Crystal and Molecular Structure of Bis[(trimethylsilyl)methyl]bis-(2,2′-bipyridyl)chromium(III) Iodide

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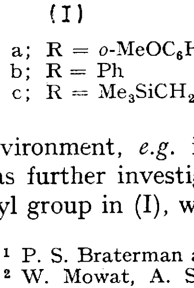
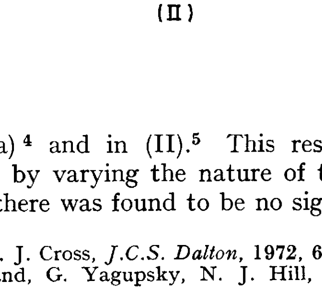
Dark red crystals of the title compound are monoclinic, space group $P2_1/c$, with cell dimensions a = 18·139(15), b = 9·611(8), c = 18·919(15) Å, β = 104·27(17)°, Z = 4. The structure was solved by direct methods. The final R for 3758 counter data refined by block-diagonal least-squares is 0·057. The *cis*-octahedral organometallic cation has an approximate two-fold symmetry axis. The Cr^{III}–C(sp^3) σ-bond length [2·107(12) Å] is the same as that found in two aryl analogues. The Cr–N bond *trans* to carbon is 2·156(7) while that *trans* to nitrogen is 2·103(7) Å, these differences are discussed in terms of σ- and π-bonding effects.

THE factors influencing the stability of σ-bonded organo-transition-metal compounds continue to arouse considerable interest.[1-3] Investigations on σ-bonded octahedral organo-chromium(III) compounds have shown that the Cr^{III}–C(aryl) bond length may vary with the environment, *e.g.* in (Ia)[4] and in (II).[5] This result was further investigated by varying the nature of the aryl group in (I), when there was found to be no significant change in the Cr–C bond length from (Ia)[4] to (Ib).[6] The present analysis of (Ic) has been undertaken to compare the structures of σ-bonded Cr^{III}–(alkyl) and Cr^{III}–(aryl) derivatives in the same environment. A difference in the Cr–C bond lengths might be expected since the aryl group can, at least in principle, participate in π-bonding with the t_{2g} orbitals of the chromium atom. A brief note describing this structure has already appeared.[7]



(I)

a; R = o-$MeOC_6H_4$
b; R = Ph
c; R = Me_3SiCH_2



(II)

EXPERIMENTAL

Crystal Data.—$C_{28}H_{38}CrIN_4Si_2$, M = 665·7, Monoclinic, a = 18·139(15), b = 9·611(8), c = 18·919(15) Å, β = 104·27(17)°, U = 3196·4 Å^3, D_c = 1380, Z = 4, D_m = 1400, Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 1440 m^{-1}. Space group $P2_1/c$ from systematic absences.

Unit-cell dimensions were obtained from zero-layer precession photographs by a least-squares procedure. Intensities were collected round c on a Hilger and Watts linear diffractometer equipped with a graphite monochromator: the 3758 strongest measured reflections were used in the analysis.

Structure Determination and Refinement.—The positions of all non-hydrogen atoms were found from an E map calculated with the phases of 323 planes obtained by an

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[1] P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657.

[2] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

[3] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. 2, Methuen, London, 1968, p. 208 ff.

[4] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *Chem. Comm.*, 1971, 243; J. J. Daly and F. Sanz, *J.C.S. Dalton*, 1972, 2584.

[5] J. J. Daly, R. P. A. Sneeden, and H. H. Zeiss, *J. Amer. Chem. Soc.*, 1966, **88**, 4287; J. J. Daly and R. P. A. Sneeden, *J. Chem. Soc.* (*A*), 1967, 736.

[6] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *J.C.S. Dalton*, 1973, 73.

