Communications to the Editor

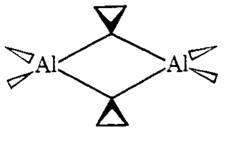
The Structure of Vinyl Bridged Aluminum Derivatives. A π-Electron Stabilized Electron Deficient Bridge Bond

Sir:

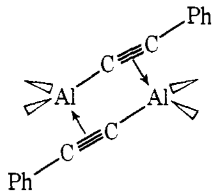
The structure and bonding of electron-deficient bridged organometallic compounds are areas of considerable interest. The geometries of the bridging groups in hydrocarbon bridged aluminum compounds have been studied in order to better understand the bonding between the metal atom and the bridging ligand. Bridging methyl groups have been shown to have their threefold axis perpendicular to the Al-Al axis.[1,2] Bridging cyclopropyl groups are oriented so that the plane bisecting the cyclopropyl group is perpendicular to the Al-Al axis and the H_2C-CH_2 bond is parallel to the Al-Al bond, as shown in I.[3] The determination of this conformation supported the earlier postulate that the p orbital on the bridging cyclopropyl carbon atom interacts with nonbonded orbitals in the aluminum atoms, thus accounting for the observed stability of the cyclopropyl group toward exchange.[4,5] Similar proposals have been put forth for the phenyl bridged dimers, which also have the bridging group oriented appropriately for such interaction.[6,7]

This type of interaction was also invoked, in the absence of any structural data, to account for the enhanced stability of vinyl bridged gallium[8,9] and aluminum compounds[10] and ethynyl bridged derivatives of aluminum, gallium, and indium.[11,12]

In a recent report of the structure of a phenylethynyl bridged aluminum dimer, Stucky et al.[13] found an unsymmetric structure with linear $Al—C\equiv C$ moieties (II), in which the bonding is best described in terms of a σ-bond between the bridging α-carbon and one aluminum atom and a π-bond between the triple bond and the vacant orbital on the other aluminum atom. Similar structural results on a phenylethynyl bridged beryllium derivative[14] support the suggestion that the bonding in ethynyl bridged systems is of a very different kind than found in alkyl bridged systems.



I



II

We now wish to report the first structure of a vinyl bridged system, di(μ-*trans*-3,3-dimethyl-1-buten-1-yl)(tetraisobutyl)dialuminum. In this compound (Figure 1), the vinyl group is bonded symmetrically through the α carbon to the two aluminum atoms with equal Al-C distances of 2.11 Å. The plane of the vinyl group is perpendicular (89.3°) to that of the Al_2C_2 moiety. It is noteworthy that this Al_2C_2 moiety is centrosymmetric and therefore planar in contradistinction to the decidedly nonplanar methyl and cyclopropyl species. It also should be noted that in this system, the Al-C-Al bridge angle (79°) is similar to that observed in the phenyl bridged dimers (76.5, 77.5°) and in the cyclopropyl bridged dimer (78°), and that the Al-Al distances in these three species are 2.70, 2.69, and 2.62, respectively, compared to 2.68 Å in the vinyl bridged system. It thus appears that π stabilization in the vinyl aluminum compound is rather like that found in the cyclopropyl or phenyl bridged dimers, and is quite similar to the bridging observed in the trimethylaluminum dimer.

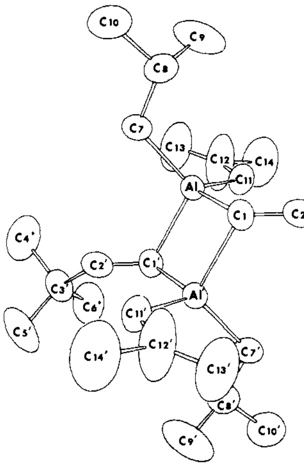


Figure 1. ORTEP drawing of di(μ-*trans*-1-buten-1-yl)(tetraisobutyl)dialuminum with 25% probability ellipsoids.

When comparison is made between these π-stabilized systems and the ethynyl bridged derivatives, it can be seen that the Al-C-Al angle (91.7°) in the ethynyl derivative is greatly altered from that observed in the other bridged species and that the Al-Al distance (~3 Å) is substantially greater, thus precluding a significant metal-metal interaction. On this basis it appears that there is competition between two kinds of bond formation: (1) the formation of an electron deficient bond stabilized by interaction of the p orbital of the carbon with the nonbonding metal orbitals and (2) the formation of a strong C-Al σ-bond and a weak π → Al bond. The result may be dictated by the sum of the two bond energies in each case and by nonbonded interactions between the substituent groups. Since the relative strengths of these bonds will be altered as a function of the metal atoms, the bridging group, and of various substituents present on the bridging group, we cannot state that the two classes of dimer bonding will always follow the pattern observed, but may in fact differ with symmetrical bridge bonding observed for ethynyl groups or unsymmetrical bridge bonding observed for other unsaturated systems. Additional studies must be carried out to establish if the reported cases represent the general type of bonding observed for each of these classes of bridging groups.

