retical and solution spectra of the free carbanion. In solution, similar systems have exhibited bathochromic shifts when the cation size was increased.[41-43] For benzyllithium in tetrahydrofuran, a transition occurs at 330 mμ, while for benzylsodium, it occurs at 355 mμ. In these solutions, increasing the metal cation size decreases its ability to be solvated and therefore promotes association and increased perturbations of the π system of the carbanion. When a strongly coordinating but sterically bulky donor is present, such as triethylenediamine, 1,2-dimethoxyethane, or N,N,N′,N′-tetramethylethylenediamine, complete solvation of such small cations as Li^+ is not possible, and partially solvated species form. The carbanion can effectively compete with the donors in this situation and use its π cloud for complexation with the metal. Here the trend will be exactly opposite to the case of nonhindering solvents, with lithium exhibiting the largest bathochromic shift. The spectral results which have obtained here for benzyllithium triethylenediamine are consistent with this conclusion.

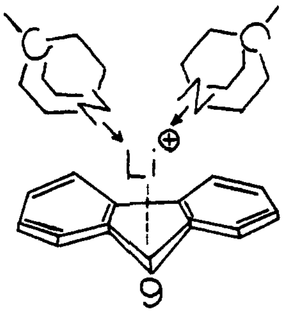

Figure 6. Predicted structure of fluorenyllithium-2-quinuclidine.

We are now in a position to predict in detail the geometry of other aromatic lithium systems. In fluorenyllithium, our molecular orbital calculations indicate that the lithium ion will penetrate the π cloud adjacent to the 9 position of the fluorenyl carbanion. Dixon has studied the structure of fluorenyllithium in solution using nuclear magnetic resonance techniques and has predicted a similar molecular arrangement.[11] The crystal structure and molecular properties of fluorenyllithium-2-quinuclidine are presently being determined in this laboratory (Figure 6), and will be reported in a subsequent publication.

(41) K. Kuwata, *Bull. Chem. Soc. Jap.*, 33, 1091 (1960).

(42) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 88, 307 (1966).

(43) H. V. Carter, B. J. McClelland, and E. Washurst, *Trans. Faraday Soc.*, 56, 455 (1960).

The Chemistry of the Bis[π-(3)-1,2-dicarbollyl] Metalates of Nickel and Palladium

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Abstract: The synthesis, reactions, and structures associated with the "sandwich"-bonded bis[π-(3)-1,2-dicarbollyl] complexes of nickel and palladium, $[M^{n+}(1,2\text{-}B_9C_2H_{11})_2]^{n-4}$ (M = Ni, Pd), and their carbon-substituted derivatives are discussed. The nickel and palladium bis(dicarbollyl) systems each contain species with the metal atoms in the formal 2+ (d^8, two unpaired electrons for nickel, diamagnetic for palladium), 3+ (d^7, one unpaired electron), and 4+ (d^6, diamagnetic) oxidation states. X-Ray diffraction studies coupled with magnetic, spectral, and electrochemical data show that the d^8 M^{II} metal complexes suffer a slip-distortion from a symmetrical π sandwich; the d^7 M^{III} anions possess a symmetrical "nonslipped" sandwich structure, while the electrically neutral d^6 M^{IV} species maintain a "cisoid" sandwich configuration in which the carbon atom pairs on opposing ligands reside on the same side of the molecule. The uncharged $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2M^{IV}$ derivatives are Lewis acids, which form addition compounds with a variety of "soft" Lewis bases, *e.g.*, halide ions, thiocyanate ion, naphthalene, phenanthrene, pyrene, etc. The binding in these adducts appears to be primarily a dipole–induced dipole interaction arising from the high dipole moment of the nickel(IV) complex (6.16 D). The C,C′-dimethyl-substituted nickel and palladium systems, $M[1,2\text{-}B_9H_9C_2(CH_3)_2]_2$, exhibit facile thermal ligand rearrangement reactions leading to three isomeric series of complexes. In these isomerization reactions, a ligand carbon atom in the icosahedral surface was found to migrate away from the metal atom while remaining adjacent to the carbon atom in the open pentagonal face of the ligand. Similar rearrangements occur in the unsubstituted $Ni(1,2\text{-}B_9C_2H_{11})_2$ complex at 360–400° in the vapor phase. Cyclic voltammetry, optical resolution studies, and nmr data and their roles in the structure elucidation of these complexes are presented.

The (3)-1,2-dicarbollide ion, $[(3)\text{-}1,2\text{-}B_9C_2H_{11}]^{2-}$ (Figure 1), has been shown to bond to a number of transition metals.[2-4] One feature associated with many of the "sandwich-bonded" bis(1,2-dicarbollyl) derivatives, $[M^{n+}(1,2\text{-}B_9C_2H_{11})_2]^{n-4}$, is their ability to undergo facile

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(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. Amer. Chem. Soc.*, 90, 879 (1968), and references therein.

(3) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, 90, 4823 (1968).

(4) H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, 7, 2279 (1968).

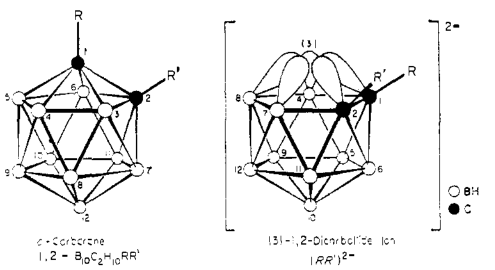

Figure 1. Schematic drawing of a C-substituted $B_{10}C_2H_{10}RR'$ carborane and its corresponding (3)-1,2-dicarbollide ion, $(R,R')^{2-}$, with numbering system.

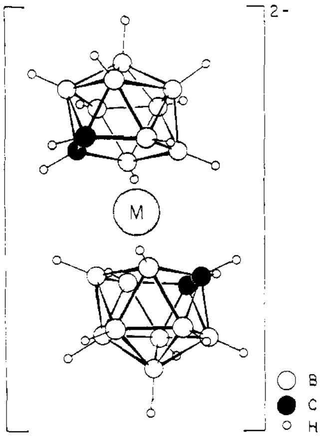

Figure 2. The structure of the d^8 bis[π-(3)-1,2-dicarbollyl] metalates: M = Ni^{II}, Pd^{II}; the "slipped-sandwich" configuration.

one-electron transfer reactions, affording species in which the metal atom exists in the *formal* 2+, 3+, and, in some cases, 4+ oxidation states. To date, all three oxidation states have been chemically accessible only with the nickel[2] and palladium[3] dicarbollide complexes.[5] Of chemical interest are the electrically neutral [π-(3)-1,2-$B_9C_2H_{11}$]$_2$M (M = Ni^{IV}, Pd^{IV}) species.[2,3] The preparation, characterization, reactions, and structures of these complexes and some of their carbon-substituted derivatives are discussed.[6]

The Parent Bis[π-(3)-1,2-dicarbollyl]nickel and -palladium and Related Systems

Structures. Details regarding the preparation and initial characterization of the parent unsubstituted bis[π-(3)-1,2-dicarbollyl]nickel and -palladium systems, [π-(3)-1,2-$B_9C_2H_{11}$]$_2$M, have been reported previously.[2,3] The pale brown, paramagnetic d^8 nickel(II) complex, $[(H_2)_2Ni^{II}]^{2-}$, was shown[3] to have the "slipped-sandwich" configuration (C_{2h} symmetry) shown in Figure 2. Boron-11 nmr evidence strongly indicated that the diamagnetic orange-brown palladium(II) complex was isostructural; *i.e.*, the spectrum contained a low-field doublet resonance which is characteristic in the ^{11}B nmr spectra of "electron-rich" diamagnetic d^8 bis[π-(3)-1,2-dicarbollyl] metalates having the slipped-sandwich structure.[3] The ^{11}B nmr spectrum of the paramagnetic $[(H_2)_2Ni^{II}]^{2-}$ ion exhibited large contact shifts extending over approximately 300 ppm and provided no structural information.

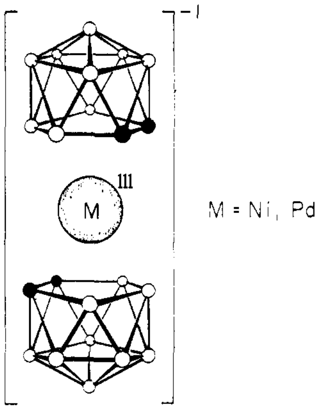

Figure 3. Schematic drawing of the d^7 bis[π-(3)-1,2-dicarbollyl] metalates of nickel(III) and palladium(III) with hydrogen atoms omitted; the symmetrical "non-slipped" sandwich configuration.

The deep yellow-brown paramagnetic, formal d^7 nickel(III) ion, $[(H_2)_2Ni^{III}]^-$, was shown to be isomorphous with its cobalt(III) analog, which has the symmetrical nonslipped sandwich structure[3,7] illustrated in Figure 3. From spectral and chemical similarities, the paramagnetic red-brown palladium(III) analog was expected to be isostructural with the nickel(III) derivative.[3] The ^{11}B nmr spectrum of the paramagnetic nickel(III) and palladium(III) complexes exhibited contact shifts and could offer no information with regard to structure.

Maintaining a closed shell electronic configuration, the diamagnetic formal d^6 M^{IV} derivatives, $(H_2)_2Ni^{IV}$ (orange) and $(H_2)_2Pd^{IV}$ (yellow), exhibited very similar spectral and redox properties.[3] Their ^{11}B nmr spectra (Figure 4) and their infrared spectra (Figure 5) demonstrate this marked similarity. The appearances of the two overlapping low-field doublet resonances in the ^{11}B nmr spectra are unique to these electrically neutral d^6 complexes,[8] and an unusual structure was expected. A single crystal X-ray diffraction study of the nickel(IV)

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(5) The [π-(3)-1,2-$B_9C_2H_{11}$]$_2$Co$^-$ ion possesses reversible formal Co^{II}–Co^{III} and Co^{III}–Co^{IV} redox couples, but at such potentials as to render isolation of the Co^{II} and Co^{IV} species exceedingly difficult. A similar situation was encountered in the [π-(3)-1,7-$B_9C_2H_{11}$]$_2$Ni system, where the Ni^{II} and Ni^{IV} derivatives were found to be much less stable than the corresponding bis(1,2-dicarbollyl) isomers (see ref 2).

(6) The nomenclature associated with the transition metal complexes of the dicarbollide ions and their carbon-substituted derivatives is often confusing and cumbersome [see "The Nomenclature of Boron Compounds," *Inorg. Chem.*, 7, 1945 (1968)]. Inasmuch as all the boron containing ligands utilized in this work were 1,2-dicarbollide derivatives, a simplified nomenclature system was devised. All bis(1,2-dicarbollyl)-metal complexes are designated by the substitution on the ligand carbon atoms and by the formal metal oxidation state. The unsubstituted [(3)-1,2-$B_9C_2H_{11}$]$^{2-}$ ligand is represented by $(H_2)^{2-}$; similarly, the 1-phenyl-1,2-dicarbollide ion is designated by $(HPh)^{2-}$, and so on for other derivatives. The following examples demonstrate this simplified nomenclature system (see Figure 1).

Dicarbollide ligand	Compound	Designation
Unsubstituted	[π-(3)-1,2-$B_9C_2H_{11}$]$_2$Ni	$(H_2)_2Ni^{IV}$
1,2-Dimethyl	[π-(3)-1,2-$B_9H_9C_2(CH_3)_2$]$_2$Pd^{2-}	$[(Me_2)_2Pd^{II}]^{2-}$
1-Methyl	[π-(3)-1,2-$B_9H_9CHC(CH_3)$]$_2$Ni$^-$	$[(HMe)_2Ni^{III}]^-$
1-Phenyl	[π-(3)-1,2-$B_9H_9CHC(C_6H_5)$]$_2$Ni	$(HPh)_2Ni^{IV}$

(7) Although the crystal structure of the $[(H_2)_2Co^{III}]^-$ ion has not been directly determined, a brominated derivative and the bis[π-(3)-1,7-dicarbollyl] analog have been structurally characterized. (See B. G. DeBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 7, 2288 (1968), and A. Zalkin, T. E. Hopkins, and D. H. Templeton, *ibid.*, 6, 1911 (1967), respectively.) Both structures exhibited the symmetrical nonslipped sandwich (C_{2h}) configuration; recent nuclear quadrupole resonance studies also confirmed this structure [C. B. Harris, *ibid.*, 7, 1517 (1968)].

(8) The charged d^6 bis[π-(3)-1,2-dicarbollyl] complexes of Fe^{II} and Co^{III} exhibited no characteristic resonances widely separated from the main body of their ^{11}B nmr spectra. The Co^{III} species has the symmetrical structure (see ref 7) shown in Figure 3, and the Fe^{II} derivative is most likely isostructural (ref 2).

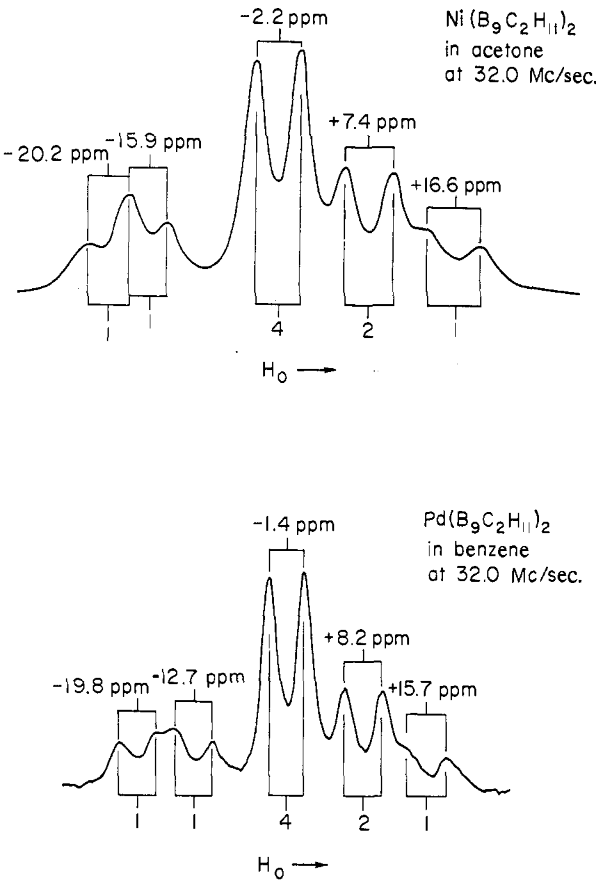

Figure 4. The 32.0-Mc/sec ^{11}B nmr spectra of the d^6 bis[π-(3)-1,2-dicarbollyl] metalates of nickel(IV) and palladium(IV); reference BF_3 etherate = 0.00 ppm.

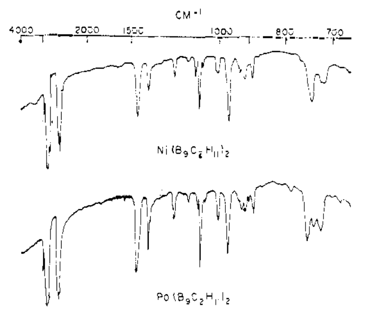

Figure 5. Infrared spectra (Nujol mulls) of the d^6 bis[π-(3)-1,2-dicarbollyl] metalates of nickel(IV) and palladium(IV).

