Metallocene Analogs of Copper, Gold, and Palladium Derived from the (3)-1,2-Dicarbollide Ion

Leslie F. Warren, Jr.,[1] and M. Frederick Hawthorne

Contribution from the Department of Chemistry, The University of California, Riverside, California 92502. *Received March 8, 1968*

Abstract: Sandwich-bonded complexes of copper, gold, and palladium using the (3)-1,2-dicarbollide ligand, $B_9C_2H_{11}^{2-}$, have been prepared and characterized. These complexes are of the type $M^{n+}(B_9C_2H_{11})_2^{n-4}$ and are formally analogous to the bis(π-cyclopentadienyl)metallocenes. The copper and gold systems each contain species with the metal atoms in the formal 2+ (d^9, one unpaired electron) and 3+ (d^8, diamagnetic) oxidation states. The crystal structures of the copper derivatives show both the Cu^{II} and Cu^{III} derivatives to be isostructural, where the anions suffer a slip-distortion from a symmetrical π sandwich. Other d^8 metal complexes ($M^{n+} = Au^{3+}, Ni^{2+}$) have been shown to be isomorphous with the copper analogs. The palladium system contains species with the metal atom in the formal 2+ (d^8, diamagnetic), 3+ (d^7, one unpaired electron), and 4+ (d^6, diamagnetic) oxidation states. Cyclic voltammetry, electronic spectra, and ^{11}B nmr data and their relationships to the chemistry and structures of these complexes are also presented.

The two isomeric (3)-1,2- and (3)-1,7-dicarbollide ions[2] have recently been shown to form novel "sandwich-bonded" complexes of the type $M^{n+}(B_9C_2H_{11})_2^{n-4}$ involving several transition metals.[2] These complexes have been formulated as analogs of the bis(π-cyclopentadienyl)metallocenes because of similarities in bonding, redox properties, and electronic structures. The (3)-1,2-dicarbollide ion, however, can stabilize "sandwich" structures with metals that have no known metallocene analogs. The recently reported "cupricene" analog,[2] $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Cu^{2-}$, is an example, as are the new complexes of gold and palladium, $M^{n+}[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2^{n-4}$ (M = Au, Pd), described in this paper. Although several $\pi\text{-}C_5H_5Pd^{II}$ [3] and some $\sigma\text{-}C_5H_5Au^{I}$ [4] compounds have been prepared, to our knowledge, the bis-(3)-1,2-dicarbollide ion complexes are the first reported analogs of the unknown bis-π-cyclopentadienylgold ("aurocene") and -palladium ("palladocene") systems. As found in these complexes and in the recently described bis-π-(3)-1,2-dicarbollylnickel,[2,5] and -copper[2] species, the ligand stabilizes unusual formal oxidation states of the metals. As examples, Cu^{III}, Pd^{III}, and Au^{II} compounds are extremely rare, being found in a few oxide and fluoride systems[6] and perhaps in the controversial square-planar bis(maleonitriledithiolene) complexes.[7a,b] Todd and coworkers have recently reported a $Cu^{3+}(B_{10}CH_{11})_2^{3-}$ species; however, no characterization data were given.[8]

The Bis(π-(3)-1,2-dicarbollyl)copper System. The preparation of the $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Cu^{2-}$ ion (**1**) has been reported previously[2] and involved the reaction of cupric salts with the $(3)\text{-}1,2\text{-}B_9C_2H_{12}^-$ ion in cold, 40% aqueous sodium hydroxide. The tetraethylammonium salt of this species is deep blue and paramagnetic (μ_{eff} = 1.70 BM) with one unpaired electron, which is consistent with a d^9 system. Acetonitrile or acetone solutions containing **1** were air sensitive, gradually turning red (*vide infra*), especially with traces of water present. Cold, basic, aqueous solutions of **1**, however, appeared to be very stable.

Upon shaking the aqueous reaction mixture from **1** with diethyl ether in the presence of air, the sodium salt of the red $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Cu^-$ ion (**2**) was extracted into the organic phase, from which **2** was isolated in high yield as the salt of a large cation. Pure **2** is a very deep red ion and diamagnetic, as expected for a d^8 configuration. The ^1H nmr spectrum of tetraphenylarsonium **2** in acetone contained a phenyl resonance of intensity 5 at −8.07 ppm (relative to tetramethylsilane) and a carborane C–H proton resonance of intensity 1 at −3.91 ppm, consistent with the assigned formulation. Solutions containing **2** were very unstable, decomposing to colored products (depending upon the solvent) in a matter of hours. Ether solvents were found to provide the most stable solutions.

Cyclic voltammetry was performed on salts of **1** and **2** in acetonitrile and the results are given in Table I.

Table I. Reduction Potentials (Volts) of the Bis(π-(3)-1,2-dicarbollyl)copper, -gold, -nickel, and -palladium Derivatives[a]

Compounds	$M^{IV} + e^- \rightarrow M^{III}$	$M^{III} + e^- \rightarrow M^{II}$	$M^{II} + e^- \rightarrow M^{I}$
$[(C_2H_5)_4N]_2Cu^{II}(B_9C_2H_{11})_2$		−0.35	−0.99
$(C_6H_5)_3CH_3PCu^{III}(B_9C_2H_{11})_2$		−0.35	∼−1.2[b]
$[(C_2H_5)_4N]_2Au^{II}(B_9C_2H_{11})_2$		−0.62	∼−0.92[b]
$(C_6H_5)_3CH_3PAu^{III}(B_9C_2H_{11})_2$		−0.62	∼−0.84[b]
$Ni^{IV}(B_9C_2H_{11})_2$	+0.18	−0.66	
$(CH_3)_4NNi^{III}(B_9C_2H_{11})_2$	+0.18	−0.66	
$Pd^{IV}(B_9C_2H_{11})_2$	−0.14	−0.56	
$[(C_2H_5)_4N]_2Pd^{II}(B_9C_2H_{11})_2$	−0.14	−0.56	

[a] Obtained by cyclic voltammetry in acetonitrile solution, 0.1 *N* tetraethyl- or tetrabutylammonium perchlorate supporting electrolyte; steady-state reduction peak potentials reported (*vs.* sce) for reversible redox couples. [b] "Quasi-" reversible redox couple.[9]

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[1] U. S. Public Health Service Predoctoral Fellow.

