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Angular Dependence of Hydrogen Magnetic Resonance Contact Shifts in Substituted Nickelocenes. Molecular Structure of Bis(η^5-isodicyclopentadienyl)nickel(II)[1]

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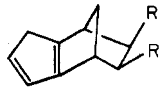
Distributions of unpaired electron spin density in a series of ring-substituted nickelocenes, specifically designed to test spin delocalization mechanisms, have been measured by proton nuclear magnetic resonance methods. Contact shifts of the cyclopentadienyl ring hydrogens are quite constant (250 ± 19 ppm) over the series of seven variously substituted nickelocenes, while in contrast the (β) hydrogen atoms on (α) carbons directly attached to the cyclopentadienyl rings exhibit contact shifts which range from zero to −312 ppm. These β contact shifts are shown to vary as $\langle\cos^2\varphi\rangle$, where φ is the dihedral angle between the cyclopentadienyl p_z orbital and the C_α–H_β bond. In two nickelocenes with rigid substituents, large contact shifts for hydrogens remote from the cyclopentadienyl ring are observed when the "W arrangement" of the remote C–H bond and a cyclopentadienyl p_z orbital is satisfied. For one such hydrogen atom a remote shift of −95.6 ppm is observed, while its geminal counterpart experiences no significant contact shift. The structure of one of the nickelocenes, bis(η^5-isodicyclopentadienyl)nickel(II), was determined by an x-ray diffraction study. The compound was found to be the C_2 symmetry isomer with the methylene bridges directed toward the nickel. The cyclopentadienyl rings are eclipsed and the nickel–ring perpendicular distance 1.824 (3) Å agrees very well with electron diffraction result for nickelocene (1.828 Å). Two formula units of the metallocene were distributed on the twofold symmetry sites (4e) of a monoclinic cell ($C2/c$) of dimensions a = 18.898 (4) Å, b = 7.578 (3) Å, c = 10.967 (4) Å, and β = 109.5 (1)°. The disagreement factor for 1621 diffractometer-collected reflections was 0.056, based on F.

Introduction

Nuclear magnetic resonance spectra which show Fermi contact interactions have been extensively used to obtain information about the bonding and electronic configuration of paramagnetic molecules.[2] The bis(η-cyclopentadienyl)metal(II) compounds (metallocenes) of the first transition series have yielded a great deal of contact shift data of theoretical interest.[3] Several interpretations of these data have been put forward. Levy and Orgel[4] attempted to explain the metallocene contact shift data by proposing either spin polarization (M = V, Cr) or electron delocalization (M = Co, Ni) from metal to ligand π orbitals. Fritz, Keller, and Schwarzhans[5] proposed the additional possibility of direct metal–hydrogen orbital overlap. Rettig and Drago[3e,6] and Prins[7] also included the possibility of electron delocalization through the σ (in-plane) orbitals.

In the present work cyclopentadienes **1–5** were utilized in the preparation of substituted nickelocenes **6–10**. We report here the synthesis, characterization, and hydrogen magnetic resonance spectra of nickelocenes **6–10**, and we show that the observed contact shifts are in agreement with the π-electron delocalization model.[4–7] This work provides the first extensive investigation of substituted nickelocenes. A number of such compounds have been reported previously,[8] but, with the exception of 1,1′-dimethylnickelocene, neither NMR nor crystallographic studies have been performed.



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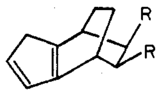

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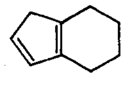

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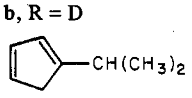

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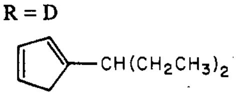

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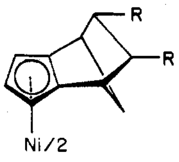
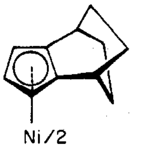


6a, R = H
b, R = D



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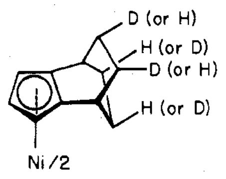

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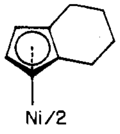

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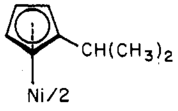

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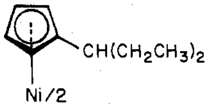

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The x-ray-determined crystalline structure reported here of bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), **6a** (common name bis(η^5-isodicyclopentadienyl)nickel(II)) is the first completed structure in the solid state of a bis(cyclopentadienyl)nickel(II) compound and is the only reported structure of any kind of a substituted nickelocene.