[7] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *Helv. Chim. Acta*, 1973, **56**, 503.

automatic direct-method [8] programme. This trial structure was refined by block-diagonal least-squares (3×3 and 1×1 or 6×6), first isotropically and then anisotropically till R was 0·059. A difference-Fourier map was then calculated from which the hydrogen atom positions were found. Further refinement of the positional parameters gave a final R of 0·057 (R' 0·0074): the hydrogen atoms were given fixed isotropic temperature factors of 0·01 units in U greater than those of the carbon atoms to which they are bonded. The weighting scheme was according to Cruickshank,[9] with $a = 2{\cdot}0$ and $c = 0{\cdot}0028$. Planes with $3|F_c| < |F_o|$ were omitted from the least-squares process and from R'.

RESULTS AND DISCUSSION

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20702 (24 pp., 1 microfiche).* Standard deviations are given in parentheses as units in the last place of decimals in this paper. Final parameters are in Tables 1 and 2, and bond lengths and angles in Table 3. Figure 1 shows the cation and the labelling of the atoms; hydrogen atoms are labelled after the carbon atom to which they are bonded.

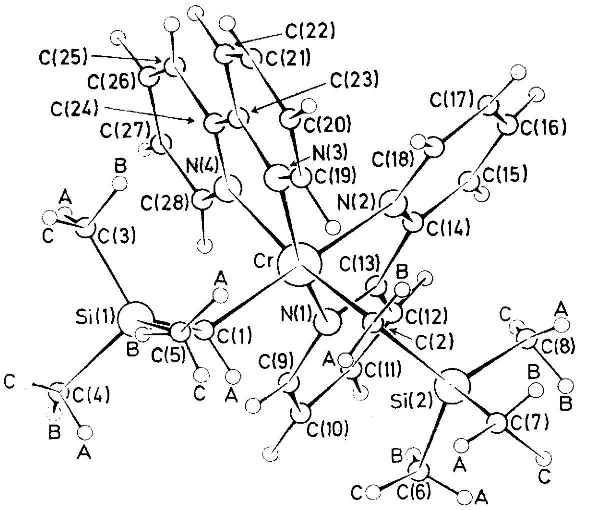

FIGURE 1 The cation of (Ic) showing the labelling of the atoms. Hydrogen atoms are labelled according to carbon atoms to which they are bonded

The cation (Figure 1) has approximate C_2 symmetry, the pseudo-two-fold axis bisecting the C–Cr–C bond angle; the bond lengths to, and the bond angles at, the chromium atom show no significant departures

TABLE 1

Final co-ordinates and standard deviations (Å)