[2] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968), and references therein.

[3] See J. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964), for a recent review.

[4] R. Huttel, U. Raffay, and H. Reinheimer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 862 (1967).

[5] L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **89**, 470 (1967).

[6] See B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964), for references regarding compounds of this type.

[7] (a) See A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963), for a possible Pd^{III} complex; (b) see J. H. Waters and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3534 (1965), regarding a Au^{II} complex.

[8] D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *ibid.*, **89**, 3342 (1967).

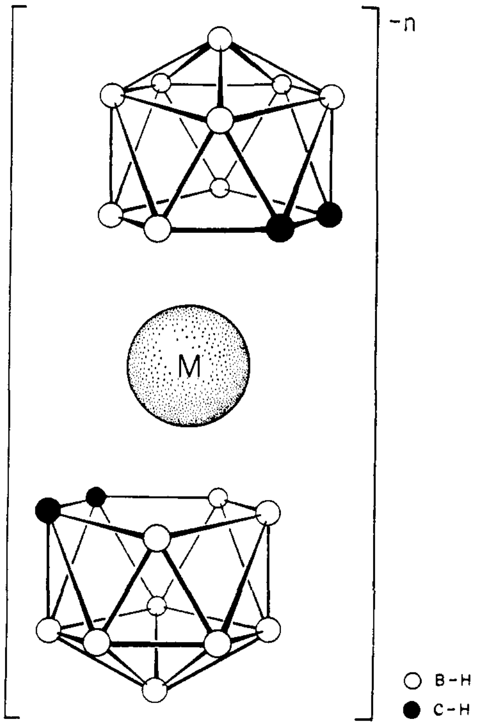

Figure 1. The structure of the d^8, d^9 systems: M = Ni^{II}, Cu^{II}, Cu^{III}, Au^{III}. The proposed structure for M = Pd^{II}, Au^{II}.

Table II. Electronic Spectra of the Bis(π-(3)-1,2-dicarbollyl)copper, -gold, -nickel, and -palladium Systems

Compound	Solvent	λ_{max}, mμ (ϵ)
$[(C_2H_5)_4N]_2Cu^{II}(B_9C_2H_{11})_2$	CH_3CN	278 (sh) (2400) 510 (sh) (4000) 610 (5300)
$[(C_2H_5)_4N]_2Au^{II}(B_9C_2H_{11})_2$	KBr disk	320 (1.0)[a] 442 (0.92) 730 (0.69)
$(CH_3)_4NCu^{III}(B_9C_2H_{11})_2$	CH_3CN	205 (sh) (∼15,000) 492 (27,300)
$(C_2H_5)_4NAu^{III}(B_9C_2H_{11})_2$	CH_3CN	208 (17,200) 447 (28,900)
$[(C_2H_5)_4N]_2Ni^{II}(B_9C_2H_{11})_2$	CH_3CN	233 (8800) 347 (12,400)
$[(C_2H_5)_4N]_2Pd^{II}(B_9C_2H_{11})_2$	CH_3CN	263 (10,200) 402 (13,600)
$(CH_3)_4NNi^{III}(B_9C_2H_{11})_2$	CH_3CN	237 (8500) 337 (21,000) 435 (sh) (3600)
$(C_2H_5)_4NPd^{III}(B_9C_2H_{11})_2$	CH_3CN	287 (13,900) 332 (19,800) ∼470 (sh) (1400)
$Ni^{IV}(B_9C_2H_{11})_2$	Cyclohexane	297 (37,100) 425 (2050)
$Pd^{IV}(B_9C_2H_{11})_2$	Cyclohexane	292 (43,800) 410 (2690)

[a] Relative absorbances from KBr disk spectrum.

Both compounds had a reversible one-electron redox couple at -0.35 V (reduction peak potential *vs.* sce) corresponding to $\mathbf{2} + e^- \rightarrow \mathbf{1}$. A second "quasi-" reversible[9] one-electron couple at ~ -1.0 V suggests the existence of a Cu^I species. It is of interest to note that Cu^{III} is the *most stable* oxidation state in the bis(dicarbollyl) system, *i.e.*, the Cu^{II} complex (**1**) is a very strongly reducing species.

The crystal and molecular structures of tetraethylammonium **1**[10] and triphenylmethylphosphonium **2**[11] were determined by Wing, who found both the ions to have the "slipped" configuration as shown in Figure 1. The ^{11}B nmr spectrum of **2** (Figure 2) contains a low-field doublet which appears to be a characteristic of the ^{11}B spectra of diamagnetic bis(dicarbollyl) complexes having this "slipped" configuration. The doublet has been tentatively assigned to the unique boron atom in the open face of the ligand. The electronic spectral data for **1** and **2** are presented in Table II.

