) *Hexachloroantimonate.*—Complex (III) (0·46 g.) in chloroform (10 ml.) was treated with 1·71 ml. of 0·14M-antimony pentachloride during 10 min. with vigorous stirring under dry nitrogen. No gas was evolved. The solution turned yellow before all the oxidising agent had been added. Ethanol (15 ml.) was added and some of the chloroform removed by rotary evaporation. The *product* (0·12 g.) was filtered off, washed with ethanol, and dried *in vacuo* (Found: Cr, 4·3; P, 9·95. $C_{56}H_{42}Cl_6CrO_2P_4Sb$ requires Cr, 4·15; P, 9·85%). The complex loses carbon monoxide in air more slowly than the corresponding tetraphenylboron salt.

Di-iodotris-(o-*diphenylphosphinophenyl*)*phosphinechromium*(III) *Tri-iodide.*—Complex (III) (0·30 g.) in dry benzene (10 ml.) was treated with iodine (0·21 g.) in dry benzene (25 ml.) during 20 min. with vigorous stirring under dry nitrogen at room temperature. After 16 hr. the solvent was removed by rotary evaporation and the residue extracted into dichloromethane and precipitated by addition of ethanol as a black powder. The *product* (0·15 g.) was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 42·6; H, 3·2; Cr, 3·3; P, 8·2. $C_{54}H_{42}CrI_5P_4$ requires C, 43·2; H, 2·8; Cr, 3·45; P, 8·25%). The complex is soluble in dichloromethane, chloroform, acetone, and nitrobenzene, but fairly rapidly decomposes. Its Λ_M in 10^{-3}M solution in nitrobenzene (33 ohm^{-1} cm.^{2}) at 20° is rather high for a 1 : 1 electrolyte although other tri-iodide salts, *e.g.*, $[CrI(CO)_2(das)_2]I_3$ [das = *o*-phenylenebis(dimethylarsine)] [4] have values of Λ_M of about 30 ohm.$^{-1}$ cm.^{2}.

Tricarbonylbis-(o-*diphenylarsinophenyl*)*phenylarsine-chromium*(0).—Resublimed chromium hexacarbonyl (0·13 g.) and TAS (0·38 g.) in dry di-n-butyl ether (50 ml.) were refluxed under dry nitrogen for 3 hr. The solvent was removed by rotary evaporation and the residue extracted into benzene. The *product* was obtained by recrystallisation from hot benzene–heptane (1 : 2) and dried *in vacuo* at 175°; yield 0·24 g. (Found: As, 25·0; Cr, 5·9. $C_{45}H_{33}As_3CrO_3$ requires As, 25·0; Cr, 5·8%).

Analyses and Physical Measurements.—These were as described elsewhere.[3]

We thank the Royal Society for a Grant-in-Aid for the purchase of chemicals and the British Petroleum Company Ltd. for a studentship (to I. V. H.).

[6/1505 *Received, November* 28*th*, 1966]