oretical calculations ${ }^{16}$ are compatible with this hypothesis.
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Registry No. 1, 157-33-5; 4, 106-99-0; cyclobutene, 822-35-5.
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# Unique Structural Features of a $\mathbf{R h}_{6}-\mu_{4}-t$-BuAs Complex, Formed via As-C Bond Cleavage. Synthesis and Structure of a $\mathbf{R h}_{6}$ Pentagonal Pyramid: $\mathrm{Rh}_{6}(\mathrm{CO})_{9}(\mu-\mathrm{CO})_{2}\left(\mu-t-\mathrm{Bu}_{2} \mathrm{As}\right)_{2}\left(\mu_{4}-t-\mathrm{BuAs}\right)$ 

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As part of a study of ditertbutylarsenido ( $t-\mathrm{Bu}_{2} \mathrm{As}^{-}$) complexes ${ }^{1}$ we investigated the reaction of $\mathrm{Li}(t-\mathrm{Bu})_{2} \mathrm{As}$ with $\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{Cl}\right]_{2}$. We report here the synthesis, characterization and X-ray crystal structure of $\mathrm{Rh}_{6}(\mathrm{CO})_{9}(\mu-\mathrm{CO})_{2}\left(\mu-t-\mathrm{Bu}_{2} \mathrm{As}\right)_{2}\left(\mu_{4}-t\right.$-BuAs $)(1)$, which displays a number of unique and unexpected structural features in transition-metal cluster chemistry. To our knowledge, $\mathbf{1}$ is the first example of a $R h_{6}$ cluster in which the $R h_{6}$ framework is a pentagonal pyramid; it has neither the commonly observed octahedral nor trigonal-prismatic geometries. ${ }^{2,3}$ The formation of $\mathbf{1}$ is also accompanied by an As-C bond cleavage which gives a tert-butylarsinidene unit ( $t$-BuAs) bound to the cluster in a unique bridging manner; one of the As-Rh bonds passes through the $\mathrm{Rh}_{5}$ plane. Although relatively few studies involving the $t$ - $\mathrm{Bu}_{2} \mathrm{As}^{-}$unit have so far been reported, As-C bond cleavage appears to be a common feature involved with the $t$ - $\mathrm{Bu}_{2}$ As unit. ${ }^{1}$ As-C cleavages have also been observed in thermal reactions involving organoarsenic species and metal carbonyls. ${ }^{4}$ Such a metal-mediated group 15 carbon bond cleavage may have considerable relevance to the deactivation of homogeneous catalysts. ${ }^{5}$

The reaction of $\mathrm{Li}(t-\mathrm{Bu})_{2}$ As with $\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{Cl}\right]_{2}(2: 1)$ in THF at $-78{ }^{\circ} \mathrm{C}$ gives a black solution from which $\mathrm{Rh}_{6}(\mathrm{CO})_{9}(\mu-$ $\mathrm{CO})_{2}\left(\mu-t-\mathrm{Bu}_{2} \mathrm{As}\right)_{2}\left(\mu_{4}-t-\mathrm{BuAs}\right)$ (1) (35\%) and [Rh( $\left.\mu-t-\mathrm{Bu}_{2} \mathrm{As}\right)$ -

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Figure 1. Overall view of 1. For clarity only the quaternary carbon atoms of the tert-butyl groups are shown.


Figure 2. The $\mathrm{Rh}_{6} \mathrm{As}_{3}$ framework of 1 showing the relevant bond lengths. $\left.(\mathrm{CO})_{2}\right]_{2}(\mathbf{2})(25 \%)$ may be isolated by fractional crystallization from hexane (eq 1). ${ }^{6}$ The structures of both $\mathbf{1}$ and $\mathbf{2}$ have been $\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{Cl}\right]_{2}+2 \mathrm{LI}\left(\mathrm{t}-\mathrm{Bu} \mathrm{A}_{2} \mathrm{As}\right) \xrightarrow[-780 \mathrm{C}]{\mathrm{THF}}$

