If the equilibrium constant for reaction 1 sufficiently deviates from unity, the reaction should provide a means of separation of the two benzophenones containing the different isotopes of carbon in the carbonyl position, since the physical and chemical properties of the ketyls are very different from those of the neutral benzophenones. Indeed, the equilibrium constant for reaction 1 was found to be less than one and the separation of the hot and cold benzophenones was realized.

The deep blue ammonia solutions were exposed to high vacuum at −78 °C until all of the ammonia was evaporated leaving the solid organometallic salt $[Na^+(NH_3)BZO^{\bullet -}]$[3] together with neutral benzophenone. The neutral hot and cold benzophenones could then be sublimed from this mixture by simply heating the sample to 130 °C under high (10^{-6} torr) vacuum. Alternatively, dry ether could be added to the solid ketyl–ketone mixture. As only the neutral ketone is soluble in the ether, this effects a separation of the ketyl and neutral material. The benzophenones recovered from the reaction mixture were recrystalized from methanol–ether and stored under vacuum to ensure complete removal of solvent.

Accurately weighed samples (about 12 mg) of the recovered neutral hot and cold benzophenones were dissolved in toluene containing Omniflour as the scintillation solvent. The radioactivity associated with each sample was determined by using a Packard Tri-carb 460C-460D liquid scintillation system. Comparison of the radioactivity of the recovered samples to that of the original unreacted mixture showed the benzophenones recovered from the anion radical mixture to be enhanced in radioactivity. The original mixture (used as the radioactivity standard) of BZO-14C + BZO-12C yields (2.676 ± 0.002) × 10^5 dpm/mmol, while a mixture recovered from a reaction of 1.43 mmol of this standard with 0.66 mmol of sodium yielded 2.97 × 10^5 dpm/mmol. Further enhancement of the radioactivity can be achieved by simply reducing the recovered materials with sodium in liquid ammonia and working up this reaction mixture in the same manner.

The specific activity of the standard in disintegration per minute/millimole (dpm[S]) can be utilized with that of the recovered material (dpm[R]) to estimate the equilibrium constant for reaction 1. This is true since the decompositions/minute of pure BZO-14C (dpm[14]) is related to that of the standard and the concentration of BZO-14C and BZO-12C in the standard, eq 2, and a similar relationship holds for the dpm[R] and the

$$\mathrm{dpm[S]} = \mathrm{dpm[14][BZO\text{-}14C]_S/([BZO\text{-}14C]_S + [BZO\text{-}12C]_S)} \quad (2)$$

concentrations of the benzophenones in the recovered material ($\mathrm{[BZO\text{-}14C]_R}$) and ($\mathrm{[BZO\text{-}12C]_R}$), eq 3. Dividing eq 2 by eq

$$\mathrm{dpm[R]} = \mathrm{dpm[14][BZO\text{-}14]_R/([BZO\text{-}14C]_R + [BZO\text{-}12C]_R)} \quad (3)$$

3 and remembering that $\mathrm{[BZO\text{-}14C]_S - [BZO\text{-}14C]_R = [BZO\text{-}14C^{\bullet -}]}$ and using the analogous expression for BZO-12C yields eq 4.

$$\mathrm{dpm[R]/dpm[S]} = \frac{K_{\mathrm{eq}} + \mathrm{[BZO\text{-}12C]_R/[BZO\text{-}12^{\bullet -}]}}{1 + \mathrm{[BZO\text{-}12C]_R/[BZO\text{-}12^{\bullet -}]}} \quad (4)$$

The only assumption made in eq 4 is that the total amount of BZO-14C is much less than that of BZO-12C. The concentration of the anion radical and the exact amount of distilled sodium used in the reduction were obtained by reacting the leftover anion radical salt with water and titrating the resulting solution with standardized HCl. Such treatment leads to a K_{eq} of about 0.7. There might be considerable error in this value, since the relative concentrations of the anions and neutral molecules in reaction 1 may deviate drastically from their equilibrium values in dilute solution during the process of evaporation of the solvent (ammonia). The ^{14}C-depleted benzophenones left in the reaction vessel in the form of $Na^+(NH_3)BZO^{\bullet -}$ can be recovered by simply adding a solution of I_2 in tetrahydrofuran to the solid salt.[4] Further, there is no theoretical limit as to how much the radioactivity of the sample can be enhanced by passing ^{14}C-enhanced material through this process consecutively, up to the point where the pure carbon-14 compound is obtained.

