Metallocene Compounds Derived from μ-1,2-Trimethylene-1,2-dicarba-*closo*-dodecaborane(10)

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Abstract: The novel carborane μ-1,2-trimethylene-1,2-dicarba-*closo*-dodecaborane(10) has been prepared and characterized. The carborane was found to undergo base degradation to form the μ-1,2-trimethylene-(3)-1,2-dicarbadecahydro-*nido*-undecaborate(1−) ion which after deprotonation would react with transition metals to form several sandwich-bonded complexes of the type $[M^{n+}(B_9C_5H_{15})_2]^{n-4}$ and $(C_5H_5)M^{III}(B_9C_5H_{15})$. The formal nickel(IV) and cobalt(III) complexes were found to undergo thermal rearrangements and the kinetics of the facile ligand isomerizations of $Ni(B_9C_5H_{15})_2$ were determined using reverse current chronopotentiometry and visible spectroscopy.

The (3)-1,2-dicarbollide ion[3-6] has been shown to form sandwich-bonded complexes of the type $[M^{n+}(B_9C_2H_{11})_2]^{n-4}$ and $[M^{n+}(C_5H_5)(B_9C_2H_{11})_2]^{n-3}$ using several transitions metals. The chemistry is now extended by the synthesis of complexes using a novel carboranyl ligand which contains a trimethylene bridge linking the carbon atoms of the icosahedral fragment. This carborane, μ-1,2-trimethylene-1,2-dicarba-*closo*-dodecaborane(10), was prepared from the reaction of the bislithio salt of *o*-carborane with 1,3-dibromopropane.[7] The carborane underwent typical boron atom removal in strong alcoholic hydroxide solution[3] to form a (3)-1,2-monoanion. Reaction of the latter with sodium hydride produced a dianion[4-6] which reacted with transition metals to form π-bonded sandwich complexes. The formal cobalt(III), nickel(III), and nickel(IV) complexes were isolated and characterized. The orange nickel(IV) complex which was prepared from the oxidation of the nickel(III) complex was found to contain a rearranged isomeric ligand. This nickel(IV) complex formed a third nickel(IV) complex when heated for a few minutes in boiling cyclooctane.

Synthesis and Characterization of μ-1,2-Trimethylene-1,2-dicarba-*closo*-dodecaborane(10) (1). The carborane (see Figure 1) was prepared from the reaction of 1 mol of *o*-carborane with 2 mol of *n*-butyllithium followed by the addition of 1,3-dibromopropane in diethyl ether.

$$B_{10}C_2H_{12} + 2n\text{-BuLi} \longrightarrow B_{10}H_{10}C_2Li_2$$

$$B_{10}H_{10}C_2Li_2 + BrCH_2CH_2CH_2Br \longrightarrow \underset{\mathbf{1}}{B_{10}C_5H_{16}} + 2LiBr$$

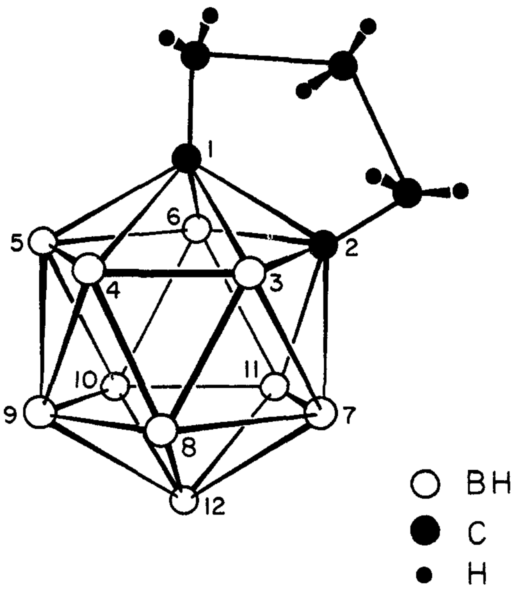

Figure 1. Proposed structure of μ-1,2-trimethylene-1,2-dicarba-*closo*-dodecaborane(10).

The product 1 was recovered in crude form by sublimation and was purified by recrystallization from ethanol–water several times followed by a final sublimation. The colorless air-stable compound had the characteristic camphor-like odor of 1,2-dodecacarboranes and sublimed slowly at 80° in high vacuum to form small needles which melted at 193° (sealed tube).

The 60-MHz ^1H nmr spectrum of 1 in carbon tetrachloride contained only a singlet centered at −2.54 ppm (relative to tetramethylsilane = 0.0). Apparently the electronic effect of the boron atoms in the carborane cage was such as to render the "inner" 4 methylene protons (adjacent to the carborane carbons) almost equivalent to the "outer" 2 methylene protons and only the single resonance pattern was observed at 60 MHz. The 250-MHz ^1H nmr spectrum of 1 in benzene exhibited a triplet (J = 6.6 Hz) at −1.65 ppm and a quintet [J = 6.6 Hz in addition to smaller (~1 Hz) couplings] at −1.42 ppm. The ^{11}B nmr spectrum at 80.5 MHz indicated three types of boron in the relative ratio of 2:2:6 (see Figure 2).

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

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

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

[6] L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 1157 (1970).

[7] (a) This compound was first reported by L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **6**, 1114 (1965). (b) V. I. Stanko and G. A. Anorova, *Zh. Obshch. Khim.*, **36**, 946 (1966), reported the preparation of this compound by the cyclization of 1-bromopropyl-1,2-carborane with magnesium. (c) L. I. Zakharkin, A. V. Grebennikov, and A. V. Kazantzer, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **9**, 2077 (1967).

