Further experiments will be directed towards spectroscopic detection and, if possible, isolation of this ion.

I wish to thank Prof. *A. Buchs*, University of Geneva, for the mass spectra, Dr. *U. Burger*, of our Department, for the NMR. measurements and Mr. *J. Pfyffer* for excellent technical assistance.

BIBLIOGRAPHY

[1] *J. D. Roberts, A. Streitwieser & C. M. Regan*, J. Amer. chem. Soc. *74*, 4579 (1952).
[2] *E. Heilbronner & H. Bock*, 'Das HMO-Modell und seine Anwendungen', p. 354, Verlag Chemie, Weinheim 1968.
[3] *J. Adamson, D. L. Forster, T. L. Gilchrist & C. W. Rees*, Chem. Commun. *1969*, 221; *M. S. Ao, E. M. Burgess, A. Schauer & E. A. Taylor*, *ibid. 1969*, 220.
[4] *B. Halton & P. J. Milsom*, Chem. Commun. *1971*, 814.
[5] *W. E. Billups, A. J. Blakeney & W. Y. Chow*, Chem. Comm. *1971*, 1461.
[6] *E. Vogel, W. Grimme & S. Korte*, Tetrahedron Letters *1965*, 3625.
[7] *P. Müller & J. Rocek*, J. Amer. chem. Soc. *93*, 7114 (1971); *94*, 2716 (1972).
[8] *H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon & D. L. Pearson*, J. Amer. chem. Soc. *79*, 4557 (1957).
[9] *D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne & R. C. Sutherland*, Tetrahedron Letters *1961*, 530.
[10] *M. A. Cooper & S. L. Manatt*, J. Amer. chem. Soc. *92*, 1605 (1970); *W. H. Mills & I. G. Nixon*, J. chem. Soc. *1930*, 2510.
[11] *P. Müller*, unpublished.
[12] *L. McDonough & H. J. Dauben, Jr.*, cited by *K. B. Wiberg & E. L. Motell*, Tetrahedron Letters *1963*, 2009; *P. Müller & J. Rocek*, unpublished.

---

45. Alkyl Transition Metal Compounds IX[1]) Synthesis and Structure of $[(Me_3SiCH_2)_2Cr(bipy)_2]$ I

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

(14. XII. 72)

Summary. Bis(trimethylsilylmethyl)-bis-(2,2'-bipyridyl)chromium(III) iodide has been synthesized and its structure determined; the Cr-C(sp^3) bond length is 2.107(9) Å.

The factors influencing the stability of σ-bonded alkyl or aryl transition metal compounds are a source of constant interest [2]–[4]. Thus it is found that many aryl metal compounds are more stable thermally than their alkyl analogues [4]–[7], and this observation is difficult to rationalize in terms of simple bond homolytic processes. It is often presumed that one of the factors contributing to this variation in thermal stability involves fundamental differences in the nature of the metal to carbon bonding in the two types of compounds. This in so far as the aryl group, in contrast to the alkyl group, may donate or accept electrons from the metal center. We have now extended our synthesis of octahedral bis-arylchromium(III) compounds of the type $[R_2Cr(bipy)_2]$I, (bipy = 2,2'-bipyridyl) [8]–[9] to the preparation of the bis-alkyl-

---

[1]) Part VIII, see [1].

analogue (R = Me_3SiCH_2 [10]). The present single crystal X-Ray structure analysis was undertaken to determine the value of the Cr(III)-C(sp^3) bond length and to find what difference, if any, exists between aryl- and alkyl-chromium bond-lengths in strictly analogous complexes.

Bis(trimethylsilylmethyl)-bis(2,2'-bipyridyl)chromium(III) iodide (Found C 51,0; H 6,10; Cr 7,94; I 18,8; N 8,4%; Calc. for $C_{28}H_{38}CrIN_4Si_2$ C 50,5; H 5,75; Cr 7,8; I 19,1; N 8,4%), μ_{eff} 3.64 BM (corresponding to three unpaired electrons); λ_{max} (EtOH) 245 ($\log\varepsilon = 4.49$); 300 ($\log\varepsilon = 4.49$); 390 nm ($\log\varepsilon = 3.30$) reacts with $HgCl_2$ in methanol to give two equivalents of Me_3SiCH_2HgCl (m.p. and mixed m.p. 74–76°). The dark red crystals of $[(Me_3SiCH_2)_2Cr(bipy)_2]I$, (**1**) were obtained from nitromethane; they are monoclinic, space group $\mathbf{P2_1/c}$ with $a = 18.139$, $b = 9.611$, $c = 18.919$ Å, $\beta = 104.3°$, $\mathbf{Z} = 4$, $\mathbf{D_m} = 1400$, $\mathbf{D_c} = 1380$ kg m^{-3}. The structure was solved by direct methods and refined by least squares to a final **R** value of 0,057 for 3758 planes. The cation is represented in Fig. 1.

