formed, $\Delta H_{-1}^{\mp}$ (= 27.7 ± 0.8) then measures the strength of the bond between Ru(II) and N_2, while $\Delta H_1^{\mp}$ measures the strength of the bond between Ru(II) and H_2O.[16] A water molecule is undoubtedly a stronger base than N_2 when each forms only σ bonds. Thus, the extra stabilization which results from the involvement of the π orbitals of Ru is likely well in excess of 9 kcal/mol.[17]

(16) A. E. Shilova and A. E. Shilov, *Kinet. Katal.*, **10**, 267 (1969). These authors conclude that the value of 23 kcal/mol which they measured as the activation energy for the decomposition of $RuN_2Cl_2(H_2O)_2$·THF in THF corresponds to the energy of the Ru–N_2 bond.

(17) NOTE ADDED IN PROOF. C. Elson, I. J. Itzkovitch, and J. A. Page, *Can. J. Chem.*, **48**, 1639 (1970), recently reported a value of $\Delta H^{\mp} = 22.0 \pm 0.1$ kcal/mol for the formation of $Ru(NH_3)_5N_2^{2-}$. Part of the discrepancy in the results may lie in the values taken for the concentration of N_2 in solution. The values listed for the solubility of N_2 in water at various temperatures appear not to have been calculated by them with

regard to the reference temperature listed in the table given in Stephen and Stephen.[11] For example, our values compare well with those obtained by other authors and techniques as listed in the "International Critical Tables" (Vol. 3, p 255): 25.0°, 6.32×10^{-4} M; 35.0°, 5.54×10^{-4} M. However, the difference in solubility does not completely explain all the differences in the results. Since we obtained similar results for $\Delta H_1°$ by both the static and kinetic methods and because of the similarity in the values of $\Delta H^{\mp}$ (16.5 to 19 kcal/mol) for the formation of $Ru(NH_3)_5X^{2-}$ complexes, where X is also N_2O (J. Armor and H. Taube, submitted for publication), and numerous neutral, nitrogen-base heterocycles (private communication with R. Shepherd and H. Taube), we believe that our value of $\Delta H_1^{\mp}$ is more nearly correct.

Determination of the Electronic Properties of Carboranes, Carborane Anions, and Metallocarboranes from Fluorine-19 Nuclear Magnetic Resonance Studies[1]

Robert G. Adler[2] and M. Frederick Hawthorne[3]

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Abstract: The preparation of the carbon-substituted *m*- and *p*-fluorophenyl derivatives of a series of carboranes, carborane anions, and metallocarboranes allowed the electronic properties of these species to be determined from ^{19}F nmr chemical shifts and the method of Taft. Species examined in this manner include the 1,2 and 1,7 isomers of the $B_{10}C_2H_{12}$ icosahedral carboranes and the corresponding $B_9C_2H_{12}^-$ and $B_9C_2H_{11}^{2-}$ ions, as well as the 1,8-$B_9C_2H_{11}$ carborane and selected transition metal derivatives of the (3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$ ions. In several instances large and negative $\sigma_R°$ values were observed, which illustrates ground-state electron donation from the carborane moiety to the substituted phenyl ring by a π mechanism. The σ_I values were affected by both the relative carbon atom positions in the carborane fragments and the presence of a negative charge delocalized in those fragments.

Work reported in the past few years has served to reveal the extensive structural variations associated with the icosahedral $B_{10}C_2H_{12}$ carboranes and their derivatives. Of utmost interest is the similarity of 1,3- and 1,7-dicarbollide ions [(3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$ ions][4] and their transition metal derivatives[5,6a] to the $C_5H_5^-$ ion and the common metallocenes derived from the $C_5H_5^-$ ion, respectively. The stereoelectronic properties associated with these and related structures have remained as unanswered questions although the

electronic properties of the 1,2 and 1,7 icosahedral carboranes have been probed[6a] by a classical Hammett σ constant determination coupled with a Taft treatment of *m*- and *p*-fluorophenyl ^{19}F chemical shifts[6b,c] of suitable derivatives. The latter work[6a] revealed that the C-substituted 1,2 carboranyl group was similar in $-I$ effect to the halogens and exhibited no ground-state resonance effect. Similar results have been reported by others using different experimental approaches.[7,8] On the other hand, the C-substituted 1,7-carboranyl group displayed a diminished $-I$ effect and a very small ground-state resonance effect, electron releasing in nature.

It was obvious from the general agreement[6a] of the Taft method with the chemical equilibrium data that the former method could rather easily be employed to elucidate the electronic properties of an extended series of carborane structures. This paper reports the results of such a study which employed carborane carbon-bonded *m*- and *p*-fluorophenyl derivatives of the various carborane species investigated.

(1) Taken in part from R. G. Adler, Ph.D. Dissertation, the University of California, Riverside, 1968.

(2) National Defense Education Act Fellow, 1964–1967; National Aeronautics and Space Administration Fellow, 1968.

(3) Address correspondence to this author at the University of California at Los Angeles, Los Angeles, California 90024.

(4) 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).

(5) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *ibid.*, **90**, 879 (1968).

(6) (a) M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *ibid.*, **87**, 4746 (1965); (b) R. N. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963); (c) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

(7) K. M. Harmon, A. B. Harmon, and B. C. Thompson, *ibid.*, **89**, 5309 (1967).

(8) N. K. Hota and D. S. Matteson, *ibid.*, **90**, 3570 (1968).

Table I. Determination of Inductive and Resonance Parameters for the Fluorophenyl Carborane Derivatives

Compound	Solvent	^{19}F chemical shift, ppm		σ_I	$\sigma_R°$
		m-FC$_6$H$_4$-	p-FC$_6$H$_4$-		
1-FC$_6$H$_4$-1,2-B$_{10}$C$_2$H$_{11}$	(CH$_3$OCH$_2$)$_2$	-1.49 ± 0.03	-1.60 ± 0.03	$+0.295 \pm 0.004$	$+0.004 \pm 0.002$
1-FC$_6$H$_4$-1,2-B$_{10}$C$_2$H$_{11}$	CCl$_4$	-1.96 ± 0.03	-2.21 ± 0.02	$+0.361 \pm 0.004$	$+0.008 \pm 0.001$
1-FC$_6$H$_4$-1,7-B$_{10}$C$_2$H$_{11}$	(CH$_3$OCH$_2$)$_2$	-0.91 ± 0.02	$+0.15 \pm 0.02$	$+0.213 \pm 0.003$	-0.036 ± 0.001
3-FC$_6$H$_4$-1,2-B$_{10}$C$_2$H$_{11}$	(CH$_3$OCH$_2$)$_2$	$+0.52 \pm 0.02$	-1.27 ± 0.03	$+0.011 \pm 0.003$	$+0.061 \pm 0.001$
1-FC$_6$H$_4$-1,8-B$_9$C$_2$H$_{10}$	CCl$_4$	-0.11 ± 0.02	-0.34 ± 0.02	$+0.100 \pm 0.003$	$+0.008 \pm 0.001$
[1-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$](CH$_3$)$_4$N	(CH$_3$OCH$_2$)$_2$	$+2.13 \pm 0.02$	$+6.95 \pm 0.06$	-0.216 ± 0.003	-0.163 ± 0.002
[1-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$](CH$_3$)$_4$N	(CH$_3$OCH$_2$)$_2$	$+3.20 \pm 0.02$	$+8.73 \pm 0.08$	-0.366 ± 0.003	-0.188 ± 0.003
[1-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]Na$_2$	(CH$_3$OCH$_2$)$_2$	$+3.98 \pm 0.02$	$+11.69 \pm 0.08$	-0.477 ± 0.003	-0.262 ± 0.003
[1-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{10}$]Na$_2$	(CH$_3$OCH$_2$)$_2$	$+5.19 \pm 0.05$	$+13.02 \pm 0.07$	-0.646 ± 0.007	-0.266 ± 0.003
[1-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$]	(CH$_3$OCH$_2$)$_2$	-0.86 ± 0.02	$+1.97 \pm 0.02$	$+0.206 \pm 0.003$	-0.096 ± 0.001
[1-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$]	(CH$_3$OCH$_2$)$_2$	$+0.17 \pm 0.02$	$+3.35 \pm 0.03$	$+0.061 \pm 0.003$	-0.108 ± 0.001
[(1-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$)$_2$-Fe]-(CH$_3$)$_4$NNa	(CD$_3$)$_2$CO	$+2.53 \pm 0.05$	$+8.02 \pm 0.05$	-0.272 ± 0.007	-0.186 ± 0.003 or -0.217 ± 0.004
		$+3.64 \pm 0.10$	$+8.93 \pm 0.10$	-0.429 ± 0.014	-0.179 ± 0.005 or -0.148 ± 0.004
[(1-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$)$_2$Co]-(CH$_3$)$_4$N	(CH$_3$OCH$_2$)$_2$	$+0.20 \pm 0.02$	$+2.74 \pm 0.02$	$+0.056 \pm 0.003$	-0.086 ± 0.001 or -0.124 ± 0.001
		$+0.69 \pm 0.02$	$+3.87 \pm 0.03$	-0.012 ± 0.003	-0.108 ± 0.001 or -0.070 ± 0.001
[1-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Ni	CH$_2$Cl$_2$	-2.94 ± 0.05	-2.81 ± 0.07	$+0.499 \pm 0.007$	-0.004 ± 0.003 or $+0.036 \pm 0.003$
		-3.98 ± 0.06	-4.00 ± 0.06	$+0.645 \pm 0.008$	$+0.001 \pm 0.003$ or -0.040 ± 0.003