Table I. Elemental Analyses of the μ-1,2-Trimethylene-1,2-dicarba-*closo*-dodecaborane(10) System

Compound	% B Calcd	% B Found	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% M Calcd	% M Found
$B_{10}C_5H_{16}$	58.65	58.45	32.58	32.33	8.77	8.46				
$[(CH_3)_4N][B_9C_5H_{16}]$	39.28	38.69	43.64	43.66	11.42	11.74	5.66	5.23		
$[(CH_3)_4N][(B_9C_5H_{15})_2Co^{III}]$	40.47	40.48	35.17	35.09	8.87	9.22	2.93	2.66	12.33	11.80
$[(C_2H_5)_4N][(B_9C_5H_{15})_2Ni^{III}$-A]	36.43	36.27	40.48	40.73	9.46	9.42	2.62	2.67	10.99	11.06
$(B_9C_5H_{15})_2Ni^{IV}$-B	48.20	48.53	29.75	30.07	7.50	6.96			14.57	14.78
$(B_9C_5H_{15})_2Ni^{IV}$-C	48.20	48.37	29.75	29.80	7.50	7.75			14.57	14.87

Preparation and Characterization of μ-1,2-Trimethylene-(3)-1,2-dicarbadecahydro-*nido*-undecaborate(1−) Ion 2. Carborane 1 was found to undergo the typical base degradation of the 1,2- and 1,7-dodecacarboranes.[3] The carborane was gently refluxed in an ethanolic potassium hydroxide solution for 24 hr and the anionic product isolated as the potassium salt. Potassium 2, a white crystalline substance, was found to be fairly hygroscopic and therefore the salt was characterized as its

$$B_{10}C_5H_{16} + 3C_2H_5OH + KOH \longrightarrow K^+[B_9C_5H_{16}]^- + H_2 + H_2O + B(OC_2H_5)_3$$

tetramethylammonium (TMA) salt. A small amount of the potassium 2 was dissolved in water and tetramethylammonium chloride added whereupon TMA 2 precipitated. The salt was isolated by filtration and recrystallized twice from ethanol–water to yield colorless needles. The trimethylammonium salt was prepared in a similar fashion. The results of elemental analysis are shown in Table I.

The ^1H nmr spectrum of TMA 2 at 60 MHz in pyridine contained a singlet at −3.28 ppm of area 12 corresponding to the tetramethylammonium protons, a poorly resolved complex multiplet of area 4 centered at −2.28 ppm corresponding to the 4 inner methylene protons of the ring, and a multiplet of sharp resonances of area 2 centered at −1.77 ppm corresponding to the 2 outer methylene protons. The proton nmr spectrum is complicated by the nonequivalence of the inner and outer proton since the (3) boron atom has been removed and the protons positioned exo with respect to the open face of the carborane fragment are different from those endo to the open face.

The ^{11}B nmr spectrum of trimethylammonium 2 in acetone indicated five types of boron atoms in the ratio of 2:1:4:1:1 (see Figure 2).

Preparation and Characterization of the Bis[π-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]cobalt(III) Complex 3. The addition of anhydrous $CoCl_2$ to a THF (tetrahydrofuran) solution of the dianion 2, $B_9C_5H_{15}^{2-}$, produced a black solution from which red crystals of bis[π-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]cobalt(III) ion, 3, were isolated. As in previous cases,[3,8] metallic cobalt was isolated and the following stoichiometry was assumed.

$$4(B_9C_5H_{15})^{2-} + 3Co^{2+} \longrightarrow Co^0 + 2[(B_9C_5H_{15})_2Co^{III}]^-$$

The ion was found to be extremely air and water stable and was isolated as a variety of salts with cations such as Rb^+, Cs^+, TMA^+, and tetraphenylarsonium. The alkali metal salts could be crystallized from hot water, while the TMA 3 could be isolated as shiny red needles from hot ethanol–water solutions. Elemental analysis results of TMA 3 are shown in Table I.

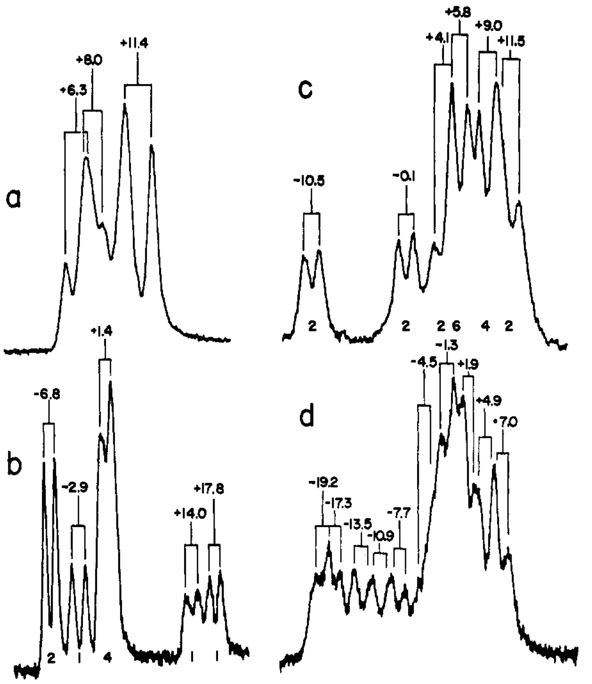

Figure 2. 80-MHz ^{11}B spectra of (a) $B_{10}C_5H_{16}$ in CCl_4, (b) $Me_3NH^+[B_9C_5H_{16}]$ in acetone, (c) $(CH_3)_4N[Co(B_9C_5H_{15})_2]$ in acetonitrile, and (d) $[Ni^{IV}(B_9C_5H_{15})_2$–B] in CH_2Cl_2.

The proton nmr spectrum of TMA 3 at 60 MHz in pyridine consisted of a broad resonance centered at −4.03 ppm of area 4, corresponding to the 4 outer methylene protons, a sharp singlet at −3.34 ppm of area 12 corresponding to the TMA protons, and a broad resonance centered at −2.58 ppm of area 8 corresponding to the 8 inner methylene protons. The ^{11}B nmr spectrum at 80.5 MHz is shown in Figure 2. The spectrum consists of a low-field doublet (−10.5 ppm) of area 2 and a series of grouped resonances of area 16. The results of cyclic voltammetry are included in Table II; TMA 3 exhibited only one reversible wave corresponding to the Co^{III}/Co^{II} couple.

Table II. Electrochemical Data for the Bis(π-μ-1,2-trimethylene-1,2-dicarbollyl)nickel and -cobalt Systems[a]

Compound	$M^{IV} - M^{III}$	$M^{III} - M^{II}$
$[(CH_3)_2N][TM_2Ni^{III}$-A]	+0.60	−0.45
TM_2Ni^{IV}-B	+0.30	−0.80
TM_2Ni^{IV}-C	+0.02	−1.20
$[(CH_3)_4N][TM_2Co^{III}]$		−1.00

[a] Half-peak potentials ($E_{p/2}$) determined by cyclic voltammetry at Pt button electrode in acetonitrile, containing 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte. Scan rate = 6 V/min; all potentials *vs.* sce.

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(8) M. F. Hawthorne and T. A. George, *J. Amer. Chem. Soc.*, **89**, 7114 (1967).