Results

1. Synthesis. Organic compounds prepared for this study were synthesized as outlined in eq 1–4. Nickelocenes **6–10** were prepared in good yields by reaction of $NiBr_2$(glyme) with the lithium salts of the anions of **1–5**, respectively.

2. Crystalline Structure of Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), 6a. The nickel atom was found to lie on a crystallographic twofold axis and thus the atom positions of the second ligand are dependent on the first. Only one set of ligand atom positional and thermal parameters were refined and the values for the other ligand atoms were generated by a twofold rotation. Final atom coordinates and bond distances are presented in Tables I and II, respectively, and two views of the molecule are shown in Figures 1 and 2.

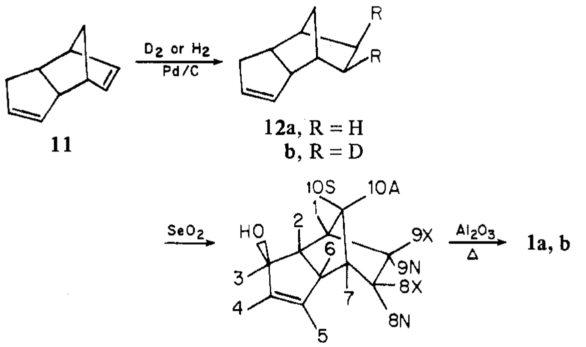
The cyclopentadienyl ring carbons are coplanar within 0.2°. The ring hydrogens are not significantly out of the cyclopentadienyl plane within the precision of the results (standard deviation σ = 5.6°): H3 is 8.5° out of plane away from the nickel, H4 is 2.2° out of plane away from the nickel, and H5 is 0.2° out of plane toward the nickel. C1 and C7 are bent out of the plane of the cyclopentadienyl ring by 6.9° away from the nickel (σ = 0.14°). The two cyclopentadienyl rings are coplanar within 0.2°, with a mean ring–ring perpendicular distance of 3.648 (12) Å. Closest crystallographic nickel–hydrogen contacts are with H1 (3.84 Å), H3 (2.97 Å), H4 (2.86 Å), H5 (2.86 Å), H7 (3.78 Å), and H10S (3.12 Å). The dihedral angle made by the C_1–H bond with the cyclopentadienyl ring (the angle between the C2–C1–H1 plane and the C2–C3–C4–C5–C6 plane) is 19 ± 3°.

Table I. Positional and Thermal Factors for Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), **6a**

Atom	x^a	y	z	$B_{11}{}^b$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.0	0.1368 (1)	0.25	15 (1)	72 (2)	45 (1)	0^c	9 (3)	0^c
C1	0.1546 (2)	0.3171 (5)	10.2142 (4)	24 (1)	128 (8)	71 (4)	−7 (3)	22 (2)	10 (5)
C2	0.1194 (2)	0.1922 (4)	0.2848 (3)	17 (11)	85 (6)	58 (4)	1 (2)	12 (2)	3 (4)
C3	0.1119 (2)	0.0118 (4)	0.3119 (4)	18 (1)	89 (7)	99 (5)	6 (2)	14 (2)	18 (5)
C4	0.0807 (2)	0.0061 (5)	0.4136 (4)	22 (1)	125 (8)	71 (4)	−5 (3)	7 (2)	42 (5)
C5	0.1119 (2)	0.0118 (4)	0.3119 (4)	22 (1)	174 (9)	42 (4)	−18 (3)	8 (2)	8 (4)
C6	0.0940 (2)	0.2965 (4)	0.3693 (3)	18 (1)	93 (7)	50 (4)	−6 (2)	11 (2)	−2 (4)
C7	0.1121 (2)	0.4856 (5)	0.3488 (4)	25 (1)	85 (7)	88 (5)	−7 (3)	20 (2)	−7 (5)
C8	0.1990 (2)	0.5016 (6)	0.4089 (5)	27 (2)	127 (9)	90 (5)	−25 (3)	9 (2)	−4 (5)
C9	0.2278 (2)	0.3863 (6)	0.3168 (5)	20 (1)	159 (9)	99 (5)	−13 (3)	19 (2)	26 (6)
C10	0.1042 (2)	0.4802 (5)	0.2041 (4)	25 (2)	117 (8)	86 (5)	−3 (3)	12 (2)	39 (5)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H1	0.162 (5)	0.267 (13)	0.131 (8)	1.4 (1.0)	H8X	0.217 (6)	0.611 (14)	0.414 (11)	3.6 (1.5)
H3	0.132 (5)	−0.092 (13)	0.0278 (10)	2.0 (1.1)	H9N	0.264 (5)	0.297 (13)	0.366 (9)	1.1 (0.9)
H4	0.068 (6)	−0.091 (14)	0.465 (10)	3.1 (1.3)	H9X	0.259 (5)	0.469 (12)	0.279 (9)	1.3 (1.0)
H5	0.048 (5)	0.219 (13)	0.520 (9)	1.7 (1.0)	H10A	0.128 (5)	0.595 (13)	0.175 (9)	2.0 (1.1)
H7	0.090 (5)	0.571 (13)	0.386 (9)	0.9 (0.9)	H10S	0.052 (5)	0.472 (12)	0.247 (9)	0.3 (0.8)
H8N	0.221 (5)	0.462 (13)	0.493 (9)	0.6 (0.9)					

