and lock compounds. Field desorption mass spectra were run on a Kratos AEI MS 30 double-focusing mass spectrometer equipped with high-temperature-activated wire emitters. Analytical and preparative high-pressure liquid chromatographies were performed on either a Waters 440 (detector UV, λ = 254 nm) or a Prep LC 500 (detector, differential refractometer) apparatus, respectively.

Materials. [2.2.2]Paracyclophane (**1**) was prepared by the modified Wurtz condensation of paraxylylene chloride in the presence of a catalytic amount of tetraphenylethylene as described by Tabushi and co-workers.[5] From the crude solid, **1** and **2** were obtained as a mixture by column chromatography (silica, hexane–benzene) and then separated by repeated recrystallization from ethanol. A more rapid and convenient separation of **1** and **2** was performed by preparative HPLC (Prep PAK-500/C_{18} column; mobile phase methanol). [2.2.2]Paracyclophane (**1**): mp 168 °C; ^1H NMR ($CDCl_3$) see Table I; ^1H NMR (CD_3OD) δ 2.47 (CH_2), 6.23 (Ar); ^{13}C NMR ($CDCl_3$) featured resonances at δ 33.56 (CH_2), 128.35, and 136.56 (Ar). *p*-bis(2-*p*-tolylethyl)benzene (**2**): mp 142–143 °C; ^1H NMR ($CDCl_3$) see Table I.

1:1 Silver Triflate Complex of 1. Into a solution of 25.7 mg (0.1 mmol) of silver triflate in 8 mL of freshly distilled THF was added 31.2 mg (0.1 mmol) of **1**. The mixture was magnetically stirred at room temperature for ten minutes and the solvent evaporated under reduced pressure to give a stoichiometric amount of the 1:1 silver triflate complex as a whitish crystalline powder. The crude complex was dissolved in hexane–dichloromethane and allowed to evaporate very slowly in the darkness at room temperature to give tiny colorless needles: mp 192 °C; ^1H NMR ($CDCl_3$) see Table I; ^1H NMR (CD_3OD) δ 2.57 (CH_2), 6.42 (Ar); ^{13}C NMR featured resonances at δ 33.01 (CH_2), 125.95, and 138.19 (Ar); field desorption mass spectrum m/e 312 (M^+), 419 ($(^{107}Ag + M)^+$), 420 ($(^{109}Ag + M)^+$). Anal. Calcd for $C_{25}H_{24}F_3SO_3Ag$: C, 52.72; H, 4.21. Found: C, 52.43; H, 4.28.

Use of up to 4:1 molar ratio of silver triflate to cyclophane did not affect the character of product or yield to any extent; only the monocomplex of **1** could be detected.

Determination of the Stability Constant. Considering the equilibrium $A + D \rightleftarrows AD$, where A and D represent the acceptor and donor molecules and AD represents the π-molecular complex, we can use the following equation, derived from the Benesi–Hildebrand equation:[7]

$$\frac{1}{\Delta} = \frac{1}{K_c}\frac{1}{\Delta_0}\frac{1}{a_0} + \frac{1}{\Delta_0}$$

where Δ = observed shift of the donor protons for the system in equilibrium relative to the shift for the pure donor in solution, Δ_0 = shift for the pure complex relative to the shift for the pure donor in solution, K_c = equilibrium constant, and a_0 = acceptor concentration. K_c was evaluated graphically, plotting $1/\Delta$ vs. $1/a_0$ (see Table II).

Table II. Values of Complexation Constant K_c from ^1H NMR Chemical Shifts with Measurement in CD_3OD at 24 °C[a]

acceptor–donor system	conditions[b]	proton measured	Δ_0, Hz	K_c, L mol^{-1}
CF_3SO_3Ag–[2.2.2]PCP	$a_0 >> d_0$	H aliph	20.2	197 ± 8
		H arom	41.7	189 ± 5

[a] For each concentration, three spectra were averaged to obtain the chemical shift of the individual protons. [b] a_0, acceptor concentration; d_0, donor concentration.

In this study, we kept the donor concentration fixed while the concentrations of the acceptor were varied and we measured the shifts of the donor protons in the complexing media. The physical method chosen here for studying weak complexes requires a large excess of the acceptor ($AgCF_3SO_3$) compared with that of the donor ([2.2.2]PCP). Deuterated methanol (CD_3OD) was used; this solvent dissolves a large amount of silver salt as well as smaller amounts of cyclophane. a standard solution of cyclophane in CD_3OD was prepared with a concentration just sufficient to observe a measurable NMR spectrum (0.01 M). Molar ratios of silver triflate to cyclophane were varied from 2 to 10 in the preparation of a series of NMR samples (200 μL in volume).

The NMR instrument was internally locked on a CD_3OD peak and chemical shifts were measured at 24 °C with Me_4Si as an external reference and an estimated accuracy of ±0.3 Hz.

Dynamic FTNMR Studies of Hindered Metal–Cage Rotation in Twelve-Vertex *closo*-Phosphinometallacarborane Complexes[†]

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Abstract: Dynamic ^1H and $^{31}P\{^1H\}$ FTNMR spectra of a series of 12-vertex *closo*-phosphinometallacarboranes are presented which suggest that the metal vertex undergoes hindered rotation with respect to the five-membered face of the carborane cage. Studies of the Rh(III) and Ir(III) complexes, $[L_2HM(carb)]$, where L = PPh_3, PEt_3, or PMe_2Ph and carb = 1,2-, 1,7-, or 1,12-$C_2B_9H_{10}R$ (R = H, Me, Ph, or *n*-Bu), the Ru(IV) complex, $[2,2\text{-}(PPh_3)_2\text{-}2,2\text{-}H_2\text{-}2,1,7\text{-}RuC_2B_9H_{11}]$, the Ru(II) complex, $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}CO\text{-}2,1,7\text{-}RuC_2B_9H_{11}]$, and the Ru(II) and Rh(I) complexes, $[3,3\text{-}(PPh_3)_2\text{-}3\text{-}(H)_n\text{-}4\text{-}C_5H_5N\text{-}3,1,2\text{-}MC_2B_9H_{10}]$ (n = 0, M = Rh; n = 1, M = Ru), constitute the first direct determination of rotational barriers in solution for $[ML_n]$ moieties with respect to planar η^5-bonded ligands in which the π system is continuous. Free energies of activation ($\Delta G^{\ddagger}$) vary from <8.4 to >17.5 kcal/mol.