Table III. Reaction Sequence and Electrochemistry of the Bis(π-μ-1,2-trimethylene-1,2-dicarbollyl)nickel System[a]

$$\mathrm{Ni(acac)_2} + \mathrm{TM^{2-}} \xrightarrow{\text{benzene–ether}}$$

$$\begin{tikzcd}
\text{Series A} & {[TM_2Ni^{II}\text{-}A]^{2-}} \arrow[r, shift left] & {[TM_2Ni^{III}\text{-}A]^{-}} \arrow[l, shift left, "-0.45\ V"] \arrow[r, shift left] \arrow[dr, "{[O]}"] & {[TM_2Ni^{IV}\text{-}A]} \arrow[l, shift left, "+0.60\ V"] \arrow[d, "0°"] \\
\text{Series B} & {[TM_2Ni^{II}\text{-}B]^{2-}} \arrow[r, shift left] & {[TM_2Ni^{III}\text{-}B]^{-}} \arrow[l, shift left, "-0.80\ V"] \arrow[r, shift left] & {[TM_2Ni^{IV}\text{-}B]} \arrow[l, shift left, "+0.30\ V"] \arrow[d, "150°"] \\
\text{Series C} & {[TM_2Ni^{II}\text{-}C]^{2-}} \arrow[r, shift left] & {[TM_2Ni^{III}\text{-}C]^{-}} \arrow[l, shift left, "-1.20\ V"] \arrow[r, shift left] & {[TM_2Ni^{IV}\text{-}C]} \arrow[l, shift left, "+0.20\ V"]
\end{tikzcd}$$

[a] $TM^{2-} = B_9H_9C_2(CH_2)_3{}^{2-}$; acac = $(CH_3COCHCOCH_3)^-$.

Bis[π-μ-1,2-Trimethylene-(3)-1,2-dicarbollyl]nickel System. {Bis[π-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]-nickel(III)}$^-$, $[TM_2Ni^{III}]^-$,[9] **4**, was isolated from the reaction of $KB_9C_5H_{16}$ with butyllithium and nickel acetylacetonate in benzene–ether solution.

$$B_9C_5H_{16}{}^- + n\text{-BuLi} \longrightarrow B_9C_5H_{15}{}^{2-} + C_4H_{10} + Li^+$$

$$2B_9C_5H_{15}{}^{2-} + Ni(acac)_2 \longrightarrow [TM_2Ni^{II}]^{2-}$$

$$[TM_2Ni^{II}]^{2-} \xrightarrow{[O]} \underset{\mathbf{4}}{[TM_2Ni^{III}]^-}$$

The anion **4** was isolated in 42% yield as its dark brown, paramagnetic (d^7), tetraethylammonium (TEA) salt. Results of the elemental analyses are shown in Table I. The tetramethylammonium salt was obtained in 88% yield using the same procedure.

Oxidation of TEA in CH_2Cl_2 yielded an orange, neutral, diamagnetic nickel(IV) species according to the following scheme.

$$TEA[TM_2Ni^{III}] + {}^3/_2I_2 \longrightarrow [TM_2Ni^{IV}]^0 + TEAI_3$$

The results of the elemental analyses are shown in Table I; the mass spectrum had a cutoff peak at *m/e* 408 corresponding to $^{11}B_{18}{}^{12}C_{10}{}^{1}H_{30}{}^{60}Ni$. Care must be taken when isolating the product; *i.e.*, the solvents must be kept at room temperature, or a mixture of compounds is obtained. Heating solutions of the orange $[TM_2Ni^{IV}]^0$ above 100° for a few minutes resulted in the formation of a bright yellow $[TM_2Ni^{IV}]^0$ species. This was analogous to the bis[π-1,2-dimethyl-(3)-1,2-dicarbollyl]nickel(IV) (abbreviated $[(Me_2)_2Ni^{IV}]^0$) system.[6] The orange isomer is designated with the letter B, corresponding to series B, while the yellow isomer designated C, corresponding to series C (see Table III). The isomeric nature of the two nickel(IV) compounds was confirmed by analysis and mass spectral data.

Polyhedral Rearrangements of Bis[π-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]nickel(IV) Systems. As in the $[(Me_2)_2Ni]$ series[6] it is believed the initial $[TM_2Ni^{II}\text{-}A]^{2-}$ isomer formed in the reaction of the dicarbollyl anion with nickel acetylacetonate has the slipped-sandwich configuration[10] (see Figure 3).

Upon oxidation of this species to the $[TM_2Ni^{III}]^-$ compound, the ligands assume the normal trans configuration which is depicted in Figure 3. Oxidation of the $[TM_2Ni^{III}\text{-}A]^-$ compound results in the rotation of the ligand to the cisoid configuration.[11] However, due to the steric interactions of the methyl groups in the $[(Me_2)_2Ni]$ system and the methylene groups in the $[TM_2Ni]$ system, a ligand rearrangement occurred. One important question that had to be solved in the $[(Me_2)_2Ni]$ system was whether the carbon atoms remained nearest neighbors (1,2) or had become separated (1,7) as observed in other rearrangement reactions observed for polyhedral borane and carborane species.[12] The $[TM_2Ni]$ system neatly resolved this

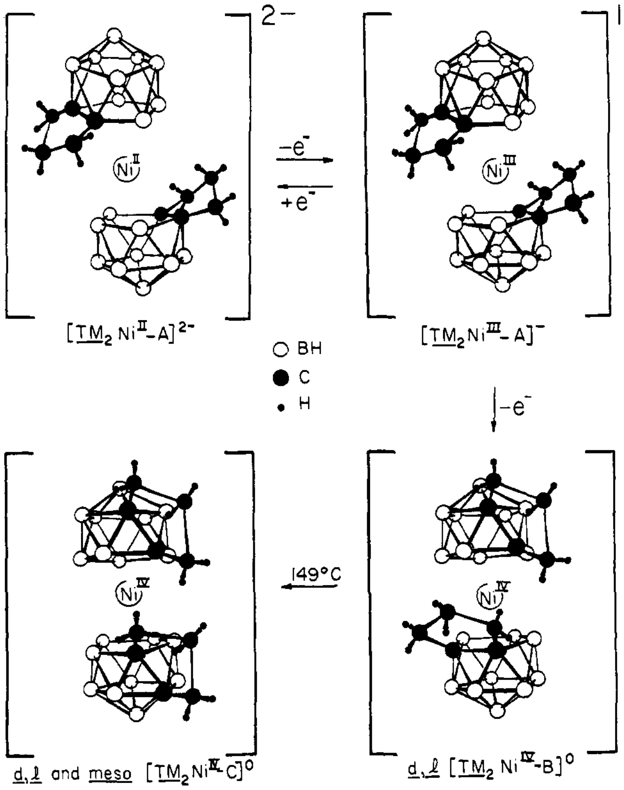

Figure 3. Reaction sequence and stereochemistry of the bis(π-μ-1,2-trimethylene-1,2-dicarbollyl)nickel system.