On the basis of the Raman and IR studies carried out upon the neutral molecules and anion radicals of tetracyanoethylene and tetracyanoquinone, the effect of an added electron is best characterized as a strengthening of single bonds and a weakening of multiple bonds with a net reduction in molecular bond energies.[5] It is this zero point energy effect that lowers the electron affinity of benzophenone when the carbonyl carbon is replaced with the heavier radioactive isotope.

Acknowledgment. We thank NSF (Grant CHE-841127) for support of this work.

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Synthesis and X-ray Crystal Structure of a Novel Bimetallic Bis(η^5-dicarbollide) Aluminum Sandwich Complex

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In the course of our investigation of the coordination chemistry of *closo*-3-C_2H_5-3,1,2-$AlC_2B_9H_{11}$ (**1**),[2] we sought to examine the reaction, if any, of **1** with carbon monoxide. Upon stirring a benzene solution of **1** under an atmosphere of CO at ambient temperature, what proved to be a CO-catalyzed reaction occurred which produced in high yield a previously unknown aluminacarborane species.[3] This species could be isolated as a colorless to slightly reddish, air-sensitive, crystalline solid. As the nature of this species could not be elucidated fully from spectroscopy alone, an X-ray structure determination was undertaken.[4] This species was shown to be the novel aluminacarborane sandwich complex, *commo*-3,3′-Al[(*exo*-8,9-(μ-H)$_2$Al(C_2H_5)$_2$-3,1,2-$AlC_2B_9H_9$)(3′,1′,2′-$AlC_2B_9H_{11}$)] (**2**), an ORTEP representation of which is shown in Figure 1.

In **2**, the planar bonding faces of the two dicarbollide ligands are nearly parallel, making an angle of 2.6° to one another and they are η^5-coordinated to a single aluminum atom in the same

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(1) Recipient of a University of California, Los Angeles, Graduate Division Research Grant Award, 1984.

(2) (a) Young, D. A. T.; Willey, G. R.; Hawthorne, M. F.; Churchill, M. R.; Reis, A. H. *J. Am. Chem. Soc.* **1970**, *92*, 6663. (b) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687.

(3) Compound **1**, *closo*-3-C_2H_5-3,1,2-$AlC_2B_9H_{11}$ (500 mg, 2.64 mmol), was dissolved in 30 mL of dry, freshly distilled benzene in a nitrogen-filled glovebox. Carbon monoxide was passed through a 3 × 30 cm column filled with P_4O_{10} and then through a liquid-N_2-cooled trap and was bubbled through benzene prior to being introduced into the reaction flask containing the solution of **1**. After purging the reaction flask with a flow of CO for 20 min, the solution was stirred under an atmosphere of CO for 12 h. After this time, CO and solvent were removed in vacuo. Recrystallization of the residue from toluene/heptane afforded 465 mg (1.23 mmol, 93% yield) of **2** (mp 147 °C, sealed tube, uncorrected) after drying for 12 h under vacuum.

(4) Crystallographic data: Suitable crystals of **2** ($C_8H_{32}B_{18}Al_2$) were grown from benzene/pentane. Crystals were sealed in 0.5-mm capillary tubes under dry N_2. Data collection was carried out at 24 °C, using a modified Picker FACS-1 automated diffractometer, Mo K_α radiation. The space group is $P2_1/n$ with a = 7.122 (2) Å, b = 27.668 (8) Å, c = 11.629 (3) Å, β = 96.246 (5)°, V = 2288 Å^3. 2335 reflections which measured $I > 3\sigma(I)$ were used for structure solution using MULTAN 78 and locally written refinement programs. The last cycle of least-squares refinement gave residuals of R = 0.065, R_w = 0.075, and GOF = 2.39.