	X	Y	Z
I	7·1364(6)	1·8228(6)	12·9883(7)
Cr	4·2112(12)	8·1762(12)	8·8301(12)
Si(1)	2·6960(26)	10·0256(27)	5·7893(25)
Si(2)	2·4369(25)	8·9959(24)	11·3998(24)
N(1)	3·246(6)	6·387(6)	9·196(6)
N(2)	5·622(7)	7·370(7)	10·622(6)
N(3)	5·719(7)	9·547(7)	8·573(7)
N(4)	5·388(7)	7·047(7)	7·664(7)
C(1)	2·705(9)	8·621(9)	6·996(8)
C(2)	3·370(8)	9·452(8)	10·078(8)
C(3)	4·223(12)	10·005(13)	5·033(13)
C(4)	1·133(13)	9·863(15)	4·289(13)
C(5)	2·614(13)	11·700(11)	6·586(11)
C(6)	0·802(12)	8·043(14)	10·693(14)
C(7)	1·931(13)	10·568(12)	12·166(11)
C(8)	3·541(15)	8·020(16)	12·813(12)
C(9)	2·013(9)	5·943(9)	8·449(9)
C(10)	1·512(11)	4·702(10)	8·655(11)
C(11)	2·277(11)	3·868(10)	9·618(10)
C(12)	3·577(11)	4·270(9)	10·391(9)
C(13)	4·028(9)	5·560(8)	10·137(8)
C(14)	5·352(8)	6·100(8)	10·944(7)
C(15)	6·128(10)	5·430(10)	12·001(9)
C(16)	7·384(10)	6·049(11)	12·785(10)
C(17)	7·634(9)	7·360(10)	12·475(9)
C(18)	6·739(8)	7·988(8)	11·392(8)
C(19)	5·809(9)	10·827(9)	9·004(10)
C(20)	6·836(11)	11·696(13)	8·874(13)
C(21)	7·816(14)	11·202(14)	8·261(15)
C(22)	7·776(11)	9·878(13)	7·795(13)
C(23)	6·729(9)	9·066(10)	7·979(9)
C(24)	6·535(9)	7·669(10)	7·506(9)
C(25)	7·462(11)	7·015(13)	6·886(12)
C(26)	7·182(13)	5·722(14)	6·400(13)
C(27)	6·006(13)	5·109(11)	6·533(11)
C(28)	5·104(11)	5·791(10)	7·197(9)
H(1A)	1·95(11)	8·58(12)	7·47(11)
H(1B)	2·67(12)	7·86(11)	6·47(11)
H(2A)	2·62(11)	10·08(12)	9·53(11)
H(2B)	4·07(11)	9·82(11)	10·64(10)
H(3A)	4·38(14)	9·28(15)	4·68(14)
H(3B)	5·13(14)	10·56(15)	5·69(14)
H(3C)	4·29(14)	10·78(15)	4·41(14)
H(4A)	0·45(14)	10·49(15)	4·71(14)
H(4B)	0·74(14)	9·07(15)	4·17(14)
H(4C)	1·22(14)	10·40(15)	3·72(14)
H(5A)	3·39(14)	12·03(14)	7·32(13)
H(5B)	2·48(14)	12·34(14)	5·91(13)
H(5C)	1·87(13)	11·80(14)	6·88(13)
H(6A)	0·42(15)	8·01(15)	11·44(15)
H(6B)	1·06(16)	7·40(16)	10·62(15)
H(6C)	0·25(15)	8·62(16)	9·83(15)
H(7A)	1·41(13)	11·22(13)	11·50(13)
H(7B)	2·65(13)	10·54(14)	12·94(13)
H(7C)	1·40(13)	10·34(14)	12·97(12)
H(8A)	3·88(15)	8·18(17)	13·44(16)
H(8B)	2·72(17)	8·01(15)	13·51(16)
H(8C)	3·73(17)	7·18(16)	12·67(16)
H(9)	1·49(12)	6·62(11)	7·80(11)
H(10)	0·63(12)	4·41(13)	8·03(12)
H(11)	2·03(13)	2·85(13)	9·73(13)
H(12)	4·23(12)	3·70(12)	11·03(12)
H(15)	6·06(12)	4·60(12)	12·19(11)
H(16)	8·04(12)	5·49(12)	13·37(12)
H(17)	8·41(12)	7·70(11)	13·08(12)
H(18)	6·80(11)	8·89(11)	11·16(10)
H(19)	4·98(12)	11·13(12)	9·53(12)
H(20)	7·13(14)	12·83(14)	9·26(14)
H(21)	8·41(16)	11·82(17)	7·88(15)
H(22)	8·52(14)	9·44(16)	7·34(14)
H(25)	8·23(14)	7·34(14)	6·89(13)
H(26)	7·80(14)	5·27(15)	5·89(14)
H(27)	5·84(13)	4·25(14)	6·22(13)
H(28)	4·25(12)	5·13(12)	7·15(12)

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[8] D. Sayre, *Acta Cryst.*, 1952, **5**, 60; W. H. Zachariesen, *Acta Cryst.*, 1952, **5**, 68; W. Cochran, *Acta Cryst.*, 1952, **5**, 65; H. Hauptman and J. Karle, 'Solution of the Phase Problem. I. The Centrosymmetric Crystal,' Amer. Cryst. Assoc., 1953.

[9] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, 'Computing Methods and the Phase Problem in X-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961, p. 32.