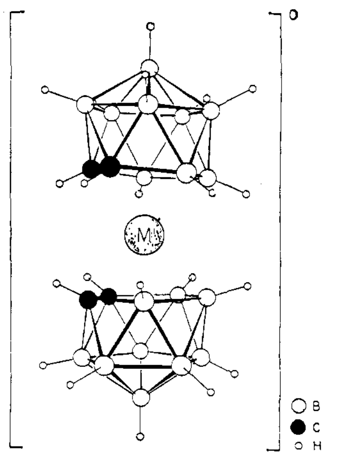

Figure 6. Structure of the d^6 bis[π-(3)-1,2-dicarbollyl]nickel(IV) and -palladium(IV) derivatives; one enantiomorphic rotational configuration in a "cisoid" configuration.

derivative was carried out by St. Clair, Zalkin, and Templeton,[9] and they observed the structure shown in Figure 6. The cisoid sandwich configuration (C_2 symmetry) is unique among the structures found for other bis[π-(3)-1,2-dicarbollyl] metalates[7,10] in that carbon atom pairs in opposing ligands resided on the same side of the molecule in a staggered, nonslipped cisoid configuration.[11] Two enantiomorphic rotational cisoid configurations were present in the crystal. The dicarbollide ion "cages" were found to be somewhat distorted at the carbon atoms which were displaced slightly toward the approximate geometric centers of their respective icosahedra. This resulted in a tip of about 6° of the facial (B_3C_2) planes with respect to one another, splaying the carbon pair in one ligand away from the carbon pair of the other ligand. Even though the ligand faces were tilted, the ligand distortions at the carbon atoms brought the facial carbons *closer* to the metal (2.07 Å) than to the facial borons (2.10 Å); a line drawn from the apex boron (B-10) of one cage through the nickel atom and through the apex boron (B-10′) of the other cage was a straight line, showing that the molecule as a whole was not bent along the *z* axis. The perpendicular distance from the metal to a best least-squares plane of either ligand face was 1.47 Å,[12] making an interligand distance of about 2.94 Å, compared to 3.32 Å, for the inter-ring distance in ferrocene.[11]

As found[13,14] in the electrically neutral carborane, $1,2\text{-}B_{10}C_2H_{12}$ (Figure 1), a region of localized electron deficiency around the carbonium ion like carbon atoms would be expected in the uncharged Ni^{IV} derivative. However, due to the presence of an adjacent highly electron-attracting metal atom, this electron deficiency should be increased in the area of the carbon atoms in $(H_2)_2Ni^{IV}$ relative to $1,2\text{-}B_{10}C_2H_{12}$.[15] Indeed, Hawthorne and Adler have shown[16] through ^{19}F nmr studies on *m*- and *p*-fluorophenyl-substituted nickel(IV) derivatives that a bis[π-(3)-1,2-dicarbollyl]nickel(IV) substituent bonded at carbon is very strongly electron-withdrawing by an inductive mechanism and its $-I$ effect (σ_I = +0.499–0.645) is the same order of magnitude as that of –CN or –F, and considerably greater than that found for the 1,2-dicarba-*closo*-dodecaboranyl substituent bonded at carbon (σ_I = +0.361).[13,16]

(9) D. St. Clair, A. Zalkin, and D. H. Templeton, *J. Amer. Chem. Soc.*, **92**, 1173 (1970).

(10) (a) R. M. Wing *ibid.*, **90**, 4828 (1968), and *ibid.*, **89**, 5599 (1967), presents the crystal structures of salts of the $[(H_2)_2Cu^{III}]^-$ and $[(H_2)_2Cu^{II}]^{2-}$ ions, respectively; (b) D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969), report an X-ray diffraction study of the $[(Me_2)_2Cr^{III}]^-$ ion.

(11) There are several examples of heteroannular substituted ferrocene derivatives which also reside in cisoid configurations in the crystal; see M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, Interscience Publishers, New York, N. Y., 1965.

(12) D. St. Clair, private communication.

(13) M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *J. Amer. Chem. Soc.*, **87**, 4746 (1965).

(14) W. N. Lipscomb, *ibid.*, **88**, 628 (1966).

(15) These effects do not appear to be as pronounced in the *anionic* d^6 bis[π-(3)-1,2-dicarbollyl] metalates of Co^{III} and Fe^{II}, and are apparently compensated by the negative charge associated with these molecules and the lower effective charges of the metal atoms.

(16) M. F. Hawthorne and R. Adler, to be submitted for publication.

Table I. Elemental Analyses, Molecular Weights, and Yields of the Carbon-Substituted Bis(π-1,2-dicarbollyl)nickel(III) and -palladium(II) Derivatives

Compound	Color	Analyses	Mol wt[a]	Yield, %
Cs[$(HMe)_2$Ni^{III}]	Orange-brown	Calcd: Ni, 12.12; B, 40.17; C, 14.87; H, 5.41; Cs, 27.43	425.7[b]	61.9
		Found: Ni, 12.46; B, 40.04; C, 15.11; H, 5.29; Cs, 27.61	409	
$(CH_3)_4$N[$(HPh)_2$Ni^{III}]	Orange-brown	Calcd: Ni, 10.68; B, 35.39; C, 43.69; H, 7.70; N, 2.55	549.9	37
		Found: Ni, 10.83; B, 35.32; C, 43.50; H, 7.61; N, 2.28	520	
$(CH_3)_4$N[$(Me_2)_2$Ni^{III}-*A*]	Deep red	Calcd: Ni, 12.94; B, 42.88; C, 31.76; H, 9.33; N, 3.09	453.8	88
		Found: Ni, 13.03; B, 43.10; C, 31.15; H, 9.33; N, 3.27	450	
$(CH_3)_4$N[$(Me_2)_2$Ni^{III}-*B*]	Yellow-brown	Calcd: Ni, 12.94; B, 42.88; C, 31.76; H, 9.33; N, 3.09	453.8	~100
		Found: Ni, 12.78; B, 42.87; C, 31.27; H, 9.39; N, 3.14	466	
$(CH_3)_4$N[$(Me_2)_2$Ni^{III}-*C*]	Deep golden	Calcd: Ni, 12.94; B, 42.88; C, 31.76; H, 9.33; N, 3.09	453.8	~100
		Found: Ni, 12.51; B, 42.03; C, 32.01; H, 9.58; N, 4.35	456	
[$(CH_3)_4$N]$_2$[$(Me_2)_2$Pd^{II}-*A*]·$(CH_3)_2$CO	Deep red-brown	Calcd: Pd, 17.23; B, 31.50; C, 36.95; H, 9.79; H, 4.54		52.8
		Found:[c] Pd, 16.43; B, 28.38; C, 35.70; H, 9.44; N, 4.29		

[a] Osmometric in acetone solution; the palladium complex was too unstable to employ osmometry. [b] Tetramethylammonium salt. [c] The thermal and air sensitivity and the possible loss of solvent of crystallization during purification may account for the poor elemental analysis of this palladium complex.

The experimentally determined dipole moments of $(H_2)_2$Ni^{IV} were 6.16 ± 0.05 D in cyclohexane solution and 6.45 ± 0.01 D in benzene solution at 25°. These values are in accord with the 4.53-D moment reported for the 1,2-icosahedral carborane, 1,2-$B_{10}C_2H_{12}$, in benzene solution.[17] The high dipole moments of the nickel(IV) complex suggested as possible solution models one in which the molecule retains a static cisoid ligand configuration as found in the crystal (Figure 6), one in which the ligands are rapidly rotating as in ferrocene, or one in which the ligands are slowly rotating (on the dipole moment measurement time scale) and a mixture of rotameric conformations is present. No definitive experiments which support or deny any of these three solution models can be presented at this time. Considering, however, the large size of the dicarbollide ligands and the possible close contact of the intercage hydrogen atoms during rotation,[18] a large energy barrier to ligand rotation might be expected.

Table II. Electronic Spectra of the Carbon-Substituted Bis(π-1,2-dicarbollyl)palladium(II) and -nickel(III) Derivatives

Compound	Solvent	λ_{max}, mμ (ϵ)
[$(CH_3)_4$N]$_2$[$(Me_2)_2$Pd^{II}-*A*]·$(CH_3)_2$CO	CH_3CN	200 (16,000) 265 (13,600) 462 (15,700)
Cs[$(HMe)_2$Ni^{III}]	CH_3OH	246 (7200) 359 (20,000) 455(sh) (~3000)
$(CH_3)_4$N[$(HPh)_2$Ni^{III}]	CH_3OH	226 (30,300) 356 (17,900)
$(CH_3)_4$N[$(Me_2)_2$Ni^{III}-*A*]	CH_3CN	249 (5760) 403 (20,200) 495(sh) (~4000)
$(CH_3)_4$N[$(Me_2)_2$Ni^{III}-*B*]	CH_3CN	245 (6800) 358 (22,000) 390(sh) (~10,000)
$(CH_3)_4$N[$(Me_2)_2$Ni^{III}-*C*]	CH_3CN	237 (7700) 333 (22,400) 370(sh) (~9000)

Mono-C-Substituted Derivatives of Nickel. The C-methyl- and the C-phenyl-substituted bis[π-(3)-1,2-dicarbollyl]nickel systems were prepared by the reaction of nickel acetylacetonate with the corresponding dicarbollide ion in tetrahydrofuran. The brown-yellow nickel(II) species thus formed were readily air oxidized to stable nickel(III) anions, which were isolated as salts of large cations. Both Cs[$(HMe)_2$Ni^{III}] and $(CH_3)_4$N[$(HPh)_2$Ni^{III}] were deep red-brown crystalline solids and paramagnetic (μ_{eff} = 1.72 and 1.73 BM, respectively) with one unpaired electron, as expected for a d^7 electronic configuration. The ^{11}B nmr spectra of these nickel(III) derivatives exhibited paramagnetic contact shifts extending over approximately 100 ppm and provided no structural information. Tables I and II present the characterization and spectroscopic data associated with these complexes.

Ferric ion oxidation of the two nickel(III) derivatives afforded the uncharged complexes $(HMe)_2$Ni^{IV} (orange) and $(HPh)_2$Ni^{IV} (deep red). These species were diamagnetic (d^6) and sparingly soluble in saturated hydrocarbons. Under high vacuum the C-methyl derivative sublimed unchanged at 200°, while severe decomposition was observed with the C-phenyl species at this temperature and a clean sublimate was not obtained. Both complexes, however, were volatile enough at lower temperatures to obtain mass spectra, and these data are presented in Table III. Tables IV and V record the characterization and spectroscopic data associated with these compounds. The proton nmr

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(17) A. W. Laubengayer and W. R. Rysz, *Inorg. Chem.*, 4, 1513 (1965).

(18) As a consequence of the assumed sp^3 hybridization of the atomic orbitals associated with the five atoms of the open face of the dicarbollide ion, substituents on these atoms are directed at an angle from the planar face in the direction of the metal atom. This is contrasted with the bis(cyclopentadienyl)metallocenes, where sp^2 hybridization directs substituents parallel to the plane of the C_5H_5 rings.

Table III. Mass Spectral Data of the Carbon-Substituted Bis(π-1,2-dicarbollyl)nickel(IV) and -palladium(IV) Derivatives

Compound	Isotopic species	Mass	Mass no. of parent peak[a]
$(D_2)_2Ni^{IV}$	$^{60}Ni^{11}B_{18}{}^{12}C_4{}^1H_{18}{}^2D_4$	Calcd: 332.298	327.552
		Found: 332.304	327
$(HMe)_2Ni^{IV}$	$^{60}Ni^{11}B_{18}{}^{12}C_6{}^1H_{26}$	Calcd: 356.304	351.582
		Found: 356.305	351
$(HPh)_2Ni^{IV}$	$^{60}Ni^{11}B_{18}{}^{12}C_{16}{}^1H_{30}$	Calcd: 480.336	475.725
		Found: 480.337	476
$(Me_2)_2Ni^{IV}$-*B*[b]	$^{60}Ni^{11}B_{18}{}^{12}C_8{}^1H_{30}$	Calcd: 384.335	379.636
		Found: 384.333	379
$(Me_2)_2Ni^{IV}$-*C*	$^{60}Ni^{11}B_{18}{}^{12}C_8{}^1H_{30}$	Calcd: 384.335	379.636
		Found: 384.333	379
$(Me_2)_2Pd^{IV}$-*C*	$PdB_{18}C_8H_{30}$ (natural abundance)	Calcd:	427.326
		Found:	427

[a] Most intense peak in parent region; compared with the calculated molecular weight. [b] Probe temperature was 100° and conversion to the isomeric form C may have taken place in the gas phase.

Table IV. Elemental Analyses and Molecular Weights of the Carbon-Substituted Bis(π-1,2-dicarbollyl)nickel(IV) and -palladium(IV) Derivatives

Compound	Color	Analyses[a]	Mol wt[b]	Yield, %
$(HMe)_2Ni^{IV}$	Orange	Calcd: Ni, 16.70; B, 55.35; C, 20.50; H, 7.45	351.6	95.3
		Found: Ni, 17.35; B, 54.00; C, 20.26; H, 7.50	347	
$(HPh)_2Ni^{IV}$	Deep red	Calcd: Ni, 12.34; B, 40.90; C, 40.40; H, 6.36	475.7	87
		Found: Ni, 13.16; B, 40.06; C, 40.60; H, 6.63	494	
$(Me_2)_2Ni^{IV}$-*B*	Orange	Calcd: Ni, 15.46; B, 51.26; C, 25.31; H, 7.97	379.6	90
		Found: Ni, 16.15; B, 49.42; C, 26.01; H, 8.08	369	
$(Me_2)_2Ni^{IV}$-*C*	Yellow	Calcd: Ni, 15.46; B, 51.26; C, 25.31; H, 7.97	379.6	~100
		Found: Ni, 15.30; B, 51.22; C, 25.34; H, 8.08	372	
$(Me_2)_2Pd^{IV}$-*C*	Yellow	Calcd: Pd, 24.90; B, 45.54; C, 22.49; H, 7.08	427.3	38
		Found: Pd, 24.96; B, 45.45; C, 22.52; H, 7.32	*c*	

[a] Purification of the strongly oxidizing nickel(IV) derivatives was difficult inasmuch as degradation products frequently appeared to cocrystallize with the compounds, leading to poor elemental analyses in some instances. [b] Osmometric in benzene solution. [c] By mass spectroscopy; see Table III.

Table V. Electronic Spectra of the Carbon-Substituted Bis(π-1,2-dicarbollyl)nickel(IV) and -palladium(IV) Derivatives in Cyclohexane

Compound	λ_{max}, mμ (ϵ)	Compound	λ_{max}, mμ (ϵ)
$(HMe)_2Ni^{IV}$	302 (15,000)	$(Me_2)_2Ni^{IV}$-*B*	308 (24,000)
	457 (2300)		440(sh) (2160)
$(HPh)_2Ni^{IV}$	224 (19,400)	$(Me_2)_2Ni^{IV}$-*C*	318 (26,600)
	289 (21,500)		410(sh) (2400)
	370 (11,200)	$(Me_2)_2Pd^{IV}$-*C*	248 (12,700)
	465(sh) (4900)		305 (49,500)
			388 (2400)

data were also consistent with these formulations and are presented in Table VI. The ^{11}B nmr spectra were not as well resolved as that obtained with the unsubstituted nickel(IV) complex, and provided no additional structural information.

The structures associated with the $[(HR)_2Ni^{n+}]^{n-4}$ ($R = CH_3$, C_6H_5) derivatives are very likely the same as those found in the unsubstituted system; *i.e.*, the nickel(II) derivatives would possess slipped-sandwich configurations (as in Figure 2), while the nickel(III) and -(IV) species would have nonslipped sandwich structures (as in Figures 3 and 6, respectively). One point of interest regarding these substituted systems is the possibility of isomers arising from the enantiomeric C-substituted dicarbollide ligands of the general type $(HR)^{2-}$, where *R* is an alkyl or aryl group[19] (Figure 1). Three isomers would be expected for a $(HR)_2Ni$ derivative, a *meso* isomer and *d* and *l* enantiomorphs. Evidence for such isomers in $(HR)_2Ni$ systems was found in the ^{19}F nmr spectra of the *m*- and *p*-fluorophenyl-substituted nickel(IV) derivatives (*R* = *m*- or *p*-FC_6H_4),[16] where two fluorine resonances were observed for each compound, corresponding to the chemically nonequivalent *meso* and *dl* racemates. The relative amounts of each isomer were not ascertained, nor were nmr assignments made.

Electrochemically, the $(HMe)_2Ni$ and the $(HPh)_2Ni$ systems closely resembled the unsubstituted $(H_2)_2Ni$ system.[3] All three systems exhibited two reversible one-electron redox couples observed by cyclic voltammetry in acetonitrile. These data are presented in Table VII.