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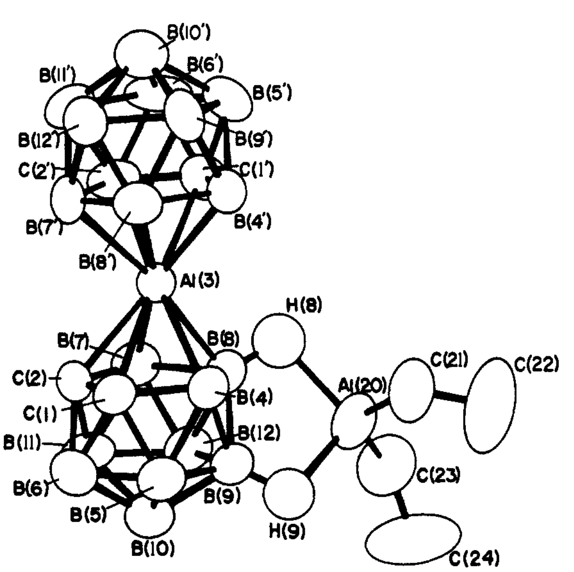

Figure 1. ORTEP representation of the structure of **2** with all hydrogen atoms except the B–H–Al bridges omitted for clarity and thermal ellipsoids at 50% probability level. Al–C(1) 2.28 (8), Al–C(1′) 2.24 (0), Al–C(2) 2.27 (1), Al–C(2′) 2.25 (4), Al–B(4) 2.23 (4), Al–B(4′) 2.17 (5), Al–B(7) 2.23 (0), Al–B(7′) 2.16 (5), Al–B(8) 2.17 (5), Al–B(8′) 2.13 (0) Å.

manner as ligands are bound in well-known transition-metal sandwich complexes, e.g., $[Fe(C_5H_5)_2]$[5] and $[Fe(C_2B_9H_{11})_2]^-$.[6] In addition, a diethylaluminum moiety is bound to one of the dicarbollide cages of **2** via two B–H–Al bridges. In a formal sense **2** is a zwitterion composed of an anionic $[Al(\eta^5\text{-}C_2B_9H_{11})_2]^-$ sandwich complexed with a $[Al(C_2H_5)_2]^+$ cation. This complex is a dimer of **1**.

In addition to the X-ray crystal structure determination, complex **2** was characterized by a combination of ^{1}H, ^{11}B, and ^{13}C NMR and IR spectroscopy.[7] The $^{11}B\{^1H\}$ NMR spectrum of **2** contained broad, ill-defined resonances attributed to one of the two nonequivalent dicarbollide cages as well as well-defined resonances for the second dicarbollide cage. Formal rapid rotation on the NMR time scale of the unsubstituted dicarbollide cage with respect to the substituted cage is inferred by the similarity between the ^{11}B NMR resonance pattern of the former cage and that of **1**. The B–H–Al bridges from one of the dicarbollide cages to the exopolyhedral diethylaluminum moiety of **2** give rise to an infrared absorption at 1584 cm^{-1}. When cage-deuterated **1** (*closo*-1,2-H_2-3-C_2H_5-3,1,2-$AlC_2B_9D_9$) was used in the preparation of **2**, this band was replaced by one at 1152 cm^{-1} in the product.

A broad ^{11}B NMR resonance which occurs at relatively high field (−32.0 ppm) and does not exhibit sharp ^{1}H splitting was assigned to the B(8) and B(9) exopolyhedral bridge sites. No evidence for "cage walking" of the distal dialkylaluminum moiety to other positions was observed in ^{11}B NMR spectra obtained between 25 and 107 °C. ^{11}B NMR spectra were obtained down to −88 °C; however, this apparently was not sufficiently low in temperature to freeze out rotation around the commo-aluminum unsubstituted cage as inferred by no loss of symmetry in the resonance pattern. Both the ^{1}H and ^{13}C NMR spectra showed broad, ill-defined ethyl resonances. This has been attributed to slow molecular tumbling on the NMR time scale caused by the molecule's relatively large size and lack of symmetry.