TABLE 2

Temperature factors and standard deviations. For the heavy atoms the form is exp $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{13} + 2hla^*c^*U_{13})$. For hydrogen, exp $-2\pi^2U[(\sin\theta)/\lambda]^2$. Values for I, Cr, are $\times 10^4$, for other atoms $\times 10^3$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
I	560(3)	496(3)	838(5)	8(6)	131(6)	152(7)
Cr	332(6)	335(6)	404(7)	−68(10)	83(11)	232(10)
Si(1)	544(14)	535(15)	474(13)	11(24)	124(23)	192(22)
Si(2)	518(13)	447(14)	533(14)	−178(22)	−81(22)	473(22)
N(1)	42(4)	37(4)	44(4)	−19(6)	−14(6)	26(6)
N(2)	43(4)	38(4)	44(4)	−4(6)	2(6)	25(6)
N(3)	44(4)	44(4)	48(4)	−9(6)	11(6)	32(6)
N(4)	46(4)	50(5)	48(4)	6(7)	5(7)	36(6)
C(1)	53(5)	55(6)	43(5)	0(9)	27(8)	8(8)
C(2)	47(5)	44(5)	55(5)	−14(8)	3(8)	38(8)
C(3)	82(8)	79(8)	99(9)	8(13)	25(14)	108(14)
C(4)	85(8)	100(10)	88(9)	−17(15)	71(15)	−49(14)
C(5)	100(9)	62(7)	63(6)	38(12)	21(10)	61(12)
C(6)	67(7)	103(10)	121(11)	−75(14)	−82(17)	85(15)
C(7)	113(9)	72(8)	67(7)	−2(14)	−33(12)	100(14)
C(8)	109(10)	147(14)	57(7)	47(9)	71(15)	65(13)
C(9)	49(5)	48(5)	65(6)	−21(8)	−15(9)	45(9)
C(10)	71(6)	59(6)	75(7)	−60(11)	−33(11)	52(11)
C(11)	97(8)	49(6)	67(7)	−62(11)	−4(10)	48(12)
C(12)	82(7)	35(5)	59(6)	−38(9)	−9(8)	49(10)
C(13)	59(5)	33(4)	48(5)	−6(8)	0(7)	52(8)
C(14)	48(4)	40(4)	37(4)	−2(7)	1(7)	30(7)
C(15)	66(6)	53(6)	57(6)	22(9)	17(9)	34(9)
C(16)	54(5)	68(7)	62(6)	15(10)	16(10)	16(9)
C(17)	45(5)	68(6)	55(5)	9(9)	5(10)	15(8)
C(18)	40(4)	49(5)	48(5)	−13(8)	0(18)	18(7)
C(19)	54(5)	48(5)	65(6)	−24(9)	10(9)	33(9)
C(20)	65(7)	87(9)	103(9)	−70(12)	−20(14)	76(13)
C(21)	85(8)	91(10)	127(11)	−85(15)	16(16)	101(16)
C(22)	52(6)	89(9)	108(9)	−25(12)	8(14)	72(12)
C(23)	45(5)	67(6)	51(5)	−2(9)	11(9)	34(8)
C(24)	46(5)	72(7)	50(5)	25(9)	15(9)	48(8)
C(25)	67(7)	89(9)	76(7)	15(13)	6(13)	53(12)
C(26)	92(9)	100(10)	84(8)	61(15)	13(15)	92(14)
C(27)	101(8)	69(7)	62(7)	34(13)	5(11)	55(12)
C(28)	94(6)	59(6)	36(5)	44(11)	−12(9)	24(10)

	U_{11}		U_{11}
H(1)	60	H(15)	69
H(2)	59	H(16)	71
H(3)	97	H(17)	66
H(4)	101	H(18)	56
H(5)	85	H(19)	66
H(6)	107	H(20)	95
H(7)	84	H(21)	111
H(8)	114	H(22)	93
H(9)	64	H(25)	87
H(10)	78	H(26)	102
H(11)	81	H(27)	87
H(12)	69	H(28)	73