Reactions. A commonly observed reaction of bis(dicarbollyl)nickel(IV) complexes was their apparent reduction to the corresponding nickel(III) anions upon treatment with "hard" Lewis bases such as hydroxide ion, amines, etc.[20] A closer investigation of these reactions, however, indicated that partial degradation of the compounds occurred to give fragments which, in turn, reduced the bulk of the nickel(IV) species to the nickel(III) ions. In a reaction of $(H_2)_2Ni^{IV}$ with hydroxide ion in tetrahydrofuran–water at room temperature, 89% of the nickel was recovered as $Rb[(H_2)Ni^{III}]$, and 8.6% of the nickel as nickel hydroxide. Hydrogen gas was also evolved. With $(H_2)_2Pd^{IV}$, a similar degradation occurred and reduction to palladium metal

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(19) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, 90, 862 (1968).

(20) Similar base degradation–reduction reactions of this nature were also noted in the bis[π-(3)-1,2-dicarbollyl]iron and -copper systems; see also ref 25 regarding similar reactions of the bis(thiaborane)iron(III) species.

Table VI. Proton Nmr Data of the Carbon-Substituted Bis(π-1,2-dicarbollyl)palladium(II) and -(IV) and -nickel(IV) Derivatives[a]

Compound	Solvent	Resonance (relative area), ppm	Assignment
$(HMe)_2\mathrm{Ni^{IV}}$	Benzene	Broad singlet (1), −3.04 Sharp singlet (3), −1.65	Carborane C–H Methyl protons
$(HPh)_2\mathrm{Ni^{IV}}$	*sym*-Tetrachloroethane[b]	Broad singlet, −3.49 Multiplet centered, −7.35	Carborane C–H Phenyl protons
$(Me_2)_2\mathrm{Ni^{IV}}$-*B*	Benzene[c]	Two close singlets (2), −2.01 −1.94 Sharp singlet (1), −1.59 Sharp singlet (1), −1.28	Methyl protons, four types
$(Me_2)_2\mathrm{Ni^{IV}}$-*C*	Benzene	Sharp singlet (1), −1.93 Sharp singlet (1), −1.38	Methyl protons, two types
$(Me_2)_2\mathrm{Pd^{IV}}$-*C*	Benzene	Sharp singlet (1), −1.90 Sharp singlet (1), −1.40	Methyl protons, two types
$[(CH_3)_4N]_2[(Me_2)_2\mathrm{Pd^{II}}\text{-}A]\cdot(CH_3)_2CO$	d_6-DMSO	Sharp singlet (4), −3.12 Sharp singlet (1), −2.10 Sharp singlet (2), −1.96	Cation methyl protons Acetone of crystallization Carborane methyl protons, one type

[a] Resonances reported in ppm relative to internal tetramethylsilane (0.00 ppm). [b] Solvent side bands interfered with integration. [c] A broad resonance of relative area 2 at room temperature resolved into the two close singlets at higher temperatures; this spectrum was recorded at 67°.

Table VII. Electrochemical Data of the Bis(π-1,2-dicarbollyl)nickel and -palladium Derivatives[a]

Dicarbollide ligand	Compound	E_p, V	
		$\mathrm{M^{IV}}$–$\mathrm{M^{III}}$ couple	$\mathrm{M^{III}}$–$\mathrm{M^{II}}$ couple
$[H_2]^{2-}$	$(CH_3)_4N[(H_2)_2\mathrm{Ni^{III}}]$	+0.18	−0.66
	$(H_2)_2\mathrm{Ni^{IV}}$	+0.18	−0.66
	$(H_2)_2\mathrm{Ni^{IV}}$-*B*	0.00	−0.95
	$(H_2)_2\mathrm{Ni^{IV}}$-*C*	−0.19	−1.22
	$[(C_2H_5)_4N]_2[(H_2)_2\mathrm{Pd^{II}}]$	−0.14	−0.56
	$(H_2)_2\mathrm{Pd^{IV}}$	−0.14	−0.56
$[HMe]^{2-}$	$\mathrm{Cs}[(HMe)_2\mathrm{Ni^{III}}]$	+0.22	−0.64
	$(HMe)_2\mathrm{Ni^{IV}}$	+0.22	−0.64
$[HPh]^{2-}$	$(CH_3)_4N[(HPh)_2\mathrm{Ni^{III}}]$	+0.35	−0.52
	$(HPh)_2\mathrm{Ni^{IV}}$	+0.35	−0.52
$[Me_2]^{2-}$	$(CH_3)_4N[(Me_2)_2\mathrm{Ni^{III}}\text{-}A]$	(~+0.5)[b]	−0.55
	$(CH_3)_4N[(Me_2)_2\mathrm{Ni^{III}}\text{-}B]$	+0.15	−1.02
	$(Me_2)_2\mathrm{Ni^{IV}}$-*B*	+0.15	−1.02
	$(CH_3)_4N[(Me_2)_2\mathrm{Ni^{III}}\text{-}C]$	−0.10	−1.19
	$(Me)_2\mathrm{Ni^{IV}}$-*C*	−0.10	−1.19
	$[(CH_3)_4N]_2[(Me_2)_2\mathrm{Pd^{II}}\text{-}A]$	(~0.0)[b]	−0.44
	$(Me_2)_2\mathrm{Pd^{IV}}$-*C*	−0.47	−0.71
$[TM]^{2-}$	$(C_2H_5)_4N[(TM)_2\mathrm{Ni}\text{-}^{III}A]$	(~+0.5)[b]	−0.60
	$(TM)_2\mathrm{Ni^{IV}}$-*B*	+0.25	−0.85
	$(TM)_2\mathrm{Ni^{IV}}$-*C*	−0.02	−1.35

[a] Determined by cyclic voltammetry in acetonitrile solution at 23°, 0.1 *N* $(C_2H_5)_4NClO_4$ supporting electrolyte; sweep rate 0.25 V/sec; reduction peak potentials reported for reversible couples; all potentials *vs.* sce. [b] Irreversible.

was observed. For this reason the palladium(IV) complex should be stored in a dry atmosphere.

Slower degradation–reduction reactions of $(H_2)_2\mathrm{Ni^{IV}}$ were observed in alcohols and in most polar solvents which may contain water, such as acetone, tetrahydrofuran, acetonitrile, etc. However, in ethanol–water mixtures acidified with hydrochloric acid, the complex was apparently stable indefinitely and could be conveniently crystallized from hot solution. The nickel(IV) complex reacted very rapidly with amines, such as trimethylamine, to give predominantly the trimethylammonium salt of $[(H_2)_2\mathrm{Ni^{III}}]^-$ with no hydrogen evolution.

One interesting feature of the $(H_2)_2\mathrm{Ni^{IV}}$ molecule was the acidity of its C–H protons, apparently arising from the relative electron deficiency of the carbon atoms. A base-degradation reaction carried out with the nickel(IV) complex in D_2O afforded the completely C-deuterated nickel(III) ion, $[(D_2)_2\mathrm{Ni^{III}}]^-$.[21] Partially C-deuterated nickel(IV) could be obtained by quenching the exchange–degradation reaction after a short period of time; the fully C-deuterated nickel(IV), however, was obtained by oxidation of the $[(D_2)_2\mathrm{Ni^{III}}]^-$ ion. (Base-catalyzed deuterium exchange on the undeuterated nickel(III) anion did not occur under the same conditions.) The infrared spectrum of $(D_2)_2\mathrm{Ni^{IV}}$ contained no C–H stretch, but a C–D stretching band at 2285 cm^{-1}. High resolution mass spectroscopy confirmed the formulation $\mathrm{Ni}(B_9H_9C_2D_2)_2$ (see Table III). Under strongly acid conditions (10% D_2SO_4 in DOAc), very slow deuterium exchange was found to occur exclusively at B–H positions.

Attempts were made to employ the $(H_2)_2\mathrm{Ni^{IV}}$ complex as an oxidizing agent, and with some substrates, such as ethanol, H_2O_2 and $(C_6H_5)_3P$, oxidation reactions did occur. However, basic conditions were required for these reactions and degradation processes could not be ruled out; hence, the mechanism of the observed oxidations could not be ascertained. In acidic media, where degradation is not likely to occur, the nickel(IV) complex is a potentially useful oxidizing agent since the nickel(III) species produced could be readily air oxidized back to $(H_2)_2\mathrm{Ni^{IV}}$, and one could thus, in principle, obtain a catalytic system using atmospheric oxygen as the electron acceptor.

The addition of certain "soft" Lewis bases such as halide ions or sulfur-containing donors to orange solutions of $(H_2)_2\mathrm{Ni^{IV}}$ in aprotic solvents turned the solutions deep red. From these mixtures crystalline 1:1 addition compounds of $(H_2)_2\mathrm{Ni^{IV}}$ could be obtained with chloride ion, bromide ion, and thiocyanate ion (isolated as the tetraphenylarsonium or triphenylmethylphosphonium salts).[22] The thiocyanate ion probably donates electrons through the sulfur atom (*vide infra*). Although iodide ion reduced the nickel(IV) complex to produce the $[(H_2)_2\mathrm{Ni^{III}}]^-$ and the I_3^- ions, the yellow palladium(IV) derivative formed a deep red 1:1 adduct. Neutral sulfur donors such as dicyclo-

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(21) Likewise, $[(DMe)_2\mathrm{Ni^{III}}]^-$ and $[(DPh)_2\mathrm{Ni^{III}}]^-$ derivatives could be obtained from the corresponding nickel(IV) species.

(22) Interactions of the $(HMe)_2\mathrm{Ni^{IV}}$ and $(HPh)_2\mathrm{Ni^{IV}}$ complexes with soft Lewis bases were noted in solution; however clean crystalline adducts were not obtained, possibly because of the lack of symmetry and the presence of the stereoisomers associated with these systems.

Table VIII. 1:1 Charge Transfer Adducts of $(H_2)_2M^{IV}$ Derivatives with Certain Soft Lewis Bases

"σ"-Type Adducts			"π"-Type adducts		
Base	Acid[a]	Color	Base	Acid[a]	Color
Cl^-	1	Orange	Benzene	1	Orange
Br^-	1	Red-orange	Naphthalene	1	Orange-red
I^-	1	(Reduces 1)	Phenanthrene	1	Deep red
I^-	2	Red	Pyrene	1	Deep green
SCN^-	1	Deep red	Pyrene	2	Brown
$(C_2H_5)_2S$	1	Red	N,N-Dimethylaniline	1	Deep green
$[(C_6H_{11})NH]_2C{=}S$	1	Deep red			

[a] 1: $(H_2)_2Ni^{IV}$ (orange); 2: $(H_2)_2Pd^{IV}$ (yellow).

hexylthiourea and diethyl sulfide also produced deep red, crystalline addition compounds with $(H_2)_2Ni^{IV}$. The latter adduct lost diethyl sulfide at room temperature, but was stable indefinitely below 0°. Tri-*n*-butylphosphine, triphenylphosphine, triphenylarsine, and triphenylstibine produced no observable effect on $(H_2)_2Ni^{IV}$ solutions and no complexes were isolated.

Crystalline adducts were also obtained with $(H_2)_2Ni^{IV}$ and certain large aromatic hydrocarbons, such as naphthalene, phenanthrene, and pyrene. The palladium(IV) complex formed an addition compound with pyrene. Benzene appeared to interact to some extent with $(H_2)_2Ni^{IV}$, as its dipole moment at 25° in that solvent was 6.45 D, somewhat higher than the 6.16 D found in cyclohexane. The nickel(IV) complex readily crystallized from benzene upon cooling with a solvent molecule of crystallization, which was rapidly lost at room temperature. A much more stable adduct was formed with N,N-dimethylaniline and $(H_2)_2Ni^{IV}$.

The $(H_2)_2M^{IV}$ molecules, then, appear to be rather strong and versatile Lewis acids, capable of forming addition compounds with a variety of soft Lewis bases. The isolated adducts and their colors are listed in Table VIII. The adducts were readily dissociated by heating (in the cases with neutral donors), by dissolution, or by treatment with a protonic solvent such as ethanol. The addition compounds in solution and in the solid state were diamagnetic, indicating incomplete charge transfer (CT) from the donor to the $(H_2)_2M^{IV}$ complex; *i.e.*, no net oxidation or reduction occurred. In order to observe charge-transfer bands in the electronic spectra of the adducts, spectral measurements in the visible and near-infrared regions were conducted on Nujol mulls of the crystalline solids. Figure 7 presents the spectra of representative $(H_2)_2Ni^{IV}$ adducts. The larger, more polarizable donors appeared to form the more stable adducts as indicated by the greater broadening of the $(H_2)_2Ni^{IV}$ electronic absorption at 425 mμ toward lower energies.

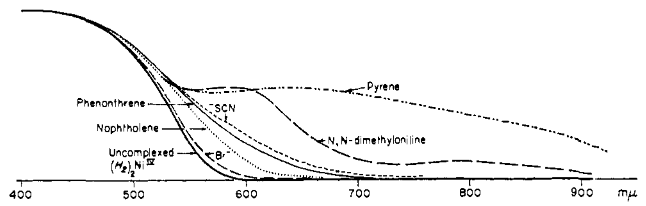

Figure 7. Electronic spectra of representative bis[π-(3)-1,2-dicarbollyl]nickel(IV) adducts (Nujol mulls); all spectra normalized to the same extinction coefficient at 400 mμ.

Preliminary X-ray diffraction studies by Wing,[23] carried out with the pyrene adduct of the $(H_2)_2Ni^{IV}$ complex, indicated that the apparent acid–base interaction was long range with the donor being about 5 Å from the metal atom. This suggested that the donor–acceptor coupling in the M^{IV} adducts may be a dipole–induced dipole type of interaction, which appears reasonable considering the large dipole moment found for the nickel(IV) complex and the high polarizabilities of the donors. Based on Wing's preliminary findings,[23] the structure of the pyrene adduct is presented in Figure 8.[24] The proposed structure of the thiocyanate ion adduct is represented in Figure 9; the Lewis acid and base are shown to align along their dipole moment vectors.

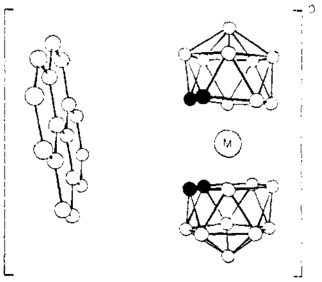

Figure 8. The structure of the pyrene-$(H_2)Ni^{IV}$ adduct in schematic form; based on preliminary X-ray diffraction studies (ref 23).

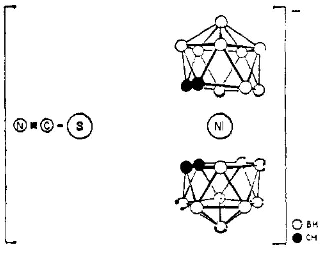

Figure 9. Proposed structure of the thiocyanate ion-$(H_2)_2Ni^{IV}$ adduct in schematic form.

Platinum-[(3)-1,2-dicarbollide] Systems. Notably missing in this series of bis[π-(3)-1,2-dicarbollyl] complexes of the nickel group elements is the congener platinum member. Several attempts to prepare this

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(23) R. M. Wing, private communication.

(24) The "face-on" coupling of the pyrene to the nickel(IV) molecule indicated that more complex interactions may take place with large aromatic donors involving quadrupoles, etc., since the induced dipole of the pyrene molecule would be expected to be in the molecular plane.

