The Novel Conformational Preferences of Five-membered Di(tertiary arsine) Chelate Complexes of Chromium Carbonyl: Determination by Nuclear Magnetic Resonance Spectroscopy

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Summary The favoured conformations of the title compounds, determined in benzene solutions by n.m.r. spectroscopy, appear to be critically dependent on the nature of the substituent attached to the chelating ligand.

ALTHOUGH the conformations of a wide variety of chelate complexes have been determined by *X*-ray crystallographic methods,[1] there is a lack of information concerning the conformations of such compounds in solution.[2] We now report a study of some five-membered, chelate complexes of chromium carbonyl which demonstrate that n.m.r. spectroscopy has considerable potential in this area.

A series of complexes have been prepared by reaction of chromium carbonyl with suitably substituted 1,2-(dimethylarsino)-ethanes.† The coupling constants of two typical complexes (**1**) and (**2**) are listed in the Table.

Coupling constants[a] (J, *Hz*) *for complexes of chromium tetracarbonyl*

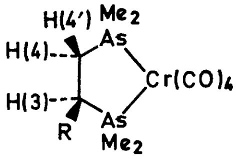
	H(3)–H(4)	H(3)–H(4′)	H(4)–H(4′)	H(3)–F	H(4)–F	H(4′)–F
(**1**)	5·1	15·9	−12·7	—	—	—
(**2**)	3·4	3·6	−13·9	49·6	48·7	15·7

[a] Data for C_6D_6 solutions at 100 MHz, using a modified Varian HA-100 spectrometer operating in the frequency-sweep mode. All data were analysed using the LAOCOON III programme with an I.B.M. 360-67 computer.

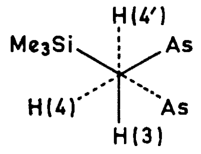
The vicinal ^1H–^1H couplings of the trimethylsilyl derivative (**1**) indicate that, to a first approximation,‡ the favoured rotamer about the C(3), C(4) bond corresponds with that depicted in the projection, (A). This implies that the five-membered ring favours a conformation in which the trimethylsilyl substituent has an "equatorial" orientation. Inspection of molecular models indicates that this effectively minimises repulsive non-bonded interactions.[4]

In marked contrast with the above findings, the vicinal ^1H–^1H and ^{19}F–^1H couplings of the fluoro-derivative (**2**) indicate unequivocally that the favoured rotamer for this compound approximates to that shown in (B). This implies that the five-membered ring must adopt a conformation which places the fluorine substituent in an "axial" orientation. We can offer no convincing explanation for this behaviour. It is possible that an attractive interaction involving the fluorine substituent is involved. Although it is well known[5] that the dipolar interactions of a C–F bond can profoundly influence conformational preferences, it is difficult to envisage how this effect could operate for (**2**). It is of interest to note that the 3-chloro-analogue (**3**) appears to have a significantly lower preference for the axial orientation (vicinal couplings for benzene solution, 7·5 and 5·2 Hz).

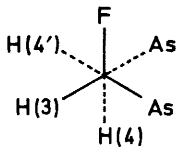
Although this discussion is expressed in terms of specific conformations it should be emphasised that this is an oversimplification. Because the energy barrier for conformational inversion processes of five-membered ring systems is generally low,[6] most conformations determined by the n.m.r. method will be subject to a greater, or lesser, degree of conformational inversion. In certain instances the conformational preference may be sufficiently high for a sensible discussion to be based on individual conformations; compounds (**1**) and (**2**) both appear to fall in this category. However, this will not usually be the case.



(1) R = SiMe$_3$
(2) R = F
(3) R = Cl



(A)



(B)

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† All substances reported here have i.r., mass, and n.m.r. spectra, and micro-analyses in accord with the assigned structures.

‡ Until the possible effect of the two arsenic substituents on the magnitudes of the vicinal couplings has been delineated, it would seem unwise to attempt any calculations based on the Karplus (ref. 3) relationship.

[1] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1362.

[2] L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *J. Amer. Chem. Soc.*, 1968, **90**, 6371; S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1969, **42**, 3184.

[3] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; *J. Amer. Chem. Soc.*, 1963, **85**, 2870.

[4] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

[5] L. D. Hall and J. F. Manville, *Canad. J. Chem.*, 1969, **47**, 19 and references therein.

[6] J. E. Kilpatrick, K. S. Pitzer, and R. S. Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2483; J. B. Hendrickson, *ibid.*, 1961, **83**, 4537; J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **8**, 1168.