

becomes the most stable $C_4H_4B_2F_2$ isomer by 2 kcal/mol and is the molecule observed experimentally.¹³ The classical structure V is also found to be greatly stabilized relative to the nonclassical structures IV and VI upon B-fluorination.

The probable existence of energetically competitive classical structures for these small carboranes suggests, and the study of the 1,2- $C_2B_4H_6$ to 1,6- $C_2B_4H_6$ rearrangement confirms, that reactions of nonclassical molecules may involve classical intermediates. While the importance of vacant orbital structures in the correct topological description of electron-deficient molecules has been previously recognized,^{14,15} our results suggest that such structures, whether purely classical (as in the small molecules studied here) or quasi-classical (involving only one or two vacant orbitals in a large nonclassical molecule), may be even more important as intermediates in reactions and rearrangements.^{16,18}

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- (16) It is important to recognize that the distinction between classical and nonclassical bonding is qualitative, and a given molecule may possess interatomic interactions that fall along a continuum between these extremes. Bond lengths, Armstrong, Perkins, Stewart bond orders,¹⁷ and atomic overlap may be used to assess the degree of interaction between boron atoms that are not formally bonded in a classical bonding network to determine whether nonclassical effects are significant. By these criteria, for example, structures VI and IX are revealed to be purely nonclassical and classical molecules, respectively, whereas the weak, nonbonded boron-boron interactions in V and, especially, I are of an intermediate "semi-classical" nature (APS bond orders are 0.20 in V and 0.25 in I for B...B interactions).
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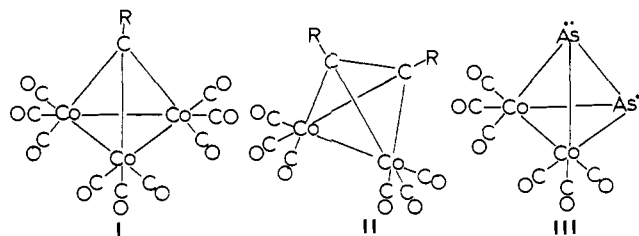
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Arsaacetylenes, $RC\equiv As$, as Ligands in Dicobalt Hexacarbonyl Complexes: Novel Main Group Element-Transition Metal Hybrid Cluster Compounds

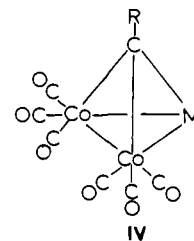
Sir:

The alkylidynetricobalt nonacarbonyl complexes, I,¹ and the related acetylenedicobalt hexacarbonyls,² which also have a cluster structure,³ II, have a well-developed chemistry. The former and, to a lesser extent, the latter show remarkable

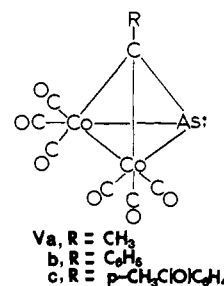
thermal and oxidative stability, compared with simple cobalt alkyls, e.g., $RCo(CO)_4$.⁴ Also known are tetrahedral cluster complexes which contain triply bridging silicon,⁵ germanium,⁶ phosphorus,⁷ arsenic,⁸ sulfur,⁹ selenium,¹⁰ boron,¹¹ and aluminum¹² in place of the RC group of I. Arsenic and phosphorus analogues of the acetylenedicobalt hexacarbonyl complexes also have been described,^{7,13} and the diarsenic compound was shown to have structure III.¹³ However, organometallic clus-



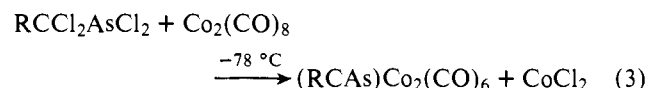
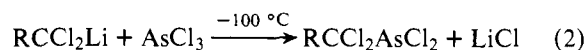
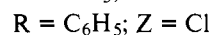
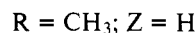
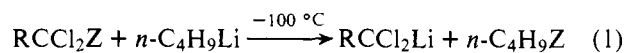
ters containing both a transition metal and a main group element in addition to the carbon function, e.g., IV, have not been



reported to date. The preparation of such complexes, a comparison of their reactivity with that of analogues of I, II, and III, and a study of their thermal and chemical decomposition with the aim of releasing and trapping an $RC\equiv M$ intermediate would be of considerable interest, and we have initiated such investigations. We report here our studies of such complexes which contain carbon, arsenic, and cobalt in the tetrahedral cluster, V.



Complexes of type $RCCO_3(CO)_9$ are prepared by the reaction of a substituted trihalomethane, RCX_3 , with dicobalt octacarbonyl,¹ while the reaction of arsenic trichloride with dicobalt octacarbonyl gives III.¹³ Our route to Va and Vb utilizes intermediates in which the C-As bond already is present, as shown in eq 1-3. The preparation of $(CH_3CAs)Co_2(CO)_6$ is described to illustrate the procedure used.