Table IX. Reaction Sequence and Electrochemistry of the Bis(π-1,2-dimethyl-1,2-dicarbollyl)nickel and -palladium Systems

$$\mathrm{Ni(acac)_2} + 2[(3)\text{-}1,2\text{-}\mathrm{B_9H_9C_2(CH_3)_2}]^{2-} \xrightarrow{\text{ether}}$$

$$\begin{tikzcd}
\text{Series A:} & {[(Me_2)_2\mathrm{Ni}^{\mathrm{II}}\text{-}A]^{2-}} \arrow[r, rightleftharpoons, "-0.55\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}A]^{-}} \arrow[d, "200^\circ"] \arrow[dr, "{[O]}"] & \\
\text{Series B:} & {[(Me_2)_2\mathrm{Ni}^{\mathrm{II}}\text{-}B]^{2-}} \arrow[r, rightleftharpoons, "-1.02\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}B]^{-}} \arrow[r, rightleftharpoons, "+0.15\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}B]^{0}} \arrow[d, "100^\circ"] \\
\text{Series C:} & {[(Me_2)_2\mathrm{Ni}^{\mathrm{II}}\text{-}C]^{2-}} \arrow[r, rightleftharpoons, "-1.19\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}C]^{-}} \arrow[r, rightleftharpoons, "-0.10\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}C]^{0}}
\end{tikzcd}$$

Series B: Red-orange
Four types of methyl protons
μ = 7.52 D in C_6H_{12}

Series C: Yellow
Two types of methyl protons
μ = 5.41 D in C_6H_{12}

$$\mathrm{Pd(acac)_2} + 2[(3)\text{-}1,2\text{-}\mathrm{B_9H_9C_2(CH_3)_2}]^{2-} \xrightarrow{\text{ether-benzene}}$$

$$\begin{tikzcd}
\text{Series A:} & {[(Me_2)_2\mathrm{Pd}^{\mathrm{II}}\text{-}A]^{2-}} \arrow[r, rightleftharpoons, "-0.44\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Pd}^{\mathrm{III}}\text{-}A]^{-}} \arrow[dr, "{[O]}"] & \\
\text{Series C:} & {[(Me_2)_2\mathrm{Pd}^{\mathrm{II}}\text{-}C]^{2-}} \arrow[r, rightleftharpoons, "-0.71\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Pd}^{\mathrm{III}}\text{-}C]^{-}} \arrow[r, rightleftharpoons, "-0.47\ \mathrm{V}"'] & {[(Me_2)_2\mathrm{Pd}^{\mathrm{IV}}\text{-}C]^{0}}
\end{tikzcd}$$

Series C: Yellow
Two types of methyl protons

system under a variety of conditions and with a variety of platinum-containing starting materials proved futile. However, one type of platinum derivative did evolve from these efforts. The reaction between 1,5-cyclooctadienedichloroplatinum(II) and the (3)-1,2-dicarbollide ion in tetrahydrofuran afforded (1,5-C_8H_{12})Pt[π-(3)-1,2-$B_9C_2H_{11}$], which could be isolated by quenching the reaction at low temperatures. Upon warming this complex with excess dicarbollide ion, the reaction mixture turned black, the inevitable result of most of the attempts to prepare bis[π-(3)-1,2-dicarbollyl]platinum derivatives.

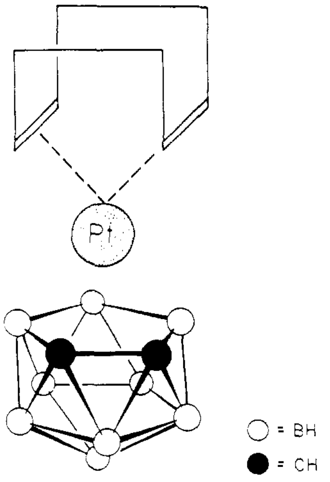

Figure 10. Proposed structure of (1,5-cyclooctadiene)-[π-(3)-1,2-dicarbollyl]platinum(II) in schematic form.

The electrically neutral (1,5-cyclooctadiene)Pt[π-(3)-1,2-$B_9C_2H_{11}$] was a stable, yellow crystalline solid which was sparingly soluble in most organic solvents. The analytical and mass spectral data confirmed the assigned formulation (see the Experimental Section), and a tentative structure of the molecule is presented in Figure 10.

The ^1H nmr spectrum of the (1,5-C_8H_{12})Pt(H_2) complex in deuteriodimethyl sulfoxide contained three principal resonances: a broad resonance at −2.71 ppm (relative to internal tetramethylsilane = 0.00 ppm) of relative area eight due to the aliphatic cyclooctadiene protons, an apparent triplet resonance at −4.37 ppm of relative area two from the carborane C–H protons, and another apparent triplet resonance at −5.47 ppm of relative area four due to the olefinic cyclooctadiene protons. The apparent triplet resonances arise from the 33.8% natural abundance ^{195}Pt (spin $^1/_2$) which couples with the carbon protons to produce doublets. The coupling constant $J(^{195}\mathrm{Pt}\text{-}^1\mathrm{H})$ for the olefinic protons was 65.8 cps and for the carborane C–H protons was 27.2 cps. No ^{195}Pt–^{11}B coupling was observed in the ^{11}B nmr spectrum of the complex.

The isolation of this platinum complex suggests that others of the general type L_2Pt[π-(3)-1,2-$B_9C_2H_{11}$], where L = a two-electron donor ligand, could be synthesized. In these complexes the platinum atom formally attains a closed shell electronic configuration. Hertler, Klanberg, and Muetterties[25] have reported an analogous type of complex, ($B_{10}H_{10}S$)Pt[P(C_2H_5)$_3$]$_2$, ultilizing the thiaborane ligand, $B_{10}H_{10}S^{2-}$.

C,C′-Dimethyl Bis[π-(3)-1,2-dicarbollyl]nickel and -palladium Systems. Icosahedral Rearrangements

Syntheses and Characterization. The reaction of the 1,2-dimethyl-1,2-dicarbollide ion with nickel acetylacetonate produced a yellow nickel(II) derivative which was readily air oxidized to a deep red [$(Me_2)_2\mathrm{Ni}^{\mathrm{III}}$]$^-$ ion. Subsequent oxidation of this species afforded a single orange, neutral nickel(IV) derivative, provided the work-up temperature was kept lower than 60°; otherwise, a mixture of products was obtained. It was then discovered that the orange compound converted completely at 100° to an uncharged yellow species which was also a nickel(IV) derivative. The orange and yellow compounds were reduced to give two new nickel(III) species, the first of which was also obtained

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[25] W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 6, 1696 (1967).

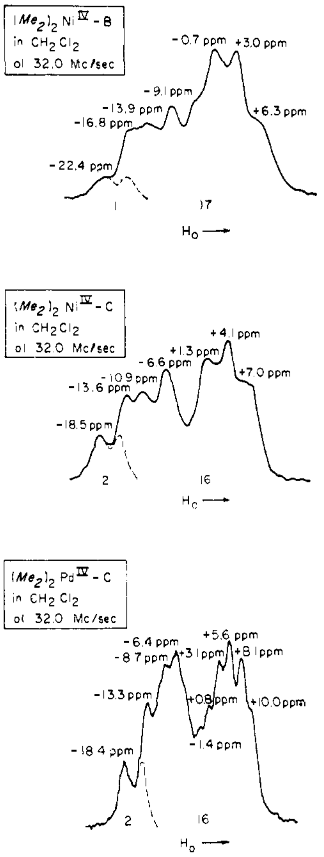

Figure 11. The 32.0-Mc/sec ^{11}B nmr spectra of the bis(π-1,2-dimethyl-1,2-dicarbollyl)nickel(IV) and -palladium(IV) derivatives; reference BF_3 etherate = 0.00 ppm.

by heating the original red nickel(III) complex at 200°. The complete reaction sequence is shown in Table IX. The initially formed nickel(II) and -(III) compounds are designated with the letter *A*, corresponding to series A; likewise, the orange nickel(IV) and its reduction products belong to series B, and the yellow nickel(IV) and its reduced species to series C.

The characterization data associated with the $[(Me_2)_2Ni^{III}]^-$ and $(Me_2)_2Ni^{IV}$ derivatives[26] (Tables I–VII) confirmed the isomeric nature of the three series of complexes. The tetramethylammonium salts of red $[(Me_2)_2Ni^{III}\text{-}A]^-$, brown $[(Me_2)_2Ni^{III}\text{-}B]^-$, and golden $[(Me_2)_2Ni^{III}\text{-}C]^-$ were found to be paramagnetic (d^7), with magnetic moments of 1.79, 1.80, and 1.86 BM, respectively. The corresponding ^{11}B nmr spectra were complex and afforded no structural information. The two diamagnetic d^6 $(Me_2)_2Ni^{IV}$ complexes, however, were more informative with regard to structure. The ^1H nmr data are presented in Table VI and the ^{11}B spectra can be seen in Figure 11. The low-field doublet resonance of relative area 1:18 in the ^{11}B nmr spectrum of the series B isomer indicated a less symmetrical structure than that of the series C isomer, where the corresponding low-field doublet resonance had a relative area 2:18. The $(Me_2)_2Ni^{IV}\text{-}B$ isomer exhibited a dipole moment in cyclohexane of 7.52 ± 0.05 D, while the $(Me_2)_2Ni^{IV}\text{-}C$ complex had a smaller moment of 5.41 ± 0.06 D. The infrared spectra of these two compounds are shown in Figure 12.

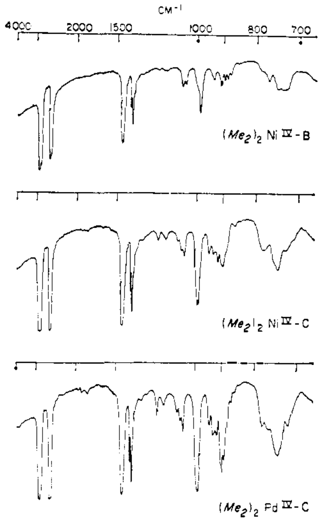

Figure 12. Infrared spectra (Nujol mulls) of the bis(π-1,2-dimethyl-1,2-dicarbollyl)nickel(IV) and -palladium(IV) derivatives.

Extension of the C,C′-dimethyl ligand system to palladium produced similar results, as seen in the scheme in Table IX. Room temperature oxidation of the initially-formed unstable red-brown $[(Me_2)_2Pd^{II}\text{-}A]^{2-}$ complex to a palladium(IV) derivative led directly to the yellow series C isomer, $(Me_2)_2Pd^{IV}\text{-}C$,[27] apparently by-passing the series B derivative. The characterization data associated with these compounds are presented in Tables I–VII. The ^{11}B nmr and the infrared spectra of the palladium(IV) derivative are seen in Figures 11 and 12, respectively, for comparison with its series C nickel(IV) analog.

The electrochemistry of the C,C′-dimethyl-substituted nickel and palladium systems was examined by cyclic voltammetry in acetonitrile solution and the results are presented in Table VII. Chemically irreversible redox couples were associated only with the series A $[(Me_2)_2M^{III}\text{-}A]^-$ ion oxidations to the unobserved series A M^{IV} species.

All of the dimethyl-substituted M^{IV} derivatives underwent base degradation–reduction reactions with hard Lewis bases. Interactions with certain soft bases were also observed in solution; however, no crystalline adducts were obtained.

The Series A Isomers. A reasonable assumption regarding the structures associated with the initially formed series A isomers (M^{II} and M^{III} derivatives) was that they possessed the analogous configurations found for the corresponding unsubstituted $[(H_2)_2Ni^{II}]^{2-}$ and $[(H_2)_2Ni^{III}]^-$ complexes. The ^{11}B nmr spectrum of the diamagnetic palladium(II) complex, $[(Me_2)_2Pd^{II}\text{-}A]^{2-}$, contained a low-field doublet resonance characteristic of a slipped-sandwich configuration.[3] This structure is represented schematically in Figure 13 and is supported by the proton nmr data (Table VI). The presumably paramagnetic $[(Me_2)_2Ni^{II}\text{-}A]^{2-}$ ion was

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[26] The strongly reducing nickel(II) isomers were not isolated, inasmuch as their probable paramagnetism would limit structural information that could be obtained through nmr. They were readily generated in diglyme solution with sodium amalgam and the corresponding nickel(III) or -(IV) derivatives. The presumed $[(Me_2)_2Ni^{II}\text{-}A]^{2-}$ ion was yellow, $[(Me_2)_2Ni^{II}\text{-}B]^{2-}$ was red-brown, and $[(Me_2)_2Ni^{II}\text{-}C]^{2-}$ was brownish yellow.

[27] The series C palladium(IV) derivative reduced smoothly in diglyme with sodium amalgam to form a brilliant red species, presumably palladium(III) and palladium(II) derivatives. These reduced species were not further characterized.

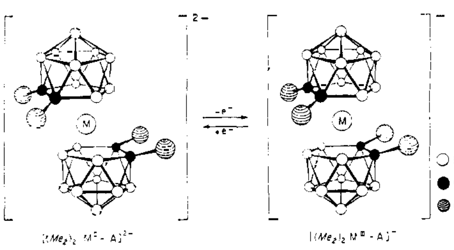


Figure 13. The proposed structures of the series A bis(π-1,2-dimethyl-1,2-dicarbollyl)nickel and -palladium derivatives in schematic form.

also expected to have this a slipped-sandwich configuration.

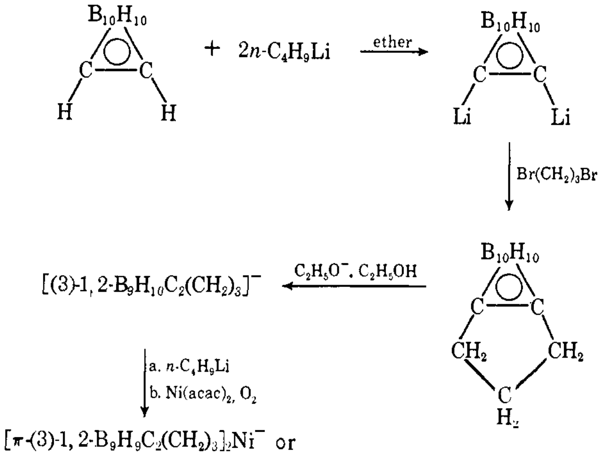
X-Ray diffraction studies[28] carried out on the paramagnetic series A nickel(III) salt, Cs[$(Me_2)_2Ni^{III}$-*A*]·H_2O, showed it to be isomorphous with its cobalt(III) analog, Cs[$(Me_2)_2Co^{III}$]·H_2O, which has a nonslipped sandwich structure[2] (*vide supra*). The ^1H nmr spectrum of the diamagnetic d^6 cobalt derivative exhibited one sharp methyl group proton resonance,[2] thus supporting the symmetrical *trans* ligand configuration shown in Figure 13 for the isostructural [$(Me_2)_2Ni^{III}$-*A*]⁻ ion.

One significant difference was noted in comparing the [$(Me_2)_2Ni^{III}$-*A*]⁻ complex with the cobalt(III) analog. Whereas the former cleanly rearranged in the solid state or in solution to a single isomer (namely, [$(Me_2)_2Ni^{III}$-*B*]⁻) at 200°, the cobalt analog was inert up to approximately 300°, at which temperature a slow series of rearrangements began, leading to a complex mixture of isomers (detected by proton nmr). This further illustrated the unique characteristics of the nickel system.

1,2 *vs.* 1,7 Rearrangements and Stereochemical Studies. Conversions of the series A isomers to the series B derivatives were irreversible, as were the series B to series C rearrangements. The possibility that the different isomers might consist of different rotameric conformations of the two dicarbollide ligands was discounted by high temperature proton nmr studies; the ^1H nmr spectra of both $(Me_2)_2Ni^{IV}$-*B* (with four sharp methyl group proton resonances) and $(Me_2)_2Ni^{IV}$-*C* (with two sharp methyl group proton resonances) in 1,1,2,2-tetrachloroethane remained unchanged from room temperature up to 140°.[29] The sharpness of the methyl group proton resonances also precluded any C-methyl group migrations to boron atoms, as B–CH_3 proton resonances are generally very broad. The only other likely type of rearrangement process involved the migration of the ligand carbon atoms to other positions in the icosahedral framework. Two possible modes of rearrangement were considered to be chemically feasible: one in which the ligand carbon atoms remained adjacent in the icosahedral surface, a "1,2 rearrangement," and one in which the carbon atoms became separated by a boron atom, a "1,7 rearrangement."[30] Polyhedral rearrangements of this type in icosahedral carboranes have been known for some time[31] and usually occur in the 400–600° temperature range.

To determine whether the isomerization reactions in the C,C′-dimethyl-substituted $(Me_2)_2M$ (M = Ni, Pd) systems (Table IX) involved 1,2 and/or 1,7 rearrangements, an analogous nickel system was prepared in which 1,7 rearrangements were prevented from occurring. From Scheme I, the details of which will be reported later,[32] a bis(1,2-dicarbollyl)nickel system was synthesized employing a 1,2-dicarbollide ligand with a trimethylene linkage bridging the ligand carbon atoms. In such a species, the ligand carbon atoms are forced to remain adjacent in an *ortho* or 1,2 position, thus prohibiting any 1,7 rearrangements.