[a] Standard deviations of last significant figures are given in parentheses. [b] Temperature factors (B_{ij}) for Ni and C are multiplied by 10^4; $T = \exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$. [c] B_{12} and B_{23} are required as a result of the C_2 site symmetry to be zero.



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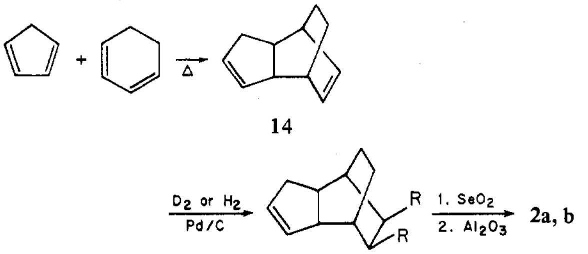
12a, R = H
b, R = D

13a, 8X, 9X = H
b, 8X, 9X = D

(1)



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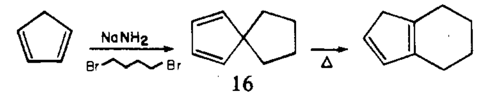
(2)



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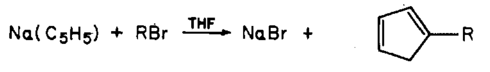


(4)

4, R = $CH(CH_3)_2$
5, R = $CH(CH_2CH_3)_2$

Table II. Bond Distances (Å) in Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), **6a**[a]

Ni–C2	2.200 (3)	C7–C8	1.556 (6)
Ni–C3	2.208 (3)	C7–C10	1.544 (7)
Ni–C4	2.167 (4)	C8–C9	1.563 (8)
Ni–C5	2.183 (4)	C1–H1	1.04 (10)
Ni–C6	2.186 (3)	C3–H3	1.00 (11)
C1–C2	1.510 (6)	C4–H4	1.00 (12)
C1–C9	1.553 (5)	C5–H5	1.01 (11)
C1–C10	1.542 (6)	C7–H7	0.95 (11)
C2–C3	1.417 (5)	C8–H8N	0.94 (9)
C2–C6	1.418 (5)	C8–H8X	0.88 (11)
C3–C4	1.426 (7)	C9–H9N	1.06 (9)
C4–C5	1.424 (5)	C10–H10A	1.08 (10)
C6–C7	1.508 (5)	C10–H10S	0.99 (8)

[a] Standard deviations are given in parentheses; x-ray crystallographic C–H bond distances are too short by ~0.13 Å.[9]

Table III. Observed and Calculated NMR Shifts for Tricyclo[5.2.1.0^{2,6}]deca-4-en-3-ol, **13a**, + Eu(dpm)$_3$

Hydrogen no.	Shift δ, Hz		Hydrogen no.	Shift δ, Hz	
	Obsd	Calcd[b,c]		Obsd	Calcd[b,c]
1	304	291	8N	233	254
2	840	831	8X	176[a]	172
3	1304	1308	9N	272	294
4	848	825	9X	168[a]	140
5	610	609	10A	184	192
6	497	508	10S	242	250
7	282	286			

[a] Not observed in **13b**. [b] See ref 10 for computational details. [c] Goodness of fit $R_1{}^2 = \Sigma(\text{obsd} - \text{calcd})^2/\Sigma\text{obsd}^2$. $R_1 = 0.036$ with Eu–O = 2.44 ± 0.10 Å and Eu–O–C = 130 ± 20°.

3. Characterization of 8,9-*exo,exo*-Dideuteriotricyclo[5.2.1.0^{2,6}]deca-4-en-3-ol, 13b. Reduction of dicyclopentadiene with D_2 using Pd on C catalyst, followed by oxidation with SeO_2, yielded **13b**, 98% dideuterated (see Experimental Section). Comparison of the NMR spectra of the dideuterated **13b** and undeuterated **13a** showed that the highest field signal, a broad singlet at δ 0.88, had decreased by an integral of two hydrogens. In an attempt to assign the NMR spectrum of **13a**, both the dideuterated and undeuterated compounds were titrated with tris(dipivaloylmethanato)europium(III), Eu(dpm)$_3$.

