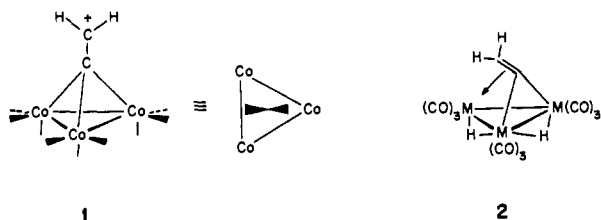


The Possibility of a Noncentered Structure for $(\text{CO})_9\text{Co}_3\text{CCR}_2^+$

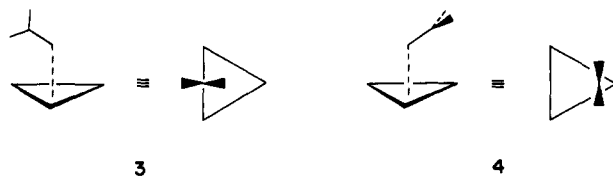
Sir:

There is an interesting and stable set of salts of carbonium ion metal cluster complexes, exemplified by the parent compound $(\text{CO})_9\text{Co}_3\text{CCH}_2^+$, **1**.¹ No crystallographic or other direct structural study of these compounds is as yet available.² If one were to reason by analogy with the many known $(\text{CO})_9\text{Co}_3\text{CR}$ structures,³ one would assume an upright positioning of the CC bond above the center of the tricobalt triangle. The resultant sixfold barrier to $\text{L}_9\text{Co}_3\text{C}-\text{CH}_2^+$ rotation should be small. This is consistent with the room-temperature NMR spectrum of these complexes.^{1,4} The IR band contours of the carbonium ion resemble those of the precursor alcohol,⁵ an argument for assigning the same framework symmetry to the two species.

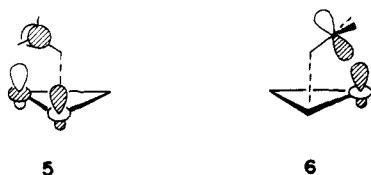


There remains, however, the possibility that the CCH_2 unit does not stand upright over the center of the ring. One is led to this line of reasoning by the structure of one of the products of the reaction of ethylene with $\text{M}_3(\text{CO})_{12}$, $\text{M} = \text{Ru}, \text{Os}$.⁶ In this molecule, **2**, two hydrogens have been stripped from the ethylene, yet retained in the cluster. Now $(\text{CO})_9\text{Co}_3\text{CCH}_2^+$ is in a sense isoelectronic with **2**, if the two bridging hydrogens are counted as protonic. Still closer to the Co cluster is $(\text{CO})_9\text{Os}_3\text{H}_3\text{CCH}_2^+$.⁷ This last molecule, as judged by NMR evidence, and **2** on the basis of its crystal structure, has the ethylidene σ bonded to two metal atoms, π bonded to the other, in a very unsymmetrical geometry.

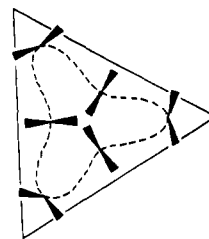
Indeed we find a deformation away from the "upright" position in an extended Hückel calculation on **1**.⁸ The potential surface is complicated, for the CH_2 rotation is coupled with bending of the CC axis away from the central perpendicular to the Co_3 plane. The preferred orientations are **3**, when the CH_2 is moving toward a bond center, and **4**, when it is moving toward a unique metal atom.



These preferences may be traced to interaction between the $-\text{CH}_2$ p orbital and an e type occupied frontier orbital of the cluster.⁸ This degenerate orbital is composed mainly of metal z^2 and has an antisymmetric and a symmetric component. When the CH_2 group bends toward a Co-Co bond midpoint, the better overlap is with the antisymmetric component, **5**, while when a metal atom is approached the best overlap is attained, in **6**, with the symmetric component. In each case the alternative orientation of the methylene group leads to a poorer interaction.



Our calculations assign the lowest energy to a structure in which the methylene tilts toward a unique metal atom, **4** or **6**, the same deformation tilts as is observed in the cited analogous structures.^{6,7} Furthermore, the theory indicates an intricate and specific circumambulation pathway, sketched schematically in **7**.⁹ The centered upright structure is avoided.¹⁰



7

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References and Notes

- (1) For a review see D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).
- (2) A crystal structure of a salt of **1** is in progress: B. H. Robinson, private communication.
- (3) See B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973), for some leading references.
- (4) D. Seyferth, G. H. Williams, and J. E. Hallgren, *J. Am. Chem. Soc.*, **95**, 266 (1973); D. Seyferth, G. H. Williams and D. D. Traficante, *ibid.*, **96**, 604 (1974).
- (5) D. Seyferth, private communication.
- (6) A. J. Deeming and M. Underhill, *J. Organomet. Chem.*, **42**, C60 (1972); *J. Chem. Soc., Chem. Commun.*, 277 (1973); *J. Chem. Soc., Dalton Trans.*, 1415 (1974).
- (7) A. J. Deeming, S. Hasso, M. Underhill, A. J. Canty, B. F. G. Johnson, W. G. Jackson, J. Lewis, and T. W. Matheson, *J. Chem. Soc., Chem. Commun.*, 807 (1974).
- (8) Details of the calculations, which form part of a general analysis of L_9M_3 -(ligand) complexes, will be given in the full publication.
- (9) The computed barrier of 16 kcal/mol is too high, but we have not yet allowed complete relaxation of the molecular framework along the rearrangement path.
- (10) The centered structure is a forbidden transition state, in the sense of R. E. Stanton and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **97**, 3632 (1975).

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Pyrolysis of the Carbonate Tosylhydrazone Salts Derived from erythro- and threo-4-Methylpentane-2,3-diol

Sir:

We have reported¹ that pyrolysis of the carbonate tosylhydrazone (CTH) salt derived from pinacol (**1**) gives, in addition to tetramethylethylene (**3**), 2,3-dimethylbutadiene (**4**) and 2,3-dimethylbuten-3-ol (**5**).² The formation of **4** and **5** is easily rationalized by mechanisms involving a diradical, produced by homolytic cleavage of one C-O bond in the 2-carbenal,1,3-dioxolane (**2**) that is presumed to be generated initially by