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[9] The trimethylene dicarbollyl ligand is hereafter abbreviated as TM, in accordance with the abbreviated notation for the nickel system as introduced by Warren.[6]

[10] The $[TM_2Ni^{II}]^{2-}$ isomers were not isolated because they readily oxidize to the nickel(III) ions.

(11) Several examples of substituted ferrocene derivatives which reside in cisoid configuration are also known: see M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part I, Interscience, New York, N. Y., 1965.

(12) (a) H. V. Hart and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **91**, 771 (1969), and references cited therein; (b) H. Schroeder and G. D. Vickers, *Inorg. Chem.*, **2**, 1317 (1963); (c) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963); (d) R. M. Salinger and C. L. Frye, *ibid.*, **4**, 1915 (1965); (e) Y. Ta-Ching, M.S. Thesis, University of California, Riverside, 1968; (f) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 5434 (1964).

problem because the outer methylene group locked the carbon atoms of the icosahedral fragment in a 1,2 configuration. If no isomers were detected in the [TM_2Ni] series, it could be assumed that a 1,7 rearrangement had occurred in the [$(Me_2)_2Ni$] system.[13] However, the facile isomerization of the initially isolated TM_2Ni^{IV}-B makes it reasonable to assume that a 1,2 shift had occurred in which one of the carbons migrated from the facial "belt" of the icosahedral fragment to the second "belt" of atoms.[14]

The [TM_2Ni^{IV}-B] exists as a *dl* enantiomorphic mixture and the [TM_2Ni^{IV}-C] may exhibit both *dl* and meso forms. The resolution of the various optically active [$(Me_2)_2Ni^{IV}$] isomers has previously been reported.[6]

This migration could occur by the "diamond-square-diamond" mechanism suggested by Lipscomb,[15] or by the "rotation of triangular faces" mechanism suggested by Muetterties,[16] or by a combination of mechanisms.[17]

The cyclic voltammetry of TMA [TM_2Ni^{III}-A] in acetonitrile at low temperature (Figure 4) indicated that a chemical reaction, *i.e.*, ligand rearrangement, had occurred following oxidation to a formal Ni(IV) complex (EC mechanism). Reverse current chronopotentiometry was used to measure the rates of the follow-up reaction. The details for the study of homogeneous chemical reactions following electron transfer have been fully described in the literature.[18]

The rates of the follow-up chemical reaction are listed in Table IV and are consistent with the following scheme.

Table IV. Rate Constants Obtained by Reverse Current Chronopotentiometry for the Rearrangement of Series A to Series B Compounds

Compound	Temp, °C	Concn, mM^a	k, sec^{-1}
[$(Me_2)_2Ni^{IV}$]	25	0.5–5.0^b	0.082 ± 0.003
	35	5.0	0.26 ± 0.01
	45	5.0	0.64 ± 0.04
[TM_2Ni^{IV}]	−1.2	5.0	0.33 ± 0.02
	5	0.5–5.0^b	0.84 ± 0.02
	15	5.0	2.60 ± 0.23

^{a} Acetonitrile solutions containing 0.1 M tetraethylammonium perchlorate. The working electrode was a platinum button. ^{b} Concentration dependence performed to verify a first-order mechanism.

$$[TM_2Ni^{III}\text{-}A]]^- \rightleftarrows [TM_2Ni^{IV}\text{-}A]^0 + e^-$$

$$[TM_2Ni^{IV}\text{-}A] \xrightarrow{k} [TM_2Ni^{IV}\text{-}B]$$

Similar behavior was observed for the [$(Me_2)_2Ni$]$^-$ system, and the rates of this rearrangement are included in Table IV.

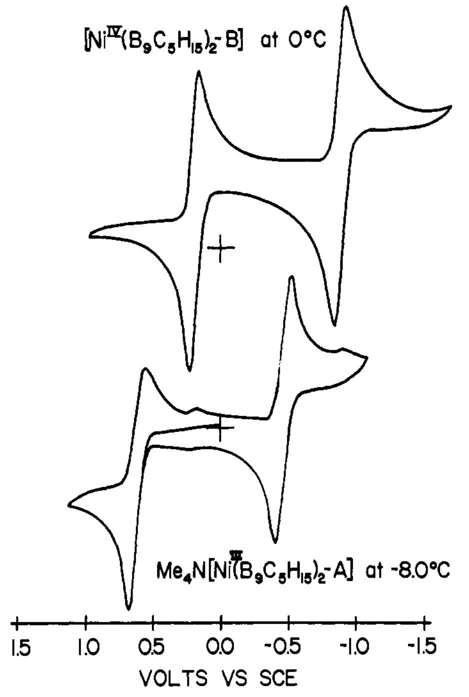

Figure 4. Cyclic voltammetry of $(CH_3)_4N[Ni^{III}(B_9C_5H_{15})_2\text{-}A]$ and [$Ni^{IV}(B_9C_5H_{15})_2$-B] in acetonitrile (0.1 M tetraethylammonium perchlorate), Pt button electrode, scan rate = 6 V/min.

The rates of the rearrangement of [$(Me_2)_2Ni^{IV}$-B] and [TM_2Ni^{IV}-B] were obtained by following the decrease of the visible absorption peaks at 480 and 460 nm, respectively, with time. The rate constants obtained from the slope of a plot of $-\log[(A_t - A_\infty)/(A_0 - A_\infty)]$ *vs.* t are shown in Table V and the activation parameters are shown in Table VI.

Table V. Rate Constants for the Rearrangement of Series B to Series C Isomers

Compound^a	Temp, °C	$k \times 10^5$, sec^{-1}
[TM_2Ni^{IV}-B]	85.0	4.81
	90.0	9.72
	95.0	18.4
[$(Me_2)_2Ni^{IV}$-B]	74.3	5.67
	79.2	11.3
	84.5	22.8

^{a} In cyclooctane solution.