Di(μ-*trans-tert*-butylvinyl)(tetraisobutyl)dialuminum was prepared by addition of diisobutyl aluminum hydride to *tert*-butylacetylene as described by Zweifel et al.;[10] single crystals were obtained by sublimation. The compound crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 9.514$ (6) Å, $b = 10.837$ (6) Å, $c = 9.803$ (3) Å, $\alpha = 90.56$ (4)°, $\beta = 105.46$ (4)°, $\gamma = 120.20$ (4)°, and one dimer per cell. Intensity data were collected with monochromatic (graphite monochromator) Mo Kα radiation by the θ-2θ scan technique on a Syntex $P2_1$ diffractometer. Iterative application of the Sayre relation[15] followed by full-matrix anisotropic least-squares refinement of all non-hydrogen atoms resulted in $R = 0.082$ and $R_w = 0.102$ for the 987 data for which $I > 3\sigma(I)$. Hydrogen atoms were included at calculated values (C-H = 1.0 Å, B assigned 10% greater than B (carbon) to which it is bonded) except for the hydrogen on the bridging vinyl carbon which was located from a difference Fourier synthesis.

Acknowledgments. M.J.A. was supported by a Wayne State University graduate fellowship (1975–1976), T.J.A. by a grant from the National Institutes of Health (AM14341), and W.M.B. by a grant from the National Science Foundation (GP-15070).

References and Notes

(1) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).
(2) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **89**, 3121 (1967).
(3) J. W. Moore, D. A. Sanders, P. A. Scherr, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, **93**, 1035 (1971).
(4) D. A. Sanders and J. P. Oliver, *J. Am. Chem. Soc.*, **90**, 5910 (1968).
(5) D. A. Sanders, P. A. Scherr, and J. P. Oliver, *Inorg. Chem.*, **15**, (1976).
(6) J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 2646 (1972).
(7) J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 2649 (1972); J. F. Malone and W. S. McDonald, *Chem. Commun.*, 280 (1970).
(8) J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, **24**, 953 (1962).
(9) H. D. Visser and J. P. Oliver, *J. Am. Chem. Soc.*, **90**, 3579 (1968).
(10) G. M. Clark and G. Zweifel, *J. Am. Chem. Soc.*, **93**, 527 (1971).
(11) E. A. Jeffery, T. Mole, and J. D. Saunders, *Aust. J. Chem.*, **21**, 137 (1968).
(12) N. S. Ham, E. A. Jeffery, and T. Mole, *Aust. J. Chem.*, **21**, 2687 (1968).
(13) G. D. Stucky, A. M. McPherson, W. E. Rhine, J. J. Eisch, and J. L. Considine, *J. Am. Chem. Soc.*, **96**, 1941 (1974).
(14) B. Morosin and J. Howatson, *J. Organomet. Chem.*, **29**, 7 (1971).
(15) (a) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FASTES, E. R. Corey's program for generation of normalized structure factors; (3) REL, R. E. Long's program for phase determination by Sayre's method; (4) FORDAP, A. Zalkin's Fourier Program; (5) ORFLS and ORFFE, W. Busing, K. Martin, and M. Levy's full matrix least-squares program and function and error program; (6) ORTEP, C. K. Johnson's program for drawing crystal models; (7) HFINDR, A. Zalkin's program for calculating idealized hydrogen coordinates. (b) Scattering factors were taken from "The International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., The Kynoch Press, Birmingham, England, 1974.

Michael J. Albright, William M. Butler, Thomas J. Anderson
Milton D. Glick, John P. Oliver*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received February 24, 1976

Intersystem Crossing in Chromium(III) Photochemistry

Sir:

We have recently suggested[1] that ${}^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing (ISC) proceeds at a comparable rate to ${}^4T_{2g}$ vibrational equilibration for the $Cr(en)_3{}^{3+}$ ion (en = ethylenediamine) in aqueous solution at 25 °C. The conclusion was based in part on the higher phosphorescence yield on 436 nm relative to 514-nm excitation (ϕ_p 514 nm/ϕ_p 436 nm = 0.63). This emission ratio was obtained after correction for the relative lamp intensities at 436 and 514 nm, using absorbance matched $Ru(bpy)_3{}^{2+}$ solutions as photon counters. We have since independently confirmed the value of this emission ratio (0.66), using ferrioxalate[2] and reinecke's salt[3] actinometry to determine the 436- and 514-nm lamp intensities, respectively.