The potential barrier to internal rotation about the *n*-fold axis in organometallic π-complexes containing a cyclic η^n-C_nR_n ligand (n = 3–8) is so low[2,3] that it evidently cannot be measured directly by dynamic FTNMR in solution. Although free energies of activation for complexes with noncontinuous π-systems (i.e., polyenes,[4] polyenyls,[5] *nido*-5,6-$C_2B_8H_{11}$,[6] and *nido*-$B_{10}H_{12}^{2-}$[7]) have been reported, no barriers have thus far appeared for complexes containing continuous but nonuniform π systems such as those containing C-substituents[8] or one or more heteroatoms in the π-bonding network.[9] Extended Hückel molecular orbital cal-

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[†] A preliminary account of this work has been presented. T. B. Marder, J. A. Doi, R. T. Baker, and M. F. Hawthorne, Pacific Conference on Chemistry and Spectroscopy, Pasadena, CA, October 1979.

(1) (a) University of California Regents' Intern Fellow, 1976–1980. (b) University of California Regents' Fellow, 1978–1979. (c) University of California Chancellor's Intern Fellow, 1977–1981.

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Table I. The 200.133-MHz ^{1}H NMR Spectral Data for Twelve-Vertex *closo*-Phosphinometallacarborane Complexes[a]

complex	δ(M–H)	δ(M–H′)	J_{Rh-H}, Hz	$J_{Rh-H'}$, Hz	$^2J_{P-H}$, Hz	$^2J_{P-H'}$, Hz	*T*, °C
Ia[c]	−8.40		17		29		−83
Ib[c]	−9.25		14		28/33		+42
Ib	−9.73 (br)	−8.36 (br)					−88
Ic	−10.19	−8.47	20	4	20/37	32[b]	−88
Id	−10.10	−8.05	22	<4	22/30	31[b]	−83
Ie[c]	−11.03				27		−73
If	−12.76	−10.54			27[b]	30[b]	−88
Ig	−13.25	−10.40			23/34	30[b]	−88
IIa	−10.74		15		24[b]		−83
IIb	−12.14	−12.57	16	10	27[b]	23/33	−88
IIc	−13.79	−12.37	13	4	30[b]	20/33	−88
IId[c]	−14.16		16		29		+27
IIe[c]	−12.22		17		31		+27
IIf	−13.00				26[b]		−80
IIg	−16.33	−14.30			29[b]	22/35	−83
IIh[c,d]	−8.94				29		−98
III[c]	−8.74		15		27		−83
IV[d]	−10.04	−9.78			29/42	33[b]	−73

[a] Spectra recorded in CD_2Cl_2. [b] $^2J_{P_1-H} \simeq {}^2J_{P_2-H}$. [c] High-temperature limiting spectrum. [d] Spectrum recorded in tetrahydrofuran-d_8.

culations by Hoffmann et al.[2e,g] indicated that substitution or heteroatom inclusion with concomitant decrease in symmetry should result in significantly higher rotational barriers.

The three isomeric *nido*-$C_2B_9H_{11}^{2-}$ (dicarbollide) dianions[10,11] possess several unique features which make them especially suitable ligands for the study of hindered rotation of $[ML_n]$ moieties with respect to the planar continuous five-membered π system.

(1) A large number of transition-metal complexes of these ligands are known which contain a wide variety of metals and exopolyhedral ligands.

(2) Although qualitative similarities exist[2d,12] between the $C_5H_5^-$ and the $C_2B_9H_{11}^{2-}$ ions, the pπ orbitals of the $C_2B_9H_{11}^{2-}$ anion are not orthogonal to the open face but are rehybridized in such a way that they tilt inward. This effect is predominantly due to the fact that the hydrogen atoms attached to the boron and carbon atoms which define the open face do not lie within the plane but above it.

(3) Metallacarborane complexes can be prepared which contain a wide variety of B- or C-substituted (7,8)-, (7,9)-, or (2,9)-dicarbollide ligands.

These features allow both electronic and steric modification ("fine tuning") of the pentagonal π-bonding network.

As part of our research on the metallacarborane-catalyzed homogeneous hydrogenation of alkenes,[13] we prepared a number of metallacarborane complexes containing C-substituted dicarbollide ligands which exhibit several modes of fluxionality in solution as evidenced by multinuclear FTNMR studies.[14]

In conjunction with continuing studies of metallacarborane solution dynamics in this laboratory,[6,15] we wish to report the direct

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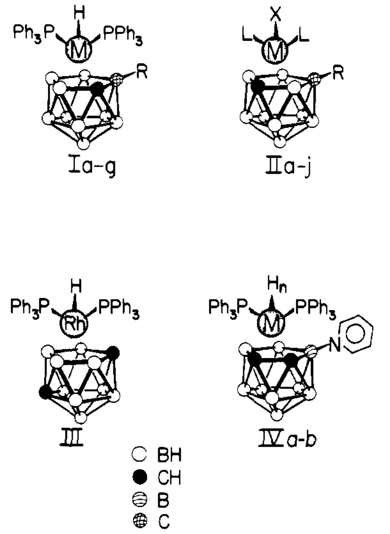

Figure 1. The *closo*-phosphinometallacarboranes. I: (a) M = Rh, R = H; (b) M = Rh, R = Me; (c) M = Rh, R = Ph; (d) M = Rh, R = *n*-Bu; (e) M = Ir, R = H; (f) M = Ir, R = Me; (g) M = Ir, R = Ph. II: (a) M = Rh, L = PPh$_3$, R = H, X = H; (b) M = Rh, L = PPh$_3$, R = Me, X = H; (c) M = Rh, L = PPh$_3$, R = Ph, X = H; (d) M = Rh, L = PEt$_3$, R = H, X = H; (e) M = Rh, L = PMe$_2$Ph, R = H, X = H; (f) M = Ir, L = PPh$_3$, R = H, X = H; (g) M = Ir, L = PPh$_3$, R = Ph, X = H; (h) M = Ru, L = PPh$_3$, R = H, X = dihydrido; (i) M = Ru, L = PPh$_3$, R = H, X = CO; (j) M = Ru, L = PPh$_3$, R = H, X = vacant. IV: (a) M = Rh, *n* = 0; (b) M = Ru, *n* = 1.

measurement of a wide range of activation energies for hindered metal–cage rotation in a series of 12-vertex *closo*-phosphinometallacarborane complexes.

