Synthesis and Crystal Structure of an Air Stable σ-Bonded Organochromium Compound, *cis*-Bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)chromium(III) Iodide Monohydrate

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Summary *cis*-Bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)-chromium(III) iodide has been synthesised by a Grignard method and the structure of its monohydrate has been determined by *X*-ray methods; the chromium–carbon bond length is 2·10(1) Å.

WE have found that the air and water stable σ-bonded organochromium(III) species (I) could be conveniently prepared by the route outlined in equation (1), where An = 2-methoxyphenyl, THF = tetrahydrofuran, bipy = 2,2′-bipyridyl. The analogous phenyl derivative of (I) has

$$\begin{tikzcd} 2\mathrm{AnMgBr} \arrow[r, "\mathrm{CrBr_2(THF)_2}"] & {[\mathrm{An_2Cr}]_n} \arrow[d, "\substack{\text{(i) bipy}\\ \text{(ii) [O]/H}_2\text{O}\\ \text{(iii) KI}}"'] \\ & {[\mathrm{An_2Cr(bipy)_2}]^+\mathrm{I}^-} \end{tikzcd} \qquad (1)$$

(I)

recently been obtained from the thermal decomposition products[1] of $Ph_3Cr(bipy)$,tetrahydrofuran. Bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)chromium iodide monohydrate; μ_{eff} 3·8 B.M. (corresponds to three unpaired electrons); λ_{max} 393 (log ε 3·49); λ_{sh} 245 (log ε 4·59); ν_{max} 3360 (H_2O), 2837 (OCH_3)cm^{-1}, reacts with mercuric chloride to give 2-methoxyphenylmercuric chloride, m.p. and mixed m.p. 178—179° (90% yield).

The dark red crystals of the hydrate of (I), $C_{34}H_{30}CrIN_4O_2,H_2O$, are triclinic with a non-reduced cell a = 12·486,

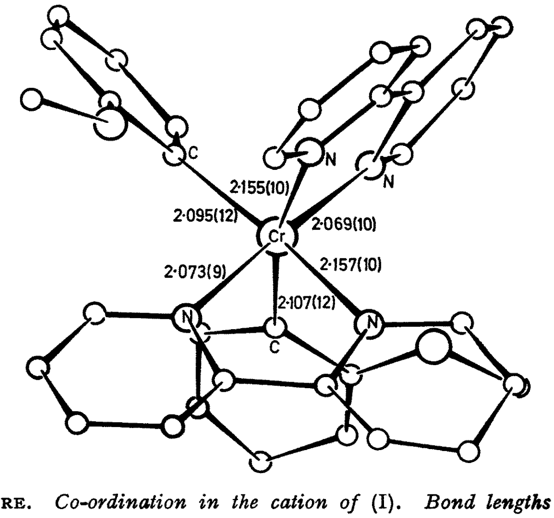

FIGURE. *Co-ordination in the cation of* (I). *Bond lengths are in* Å.

$b = 16{\cdot}657$, $c = 12{\cdot}593$ Å, $\alpha = 129°42'$, $\beta = 51°28'$, $\gamma = 120°7'$, $D_m = 1497$, $Z = 2$, $D_c = 1505$ kg m^{-3}. The water molecule was initially ignored and the structure was determined from 3157 diffractometer data by Patterson and Fourier methods and refined to an R value of 0·070 in the space group $P\bar{1}$. A final difference map gave the positions of the hydrogen atoms and suggested that the water molecule was statistically disordered.

The structure of the cation of (I) is shown in the Figure. The co-ordination round the central chromium atom is distorted octahedral and an approximate twofold axis bisects the C–Cr–C angle and lies in the plane of this angle; the anisyl groups are in the predictable[2] *cis*-configuration. The C–Cr bond lengths are equal with an average length of 2·10(1) Å, 0·09 Å longer than that found[3] in the less (air and water) stable p-$MeC_6H_4{\cdot}CrCl_2,3C_4H_8O$, and 0·10 Å shorter than that found[4] in $Li_4Cr_2Me_8,4C_4H_8O$. In chromium–carbene complexes the chromium–carbon (carbene) bond lengths range[5] from 2·00—2·16 Å and in dibenzenechromium[6] the average of the Cr–C distances is 2·142 Å. The Cr–N bond lengths split into two groups; those *trans* to carbon, 2·16(1) Å, are longer than those *trans* to nitrogen, 2·07(1) Å.

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[1] H. Müller, *Z. Chem.*, 1969, **9**, 311.

[2] F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Austral. J. Chem.*, 1963, **16**, 544; I. M. Proctor and F. S. Stephens, *J. Chem. Soc.* (*A*) 1969, 1248; H. Nakai, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1970, **43**, 577.

[3] J. J. Daly and R. P. A. Sneeden, *J. Chem. Soc.* (*A*), 1967, 736.

[4] J. Krausse, G. Marx, and G. Schödl, *J. Organometallic Chem.*, 1970, **21**, 159.

[5] P. E. Baikie, E. O. Fischer, and O. S. Mills, *Chem. Comm.*, 1967, 1199; O. S. Mills and A. D. Redhouse, *J. Chem. Soc.* (*A*), 1968, 642 ; J. A. Connor and O. S. Mills, *ibid.*, 1969, 334; G. Huttner, S. Schelle, and O. S. Mills, *Angew. Chem.*, 1969, **81**, 536.

[6] E. Keulen and F. Jellinek, *J. Organometallic Chem.*, 1966, **5**, 490; see also F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Amer. Chem. Soc.*, 1963, **85**, 1543; E. Förster, G. Albrecht, W. Dürselen, and E. Kurras, *J. Organometallic Chem.*, 1969, **19**, 215; E. Weiss and E. O. Fischer, *Z. anorg. Chem.*, 1956, **286**, 142.