Scheme I



[$(TM)_2Ni^{III}$-*A*]⁻ (*TM* = μ-1,2-trimethylene-1,2-dicarbollide)

The deep red-brown series A [$(TM)_2Ni^{III}$-*A*]⁻ complex underwent reactions similar to those shown in Table IX; *i.e.*, it was oxidized to an orange $(TM)_2Ni^{IV}$-*B* derivative, which rearranged in boiling cyclooctane (149°) to a yellow $(TM)_2Ni^{IV}$-*C* species. The analytical and mass spectral data associated with these nickel(IV) derivatives confirmed the assigned formulations.[32] The electrochemical data associated with these complexes was completely analogous with that of the $(Me_2)_2Ni$ system and are presented in Table VII. This behavior provided nearly conclusive evidence that the two thermal isomerization reactions which take place in these disubstituted bis(1,2-dicarbollyl)nickel rearrangements involve only 1,2 rearrangements in which the ligand carbon atoms remain adjacent.

Examination of molecular models of possible configurations of the rearranged $(Me_2)_2Ni$ isomers revealed that *d* and *l* enantiomers would be expected to exist in some instances. If the presence of these enantiomers could be demonstrated, certain structures could be eliminated from consideration. An optical resolution study was therefore undertaken, and one enantiomer of the [$(Me_2)_2Ni^{III}$-*B*]⁻ ion was, in fact, obtained in an apparently optically pure condition by resolution of a *dl* mixture with the *d*-N,N,N-trimethyl-α-phenylethylammonium cation.[33] To completely separate the diastereomeric quaternary ammonium salts, 34 frac-

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(28) D. St. Clair, private communication.

(29) The series B isomer began to rearrange to the series C derivative at the higher temperatures, but the individual proton resonances of each isomer remained sharply defined.

(30) The 1,2 rearrangement involves the conversion of a 1,2 isomer to another 1,2 isomer (1,2 → 1′,2′), while the 1,7 rearrangement converts a 1,2 isomer to a 1,7 derivative (1,2 → 1,7).

(31) (a) H. V. Hart and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **91**, 771 (1969), and references therein; (b) W. N. Lipscomb, *Science*, **153**, 373 (1966); (c) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, pp 69–71.

(32) M. F. Hawthorne and T. Paxson, to be submitted.

(33) D. N. Kursanov and S. V. Vitt, *Dokl. Akad. Nauk SSSR*, **113**, 607 (1957).

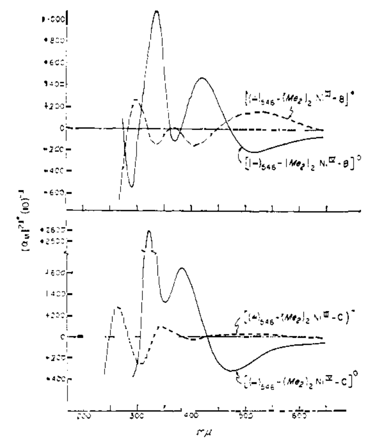

Figure 14. Optical rotatory dispersion curves of the optically active $(Me_2)_2$Ni complexes; salts in ethanol solution, neutral complexes in cyclohexane.

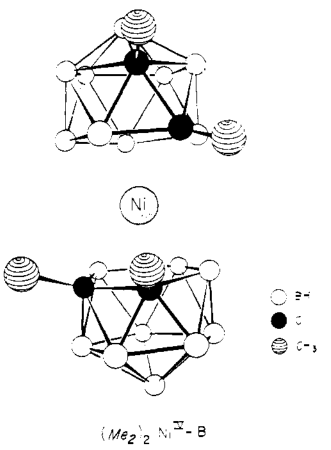

Figure 15. Structure of the series B bis(π-1,2-dimethyl-1,2-dicarbollyl)nickel derivative in schematic form; one *dl* enantiomer shown.

tional recrystallizations from ethanol–water mixtures were required.

The resolved $[(+)_{546}\text{-}(Me_2)_2\text{Ni}^{\text{III}}\text{-}B]^-$ ion was subjected to the reaction sequence shown in Table IX. Oxidation of the optically pure ion (tetraethylammonium salt) afforded neutral crystalline $[(-)_{546}\text{-}(Me_2)_2\text{Ni}^{\text{IV}}\text{-}B]^0$, which rearranged in boiling cyclooctane to $[(-)_{546}\text{-}(Me_2)_2\text{Ni}^{\text{IV}}\text{-}C]^0$, which was subsequently reduced to the corresponding $[(+)_{546}\text{-}(Me_2)_2\text{Ni}^{\text{III}}\text{-}C]^-$ ion. The specific rotations of these four derivatives are presented in Table X. The optical rotatory dispersion curves are presented in Figure 14.

Table X. Optical Resolution Data of Optically Active $(Me_2)_2\text{Ni}_2$ Complexes[a]

Optically active complex	$[\alpha]^{23}_{546}$, deg	$[\alpha]^{23}_{578}$, deg
$(C_2H_5)_4N[(Me_2)_2\text{Ni}^{\text{III}}\text{-}B]$	+284	+196
$\downarrow$ oxidize		
$(Me_2)_2\text{Ni}^{\text{IV}}\text{-}B$	−448	−333
$\downarrow \Delta$		
$(Me_2)_2\text{Ni}^{\text{IV}}\text{-}C$	−262	−183
$\downarrow$ reduce		
$(C_2H_5)_4N[(Me_2)_2\text{Ni}^{\text{III}}\text{-}C]$	+31	0

[a] Rotations of salts measured in ethanol, neutral complexes in cyclohexane; due to the intense absorption of these species in solution, very dilute concentrations ($\sim 10^{-3}$ *M*) were employed, leading to an error in the rotations of about ±10°.

The Series B Isomers. Given the above information, reasonable conjectures could be made regarding the structures of the rearranged series B isomers. The physical properties associated with the $(Me_2)_2\text{Ni}^{\text{IV}}\text{-}B$ complex, *i.e.*, existence of enantiomeric forms, the observation of four types of C-methyl proton nmr resonances, and a high dipole moment, coupled with the assumptions that a 1,2 rearrangement[30] has occurred and that methyl groups on opposing ligands cannot pass through an eclipsed configuration, led to only one reasonable structure, which is shown in Figure 15. Subsequent single crystal X-ray diffraction studies by Gold and Churchill[34] using *dl*-$(Me_2)_2\text{Ni}^{\text{IV}}\text{-}B$ have recently confirmed this unique structure in which a facial carbon atom in one of the dicarbollide ligands has migrated away from the adjacent metal atom while remaining a nearest neighbor (1,2) of the second carbon atom. The $(Me_2)_2\text{Ni}^{\text{IV}}\text{-}B$ molecule retained a cisoid arrangement with the carbon pairs in the staggered ligands as near to each other as possible without having methyl groups in a locked configuration. There was no apparent distortion of the ligands at the carbon atoms as found in the unsubstituted complex.[9] The facial planes of the cages were tilted about 15° with respect to one another such that the interligand C–C distances were significantly larger than the interligand B–B distances. This may be due to methyl hydrogen van der Waals repulsions between ligands.

The formal designation for the $(Me_2)_2\text{Ni}^{\text{IV}}\text{-}B$ complex is (*dl*)-$\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9H_9C_2(CH_3)_2]\text{Ni}[\pi\text{-}(4)\text{-}1,2\text{-}B_9H_9C_2(CH_3)_2]\}$, indicating that the nickel atom lies in the 3 position of an icosahedron formed by one of the 1,2-dicarbollide ligands and in the 4 position of the other (see Figure 1). The series B nickel(III) species would be expected to have a normal sandwich arrangement ("*trans*" with respect to ligand C atoms), while the corresponding nickel(II) species may reside in a slipped-sandwich configuration.

The Series C Isomers. The thermal conversion of $(Me_2)_2\text{Ni}^{\text{IV}}\text{-}B$ to $(Me_2)_2\text{Ni}^{\text{IV}}\text{-}C$ could involve either a further rearrangement of the same ligand or a similar rearrangement of the yet unchanged ligand. Here again, the physical properties associated with the series C isomer, *i.e.*, optical activity, two types of C-methyl group proton nmr resonances, lower dipole moment and higher symmetry than the series B isomer (*vide supra*), and the assumption that a 1,2 rearrangement has occurred, led to only one consistent possibility: the unchanged cage had undergone the same type of rearrangement as that ascribed to the series A to B isomerization. The rearrangement of this ligand, however, could proceed in two directions relative to the stereochemistry of the initially rearranged ligand, affording *meso* and *dl* products as depicted in Figure 16. As seen in the structures of these $(Me_2)_2\text{Ni}^{\text{IV}}\text{-}C$ isomers, the chemical environments of the methyl

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(34) M. R. Churchill, and K. Gold *J. Amer. Chem. Soc.*, **92**, 1180 (1970).

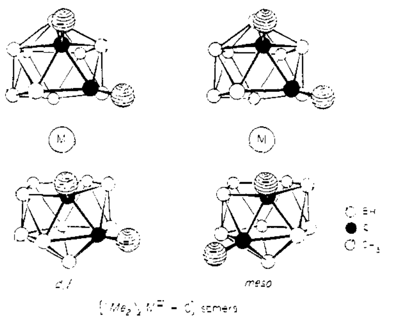

Figure 16. Proposed structures of the series C bis(π-1,2-dimethyl-1,2-dicarbollyl)nickel and -palladium derivatives in schematic form.

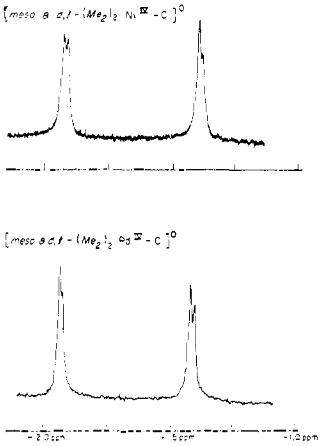

Figure 17. The 100-Mc/sec ^1H nmr spectra of the series C bis(π-1,2-dimethyl-1,2-dicarbollyl)nickel(IV) and -palladium(IV) derivatives in benzene solution; reference, internal tetramethylsilane = 0.00 ppm.

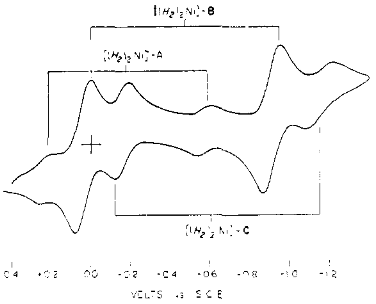

Figure 18. Cyclic voltammogram of a mixture of thermally rearranged unsubstituted bis(π-1,2-dicarbollyl)nickel(IV) isomers in acetonitrile solution.

groups would be slightly different in the *meso* and in the *dl* racemate. Although at 60 Mc/sec, the ^1H nmr spectrum of the $(Me_2)_2Ni^{IV}$-*C* complex showed only two sharp resonances corresponding to the methyl group protons adjacent and nonadjacent to the metal atom, the 100-Mc/sec ^1H nmr spectrum revealed additional splitting of these proton resonances as shown in Figure 17. This observation confirmed the presence of *meso* and *dl* isomers in the series C system. Consequently, the optically active series C complexes obtained from the thermal rearrangement of the resolved series B $(Me_2)_2Ni^{IV}$-*B* complex must have contained some *meso* isomer.

In the analogous C,C′-dimethyl-substituted palladium system, the room temperature oxidation of the series A system directly afforded a yellow series C isomer, $(Me_2)_2Pd^{IV}$-*C*, apparently by-passing series B. The infrared spectrum (Figure 12) and the ^{11}B and ^1H nmr spectra (Figure 11 and Table VI, respectively) of this palladium(IV) derivative were nearly identical with its series C nickel analog. The 100-Mc/sec ^1H nmr spectrum of this compound is presented in Figure 17, and the presence of *meso* and *dl* isomers (Figure 16) as found in the series C nickel complex was thus confirmed.

In the series C $(Me_2)_2M$ complexes (M = Ni, Pd), both dicarbollide ligands have undergone intramolecular rearrangements such that the metal atom now fills the vacant icosahedral 4 positions. Hence, the formal designations for these M^{IV} species are (*dl*)- and (*meso*)-$[\pi\text{-}(4)\text{-}1,2\text{-}B_9H_9C_2(CH_3)_2]_2M$. The series C M^{III} derivatives would be expected to reside in a *trans* sandwich configuration and the M^{II} complexes may possess a slipped-sandwich type of structure.

Base degradation reactions were conducted on the $(Me_2)_2Ni$-*C* complexes in the hope of obtaining the free rearranged ligand, $[(4)\text{-}1,2\text{-}B_9H_9C_2(CH_3)_2]^{2-}$, as its protonated monoanion. These complexes were extremely difficult to degrade cleanly and very strongly reducing conditions were required, such as excess sodium amalgam for 2 days in tetrahydrofuran, or a NaOH, NaCN, hydrazine mixture in ethylene glycol–water at 100° for 1 hr. Recovery of only 20% of uncomplexed ligand was obtained in any case, and this was identified as the initial starting material, the $[(3)\text{-}1,2\text{-}B_9H_{10}C_2(CH_3)_2]^-$ ion. This apparent reversion of the free $[(4)\text{-}1,2\text{-}B_9H_9C_2(CH_3)_2]^{2-}$ ligand, obtained by degradation of the $(Me_2)_2Ni$-*C* complexes, back to the original (3)-1,2 ion indicated that the latter ligand is more stable in the uncomplexed state.

Thermal Rearrangement of Unsubstituted $(H_2)_2Ni^{IV}$. There was no reason to expect that other bis(1,2-dicarbollyl)M^{IV} (M = Ni, Pd) complexes should not undergo thermal isomerization reactions analogous to those in the C,C′-dialkyl-substituted derivatives. However, the temperatures required for such rearrangements were expected to be higher in systems that did not have the steric requirements of the $(Me_2)_2M$ systems. Attempts to thermally rearrange the unsubstituted $(H_2)_2Ni^{IV}$ complex in the solid state at 270° or higher led to extensive decomposition. However, in the *vapor phase*, the orange compound rearranged at 360–400° to afford a bright yellow sublimate from which orange-yellow crystals were obtained. The cyclic voltammogram of this crystalline material is shown in Figure 18, and demonstrates the presence of three compounds, each exhibiting two reversible redox couples, presumably Ni^{II}–Ni^{III} and Ni^{III}–Ni^{IV} couples. The least intense pair of couples, $E_p = +0.18$ and -0.66 V, showed that a small amount of unchanged $(H_2)_2Ni^{IV}$-*A* was still present (the ligand carbon atoms maintaining the same positions as in the series A dimethyl-substituted ligand systems). The four remaining couples must have arisen due to the presence of two rearranged isomers. By analogy with the $(Me_2)_2Ni$ and $(TM)_2Ni$ systems above, the larger pair of couples at $+0.00$ and -0.95 V were associated with a series B isomer, and the remaining couples at -0.19 and -1.22 V corresponded to a series C isomer. These data are presented in Table VII for comparison with the dimethyl- and the μ-trimethylene-substituted systems. Due to the small amounts of the rearranged $(H_2)_2$Ni species obtained and the difficulty in separating them from one another, no other characterization data can be presented at this time. However, the trend in the electrochemistry of these complexes, *i.e.*, the progressive decrease in both the Ni^{II}-Ni^{III} and Ni^{III}-Ni^{IV} couples upon successive ligand rearrangements, was so similar to that found in the $(Me_2)_2$Ni and $(TM)_2$Ni systems that it is virtually certain that the rearranged isomers in the unsubstituted system are actually $(H_2)_2Ni^{IV}$-*B* and $(H_2)_2Ni^{IV}$-C. The structures associated with these complexes would be analogous to those of the corresponding $(Me_2)_2$Ni-*B* and -*C* isomers (Figures 15 and 16, respectively).

Discussion

The conversion of the (3)-1,2-dicarbollide ligand to the (4)-1,2- moiety appeared to proceed only through the intervention of complexation with a transition metal ion. An explanation for the occurrence of such ligand rearrangements in the nickel and palladium systems arises from the formation of regions of highly localized electron deficiency, particularly in those bis(1,2-dicarbollyl) metal complexes with high (4+) formal metal oxidation states. On each icosahedral surface of a series A derivative this accumulation of positive charge would be centered around the triangle formed by the two facial carbon atoms and the metal atom. The separation of one of the carbon atoms away from the metal (to produce a series B or series C complex) would be expected to effectively lower this electron deficiency. It is this relief of localized electron deficiency which may provide the "driving force" for the facile thermal rearrangements of the complexed (3)-1,2 ligands to the (4)-1,2 ligands.