TABLE 3

Bond length (Å) and angles (°) with standard deviations in parentheses

(*a*) Bond lengths

(i) Chromium octahedron

Cr–C(1)	2·113(9)	Cr–N(3)	2·100(7)
Cr–C(2)	2·100(9)	Cr–N(2)	2·146(7)
Cr–N(1)	2·106(6)	Cr–N(4)	2·166(7)

(ii) To silicon

Si(1)–C(1)	1·850(9)	Si(2)–C(6)	1·873(14)
Si(2)–C(2)	1·853(9)	Si(2)–C(7)	1·873(12)
Si(1)–C(3)	1·864(13)	Si(2)–C(8)	1·844(15)
Si(1)–C(4)	1·887(14)		
Si(1)–C(5)	1·865(12)	Mean Si–C	1·863

TABLE 3 (*Continued*)

(iii) In bipy groups

N(1)–C(9)	1·350(11)	C(11)–C(12)	1·397(14)
N(1)–C(13)	1·349(10)	C(12)–C(13)	1·410(12)
N(2)–C(14)	1·354(10)	C(14)–C(15)	1·366(12)
N(2)–C(18)	1·341(10)	C(15)–C(16)	1·381(14)
N(3)–C(19)	1·347(11)	C(16)–C(17)	1·384(14)
N(3)–C(23)	1·378(11)	C(17)–C(18)	1·375(13)
N(4)–C(24)	1·348(11)	C(19)–C(20)	1·376(15)
N(4)–C(28)	1·346(12)	C(20)–C(21)	1·369(19)
		C(21)–C(22)	1·401(19)
Mean N–C	1·352	C(22)–C(23)	1·372(15)
		C(24)–C(25)	1·398(15)
C(13)–C(14)	1·472(11)	C(25)–C(26)	1·386(18)
C(23)–C(24)	1·473(13)	C(26)–C(27)	1·362(17)
		C(27)–C(28)	1·420(15)
Mean	1·473		
		Mean	1·383
C(9)–C(10)	1·373(14)		
C(10)–C(11)	1·358(15)	Mean C–H	0·96

(*b*) Bond angles

(i) In chromium octahedron, grouped to show approximate C_2 symmetry

N(1)–Cr–N(2)	76·8(3)	N(2)–Cr–C(2)	90·5(3)
N(3)–Cr–N(4)	76·8(3)	N(4)–Cr–C(1)	90·5(3)
N(1)–Cr–N(4)	89·1(3)		
N(2)–Cr–N(3)	90·2(3)	N(2)–Cr–C(1)	170·0(3)
		N(4)–Cr–C(2)	170·5(3)
N(1)–Cr–C(1)	94·1(3)		
N(3)–Cr–C(2)	94·6(3)	N(1)–Cr–N(3)	161·6(3)
		N(2)–Cr–N(4)	85·5(3)
N(1)–Cr–C(2)	98·3(3)	C(1)–Cr–C(2)	94·8(3)
N(3)–Cr–C(1)	97·8(3)		

(ii) Other angles involving chromium

Cr–C(1)–Si(1)	127·9(5)	Cr–N(2)–C(18)	126·1(5)
Cr–C(2)–Si(2)	128·3(5)	Cr–N(3)–C(23)	116·8(5)
Cr–N(1)–C(13)	115·5(5)	Cr–N(3)–C(19)	125·1(6)
Cr–N(1)–C(9)	125·5(6)	Cr–N(4)–C(24)	114·5(6)
Cr–N(2)–C(14)	115·0(5)	Cr–N(4)–C(28)	125·2(6)