The Bis(π-(3)-1,2-dicarbollyl)gold System. The addition of a dioxane suspension of anhydrous $AuCl_3$ to a large excess of the (3)-1,2-dicarbollide ion, $B_9C_2H_{11}^{2-}$, in glyme (1,2-dimethoxyethane) produced a deep blue species (*vide infra*) which dissolved in water giving a brown solution. Treatment of this aqueous solution with tetraethylammonium or triphenylmethylphosphonium bromide afforded blue precipitates which were oxidized in dichloromethane with acidic hydrogen peroxide to red salts of the very stable ion $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Au^-$ (**3**). Salts of **3** are deep red and diamagnetic, as is its d^8 Cu^{III} analog, **2**. The ^1H nmr spectrum of tetraethylammonium **3** in acetone was consistent with our formulation: a broad carborane C–H proton resonance at -4.12 ppm and ethyl proton resonances which integrated as one carborane C–H proton per ethyl group. Cyclic voltammetry with **3** in acetonitrile (Table I) showed a reversible one-electron redox couple at -0.62 V (*vs.* sce) and a quasi-reversible,[9] one-electron couple at ~ -0.9 V, indicating the existence of a Au^{II} and possibly a Au^I species, as in the copper system. Thus, sodium amalgam reduction of tetraethylammonium **3** in tetrahydrofuran produced a new ion, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Au^{2-}$ (**4**). Tetraethylammonium **4** is deep blue-green and paramagnetic (μ_{eff} = 1.79 BM), consistent with a d^9 formulation. The cyclic voltammetry data of **4** are given in Table I.

An X-ray diffraction study of triphenylmethylphosphonium **3** by Wing[11] showed that the salt was isomorphous with its Cu^{III} analog, **2** (Figure 1). The ^{11}B nmr spectrum of **3** is shown in Figure 2. In view of the great similarities in the polarographic, magnetic, and electronic spectral data (Table II) of the gold and copper systems, it is reasonable to expect that the Au^{II} species, **4**, also has this same structure.

Attempts to prepare an analogous bis(dicarbollyl)silver system employing an aqueous procedure (as with copper) and a nonaqueous procedure (as with gold) have thus far been unsuccessful.

The Bis(π-(3)-1,2-dicarbollyl)palladium System. The addition of the (3)-1,2-$B_9C_2H_{11}^{2-}$ ion to simple Pd^{II} salts in ether solvents resulted in black, spontaneously imflammable materials. Reversing the mode of addition gave the same results unless the ligand was present in a *large* excess. Thus, upon slowly adding palladium acetylacetonate in glyme to a cold solution containing a 2.5-fold excess of dicarbollide ion in the same solvent, the unstable, air-sensitive ion $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Pd^{2-}$ (**5**) was isolated from water in 80% yield as its orange-brown, diamagnetic (d^8), tetraethylammonium salt. Solutions containing **5** decomposed upon standing after

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[9] A "quasi-"reversible couple contained a cathodic wave with a varying peak potential and an anodic wave with a more or less constant peak potential.

[10] R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).

[11] R. M. Wing, *ibid.*, **90**, 4828 (1968).

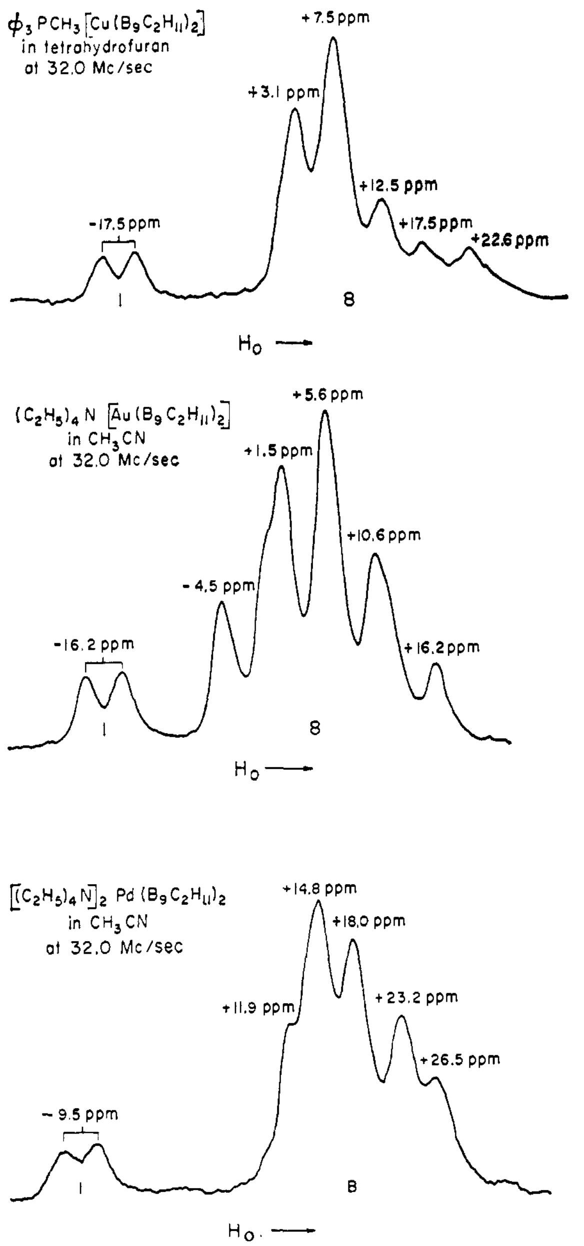

Figure 2. 32.0-Mc/sec ^{11}B nmr spectra of diamagnetic d^8 bis(π-(3)-1,2-dicarbollyl)metalates; reference $BF_3 \cdot O(C_2H_5)_2$ = 0 ppm.

several hours, depositing palladium metal. Decomposition was more rapid in the presence of air. The ^1H nmr spectrum of tetraethylammonium **5** in deuterioacetonitrile contained a carborane C–H resonance at -2.31 ppm and cation resonances in the expected ratios. The ^{11}B nmr spectrum of **5** shown in Figure 2 has a low-field doublet as the other d^8 species, **2** and **3**. Wing[11] has shown that the Ni^{II} analog[2] of **5**, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_1Ni^{2-}$, is isomorphous with **1** (Figure 1), and it is very reasonable to expect that the palladium compound has this same configuration. The electronic spectrum of **5** is given in Table II along with that of the nickel analog for purposes of comparison.