Results

The m- and p-fluorophenyl derivatives of 13 carborane structures were prepared by known methods described in the Experimental Section. An attempt was made to study representative examples of compounds which had been prepared in many of the earliest carborane investigations and which included several classes of compounds of known structure.

Care was taken as to the choice of solvents employed in the nmr measurements, although Taft[6b,c] has indicated that solvent effects are small so long as an internal standard is employed for reference. However, in order to avoid as much as possible any variations due to solvent effects, an attempt was made to find a chemically inert solvent which would dissolve all of the compounds studied. The solvent of choice for most of the ^{19}F nmr studies was 1,2-dimethoxyethane (DME). However, DME could not be used for all of the compounds investigated, either because of chemical reactivity or insufficient compound solubility, in which case a solvent was employed which greatly differed from DME in polarity.

In order to detect any possible concentration effects, particularly ion-pair formation in the case of the ionic species, all compounds were examined at two or more concentrations, with the most dilute solutions being of the order of 0.1 M. Only very small concentration effects, if any, were observed. The chemical shifts reported are those which were determined by extrapolation of the observed results to low concentrations and they differ very little, if at all, from the values actually observed.

The ^{19}F chemical shifts were determined in parts per million relative to fluorobenzene as an internal standard and the σ_I and $\sigma_R°$ values were calculated from the ap-

propriate Taft equations.[6b,c] The results are presented in Table I.

Discussion

Neutral Carborane Species. Four neutral carborane systems were investigated; 1-substituted-1,2- and -1,7-B$_{10}$C$_2$H$_{12}$,[6a] 3-substituted-1,2-B$_{10}$C$_2$H$_{12}$ (Figure 1),[9] and 1-
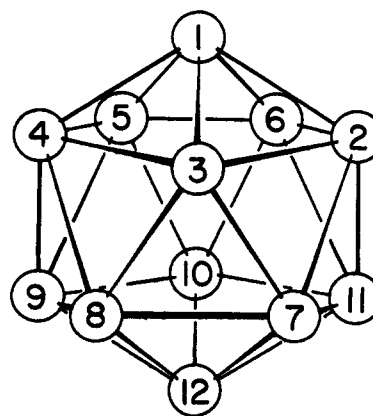

Figure 1. Icosahedral carborane structure and numbering system without terminal H atoms.

substituted-1,8-B$_9$C$_2$H$_{11}$[10] (Figure 2). The chemical shift data obtained for the 1-substituted-1,2- and -1,7-B$_{10}$-C$_2$H$_{12}$ systems in this study (DME solvent) are in qualitative agreement with the σ_I and $\sigma_R°$ values previously obtained in cyclohexane solution[6a] ($\sigma_I^{1,2}$ = $+0.38$,

(9) Prepared by the method of M. F. Hawthorne and P. A. Wegner, J. Amer. Chem. Soc., 90, 896 (1968).
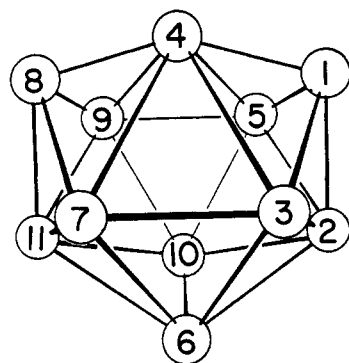(10) Prepared by the method of F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, ibid., 90, 869 (1968).

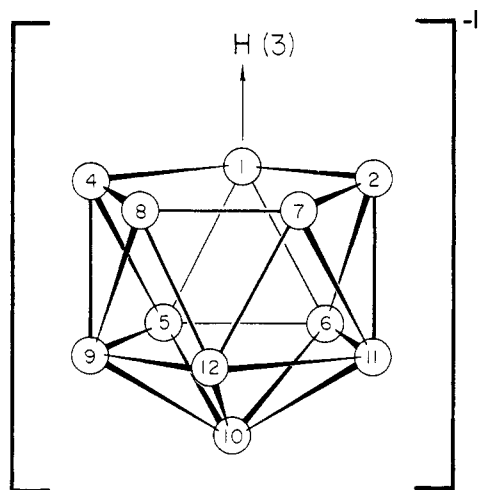Figure 2. $1,8$-$B_9C_2H_{11}$ structure with carbon atoms at positions 1 and 8 without terminal H atoms.

Figure 3. (3)-$1,2$- and (3)-$1,7$-$B_9C_2H_{12}^-$ structures without terminal H atoms.

$\sigma_{R^0}{}^{1,2} = +0.003$ and $\sigma_I{}^{1,7} = +0.19$, $\sigma_{R^0}{}^{1,7} = -0.04$). In both studies, the 1-substituted-1,2-$B_{10}C_2H_{12}$ system displayed a greater $-I$ effect than that of the corresponding $1,7$-$B_{10}C_2H_{12}$ derivative. This effect has been previously associated[6a] with the greater geometrical localization of the carbon atoms present in the icosahedral surface of the 1,2 isomer coupled with the formal carbonium ion character of these six-coordinate carbon atoms. While the σ_{R^0} value for the 1-substituted-$1,2$-$B_{10}C_2H_{12}$ system is zero within experimental uncertainty, the corresponding parameter for the 1-substituted-$1,7$-$B_{10}C_2H_{12}$ system exhibits a very small and negative value. The weak electron donation suggested by this σ_{R^0} value may be real, but results obtained with the boron-substituted 3-substituted-1,2-$B_{10}C_2H_{12}$ system indicate a σ_{R^0} value of $+0.06$ and mitigate an interpretation at this time. It is significant that the σ_I value of the 3-substituted-1,2-$B_{10}C_2H_{12}$ system is virtually zero, since this suggests that the transmission of the coulombic effect of the carbon atoms decreases rather rapidly with distance across the icosahedral surface. Chemical evidence[4] suggests that the 3 (6) position of the $1,2$-$B_{10}C_2H_{12}$ carborane is the most electrophilic BH position on the icosahedral surface. This further suggests, when coupled with the observed σ_I value seen at the 3 (6) position, that substitutents placed further away from the carbon atom pair (7, 8, 9, 10, 11, and 12)
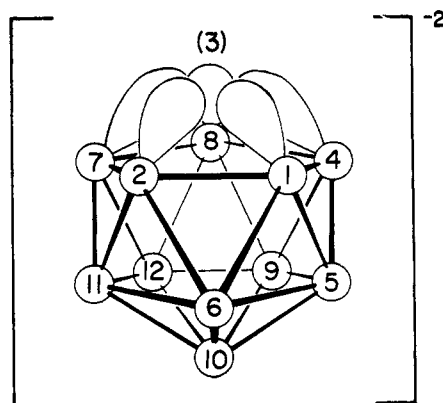

Figure 4. (3)-$1,2$- and (3)-$1,7$-$B_9C_2H_{11}{}^{2-}$ ion structures without terminal H atoms. Approximately sp^3 hybrid orbitals are shown directed toward the open vertex.

would be subject to a detectable $+I$ effect of the icosahedron.

The 1-substituted-1,8-$B_9C_2H_{11}$ carborane system may be best described as exhibiting only a very weak $-I$ effect and a negligible resonance effect. The relatively small $-I$ effect may be due to the wide separation of the carborane carbon atoms from one another as in the $1,7$-$B_{10}C_2H_{12}$ system.