It is noteworthy that Adamson et al. have previously postulated that ISC may successfully compete with ${}^4T_{2g}$ equilibration for Cr(III) complexes at very low temperatures.[4-6] They attribute[5,6] the phenomenon to solvent restricted (and therefore temperature dependent) quartet relaxation, associated with the substantial distortion of the equilibrated ${}^4T_{2g}$ state from ground state geometry. If this explanation also applies at room temperature, it would seriously compromise the widely held contention[7-10] that the photoreactivity of Cr(III) systems of O_h and D_3 symmetry originates solely out of the ${}^4T_{2g}$ excited level. A critical argument for exclusive quartet reactivity has been the high activation energy observed for Cr(III) phosphorescence in these systems.[7,8] It is apparent that solvent restricted quartet relaxation would provide an alternative explanation for this high activation energy.[6] Therefore, thermal ${}^2E_g \rightarrow {}^4T_{2g}$ back-ISC *may* not be the principal fate of ${}^2E_g$ state molecules, and that part of the overall photoreaction that is quenched upon ${}^2E_g$ state quenching may in fact be associated with *direct* reaction out of the doublet level. A doublet reaction component would also be in keeping with recent studies on C_{4v} systems such as $Cr(NH_3)_5NCS^{2+}$[11] and $Cr(NH_3)_5Cl^{2+}$.[12]

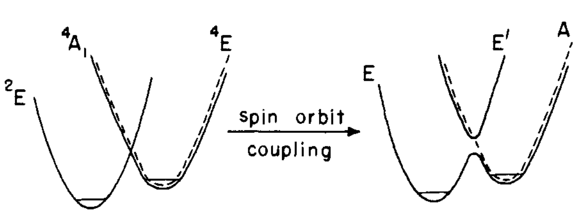


Figure 1.

We present here experimental evidence against solvent restricted quartet relaxation playing an important role in aqueous solution Cr(III) photochemistry near room temperature. The wavelength dependence of the activation energy for phosphorescence has been examined for the species $Cr(en)_3{}^{3+}$ and $Cr(NH_3)_6{}^{3+}$, using emission equipment and procedures described elsewhere.[1] Excitation wavelengths of 460 and 514 nm were employed. The former wavelength corresponds to population of the ${}^4T_{2g}$ state above the anticipated "cross-over point" between the ${}^4T_{2g}$ and ${}^2E_g$ surfaces, whereas 514-nm excitation corresponds to generation of the ${}^4T_{2g}$ level below the crossing point and near its vibrationally equilibrated configuration.[1,6] For both compounds, no wavelength dependence was observed. Activation energies of 10.5 and 10.3 kcal mol^{-1} were obtained for $Cr(en)_3{}^{3+}$ on 460- and 514-nm excitation, respectively, while the corresponding values for $Cr(NH_3)_6{}^{3+}$ were 10.4 and 10.3 kcal mol^{-1}. On the basis of Adamson's "solvent-restricted" model, essentially no activation energy is predicted for the case of 514-nm irradiation. Further, this model requires large and small activation energies for the phosphorescence intensity and lifetime, respectively, on 460-nm excitation. The observation by Ballardini et al.[8] that intensity and lifetime activation energies parallel each other for $Cr(en)_3{}^{3+}$ is therefore also inconsistent with the model.

In addition, we have investigated the temperature dependence of percent photoracemization quenching of (+)-D-$Cr(en)_3{}^{3+}$ by hydroxide ion (a selective doublet state-quencher)[1] on 436-nm excitation. Optical rotation measurements were obtained using a Bendix automatic polarimeter (Model 1164). Over the temperature range studied (5–35 °C) percent reaction quenching remained essentially constant (58–60%).[13,14] This is consistent with back-ISC as the principal deactivation mode of doublet molecules, whereas Adamson's hypothesis requires percent quenching to decrease with rising temperature.

On the basis of the foregoing discussion, an alternative explanation must therefore be sought for ${}^4T_{2g} \rightarrow {}^2E_g$ ISC successfully competing with ${}^4T_{2g}$ relaxation for $Cr(en)_3{}^{3+}$ in room temperature solution. Beattie has recently noted[15] in an analysis of Fe^{2+} (d^6) systems, that formally spin-forbidden transitions can occur rapidly along a single potential energy surface (adiabatically) provided the states involved have an irreducible representation in common. For $Cr(en)_3{}^{3+}$ under D_3 symmetry, the ${}^4T_{2g}$ level splits into ${}^4A_1$ and ${}^4E$ components. In the presence of strong spin-orbit coupling the spin designations may have limited significance,[16] and the quartet and doublet surfaces have two irreducible representations (E) in common. The noncrossing rule may therefore be invoked[17] as depicted in Figure 1, resulting in a single surface (E) connecting the two potential energy minima. We suggest this then provides a mechanism for ISC to compete with quartet vibrational equilibration.