The relatively low temperatures required for the internal ligand rearrangements observed in the C,C′-dialkyl-substituted $(Me_2)_2$M and $(TM)_2$Ni systems, compared to the unsubstituted $(H_2)_2$Ni system, may be attributed to steric effects. When oxidation of the disubstituted series A complexes to the corresponding M^{IV} derivatives occurred, alkyl groups on each cage effectively prevented the rotational crossover necessary to attain the cisoid configuration like that found in the unsubstituted complex (Figure 6). A sterically accelerated ligand rearrangement then took place to form a series B isomer (Figure 15). The steric interactions due to the facial alkyl groups were apparently still significant in the disubstituted series B complexes and mild heating resulted in a second rearrangement to produce the series C isomers (Figure 16).

Definitive statements concerning the mechanism of the thermal ligand isomerization reactions which occur in these bis(1,2-dicarbollyl) metal complexes cannot be made. The icosahedral rearrangements might proceed *via* either of the two previously described mechanisms: the "diamond–square–diamond" mechanism of Lipscomb[31b] through a cubeoctahedral intermediate, or by the "rotation of triangular faces" mechanism suggested by Muetterties.[31c]

Successive introduction of a (4)-1,2-dicarbollide ligand into bis(dicarbollyl)nickel and -palladium complexes brought about a corresponding decrease in the M^{III}-M^{IV} redox potential, *i.e.*, the M^{IV} species became more difficult to reduce. This suggested that the rearranged ligand with its pentagonal B_4C bonding face donates more electron density to the metal atom than the unrearranged (3)-1,2-dicarbollide ligand with a B_3C_2 face. Other workers have prepared analogous formal nickel(IV) complexes employing B_4C ligands derived from the monocarbollide ion $[1\text{-}(2)\text{-}B_{10}H_{10}CH]^{3-}$,[35] and have indicated that these ligands were also superior to the B_3C_2 (3)-1,2-dicarbollide ion in "stabilizing" the high 4+ metal oxidation state.

Experimental Section

Physical Measurements. Ultraviolet-visible, infrared, proton nmr, ^{11}B nmr, and mass spectra were obtained as described previously.[2,3] A Varian HA-100 spectrometer at 100 Mc/sec was employed for obtaining some ^1H nmr spectra. Molecular weights, magnetic susceptibilities, and cyclic voltammograms were measured as before.[2,3]

The dielectric constants of nickel(IV) solutions were determined by the standard heterodyne-beat oscillator method,[36] and indices of refraction obtained with an Abbé refractometer. All measurements were made at 25°. Dipole moments were calculated using a modification of the Guggenheim method.[37] The dipole moments obtained by this procedure for triphenylphosphine and triphenylphosphine sulfide compared favorably with the literature values, serving as a check on the equipment and method of calculation. In benzene solution four different solute concentrations were employed ranging from zero to *ca.* 25 × 10^{-3} *M*; in cyclohexane three different concentrations were used ranging from zero to *ca.* 3 × 10^{-3} *M*.

Optical rotations were taken on a Zeiss photoelectric precision polarimeter in absolute ethanol for the salts, and in spectrograde cyclohexane for the neutral species; concentrations employed were approximately 5 mg in 10 ml of solvent in a 1-dm path length cell. Optical rotatory dispersion curves were obtained on a Jasco Model ORD/UV-5 recorder; scale settings were maximum, 0.005° full scale, and concentrations run were approximately 1.2 × 10^{-4} *M* to 4.7 × 10^{-4} *M* in a 1-cm path length cell. Mull spectra were recorded on a Cary Model 14 spectrophotometer. A Nujol mull of the compound was thinly spread on filter paper and placed in the sample beam; filter paper moistened with Nujol was placed in the reference beam.

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

Materials. The preparation of most of the starting materials has been described previously.[2,3,19] The preparation and properties of the $[TM]^{2-}$ complexes will be presented in a later paper.[32] Tetraphenylarsonium thiocyanate was prepared by mixing concentrated aqueous solutions of tetraphenylarsonium chloride and sodium thiocyanate and recrystallizing the resulting precipitate from hot water. Triphenylmethylphosphonium iodide was prepared in the same fashion. The 1,5-cyclooctadienedichloroplatinum complex was made by shaking an aqueous solution of K_2PtCl_4 with 1,5-cyclooctadiene (a gift from Cities Service Research and Development Co., New York, N. Y.) and recrystallizing the resulting white compound from CH_2Cl_2-hexane.

Solvents were dried as discussed before[2,3] and stored under nitrogen. Diglyme was dried by refluxing under nitrogen with sodium metal for 12 hr, distilling from the sodium under nitrogen at atmospheric pressure, and vacuum distilling the distillate from lithium aluminum hydride at approximately 0.5 mm. *sym*-Tetrachloro-

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[35] (a) D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *J. Amer. Chem. Soc.*, **89**, 3342 (1967); (b) W. H. Knoth, *ibid.*, **89**, 3342 (1967).

[36] D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 275.

[37] J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950): moments were calculated from the expression

$$\mu^2 = \frac{3kt}{4\pi N_0/3}\left\}\frac{3}{(\epsilon_1 + 2)^2}\lim_{C_2=0}\partial(\epsilon_{12} - n_{12}{}^2)/\partial C_2\right\{$$

or

$$\mu(\text{benzene solvent}) = 0.0896(10)^{-18}\{\lim_{C_2=0}\partial(\epsilon_{12} - n_{12}{}^2)/\partial C_2\}^{1/2}$$

and

$$\mu(\text{cyclohexane solvent}) = 0.0953(10)^{-18}\{\lim_{C_2=0}\partial(\epsilon_{12} - n_{12}{}^2)/\partial C_2\}^{1/2}$$

for benzene and cyclohexane solutions at 25°, respectively.

ethane was distilled from phosphorus pentoxide. Cyclooctane was distilled, collecting the intermediate fractions.

Ultraviolet and visible spectra were measured in spectrograde solvents. Proton and ^{11}B nmr spectra were measured in dried solvents.

Preparation of the Carbon-Substituted Bis(1,2-dicarbollyl)nickel **and -palladium Complexes.** The preparation of the unsubstituted $(H_2)_2$Ni and $(H_2)_2$Pd derivatives has been described previously.[2,3]

A. $\mathrm{Cs}[(HMe)_2\mathrm{Ni}^{\mathrm{III}}]$. A solution of nickel acetylacetonate (3.10 g, 12.1 mmol) in tetrahydrofuran was added dropwise under nitrogen to a stirring solution of $\mathrm{Na}_2(HMe)$ (24.1 mmol) prepared in the same solvent from 5.0 g of $(\mathrm{CH_3})_3\mathrm{NH}[(3)\text{-}1,2\text{-}\mathrm{B_9H_{10}CHC(CH_3)}]$[19] in the manner described previously.[2] After the mixture was allowed to stir under nitrogen at 40° for 3 hr, the cooled solution was stirred in the presence of air for 30 min, changing from a brown to a deep orange-brown color. The mixture was filtered, the filtrate solvent removed *in vacuo*, and the residue extracted with ether (*ca.* 300 ml) and filtered. The sodium salt of the brown nickel(III) complex was extracted into 300 ml of water upon the addition of pentane to the ether layer. Addition of 2.5 g (14.8 mmol) of cesium chloride to the heated aqueous solution (70°) gave upon cooling 3.61 g (7.45 mmol, 61.9%) of $\mathrm{Cs}[(HMe)_2\mathrm{Ni}^{\mathrm{III}}]$ as stable glittering red-brown plates, $d \sim 250°$. The product could be further purified by crystallization from hot water. The infrared spectrum (Nujol mull) contained absorptions at 2532(s), 1074(m), 1058(m), 1021(m), 990(m), 903(m), 870(w), 820(w), 772(w), and 732(m) cm^{-1}. (Only the more prominent infrared bands useful for characterization purposes are reported, including the cation bands in the salts.)

B. $(\mathrm{CH_3})_4\mathrm{N}[(HPh)_2\mathrm{Ni}^{\mathrm{III}}]$. Employing the procedure above, 20 mmol of $\mathrm{Na}_2(HPh)$ afforded 2.087 g (3.72 mmol, 37.2%) of $\mathrm{Rb}(HPh)_2\mathrm{Ni}^{\mathrm{III}}]$ as small red-brown plates. The rubidium salt dissolved with difficulty in hot water, from whence the tetramethylammonium salt was precipitated and crystallized from aqueous acetone to give stable brown needles of $(\mathrm{CH_3})_4\mathrm{N}[(HPh)_2\mathrm{Ni}^{\mathrm{III}}]$, dec pt ~250°. The infrared spectrum (Nujol mull) of this salt contained absorptions at 2525(s), 1589(w), 1189(w), 1170(w), 1084(w), 1060(m), 1040(w), 999(w), 982(m), 946(m), 869(w), 844(w), 778(m), 761(w), 749(m), 723(w), and 698(m) cm^{-1}.

C. **The** $[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}A]^-$ **Ion.** Employing the same procedures with $\mathrm{Na}_2(Me_2)$ in tetrahydrofuran, consistent yields of only 30–35% of the corresponding nickel(III) complex were obtained. However, much higher yields were realized in a benzene–ether solvent mixture. The anhydrous potassium salt of the $[(3)\text{-}1,2\text{-}\mathrm{B_9H_{10}C_2(CH_3)_2}]^-$ ion[19] (5.0 g, 25 mmol) was dissolved in a minimum amount of diethyl ether and the solution diluted with a large excess of benzene. To the rapidly stirring solution (under nitrogen) was added 15.6 ml of 1.6 *M n*-butyllithium in hexane (25 mmol) to give a white suspension of $\mathrm{KLi}(Me_2)$. Nickel acetylacetonate was added in bulk (3.2 g, 12.5 mmol), the mixture stirred rapidly for 30 min, heated to reflux for about 5 min, let cool, and stirred for an additional 12 hr. The yellow-brown mixture was filtered and the residue dissolved in ether by shaking with a small amount of dilute aqueous hydrochloric acid. The red ether layer was worked up as described above using, however, potassium chloride as the precipitant to afford 4.80 g (11.0 mmol, 88%) of $\mathrm{K}[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}A]\cdot\mathrm{H_2O}$ as black crystals from hot water. The infrared spectrum of the red tetramethylammonium salt contained absorptions at 2532(s), 1478(s), 1412(w), 1072(m), 1020(m), 1003(m), 948(m), 910(m), 784(m), 740(m), and 700(m) cm^{-1}. The tetramethylammonium salt converted to the brown series B isomer in the solid state at 200–210°.

D. $[(\mathrm{CH_3})_4\mathrm{N}]_2[(Me_2)_2\mathbf{Pd}^{\mathrm{II}}\text{-}A]$. The palladium(II) complex was prepared in benzene–ether solvent as above. To 15 mmol of $\mathrm{KLi}(Me_2)$ in benzene–ether at 0° was very slowly added 0.926 g (3.05 mmol) of palladium acetylacetonate dissolved in benzene. The color of the reaction mixture turned from white to orange to a deep orange-brown color. The mixture was filtered under a blanket of nitrogen and the residue taken up in cold water previously flushed with nitrogen to give a deep red solution which was treated with tetramethylammonium chloride. The pink precipitate was filtered, dried in a vacuum desiccator over $\mathrm{P_2O_5}$, washed with tetrahydrofuran (in a drybox) to remove soluble $(\mathrm{CH_3})_4\mathrm{N}[(3)\text{-}1,2\text{-}\mathrm{B_9H_{10}C_2(CH_3)_2}]$, and the red residue crystallized from concentrated acetone solution by slowly adding heptane (see ref 2 regarding the purification of $[(\mathrm{C_2H_5})_4\mathrm{N}]_2[(H_2)_2\mathrm{Cu}^{\mathrm{II}}]$). Brown, crystalline, air-sensitive $[(\mathrm{CH_3})_4\mathrm{N}]_2[(Me_2)_2\mathrm{Pd}^{\mathrm{II}}\text{-}A]\cdot(\mathrm{CH_3})_2\mathrm{CO}$ (0.995 g, 1.61 mmol) was thus obtained in 52.8% yield. The infrared spectrum (Nujol mull) contained absorptions at 2544(s), 1724(m), 1288(m), 1219(m), 1070(s), 1003(m), 954(s), 930(w), 905(m), 844(w), 824(w), 730(m), and 701(m) cm^{-1}. The ^{11}B spectrum in acetonitrile contained a low-field doublet resonance of relative area one centered at −10.6 ppm (relative to $\mathrm{BF_3}$ ethereate) plus complex higher field resonances of relative area eight.

E. $(HMe)_2\mathrm{Ni}^{\mathrm{IV}}$. To a stirring hot aqueous solution (1.1 l.) containing 1.82 g (3.76 mmol) of $\mathrm{Cs}[(HMe)_2\mathrm{Ni}^{\mathrm{III}}]$ was slowly added an aqueous solution of $\mathrm{FeCl_3\cdot 6H_2O}$ (1.27 g, 4.70 mmol). Concentrated hydrochloric acid (50 ml) was added to aid coagulation of the orange precipitate. The product was filtered, washed with water, and dried *in vacuo*. Rapid chromatography of the material on a 2-in. silica gel column eluting with 1:1 heptane:benzene afforded 1.26 g (3.58 mmol, 95.3%) of $(HMe)_2\mathrm{Ni}^{\mathrm{IV}}$ as stable red-orange crystals upon removing the solvent under reduced pressure. The infrared spectrum (Nujol mull) contained absorptions at 2952(w), 2580(s), 1079(m), 1016(w), 975(s), 934(w), 907(w), 896(w), 750(m), and 720(m) cm^{-1}. The ^{11}B nmr spectrum in acetone resembled that of the unsubstituted derivative but was not as well resolved.

F. $(HPh)_2\mathrm{Ni}^{\mathrm{IV}}$. A solution of 0.628 g (1.14 mmol) of $(\mathrm{CH_3})_4\mathrm{N}[(HPh)_2\mathrm{Ni}^{\mathrm{III}}]$ was ion exchanged to the sodium salt on a 1 × 12 in. sodium column of Dowex ion-exchange resin 50W × 8 in a 3:5 acetonitrile–water mixture. The solution of the sodium salt was gently heated *in vacuo* to remove the acetonitrile, acidified with concentrated hydrochloric acid, and treated with ferric chloride as above. The crude red product was dried and chromatographed as described to give 0.472 g (0.994 mmol, 87.2%) of $(HPh)_2\mathrm{Ni}^{\mathrm{IV}}$ as deep red, nearly black crystals. The infrared spectrum (Nujol mull) contained absorptions at 2583(s), 1240(w), 1170(w), 1064(m), 1033(m), 976(s), 874(w), 830(w), 765(m), 723(m), 691(s), and 686(m) cm^{-1}. The ^{11}B nmr spectrum in dichloromethane was broad and very poorly resolved.

G. $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}B$. The potassium or rubidium salt of the red $[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}A]^-$ ion could be oxidized in aqueous media with ferric chloride as described above or by a more convenient nonaqueous oxidation with iodine. This general procedure could be used for any of the above-mentioned oxidation reactions. To a solution or suspension of 1.37 g (2.68 mmol) of $(\mathrm{C_2H_5})_4\mathrm{N}[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}A]$ (any salt will suffice) in dichloromethane (150 ml) was added 1.04 g of iodine (8.19 mmol or 3.06 equiv). (Only 1 equiv of iodine was required for oxidation of the potassium salt.) After stirring for 20 min, 225 ml of hexane was added, the brown mixture filtered, and the orange solution passed through a short silica gel column (1.5 in.). Upon removal of most of the solvent *in vacuo*, 0.945 g (2.49 mmol, 93%) of $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}B$ was obtained as small, deep orange plates. Care must be taken to keep any solutions of this compound at room temperature or lower, due to its facile rearrangement to another isomer. The infrared spectrum (Nujol mull) of $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}B$ (see Figure 12) contained absorptions at 2572(s), 1071(m), 1057(m), 990(s), 939(m), 913(m), 898(w), 890(w), 880(w), 770(m), and 738(m) cm^{-1}. The ^{11}B nmr spectrum is shown in Figure 11. The dipole moment in benzene at 25° was 7.65 ± 0.01 D.