Although attempts to oxidize aqueous solutions of **5** were not successful (*cf.* the analogous nickel system[2]), tetraethylammonium **5** was readily oxidized in dichloromethane with 2 equiv of iodine, producing the neutral

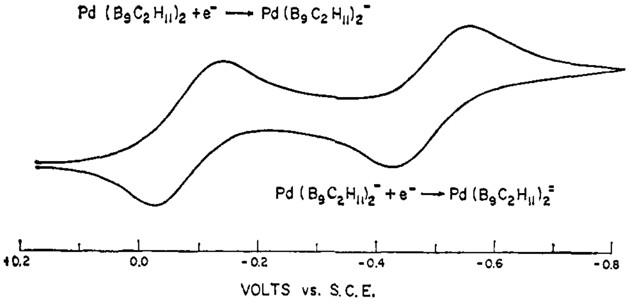

Figure 3. Cyclic voltammogram of the bis(π-(3)-1,2-dicarbollyl)palladium system, determined in CH_3CN (steady state).

species, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Pd$ (**6**), in 84% yield. The electrically neutral **6** is a diamagnetic (d^6), yellow crystal-

$$[(C_2H_5)_4N]_2Pd(B_9C_2H_{11})_2 + 3I_2 \xrightarrow{CH_2Cl_2} Pd(B_9C_2H_{11})_2 + 2(C_2H_5)_4NI_3$$

line solid, soluble in saturated hydrocarbon solvents, stable in dry air, and sublimes *in vacuo* at 200°. High-resolution mass spectroscopy verified the formulation $PdB_{18}C_4H_{22}$: Calcd for $^{108}Pd^{11}B_{18}{}^{12}C_4{}^1H_{22}$: mol wt, 376.2427. Found: mol wt, 376.2435. The ^1H nmr spectrum of **6** in benzene contained only a single carborane C–H proton resonance at -3.20 ppm. The infrared and ^{11}B nmr spectra of **6** are virtually identical with those of its Ni^{IV} analog,[2,5] $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Ni$, and the electronic spectra of these two compounds are given in Table II.

Tetraethylammonium **5** and **6** gave identical cyclic voltammograms, as shown in Figure 3. The two reversible redox couples at -0.14 and -0.56 V were found by controlled-potential coulometry to be two one-electron processes, which correspond to $\mathbf{6} + e^- \rightarrow Pd^{III}$ and $Pd^{III} + e^- \rightarrow \mathbf{5}$, respectively. The analogous nickel complexes give this same redox behavior.[2] Consequently, upon mixing equimolar quantities of **5** and **6** in dichloromethane the red species $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Pd^-$ (**7**) was obtained as its tetraethylammonium salt. Reduction of **6** in nonaqueous media with cadmium amalgam also gave **7**, but the presence of water destroyed the complex (in contrast to its water-stable Ni^{III} analog). Tetraethylammonium **7** is red-brown and paramagnetic ($\mu_{eff} = 1.68$ BM), as expected for a d^7 configuration. Nonaqueous solutions containing **7** rapidly decomposed upon standing and were very air and water sensitive. Stucky[12] and Wing[11] have shown that the Ni^{III} analog of **7**, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Ni^-$, has the structure shown in Figure 4. It is very likely that the Pd^{III} species is isostructural. Similarities in the electronic spectra of these two compounds are seen in Table II.

In addition to spectroscopic and redox similarities of the bis(dicarbollyl)palladium and -nickel[2,5] systems, there are chemical analogies. For example, the neutral Pd^{IV} (**6**) and Ni^{IV} species[2] are strong Lewis acids, both forming crystalline adducts with certain π and Lewis bases (halide ions, SCN^-, pyrene, phenanthrene, N,N-dimethylaniline, etc.). Also, the C,C′-dimethyl-substituted derivatives exhibit a series of molecular rearrangements to form isomeric systems. These aspects

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[12] G. D. Stucky, private communication regarding the X-ray crystal structure of $(CH_3)_4NNi(B_9C_2H_{11})_2$.

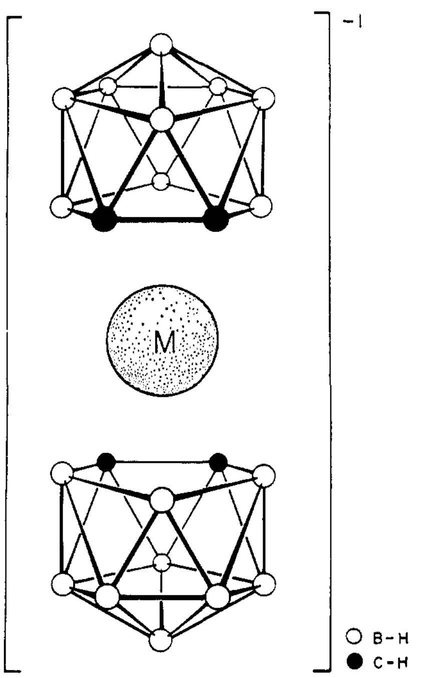

Figure 4. The structure of the d^7 system: M = Ni^{III}. The proposed structure for M = Pd^{III}.

of the chemistry and structures involved in the nickel and palladium systems will be reported at a later date.

