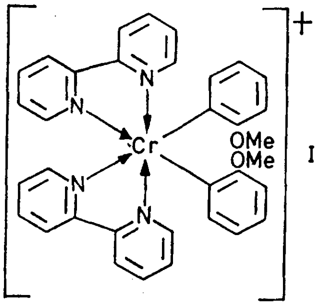
Crystal and Molecular Structure of *cis*-Diphenylbis-(2,2'-bipyridyl)-chromium(III) Iodide

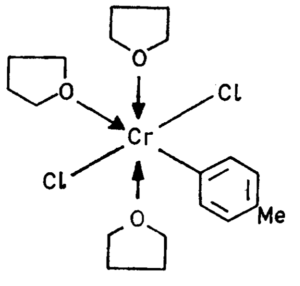
By **J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss,*** Monsanto Research S.A., Eggbühlstrasse 36, CH-8050 Zürich, Switzerland

Crystals of the title compound are monoclinic, space group *C*2/*c*, with cell dimensions *a* = 11·034, *b* = 16·021, *c* = 16·183 Å, β = 103° 31', *Z* = 4. The final *R* for 2227 counter data refined by a block-diagonal least-squares method is 0·054. The organometallic cation, which has the *cis*-octahedral configuration, possesses a crystallographic two-fold symmetry axis. The chromium–carbon σ bond length [2·087(4) Å] is no different from the corresponding length in the *cis*-$[(2\text{-methoxyphenyl})_2Cr(bipy)_2]^+$ (bipy = 2,2'-bipyridyl) cation. The chromium–nitrogen bonds which are not related by the two-fold symmetry axis have different lengths; those *trans* to nitrogen [2·087(4)] being shorter than those *trans* to carbon [2·147(4) Å].

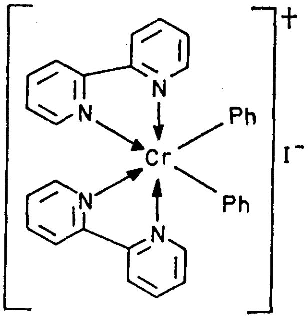
THE previous paper[1] describes the structure of $[(o\text{-MeOC}_6H_4)_2Cr(bipy)_2]^+I^-$, (I; bipy = 2,2'-bipyridyl), an air- and water-stable σ bonded organo-chromium compound. The analysis showed that the Cr–C bond length of 2·101(12) Å was considerably longer than the Cr–C bond length of 2·014(10) Å in the unstable $p\text{-MeC}_6H_4\text{-CrCl}_2,3\text{THF}$,[2] (II; THF = tetrahydrofuran), which suggested that this bond length is a function of the environment of the chromium atom. In an attempt to analyse the effects of the various ligands on this Cr–C length we have now determined the structure of $[Ph_2Cr(bipy)_2]^+I^-$, (III), also air- and water-stable, which differs from (I) in that the MeO groups have been replaced by hydrogen atoms. The compound (III) was prepared by a modified version of the synthesis[3] already described; it had previously been isolated[4] from the thermal decomposition products of $Ph_3Cr(bipy)(THF)$.



(I)



(II)



(III)

EXPERIMENTAL

Synthesis of $[Ph_2Cr(bipy)_2]I$.—A tetrahydrofuran solution of phenylmagnesium bromide (20 ml, 21·96 mmol) was added, under argon, to a stirred suspension of $CrCl_2$ (1·35 g, 10·98 mmol) in tetrahydrofuran containing 2,2'-bipyridyl (3·42 g, 21·9 mmol) at −70 °C. The reaction mixture was allowed to warm to room temperature and subsequently (8 h) concentrated and filtered under argon. The deep-blue solid obtained, was disolved in aqueous methanol containing KI (5 g), and the clear solution subjected to a stream of air. The orange-red solid obtained was then dried, and extracted with small portions of hot nitromethane which, when cooled, gave chunky orange-red crystals which were recrystallized from methanol. (Found: C, 58·9; H, 4·1; Cr, 8·0; I, 20·2; N, 8·7. Calc. for $C_{32}H_{26}CrIN_4$: C, 59·4; H, 4·1; Cr, 8·1; I, 19·7; N, 8·7%; μ_{eff} 3·82 B.M.; $\lambda_{max.}$ (EtOH) (log ε in parentheses) 245 (4·60), 303 (4·77), λ_{sh} 390nm (2·94). The compound reacts with $HgCl_2$, in methanol, to give two equivalents of phenylmercuric chloride m.p. and mixed m.p. 253—255 °C.