(1) (35\%)
(2) $(25 \%)$
determined by X-ray crystallography. ${ }^{7}$ The structure of $\mathbf{2}$ consists of two planar $\mathrm{Rh}(\mathrm{I})$ atoms each bearing two CO ligands and bridged by two $t$ - $\mathrm{Bu}_{2} \mathrm{As}^{-}$units (eq 1). It will be described fully in another paper. ${ }^{6}$
$\mathbf{1}$ is a black crystalline material which is air stable for short periods in the solid state but decomposes in solution when exposed to the air. An ORTEP view of the molecule is shown in Figure 1 and the key features of the $\mathrm{Rh}_{6} \mathrm{As}_{3}$ core are shown in Figure 2.
There are several unique features. ${ }^{8}$ The central core contains
(6) Full experimental details will be published with the characterization and X-ray structure of 2; Jones, R. A.; Seeberger, M. H.; Whittlesey, B. R.; Wright, T. C., manuscript in preparation. Both 1 and 2 may be crystallized from hexane solution. 1 is less soluble than 2 and crystallizes first at $-20^{\circ} \mathrm{C}$. 1: mp 192-198 ${ }^{\circ} \mathrm{C} \mathrm{dec} ;{ }^{1} \mathrm{H}$ NMR ( 90 MHz , in $\mathrm{PhMe}-d_{8}$ at $35^{\circ} \mathrm{C}$, rel. to $\left.\mathrm{Me}_{4} \mathrm{Si}(\delta 0.0)\right) \delta 1.28(\mathrm{~s}, 9 \mathrm{H}), 1.32(\mathrm{~s}, 9 \mathrm{H}), 1.37(\mathrm{~s}, 9 \mathrm{H}), 1.40(\mathrm{~s}, 9 \mathrm{H}), 1.48$ ( $\mathrm{s}, 9 \mathrm{H}$ ) (all $t$-BuAs); IR (hexane solution, matched KBr cells) $2066 \mathrm{w}, 2044$ w, 2026 sh, $2006 \mathrm{~s}, 2002 \mathrm{sh}, 1982 \mathrm{~m}, 1947 \mathrm{~m}, 1857 \mathrm{w}, 1832 \mathrm{w}, 1820 \mathrm{w}$, (KBr disc) 2900 v br m, $2020 \mathrm{~m}, 1986 \mathrm{~s}, 1948 \mathrm{~s}, 1826 \mathrm{~m}, 1800 \mathrm{~m}, 1455 \mathrm{br} \mathrm{w}, 1382$ $\mathrm{w}, 1361 \mathrm{w}, 1254 \mathrm{w}, 1152 \mathrm{~m}, 1010 \mathrm{w}, 790 \mathrm{w} \mathrm{cm}^{-1}$. Microanal. Calcd for $\mathrm{Rh}_{6} \mathrm{As}_{3} \mathrm{C}_{31} \mathrm{O}_{11} \mathrm{H}_{45}: \mathrm{C}, 25.93 \%$; $\mathrm{H}, 3.16 \%$. Found: $\mathrm{C}, 25.84 \%$; $\mathrm{H}, 3.01 \%$.
(7) CAD-4, crystal data: $\mathrm{Rh}_{6} \mathrm{As}_{3} \mathrm{C}_{31} \mathrm{O}_{11} \mathrm{H}_{45}, M=1435.89$, monoclinic, space group $P 2_{1} / n$ (nonstandard setting of $P 2_{1} / c$, No. 14), $a=10.130$ (2) $\AA, b=27.446$ (4) $\AA, c=15.904$ (2) $\AA, \beta=98.563(9)^{\circ}, U=4372.8 \AA^{3}, D_{c}$ $=2.181 \mathrm{~g} \mathrm{~cm}^{-3}, Z=4, \lambda(\mathrm{Mo} \mathrm{K} \alpha)=0.71069 \AA$ (graphite monochromator), $\mu(\mathrm{Mo} \mathrm{K} \alpha)=44.77 \mathrm{~cm}^{-1}$. Methods: multan, difference Fourier, full matrix least squares. Refinement of 4470 reflections $(I>3 \sigma(I)$ ) out of 4837 unique observed reflections measured ( $2^{\circ}<2 \theta<50^{\circ}$ ) gave $R=0.0351$ and $R_{w}=$ 0.0388 . All non-hydrogen atoms were refined anisotropically; hydrogen atoms were not located. The final difference Fourier map showed no unusual features. ${ }^{8}$
(8) See paragraph at end of paper regarding supplementary material.
a virtually planar $R h_{5}$ pentagon ( $\mathrm{Rh}(1)$ to $\left.R h(5)\right),{ }^{9}$ which is capped on one face by a sixth Rh atom $\mathrm{Rh}(6)$ and on the other by a $t$-BuAs unit. The five $\mathrm{Rh}-\mathrm{Rh}$ distances that describe the pentagon are all within the range for $\mathrm{Rh}-\mathrm{Rh}$ single bonds (see Figure 2) $(\mathrm{Rh}-\mathrm{Rh} \min =2.727$ (1), $\max =2.930(1) \AA) . R h_{6}$ is also bonded to each of these with an average $\mathrm{Rh}-\mathrm{Rh}$ distance of $2.799 \AA$. The $t$-BuAs group on the other face of the pentagon lies somewhat closer to the $\mathrm{Rh}_{5}$ plane than $\mathrm{Rh}(6) .{ }^{9}$ Minor deviations in planarity for this central $\mathrm{Rh}_{5}$ unit are sufficient to permit $\mathrm{As}(3)$ of this arsinidene unit to be within bonding distance of only three Rh atoms of the ring ( $\mathrm{Rh}(1), \mathrm{Rh}(3)$, and $\mathrm{Rh}(4)$ ), which are all bent slightly toward it, in addition to $\mathrm{Rh}(6)$. The nonbonded Rh atoms, $\mathrm{Rh}(2)$ and $\mathrm{Rh}(5)$, are bent slightly away from the $t$-BuAs side of the ring. Thus the average As(3)-Rh bonding distance is $2.479 \AA$ while the nonbonded distances average $2.875 \AA$, 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 $\mathrm{Rh}_{5}$ ring which is part of a unique $R h_{6}$ 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 $\mathrm{Rh}-\mathrm{Rh}$ bonds in the $\mathrm{Rh}_{5}$ pentagon and although they both bridge nearly symmetrically they are bent slightly away from the $\mu-t$-BuAs face of the ring. There are 11 CO ligands in the structure. Nine are terminally bound with two each to $\mathrm{Rh}(1), \mathrm{Rh}(3)$, and $\mathrm{Rh}(4)$ and one each to $\mathrm{Rh}(2), \mathrm{Rh}(5)$, and $\mathrm{Rh}(6)$. In addition there are two bridging CO's which span the $\mathrm{Rh}(2)-\mathrm{Rh}(6)$ and $\mathrm{Rh}(5)-\mathrm{Rh}(6)$ bonds.