Experimental Section

The *closo*-phosphinoruthena-,[16] *closo*-phosphinorhoda-,[11b,e,13a,17] and *closo*-phosphinoiridacarborane[13a,b,17,18] complexes employed in this study were prepared by previously published procedures. NMR solvents were obtained from commercial sources and were dried (CD$_2$Cl$_2$ (P$_2$O$_5$); C$_6$D$_5$CD$_3$, C$_4$D$_8$O (tetrahydrofuran-d_8), and C$_6$D$_6$ (CaH$_2$)), degassed, condensed into the NMR tubes (^{1}H, 5 mm; ^{31}P, 10 mm) containing the solid samples at −196 °C and sealed in vacuo. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WP-200 spectrometer at 200.133 and 81.02 MHz, respectively, operating in the Fourier transform mode. Typical spectrometer settings were as follows: spectral width, 10,000 Hz; number of data points, 8K; and pulse angle, 30°. The spectrometer was locked on a solvent deuterium resonance, and sample temperatures were measured with the B-VT-1000 digital temperature controller by means of a thermocouple situated in the cooling gas a few centimeters below the sample. Proton chemical shifts are referenced to residual protons in the solvent (dichloromethane, δ 5.32, toluene methyl, δ 2.09, tetrahydrofuran, δ 3.58, with respect to tetramethylsilane). Phosphorus chemical shifts were determined as follows: because the spectrometer was locked on different solvent deuterium resonances (i.e., CD_2Cl$_2$, C$_6$D$_6$, or C$_6$$D_5$–CD$_3$), it was necessary to calibrate spectra obtained with the use of each of these lock signals. This was achieved by determining the chemical shift of PPh$_3$ in all the solvent systems used under spectrometer conditions identical with those employed in this study. The ^{31}P chemical shifts are reported with respect to 85% H$_3$PO$_4$ by taking the chemical shift of PPh$_3$ with respect to 85% H$_3$PO$_4$ as −6 ppm.[19]

Free energies of activation ($\Delta G^{\ddagger}$) were obtained at the coalescence temperature by means of the Eyring equation and the expression $k = \pi\Delta\nu/2^{1/2}$, where k is the rate constant (s^{-1}) for internal rotation and $\Delta\nu$ is the chemical shift difference in hertz. In those cases in which the dynamic NMR effects involve spin-coupled nuclei, $|\Delta\nu| \gg |J|$ for all J's and thus the simple expression given above should be an excellent approximation. Since the chemical shift differences are fairly large, errors due to natural line widths are negligible. In the case of complexes which show unequal populations at low temperatures the value of the rotational barrier given is that for the conversion from the minor to the major rotamer (i.e., complexes Ib,c,g, IIc,g, and IVb). In these cases, the values of $\Delta G^{\ddagger}$ are most probably within ±0.5 kcal/mol, whereas for the remaining complexes, the maximum error in $\Delta G^{\ddagger}$ is ±0.3 kcal/mol. Due to the nature of the observed dynamic NMR spectra, computer simulation was not undertaken and all calculations were performed by using a program written for a Texas Instruments TI-59 magnetic card programmable calculator by Mr. T. B. Marder.

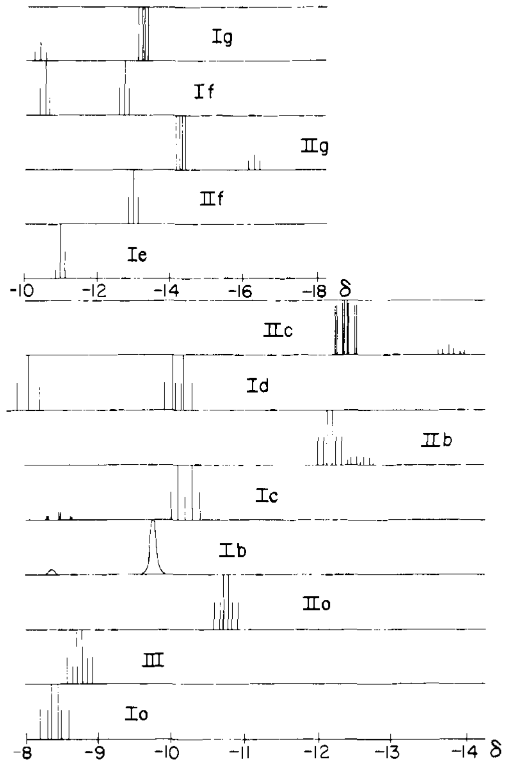

Figure 2. Graphic representation of the low-temperature 200.133-MHz ^{1}H NMR spectra of the closo complexes.