Anionic Carborane Species. Four anionic species derived from the 1,2- and 1,7-$B_{10}C_2H_{12}$ carboranes were investigated. These are the 1-substituted-(3)-1,2- and -(3)-1,7-$B_9C_2H_{12}^-$ and $B_9C_2H_{11}{}^{2-}$ ions (Figures 3 and 4).

The 1-substituted-(3)-1,2- and -(3)-1,7-$B_9C_2H_{12}^-$ ions exhibit large $+I$ and $+R$ effects commensurate with their unit negative charges and the apparent ability of the π system of the attached aryl group to overlap with a filled orbital of the icosahedral fragment. The 1,2 isomer, as expected from the nearest neighbor relationship of the framework carbon atoms, is the least electron-releasing group in the inductive sense. The ordering of $+R$ electron release is also seen to lie in the same direction. Since the position of the face-bound proton of the two $B_9C_2H_{12}^-$ ions is uncertain, no strict interpretation can be given at this time. However, it is clear that ground-state charge delocalization into the aryl substituent does exist in both isomeric ions.

In the case of the isomeric 1-substituted-(3)-1,2- and -(3)-1,7-$B_9C_2H_{11}^{-2}$ ions, the face-bound proton has been removed and arguments presented earlier[4,5] suggest that six electrons are delocalized about the open pentagonal face in five sp^3-like atomic orbitals. Such a system resembles the $C_5H_5^-$ ion, which should obviously be capable of enormous π-electron release to an attached aryl group. This analogy is observed in the isomeric $B_9C_2H_{11}{}^{2-}$ ions, since large $+R$ effects are observed in both cases. As expected from the $2-$ charge present on these ions, large $+I$ effects are observed with both isomeric ions, with the 1,7 isomer having a larger $+I$ effect than the 1,2 isomer ion. Again, the latter effect may be attributed to the relative positions of the carbon atoms present in the isomeric ions.

Metallocarboranes Containing the Dicarbollide Ion. Four metallocarborane derivatives of known structure were examined. In each case a formally d^6 transition metal ion was employed as the coordination site (Fe(II), Co(III), Ni(IV)). Basic structures of the iron and co-
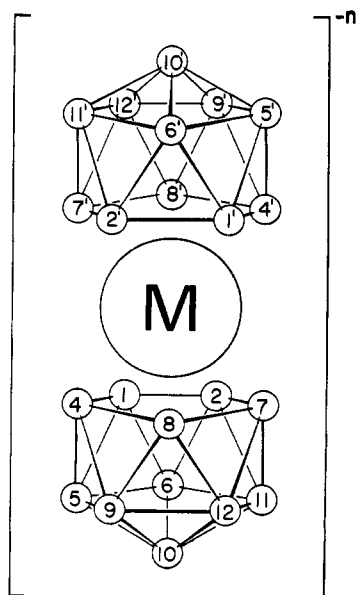
Figure 5. Skeletal structure of d^6 transition metal complexes of bisdicarbollide ions.

Figure 6. Skeletal structure of d^6 transition metal complexes containing the dicarbollide ion and C_5H_5 ligands.

balt species are presented in Figure 5. Two members of this series were uncharged hybrid Co(III) complexes which contained a cyclopentadienide and a 1-fluoro-phenyl-(3)-1,2- or -1,7-$B_9C_2H_{11}^{2-}$ ligand (Figure 6). In these two compounds a $-I$ effect was observed with the 1-substituted-1,2-$B_9C_2H_{11}^{-2}$ ligand giving the greater effect ($+0.206$ vs. $+0.061$), as expected. Chemical equilibria studies by Nesmeyanov and coworkers[11,12] produced a σ_m value of -0.07 for ferrocene. Comparison of the σ_I values obtained in this study with the σ_m value for ferrocene serves to point out the relatively strong $-I$ effect associated with the carbon atoms of uncharged carboranes or fragments of same with near neighbor carbon atom configurations giving much larger effects.

Resonance effects seen in the isomeric 1,2 and 1,7 systems were of a weakly electron-releasing type with σ_R values of -0.096 and -0.108 for the 1,2 and 1,7 isomers, respectively. These values may be compared with a σ_p value of -0.17 determined previously for ferrocene.[11,12] While this effect is relatively weak in the compounds under discussion, conjugation of the aryl substituent with the delocalized and complexed ligand is indicated.

The bis-1-substituted-(3)-1,2- and -1,7-$B_9C_2H_{11}^{-2}$ complexes of Fe(II) and Co(III) were negatively charged species which in every case were obtained as an inseparable mixture of diastereomeric isomers (dd and ll vs. dl) which arise from the molecular asymmetry of the monosubstituted (3)-1,2-$B_9C_2H_{11}^{2-}$ ion ligands. The required neutral d^6 Ni(IV) complexes (vide infra) were obtained in a similar condition. Since separation and identification of the diastereomeric complexes proved to be impossible in our hands, ^{19}F nmr chemical shift measurements were made using the diastereomer mixtures themselves. Thus, two ^{19}F resonances were observed in all cases whether the m- or p-fluorophenyl substituent was under examination. Such data sets

could not be precisely refined nor could the stereochemical identity of the species providing each resonance be defined. Therefore, Table I records the two extreme limits of the possible σ_I and σ_{R^0} functions which were obtained for each system. Although this is admittedly imprecise, definite qualitative trends are obvious.

The iron bis complexes, being $2-$ ions, give rather large $+I$ effects comparable in magnitude to those of the $B_9C_2H_{11}^{2-}$ systems discussed above. On the other hand, the cobalt complexes, although they bear a $1-$ charge, exhibit very small I values with the extremes bracketing a zero value. Comparison of these extremes with the large σ_I values observed with the $B_9C_2H_{12}^-$ ions suggests that the coordinated formal Co(III) ion effectively reduces the $+I$ effect which might be present due to charge alone. This effect also appears in the two $C_5H_5Co(B_9C_2H_{11})$ isomers and may well be attributed to the higher effective nuclear charge of d^6 Co(III) when compared to d^6 Fe(II).

Examination of the σ_{R^0} values obtained with these iron and cobalt complexes suggests, as in the case of the $C_5H_5Co(B_9C_2H_{11})$ complexes, that delocalization of electron density in the dicarbollide ligand extends into the attached aryl substituent.

The formal d^6 Ni(IV) complexes present an unusual case in that they are not closely related structurally to the corresponding d^6 cobalt and iron systems. Figure 7 presents the structure of the unsubstituted nickel complex which was recently obtained by X-ray diffraction studies.[13] In the formal Ni(IV) complex one sees a cisoid arrangement of all carbon atoms and somewhat distorted dicarbollide ligands. The localizations of the carbons in the cisoid manner plus the high effective nuclear charge of the formal d^6 Ni(IV) ion and electrical neutrality of the complex would be expected to militate against inductive electron release to the substituent aryl group. Such is the case, since the limiting σ_I

(11) A. N. Nesmeyanov, E. G. Perevalova, and R. V. Golovyna, Dokl. Akad. Nauk SSSR, 103, 81 (1955).
(12) A. N. Nesmeyanov, Proc. Roy. Soc., Ser. A, 246, 495 (1958).

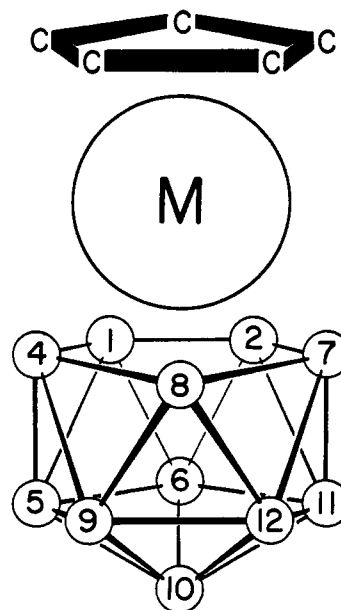(13) D. St. Clair, A Zalkin, and D. H. Templeton, J. Amer. Chem. Soc., 92, 1173 (1970).