The IR spectrum of $\mathbf{1}$ in the solid state ( KBr disc) shows five bands in the CO region while in solution ten are observed. The ${ }^{1} \mathrm{H}$ NMR in toluene- $d_{8}$ shows a multiplet consisting of five peaks. ${ }^{6}$ Thus, although the solid-state structure has a pseudomirror plane containing $\mathrm{As}(3), \mathrm{Rh}(6)$, and $\mathrm{Rh}(1)$ and passing through the midpoint between $\operatorname{Rh}(4)$ and $\operatorname{Rh}(3)$, 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 $\mathrm{R}_{2} \mathrm{As}^{-}$or $\mathrm{RAs}^{2-}$ units may shortly be discovered. Further studies are in progress.

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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 $(\AA)$ from the least-squares plane through the $R h_{5}$ pentagon and $\operatorname{As}(1)$ and $\operatorname{As}(2)$ are as follows: $\operatorname{Rh}(1), 0.245$ (1); $\operatorname{Rh}(2),-0.132$ (1); $\operatorname{Rh}(3), 0.263$ (1); $\operatorname{Rh}(4), 0.165$ (1); $\operatorname{Rh}(5),-0.115$ (1); $\mathrm{As}(1),-0.226$ (1); $\mathrm{As}(2),-0.200$ (1). Deviations ( $\AA$ ) from this plane for $\mathrm{Rh}(6)$ and $\mathrm{As}(3)$ are as follows: $\mathrm{Rh}(6),-1.373$ (1); $\mathrm{As}(3), 1.204$ (1). Key bond lengths are given in Figure 3. For convenience key angles (deg) are as follows: $\mathrm{Rh}(1)-\mathrm{Rh}-$ (2) $-\mathrm{Rh}(3)=98.89$ (2), $\mathrm{Rh}(2)-\mathrm{Rh}(3)-\mathrm{Rh}(4)=109.60$ (2), $\mathrm{Rh}(3)-\mathrm{Rh}(4)-$ $\operatorname{Rh}(5)=107.76(2), \operatorname{Rh}(4)-\operatorname{Rh}(5)-\operatorname{Rh}(1)=101.12(2), \operatorname{Rh}(5)-\operatorname{Rh}(1)-\operatorname{Rh}(2)$ $=118.28$ (2) $, \operatorname{Rh}(6)-\operatorname{As}(3)-\mathrm{C}(300)=165.9(2), \operatorname{Rh}(3)-\mathrm{As}(1)-\operatorname{Rh}(2)=75.46$ (2), $\mathrm{Rh}(4)-\mathrm{As}(2)-\mathrm{Rh}(5)=74.19$ (2), $\mathrm{Rh}(1)-\mathrm{As}(3)-\mathrm{Rh}(3)=119.18$ (3), $\operatorname{Rh}(1)-\operatorname{As}(3)-\operatorname{Rh}(4)=121.28$ (3), $\mathrm{Rh}(1)-\mathrm{Rh}(6)-\mathrm{Rh}(2)=58.97$ (2), $\mathrm{Rh}-$ (1) $-\mathrm{Rh}(6)-\mathrm{Rh}(5)=59.51$ (2).
(10) Typical Rh-As bonding distances fall in the range 2.4-2.5 $\AA$; 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, B3l, 2223. Mague, J. T. Inorg. Chem. 1973, l2, 2649. We consider Rh-As distances longer than ca. $2.7 \AA$ to be nonbonding; see, for example: Vidal, J. L. Inorg. Chem. 1984, 20, 243 and references therein.
(11) Counting the $\mu_{4}-t-\mathrm{BuAs}$ and $\mu-t-\mathrm{Bu}_{2}$ As units as four- and threeelectron donors, respectively, the $\mathrm{Rh}_{6}$ 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 $\mu_{4}-t$-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 $\mathrm{Rh}_{5}$ plane.

## Evidence for Two Different Radical Cation Types Derived from Methylenecyclopropane

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The photoreactions of quinones with appropriately substituted methylenecyclopropanes, $\mathbf{1}$ and $\mathbf{2}$, 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 to the photoreactions of quinones with two types of gemdiarylmethylenecyclopropanes 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 ( $\mathbf{1 a}$ and $\mathbf{1 b}, \mathrm{H}^{\prime}=\mathrm{D}$ ) are readily inter-


1a


1b


2
converted in the electron-transfer-sensitized reactions with quinones but that the third isomer (2) was not formed.
The irradiation of deaerated acetone $\cdot d_{6}$ solutions of chloranil containing 2,2-dianisyl-1-methylenecyclopropane (1, $\mathrm{Ar}=\mathrm{C}_{6}-$ $\mathrm{H}_{4} \mathrm{OCH}_{3}, \mathrm{H}^{\prime}=\mathrm{H}$ ) 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 dioxolanes ${ }^{3}$ 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 2,2bis ( $p$-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 $\mathrm{CH}_{2}$ groups, and in each product

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