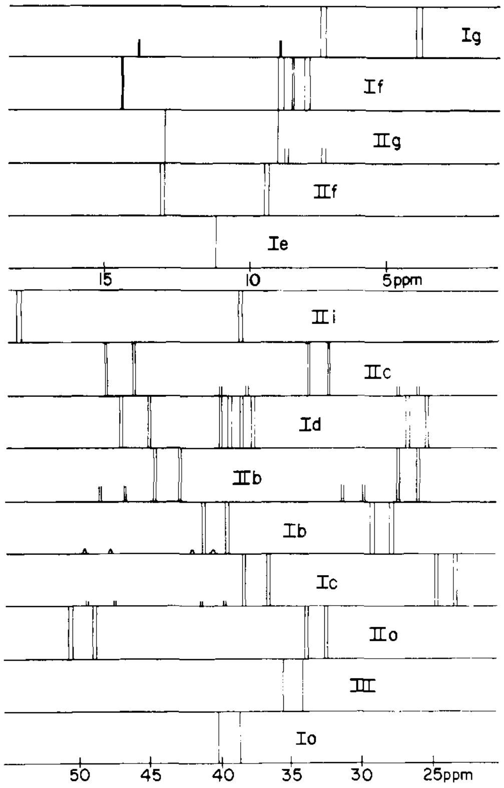

Figure 3. Graphic representation of the low-temperature 81.02-MHz ^{31}P{^{1}H} NMR spectra of the closo complexes.

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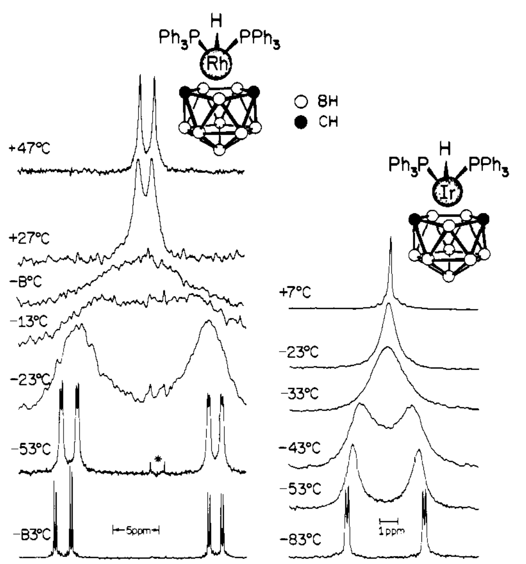


Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complexes IIa,f (asterisk = trace impurity of Ia).

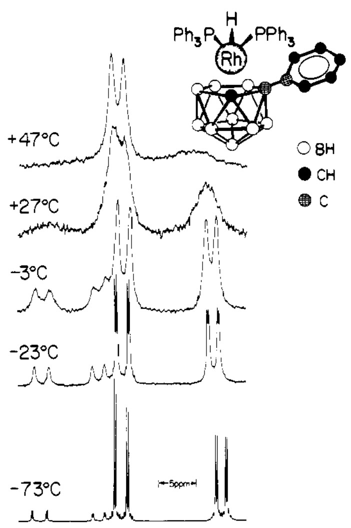


Figure 5. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex Ic.

Results

The *closo*-phosphinometallacarborane complexes employed in this study are shown in Figure 1. The ^1H and $^{31}P\{^1H\}$ FTNMR spectral data are presented in Tables I and II, respectively, and graphic representations of the low-temperature spectra are shown in Figures 2 and 3. Coupling constants (J_{Rh-H} and $^2J_{P-H}$) were deduced by comparison of the rhodium complexes with the iridium analogues and by single frequency, and/or broad-band ^{31}P decoupling of the hydride resonance. The spectra of the analogous unsubstituted complexes Ia and III, IIh, Ie, and IIj consisted of apparent A_2MX ($M = {}^{103}Rh$, 100% abundance, $I = {}^1/_2$), A_2X_2, A_2X, and A_2 spin systems, respectively, and were invariant from −80 to +40 °C. The unsubstituted complexes IIa and IId–f, however, exhibited broad resonances in the $^{31}P\{^1H\}$ FTNMR spectra at room temperature, as shown in Figure 4 for complexes IIa and f. At ca. −80 °C the AA′ portion of an AA′MX (AA′X for IIf) spectrum was observed, implying the absence of a mirror plane bisecting both the carborane ligand and the P–Rh–P angle. The ^1H FTNMR spectra of IIa and f were invariant over the temperature range −88 to +27 °C and the metal hydride retained coupling to the phosphorus (and rhodium for IIa) throughout, demonstrating that phosphine dissociation cannot account for the observed dynamic process. The $^{31}P\{^1H\}$ FTNMR spectra of IIi and boron-substituted IVa exhibited similar behavior to that of IIa,f.

The dynamic FTNMR spectra of the carbon-substituted *closo*-phosphinometallacarborane complexes were more complex. The

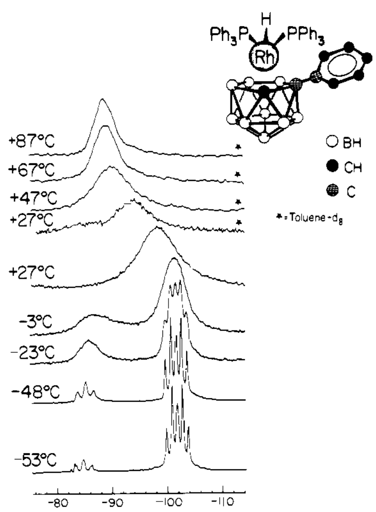


Figure 6. Variable-temperature ^1H NMR spectra of complex Ic.

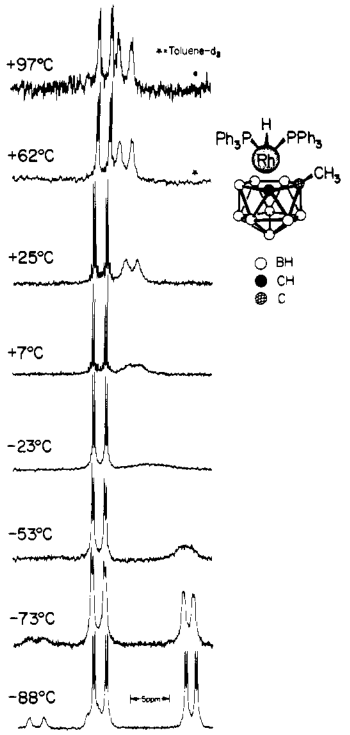


Figure 7. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex Ib.