Table VI. Activation Parameters for the Polyhedral Rearrangements of Ni(IV) Complexes

Reaction	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
[$(Me_2)_2Ni^{IV}$] A → B	19 ± 2	3 ± 3
[TM_2Ni^{IV}] A → B	20 ± 2	14 ± 7
[$(Me_2)Ni^{IV}$] B → C	34 ± 1	20 ± 5
[TM_2Ni^{IV}] B → C	35 ± 1	22 ± 5

Discussion

The μ-1,2-trimethylene-(3)-1,2-dicarbadecahydro-*nido*-undecaborate(1−) ion forms complexes after deprotonation analogous to the other dicarbollide ligand systems. The overall chemistry of the nickel complexes is very similar to the previously reported complexes of

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(13) The sharpness of the methyl protons in the ^1H nmr spectra of the [$(Me_2)_2Ni$] series precluded any methyl group migrations from carbon to boron atoms, as B–CH_3 resonances are generally very broad.

(14) This structure has since been conclusively verified by an X-ray structure carried out on the orange [$(Me_2)_2Ni^{IV}$-B]^0 isomer: K. Gold and M. R. Churchill, *J. Amer. Chem. Soc.*, **92**, 1180 (1970).

(15) W. N. Lipscomb, *Science*, **153**, 373 (1966).

(16) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, pp 69–71.

(17) M. K. Kaloustian, Richard J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, in press.

(18) D. Hawley and R. N. Adams, *J. Electroanal. Chem.*, **10**, 376 (1965).

the 1,2-dimethyl-(3)-1,2-dicarbollide ion and is shown schematically in Table III. Both systems involve di-C-substituted ligands and exhibit facile ligand rearrangements. The formal designation of the [TM_2Ni^{IV}-B] complex is *dl*-[π-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]nickel(IV)[π-μ-1,6-trimethylene-(3)-1,6-dicarbollyl]. The series C isomer is designated *dl*- or *meso*-bis[π-μ-1,6-trimethylene-(3)-1,6-dicarbollyl]nickel(IV).

The facile ligand rearrangement is presumably a result of steric interactions between the carbon substituents on opposite cages. The isoelectronic (d^6) Fe(II) and Co(III) compounds do not exhibit this phenomenon, except at high temperature (400–600°).[19] The [$Ni^{IV}(B_9C_2H_{11})_2$] complex retains a cisoid ligand arrangement in the solid state with a very short metal ligand distance (1.47 Å) presumably brought about by high nuclear charge existing on the metal in the complex.[20]

The activation parameters which have been determined for a number of various polyhedral rearrangements involving carboranes and metallocarboranes are shown in Table VII. In a majority of the cases examined to date the driving force for the rearrangement appears to be the separation of the carbon atoms to alleviate the electrostatic repulsions of the carbon atoms when they are directly bonded.[12a] Available data[12d] suggest that the introduction of bulky substituents lowers the enthalpy of activation, presumably due to steric interactions. The entropy of activation has been approximately zero or slightly positive in all cases observed thus far and indicates only a modest relief of steric interaction in forming the transition state.

Table VII. Activation Parameters for Polyhedral Rearrangements

Compound	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
1,2-$B_{10}C_2H_{12}$ → 1,7-$B_{10}C_2H_{12}$	62	+7	12d
1,2 → 1,7-bis(methyldiphenylsilyl)-carborane	45	−1	12d
(1,6-$B_7C_2H_9$)Co(π-C_5H_5) → (1,10-$B_7C_2H_9$)Co(π-C_5H_5)	34	+3	12e
1,6-$B_8C_2H_{10}$ → 1,10-$B_8C_2H_{10}$	49	+5	12e
1,6-$B_8C_2H_8(CH_3)_2$ → 1,10-$B_8C_2H_8(CH_3)_2$	50	+5	12e
2,3-$B_{10}H_8[N(CH_3)_3]_2$ → 1,6-$B_{10}H_8[N(CH_3)_3]_2$	37	+2.4	12f

In the case of the $(Me_2)_2Ni^{IV}$ and TM_2Ni^{IV} the rearrangements do not involve separation of carbon atoms, but only migration of one carbon atom away from the metal-bonding face of the complexed ligand. Consequently the lowering of the enthalpy of activation must certainly be a reflection of the gross steric interactions which are present when the substituents are brought into a "cisoid" configuration in the Ni^{IV} species. This relief of steric interaction is observed in the higher enthalpy of activation in the second rearrangement (B → C). The exact nature of the transition state involved in rearrangement of metal-coordinated carboranes is unknown, and therefore the specific interactions which effect the activation parameters can only be qualitatively evaluated. The decrease in the enthalpy of activation in both of these rearrangements can be explained on the basis of ligand repulsions; however, the geometry of the transition state which gives rise to the higher values of $\Delta S^{\ddagger}$ can only be ascribed to a gross relief of steric interactions in a transition state which is obviously quite different from all previous types of polyhedral rearrangements.

The isomerization of a (3)-1,2- to a (3)-1,6-dicarbollide ligand in the bis(dicarbollyl)nickel complexes results in a lowering of the Ni^{III}/Ni^{IV} and Ni^{III}/Ni^{II} redox couple. This suggests that the rearranged ligand with its pentagonal B_4C bonding face donates more electron density to the metal atom than the B_3C_2 face. The same effect has been observed in the Co^{III}/Co^{II} couple in the rearranged (π-C_5H_5)Co($B_9C_5H_{15}$) system.[19] The rearranged ligands in the nickel system therefore tend to stabilize the higher (4+) oxidation state and by the same reasoning to destabilize the lower (2+) oxidation state.

Experimental Section

Physical Measurements. Infrared spectra were obtained using a Perkin-Elmer Model 137 infrared spectrophotometer. Proton nmr spectra at 60 MHz were obtained using a Varian A-60 spectrometer. ^1H and ^{11}B nmr spectra at 250 and 80.5 MHz, respectively, were obtained on an experimental superconducting system designed and constructed by Professor F. A. L. Anet of this department.

The electrochemical apparatus for cyclic voltammetry and reverse current chronopotentiometry was based on the design of Hawley.[21] The apparatus for controlled potential electrolysis and coulometry was of conventional design,[22] employing a Hewlett-Packard Model 301A operational amplifier/power supply (±50 V, 1 amp) and a Dymec Model 2211BR voltage to frequency converter and Hewlett-Packard Model 521 C electronic counter. Current–voltage and voltage–time curves were obtained on a Hewlett-Packard Model 7030A X-Y recorder. All measurements were made in acetonitrile using 0.1 *M* tetraethylammonium perchlorate as the supporting electrolyte. The working electrode was a Pt inlay electrode (Beckman Model 39273). Potentials were measured *vs.* a saturated calomel electrode.