Crystal Data.—$C_{32}H_{26}CrIN_4$, *M* = 645·5, Monoclinic *a* = 11·034(6), *b* = 16·021(8), *c* = 16·183(8) Å, β = 103° 31(5)', *U* = 2781·6 Å^3, D_c = 1542, *Z* = 4, D_m = 1549. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 15·9 cm^{-1}. Space group, from extinctions and successful analysis, *C*2/*c*. Unit-cell dimensions were obtained by a least-squares process from precession photographs.

Intensities were collected round *b* on a Hilger and Watts linear diffractometer; 2227 reflections with $\theta \ngtr 22{\cdot}5°$ were measured and used in the refinement.

Structure Determination and Refinement.—A systematic weakness of reflections with *l* odd suggested that an application of direct methods would lead to an ambiguous solution so the structure was solved, in the space group *C*2/*c*, from the three-dimensional Patterson function. Refinement was carried out by a block-diagonal (3 × 3 and 1 × 1 or 6 × 6) process till there was no improvement in *R* and then a three-dimensional difference map was calculated which showed all the hydrogen atoms in their expected positions. Further refinement of the positional parameters led to final values of *R* 0·054 for 2227 planes and of *R'* 0·006 ($R' = \Sigma w\Delta^2/\Sigma wF_o^2$) for 2187 planes. Planes with $3|F_c| < |F_o|$ were omitted from the least-squares totals and from *R'*. All calculations were carried out on an Elliott 803 B computer with programs written in this laboratory.[5]

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[1] J. J. Daly and F. Sanz, *J.C.S. Dalton*, 1972, 2584.

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

[3] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *Chem. Comm.*, 1971, 243.

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

[5] J. J. Daly, F. S. Stephens, and P. J. Wheatley, unpublished work.

RESULTS AND DISCUSSION

The results of the analysis are summarised in Tables 1—4: Table 1 analyses R as a function of the layer index and of the magnitude of $|F_o|$, Table 2 gives the co-ordinates, Table 3 thermal parameters, and Table 4 bond lengths and angles.* Figure 1 is a drawing of the cation projected down [b] and shows the labelling of the atoms.

The cation of (III) (Figure 1) is very similar to that [1] of (I). It exhibits its maximum possible symmetry, a two-fold axis which bisects the C–Cr–C bond angle. This symmetry leaves only two of the chromium d orbitals (Figure 2) degenerate, d_{xz} and d_{yz}, and equality of the Cr–N(1) and Cr–N(2) bond lengths is no longer required since the d_{z^2} and $d_{x^2-y^2}$ orbitals are not degenerate. Thus a Cr–X bond length will depend on its environment and may change if this environment is altered. Two different Cr–N bind lengths are, in fact, observed; that *trans* to nitrogen (2·087 Å) is shorter than that *trans* to carbon (2·147 Å).

