

a virtually planar Rh₅ pentagon (Rh(1) to Rh(5)),⁹ which is capped on one face by a sixth Rh atom Rh(6) and on the other by a *t*-BuAs unit. The five Rh-Rh distances that describe the pentagon are all within the range for Rh-Rh single bonds (see Figure 2) (Rh-Rh min = 2.727 (1), max = 2.930 (1) Å). Rh₆ is also bonded to each of these with an average Rh-Rh distance of 2.799 Å. The *t*-BuAs group on the other face of the pentagon lies somewhat closer to the Rh₅ plane than Rh(6).⁹ Minor deviations in planarity for this central Rh₅ unit are sufficient to permit As(3) of this arsinidene unit to be within bonding distance of only three Rh atoms of the ring (Rh(1), Rh(3), and Rh(4)), which are all bent slightly toward it, in addition to Rh(6). The nonbonded Rh atoms, Rh(2) and Rh(5), are bent slightly away from the *t*-BuAs side of the ring. Thus the average As(3)-Rh bonding distance is 2.479 Å while the nonbonded distances average 2.875 Å, and these values compare well with other Rh-As bonding and nonbonding distances in other systems.¹⁰ To our knowledge this geometry is unique, an As-Rh bond passing through a Rh₅ ring which is part of a unique Rh₆ pentagonal pyramid. The cluster with 86 valence shell electrons appears to be in violation of "Wade's rules".

Two di-*tert*-butylarsenido groups bridge two of the Rh-Rh bonds in the Rh₅ pentagon and although they both bridge nearly symmetrically they are bent slightly away from the μ -*t*-BuAs face of the ring. There are 11 CO ligands in the structure. Nine are terminally bound with two each to Rh(1), Rh(3), and Rh(4) and one each to Rh(2), Rh(5), and Rh(6). In addition there are two bridging CO's which span the Rh(2)-Rh(6) and Rh(5)-Rh(6) bonds.

The IR spectrum of **1** in the solid state (KBr disc) shows five bands in the CO region while in solution ten are observed. The ¹H NMR in toluene-*d*₈ shows a multiplet consisting of five peaks.⁶ Thus, although the solid-state structure has a pseudomirror plane containing As(3), Rh(6), and Rh(1) and passing through the midpoint between Rh(4) and Rh(3), in solution the molecule must exist in a less symmetrical form resulting in the nonequivalence of all five of the *t*-BuAs groups and increasing the number of CO stretches observed in the IR.

The isolation and characterization of **1** suggests that other unusual structures involving metal clusters and R₂As⁻ or RAs²⁻ units may shortly be discovered. Further studies are in progress.

Acknowledgments. We thank the National Science Foundation (CHE82-11883) and the Robert A. Welch Foundation (F-816) for support. We also thank Johnson-Matthey Ltd. for a generous loan of RhCl₃·xH₂O. The X-ray diffractometer was purchased with funds from the National Science Foundation (CHE82-05871) and the University of Texas at Austin.

Supplementary Material Available: Complete listings of bond lengths, angles, atomic coordinates, thermal parameters, and structure factors (57 pages). Ordering information is given on any current masthead page.

(9) Deviations (Å) from the least-squares plane through the Rh₅ pentagon and As(1) and As(2) are as follows: Rh(1), 0.245 (1); Rh(2), -0.132 (1); Rh(3), 0.263 (1); Rh(4), 0.165 (1); Rh(5), -0.115 (1); As(1), -0.226 (1); As(2), -0.200 (1). Deviations (Å) from this plane for Rh(6) and As(3) are as follows: Rh(6), -1.373 (1); As(3), 1.204 (1). Key bond lengths are given in Figure 3. For convenience key angles (deg) are as follows: Rh(1)-Rh(2)-Rh(3) = 98.89 (2), Rh(2)-Rh(3)-Rh(4) = 109.60 (2), Rh(3)-Rh(4)-Rh(5) = 107.76 (2), Rh(4)-Rh(5)-Rh(1) = 101.12 (2), Rh(5)-Rh(1)-Rh(2) = 118.28 (2), Rh(6)-As(3)-C(300) = 165.9 (2), Rh(3)-As(1)-Rh(2) = 75.46 (2), Rh(4)-As(2)-Rh(5) = 74.19 (2), Rh(1)-As(3)-Rh(3) = 119.18 (3), Rh(1)-As(3)-Rh(4) = 121.28 (3), Rh(1)-Rh(6)-Rh(2) = 58.97 (2), Rh(1)-Rh(6)-Rh(5) = 59.51 (2).