Mass spectra were obtained using an Associated Electrical Industries MS-9 spectrometer and visible spectra were obtained using a Beckman Model DB spectrophotometer.

Materials. 1,2-Dicarba-*closo*-dodecaborane(12) was sublimed in high vacuum prior to use. Butyllithium, as a 1.6 *M* solution in *n*-hexane, was used as received from Foote Mineral Co. Tetraethylammonium perchlorate was obtained from Eastman Organic Chemicals and was recrystallized from water and dried at 80° under high vacuum.

Tetrahydrofuran and diethyl ether were freshly distilled from $LiAlH_4$ and collected under nitrogen. Benzene and cyclooctane were distilled from CaH_2 and collected under nitrogen. Hexane and dichloromethane were reagent grade and dried over molecular sieves. Baker "Analyzed Reagent" silica gel was employed in chromatography.

Anhydrous $CoCl_2$ was prepared by heating (at ~100°) $CoCl_2 \cdot 6H_2O$ in a 500-ml round-bottom flask attached to a vacuum line for approximately 10 hr. The anhydrous $CoCl_2$ was then stored in a nitrogen-filled drybox. Nickel acetylacetonate was purchased from Research Organic/Inorganic Chemical Corp., Sun Valley, Calif. The compound was first crystallized from benzene and then sublimed in high vacuum. The pure material was then stored in a nitrogen atmosphere. Aldrich Chemical Co. supplied the 1,3-dibromopropane which was distilled from molecular sieves prior to use.

Preparation of μ-1,2-Trimethylene-1,2-dicarba-*closo*-dodecaborane(10), $B_{10}C_5H_{16}$ (1). To a 500-ml, three-necked flask equipped with

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[19] M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 4912 (1971).

[20] D. St. Clair, A. Zalkin, and D. H. Templeton, *ibid.*, **92**, 1173 (1970).

[21] J. D. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969).

[22] (a) J. G. Lawless, D. E. Bantak, and M. D. Hawley, *J. Amer. Chem. Soc.*, **91**, 7121 (1969); (b) A. J. Bard, *Anal. Chem.*, **35**, 1125 (1963).

stirring apparatus and a reflux condenser was added 10.0 g (0.0695 mol) of 1,2-dicarba-*closo*-dodecaborane(12). The flask was flushed with dry nitrogen and approximately 250 ml of dry ethyl ether added to dissolve the carborane. The solution was cooled to 0° and *n*-butyllithium (0.160 mol, 100 ml) was introduced from a syringe. The bislithium salt of the carborane immediately precipitated from solution and the mixture was stirred for 2 hr.

Dry 1,3-dibromopropane (0.0695 mol, 7.1 ml) was added to the mixture and the solution was allowed to stir 4.8 hr at reflux. At the end of that time the solution was hydrolyzed and washed with water three times. The organic layer was dried over anhydrous $\mathrm{MgSO_4}$ and filtered. The solvent was removed by rotary evaporation, unreacted dibromopropane was distilled past a 0° cold finger, and the residue sublimed under high vacuum. The crude carborane **1** was obtained as a white solid in 61.3% yield. The carborane could be further purified by crystallization from ethanol–water followed by a final sublimation. The infrared spectrum of $\mathrm{B_{10}C_5H_{16}}$ (Nujol mull) exhibited bands at 2577 vs, 1333 w, 1179 s, 1024 s, 970 m, 939 m, 914 m, 833 s, 759 vs $\mathrm{cm^{-1}}$.

Preparation of μ-1,2-Trimethylene-(2)-1,2-dicarbadecahydro-*nido*-undecaborate(1−) Ion, $\mathrm{B_9C_5H_{16}^-}$ (2). To a 500-ml, three-necked flask equipped with a reflux condenser, nitrogen bubbler, and magnetic stirring apparatus were added 8.3 g (0.140 mol) of KOH and 135 ml of ethyl alcohol. After the KOH had dissolved 13.6 g (0.074 mol) of carborane **1** was added and the solution heated to gentle reflux for 24 hr. The solution was then cooled and small chunks of solid $\mathrm{CO_2}$ were added until precipitation of $\mathrm{K_2CO_3}$ ceased. The solution was filtered and the addition of $\mathrm{CO_2}$ repeated. The solution was then stripped and the resulting oil taken up in about 300 ml of benzene. The remaining ethanol and $\mathrm{H_2O}$ were azeotroped from the solution and the solid potassium salt of the monoanion (hygroscopic) was isolated by filtration under a nitrogen atmosphere. The solid was transferred to a Soxhlet thimble and extracted 36 hr with dry benzene. The crystalline monoanion **2** was collected by filtration and stored in a nitrogen-filled drybox. The yield was 11.7 g (74.3%) of pure potassium monoanion **2**. The infrared spectrum of $\mathrm{KB_9C_5H_{16}}$ (Nujol mull) exhibited bands at 2519 vs, 1307 m, 1259 w, 1227 w, 1188 m, 1082 w, 1035 s, 1006 m, 946 m, 899 s, 722 m $\mathrm{cm^{-1}}$.

A small amount of the monoanion **2** was dissolved in a small amount of water and precipitated by the addition of tetramethylammonium chloride. The tetramethylammonium salt of **2** was recrystallized from ethanol–water. The infrared spectrum of $\mathrm{[(CH_3)_4N]B_9C_5H_{16}}$ (Nujol mull) exhibited bands at 2519 vs, 2457 s, 1475 s, 1167 w, 1067 w, 1026 m, 950 s, 897 m, 722 m $\mathrm{cm^{-1}}$.