Table 1

R as a function of the magnitude of $|F_o|$ and of the layer index k

Range of $\|F_o\|$	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N *	R
0—9·18	1604·92	1400·20	611·76	294	0·381
9·18—18·36	5410·68	5302·70	697·36	398	0·129
18·36—27·54	7666·29	7642·12	523·37	334	0·068
27·54—36·72	7842·03	7895·08	402·51	245	0·051
36·72—45·90	8373·94	8450·71	414·13	204	0·049
45·90—192·78	59377·22	59452·27	1866·69	715	0·031
192·78—247·86	4445·97	4177·13	268·84	21	0·060
247·86—459·00	5064·21	4582·82	511·75	16	0·109
k					
0	11473·32	11056·15	553·55	102	0·048
1	6109·04	5972·76	387·34	166	0·063
2	12750·84	12480·03	610·21	185	0·048
3	9014·01	9016·25	438·24	162	0·049
4	9588·26	9450·39	430·85	172	0·045
5	9877·46	9790·20	372·44	156	0·038
6	5159·06	5260·12	339·64	177	0·066
7	8808·57	8841·44	298·73	164	0·034
8	2855·90	2879·56	291·34	150	0·102
9	6826·11	7069·91	365·90	164	0·054
10	3711·13	3842·62	283·93	155	0·077
11	4759·08	4906·73	260·65	147	0·055
12	3917·76	3662·72	287·74	116	0·073
13	1977·37	1896·49	214·34	109	0·108
14	2917·35	2777·66	201·51	102	0·069
All planes	99745·26	98903·03	5336·41	2227	0·054

* Number of planes.

A comparison of the Cr–X bond lengths in (I)—(III) [1,2] (Table 5) shows that there is an inverse relationship between the Cr–X length and the electronegativity of the atom *trans* to X, for example Cr–C *trans* to oxygen is shorter than Cr–C *trans* to nitrogen. This simple inverse relation does not apply to all octahedral Cr^{III} compounds and exceptions are found in a $Cr^{III}(en)_2$ oxalate complex [6] and in a Cr^{III} [(salen)$(H_2O)_2$] complex.[7]

Table 2

Atomic co-ordinates in Å with standard deviations in parentheses

	X	Y	Z
I	0	8·0059(5)	4·0460(00)
Cr	0	1·0423(8)	4·0460(00)
N(1)	−0·693(4)	−0·554(4)	5·152(3)
N(2)	1·625(3)	0·848(3)	5·776(3)
C(1)	−1·845(5)	−1·253(5)	4·733(5)
C(2)	−2·186(5)	−2·328(6)	5·477(6)
C(3)	−1·276(6)	−2·680(6)	6·701(6)
C(4)	−0·079(5)	−1·965(5)	7·146(5)
C(5)	0·197(4)	−0·902(4)	6·358(4)
C(6)	1·467(5)	−0·079(3)	6·720(4)
C(7)	2·469(5)	−0·260(5)	7·935(5)
C(8)	3·652(5)	0·499(6)	8·192(5)
C(9)	3·813(5)	1·423(6)	7·224(5)
C(10)	2·784(5)	1·572(5)	6·048(4)
C(11)	−0·899(4)	2·469(4)	5·083(4)
C(12)	−2·230(4)	2·277(5)	5·310(4)
C(13)	−2·865(5)	3·239(5)	5·972(5)
C(14)	−2·214(7)	4·405(5)	6·408(6)
C(15)	−0·916(7)	4·638(5)	6·223(5)
C(16)	−0·269(5)	3·673(5)	5·576(5)
H(1)	−2·54(7)	−1·03(6)	3·82(7)
H(2)	−3·13(7)	−2·73(6)	5·00(7)
H(3)	−1·45(8)	−3·39(7)	7·24(7)
H(4)	0·54(7)	−2·21(7)	8·05(6)
H(7)	2·40(6)	−0·98(6)	8·60(6)
H(8)	4·33(8)	0·37(7)	9·06(7)
H(9)	4·64(7)	1·91(6)	7·33(7)
H(10)	2·83(6)	2·25(6)	5·35(6)
H(12)	−2·79(6)	1·46(6)	5·06(6)
H(13)	−3·86(6)	3·05(7)	6·01(7)
H(14)	−2·67(7)	5·06(7)	6·67(7)
H(15)	−0·46(8)	5·41(7)	6·42(7)
H(16)	0·54(7)	3·87(6)	5·39(6)

