oretical calculations¹⁶ are compatible with this hypothesis.

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Unique Structural Features of a $Rh_6-\mu_4$ -t-BuAs Complex, Formed via As-C Bond Cleavage. Synthesis and Structure of a Rh₆ Pentagonal Pyramid: $Rh_6(CO)_9(\mu-CO)_2(\mu-t-Bu_2As)_2(\mu_4-t-BuAs)$

Richard A. Jones* and Bruce R. Whittlesey

Department of Chemistry The University of Texas at Austin Austin, Texas 78712

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As part of a study of ditertbutylarsenido (t-Bu₂As⁻) complexes¹ we investigated the reaction of $Li(t-Bu)_2As$ with $[Rh(CO)_2Cl]_2$. We report here the synthesis, characterization and X-ray crystal structure of $Rh_6(CO)_9(\mu-CO)_2(\mu-t-Bu_2As)_2(\mu_4-t-BuAs)$ (1), which displays a number of unique and unexpected structural features in transition-metal cluster chemistry. To our knowledge, 1 is the first example of a Rh₆ cluster in which the Rh₆ framework is a pentagonal pyramid; it has neither the commonly observed octahedral nor trigonal-prismatic geometries.^{2,3} The formation of 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 Rh, plane. Although relatively few studies involving the t-Bu₂As⁻ unit have so far been reported, As-C bond cleavage appears to be a common feature involved with the t-Bu₂As 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 $Li(t-Bu)_2As$ with $[Rh(CO)_2Cl]_2$ (2:1) in THF at -78 °C gives a black solution from which $Rh_6(CO)_9(\mu$ - $CO_{2}(\mu-t-Bu_{2}As)_{2}(\mu_{4}-t-BuAs)$ (1) (35%) and $[Rh(\mu-t-Bu_{2}As)-t-Bu_{2}As)_{2}(\mu_{4}-t-Bu_{2}As)_{$



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



Figure 2. The Rh₆As₃ framework of 1 showing the relevant bond lengths.

 $(CO)_2]_2$ (2) (25%) may be isolated by fractional crystallization from hexane (eq 1).⁶ The structures of both 1 and 2 have been

$$\binom{(CO)_{2}CI}{2} + 2L1(t-Bu_{2}As) \xrightarrow{-780C} Rh_{6}(CO)_{9}(t-CO)_{2}(u-t-Bu_{2}As)_{2}(u_{4}-t-BuAs) + 0C + Rh_{5} \xrightarrow{t-Bu_{2}} Rh_{5} \xrightarrow{C} C_{0}$$
(1)
(1) (357) (2) (2) (253)

determined by X-ray crystallography.⁷ The structure of 2 consists of two planar Rh(I) atoms each bearing two CO ligands and bridged by two t-Bu₂As⁻ units (eq 1). It will be described fully in another paper.6

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 Rh_6As_3 core are shown in Figure 2. There are several unique features.⁸ The central core contains

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[R]

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⁽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 °C. 1: mp 192–198 °C dec; ¹H NMR (90 MHz, in PhMe- d_8 at 35 °C, rel. to Me₄Si (δ 0.0)) δ 1.28 (s, 9 H), 1.32 (s, 9 H), 1.37 (s, 9 H), 1.40 (s, 9 H), 1.48 (s, 9 H) (all t-BuAs); IR (hexane solution, matched KBr cells) 2066 w, 2044 w, 2026 sh, 2006 s, 2002 sh, 1982 m, 1947 m, 1857 w, 1832 w, 1820 w, (KBr w, 2020 sn, 2000 s, 2002 sn, 1982 m, 1947 m, 1857 w, 1852 w, 1852 w, 1851 w, 1851 disc) 2900 v br m, 2020 m, 1986 s, 1948 s, 1826 m, 1800 m, 1455 br w, 1382 w, 1361 w, 1254 w, 1152 m, 1010 w, 790 w cm⁻¹. Microanal. Calcd for Rh₆As₃C₃₁O₁₁H₄₅: C, 25.93%; H, 3.16%. Found: C, 25.84%; H, 3.01%. (7) CAD-4, crystal data: Rh₆As₃C₃₁O₁₁H₄₅, M = 1435.89, monoclinic, space group $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14), a = 10.130 (2) Å, b = 27.446 (4) Å, c = 15.904 (2) Å, $\beta = 98.563$ (9)°, U = 4372.8 Å³, D_c = 2.181 g cm⁻³, Z = 4, λ (Mo K α) = 0.710 69 Å (graphite monochromator), μ (Mo K α) = 44.77 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.

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). Rh_{6} 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 Rh_5 plane than Rh(6).⁹ Minor deviations in planarity for this central Rh, 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 Rh, 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.

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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.

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 (11) Counting the µ₄-t-BuAs and µ-t-Bu₂As units as four- and threeelectron 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

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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 to the photoreactions of guinones 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 (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, $Ar = C_6$ - H_4OCH_3 , 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 2,2bis(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 CH₂ groups, and in each product

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