H. **The** $[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}B]^-$ **Ion.** This nickel(III) salt was obtained in nearly quantitative yields by the borohydride reduction of the corresponding nickel(IV) derivative. An ethanolic suspension of $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}B$ was treated with approximately twice the required amount of sodium borohydride and let stir for 15 min. The brown solution was diluted with water and tetramethylammonium chloride added. (The cesium and tetraethylammonium salts were similarly obtained.) Stable $(\mathrm{CH_3})_4\mathrm{N}[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}B]$ crystallized from methanol-water as brown flakes; its infrared spectrum (Nujol mull) contained absorptions at 2520(s), 1478(s), 1410(w), 1078(m), 1003(s), 941(s), 910(m), 881(m), 780(m), 746(m), 738(m), and 722(m) cm^{-1}.

The $[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}B]^-$ ion was also obtained by the clean thermal conversion of the red series A ion, $[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}]\text{-}A]^-$, at 200°. In the solid state the tetramethylammonium salt of the series A isomer rapidly turned a brown color at 200–210°. Cyclic voltammetry conducted on this material afforded the two reversible redox couples associated with the series B derivatives, confirming the presence of the $[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}B]^-$ ion. Similarly, in solution, when a thick-walled nmr tube containing $(\mathrm{CH_3})_4\mathrm{N}[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}A]$ in dry, degassed diglyme (sealed off under vacuum) was heated at 190° for 15 min, the mixture turned from deep red to brown. Cyclic voltammetry of the crystallized brown material showed it to be the series B derivative. When the series A cobalt analog,[2] $[(Me_2)_2\mathrm{Co}^{\mathrm{III}}]^-$, was subjected to the same conditions, no changed was observed until 300° (cesium salt, solid state) when a complex mixture of isomers was obtained and detected by proton nmr.

I. $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}C$. Upon heating a toluene or cyclooctane solution of $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}B$ to boiling (110° and 149°, respectively) for 3 min, the compound was converted to the yellow $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}C$ isomer, which could be recovered in essentially quantitative yield after removal of the solvent. This series C isomer was obtained as a stable, bright yellow microcrystalline powder (well-defined crystals were never obtained) whose infrared spectrum (Nujol mull) contained absorptions at 2572(s), 1199(w), 1152(w), 1060(m), 995(s), 951(m), 935(w), 918(w), 899(m), 778(m), and 743(m) cm^{-1} (see Figure 12). The ^{11}B nmr spectrum is shown in Figure 11.

J. The $[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}C]^-$ Ion. This nickel(III) derivative was prepared in high yields by reduction of $(Me_2)_2\mathrm{Ni}^{\mathrm{IV}}\text{-}C$ in the manner described above for the series B isomer. The potassium, cesium, tetramethylammonium, and tetraethylammonium salts were readily obtained. The tetramethylammonium salt, $(\mathrm{CH_3})_4\mathrm{N}[(Me_2)_2\mathrm{Ni}^{\mathrm{III}}\text{-}C]$, crystallized from acetone–water as golden plates which contained the following bands in its infrared spectrum: 2522(s), 1478(s), 1412(w), 1205(w), 1178(w), 1078(m), 1063(m), 1005(s), 949(s), 914(w), 889(m), 877(m), 818(w), 770(w), 744(m), and 722(m) cm^{-1}.

K. $(Me_2)_2\mathrm{Pd}^{\mathrm{IV}}\text{-}C$. To a stirring suspension of $[(\mathrm{CH_3})_4\mathrm{N}]_2\text{-}[(Me_2)_2\mathrm{Pd}^{\mathrm{II}}\text{-}A]\cdot(\mathrm{CH_3})_2\mathrm{CO}$ (0.775 g, 1.26 mmol) in dichloromethane was slowly added *1* equiv of iodine (0.16 g, 1.26 mmol) dissolved in the same solvent. Approximately 0.5 g of $(\mathrm{C_2H_5})_4\mathrm{NBr}$ and some anhydrous magnesium sulfate were added to the stirring mixture to increase solubilities and to keep the solvent dry, respectively. The black solution was filtered and poured over a 7-in. silica gel column made up with dichloromethane. The absorbed oxygen on the column acted as a mild oxidizing agent and a yellow band appeared, followed by a narrow black band (Pd$^{\mathrm{III}}$?) which was followed by a broad orange band (Pd$^{\mathrm{II}}$?), leaving black decomposition behind. The yellow fraction was collected and the remaining fractions recycled on a new column. The combined yellow fractions afforded 0.205 g (0.48 mmol, 38%) of pale yellow, microcrystalline $(Me_2)_2\mathrm{Pd}^{\mathrm{IV}}\text{-}C$. The compound was unstable to moist air over long periods of time like its unsubstituted analog[3] and was somewhat thermally unstable. The infrared spectrum (Nujol mull) is shown in Figure 12 and contained absorptions at 2580(s), 1199(m), 1160(w), 1090(w), 1072(w), 1060(m), 995(s), 949(w), 921(m), 905(s), 896(w), and 744(s) cm^{-1}. The ^{11}B nmr spectrum is shown in Figure 11.

The analytical data, electronic spectra, and electrochemical data for the bis(1,2-dicarbollyl)nickel and -palladium derivatives are given in Tables I–VII.

Platinum-1,2-dicarbollide Derivatives. Platinum dichloride, platinum tetrachloride, cesium ethylenetrichloroplatinate(II), disodium tetrachloroplatinate(II), and chloroplatinic acid all reacted with excess Na$_2$- or KLi(H_2) in tetrahydrofuran or monoglyme at 0° to produce intractable brown to black materials. Even at lower temperatures (−78°) the dichloride and tetrachloride still afforded black material. Employing dimethyl sulfoxide as solvent did not alter the results. Platinum acetylacetonate appeared inert to excess dicarbollide ion in refluxing tetrahydrofuran.

The compound 1,5-cyclooctadieneplatinum dichloride produced a bright yellow color in tetrahydrofuran with excess $\mathrm{Na_2}(H_2)$ at −78°. The yellow material could be obtained at this stage by quenching the reaction mixture at low temperatures with heptane. However, upon warming up to about −10°, the solution turned black. This yellow material was also obtained by stirring 0.64 g (1.71 mmol) of $(1,5\text{-}\mathrm{C_8H_{12}})\mathrm{PtCl_2}$ for 24 hr with 8.57 mmol of a $\mathrm{Li_2}(H_2)$ slurry in benzene (prepared from 1.66 g of $(\mathrm{CH_3})_3\mathrm{NH}[(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{12}}]$ and 10.7 ml of 1.6 *M* *n*-butyllithium and refluxing for 12 hr). The black mixture was filtered, the filtrate evaporated to dryness *in vacuo*, and the residue extracted with dichloromethane and chromatographed on silica gel. Repeated chromatography with 1:1 dichloromethane–hexane afforded 0.194 g (0.445 mmol, 38.4%) of pale yellow [$\lambda_{\max}^{\mathrm{CH_3CN}}$ (ϵ): 252 (25,900), 389 (220)], crystalline (1,5-cyclooctadiene)[π-(3)-1,2-dicarbollyl]platinum(II). The elemental analysis of the crystalline compound was poor for unknown reasons; however, the mass spectral data confirmed the assigned formulation. *Anal.* Calcd for $(\mathrm{C_8H_{12}})\mathrm{Pt}(\mathrm{B_9C_2H_{11}})$: Pt, 44.78; B, 22.33; C, 27.57; H, 5.32. Found: Pt, 45.93; B, 20.50; C, 28.35; H, 5.77. The mass spectrum exhibited a peak at mass number 436 (mol wt, 435.685) as the most intense peak in the parent region. The infrared spectrum (Nujol mull) contained absorptions at 3080(w), 2564(s), 1331(m), 1305(w), 1223(m), 1178(w), 1163(w), 1081(m), 1059(w), 1019(m), 987(m), 920(w), 880(w), 873(w), 830(m), 815(w), 784(w), 757(w), and 724(m) cm^{-1}.

Deuteration and Degradation Reactions of $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$. A mixture of 1.006 g (3.10 mmol) of $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$ and 0.180 g (4.5 mmol) of sodium hydroxide (pellets) was allowed to stir under nitrogen for 2.5 hr at room temperature in 12 ml of tetrahydrofuran and 20 ml of D$_2$O. Upon filtering, nickel hydroxide was obtained and converted to the dimethylglyoxime complex, which corresponded to 8.6% of the nickel originally present. The tetrahydrofuran was removed from the brown filtrate under reduced pressure. The addition of 0.373 g (3.08 mmol) of rubidium chloride to the warm D$_2$O solution afforded 1.14 g (2.76 mmol, 89%) of completely C-deuterated $\mathrm{Rb}[(D_2)_2\mathrm{Ni}^{\mathrm{III}}]$ upon cooling. The infrared spectrum (Nujol mull) of the tetramethylammonium salt of the $[(D_2)_2\mathrm{Ni}^{\mathrm{III}}]^-$ ion contained absorptions at 2544(s), 2300(m), 1065(m), 1021(s), 967(m), 949(s), 912(m), 879(w), 860(w), 794(w), 766(w), 757(w), 729(m), and 695(w) cm^{-1}. No deuteration occurred when the $[(H_2)_2\mathrm{Ni}^{\mathrm{III}}]^-$ ion was subjected to the same conditions.

To a D$_2$O solution of $\mathrm{Rb}[(D_2)_2\mathrm{Ni}^{\mathrm{III}}]$ was added an equivalent amount of anhydrous FeCl$_3$. The resulting yellow precipitate was filtered, dried *in vacuo*, and extracted with boiling *n*-hexane in a Soxhlet apparatus to afford orange, crystalline $(D_2)_2\mathrm{Ni}^{\mathrm{IV}}$. The mass spectral data for this compound are presented in Table III. The infrared spectrum (Nujol mull) contained absorptions at 2592(s), 2283(m), 1045(m), 1009(s), 946(s), 925(m), 918(m), 909(w), 896(m), 856(w), 820(m), 810(m), 754(m), 744(m), 734(s), and 712(m) cm^{-1}.

In another experiment, 1.00 g (3.09 mmol) of $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$ and 0.42 g (5.7 mmol) of calcium hydroxide were sealed in a Toepler system with 5 ml of toluene and 10 ml of water (degassed before sealing). The system was heated at 95° for 2.5 hr, after which time the orange color disappeared from the toluene and the aqueous layer became deep brown. The evolved gas was measured and amounted to 1.25 mmol of hydrogen (as determined by mass spectroscopy). From the aqueous phase, 91.8% of the nickel was recovered as $(\mathrm{CH_3})_4\mathrm{N}[(H_2)_2\mathrm{Ni}^{\mathrm{III}}]$ (1.13 g). The reaction by-products were not characterized but were probably borates.

Amines were also employed as degradation agents. Trimethylamine was condensed into a Toepler bulk containing $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$ and dry benzene, and the system sealed off. Upon warming to room temperature, a transient green color was seen at low temperatures as the amine melted upon the orange nickel(IV) compound, and at higher temperatures turned to the yellow-brown color of the nickel(III) anion. No hydrogen gas was evolved. The molar ratio of reacted trimethylamine to $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$ was 1.3:1. The infrared spectrum of the final product was practically identical with that of authentic $(\mathrm{CH_3})_3\mathrm{NH}[(H_2)_2\mathrm{Ni}^{\mathrm{III}}]$, including a strong N–H stretching band at 3100 cm^{-1}. Similar results were observed with ammonia. When diethylamine was added to a benzene solution of $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$, the transient green color persisted even at room temperature, but reverted to yellow-brown upon standing. The nature of these intermediates and the reaction by-products are presently not known.

Attempted Oxidation Reactions Involving $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$. Ethanol, hydrogen peroxide, and triphenylphosphine were all oxidized to some extent under basic conditions to form acetaldehyde, oxygen, and triphenylphosphine oxide, respectively. In all cases, some degradation of the nickel complex was observed. The more interesting ethanol oxidation is discussed below.

To a refluxing solution of sodium ethoxide (6.49 mmol) in 75 ml of absolute ethanol was added under nitrogen 1.00 g (3.09 mmol) of $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$. Nitrogen was bubbled through the system at a slow rate to entrain any acetaldehyde formed and then through a cooled (0°) stirring solution of 2,4-dinitrophenylhydrazine.[38] After 3 min a yellow precipitate began to form in the 2,4-DNP solution, and the refluxing was continued for 1 hr. Benzene extraction of the 2,4-DNP solution, followed by column chromatography on alumina, gave 0.076 g (0.34 mmol, 22%) of the yellow acetaldehyde 2,4-dinitrophenylhydrazone, mp 146° (lit. 147°). Recovered from the ethanol solution was 1.023 g (2.58 mmol, 83.3%) of $(\mathrm{CH_3})_4\mathrm{N}[(H_2)_2\mathrm{Ni}^{\mathrm{III}}]$.

Reactions of $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$ with Soft Bases. A. Bromide Ion. A mixture of 0.602 g (1.86 mmol) of $(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$ and 0.647 g (1.81 mmol) of triphenylmethylphosphonium bromide was dissolved in *ca.* 40 ml of warm dichloromethane. Hexane was slowly added while scratching the sides of the vessel until crystallization was initiated, and the solution allowed to stand for 1 hr (open to the air). Obtained in the first crop was 1.10 g (1.62 mmol, 89.4%) of orange, crystalline $[(\mathrm{C_6H_5})_3\mathrm{P}(\mathrm{CH_3})]\mathrm{Br}\cdot(H_2)_2\mathrm{Ni}^{\mathrm{IV}}$. Purification was achieved by recrystallizing from the same solvent system, keeping the volumes to a minimum. The ease of dissociation of this type of adduct, coupled with possible difficulty in completely burning the samples, led to somewhat poor elemental analyses; however, the data did support the 1:1 stoichiometries of the addition compounds. *Anal.* Calcd for $(\mathrm{C_6H_5})_3\mathrm{P}(\mathrm{CH_3})\mathrm{BrNi}(\mathrm{B_9C_2H_{11}})_2$: Ni, 8.62; B, 28.59; C, 40.58; H, 5.92; Br, 11.74. Found: Ni, 8.71; B, 28.16; C, 39.46; H, 5.94; Br, 10.30. The infrared spectrum (Nujol mull)

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[38] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 29.

contained absorptions at 2580(s), 1585(w), 1481(w), 1438(s), 1264(w), 1223(w), 1164(w), 1128(s), 1016(m), 998(m), 975(s), 915(s), 908(m), 894(w), 789(m), 748(s), 720(s), and 692(s) cm^{-1}.

A red, crystalline material was obtained in the same manner with tetraethylammonium bromide and $(HMe)_2\text{Ni}^{\text{IV}}$; however, elemental analysis indicated a mixture was present; *i.e.*, the crystals did not correspond to a 1:1 adduct. Attempts to prepare similar bromide ion adducts with the monophenyl- and dimethyl-substituted nickel(IV) complexes were unsuccessful, although slight solution interactions were noted.

B. Chloride Ion. Employing the procedure described above for the bromide ion adduct, yellow-orange needles of the tetraphenylarsonium chloride addition compound with $(H_2)_2\text{Ni}^{\text{IV}}$ were obtained in high yields from dichloromethane–hexane solutions. An analogous triphenylmethylphosphonium chloride adduct was prepared similarly. *Anal.* Calcd for $(C_6H_5)_4AsClNi(B_9C_2H_{11})_2$: Ni, 7.91; B, 26.21; C, 45.30; H, 5.70; Cl, 4.78. Found: Ni, 8.42; B, 25.20; C, 44.72; H, 5.61; Cl, 5.34. The elemental analysis indicated that there may be some dichloromethane of crystallization in the complex. The infrared spectrum (Nujol mull) of the tetraphenylarsonium salt contained absorptions at 2583(s), 1440(s), 13111(w), 1266(w), 1111(m), 1083(m), 1014(m), 999(m), 976(s), 920(m), 893(w), 742(s), and 688(s) cm^{-1}.