Table 3

Final anisotropic temperature factors ($10^4 \times U_{ij}$) for I and Cr, ($10^3 \times U_{ij}$) for N and C,* and isotropic temperature factors ($10^3 \times U_{iso}$) for hydrogen

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
I	382(3)	788(5)	502(3)	0(0)	0(0)	7(5)
Cr	260(5)	292(6)	212(5)	0(0)	0(0)	49(7)
N(1)	40(2)	29(2)	38(2)	3(4)	3(3)	19(3)
N(2)	32(2)	38(3)	29(2)	−1(3)	−2(3)	3(3)
C(1)	42(3)	40(4)	53(3)	−26(4)	2(4)	21(5)
C(2)	48(4)	58(4)	60(3)	−18(5)	18(5)	17(6)
C(3)	61(4)	57(4)	64(4)	−11(6)	35(5)	42(6)
C(4)	51(3)	46(4)	48(3)	4(5)	19(5)	33(5)
C(5)	38(2)	28(3)	35(3)	6(3)	0(3)	22(4)
C(6)	41(3)	29(3)	26(3)	4(3)	1(3)	21(4)
C(7)	46(3)	46(3)	39(3)	17(4)	9(4)	−3(5)
C(8)	53(3)	60(4)	37(3)	7(6)	2(5)	−16(5)
C(9)	42(3)	70(4)	45(3)	−12(5)	−4(5)	−14(5)
C(10)	46(3)	43(3)	36(3)	−10(4)	0(4)	5(4)
C(11)	38(2)	34(3)	25(2)	−4(5)	0(4)	22(3)
C(12)	44(3)	45(3)	37(3)	8(4)	6(4)	27(4)
C(13)	52(3)	51(4)	45(3)	30(5)	5(4)	39(5)
C(14)	95(5)	37(4)	53(4)	44(6)	8(5)	61(7)
C(15)	101(5)	39(4)	38(3)	−2(6)	16(4)	33(6)
C(16)	56(3)	42(3)	42(3)	−24(5)	−9(4)	15(5)

	U_{iso}		U_{iso}
H(1)	45	H(9)	52
H(2)	55	H(10)	42
H(3)	61	H(12)	42
H(4)	49	H(13)	49
H(7)	44	H(14)	62
H(8)	50	H(15)	59
		H(16)	47

* In the form $\exp - 2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$.

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* Final observed and calculated structure factors are in Supplementary Publication No. SUP 20510 (15 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[6] J. W. Lethbridge, L. S. D. Glasser, and H. F. W. Taylor, *J. Chem. Soc.* (*A*), 1970, 1862.

[7] P. Coggon, A. T. McPhail, F. E. Mabbs, A. Richards, and A. S. Thornley, *J. Chem. Soc.* (*A*), 1970, 3296.

TABLE 4

Bond lengths (Å) and angles (°) with standard deviations. Mean values only are given when a hydrogen atom is involved

(*a*) Chromium octahedron	
Cr–N(1)	2·147(4)
Cr–N(2)	2·087(4)
Cr–C(11)	2·087(4)
N(1)–Cr–N(2)	77·68(13)
N(1)–Cr–N(1′)	83·93(13)
N(1)–Cr–N(2′)	94·29(13)
N(1)–Cr–C(11)	91·38(14)
N(2)–Cr–C(11)	89·67(14)
N(2)–Cr–C(11′)	97·64(14)
C(11)–Cr–C(11′)	93·72(15)
N(1)–Cr–C(11′)	173·07(14)
N(2)–Cr–N(2′)	169·32(13)