Preparation of Bis[π-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]cobalt(III) $\mathrm{[(B_9C_5H_{15})_2Co^{III}]^-}$ (3). A 200-ml, three-necked flask was fitted with a reflux condenser and magnetic stirring apparatus. The potassium salt of the monoanion **2** was weighed in a nitrogen-filled drybox (2.0 g, 9.4 mmol) and placed in the reaction flask which was maintained in a nitrogen atmosphere. Approximately 75 ml of dry THF was added and 6.3 ml of *n*-butyllithium added with a syringe. The solution was stirred for 1 hr. Anhydrous $\mathrm{CoCl_2}$ (1.9 g, 14.4 mmol) was added and an immediate darkening of the solution was noted. The solution was briefly heated to reflux and the solution allowed to cool slowly while constantly stirring. After stirring the mixture for an additional 2 hr, the solution was filtered through Celite and the solvent removed. The residue was dissolved in ether and filtered, and the ether was removed by rotary evaporation. Finally the residue was dissolved in 100 ml of water and divided into two equal portions. To one portion an aqueous solution of CsCl was added, while an aqueous solution of tetramethylammonium (TMA) chloride was added to the other. Both salts were isolated by filtration and recrystallized from ethanol–water to yield small red blocks of the cesium complex **3** and red needles of the TMA complex **3**. The total yield was 46.3%. The infrared spectrum of $\mathrm{Cs[(B_9C_5H_{15})_2Co^{III}]}$ (Nujol mull) exhibited bands at 2532 vs, 1307 w, 1286 w, 1208 m, 1070 s, 1013 s, 936 w, 922 w, 900 m, 797 m, 772 m, 743 m $\mathrm{cm^{-1}}$. The infrared spectrum of $\mathrm{(CH_3)_4N[(B_9C_5H_{15})_2Co^{III}]}$ (Nujol mull) exhibited bands at 2525 vs, 1314 w, 1198 w, 1066 s, 1008 s, 966 m, 945 s, 921 w, 894 m, 796 m, 718 m $\mathrm{cm^{-1}}$.

Bis[π-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]nickel System. (a) **$\mathrm{(C_2H_5)_4N[TM_2Ni^{III}]}$ (4).** Potassium **2** (3.0 g, 14.1 mmol) was dissolved in the minimum amount of dry ethyl ether (21–22 ml) in a 500-ml, three-necked flask equipped with a reflux condenser and high-speed stirring apparatus. The system was maintained under a dry nitrogen atmosphere. Approximately 200 ml of dry benzene was added followed by the addition of 10 ml of *n*-butyllithium *via* syringe. A white precipitate formed immediately and the slurry was stirred for 1 hr. Nickel acetylacetonate (1.6 g, 7.05 mmol) dissolved in hot benzene was added and the mixture heated to a gentle reflux for 6 hr.

The resulting straw-colored solution was cooled and the solvent removed by rotary evaporation. The residue was dissolved in ethyl ether and a small amount of HCl added to catalyze the oxidation of nickel from the formal 2+ oxidation state to the formal 3+ oxidation state. The solution darkened to a red-brown color and the solution was filtered and stripped. The resulting oil was dissolved in the minimum amount of $\mathrm{CH_2Cl_2}$ and combined with a $\mathrm{CH_2Cl_2}$ solution of $\mathrm{(C_2H_5)NBr}$ (3.0 g, 14.1 mmol). The solution was quickly chromatographed through silica gel and crystallized from $\mathrm{CH_2Cl_2}$–hexane by slow rotary evaporation; yield, 1.6 g of dark brown $\mathrm{(C_2H_5)_4N[(B_9H_5H_{15})_2Ni^{III}]}$ (42.6%). The infrared spectrum of $\mathrm{(C_2H_5)_4N[(B_9C_5H_{15})_2Ni^{III}]}$ (Nujol mull) exhibited bands at 2551 vs, 1302 w, 1174 m, 1066 m, 1053 w, 1020 w, 1002 m, 908 m, 853 m, 701 m, 725 m $\mathrm{cm^{-1}}$.

(b) **Preparation of $\mathrm{[TM_2Ni^{IV}–B]}$ (5).** To a stirred dichloromethane solution of complex **4** (1.0 g, 1.82 mmol) was added a dichloromethane solution of iodine (0.713 g, 2.81 mmol). The solution was stirred for 0.5 hr and then diluted twofold with hexane. The solution was filtered and quickly passed through a short column of silica gel (~1.5 in.). The resulting red-orange solution was then slowly stripped to yield 0.49 g (67%) of orange crystalline $\mathrm{[TM_2Ni^{IV}–B]}$ (**5**). The infrared spectrum of $\mathrm{[TM_2Ni^{IV}–B]}$ (Nujol mull) exhibited bands at 2564 vs, 1302 w, 1156 w, 1117 w, 1081 w, 1067 m, 1010 w, 993 s, 962 m, 913 m, 886 w, 887 w, 860 w, 735 m $\mathrm{cm^{-1}}$.

(c) **Preparation of $\mathrm{[TM_2Ni^{IV}–C]}$ (6).** Upon heating a cyclooctane solution of complex **5** to 150° for 30 min, the compound was converted to the yellow $\mathrm{[TM_2Ni^{IV}–C]}$ (**6**). The solution of **6** was quickly passed through a short column (~1.5 in.) of silica gel packed in a 2:1 solution of hexane–dichloromethane and was recovered in essentially quantitative yield after removal of the solvent. The infrared spectrum of $\mathrm{[TM_2Ni^{IV}–C]}$ (Nujol mull) exhibited bands at 2584 s, 1316 w, 1157 w, 1085 w, 1012 m, 996 m, 897 m, 741 m $\mathrm{cm^{-1}}$.

Electrochemical Kinetics. The cell was a sample jar with a Teflon top which was drilled to accommodate the Pt button working electrode, the sce reference electrode, the Pt foil auxiliary electrode, and a nitrogen bubbler. The temperature was maintained by a thermoregulator connected to a DPDT laboratory relay. For the temperature studies at and above room temperature $\mathrm{[(Me_2)_2Ni^{III}}$: 25, 35, and 45°] a heater and large water bath served as the thermostat. In the low-temperature studies $\mathrm{[TM_2Ni^{III}}$: −1.2, 5, and 15°] a refrigeration unit was used with the inverse outlet of the relay and a large Dewar held the equipment. A presaturation bubbler filled with acetonitrile and maintained at the temperature of the experiment was used to degas the solution. All solutions were 0.1 *M* in tetraethylammonium perchlorate. The solutions were degassed for at least 15 min with presaturated, dry, oxygen-free nitrogen.