C. Thiocyanate Ion. Employing the same procedure above, the tetraphenylarsonium thiocyanate-$(H_2)_2\text{Ni}^{\text{IV}}$ adduct was obtained in high yields as deep red-orange needles. *Anal.* Calcd for $(C_6H_5)_4AsNCSNi(B_9C_2H_{11})_2$: Ni, 7.67; B, 25.44; C, 45.53; H, 5.53; S, 4.19; N, 1.83. Found: Ni, 6.85; B, 22.78; C, 42.06; H, 5.13; S, 4.02; N, 2.08. (Some dichloromethane may be present in the crystalline complex.) The infrared spectrum (Nujol mull) contained absorptions at 2580(s), 2045(s), 1481(m), 1440(s), 1337(w), 1390(w), 1264(m), 1200(w), 1188(m), 1097(m), 1083(s), 1022(w), 1010(w), 998(m), 968(s), 919(m), 890(m), 844(w), 739(s), and 687(s) cm^{-1}. The C≡N stretching frequency at 2045 cm^{-1} was virtually the same in $[(C_6H_5)_4As]SCN$ and in $[(C_6H_5)_4As]SCN \cdot (H_2)_2\text{Ni}^{\text{IV}}$.

D. Iodide Ion. When equimolar amounts of triphenylmethylphosphonium iodide and $(H_2)_2\text{Ni}^{\text{IV}}$ were treated as described for the adducts above, large deep brown crystals were obtained. Elemental analysis of the material gave a low iodine percentage for a 1:1 adduct and the crystals were paramagnetic as determined by Faraday measurements. Subsequent X-ray diffraction studies carried out by Wing[23] on a single crystals of the "iodide adduct" showed that it was the same as authentic $(C_6H_5)_3P(CH_3)[(H_2)_2\text{Ni}^{\text{III}}]$. It appeared, therefore, that iodide ion was oxidized by $(H_2)_2\text{Ni}^{\text{IV}}$ in dichloromethane to produce the nickel(III) anion and the triiodide anion, both of which cocrystallize as their triphenylmethylphosphonium salts.

The $(H_2)_2\text{Pd}^{\text{IV}}$ derivative, however, was not reduced by iodide ion and a deep red crystalline adduct was obtained with triphenylmethylphosphonium iodide by the usual procedure. *Anal.* Calcd for $(C_6H_5)_3P(CH_3)IPd(B_9C_2H_{11})_2$: Pd, 13.72; B, 25.09; C, 35.63; H, 5.20; I, 16.37. Found: Pd, 14.53; B, 25.09; C, 34.37; H, 5.02; I, 14.03. The infrared spectrum (Nujol mull) contained absorptions at 2580(s), 1585(w), 1266(w), 1221(w), 1164(w), 1117(s), 1011(m), 998(w), 973(s), 906(s), 885(w), 788(m), 745(s), 720(s), and 691(s) cm^{-1}.

E. Neutral Sulfur Donors. A concentrated solution of $(H_2)_2\text{Ni}^{\text{IV}}$ in 1:1 diethyl sulfide–methylcyclohexane was allowed to slowly cool to −20°, whereupon large red crystals of an adduct crystallized. The diethyl sulfide was readily lost when the crystals were taken out of the solution at room temperature, leaving orange, powdery $(H_2)_2\text{Ni}^{\text{IV}}$. The solid adduct was more stable at low temperatures, however.

Solutions of $(H_2)_2\text{Ni}^{\text{IV}}$ with excess thiourea in acetone were a deep red, yet no solid addition compound could be obtained. When the more soluble dicyclohexylthiourea was substituted, a red crystalline complex could be isolated by cooling a concentrated dichloromethane solution containing equimolar amounts of the donor and nickel(IV) derivative. The infrared spectrum (Nujol mull) contained absorptions at 3440(w), 3280(m), 2600(s), 1558(s), 1496(m), 1412(w), 1340(m), 1295(w), 1273(w), 1253(m), 1228(m), 1190(w), 1148(m), 1102(m), 1087(m), 1030(w), 1012(m), 969(s), 916(m), 895(m), 852(w), 817(w), 773(m), 744(s), and 732(w) cm^{-1}.

Other sulfur donors such as phenyl isothiocyanate, thiophene, thioacetamide, and triphenylphosphine sulfide did not appear to interact appreciably with $(H_2)_2\text{Ni}^{\text{IV}}$.

F. Aromatic Hydrocarbons. By cooling hot solutions of $(H_2)_2\text{Ni}^{\text{IV}}$ containing a large molar excess of an aromatic hydrocarbon, crystalline adducts were readily obtained.

Red-orange crystals of the naphthalene addition compound of $(H_2)_2\text{Ni}^{\text{IV}}$ were isolated from dichloromethane. The complex would slowly lose naphthalene upon standing in the open air. Its infrared spectrum (Nujol mull) contained absorptions at 2560(s), 1599(w), 1264(w), 1209(m), 1138(m), 1099(m), 1081(s), 1008(m), 966(s), 914(m), 897(w), 790(s), 744(s), and 720(m) cm^{-1}. The most prominent absorption shift observed was the 784 cm^{-1} band of naphthalene moving to 790 cm^{-1} in the complex.

The phenanthrene-$(H_2)_2\text{Ni}^{\text{IV}}$ adduct was obtained from dichloromethane as large deep-red plates. The infrared spectrum (Nujol mull) contained absorptions at 2600(s), 1609(w), 1300(w), 1243(m), 1208(w), 1142(m), 1080(s), 1034(w), 1009(w), 966(s), 920(w), 899(w), 874(m), 824(s), 816(s), 743(s), and 715(m) cm^{-1}. The major band shift of phenanthrene was the 820 cm^{-1} absorption moving to 824 cm^{-1} in the adduct.

Deep green needles of the pyrene addition compound with $(H_2)_2\text{Ni}^{\text{IV}}$ were obtained from methylcyclohexane. The solid adduct was diamagnetic, having a molar susceptibility of −413 × 10^{-6} cm^3 mol^{-1}. *Anal.* Calcd for $C_{16}H_{10}Ni(B_9C_2H_{11})_2$: Ni, 11.17; C, 45.69; H, 6.13. Found: Ni, 10.59; C, 43.52; H, 6.79. Its infrared spectrum (Nujol mull) contained absorptions at 3070(m), 2603(s), 1602(m), 1311(w), 1242(w), 1210(m), 1188(m), 1139(m), 1102(m), 1084(s), 1070(m), 1010(m), 966(s), 918(m), 894(m), 851(s), 845(s), 823(m), 756(s), 744(s), and 715(s) cm^{-1}. The 851, 756, and 715 cm^{-1} pyrene bands were shifted to slightly higher energies in the adduct relative to pyrene itself.

Brown needles of the $(H_2)_2\text{Pd}^{\text{IV}}$-pyrene adduct were prepared in the same manner as the nickel derivative. The infrared spectrum (Nujol mull) contained absorptions at 3080(m), 2603(s), 1608(m), 1310(w), 1240(w), 1209(m), 1185(m), 1132(w), 1093(m), 1079(s), 1059(w), 1007(m), 996(s), 882(m), 849(s), 822(m), 749(s), and 715(s) cm^{-1}.

When a warm, concentrated $(H_2)_2\text{Ni}^{\text{IV}}$ solution in N,N-dimethylaniline was treated with approximately twice the volume of hexane and cooled to 0°, dark-green needles of $[C_6H_5N(CH_3)_2] \cdot (H_2)_2\text{Ni}^{\text{IV}}$ were obtained. The adduct lost dimethylaniline upon standing in the open, leaving the orange nickel(IV) complex. The infrared spectrum (Nujol mull) contained absorptions at 2603(s), 1609(s), 1579(m), 1510(s), 1340(s), 1231(s), 1209(m), 1193(m), 1161(w), 1139(m), 1101(m), 1083(s), 1064(m), 1034(w), 1011(m), 993(m), 968(s), 940(w), 921(m), 905(w), 897(w), 871(m), 809(w), 761(s), 723(m), and 699(s) cm^{-1}.

Optical Resolution Studies. Aqueous solutions of Na[*dl*-$(Me_2)_2\text{Ni}^{\text{III}}$-*B*] and *d*-N,N,N-trimethyl-α-phenylethylammonium iodide,[33] (*d*-TMPEA)I, $[\alpha]^{23}\text{D}$ +16.7°, were mixed producing 5.4 g (10.1 mmol) of (*d*-TMPEA)[*dl*-$(Me_2)_2\text{Ni}^{\text{III}}$-*B*]. The product was recrystallized from hot ethanol–water mixtures until the melting point and rotation ceased to increase. This occurred after 34 recrystallizations to afford 0.184 g (0.34 mmol) of (*d*-TMPEA)[$(+)_{546}$-$(Me_2)_2\text{Ni}^{\text{III}}$-*B*], mp 164.5–165°, $[\alpha]^{23}\text{D}$ 140 ± 10°. This resolved material was passed through a sodium ion-exchange column and precipitated from water with $(C_2H_5)_4NBr$. The crude solid was run through a 2-in. silica gel column with dichloromethane and crystallized from CH_2Cl_2–hexane to afford long brown needles of $(C_2H_5)_4N[(+)_{546}$-$(Me_2)_2\text{Ni}^{\text{III}}$-*B*], dec pt 169–170° (turns dark, does not melt up to 200°). The racemic tetraethylammonium salt melted with decomposition at 157–158°. The infrared spectra of the resolved and racemic tetraethylammonium salts were identical.

In dichloromethane, $(CH_5)_4N[(+)_{546}$-$(Me_2)_2\text{Ni}^{\text{III}}$-*B*] was treated with iodine as previously described; the mixture was diluted with an equal volume of hexane, filtered from $(C_2H_5)NI_3$, and rapidly passed through a short (1-in.) silica gel column made up with the same solvent mixture. Evaporation of the solvent *in vacuo* afford orange crystalline $[(-)_{546}$-$(Me_2)_2\text{Ni}^{\text{IV}}$-*B* slowly darkening at 215–219°, not melting up to 230°. The racemic compound darkened at 204–206° and melted with decomposition at *ca.* 208°.

Optically active $[(-)_{546}$-$(Me_2)_2\text{Ni}^{\text{IV}}$-$B]^0$ from above was heated in boiling cyclooctane for 1 min. The solvent was removed *in vacuo*, the residue taken up in 1:2 CH_2Cl_2–hexane, and the solution passed through a 1-in. silica gel column as above. Bright yellow clumps of semicrystalline [*meso*- and $(-)_{546}$-$(Me_2)_2\text{Ni}^{\text{IV}}$-*C*] (*vide supra*) were obtained. The decomposition points of this material and of the optically inactive compound were the same, both blackening at *ca.* 230°.

Optically active [*meso*- and $(-)_{546}$-$(Me_2)_2\text{Ni}^{\text{IV}}$-$C]^0$ from above was treated with sodium borohydride in absolute ethanol, followed by $(C_2H_5)_4NBr$ and water. Pale green-brown crystals formed and were crystallized from dichloromethane–hexane to give green-brown plates of $(C_2H_5)_4N$[*meso*- and $(+)_{546}$-$(Me_2)_2\text{Ni}^{\text{III}}$-*C*] darkening at *ca.* 225–228°, the same decomposition temperature observed for the optically inactive compound.

The rotations of all the optically active derivatives described above at 546 and 578 mμ are presented in Table X. The ORD curves of these compounds are shown in Figure 14.

Degradation of $(Me_2)_2$Ni-*C* Derivatives. A tetrahydrofuran solution containing 0.145 g (0.38 mmol) of $(Me_2)_2$Ni^{IV}-*C* with an excess of sodium amalgam was allowed to stir under nitrogen for 2 days. The resulting black mixture was poured into water, the tetrahydrofuran removed *in vacuo*, and the aqueous solution treated with $(CH_3)_4NCl$. Fractional recrystallization of the crude precipitate from acetone–water mixtures afforded 0.0346 g (0.147 mmol, 20%) of $(CH_3)_4N[(3)\text{-}1,2\text{-}B_9H_{10}C_2(CH_3)_2]$ and a very small amount (0.006 g, 0.013 mmol) of red $(CH_3)_4N[(Me_2)_2Ni^{III}\text{-}A]$, which was probably formed *after* the degradation of the series C derivative.

In another reaction, 0.249 g (0.594 mmol) of K[$(Me_2)_2$Ni^{III}-*C*], 2 ml of hydrazine hydrate, and 1 g of sodium cyanide in an ethylene glycol–water solution were heated in a steam bath. Solid NaOH pellets (0.7 g) were slowly added and the heating continued for 1 hr. The mixture was diluted, treated with $(CH_3)_4NCl$, and the crude precipitate fractionally crystallized from ethanol-water to afford 0.060 g (0.255 mmol, 21.4%) of $(CH_3)_4N[(3)\text{-}1,2\text{-}B_9H_{10}C_2(CH_3)_2]$. In this experiment and in the one described above, the degradation products were identified by their proton nmr spectra and/or infrared spectra.

Thermal Rearrangement of Unsubstituted $(H_2)_2$Ni^{IV}. In a high vacuum system, $(H_2)_2$Ni^{IV} was allowed to slowly sublime through a 9-in. glass tube which was heated to 360–400°. An oil bath at the bottom of the assembly was maintained at 150°. The level of the oil bath was always just below the level of the $(H_2)_2$Ni^{IV} sublimate so as not to force too much through the hot column at once; otherwise, serious decomposition occurred. The process was allowed to continue for 1 week, after which time a small amount (*ca.* 0.2 g) of yellow material had condensed at the top of the strongly heated portion of the tube. This material was crystallized from dichloromethane–hexane to afford a small amount of crystalline yellow-orange flakes as the least soluble fraction. It was this fraction that contained the majority of the rearranged products, the more soluble fractions containing considerable amounts of starting material. The cyclic voltammogram of the least soluble material is shown in Figure 18, and the potential data are presented in Table VII.

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The Crystal Structure of 3,3′-*commo*-Bis[undecahydro-1,2-dicarba-3-nickela-*closo*-dodecaborane], a Nickel(IV) Complex of the Dicarbollide Ion[1]

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Abstract: The crystal structure of the neutral molecule, 3,3′-*commo*-bis[undecahydro-1,2-dicarba-3-nickela-*closo*-dodecaborane], $Ni(B_9C_2H_{11})_2$, has been determined from 3242 independent X-ray data obtained from a single crystal using a scintillation counter and the θ-2θ scanning technique. The monoclinic unit cell has dimensions $a = 13.371$, $b = 10.398$, $c = 13.556$ Å, and $\beta = 119.16°$. The space group is $P2_1/c$. There are four molecules in the unit cell and the calculated density is 1.31 g/cc. The model was refined to a conventional discrepancy factor of $R = 0.035$. The molecule has the shape of two icosahedra, each composed of nine boron atoms, two carbon atoms, and a nickel atom, which have one vertex position occupied by the nickel shared in common. The positions of the carbon atoms in the cage were determined and all hydrogen atoms were located. The carbon atoms in opposite cages are as close to each other as is possible in the staggered configuration. The molecule has point symmetry C_2. There are two enantiomorphic rotational isomers present in the crystal.

Another in the series of transition metal complexes of the dicarbollide ion, $(B_9C_2H_{11})^{2-}$, has been prepared.[2,3] This complex, $Ni(B_9C_2H_{11})_2$, 3,3′-*commo*-bis[undecahydro-1,2-dicarba-3-nickela-*closo*-dodecaborane],[4] is a neutral molecule in which the nickel is in a formal 4+ valence state. Warren and Hawthorne predicted the structure as having the nickel ion sandwiched between the open fivefold faces of two $(B_9C_2H_{11})^{-2}$ icosahedral fragments. Because of the unusual chemical and spectral properties of this compound, such as the high dipole moment and two low-field doublets in the 32.0-Mc/sec ^{11}B nmr spectrum, observed for this molecule and an analogous $Pd(B_9C_2H_{11})_2$ neutral molecule,[5] an unusual structure was expected.

In this paper are reported the results of a single-crystal X-ray analysis which confirms the sandwich type structure in the molecule, shown in Figure 1. We show that there are two enantiomorphic rotational configurations present in the crystal and that the cages are staggered. The structure is novel among the unsubstituted metallocarboranes containing two dicarbollide ions, in that the pairs of carbon atoms in opposite cages are as

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