(*b*) Phenyl group	
C(11)–C(12)	1·415(6)
C(12)–C(13)	1·401(7)
C(13)–C(14)	1·357(8)
C(14)–C(15)	1·373(8)
C(15)–C(16)	1·402(7)
C(16)–C(11)	1·394(6)
Mean C⋯C	1·390
Mean C–H	0·93
C(16)–C(11)–C(12)	115·16(38)
C(11)–C(12)–C(13)	121·97(41)
C(12)–C(13)–C(14)	120·38(47)
C(13)–C(14)–C(15)	120·02(53)
C(14)–C(15)–C(16)	119·88(52)
C(15)–C(16)–C(11)	122·57(46)
Mean C⋯C⋯C	120·0
Cr–C(11)–C(12)	121·16(29)
Cr–C(11)–C(16)	123·68(31)
Mean C⋯C–H	119

(*c*) Bipyridyl group	
N(1)–C(1)	1·328(6)
N(1)–C(5)	1·367(5)
N(2)–C(6)	1·358(5)
N(2)–C(10)	1·340(5)
Mean N⋯C	1·348
C(1)–C(2)	1·394(7)
C(2)–C(3)	1·389(8)
C(3)–C(4)	1·376(8)
C(4)–C(5)	1·389(6)
C(6)–C(7)	1·395(7)
C(7)–C(8)	1·378(7)
C(8)–C(9)	1·374(8)
C(9)–C(10)	1·378(7)
Mean C⋯C	1·384
C(5)–C(6)	1·485(6)
Mean C–H	1·00
N(1)–C(1)–C(2)	122·68(44)
C(1)–C(2)–C(3)	118·27(49)
C(2)–C(3)–C(4)	119·68(51)
C(3)–C(4)–C(5)	119·15(46)
C(4)–C(5)–N(1)	121·38(38)
C(5)–N(1)–C(2)	118·84(37)
N(2)–C(6)–C(7)	121·14(40)
C(6)–C(7)–C(8)	120·09(45)
C(7)–C(8)–C(9)	118·44(48)
C(8)–C(9)–C(10)	119·13(48)
C(9)–C(10)–C(2)	123·54(42)
C(10)–N(2)–C(6)	117·65(36)
C(4)–C(5)–C(6)	123·94(39)
C(5)–C(6)–C(7)	122·65(40)
N(1)–C(5)–C(6)	114·67(35)
N(2)–C(6)–C(5)	116·19(36)
Cr–N(1)–C(5)	114·93(26)
Cr–N(2)–C(6)	116·38(27)
Cr–N(1)–C(1)	126·12(30)
Cr–N(2)–C(10)	125·94(28)
Mean C–C–H, N–C–H	119

The Cr–C bond length of 2·087(4) in (III) is not significantly different from that observed in (I) (Table 5) and so we conclude that it is unaffected by substitution in the aromatic ring. It seems premature at this stage to assign a bond order to this bond on the basis of its length but we may note that it is not a long one since it is no different from the shorter Cr–N bond length of 2·087(3) Å. For comparison Cr^0–C(carbene) bond lengths, which are also sensitive to environment, vary from 2·00—2·16 Å [8] while Cr^{II}–C(Me) bond lengths, in non-octahedral complexes, of 2·20 and 2·24 Å have been reported.[9]

The shorter Cr–N bond length of 2·087(3) Å is close to Cr–N lengths found in $Cr^{III}(en)_3$ [2·081(5) [10] and 2·075(3) Å [11]], and to that observed [12] in $Cr^0(bipy)_3$ [2·08(3) Å]. The other Cr–N bond length, 2·147(3) Å, is a little longer than normally observed values but less than that found [13] in Cr^0 $(CO)_3$(dien), 2·185(4) Å.

The angular deviations of the bond angles at the chromium atom from the ideal octahedral values are considerable. Thus the root-mean-square deviation from 90° of the 12 bond angles close to 90° at the chromium atom is 6·37°; the minimum deviation is 0·33° and the maximum 12·32°.