$^{31}P\{^1H\}$ FTNMR spectrum of Ic at −73 °C, shown in Figure 5, exhibited four different phosphorus resonances and was consistent with the AA′ portions of two separate AA′MX spin systems of approximate ratio 10:1. If P_1 and P_1' are arbitrarily designated to be those phosphorus resonances possessing the smaller chemical shift difference ($\Delta\nu$), then the coalescence of P_1 and P_1' is observed at ca. 15 °C, while that of P_2 and P_2' occurs at 40 °C. The ^1H FTNMR spectrum of Ic at −88 °C, shown in Figure 6, consisted of two rhodium hydride resonances, with an approximate intensity ratio of 10:1, which coalesced at ca. 20 °C; however, the high-temperature limiting spectrum was not obtained for either nucleus. The FTNMR spectra of the analogous iridacarborane complex, Ig, displayed similar behavior, although the intensity ratio of the two species at the low-temperature limit was ca. 5:1. The dynamic FTNMR spectra of Ib were similar to that of Ic; however, the lower activation energy for this complex permitted the observation of the high-temperature limiting spectrum but precluded that of the low-temperature limiting spectrum, as shown in Figures 7 and 8. The spectra of Id and f were also similar to those of Ic, except that the ratio of the two species observed at low temperature was approximately unity. Complexes IIb,c,g and IVb all possessed

Table II. The 81.02-MHz $^{31}P\{^1H\}$ NMR Spectral Data for Twelve-Vertex *closo*-Phosphinometallacarborane Complexes[a]

complex	$\delta(P_1)$ (J_{Rh-P_1})	$\delta(P_2)$ (J_{Rh-P_2})	$\delta(P_1')$ ($J_{Rh-P_1'}$)	$\delta(P_2')$ ($J_{Rh-P_2'}$)	$^2J_{P_1-P_2}$	$^2J_{P_1-P_2'}$	T, °C
Ia	39.5 (125)						−83
Ib[b,d]	40.0 (131)	37.4 (131)			18		+100
Ib	40.3 (134)	28.5 (108)	41.2 (122)	48.6 (153)	22	br[f]	−88
Ic	37.5 (134)	24.1 (110)	40.5 (127)	48.5 (158)	20	15	−88
Id	38.5 (134)	26.1 (110)	39.2 (122)	46.0 (159)	22	17	−88
Ie	11.0						−73
If	7.8	8.7	8.3	14.3	16	5	−80
Ig	7.2	3.8	8.7	13.8	15	5	−88
IIa[d]	41.7 (125)						+27
IIa	49.7 (139)	33.2 (112)			21		−83
IIb[c]	26.6 (116)	43.7 (143)	30.5 (122)	47.5 (145)	13	12	−83
IIc	26.7 (112)	39.0 (147)	33.3 (127)	47.1 (157)	15	10	−88
IId[b,c]	30.5 (125)						+27
IId[c]	41.4 (129)	22.7 (115)			22		−103
IIe[b,c]	10.9 (127)						−23
IIe[c]	19.0 (134)	7.2 (110)			24		−103
IIf[b]	10.8						+27
IIf	13.5	9.2			12		−80
IIg	7.2	8.5	8.8	12.8	10	<3	−83
IIh[b,c]	61.8						−88
IIi[b,c]	43.6						+47
IIi[c]	52.2	36.7			22		−83
IIj[b]	32.8						−53
III	34.8 (112)						−83
IVa[b]	46.1 (198)						+42
IVa	52.8 (221)	32.0 (170)			45		−83
IVb[c]	57.7	60.8	49.8[e]	49.8[e]	32		−48

[a] Spectra recorded in 20% CD_2Cl_2/CH_2Cl_2. P_1/P_1' is arbitrarily defined as the phosphine ligand pair with the smaller $\Delta\nu$. Coupling constants are in Hz. [b] Spectrum recorded in 20% $C_6D_5CD_3/C_6H_5CH_3$. [c] Spectrum recorded in 10% C_6D_6/tetrahydrofuran. [d] High-temperature limiting spectrum. [e] Coincidental overlap, becomes AB resonance at higher temperatures. [f] Broad.

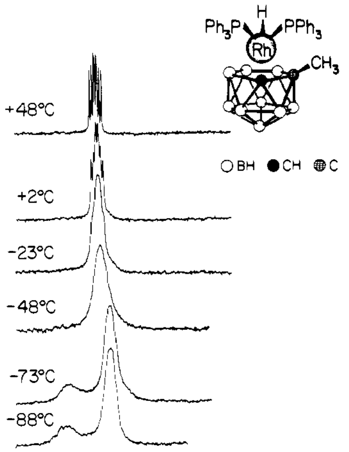


Figure 8. Variable-temperature ^1H NMR spectra of complex Ib.

higher activation energies and resonances due to two species were present even at 27 °C. The coalescence temperature was obtained only for complex IIb and thus only lower limits for the activation energies of complexes IIc,g and IVb were obtained.

The calculated free energies of activation ($\Delta G^{\ddagger}$) for the 12-vertex *closo*-phosphinometallacarborane complexes are presented in Table III.

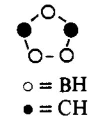
Discussion

The dynamic FTNMR spectra of the 12-vertex *closo*-phosphinometallacarborane complexes I–IV all appear to result from the same dynamic process and differ only in the magnitude of the activation energies, and the number of conformations which are observed at the low-temperature limit. These differences depend in part on the local symmetries of the transition-metal vertex and the carborane cage ligand. Thus, the metal vertex may possess local C_{2v} (MP_2 and H_2MP_2) or C_s (mirror) symmetry (HMP_2 and $(CO)MP_2$), and the carborane cage ligand may either possess local C_s symmetry (unsubstituted) or no symmetry (B or C substituted). The complexes may then be divided into four different categories: (1) C_{2v} metal vertex and C_s carborane cage (IIh,j); (2) C_{2v} metal vertex and asymmetric carborane cage (IVa); (3) C_s metal vertex and C_s carborane cage (Ia,e, IIa,d–f,i, III); (4) C_s metal vertex and asymmetric carborane cage (Ib–d,f,g, IIb,c,g, IVb). Complexes belonging to categories 1 and 3 are the only phosphinometallacarborane complexes discussed above which may possess overall C_s symmetry, and these complexes should exhibit relatively small activation energies (cf. monosubstituted cyclopentadienyl complexes[8]). Recent extended Hückel molecular orbital studies by Hoffmann et al.,[9c] suggest that the largest rotational barriers for $[ML_3]$ moieties with respect to pentagonal η^5-π-bonding ligands will be observed for those ligands possessing the substitution pattern shown (cf. $(7,9\text{-}C_2B_9H_{11})^{2-}$).