Table II. Elemental Analyses of m- and p-Fluorophenyl Carborane Derivatives

Compound	Isomer[a]	% B	% C	% H	% N	% Fe, Co, or Ni
3-FC₆H₄-1,2-B₁₀C₂H₁₁	Calcd	45.36	40.32	6.34		
	Found (m)	45.13	40.35	6.50		
	Found (p)	45.52	39.90	6.03		
1-FC₆H₄-1,8-B₉C₂H₁₀	Calcd	42.96	42.42	6.23		
	Found (m)	42.57	42.24	6.25		
	Found (p)	42.32	42.60	6.35		
(CH₃)₄N[1-FC₆H₄-(3)-1,2-B₉C₂H₁₁]	Calcd	32.26	47.78	9.02	4.64	
	Found (m)	31.99	47.12	9.38	4.96	
	Found (p)	32.11	47.40	9.04	4.75	
(CH₃)₄N[1-FC₆H₄(3)-1,7-B₉C₂H₁₁]	Calcd	32.26	47.78	9.02	4.64	
	Found (m)	32.28	47.28	8.94	4.98	
	Found (p)	32.13	46.71	9.10	4.87	
[1-FC₆H₄-(3)-1,2-B₉C₂H₁₀]Co[C₅H₅]	Calcd	27.76	44.55	5.46		16.81
	Found (m)	26.14	44.13	5.49		16.53
	Found (p)	26.04	45.18	5.32		16.91
[1-FC₆H₄-(3)-1,7-B₉C₂H₁₀]Co[C₅H₅]	Calcd	27.76	44.55	5.46		16.81
	Found (m)	27.93	44.68	5.46		16.38
	Found (p)	27.28	44.86	5.77		16.54
(CH₃)₄N[1-FC₆H₄-(3)-1,2-B₉C₂H₁₀)₂Fe]	Calcd	33.38	41.21	6.92	2.40	9.58
	Found (m)	31.68	41.25	7.34	2.57	9.48
	Found (p)	32.03	43.11	7.35	2.48	10.15
(CH₃)₄N[(1-FC₆H₄-(3)-1,2-B₉C₂H₁₀)₂Co]	Calcd ·	33.20	40.99	6.88	2.39	10.06
	Found (m)[b]	31.08	42.09	7.46	2.14	9.28
	Found (p)	32.33	41.32	7.16	2.31	10.23
[1-FC₆H₄-(3)-1,2-B₉C₂H₁₀]₂Ni	Calcd	38.03	37.56	5.52		11.47
	Found (m)	37.63	38.87	5.85		12.03
	Found (p)	38.60	36.99	5.52		11.96

[a] m indicates the m-fluorophenyl compound; p, the p-fluorophenyl. [b] ¹H nmr spectrum indicated that acetone of crystallization was present in the solid compound before drying under normal conditions.

values seen for the two diastereomers of the complex in Table I are high and positive. Not surprisingly, the σ_{R^0} limiting values range near zero and contrast sharply with the corresponding σ_{R^0} values observed for the
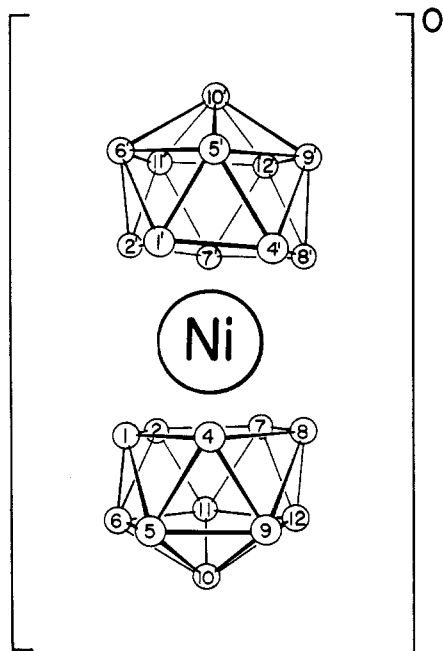

Figure 7. Skeletal structure of a d⁶ nickel bisdicarbollide ion complex.

cobalt and iron complexes. It must be concluded from these results that the bonding of the distorted ligand present in the d⁶ nickel complexes prevents effective overlap of ligand and aryl substituent molecular orbital systems.

Although only ¹⁹F nmr results are reported in this paper, extensive ¹H and ¹¹B nmr data were obtained and are available elsewhere.[1]

Experimental Section

Physical Measurements. Approximately one-half of the ¹⁹F nmr spectra were obtained with a Varian HA-60 spectrometer (at the University of California, Irvine) equipped with a Varian 1024 computer of average transits (CAT) and an NMR Specialties heteronuclear decoupler, Model SD60-B. Use of the decoupler made possible the decoupling of the protons in the aromatic ring from the fluorine, thus greatly sharpening and intensifying the ¹⁹F signal in both the compound being studied and in the internal fluorobenzene standard employed. Accuracy of chemical shift determination was thus increased and chemical shifts which were so small that sample and reference peaks would have overlapped without decoupling could be determined. The remaining ¹⁹F nmr spectra were determined with a Varian HR-60 spectrometer equipped with a Hewlett-Packard wide-range oscillator and a Hewlett-Packard electronic counter, Model 521C. Both spectrometers were operated at a radiofrequency of 56.4 Mc/sec. For HA-60 determinations, a sealed capillary tube containing a solution of 50 wt % tetrafluorotetrachlorocyclobutane (Peninsular ChemResearch) in carbon tetrachloride was included in each nmr tube for the instrument to lock on to. An error of ±0.02 ppm was estimated for the shifts determined with the HA-60 (250-cps-range runs requiring a higher frequency range scan had a proportionately higher error). Runs obtained on the HR-60 were repeated for a total of four to ten runs (including both up- and downfield scans) for each compound at each concentration studied, and results were averaged. The error given for each compound represents the average deviation determined for the series of runs obtained. Concentrations examined ranged from ca. 1 M down to less than 0.1 M. All runs were performed at room temperature.

Infrared spectra were determined using a Beckman IR5 infrared spectrophometer and a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Melting points were determined with a Thomas–Hoover capillary melting point apparatus and are uncorrected. Analyses of previously unreported compounds were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and are reported in Table II.

Materials. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were freshly distilled from lithium aluminum hydride and

collected under nitrogen. Sodium hydride as a 54% dispersion in mineral oil was obtained from Metal Hydrides, Inc. Other chemicals employed were reagent grade and were used without further purification except where indicated.

Dimethoxyethane (Matheson Coleman and Bell) used for nmr spectra was distilled from lithium aluminum hydride and stored under nitrogen in a rubber-septum-capped flask. Fluorobenzene employed as an internal standard in the ^{19}F nmr studies (at concentrations of 0.1–0.3 M) was obtained from the Pierce Chemical Co.

Preparation of 1-m- and 1-p-Fluorophenyl-1,2-dicarba-$closo$-decaborane(12). The two isomeric compounds were prepared as described previously, employing acetonitrile, sublimed decaborane, distilled m- and p-fluorophenylacetylenes, and sodium-dried benzene as solvent.[6a] The final purification of each of the crude compounds was carried out by recrystallization from methanol followed by sublimation *in vacuo* to a 0° cold finger. The corrected melting points obtained were 65.5–66.5° for the m-fluorophenyl isomer and 13.5–136.5° for the p-fluorophenyl isomer.

Preparation of 1-m- and 1-p-Fluorophenyl-1,7-dicarba-$closo$-decaborane(12). (a) **1-m-FC$_6$H$_4$-1,7-B$_{10}$C$_2$H$_{11}$.** A sample of 1-m-FC$_6$H$_4$-1,2-B$_{10}$C$_2$H$_{11}$ (6.8 g, 0.029 mol) was sealed in an evacuated heavy-wall glass ampoule. The ampoule was placed in a stainless steel bomb which contained diphenyl ether to serve as a heat transfer medium and to help maintain bomb pressure during pyrolysis. The bomb was evacuated, sealed, and heated to 405° for 55 hr. After the bomb had cooled, the ampoule was opened behind a shield. A very small quantity of white fumes was emitted. *Caution:* heating the carborane in a sealed glass ampoule gives a superior preparation to heating the compound directly in the steel bomb, since losses due to leakage or reaction with bomb residues are eliminated. However, the carborane employed *must be pure*, otherwise large quantities of gaseous decomposition products may be produced, leading to a dangerously high pressure in the ampoule. The compound was sublimed *in vacuo* at 120° to a 0° cold finger, yielding 5.6 g of product (0.024 mol, 82% recovery). The compound was dissolved in hexane and the solution was applied to an 8 ft × 1 in. column of Baker chromatographic silica gel in an upflow liquid-phase chromatographic apparatus. The column was prewet with about 200 ml of hexane and the sample was eluted with hexane. The separation was monitored by permitting a few drops of the eluate to evaporate on a watch glass and noting any solid film remaining. The solutions containing the separated isomers were stripped and the purity was checked with an Aerograph gas chromatograph apparatus employing an Apiezon L–Chromosorb P column at 208° and using helium as a sweep gas. Clean separation of the 1,2 and 1,7 isomers had occurred. Afforded were 3.8 g and 1.7 g of the 1,7 and 1,2 isomers, respectively. The 1,7 isomer was given a final purification by briefly heating at 40° in an evacuated sublimer, discarding the initial oily material which sublimed out, and then subliming the remaining material at 72° to a 0° cold finger. Afforded was 3.6 g (0.015 mol) of white 1-m-FC$_6$H$_4$-1,7-B$_{10}$C$_2$H$_{11}$, representing 52% of the starting 1,2 isomer used. The melting point was 47–48.5°.