In **13a**, the hydrogens in the cyclopentenol ring showed large downfield shifts, linear with the addition of Eu(dpm)$_3$. The hydrogens in the norbornane ring showed much smaller shifts upon the addition of Eu(dpm)$_3$. In addition, large geminal couplings of 8N–8X, 9N–9X, and 10A–10S and large vicinal couplings of 8N–9N and 8X–9X obscured the individual resonances. The spectra obtained by Eu(dpm)$_3$ addition to 8X,9X-dideuterated **13b** simplified the high-field region greatly. With the removal of the 8X and 9X resonances and the absence of the 8N–8X and 9N–9X couplings the linear shifts of the remaining hydrogens could be followed readily.

Undeuterated **13a** showed two peaks consistently to higher field that were absent in dideuterated **13b**. The observed shifts for the last addition of Eu(dpm)$_3$ to **13a** were used to assign the spectra. The observed and calculated shifts for the final

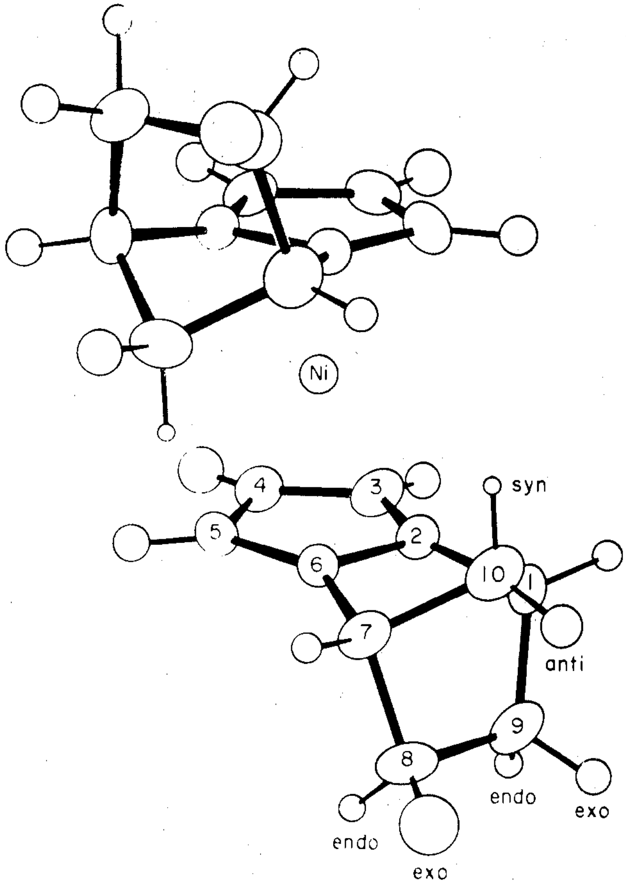


Figure 1. Drawing of bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), **6a**, looking along the C_2 axis.

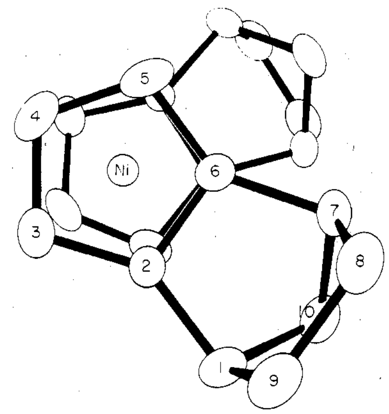


Figure 2. View of bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), looking down the ring-nickel-ring axis.

addition are given in Table III. The disagreement factor R_1 was 0.0358.

The proton–proton coupling constants observed for **13b** are also in agreement with the Eu(dpm)$_3$ results. The observed proton–proton coupling constants for **13b** are listed in Table IV. The assignments of the coupling constants were obtained as follows. The resonances assigned to H1 and H7 show only one large coupling of 5 Hz, which was assigned to coupling with the exo H2 and H6, respectively (H8X and H9X are deuterated). This 5-Hz coupling is also present in the resonances assigned to H2 and H6, each of which also show a large 9-Hz coupling with each other due to their eclipsed arrangement. H2 shows an additional small coupling of <2 Hz which is due to H3. H6 shows two additional couplings of ~2 Hz due to H4 and H5. These 2-Hz couplings are present in the resonances assigned to H4 and H5 plus an additional 5-Hz coupling to each other.