(10) Typical Rh-As bonding distances fall in the range 2.4-2.5 Å; see, for example: Hewitt, T. G.; DeBoer, J. J.; Anzenhofer, K. *Acta Crystallogr., Sect. B* 1970, B26, 1244. Nolte, M. J.; Singleton, E. *Acta Crystallogr., Sect. B* 1975, B31, 2223. Mague, J. T. *Inorg. Chem.* 1973, 12, 2649. We consider Rh-As distances longer than ca. 2.7 Å to be nonbonding; see, for example: Vidal, J. L. *Inorg. Chem.* 1984, 20, 243 and references therein.

(11) Counting the μ_4 -*t*-BuAs and μ_3 -*t*-BuAs units as four- and three-electron donors, respectively, the Rh₆ cluster has 86 valence shell electrons and should have a "closo" octahedral structure with seven skeletal bonding pairs. Electron counting schemes in which the As atom of the μ_4 -*t*-BuAs unit is considered a part of the cluster framework also fail. This approach is also controversial since this unit is not bonded to all the Rh atoms in the Rh₅ plane.

Evidence for Two Different Radical Cation Types Derived from Methylenecyclopropane

Tsutomu Miyashi,* Yasutake Takahashi, and Toshio Mukai

Photochemical Research Laboratory
Faculty of Science, Tohoku University
Sendai 980, Japan

Heinz D. Roth* and Marcia L. M. Schilling

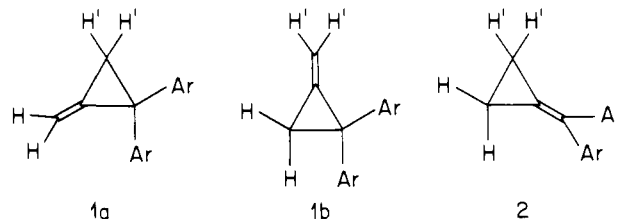
AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received October 1, 1984

The photoreactions of quinones with appropriately substituted methylenecyclopropanes, **1** and **2**, give rise to nuclear spin polarization effects supporting the existence of two different radical cation structures, **5** and **6**.

The structure and reactivity of organic radical cations continue to attract much interest and a variety of techniques continue to be employed in their study.¹⁻⁶ We are interested especially in the radical cations of strained ring systems because they can assume a variety of interesting structure types.^{2,3,7,8} The relative energies of the accessible states are subject to substituent effects, and in selected cases, appropriately chosen substituents can alter the ordering of states.^{9,10}

In this paper we describe the application of the CIDNP technique in the photoreactions of quinones with two types of *gem*-diarylmethylenecyclopropanes in order to elucidate the structures of the intermediate radical cations. This work was stimulated by the interesting observation,³ that two of the *gem*-diarylmethylenecyclopropanes (**1a** and **1b**, H' = D) are readily inter-



converted in the electron-transfer-sensitized reactions with quinones but that the third isomer (**2**) was not formed.

The irradiation of deaerated acetone-*d*₆ solutions of chloranil containing 2,2-dianisyl-1-methylenecyclopropane (**1**, Ar = C₆H₄OCH₃, H' = H) gave rise to strong nuclear spin polarization effects for the starting material and for two [3 + 2] cycloadducts, **3** and **4**.¹¹ These products are formed only in thoroughly deaerated solutions whereas the previously described dioxolanes³ are formed in oxygen-containing solutions. Similar but weaker effects were observed for the 2,2-ditolyl derivative, whereas no CIDNP results were observed for the 2,2-diphenyl and the 2,2-bis(*p*-chlorophenyl) derivatives.

The structure of the intermediate radical cations can be derived from the observed polarization patterns. Each product shows polarization only for the two CH₂ groups, and in each product

(1) Miller, T. A.; Bondybyev, V. *Appl. Spectrosc. Rev.* 1982, 18, 105-169.

(2) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* 1983, 61, 1027-1035.

(3) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* 1983, 105, 6511-6513.

(4) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* 1983, 202-204. Toriyama, K.; Nunome, K.; Iwasaki, M. *Ibid.* 1983, 1346-1347.

(5) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* 1984, 17, 180-186.

(6) Knight, L. B., Jr.; Steadman, J.; Teller, D.; Davidson, E. R. *J. Am. Chem. Soc.* 1984, 106, 3700-3701.

(7) Roth, H. D.; Schilling, M. L. M.; Mukai, T.; Miyashi, T. *Tetrahedron Lett.* 1983, 5815-5818.

(8) Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* 1984, 106, 253-255.

(9) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* 1980, 102, 7956-7958.

(10) Haddon, R. C.; Roth, H. D. *Croat. Chim. Acta* 1984, 57, 1165-1176.