Preliminary experiments were performed to determine the time range which would give reproducible results. Owing to non-Faradic processes at short times and convection at long times,[23] the nickel III/II reversible couple was examined by reverse current chronopotentiometry. With a current ratio of $(i_r/i_f) = 0.414$ the nickel III/II couple exhibited the theoretical ratio of $(\tau_r/t_f) = 1.00 \pm 0.05$ when $1.00 \leq t_f \leq 5.00$ sec. The reverse transition time was measured using the Kuwana method.[24]

For each temperature, the current ratio (i_r/i_f) was set (0.225, 0.110, or 0.050) to make $0.5 \leq \tau_r/t_f \leq 1.5$. From the experimental value of τ_r/t_f a value of kt_f was obtained from the working curve of (τ_r/t_f) *vs.* kt_f. The rate constant was determined from the slope of the linear plot of kt_f *vs.* t_f. A minimum of ten points was determined on each solution.

Kinetics of Series B to Series C Isomerization. Cyclooctane solutions of $\mathrm{[TM_2Ni^{IV}–B]}$ and $\mathrm{[(Me_2)_2Ni^{IV}–B]}$, approximately 1×10^{-4}, were prepared. The absorption spectrum of each compound was obtained (A_0). The solutions were then placed in an oil bath maintained at the appropriate temperature. Samples were withdrawn by a syringe at various intervals and cooled in an ice bath. The absorption spectra were recorded on each of these samples to yield A_t. A small portion of the original cyclooctane

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(23) A. J. Bard, *Anal. Chem.*, **35**, 340 (1963).

(24) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, pp 172–185.

solution was heated to 150° for 5 min [$(Me_2)_2Ni^{IV}$] or 30 min (TM_2Ni^{IV}) and cooled and the absorption spectra were obtained to yield A_∞. The rate constants were obtained from linear plots of $-\log (A_t - A_\infty/A_0 - A_\infty)$ *vs.* t. Plots of $\log k$ *vs.* $1/T$ gave the activation parameters.

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Acidity of Hydrocarbons. XXXIX. H_- Acidity Function for Methanolic Sodium Methoxide (H_M) Based on Ionization of a Hydrocarbon Acid[1]

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Abstract: p*K* values of 1,3-diphenylindene and fluoradene were determined to be 19.8 and 18.2, respectively, in methanol at 25°. An H_- scale for methanolic sodium methoxide (H_M) has been constructed from the ionization of 1,3-diphenylindene. This H_M scale gives an excellent linear correlation with the logarithm of the pseudo-first-order rate constants of base-catalyzed protodetritiation reaction of fluorene in NaOMe–MeOH.

The H_- acidity function[2] measures the ability of a basic medium to ionize an acid, HA, to form the anion A^-, and is defined as

$$H_- = pK_{HA} - \log [HA]/[A^-] = -\log (a_{H^+}f_{A^-})/f_{HA} \quad (1)$$

For a methanol solution, pK_{HA} is the ionization constant of HA in methanol and the activity coefficient, f, refers to methanol as standard state. Several authors have used H_M for H_- in methanol, where the use of subscript, M, denotes the acidity function for methanol instead of water as standard state.

The existing H_M scales have been determined by using nitrogen and oxygen acids as indicators, whereas most kinetic investigations involve base-catalyzed breaking of C–H bonds. In fact, for acids of different structure the ratio f_{A^-}/f_{HA} cannot be assumed to be the same at a given solvent composition. Thus, $H_-(H_M)$ scales depend on the type of indicator used.[3,4] With substituted anilines and diphenylamines as indicators, H_M scales for methanolic sodium methoxide have been reported by Schaal and Lambert,[5] and More O'Ferrall and Ridd.[6] The two scales agree satisfactorily when the same value of pK_{MeOH} is used. Rochester[7] used *o-tert*-butylphenol, di-*o-tert*-butylphenol, and pentamethylphenol to set up three H_M scales which differ slightly from one another but differ substantially from the H_M acidity function derived from amine indicators.

Bowden and Stewart[8] constructed an H_- scale for the system DMSO–EtONa using only carbon acids as indicators. They started with malononitrile in water and established the p*K* values of 9-cyanofluorene, 9-methoxycarbonylfluorene, and tris- and bis(4-nitrophenyl)-methane. The latter compound was compared with 9-phenylfluorene and with fluorene. However, it is by no means certain that the various substituted carbon acids used are really more similar to hydrocarbon acids than nitrogen acids. That is, an important contributor to variations in f_{A^-}/f_{HA} is hydrogen-bonding solvation toward A^-.[9] In the present work we report an H_M acidity function derived solely from hydrocarbons whose conjugate bases are delocalized carbanions for which hydrogen-bonding solvation is minimal.

Experimental Section

The preparations of 1,3-diphenylindene, DPI, and fluoradene, FD, have been described.[10] The sodium methoxide solutions were prepared by adding freshly cut and cleaned sodium to cooled absolute methanol under argon or nitrogen atmosphere. The resulting sodium methoxide solutions were degassed on the vacuum line and pressured with argon. The sodium methoxide concentrations were determined by titration with standard acid.

Since the carbanions studied here are sensitive to air, all materials were handled under an argon atmosphere. The apparatus for equilibrium measurements has been described.[11] For runs in which the sodium methoxide concentration was less than 0.5 *M*, a modified apparatus was used in which a cylindrical Pyrex absorption cell of path length 4.54 cm replaced the 1.00-cm cell. The solid hydrocarbon was added to either apparatus which was then attached to the vacuum line and evacuated. The entire system was pressured with argon. A known amount of degassed absolute methanol was added to the apparatus and the mixture was shaken until the hydrocarbon dissolved. A known amount of sodium methoxide solution was introduced by a syringe. After mixing

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(1) This research was supported in part by Grant No. 12855 of the National Institutes of Health, U. S. Public Health Service.

(2) (a) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932); (b) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957); (c) K. Bowden, *ibid.*, **66**, 119 (1966).

(3) E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, **89**, 2751 (1967).

(4) R. H. Boyd, *ibid.*, **85**, 1555 (1963).

(5) R. Schaal and G. Lambert, *J. Chim. Phys.*, 1164 (1962).

(6) R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5030 (1963).

(7) (a) C. H. Rochester, *Quart. Rev., Chem. Soc.*, 511 (1966); (b) C. H. Rochester, "Acidity Functions," Academic Press, London and New York, 1970, Chapter 7.

(8) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

(9) C. D. Ritchie in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 219.

(10) A. Streitwieser, Jr., C. J. Chang, and W. Hollyhead, *J. Amer. Chem. Soc.*, in press.

(11) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin and J. I. Brauman, *J. Amer. Chem. Soc.*, **89**, 59 (1967); G. Häfelinger and A. Streitwieser, Jr., *Chem. Ber.*, **101**, 657 (1968).