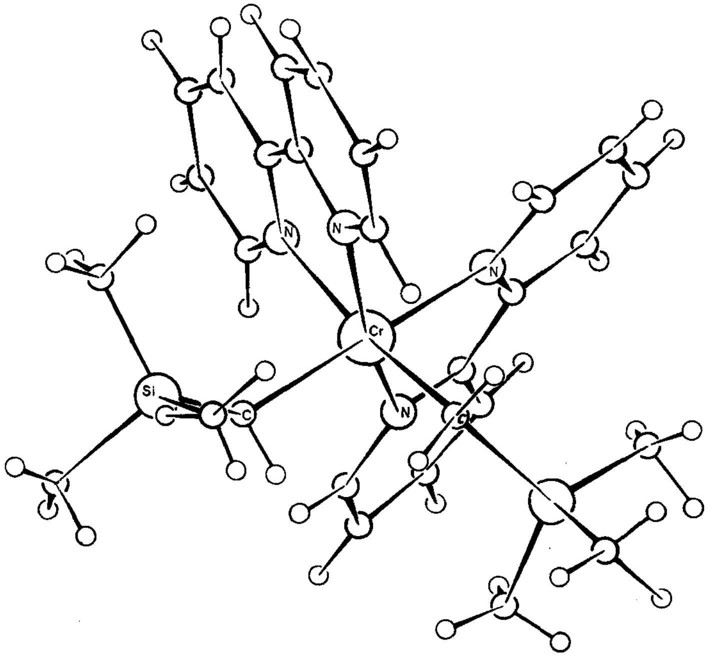


Fig. 1. *The cation* $[(Me_3SiCH_2)_2Cr(bipy)_2]^+$

The bond lengths and angles involving the chromium atom show no significant deviations from $\mathbf{C_2}$ symmetry, the pseudo-twofold axis bisecting the C–Cr–C bond angle. The mean Cr(III)-C(sp^3) bond length of 2.107(9) Å is not significantly different from the Cr(III)-C(sp^2) lengths in the analogous $[Ar_2Cr(bipy)_2]^+$ cations which have Cr–C bonds of 2.101(12) (Ar = o-$MeOC_6H_4$, **2**) [11] and 2.087(4) Å (Ar = Ph, **3**) [9]. The Cr–N bond lengths in **1** exhibit precisely the same pattern as that found in **2** and **3**; Cr–N *trans* to carbon, 2.156(7), is longer than Cr–N *trans* to nitrogen, 2.103(7)

Å. Thus the bond lengths to the chromium atoms in these three structures provide no evidence for a fundamental difference in bonding between the Cr(III)-C(alkyl) and Cr(III)-C(aryl) compounds.

Two factors may reinforce one another in the lengthening of the Cr–N(2) and Cr–N(4) bonds (Fig. 2); first the *trans* influence of the organic group operating on the σ-bond framework of the chromium atoms [12] and second the π-acceptor properties of the bipyridyl groups. Non-bonded intramolecular repulsions force the aryl groups of **2** and **3** out of the xy plane of Fig. 2 and so these rings are poorly oriented to give effective π-bonding with the t_{2g} orbitals of the chromium atom. The Me_3SiCH_2 groups in **1** also should not form strong π-bonds to chromium [4] and so the near equality of the Cr–C bond lengths in **1**, **2** and **3** is understandable. The bipyridyl groups are classified as π-acceptors [13], one lies in the xz and the other in the yz plane of Fig. 2. Two different types of pyridine rings may be distinguished; those containing N(2) and N(4) which compete with one another for the electron of only one d orbital, d_{xy} (no longer degenerate with d_{yz} and d_{xz}), and those containing N(1) and N(2) which have no effective competition from the organic groups C(1) and C(2) for the electrons of d_{yz} and d_{xz} respectively. Thus, as observed, the Cr–N(2) and Cr–N(4) bonds should be weaker and longer than the Cr–N(1) and Cr–N(3) bonds.

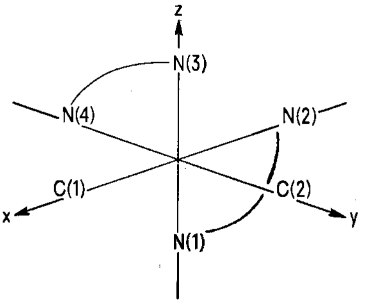


Fig. 2. *Labelling for atoms bonded to chromium in* **1**, **2** and **3** with axes for d orbitals

It is interesting to note that π-bonding effects seem to predominate in phosphine chromium carbonyl compounds [14–16] while σ-bonding effects seem to be more important in (*p*-tolyl)-$CrCl_2 \cdot 3C_4H_8O$ [5].