Table III. Free Energies of Activation for Hindered Metal–Cage Rotation in Twelve-Vertex *closo*-Phosphinometallacarborane Complexes[a]

complex	$\Delta\nu$ (±5 Hz)	T_c, °C (±5 °C)	$\Delta G^{\ddagger}{}_{T_c}$
Ib	1628	−28	10.3
Ic	1976	+42	13.2
Id	1612/411	+27/−13	12.1[c]
If	460	−38	10.4
Ig	818	+10	12.3
IIa	1336	−11	11.1
IIb	308	+70	15.7
IIc	284	>87	>17[b]
IId	1514	−58	9.0
IIe	958	−76	8.4
IIf	348	−38	10.5
IIh	1262	−11	11.1
IVa	1685	−38	9.8
IVb	53	>82	>17.5[b]

[a] Calculated from $^{31}P\{^1H\}$ NMR spectra; for error limits in $\Delta G^{\ddagger}$ see Experimental Section. [b] Calculated from ^1H NMR spectra. [c] Calculated from ^1H and $^{31}P\{^1H\}$ NMR spectra.



The dynamic FTNMR spectral data presented above are consistent with this hypothesis, as complexes Ia,e and III exhibit no observable dynamic behavior (low rotational barriers) while complexes IIa,d–f,i have measurable activation energies ranging from 8.4 to 11.1 kcal/mol (see Table III). The asymmetry of the static conformation of complexes IIa,d–f,i at the low-temperature limit permitted the observation of this dynamic process. The dynamic behavior observed for these complexes is in accord with a simple hindered rotation of the [XMP_2] vertex with respect to the pentagonal bonding face of the carborane ligand. The trends in the measured values of $\Delta G^{\ddagger}$ for these complexes depend on the local symmetry and the steric requirements of the metal vertex. Thus, while complexes IIh and j, which possess local C_{2v} symmetry at the metal vertex ([H_2MP_2] and [MP_2]), presumably undergo rapid rotation at −90 °C, complexes IIa,d–f,i which possess local C_s symmetry at the metal vertex ([HMP_2] and [(CO)MP_2]), all exhibited significant rotational barriers. It is interesting to note that the isoelectronic and presumably isostructural (vide infra) complexes IIa and i exhibit identical $\Delta G^{\ddagger}$ values, thus demonstrating the similarity between the [$HRh(PPh_3)_2$] and [(CO)$Ru(PPh_3)_2$] vertices. For complexes IIa, d, and e in which the phosphine ligands of the [$HRhP_2$] vertex are PPh_3, PEt_3, and PMe_2Ph, respectively, the observed values of $\Delta G^{\ddagger}$ decrease monotonically with decreasing cone and angle[20] of the phosphine ligands (i.e., $PPh_3 > PEt_3 > PMe_2Ph$; the ordering of the electronic parameters (ν) of Tolman, which correlate with the phosphine ligand basicities, are $PPh_3 > PMe_2Ph > PEt_3$). Complex IVa, which contains a metal vertex with local C_{2v} symmetry and an asymmetric B-substituted carborane ligand, also exists in a single conformation at −90 °C and exhibits a significant rotational barrier (9.8 kcal/mol).

The complexes belonging to category 4 all exist in two conformations at the low-temperature limit as shown in Figures 2 and 3. The large values of $\Delta G^{\ddagger}$ observed for these complexes (10.3–>17.5 kcal/mol) increase with the steric bulk of the substituent on the carborane cage carbon (i.e., Me < *n*-Bu < Ph). The observed rotational barriers are, again, significantly greater for those complexes containing the $(7\text{-R-}7,9\text{-}C_2B_9H_{10})^{2-}$ ligand than for the isomeric complexes containing the $(7\text{-R-}7,8\text{-}C_2B_9H_{10})^{2-}$ ligand. In addition, the values of $\Delta G^{\ddagger}$ obtained for the iridacarborane complexes If,g and IIf were slightly less than or equal to those obtained for their rhodium congeners Ib,c and IIa.

Extended Hückel molecular orbital studies regarding conformational preferences of [ML_2] and [ML_3] moieties with respect to pentagonal π systems have been reported by Hoffmann et al.[9c] and by Mingos et al.[2d,21,22] In particular, the interactions which give rise to preferred orientations in the isomeric, unsubstituted [$3,1,2\text{-}HL_2MC_2B_9H_{11}$] and [$2,1,7\text{-}HL_2MC_2B_9H_{11}$] complexes are primarily those of the filled, nondegenerate d_{xz}, and d_{yz} [HML_2] frontier orbitals[21] with the a′ and a″ HOMO–LUMO frontier orbital pair of the carborane ligands[2d,22] shown in Figure 9. The salient features of these orbitals are as follows.

(1) The carborane ligand orbitals exhibit the "ene–enyl" and "diene" localization patterns similar in nature to the dengerate e_1 frontier orbitals of the cyclopentadienyl ligand, although, as discussed previously, the carborane ligand orbitals are tilted toward the metal vertex. In addition, the carborane ligand orbitals are nondegenerate, the ordering is inverted for the two isomers, and the HOMO–LUMO energy difference for $(7,9\text{-}C_2B_9H_{11})^{2-}$ is greater than that for $(7,8\text{-}C_2B_9H_{11})^{2-}$.[22]

(2) The [HML_2] frontier oribtals are mutually orthogonal, as are those of the carborane ligands.