Preparation of the bis(dicarbollyl)platinum system has so far been unsuccessful, although a number of platinum-containing starting materials have been employed. This could be due to the fact that Pt^{II} complexes invariably have square-planar coordination, which is difficult, if not impossible, to attain with the known dicarbollide ion ligands.

Conclusion

To date, bis(π-(3)-1,2-dicarbollyl) complexes of the first-row transition metals have been synthesized and characterized for metals whose d electron configurations have been d^3 and d^5 through d^9. X-Ray diffraction studies[2,10–14] have shown that all the characterized anionic complexes with seven or less metal d electrons have the symmetrical sandwich structure shown in Figure 4. All anionic d^8 and d^9 complexes, however, have the "slipped" configuration shown in Figure 1. Wing[10,11] describes this latter type of bonding as π-allylic, where the primary coordination sphere of the metal is six borons, three from each dicarbollide ion ligand. He rationalizes this distortion as due to both the electron-richness of the system and to the ligand asymmetry. However, π-allylic bonding does not fully describe the over-all picture. For example, bis(π-allyl)nickel(II) (d^8) is diamagnetic,[15] while the bis(π-(3)-1,2-dicarbollyl)nickel(II) is paramagnetic[2] with two unpaired electrons (*cf.* nickelocene).

An alternative viewpoint of the bonding in the d^8 and d^9 bis(dicarbollyl)metal systems is found in the d^{10} benzene complexes of Ag^{I} [16] and Cu^{I}.[17] The rationale[18,19] for the asymmetric binding in these species is that the empty (n + 1)s acceptor orbital of the metal is not of the correct symmetry to interact with the filled benzene e$_1$ molecular orbital and maintain C$_6$ symmetry; π-backbonding from a filled nd metal orbital to the empty e$_2$ molecular orbital of benzene would also require a distortion from C$_6$ asymmetry. For the d^8 and d^9 bis(dicarbollyl)metal complexes, the empty (or partially filled) metal orbital would be a ka$_g$-type orbital, a nd$_{z^2}$–(n + 1)s hybrid orbital as in Moffitt's treatment of ferrocene.[20] These metal–ligand orbital interactions are illustrated schematically in Figure 5.[21] Bonding in this manner does not significantly freeze the bonding electrons of the B$_9$C$_2$H$_{11}$$^{2-}$ ligand itself, whereas the π-allyl model would, resulting in some loss of the electron delocalization energy associated with the ligand.

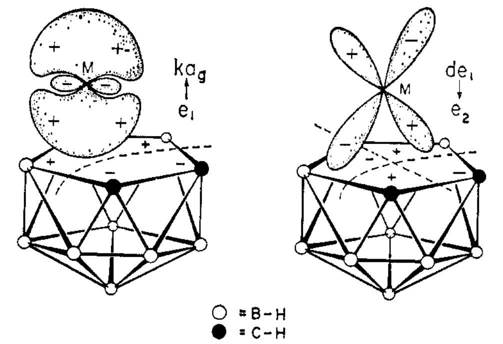

Figure 5. The metal–ligand orbital interactions in the d^8 and d^9 bis(π-(3)-1,2-dicarbollyl)metal complexes.[21]

The ^{11}B nmr spectra have been useful in structural assignments. Certain characteristics in these spectra are common to complexes having a particular configuration. A good example is the low-field doublet observed with the diamagnetic d^8 bis-π-(3)-1,2-carbollyl "slipped-sandwich" compounds (Figures 1 and 2), which is not seen in the ^{11}B spectra of diamagnetic (d^6) complexes having the more symmetrical sandwich structure (Figure 4). The ^{11}B nmr spectra of the neutral d^6 [(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni and [(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Pd species have *two* low-field doublets, a characteristic found only with these complexes. This and other information (*e.g.*, adduct formation) indicate a possible unique structure for these compounds. Further data regarding these observations will be presented in a later paper.

Experimental Section

Physical Measurements. Ultraviolet-visible spectra were measured with a Cary Model 14 spectrophotometer. Infrared spectra were obtained using a Beckman IR5 infrared spectrophotometer. Proton nmr spectra were obtained by means of a Varian A-60 spectrometer. The ^{11}B nmr spectra were recorded with a Varian HA-100 spectrometer at 32.0 Mc/sec. Molecular weights were determined with a Mechrolab Model 301A osmometer.

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(13) A. Zalkin and D. H. Templeton, private communication regarding the crystal structure determination of a bis(dicarbollylchromium(III)) complex.

(14) A. Zalkin, T. B. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **6**, 1911 (1967).

(15) G. Wilke and B. Bogdanović, *Angew. Chem.*, 73, 756 (1961).

(16) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 5075 (1958); R. W. Turner and E. L. Amma, *ibid.*, **88**, 3243 (1966).

(17) R. W. Turner and E. L. Amma, *ibid.*, **88**, 1877 (1966).

(18) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(19) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, c. 79 (1951).

(20) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).