(b) **1-p-FC$_6$H$_4$-1,7-B$_{10}$C$_2$H$_{11}$.** Starting with 7.0 g of 1-p-FC$_6$H$_4$-1,2-B$_{10}$C$_2$H$_{11}$, the same procedure was employed as for the meta isomer described above, affording 4.9 g (70%) of 1-p-FC$_6$H$_4$-1,7-B$_{10}$C$_2$H$_{11}$, mp 59–61°.

Preparation of the 1-m- and 1-p-Fluorophenyl-(3)-1,2-dicarbado-decahydroundecarborate(1−) Ion Derivatives. (a) **Potassium Salts.** The crude potassium salts were prepared by the ethanolic potassium hydroxide degradation of the 1-m- and 1-p-FC$_6$H$_4$-1,2-B$_{10}$C$_2$H$_{11}$ compounds using essentially the same process as described previously for the preparation of other carborane monoanion derivatives.[4]

(b) **(CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$].** A sample of 2.5 g (0.0094 mol) of crude K[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] was dissolved in a small amount of water and excess (CH$_3$)$_4$NCl solution was added. The solid was collected, washed with water, and recrystallized. The recrystallization was carried out by adding the compound to 125 ml of hot water and adding sufficient ethanol to dissolve the solid. The solution was permitted to cool slowly to 0°. The white crystalline solid was collected and dried *in vacuo* at 78° to afford 2.5 g of (CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] (88% yield), mp 163–164°.

(c) **(CH$_3$)$_4$N[1-p-FC$_6$H$_4$-1,2-B$_9$C$_2$H$_{11}$].** Starting with K[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$], the same procedure was followed as described above for the meta compound, to afford 2.2 g of white crystalline (CH$_3$)$_4$N[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$], mp 330° dec.

(d) **(CH$_3$)$_3$NH[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$.** A typical preparation is as follows. Samples of K[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] (7.5

g, 0.028 mol) and (CH$_3$)$_3$NHCl (3.0 g, 0.031 mol) were dissolved in separate small portions of water. The solutions were heated to boiling, the (CH$_3$)$_3$NHCl solution was added to the carborane salt solution, and the mixed solution was allowed to stand at 0°. The desired compound separated as an oil. A few crystals of the corresponding (CH$_3$)$_4$N$^+$ salt were added and the solution was returned to the refrigerator. After 1 hr the oil had solidified to a yellowish, waxy solid. The solid was washed with a few small portions of water and left in a vacuum desiccator over P$_2$O$_5$. Afforded was 7.0 g of product (86% yield). Repeated preparations always resulted in oil formation, as was observed in the initial preparation, but these now could be seeded with previously prepared (CH$_3$)$_3$NH$^+$ compound. The compound was purified by recrystallization from water; *e.g.*, 6.0 g was dissolved in 500 ml of hot water and the insoluble yellowish material remaining was filtered off. The solution was allowed to cool slowly, seeded with a few particles of the crude starting material, and left in the refrigerator overnight. The solutions were filtered and the white, crystalline solid was collected and pumped at high vacuum over P$_2$O$_5$ overnight to afford 5.0 g of (CH$_3$)$_3$NH[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$], mp 72–74°.

(e) **(CH$_3$)$_3$NH[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$].** Starting with the corresponding para potassium salt, (CH$_3$)$_3$NH[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] was prepared following the procedure described above. However, this compound always separated as a solid from solution. The solid was recrystallized from hot water, mp 127–128°.

(f) **Cesium Salts.** The cesium salts were prepared by essentially the same procedure as the (CH$_3$)$_3$NH$^+$ salts, but using cesium chloride. After addition of the hot cesium chloride solution to the hot potassium carborane salt solution, the mixed solutions were cooled to 0°, filtered, and the white, finely crystalline cesium salts were dried *in vacuo* at 78° for 3 hr.

Preparation of the 1-m- and 1-p-Fluorophenyl-(3)-1,7-dicarbado-decahydroundecaborate(1−) Ion Derivatives. (a) **K[1-m-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$] Solution.** To 7.6 g (0.032 mol) of 1-m-FC$_6$H$_4$-(3)-1,7-B$_{10}$C$_2$H$_{11}$ was added 60 ml (0.61 mol) of piperidine. The piperidine had previously been distilled and a middle cut taken of bp 104–105°. The solution was stirred and refluxed under nitrogen for 4 days. After cooling, the piperidine was removed *in vacuo*, leaving a viscous liquid. A solution of 12 g (0.21 mol) of potassium hydroxide in 50 ml of water was added to decompose the piperidinium and [(CH$_3$)$_3$N]$_2$BH present. Rapid gas evolution took place and two liquid phases remained. The solution was evaporated *in vacuo*, leaving a white solid. Absolute ethanol (100 ml) was added and the material was almost completely dissolved. Dry Ice (*ca.* 50 g) was added to react with remaining potassium hydroxide and precipitate potassium carbonate. The solution was filtered and the large amount of white solid which remained was washed three times with ethanol. The solution was evaporated *in vacuo*, leaving an oil. The oily residue was treated with 125 ml of water, yielding a milky solution with some oily residues. After filtering the solution through Celite (filter aid), the solution was shaken in a separatory funnel with a heptane–benzene solution, then with ether, to remove the oil. The clear aqueous solution was then used for conversion to the tetra- and trimethylammonium salts as described below.

(b) **K[1-p-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$] Solution.** Starting with 1-p-FC$_6$H$_4$-1,7-B$_{10}$C$_2$H$_{11}$, the procedure leading to the formation of the K$^+$ solution was identical with that used for the meta isomer.

(c) **(CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$].** Tetramethylammonium chloride (6 g of a 50% solution) was added to 37.5 ml (30%) of the K[1-m-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$] solution prepared as described above. The white precipitate was filtered and washed twice with small portions of water. It was recrystallized by adding 100 ml of water, heating to nearly boiling, and then adding sufficient ethanol to effect complete solution. The hot solution was then permitted to slowly cool to 0°. The compound was separated by filtration and washed twice with ice-cold water. The compound was recrystallized once more from ethanol–water and once from absolute ethanol. It was dried for 2 hr *in vacuo* at 78°. The yield was 1.08 g (0.0036 mol) of (CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$] (37% yield based on 30% of the starting carborane). The 1,7 isomer appears to be much less stable than the 1,2 compound upon long storage, since solid material formed which was insoluble in acetone, DME, or acetonitrile and which appeared to be boric acid.

(d) **(CH$_3$)$_4$N[1-p-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{12}$].** Starting with K[1-p-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$], the same procedure was followed as for the meta compound, except that only one ethanol–water recrystallization was required to achieve the purity. The compound remained solid until decomposition set in at 320°. Afforded was 0.71 g of

$(CH_3)_4N[1\text{-}p\text{-}FC_6H_4\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$ (28% yield). Like the meta isomer, it also tended to deteriorate with time, yielding boric acid.

(e) $(CH_3)_3NH[1\text{-}m\text{-}FC_6H_4\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$. A sample of 8.0 g of $(CH_3)_3NHCl$ was dissolved in 25 ml of water and added to 87.5 ml (70%) of the corresponding K$^+$ solution prepared as described above. The solution was left in the refrigerator overnight. The next day the compound had separated as an oil. A few crystals of the corresponding $(CH_3)_4N^+$ compound were added and the solution was returned to the refrigerator. The next day the oil had solidified. The solid was dissolved in 350 ml of boiling water and cooled. Some material separated as a colorless oil. A few particles of the crude starting material were added and the solution was left in the refrigerator. The resulting crystalline solid was filtered, washed twice with ice-cold water, and pumped in a vacuum desiccator over P$_2$O$_5$ for 3 days. The yield was 6.4 g (0.022 mol, 47%) of $(CH_3)_3NH[1\text{-}m\text{-}FC_6H_4\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$, mp 78.5–80°.