1,1-Dichloroethyl lithium was prepared at $-100^\circ C$ in 4:1:1 THF/Et₂O/pentane using our published procedure.¹⁴ This

reagent solution was forced by nitrogen pressure through a cannula which was cooled to -78°C into a solution containing 1 molar equiv of arsenic trichloride in THF at -100°C . The 1,1-dichloroethyldichloroarsine thus prepared was not isolated. Instead, the solution containing this material was cannulated (cooled to -78°C) into a solution of 2 molar equiv of dicobalt octacarbonyl in THF at -78°C . (For best results, a dilute solution (1000 ml of THF/100 mmol) of the carbonyl should be used.) When the resulting mixture was allowed to warm slowly, a vigorous evolution of gas commenced at 0°C and subsided after 15 min. After 24 h at room temperature, it was evaporated at reduced pressure and extracted with pentane. Removal of pentane left a red oil which was chromatographed (silicic acid) to give $(\text{CH}_3\text{CAs})\text{Co}_2(\text{CO})_6$, an orange oil (27% yield, based on 1,1-dichloroethane), which could be short path distilled at 40°C (0.02 Torr). Anal. Calcd for $\text{C}_8\text{H}_3\text{O}_6\text{AsCo}_2$: C, 24.77; H, 0.78; As, 19.32. Found: C, 24.97; H, 0.89; As, 20.39. In the mass spectrometer (70 eV) the complex underwent stepwise loss of CO, and fragment ions at m/e corresponding to $(\text{CH}_3\text{CAs})\text{Co}_2(\text{CO})_n^+$ ($n = 0-5$) were observed. Its ^1H NMR spectrum (in CCl_4) showed δ_{CH_3} at 3.13 ppm, and its infrared spectrum showed three bands in the terminal carbonyl region at 2100, 2060, and 2030 cm^{-1} , which are consistent with the presence of the $\text{Co}_2(\text{CO})_6$ unit. Treatment of the product, Va, with 2 equiv of triphenylphosphine in refluxing benzene gave the crystalline 1,2-bis(triphenylphosphine) substitution product, $(\text{CH}_3\text{CAs})\text{Co}_2(\text{CO})_4(\text{Ph}_3\text{P})_2$, which apparently is a mixture of the two possible 1,2 isomers since its ^1H NMR spectrum showed two CH_3 resonances. A 1:1 reaction of Va and triphenylphosphine at room temperature for 48 h gave the nicely crystalline monotriphenylphosphine substitution product, mp $121-122^{\circ}\text{C}$. As expected, δ_{CH_3} of these complexes depended on the degree of triphenylphosphine substitution. In the ^1H NMR spectrum of the monotriphenylphosphine adduct, δ_{CH_3} was observed at 2.43 ppm (in CDCl_3); in the spectrum of the bis(triphenylphosphine) adduct the two methyl resonances were observed at δ 1.62 and 1.82 ppm (in CDCl_3).

A similar procedure in which α,α -dichlorobenzylolithium¹⁵ was used gave 2-phenylarsacetylenedicobalt hexacarbonyl, Vb, an air-stable red oil, in 28% yield based on starting benzotrichloride. Its mass spectrum showed the molecular ion, fragment ions with m/e corresponding to products of successive CO loss, $[\text{M} - \text{CO}]^+$ through $[\text{M} - 6\text{CO}]^+$, as well as PhCAsCo^+ and Co^+ . Three $\nu_{\text{C}\equiv\text{O}}$ bands were observed at 2090, 2060, and 2035 cm^{-1} . A crystalline 1,2-bis(triphenylphosphine) substitution product could be prepared.

In the ^{13}C NMR spectra of Va and Vb (in CDCl_3) the resonances due to the carbon atoms in the CAsCo_2 cluster were observed at δ_{C} 170.4 and 165.9 ppm, respectively. In comparison, the cluster carbon atom resonances in the $\text{RCCo}_3(\text{CO})_9$ and $(\text{RC}_2\text{R})(\text{Co}_2(\text{CO})_6)$ complexes were found in the ranges δ_{C} 275–310¹⁶ and δ_{C} 91–95¹⁷ ppm, respectively.

These $(\text{RCAs})\text{Co}_2(\text{CO})_6$ complexes appear to be chemically quite robust. Both are air stable. The phenyl derivative Vb may be para-acetylated in quantitative yield by adding it to a solution of acetyl chloride and aluminum chloride in dichloromethane, a procedure which served well in the acetylation of $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_6$ ¹⁸ and $\text{PhCCo}_3(\text{CO})_9$.¹⁹ The product, Vc, was isolated as a red oil but could be converted to a crystalline 1,2-bis(triphenylphosphine) derivative. Attempted methylation of the arsenic atom in Vb with methyl fluorosulfonate, a powerful alkylating agent, and attempted reactions of Va with $(\text{OC})_5\text{Cr}\cdot\text{THF}$ and of Vb with $(\text{OC})_5\text{W}\cdot\text{THF}$ were unsuccessful.

Since these $(\text{RCAs})\text{Co}_2(\text{CO})_6$ complexes may be regarded as derivatives of the as yet unknown arsaacetylenes, $\text{RC}\equiv\text{As}$,²⁰ it seemed possible that their thermolysis might release this

species. However, thermal decomposition of Vb at 200°C in the presence of tetraphenylcyclopentadienone did not give the hoped-for pentaphenylarsabenzene. Instead, the decomposition of Vb resulted in the formation of a shiny black mirror on the walls of the flask which was identified by analysis as Co_2As . Oxidation of Vb with ceric ammonium nitrate in methanol solution resulted in C–As bond cleavage, the organic products which were isolated being $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$ and $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CO}_2\text{CH}_3$.

Our synthesis of Va and Vb should be capable of extension to other cluster complexes of general type IV, and such hybrid clusters should have interesting properties and chemistry. Applications to systems of type IV where M is an element other than arsenic are under investigation.

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Structure of Antibiotic X-14547A, a Carboxylic Acid Ionophore Produced by *Streptomyces antibioticus*, NRRL 8167¹

Sir:

Of the 30 structurally defined carboxylic acid ionophores² known as polyether antibiotics,³ only A23187⁴ contains nitrogen. A second example, designated X-14547A, is reported here.