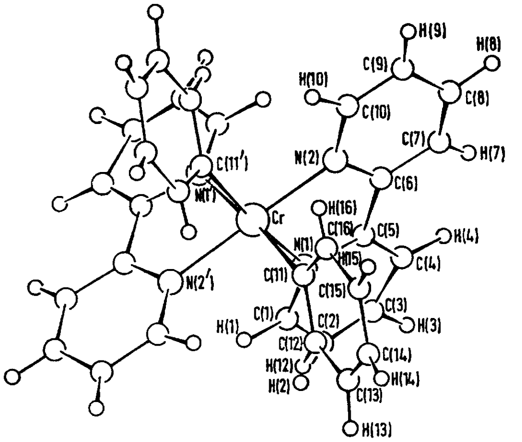

FIGURE 1 The cation of (III) projected down [*b*], showing the atom labelling

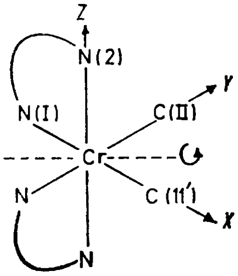

FIGURE 2 Labelling of molecular axes for *d* orbitals

TABLE 5

Cr–X bond lengths in (I)—(III), assuming that the small deviations from symmetry $2(C_2)$ in (I) and (II) may be ignored

Compound	Cr–C(*trans* to Y)	Cr–Y(*trans* to C)	Cr–Y(*trans* to Y)
(I), Y = N	2·101(12)	2·156(10)	2·071(10)
(II), Y = O	2·014(10)	2·214(10)	2·045(8)
(III), Y = N	2·087(4)	2·147(3)	2·087(3)

The torsion angles (°) round the bonds of the chelate five-membered ring are: −2·2(2) N(1)–C(5), 4·1(2) C(5)–C(6), −4·0(2) C(6)–N(2), 2·1(3) N(2)–Cr, and 0·2(2)° Cr–N(1). In this ring therefore only the four atoms N(2), Cr, N(1), and C(5) are coplanar while C(6) is displaced from this plane.

The bond lengths and angles in the bipyridyl group are

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[8] 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.

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close to the values measured in 2,2′-bipyridyl[14] itself which, however, adopts the *anti*-conformation in the solid state. Both pyridine rings are planar (maximum deviation for the heavy atoms 0·006 Å) but the two planes make an angle of 5·10° with one another. The chromium atom lies 0·12 Å from the plane of the ring containing N(1) and 0·06 Å from that of the ring containing N(2).

The carbon atoms of the phenyl group are also coplanar, maximum deviation 0·007 Å, and the chromium atom is displaced by 0·07 Å from this plane. The C$\overset{\cdots}{-}$C bond lengths in this ring have a mean value of 1·390 Å but the lengths to the *para*-carbon atom, mean 1·365 Å, are rather less than the other four, mean 1·403 Å. At least a part of this difference may arise from neglect of thermal motion effects. The ring angle of 115·2° at C(11), the carbon atom bonded to chromium, is considerably less than the normal benzenoid value of 120° and this contraction is also observed in many other metal–aryl compounds.[15]

Since the two phenyl groups are related by a two-fold symmetry axis it can be calculated[16] that the C(16)–C(11)–Cr–C(11′) torsion angle must exceed 31·5° if H(16) · · · H(16′) is to exceed 2·4 Å. As the torsion angle exceeds this value, the H(12) · · · H(10′) contact decreases rapidly; the observed angle is 37·1° with H(16) · · · H(16′) 2·7 Å and H(12) · · · H(10′) 2·4 Å.

The shortest contacts involving the iodide ion are to hydrogen, 3·05 Å, and to carbon, 3·79 Å. The van der Waals' contacts show no unusual features.

We thank Drs. S. and G. Olivé for measurement of μ_{eff} for compound (III).

[2/561 *Received*, 9*th March*, 1972]

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