Catalytic formation of **2** proceeds smoothly within 12 h in benzene solution at 25 °C and 1 atm. of CO to give the product in 93% yield based on **1** (eq 1). In experiments designed to

$$2[\textit{closo}\text{-}3\text{-}\underset{\mathbf{1}}{C_2H_5}\text{-}3,1,2\text{-}AlC_2B_9H_{11}] \xrightarrow[C_6H_6]{CO}$$
$$\textit{commo}\text{-}3,3'\text{-}Al[(\textit{exo}\text{-}8,9\text{-}(\mu\text{-}H)_2\underset{\mathbf{2}}{Al}(C_2H_5)_2\text{-}3,1,2\text{-}AlC_2B_9H_9)\text{-}(3',1',2'\text{-}AlC_2B_9H_{11})] \quad (1)$$

quantify the loss of CO during reaction, CO recoveries of over 95% were consistently measured.[8] The facile reaction of carbon monoxide with **1** contrasts markedly with its reported reaction with neat triethylaluminum in an autoclave at 78 °C to give a mixture of 2-pentene and isobutylene.[9] The reaction of **1** with other donor ligands such as tetrahydrofuran, acetonitrile, and triethylphosphine does not result in dimerization but rather results in the formation of adducts of the type **1**·2L (L = donor ligand).[10]

Complex **2** is an unusual example of a complex which contains a non-transition element bonded between the parallel faces of two planar π-donor ligands.[11] While sandwich compounds based on main-group elements have been prepared [e.g. $Sn[C_5(CH_3)_5]_2$ and $Pb(C_5H_5)_2$], these are 14 interstitial electron systems involving a nonbonding electron pair on the central metal atom. Complex **2**, on the other hand, contains a formal Al(III) atom. The central aluminum atom in **2** is bound nearly symmetrically with respect to the five atoms in each C_2B_3 bonding face of the two dicarbollide ligands. As each of these ligands is regarded as a six-electron donor, the central metal atom formally has 12 electrons in its valence shell. Furthermore, there are no distortions in the structure of **2** which might be indicative of the presence of localized nonbonding electrons. Thus, **2** represents a 12 interstitial electron system and the first formal commo-[Ne]-core main-group-element sandwich complex, as well as the first aluminum sandwich complex of any kind of which we are aware. Extension of the chemistry of formal commo-[Ne]-core main-group-element bis(dicarbollide) sandwich complexes to include the neutral silicon compound is described in the following paper.[13]

Acknowledgment. The support of the National Science Foundation (Grant CHE-84-01433) is gratefully acknowledged. We also thank NSF for use of the Bruker WM-500 FTNMR spectrometer at the Southern California Regional Magnetic Resonance Facility (Grant CHE-79-16324).

Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(7) Spectroscopic data for **2**: $^{11}B\{^1H\}$ NMR (C_6D_6; referenced to external $BF_3{\cdot}OEt_2$, 0 ppm, with chemical shift values upfield of 0 ppm reported as negative; ambient temperature; areas given in parentheses) δ −8.6(3), −14.6(1), −15.6(1), −16.6(3), −17.4(3), −19.7(3), −26.1(2), −32.0(2) (br); ^{1}H NMR (C_6D_6; referenced to residual protons in C_6D_6, 7.15 ppm; ambient temperature) δ 0.87 (q, ill defined, area 2), 1.36 (t, area 3), 1.58 (s, area 1), 2.55 (s, area 1); $^{13}C\{^1H\}$ NMR (C_6D_6; referenced to C_6D_6, 128.0 ppm; ambient temperature) δ 20.70 (CH_2 by APT), 29.99 (CH_3 by APT), 50.97 (br), 45.64 (br); IR (NaCl; Nujol mull) 3039 (w), 3033 (w), 2602 (m), 2589 (m), 2579 (s), 2569 (m), 2553 (m), 2533 (vs), 2502 (w), 2489 (w), 2466 (w), 1584 (s), 1265 (m), 1134 (s), 1082 (s), 1005 (vs), 946 (s), 828 cm^{-1} (s).

(8) A typical experiment for monitoring CO uptake was carried out as follows. A solution of **1** (0.53 mmol in 5 mL of benzene) was added in a nitrogen-filled glovebox to a dry glass vessel equipped with a high-vacuum stopcock. After attachment to a calibrated vacuum line, the solution was degassed with three freeze–pump–thaw cycles. Dry, $Fe(CO)_5$- and oxygen-free CO (0.57 mmol) was introduced into the vessel and it was isolated. The solution was stirred for 12 h after which time all volatiles were removed in vacuo and passed through a −78 °C trap using a Toepler pump. Recovered CO (>95%) was measured volumetrically. Product **2** was identified by ^{11}B NMR spectroscopy.

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