(21) In this qualitative scheme the open face of the (3)-1,2-B$_9$C$_2$H$_{11}$$^{2-}$ ligand is treated as a symmetrical C$_5$H$_5$$^-$ system with a (filled), e$_1$ (filled), and e$_2$ (empty) molecular orbitals; the de$_1$ orbital is a filled nd_{xz} (or nd_{yz}) orbital.

Controlled-potential cyclic voltammetry was carried out using an instrument based on the design of Alden, Chambers, and Adams.[22] The measurements were made in acetonitrile using 0.1 *N* tetraethylammonium perchlorate as the supporting electrolyte. Potentials were measured at a platinum electrode *vs.* a saturated calomel electrode. The concentration of metal complex was approximately 10^{-3} *M*.

Controlled-potential coulometry on the palladium complexes was performed in acetonitrile solution with an instrument constructed from Philbrick operational amplifiers following the design of DeFord.[23]

Magnetic susceptibilities were measured utilizing an Alpha Scientific Laboratory, Inc., Model AL7536 water-cooled electromagnet with Models AL 7500 and AL 7500R power supply and current regulator, and a Mettler analytical balance with a sensitivity of 0.05 mg. Measurements were run on solid samples employing the Faraday technique,[24] using copper sulfate pentahydrate as standard. Diamagnetic corrections to the molar susceptibilities were made from Pascal's constants.

Mass spectra were determined with a CEC Type 21-103B mass spectrometer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. The preparation of the dicarbadodecahydroundecaborate(−1) ion, (3)-1,2-$B_9C_2H_{12}^-$, has been described.[25] Palladium acetylacetonate was obtained using the published procedure.[26] Anhydrous auric chloride was obtained by heating chloroauric acid, $H_3O^+AuCl_4^-$ (Alfa Inorganics, Inc.), at 100° *in vacuo* for 20 hr. Butyllithium, as a 1.6 *M* solution in hexane, was obtained from Foote Mineral Co. Tetraethylammonium bromide was obtained from Matheson Coleman and Bell; triphenylmethylphosphonium bromide was prepared from triphenylphosphine and excess methyl bromide in benzene solution.

All 1,2-dimethoxyethane and tetrahydrofuran were freshly distilled from lithium aluminum hydride and collected under nitrogen. Dioxane was dried by the procedure of Fieser.[27] Hexane, heptane, benzene, dichloromethane, and acetone were reagent grade and dried over molecular sieves. Baker Analyzed Reagent silica gel was employed in the chromatography.

Ultraviolet and visible spectra were measured in Spectrograde acetonitrile.

Preparation of the Bis(π-(3)-1,2-dicarbollyl)copper System. The preparation of the [π-(3)-1,2-$B_9C_2H_{11}$]$_2$$Cu^{2-}$ ion (**1**) has been described elsewhere.[2]

[$(C_6H_5)_3PCH_3$][π-(3)-1,2-$B_9C_2H_{11}$]$_2$Cu (2). A cold, 40% aqueous sodium hydroxide solution (35 ml) was treated with 0.993 g (5.14 mmoles) of $(CH_3)_3NH$[(3)-1,2-$B_9C_2H_{12}$] and 1.5 g (6 mmoles) of $CuSO_4 \cdot 5H_2O$ as previously described.[2] This deep blue mixture was diluted with 100 ml of cold water and rapidly extracted with four 100-ml portions of diethyl ether. The combined red ether layer was immediately shaken with a nearly saturated aqueous solution of triphenylmethylphosphonium bromide, and the brown-red precipitate was separated by filtration, washed with water, and dried in a vacuum desiccator. The yield of crude $(C_6H_5)_3PCH_3$–**2** was 1.293 g (2.14 mmoles, 83%). Other salts, *e.g.*, tetraethylammonium, tetramethylammonium, and tetraphenylarsonium, were obtained in the same manner. The $(C_6H_5)_3PCH_3^+$ salt was easily purified by rapidly chromatographing a fresh dichloromethane solution through a short (2–3 in.) silica gel column and adding hexane to the filtrate until crystallization was initiated to give deep red needles. The infrared spectrum (Nujol mull) of $(C_6H_5)_3PCH_3$–**2** contained absorptions at 3050 (w), 2525 (s), 1587 (w), 1438 (s), 1250 (w), 1183 (w), 1168 (w), 1119 (s), 1060 (m), 1033 (m), 999 (w), 975 (m), 945 (w), 898 (s), 790 (m), 743 (s), 720 (s), and 689 (s) cm^{-1}. (Only the more prominent infrared bands useful for characterization purposes are reported, including the cation bands in the salts.)