(f) $(C_3H)_3NH[1\text{-}p\text{-}FC_6H_4\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$. The para compound was prepared in an analogous manner to that of the meta. However, the compound separated initially as a solid rather than as an oil. The yield of purified $(CH_3)_3NH[1\text{-}p\text{-}FC_6H_4\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$ was 5.6 g (29%), mp 95.9–96.5°.

Preparation of the 1-*m*- and 1-*p*-Fluorophenyl-(3)-1,2-dicarbollide Ion Solutions for Nmr Determinations. (a) $Na_2[1\text{-}m\text{-}FC_6H_4\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}]$. To 4 ml of freshly distilled DME and 0.32 g of sodium hydride (0.013 mol) (0.60 g of a 54% dispersion in mineral oil which had been washed twice with DME) was added 0.575 g (0.0020 mol) of $(CH_3)_3NH[1\text{-}m\text{-}FC_6H_4\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ under nitrogen. The solution was refluxed and nitrogen was periodically swept for a short time over the surface until the evolved trimethylamine was removed. The solution was transferred to the drybox, sufficient DME was added to compensate for the solvent lost during refluxing, and the solid was permitted to settle. The following solutions were made up in separate nmr tubes: (1) 0.4 ml of stock solution and 1 drop of tetramethylsilane; (2) 0.4 ml of stock solution and 4 μl of fluorobenzene; (3) 0.2 ml of stock solution, 0.3 ml of DME, and 5 μl of fluorobenzene; and (4) 0.2 ml of stock solution, 0.8 ml of DME, and 10 μl of fluorobenzene. To each of the last three tubes was also added a sealed capillary tube containing 50% tetrafluorotetrachlorocyclobutane in carbon tetrachloride solution. These last three dicarbollide solutions were designed for ^{19}F nmr analysis with the HA-60 at three different concentrations. The first tube described above was for ^{1}H and ^{11}B spectra. All tubes were removed from the drybox and connected to a vacuum line, the solutions were frozen, and the tubes were evacuated and sealed. All solutions were stored in Dry Ice to retard deterioration.

(b) $Na_2[1\text{-}p\text{-}FC_6H_4\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}]$. Starting with the corresponding para monanion, solutions for the nmr determinations were prepared in the same manner as described for the meta compound.

Preparation of the 1-*m*- and 1-*p*-Fluorophenyl-(3)-1,7-dicarbollide Ion Solutions for Nmr Determinations. The solutions of these ions were prepared in an analogous manner to that employed for the 1,2 isomers. However, centrifuging was necessary to affect settling of the solid in the reaction solutions. The nmr solutions were prepared in the same manner as for the 1,2 compounds. However, since the ^{19}F nmr spectra were being taken with the HR-60, the fluorobenzene concentration was made three times as great to improve the reference peak, and the tetrafluorotetrachlorocyclobutane-containing tube was omitted.

Preparation of 1-*m*- and 1-*p*-Fluorophenyl-1,8-dicarba-*closo*-undecaborane(11). (a) $1\text{-}p\text{-}FC_6H_4\text{-}1,8\text{-}B_9C_2H_{10}$. A sample of 4.0 g (0.011 mol) of $Cs[1\text{-}p\text{-}FC_6H_4\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ was mixed with 28 g of polyphosphoric acid. The flask was connected to an alembic distillation column and was pumped to remove the air. The mixture was then heated at 135° for 2 hr under nitrogen at *ca* 0.75 atm. After the mixture had cooled, the system was evacuated. The temperature of the mixture was raised to 135° and then gradually increased to 170° to distill over the desired compound. The apparatus was filled with nitrogen and the compound was transferred to the drybox for storage. Afforded was 0.88 g (0.0039 mol) of very pale yellow $1\text{-}p\text{-}FC_6H_4\text{-}1,8\text{-}B_9C_2H_{10}$ (35% yield), mp 24.5–25.2°.

(b) $1\text{-}m\text{-}FC_6H_4\text{-}1,8\text{-}B_9C_2H_{10}$. Starting with 4.0 g of $Cs[1\text{-}m\text{-}FC_6H_4\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}]$, the corresponding meta compound was prepared. However, a slight air leak to the system during the 135° heating period appeared to have been responsible for a lower yield (0.40 g, 16%). The $1\text{-}m\text{-}FC_6H_4\text{-}1,8\text{-}B_9C_2H_{10}$ was afforded as a very pale yellow liquid which remained liquid at 0°.

Preparation of *m*-Fluorophenylboron Dichloride. A sample of *m*-fluoroaniline (Pierce Chemical Co.) was converted to the diazonium borofluoride, and then with stannous and mercuric chlorides to *m*-fluorophenylmercuric chloride by the method of Dunker, Starkey, and Jenkins.[14,15] It was found necessary to increase the volume of the final acetone reaction solution by 75% by the addition of water before the fluorophenylmercuric chloride crystallized out. The crude compound had a melting point of 247.5–248.5°.

The compound was converted to *m*-fluorophenylboron dichloride by reaction with boron trichloride according to a modified procedure of Gerrard, Howarth, Mooney, and Pratt.[16] The *m*-fluorophenylmercuric chloride (16.8 g, 0.0508 mol) and 60 ml of toluene were mixed, placed under dry nitrogen, and cooled to 10°. Boron trichloride (7.0 g, 0.060 mol) was then added. The solution was stirred under nitrogen at room temperature for 40 min and then heated with an oil bath to 70–75° for 4 hr. After the reaction mixture had cooled, it was transferred to the drybox for filtration to remove the precipitated mercuric chloride. The solution was vacuum distilled, using a small vertical condenser equipped with a cold finger containing ice water. The toluene was stripped (toluene rather than benzene had been used as solvent to avoid solidification on the cold finger). The system was then closed off, the solution temperature raised to 70°, and the compound was distilled, condensed on the cold finger, and drained into the receiver, affording 7.22 g (6.37 ml) of distillate which was stored under nitrogen. Recovery of chloride ion in the carborane preparation described below indicated that the product contained at least 75% *m*-fluorophenylboron dichloride, with the balance most likely being toluene. The yield of desired compound was thus at least 5.4 g (0.031 mol, 60% minimum).

The product was characterized by conversion to the corresponding 2-(*m*-fluorophenyl)benzo-1,3-diaza-2-borole, according to the method of Dewar, Kubba, and Pettit.[17] A sample of 2.27 g of the solution was treated with sublimed *o*-phenylenediamine and the product was recrystallized twice from benzene to afford a crystalline white derivative, which was dried by pumping for 2 hr at room temperature (mp 157.5–158.5°). *Anal.* Calcd for $C_{12}H_{10}N_2BF$: C, 67.98; H, 4.75; B, 5.10; N, 13.21. Found: C, 67.62; H, 4.59; B 5.21; N, 13.06. The ^{1}H nmr (in acetone-d_6) consisted of a broad peak at −8.45 ppm relative to TMS (assigned to N–H) and a series of peaks from −7.83 to −6.73 ppm (assigned to the aromatic protons). The corresponding area ratio was 1:4.3.

Preparation of 3-*m* and 3-*p*-Fluorophenyl-1,2-dicarba-*closo*-dodecaborane(12). (a) $3\text{-}m\text{-}FC_6H_4\text{-}1,2\text{-}B_{10}C_2H_{11}$. A sample of 7.0 g of $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_{10}C_2H_{12}]$ (0.036 mol) was converted to the dicarbollide ion which was in turn treated with 4.37 ml (4.95 g) of the $m\text{-}FC_6H_4BCl_2$ solution prepared as described above, using the procedure described previously ("General Procedure for the Insertion Reaction. 3-Phenyl-1,2-dicarbaclovododecaborane(12)").[18] After the THF was stripped, 150 ml of heptane was added to the residual oil and refluxed for 1 hr. The heptane solution was decanted and the heptane extraction repeated two more times. The heptane was stripped and the solid obtained was twice sublimed *in vacuo*. During the second sublimation the temperature was raised no higher than 60° and the oily material which initially sublimed out was discarded. The sublimation was then continued upon raising the temperature to 90°, affording 2.48 g (0.0104 mole) of white, fluffy $3\text{-}m\text{-}FC_6H_4\text{-}1,2\text{-}B_{10}C_2H_{11}$. The yield, based on recovered chloride ion (see below), was 50%. An analytical sample (mp 62–63°) was obtained by two recrystallizations from heptane followed by sublimation.