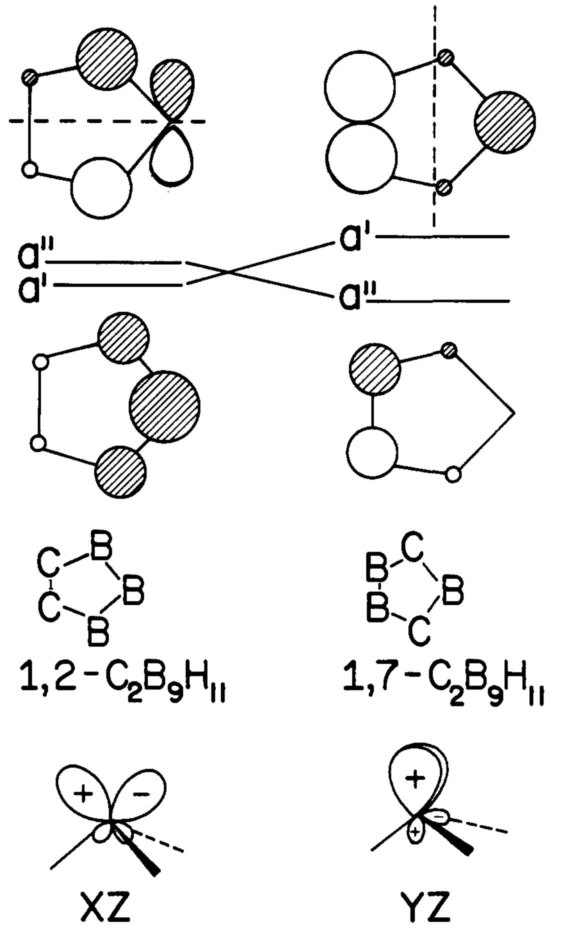
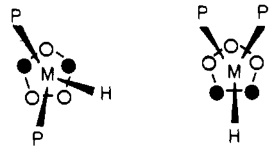


Figure 9. Frontier orbitals of the unsubstituted carborane cages and the [L_2MH] fragment.

Features 1 and 2 taken together, suggest that the preferred conformations of the [$3,1,2\text{-}HL_2MC_2B_9H_{11}$] and [$2,1,7\text{-}HL_2MC_2B_9H_{11}$] isomers will be mutually orthogonal. As the observed conformation A of the [$2,1,7\text{-}HL_2MC_2B_9H_{11}$] complexes, IIa,d–f, is asymmetric, the preferred orientations will be those shown below. Although the rotational barriers for the [$3,1,2\text{-}HL_2MC_2B_9H_{11}$] complexes Ia and e, are small, a recent X-ray diffraction structural determination of the symmetrically disubstituted *C,C′-o*-xylyl complex, [$3,1,2\text{-}H(PPh_3)_2RhC_2R_2B_9H_9$],[23] confirms the symmetric conformation B predicted for this isomer. The Rh–H and Rh–P coupling constants for several C,C′-disubstituted [$3,1,2\text{-}HL_2MC_2R_2B_9H_9$] complexes prepared in this laboratory[13i,14,23] do not resemble those of their unsubstituted counterparts and suggest that these complexes exist only in the symmetric conformation in solution as well (i.e., high rotational barriers).[24]



A B

The magnitude of the Rh–P coupling constants of complexes IIa,d,e, which exist in conformation A at low temperatures, reflects the specific region of the pentagonal carborane face which is trans

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(20) (a) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977); (b) C. A. Tolman, W. C. Seidel, and L. W. Gosse, *J. Am. Chem. Soc.*, **96**, 53 (1974); (c) C. A. Tolman, *ibid.*, **92**, 2953, 2956 (1970).

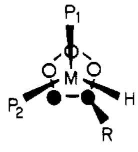
(21) D. M. P. Mingos, P. C. Minshall, M. B. Hursthouse, K. M. A. Malik, and S. D. Willoughby, *J. Organomet. Chem.*, **181**, 169 (1979).

(22) D. M. P. Mingos, M. I. Forsyth, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 605 (1977); *J. Chem. Soc., Dalton Trans.*, 1363 (1978).

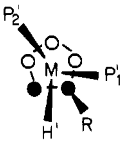
(23) C. B. Knobler, T. B. Marder, E. A. Mizusawa, R. G. Teller, J. A. Long, P. E. Behnken, and M. F. Hawthorne, *J. Am. Chem. Soc.*, to be submitted.

(24) In contrast, it should be noted that there is only limited conformational preference in the solid state for complex Ia., determined by X-ray crystallography (see ref 13g). On the basis of temperature factors and bond lengths, one of the atoms in the five-membered face coordinated to the rhodium atom was identified as a carbon and the two adjacent atoms in this face were assigned scattering factors of statistically disordered carbon and boron atoms.