We thank Drs. *G.* and *S. Olivé* for the magnetic measurement.

REFERENCES

[1] *R. P. A. Sneeden & H. H. Zeiss*, J. organometal. Chem. *27*, 89 (1971).
[2] *P. S. Braterman & R. J. Cross*, J. chem. Soc. (Dalton) *1972*, 657.
[3] *W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky & G. Wilkinson*, J. chem. Soc. (Dalton) *1972*, 533.
[4] *G. E. Coates, M. L. H. Green & K. Wade*, 'Organometallic Compounds', Methuen and Co. Ltd., London 1968, vol. 2, p. 208 *et seq.*
[5] *J. J. Daly, R. P. A. Sneeden & H. H. Zeiss*, J. Amer. chem. Soc. *88*, 4287 (1966).
[6] *R. P. A. Sneeden & H. H. Zeiss*, J. organometal. Chem. *13*, 369 (1968).
[7] *K. Nishimura, H. Kuribayashi, A. Yamamoto & S. Ikeda*, J. organometal. Chem. *37*, 317 (1972).

[8] *R. P. A. Sneeden & H. H. Zeiss,* J. organometal. Chem. *47,* 125 (1973).
[9] *J. J. Daly, F. Sanz, R. P. A. Sneeden & H. H. Zeiss,* J. chem. Soc. (Dalton), in press.
[10] *M. R. Collier, M. F. Lappert & M. M. Truelock,* J. organometal. Chem. *25,* C 36 (1970).
[11] *J. J. Daly & F. Sanz,* J. chem. Soc., Dalton *1972,* 2284.
[12] *A. Pidcock, R. E. Richards & L. M. Venanzi,* J. chem. Soc. (A) *1966,* 1707.
[13] *C. S. G. Phillips & R. J. P. Williams,* 'Inorganic Chemistry', Vol. 2, p. 214, Oxford University Press, Oxford, 1966.
[14] *M. J. Bennett, F. A. Cotton & M. D. LaPrade,* Acta Cryst., *B27,* 1899 (1971).
[15] *G. Huttner & S. Schelle,* J. organometal. Chem. *19,* P9 (1969).
[16] *G. Huttner & S. Schelle,* J. Cryst. Mol. Struct. *1,* 69 (1971).

46. Chemically Induced Dynamic Nuclear Polarization XI[1]) Intermediary Vinyl Alcohol During Photochemical Reactions of Acetaldehyde and of Acetoin

by **B. Blank** and **H. Fischer**

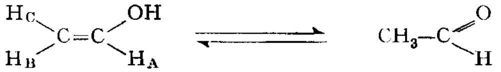
Physikalisch-Chemisches Institut der Universität Zürich

Herrn Prof. Dr. *M. Viscontini* zum 60. Geburtstag gewidmet

(11. XII. 72)

Summary. Vinylalcohol, formed by disproportionation of α-hydroxyethyl radicals, is detected by NMR. spectroscopy during photoreactions of acetaldehyde and acetoin in solution and slowly tautomerizes to acetaldehyde.

At room temperature, the equilibrium concentration of vinyl alcohol **1** has been estimated to be at least seven orders of magnitude lower than that of the keto isomer, acetaldehyde **2**, *i.e.* to be lower than the detection limit of most physical techniques [2] [3]. This has impeded the determination of spectroscopic properties of this most simple enol.



1 **2** (1)

During photolysis of **2** and of 2-hydroxybutan-3-one (acetoin, **3**) in the probe of a modified HA-100 ^{1}H-NMR. spectrometer, we detect **1** as thermally unstable radical reaction product, and observe its vinyl proton spectrum highly enhanced by chemically induced dynamic nuclear polarization (CIDNP.) [4] [5] [6]. Fig. 1 shows ^{1}H-NMR.-spectra taken at room temperature during irradiation of **2** (a) and **3** (b), 0.2 M in benzene, with the beam of a high pressure mercury capillary lamp filtered to transmit radiation of wavelength 300 nm $\leqslant \lambda \leqslant$ 350 nm. During the periods of observation conversion was less than 10%. The same CIDNP. effects were found with benzene-h_6, benzene-d_6, cyclohexane-h_{12}, cyclohexane-d_{12}, and octamethyltetrasiloxane as solvents.

The Table gives the assignments of the transitions 1 through 10 of Fig. 1 to the various reaction products together with the description of the CIDNP.-effects in the

---

[1]) For part X of this series: see [1].