The chloride ion generated in the reaction was removed from the reaction residues with water. Remaining carborane anion species were removed with tetramethylammonium hydroxide, and the chloride ion was precipitated with silver ion, dissolved with ammonium hydroxide, filtered, reprecipitated with nitric acid, collected, dried, and weighed, yielding 5.9707 g of AgCl (0.0417 mol). The original $m\text{-}FC_6H_4BCl_2$ solution employed in the reaction thus contained 0.0209 mol (3.7 g, 75%) of $m\text{-}FC_6H_4BCl_2$.

(b) $3\text{-}p\text{-}FC_6H_4\text{-}1,2\text{-}B_{10}C_2H_{11}$. A sample of 0.5 g (0.0028 mol) of $p\text{-}FC_6H_4BCl_2$ was very kindly provided by Professor R. W. Taft. It was treated with the dicarbollide ion prepared from 1.0 g (0.0052 mol) of $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_9C_2H_{12}]$ according to the procedure described for the meta compound. The product obtained from

(14) M. F. W. Dunker, E. B. Starkey, and G. L. Jenkins, *J. Amer. Chem Soc.*, **58**, 2308 (1936).

(15) M. F. W. Dunker and E. B. Starkey, *ibid.*, **61**, 3005 (1939).

(16) W. Gerrard, M. Howarth, E. F. Mooney, and D. E. Pratt, *J. Chem. Soc.*, 1582 (1963).

(17) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *ibid.*, 3076 (1958).

(18) M. F. Hawthorne and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 896 (1968).

the heptane extraction was sublimed and recrystallized from fresh heptane to yield white crystalline 3-p-FC$_6$H$_4$-1,2-B$_{10}$C$_2$H$_{11}$, mp 103.5–105°.

Preparation of the Bis-1-m- and Bis-1-p-fluorophenyl-(3)-1,2-dicarbollyliron(III) Derivatives. (a) (CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe. Following essentially the procedure described previously ("Nonaqueous Preparation of the π-(3)-1,2-Dicarbollyl-iron(III) Derivatives"),[5] 5.0 g (0.0174 mol) of (CH$_3$)$_3$NH[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] was converted to the dicarbollide ion and this in turn was treated with 0.037 mol of ferrous chloride in THF. After the THF was stripped, the residue was extracted with small portions of ether and benzene while exposed to the air, and the extraction solutions were combined and stirred with dilute hydrochloric acid. The aqueous phase was removed and the dark, reddish purple organic phase was filtered and stripped until only a small amount of liquid remained. Water and pentane (300 ml of each) were added, with the desired compound being transferred to the aqueous phase. The organic phase was discarded and the aqueous phase was washed four more times with 150-ml portions of pentane. The aqueous phase was filtered through Celite, and 20 ml of a 50% (CH$_3$)$_4$NCl aqueous solution was added with stirring. The precipitate was collected and washed three times with water. It was purified by dissolving in an acetone–water mixture and allowing the solvent to evaporate slowly at ambient conditions until crystallization occurred. The crystallization process was performed three times (considerable difficulty with oil formation was encountered). After washing with water, the purple, almost black solid from the final recrystallization was dried *in vacuo* at 78° for 6 hr, to yield 2.50 g of (CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe (0.00430 mol, 49%). A melting point determination indicated slight melting at 160°, followed by extensive melting with decomposition at 200°.

(b) (CH$_3$)$_4$N[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe. Samples of (CH$_3$)$_3$-NH[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] and ferrous chloride were employed using the same procedure described above in order to afford (CH$_3$)$_4$N[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe. A melting point determination indicated a very slight melting at 180°, followed by extensive melting with decomposition at 251°; yield, 50%.

Preparation of the Bis-1-m- and Bis-1-p-fluorophenyl-(3)-1,2-dicarbollyliron(II) Derivative Solutions for Nmr Determinations. (a) (CH$_3$)$_4$NNa[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe. A sample of (CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe (0.281 g, 0.482 mol) was dissolved in 1.2 ml of deuterioacetone in the drybox, excess sodium amalgam was added, and the mixture was stirred for 1 hr. The color rapidly changed to a deep violet. Some compound, which precipitated out, was permitted to settle. The following (CH$_3$)$_4$-NNa[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe solutions were made up in separate nmr tubes: (1) 0.35 ml of stock solution and 10.5 μl of fluorobenzene; (2) 0.2 ml of stock solution, 0.2 ml of acetone-d_6, and 12 μl of fluorobenzene; and (3) 0.1 ml of stock solution, 0.3 ml of acetone-d_6, and 12 μl of fluorobenzene. The tubes were removed from the drybox, frozen, evacuated, and sealed. All nmr tubes were stored in Dry Ice and in the absence of light to retard decomposition. Deuterioacetone was chosen for the ^{16}Fe as well as the ^{1}H and ^{11}B nmr studies since preliminary work had shown that the iron(II) compounds were not sufficiently soluble in DME for successful nmr spectra to be obtained.

(b) (CH$_3$)$_4$NNa[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe. Starting with 0.281 g of (CH$_3$)$_4$N[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe, the same procedures were carried out as for the meta isomer. A portion of the starting compound was material which had been recovered from earlier nmr tests and recrystallized from dichloromethane–hexane. The (CH$_3$)$_4$NNa[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Fe obtained appeared to be somewhat less soluble in acetone-d_6 than was the meta isomer.

Preparation of the Bis-1-m- and Bis-1-p-fluorophenyl-(3)-1,2-dicarbollylcobalt(III) Derivatives. (a) (CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Co. A sample of (CH$_3$)$_3$NH[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] (2.0 g, 0.0070 mol) was converted to the dicarbollide ion and then treated with anhydrous cobaltous chloride (1.36 g, 0.0105 mol) in THF essentially according to the procedure described previously for the nonaqueous preparation of dicarbollylcobalt(III) derivatives.[5] The THF was removed *in vacuo* and water was added to the residue. After briefly heating with stirring, the mixture was filtered through Celite to yield a clear, deep red solution. Addition of excess (CH$_3$)$_4$NCl solution yielded a brick red precipitate. The compound was dried overnight in a vacuum desiccator and afforded 1.6 g (0.0027 mol, 78% yield) of crude product. The compound was dissolved in a benzene–acetone solution (volume ratio 9:1) and chromatographed on a short silica gel column, using solutions of increasing acetone content as eluent. The solvent was removed

in vacuo and the compound was crystallized from a water–acetone solution by permitting the solvent to evaporate slowly at ambient conditions. The recrystallization procedure was repeated until the mother liquor tended to remain fairly clear (considerable difficulty with oil formation was encountered). The final crystalline material was washed with water and dried *in vacuo* at 78° for 4.5 hr to afford (CH$_3$)$_4$N[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Co as light red crystals.

(b) (CH$_3$)$_4$N[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Co. Starting with (CH$_3$)$_3$NH[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] the same procedure was followed as for the meta compound. Less difficulty was encountered in recrystallizing the para compound from acetone–water solutions than was the case for the meta preparation. The (CH$_3$)$_4$N[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Co was obtained as a dark red crystalline material.

Preparation of Bis-1-m- and Bis-1-p-fluorophenyl-(3)-1,2-dicarbollylnickel(IV). (a) [1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Ni. A sample of (CH$_3$)$_3$NH[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] (4.0 g, 0.0139 mol) was converted to the dicarbollide ion and then treated with anhydrous nickel(II) acetylacetonate (1.79 g, 0.00697 mol) in THF according to the procedure described previously for the nonaqueous preparation of the bisdicarbollylnickel(III) anions.[5] After oxidizing the resulting nickel(II) complex to the nickel(III) form and filtering the THF solution, the THF was removed *in vacuo*. The residue was extracted with several portions of ether. The ether solutions were added to *ca.* 200 ml of water and the ether was stripped, transferring the compound to water. The nickel(III) complex was precipitated by adding a large excess of rubidium chloride solution and collecting the solid by filtration. The solid was dissolved in 1100 ml of hot water, the solution was acidified with hydrochloric acid, and excess ferric chloride solution was added to oxidize the nickel(III) compound to the nickel(IV) state. The brick red precipitate was collected and dried *in vacuo* overnight. Starting with the stripped THF residue, reddish, water-insoluble precipitates were observed to form at various stages during the course of the preparation. These deposits were assumed to be nickel(IV) complex forming as a result of air oxidation. The deposits were collected and dissolved in benzene, and the benzene was stripped. The solid remaining was treated along with the material obtained from the iron(III) oxidation. The compound was chromatographed using a silica gel column and heptane–benzene (5:3 volume ratio) as solvent. When the solvent was stripped, red crystals were obtained. The solid was dissolved in 100 ml of heptane to which enough benzene had been added to effect solution of the solid. The solution was filtered and partially stripped at room temperature employing an aspirator vacuum until 25–50 ml of solution was left. The red crystalline [1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Ni which formed was collected, recrystallized from CH$_2$Cl$_2$–hexane, and dried *in vacuo* overnight; yield, 0.55 g (0.00108 mol, 15.5%). The compound decomposed at 190°. The compound appeared to react slowly with DME and ^{19}F nmr resonance peaks could not be detected with the HA-60 for a solution of the compound in DME. Methylene chloride was used as the ^{19}F nmr solvent.