Preparation of the Bis(π-(3)-1,2-dicarbollyl)gold System. (a) The [π-(3)-1,2-$B_9C_2H_{11}$]$_2$$Au^-$ Anion (3). The (3)-1,2-$B_9C_2H_{11}^{2-}$ ion (18.1 mmoles) was prepared by gently refluxing 3.5 g of $(CH_3)_3NH$-[(3)-1,2-$B_9C_2H_{11}$] with 22.6 ml of 1.6 *M* butyllithium in hexane (36.2 mmoles) under nitrogen for ~1.5 hr in 250 ml of 1,2-dimethoxyethane. The turbid solution was cooled to 0°, and a suspension of 1.0 g of Au_2Cl_6 (3.3 mmoles) in dry dioxane was slowly added under nitrogen with stirring. A deep blue solution was formed, which, when treated with hexane, precipitated a blue material. The supernatant was decanted; the blue material was dissolved in deoxygenated water and filtered to give a deep brown filtrate. The brown solution was divided into two portions, one of which was treated with $(C_6H_5)_3PCH_3Br$, the other with $(C_2H_5)_4NBr$, to give blue precipitates. The precipitates were separated by filtration, washed with water, and dissolved in dichloromethane forming blue-green solutions which were shaken with a few drops of 30% hydrogen peroxide acidified with hydrochloric acid until they turned red. The dichloromethane solutions were washed with water, passed through short (2–3 in.) silica gel columns, and treated with hexane to give upon slow evaporation 1.283 g of $(C_6H_5)_3PCH_2$–**3** as large red crystals and 0.566 g of $(C_2H_5)_4N$–**3** as glittering red plates. The total yield was 2.70 mmoles, 82% based on $AuCl_3$. *Anal.* Calcd for $(C_2H_5)_4NAu(B_9C_2H_{11})_2$: Au, 33.27; B, 32.87; C, 24.34; H, 7.15; N, 2.37; formula wt, 592.04. Found: Au, 33.03; B, 31.31; C, 24.57; H, 7.33; N, 2.56; formula wt, 585 (osmometric). The infrared spectrum (Nujol mull) of $(C_2H_5)_4N$–**3** contained absorptions at 3050 (w), 2603 (m), 2520 (s), 1362 (m), 1258 (m), 1183 (m), 1172 (m), 1058 (s), 1038 (w), 1012 (w), 999 (m), 985 (m), 965 (m), 920 (m), 905 (s), 864 (m), 811 (w), 785 (s), 737 (w), 727 (m), 708 (m), 679 (m), and 647 (w) cm^{-1}.

(b) [$(C_2H_5)_4N$]$_2$[π-(3)-1,2-B_9CH_{11}]$_2$Au (4). A tetrahydrofuran solution containing 0.202 g (0.341 mmole) of $(C_2H_5)_4N$–**3** was stirred with dilute sodium amalgam in an inert atmosphere. After 5 min, the solution was nearly colorless. The suspension was decanted from the amalgam and filtered to give 0.086 g (0.119 mole) of [$(C_2H_5)_4N$]$_2$–**4** as a blue, microcrystalline solid. *Anal.* Calcd for [$(C_2H_5)_4N$]$_2$$Au(B_9C_2H_{11})_2$: C, 33.26; H, 8.65; N, 3.88. Found: C, 30.71; H, 8.27; N, 4.18. The colorless tetrahydrofuran filtrate was air-oxidized to give the red, water-soluble sodium salt of **3**, which was converted to the tetraethylammonium salt (0.054 g, 0.091 mmole). The deep, blue-green solutions containing **4** were readily air-oxidized to the red Au^{III} species (**3**). The infrared spectrum (Nujol mull) of [$(C_2H_5)_4N$]$_2$–**4** contained absorptions at 2580 (m), 2500 (s), 1385 (m), 1171 (s), 1070 (s), 1057 (w), 1025 (w), 998 (m), 966 (m), 949 (m), 928 (w), 907 (w), 896 (m), 888 (w), 779 (s), 735 (m), 712 (w), and 655 (w) cm^{-1}.

Preparation of the Bis(π-(3)-1,2-dicarbollyl)palladium System. (a) [$(C_2H_5)_4N$]$_2$[π-(3)-1,2-$B_9C_2H_{11}$]$_2$Pd (5). The (3)-1,2-dicarbollide ion (15.5 mmoles) was prepared in 1,2-dimethoxyethane using butyllithium as in the case of the gold complex. A 1,2-dimethoxyethane solution containing 1.0 g (3.29 mmoles) of palladium acetylacetonate was slowly added to the cold dicarbollide ion solution to give a red-orange solution. Heptane precipitated the red-orange dilithium salt of **5**, which was dissolved in deoxygenated water and filtered, and the filtrate was treated with $(C_2H_5)_4NBr$. The crude orange precipitate was dried *in vacuo* and rapidly crystallized in an inert atmosphere from acetone–heptane to give 1.66 g (2.63 mmoles, 80%) of rust-red to brown, air-sensitive, crystalline [$(C_2H_5)_4N$]$_2$–**5**. *Anal.* Calcd for [$(C_2H_5)_4N$]$_2$$Pd(B_9C_2H_{11})_2$: Pd, 16.84; B, 30.80; C, 38.03; H, 9.89; N, 4.43. Found: Pd, 18.46; B, 28.28; C, 38.33; H, 9.80; N, 4.68. The infrared spectrum (Nujol mull) of tetraethylammonium **5** contained absorptions at 2565 (m), 2515 (s), 2422 (m), 1302 (m), 1182 (m), 1060 (w), 1031 (m), 1003 (w), 982 (w), 966 (w), 909 (m), 790 (m), and 692 (w) cm^{-1}.

(b) [π-(3)-1,2-$B_9C_2H_{11}$]$_2$Pd (6). A dichloromethane solution–suspension of [$(C_2H_5)_4N$]$_2$–**5** (0.477 g, 0.755 mmole) was stirred with a solution of iodine (0.6 g, 2.37 mmoles) in the same solvent for 5 min. Twice the volume of hexane was added, the mixture separated from the $(C_2H_5)_4NI_3$ by filtration, and the yellow filtrate passed through a short silica gel column (3 in.), eluting with 2:1 hexane–CH_2Cl_2. The solvent and excess iodine were completely removed *in vacuo*. The yellow residue was then rechromatographed on silica gel (3 in.) with a 7:10 CH_2Cl_2–hexane mixture, and the solvent was slowly removed with a water aspirator vacuum to give 0.235 g (0.634 mmole, 84%) of bright yellow **6**. *Anal.* Calcd for $Pd(B_9C_2H_{11})_2$: Pd, 28.66; B, 52.42; C, 12.94; H, 5.97. Found: Pd, 27.91; B, 52.70; C, 13.04; H, 6.04. Solid **6** slowly decomposed in moist air. The infrared spectrum (Nujol mull) of **6** contained absorptions at 3030 (w), 2583 (s), 1210 (m), 1138 (w),

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1095 (w), 1080 (s), 1006 (m), 966 (s), 921 (w), 910 (m), 885 (m), 746 (m), 734 (w), and 721 (m) cm^{-1}.