(iii) Angles at silicon

C(1)–Si(1)–C(3)	112·6(5)	C(2)–Si(2)–C(6)	113·7(5)
C(1)–Si(1)–C(4)	108·9(5)	C(2)–Si(2)–C(7)	108·6(5)
C(1)–Si(1)–C(5)	113·4(5)	C(2)–Si(2)–C(8)	111·4(5)
C(3)–Si(1)–C(4)	106·1(6)	C(6)–Si(2)–C(7)	106·4(6)
C(4)–Si(1)–C(5)	107·6(6)	C(7)–Si(2)–C(8)	107·5(6)
C(3)–Si(1)–C(5)	108·0(5)	C(6)–Si(2)–C(8)	108·9(6)

(iv) Bond angles in bipy groups

C(13)–N(1)–C(9)	118·5(7)	C(23)–N(3)–C(19)	118·1(7)
N(1)–C(9)–C(10)	122·2(8)	N(3)–C(19)–C(20)	124·2(9)
C(9)–C(10)–C(11)	119·9(10)	C(19)–C(20)–C(21)	116·6(11)
C(10)–C(11)–C(12)	120·0(10)	C(20)–C(21)–C(22)	121·6(12)
C(11)–C(12)–C(13)	117·3(9)	C(21)–C(22)–C(23)	118·4(11)
C(12)–C(13)–N(1)	122·1(8)	C(22)–C(23)–N(3)	121·0(9)
C(14)–N(2)–C(18)	118·9(7)	C(24)–N(4)–C(28)	120·2(8)
N(2)–C(18)–C(17)	122·0(8)	N(4)–C(28)–C(27)	120·4(9)
C(18)–C(17)–C(16)	119·4(9)	C(28)–C(27)–C(26)	119·5(1)
C(17)–C(16)–C(15)	118·1(9)	C(27)–C(26)–C(25)	119·4(12)
C(16)–C(15)–C(14)	120·3(9)	C(26)–C(25)–C(24)	119·5(11)
C(15)–C(14)–N(2)	121·2(8)	C(25)–C(24)–N(4)	120·9(9)
N(1)–C(13)–C(14)	116·5(7)	N(3)–C(23)–C(24)	114·6(8)
N(2)–C(14)–C(13)	114·8(7)	N(4)–C(24)–C(23)	116·6(8)

from C_2 symmetry. The mean Cr$^{\text{III}}$–C(sp^3) bond length [2·107(9)] is not significantly different from the Cr$^{\text{III}}$–C(sp^2) lengths in (Ia) [4] [2·101(12)] and (Ib) [6] [2·087(4) Å]. The Cr–N bond lengths in (Ic) exhibit precisely the same pattern as that found in (Ia) and

(Ib), Cr–N(*trans* to C) [2·156(7)] is longer than Cr–N(*trans* to N) [2·103(7) Å]. The remaining bond lengths (Table 3) show no unusual features.

The angular deviations of the bond angles at chromium from the ideal octahedral values are, as in (Ia)[4] and (Ib),[6] quite large; twelve of these angles should be 90° and the root-mean-square deviation from this is 7·49°, maximum 13·2° and minimum 0·2°. Of the other bond angles in the cation, only Cr–C(1)–Si(1), 127·9(5), and Cr–C(2)–Si(2), 128·3(5)°, are unusual. These large values may be caused by intramolecular repulsions involving the bulky Me_3Si groups or by electronic effects related to those which give rise to a small ring angle at the carbon atom attached to a metal atom in σ-bonded aryl–metal compounds, *e.g.* (Ia),[4] (Ib),[6] and (II).[5]

The pyridyl groups are individually planar (Table 4) but within a bipyridyl ligand they are mutually inclined at a small angle: 7·0° between the rings of N(1) and N(2), and 5·3° between the rings of N(3) and N(4). The chromium atom is displaced from the pyridyl rings by 0·07—0·20 Å; similar distortions are found also in (Ia)[4] and (Ib).[6] The five-membered chelate rings are not planar; the torsion angles about the ring bonds are, in the first ring: −9·7(4) N(1)–C(13), 0·5(5) C(13)–C(14), 8·6(4) C(14)–N(2), −10·4(5) N(2)–Cr, and 10·7(5) Cr–N(1); and in the second ring: −4·7(4) N(3)–C(23), −2·1(5) C(23)–C(24), 7·6(4) C(24)–N(4), −7·6(5) N(4)–Cr, and 6·5(5)° Cr–N(3). Thus in both rings the distortion is mainly a displacement of the chromium atom from the plane of the remaining four atoms.