(b) [1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Ni. Starting with 4.0 g (0.0139 mol) of (CH$_3$)$_3$NH[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$], and using the same procedure as for the meta compound, 1.14 g (0.00223 mol, 32% yield) of red [1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Ni was obtained from the heptane–benzene recrystallization step. The compound, like the meta isomer, decomposed at 190°. A fresh solution of the compound in DME gave a ^{11}B nmr very similar to the ^{11}B nmr obtained on a solution of the compound in dichloromethane; however, after 3 hr, the spectrum had changed (new peaks had appeared and the assembly of peaks had broadened). No ^{19}F nmr spectrum could be obtained with the HA-60 on a solution of the compound in DME. Methylene chloride was used as the ^{19}F nmr solvent.

Preparation of 1-m- and 1-p-Fluorophenyl-(3)-1,2-dicarbollyl-cyclopentadienylcobalt(III). (a) [1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]Co-[C$_5$H$_5$]. A THF solution of 1.76 g (0.027 mol) of freshly cracked cyclopentadiene and 3.0 g (0.0104 mol) of (CH$_3$)$_3$NH[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] was treated with excess sodium hydride as described previously.[5] The resulting solution of NaC$_5$H$_5$ and Na$_2$[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$] was added under nitrogen to a mixture of 5.31 g (0.0410 mol) of cobaltous chloride in THF. The mixture was refluxed for 30 min, cooled, and filtered. The residue was washed with a few small portions of ether which were than added to the THF solution. The solvent was stripped *in vacuo* leaving a green residue. The residue was extracted with several portions of hot benzene and dichloromethane, the extracts were combined, silica gel was added to the mixed solution, and the solvent was stripped. The compound was chromatographed with hexane–

dichloromethane solutions using a silica gel column. A bright yellow band which separated was collected and saved. Further elution of the column with dichloromethane–acetone solutions resulted in the separation of a dark red band followed by a broad yellow band. An infrared spectrum taken of the material in the second yellow band indicated peaks characteristic of 1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}^-$ compounds, together with a peak at 11.64 μ characteristic of C$_5$H$_5^-$ compounds. The red band appeared to be (C$_5$H$_5$)$_2$Co[1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]$_2$Co and the yellow band to be (C$_5$H$_5$)$_2$Co(1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$). The compound obtained from the first yellow band to separate was recrystallized once from benzene–heptane and twice from dichloromethane–heptane, washed with a few small portions of heptane, and dried $in\ vacuo$ at 78° for 3 hr, to afford 1.03 g (0.0029 mol) of yellow-orange, crystalline [1-m-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$], mp 229–230°. The yield was 28% based on initially employed carborane salt.

(b) [1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$]. Starting with 3.0 g of (CH$_3$)$_3$NH[1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{11}$] and following the procedure described above afforded 0.86 g (0.0025 mol) of yellow, finely crystalline [1-p-FC$_6$H$_4$-(3)-1,2-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$], mp 250–251.8°. The yield was 24% based on the starting carborane salt.

Preparation of 1-m- and 1-p-Fluorophenyl-(3)-1,7-dicarbollyl-cyclopentadienylcobalt(III). (a) [1-m-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$]. Starting with 1.50 g (0.00522 mol) of (CH$_3$)$_3$NH[1-m-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$], 2.42 g (0.0365 mol) of cyclopentadiene, and 6.10 g (0.0470 mol) of cobaltous chloride, the same general procedure was followed as was employed for the 1,2 isomers. The

residue obtained upon removal of the THF from the filtered reaction solution was extracted with several portions of boiling benzene and the residue was chromatographed using the same solvent systems as described above. A series of colored bands was obtained, but only one (a dark yellow, broad band) afforded a crystalline solid upon solvent removal; solvent removal from the other fractions afforded only small amounts of oils. The yellow solid was recrystallized twice from dichloromethane–heptane and dried $in\ vacuo$ at 78° for 2.5 hr to afford 0.19 g (0.54 mmol) of yellow crystalline [1-m-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$], mp 186–186.5°. The yield was 10% based on the starting carborane salt.

(b) [1-p-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$]. Starting with 0.90 g (0.0031 mol) of (CH$_3$)$_3$NH[1-p-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{11}$], 1.45 g (0.022 mol) of cyclopentadiene, and 3.65 g (0.028 mol) of cobaltous chloride, the same procedure employed in the meta compound preparation was used to afford 0.08 g (0.23 mmol) of yellow crystalline [1-p-FC$_6$H$_4$-(3)-1,7-B$_9$C$_2$H$_{10}$]Co[C$_5$H$_5$], mp 209–210°. The yield was 7% based on the starting carborane salt.

The Nature of So-Called Titanocene, (C₁₀H₁₀Ti)₂

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Abstract: Mass spectral and chemical evidence indicates that the compound (C₁₀H₁₀Ti)₂, sometimes referred to as "titanocene", is in fact the dimer of a cyclopentadienyltitanium hydride, containing one cyclopentadienylidene moiety (C$_5$H$_4$) per subunit: ((C$_5$H$_5$)(C$_5$H$_4$)TiH)₂. Ir data are consistent with the presence of a double hydrogen bridge in the dimer. The instability of (h^5-C$_5$H$_5$)$_2$Ti toward rearrangement to this metal hydride structure is in accord with the view that the reaction intermediate (h^5-C$_5$H$_5$)$_2$Ti has a carbene-like reactivity.

The compound (C₁₀H₁₀Ti)₂ is prepared by reaction of (h^5-C$_5$H$_5$)$_2$Ti(CH$_3$)$_2$ with H₂ gas in hexane[1] or by reduction of (h^5-C$_5$H$_5$)$_2$TiCl$_2$ with sodium naphthalide[2] or sodium sand.[3] Initially thought of as a dimer of titanocene, (h_5-C$_5$H$_5$)$_2$Ti, the compound was recently shown to exhibit ir and nmr spectra far too complex for such a structure.[3] Although (C₁₀H₁₀Ti)₂ is of considerable interest because of its participation in various catalytic reactions[4-7] and in the reduction of nitrogen,[8] an acceptable structure has not been proposed yet. We want to report evidence that (C₁₀H₁₀Ti)₂ is a titanium

hydride complex and contains two of its four ring ligands in form of C$_5$H$_4$ units.

Reaction to ((C$_5$H$_5$)(C$_5$H$_4$)TiCl)₂

When solutions of (C₁₀H₁₀Ti)₂ in ether are treated with HCl gas, formation of a purple chloride is observed, which differs from either (h^5-C$_5$H$_5$)$_2$TiCl or (h^5-C$_5$H$_5$)$_2$-TiCl$_2$.[3] We find that formation of the purple chloride from (C₁₀H₁₀Ti)₂ occurs under evolution of exactly 1 mol of H₂ gas per mol of titanium. This establishes the stoichiometry of the reaction product as C₁₀H₉TiCl or a multiple thereof. Mass spectra (see below) confirm this formulation and show that the compound is in fact the dimer (C₁₀H₉TiCl)₂. The exchange of chlorine for one hydrogen in each C₁₀H₁₀Ti unit by HCl gas indicates the presence of a hydride moiety in this unit. This suspicion is confirmed by reaction of (C₁₀H₁₀Ti)₂ with DCl. The evolved hydrogen is now essentially pure HD and must therefore originate from interaction of a hydride with DCl. To judge from this reaction, "titanocene" should therefore be formulated as (C₁₀H₉-TiH)₂.

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