(c) **$(C_2H_5)_4N[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Pd$ (7).** A mixture of 0.361 g (0.571 mmole) of $[(C_2H_5)_4N]_2$–**5** and 0.215 g (0.580 mmole) of **6** was stirred in 30 ml of dichloromethane for 2 min. The solution, which became deep red, was filtered, hexane was added until crystallization was initiated, and, upon standing for 10 min, 0.373 g (0.744 mmoles, 65%) of $(C_2H_5)_4N$–**7** separated as lustrous brown leaflets. *Anal.* Calcd for $(C_2H_5)_4NPd(B_9C_2H_{11})_2$: Pd, 21.22; B, 38.81; C, 28.74; H, 8.44; N, 2.79. Found: Pd, 22.02; B, 37.96; C, 26.35; H, 8.62; N, 2.18. The compound was very air and moisture sensitive, both in the solid state and in solution. The infrared spectrum (Nujol mull) of $(C_2H_5)_4N$–**7** contained absorptions at 3050 (w), 2533 (s), 1300 (w), 1218 (w), 1181 (m), 1143 (w), 1079 (s), 1031 (w), 1011 (m), 970 (s), 915 (m), 861 (m), 790 (m), 745 (m), and 721 (w) cm^{-1}.

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Carborane Analogs of π-Allyls. The Crystal and Molecular Structure of Triphenylmethylphosphonium Bis((3)-1,2-dicarbollyl)cuprate(III)[1]

Richard M. Wing

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received February 21, 1968*

Abstract: The crystal structure of $[(C_6H_5)_3PCH_3]Cu(C_2B_9H_{11})_2$ has been determined from a single-crystal X-ray diffraction study. The triclinic cell I$\bar{1}$ with a_0 = 11.74 Å, b_0 = 15.30 Å, c_0 = 19.96 Å, α = 97.9°, β = 94.2°, and γ = 99.0° contains four formula units. The carbametallic anion $Cu(C_2B_9H_{11})_2^-$ (isostructural with the corresponding Cu(I)) is distorted from a π-sandwich configuration by a slippage of the carborane moieties parallel to one another so that the primary coordination sphere of copper is six borons, three from each carborane cage. The molecular symmetry of the anion is C_{2h}, and the copper–boron stereochemistry has a striking likeness to bis(π-allyl)nickel(II). This similarity lends further support to the description of the bonding in the electron-rich carbametallics as π-allylic. Also the bisdicarbollyls of Au(III), Ni(II), and Ni(III) have been shown to be isomorphous with the Cu(III), Cu(II), and Co(III) compounds, respectively. Thus for the 3d metallo bisdicarbollyls, it has been established that the d^8 and d^9 complexes have suffered a slip distortion, while those with seven or less d electrons are symmetrical π sandwiches.

Copper forms a series of electron-rich bisdicarbollyls. These compounds are related by one-electron changes in oxidation state, the formal metal valence ranging from one to three.[2]

A very unusual and interesting stereochemistry was revealed in the structure of the middle member of this series,[3] in which a severe slip distortion from the geometry of a π-sandwich compound was extant. From considerations of the molecular geometry, single-crystal visible dichroism, and single-crystal electron spin resonance, a description of the molecule as a carborane analog of a bis(π-allyl) was formulated.

Preliminary molecular orbital calculations indicate that tendencies toward distortion lie in a delicate balance of two factors, the electron-rich nature of the system and the heterocyclic character of the ligand.[4]

Because of the unusual structure observed for the blue copper(II) species, and the possibility of a molecular geometry change in going to Cu(III), as well as the unusual oxidation state for copper (unknown in organometallic chemistry), it was decided to determine the crystal structure of the copper(III) dicarbollide when it became available.

An added attraction was the fact that the copper(III) species is formally isoelectronic with the fully characterized diamagnetic bis(π-allyl)nickel(II),[5] in the same manner that the iron carbametallics are isoelectronic with ferrocene and ferrocenium ion.[6,7]

Experimental Section

Dark blood red needles of the triphenylmethylphosphonium salt of $Cu(C_2B_9H_{11})_2^-$ were provided by Professor M. F. Hawthorne and Mr. L. F. Warren of this department.

Using a polarizing microscope, a very small single crystal (0.4 × 0.04 × 0.01 mm) was selected and mounted in a borosilicate capillary. The crystals are dichroic, changing in color from dark red to orange. This dichroism was surveyed using a Donnay optical analyzer, and its relationship to the structure will be discussed below.

Precession (Mo K$\bar{\alpha}$) and Weissenberg (Cu Kα) photographs indicated that the crystal was triclinic with a_0 = 11.74 Å, b_0 = 15.30 Å, c_0 = 19.96 Å, α = 97.9°, β = 94.2°, γ = 99.0°. Systematic absences for $h + k + l = 2n + 1$ indicated a body-centered unit cell. A Delaunay reduction failed to reveal any hidden symmetry, so the centered triclinic cell was retained as this was the most con-

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