TABLE 4

Normalised equations of least-square planes of the pyridyl groups in an orthogonal co-ordinate system in the form $lX' + mY' + nZ' - p = 0$ where $X' = X + Z\cos\beta$, $Y' = Y$, $Z' = Z\sin\beta$. Deviations (Å) at atoms from the planes are given in square brackets

	l	*m*	*n*	*p*	
Plane (1): N(1), C(9)—(13)	−0·6154	0·3765	0·6925	7·9620	[Cr −0·209, N(1) 0·0012, C(9) −0·011, C(10) 0·000, C(11) 0·007, C(12) −0·005, C(13) −0·006]
Plane (2): N(2), C(14)—(18)	−0·7072	0·3312	0·6246	6·7583	[Cr −0·014, N(2) −0·011, C(14) 0·010, C(15) 0·000, C(16) −0·008, C(17) 0·007, C(18) 0·004]
Plane (3): N(3), C(19)—(23)	0·3422	−0·2813	0·8959	5·9809	[Cr 0·067, N(3) −0·006, C(19) 0·000, C(20) 0·004, C(21) −0·002, C(22) −0·006, C(23) 0·010]
Plane (4): N(4), C(24)—(28)	0·2899	−0·3595	0·8870	5·0647	[Cr 0·176, N(4) 0·005, C(24) −0·010, C(25) 0·005, C(26) 0·005, C(27) −0·010, C(28) 0·006]

The close similarity of the Cr–X (X = C or N) bond lengths in the three cations of (Ia),[4] (Ib),[6] and (Ic) provides no evidence for a fundamental difference in bonding between the Cr^{III}–C(alkyl) and Cr^{III}–C(aryl) derivatives.

The two-fold symmetry of the chromium octahedra in (Ia), (Ib), and (Ic) leaves only two (d_{yz} and d_{xz} in Figure 2) of the *d* orbitals degenerate and there is no longer any reason to expect equality of the four Cr–N bond lengths since two of them are associated with d_{z^2} and the remaining two with $d_{x^2-y^2}$ (Figure 2). In this low-symmetry system σ- and π-bonding effects may reinforce one another to give a long Cr–N bond *trans* to carbon. First the *trans*-influence[10] of the organic group operating on the σ-bond framework, and secondly the π-acceptor properties of the bipy groups[11] lying in the *xz* and *yz* planes of Figure 2. Two different types of pyridyl ring may be distinguished: those [N(2) and N(4) of Figure 2] which compete with one another for the electron of the d_{xy} orbital, and those [N(1) and N(3)] which compete with organic groups, C(1) and C(2), for the electrons of the d_{yz} and d_{xz} orbitals of the chromium atom. Now the aryl groups of (Ia) and (Ib) are poorly oriented to interact with the d_{xz} and d_{yz} orbitals and in (Ic) the alkyl group should not give effective π-bonding with these orbitals.[3] Thus the pyridyl rings, N(1) and N(3), have no effective competition for the d_{yz} and d_{xz} electrons and so, as observed, the Cr–N(1) and Cr–N(3) bonds should be stronger and shorter than the Cr–N(2) and Cr–N(4) bonds. σ-Bonding effects seem to predominate in (II)[5] while in carbonyl(phosphine)chromium compounds π-bonding seems to be more important.[12-14]

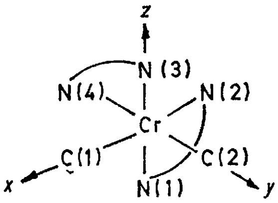

FIGURE 2 Labelling and axes of (I) (a)—(c) for π-bonding with *d* orbitals

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