to the Rh–P bond.[25] The empirical data listed in Table II suggest that the phosphorus nucleus that is trans to a B–H vertex exhibits $J_{\mathrm{Rh-P}}$ values ranging from 110 to 115 Hz, while that trans to a B–C bond exhibits $J_{\mathrm{Rh-P}} = 129$–139 Hz. The Rh–P coupling constant for the disubstituted $[3,1,2\text{-}HL_2MC_2R_2B_9H_9]$ complex (where R_2 = *o*-xylyl), which contains both phosphine ligands trans to a C–R vertex (conformation B) is 146 Hz. In addition, the Rh–H coupling constant for the latter complex, in which the hydride ligand is projected over a C–C bond, is less than 5 Hz, while the magnitude of $J_{\mathrm{Rh-H}}$ for complexes IIa,d,e (conformation A) is ca. 16 Hz. An inspection of the coupling constant data for the C-substituted complexes, $[3,1,2\text{-}HL_2MRhC_2RB_9H_{10}]$ (Ib–d), reveals that the coupling constants fall into well-defined ranges: 108–110, 122–134, and 153–159 Hz for $J_{\mathrm{Rh-P}}$ and 4 and 20–22 Hz for $J_{\mathrm{Rh-H}}$. A number of possible conformations for these complexes were tested by utilizing the empirical correlations discussed above with the constraint that the rotation must interchange P_1 (P_2) and P_1' (P_2'). The two conformations which gave the best correlation are shown below. Thus, for conformation C, $J_{\mathrm{Rh-P_1}}$ (trans to the C–CR bond) = 134 Hz, $J_{\mathrm{Rh-P_2}}$ (trans to a B–B bond) = 108–110 Hz, and $J_{\mathrm{Rh-H}}$ (not over the C–CR bond) = 20–22 Hz, and for conformation D, $J_{\mathrm{Rh-P_1'}}$ (trans to a B–C bond) = 122–127 Hz, $J_{\mathrm{Rh-P_2'}}$ (trans to the C–R vertex) = 153–159 Hz, and $J_{\mathrm{Rh-H'}}$ (over the C–CR bond) < 4 Hz. The relative intensities (Figures 2 and 3) of the two conformations indicate that conformation C is favored when R = Me, Ph, as would be expected on the basis of steric arguments. The equal populations of both conformations observed for R = *n*-Bu are not readily accounted for and may suggest an electronic preference for conformation D when R is a good electron-releasing substituent. Some credence for this proposal is provided by the isomeric iridacarborane complexes If,g in which conformation C is favored when R = Ph and the conformation populations are equal when R = Me. In addition, the two-bond phosphorus–phosphorus coupling constants, $^2J_{\mathrm{P-P}}$ are consistently smaller for conformation D than for conformation C, as might be expected[25] if the steric influence of the C-substituent results in a compression of the P–M–P angle in conformation D. This effect is particularly significant for the iridacarborane complexes in which $^2J_{\mathrm{P-P}}(\mathrm{C}) = 15$–16 Hz and $^2J_{\mathrm{P-P}}(\mathrm{D}) < 5$ Hz.

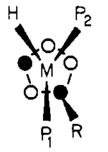


C

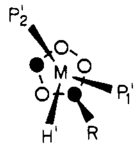


D

The application of a similar analysis to the isomeric $[2,1,7\text{-}HL_2MC_2RB_9H_{10}]$ complexes IIb,c,g yielded the preferred conformations shown below. Thus, for conformation E, $J_{\mathrm{Rh-P_1}}$ (trans to a B–H vertex) = 112 and 116 Hz, $J_{\mathrm{Rh-P_2}}$ (trans to the B*–C bond) = 147 and 143 Hz, and $J_{\mathrm{Rh-H}}$ (not over the B*–CR bond) = 13 and 15 Hz. For conformation F, $J_{\mathrm{Rh-P_1'}}$ (trans to a B–C bond) = 127 and 122 Hz, $J_{\mathrm{Rh-P_2'}}$ (trans to the C–R vertex) = 157 and 145 Hz, and $J_{\mathrm{Rh-H'}}$ (over the B*–CR bond) = 4 and 10 Hz, where B* is the boron atom which is bonded to both carbon atoms. A conformational population inversion is observed for these complexes, with conformation E being favored when R = Me and conformation F predominating when R = Ph, as would be expected on the basis of steric arguments. As before, the values of $^2J_{\mathrm{P-P}}$ are smaller for conformation F than for conformation E, particularly for iridacarborane complex IIg, in which $^2J_{\mathrm{P-P}}(\mathrm{E}) = 10$ Hz and $^2J_{\mathrm{P-P}}(\mathrm{F}) < 3$ Hz.



E



F

The correlation of the magnitude of the $J_{\mathrm{Rh-P}}$ coupling constant with the nature of the ligand trans to the Rh–P bond is a common one, and the theoretical basis for such a correlation has been discussed.[25] An empirical correlation of the magnitude of the $J_{\mathrm{Rh-H}}$ coupling constant with the nature of the cis ligand (i.e., H over a C–C bond), however, has not been previously observed, although Church and Mays noted[26] that the effect on $J_{\mathrm{P-H}}$ of changing a cis ligand was the reverse of the effect when the trans ligand was changed. At this time, no firm theoretical basis exists for the correlation of $J_{\mathrm{M-H}}$ with the nature of the cis ligands in octahedral complexes. This correlation has to be invoked, however, in order to obtain reasonable conformations for the $[3,1,2\text{-}HL_2MC_2RB_9H_{10}]$ complexes. Although conformations A and B presented above are easily derived from oribtal symmetry arguments, it should be emphasized that conformations C–F for the asymmetric C-substituted complexes are proposed on the basis of empirical correlations and a detailed discussion of the electronic conformational preferences for these complexes must await further theoretical studies.

Acknowledgment. We wish to thank Mr. R. E. King III for providing spectra of complexes IId,e, Mr. M. S. Delaney and Drs. D. C. Busby, B. A. Sosinsky, and E. Wong for providing samples of some of the complexes used in this work. We also wish to thank Dr. J. Strouse and Professor F. A. L. Anet (both at UCLA) for helpful discussions. In addition, we would like to thank the National Science Foundation for support of this work (NSF Grant No. CHE77-22910) and for the purchase of the Bruker WP-200 NMR spectrometer (NSF Grant No. CHE76-05926).

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(25) P. S. Pregosin and R. W. Kunz, "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes", Springer-Verlag, Berlin, 1979.

(26) M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1938 (1970).

(27) **Notes Added in Proof:** Since this manuscript was submitted the following relevant studies have appeared: (1) A barrier of ca. 12.2 kcal/mol has been determined by ^{1}H and ^{13}C NMR for the restricted rotation of the arene ring about the ruthenium atom in the complex $[(p\text{-}t\text{-}Bu_2C_6H_4)Ru(CO)(SiCl_3)_2]$. R. K. Pomeroy and D. J. Harrison, *J. Chem. Soc., Chem. Commun.*, 661 (1980). (2) Although no activation energies were given, it was reported that the barrier to rotation of a metal fragment with respect to the five-membered face of a carborane cage is lower for the C_2B_4 cage than for the C_2B_9 cage as determined by variable temperature NMR studies. G. K. Barker, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton. Trans.*, 1186 (1980).