Table IV. Proton–Proton Coupling Constants, J_{xy}, for 8,9-*exo,exo*-Dideuteriotricyclo[5.2.1.0^{2,6}]deca-4-en-3-ol, **13b**

Protons		Obsd J_{xy} ±1, Hz	Expected J_{xy}, Hz
x	y		
1	2	5	4.3–4.8[a]
2	3	≤2	2[b]
2	6	9	5.1–7.0[c]
4	5	5	5.1–7.0[c]
4	6	2	0.5–3.0[c]
5	6	2	0–5[c]
6	7	5	4.3–4.8[a]
8N	9N	10[d]	9.1[a]
10A	10S	10[d]	10.1[a]

[a] For bicyclo[2.2.1]heptan-2-one [J. L. Marshall and S. R. Walter, *J. Am. Chem. Soc.*, **96**, 6358 (1974)]. [b] From the Karplus relationship; dihedral angle is 120°. [c] Normal range for cyclopentenes (D. J. Pasto and C. R. Johnson, "Organic Structure Determination", Prentice-Hall, Englewood Cliffs, N. J., 1969). [d] ±3 Hz due to extensive line broadening by Eu(dpm)$_3$.

The assumption that the hydroxyl group is in the exo 3 position is verified by the small (≤2 Hz) coupling constant for H2–H3. If the hydroxyl group were endo, H2 and H3 would be eclipsed, and a coupling constant of ~8 Hz would be expected.

All other coupling constants are in agreement with the assignments made. H2 and H6 are eclipsed and have a large (9 Hz) coupling. H6 is also extensively split by H5 (vicinal) and H4 (allylic). H1–H2 and H6–H7 couplings are typical of bridgehead–exo couplings in norbornane rings. H8N and H9N are eclipsed and show a large (10 Hz) coupling, and H10A and H10S are geminal and show a large (10 Hz) coupling. The couplings between hydrogens on C8, C9, and C10 are observed only at high concentrations of Eu(dpm)$_3$, for which resolution is poor (line widths ~5 Hz).

These results demonstrate that **13b** is dideuterated in the 8,9 exo,exo positions. Since subsequent reactions leading to **6b** do not involve the norbornane ring, it is assumed that no deuterium loss or scrambling occurs. The NMR spectrum of **6b** shows a 98 ± 3% reduction in the intensity of the resonance at −95.6 ppm, confirming the assignments discussed below.

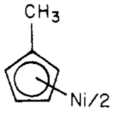
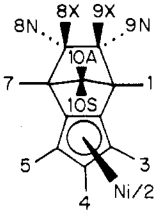
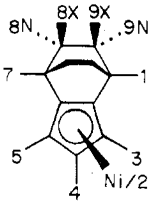
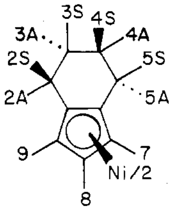
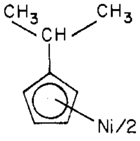
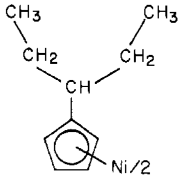
4. NMR Contact Shifts. NMR spectra of nickelocenes **6–10** were obtained in either benzene-d_6 or toluene-d_8. The results are given in Table V. In addition, variable-temperature studies were carried out for 1,1′-dimethylnickelocene[3e] and nickelocenes **8–10**. In all cases the isotropic shifts gave acceptable linear plots vs. $1/T$. In all cases except the methine resonance in **10**, the $\Delta\nu$ vs. $1/T$ plots intercepted near the origin. For the methine resonance in **10**, the $\Delta\nu$ vs. $1/T$ plot intercepted at −56 ppm at $T = \infty$ (plotted over a temperature range of 195–352 K). In addition, for the methine resonance in nickelocene **10**, the product $T(\Delta\nu_{\text{methine}})$ is strongly temperature dependent while $T(\Delta\nu_{\text{ring}})$ shows the normal temperature independence. In this case $T(\Delta\nu_{\text{methine}})$ decreases by 13% when the temperature is lowered from +79 to −78 °C. The plot of $T(\Delta\nu_{\text{methine}})$ vs. T is linear. In no other case did we observe significant temperature dependence of $T\Delta\nu$.

Discussion

A. Molecular Structure of Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), 6a. Electron diffraction studies have been published for nickelocene at 90[11] and 110 °C.[12] The results of the better of these[12] are compared to results obtained for **6a** in Table VI.

There is remarkable agreement between the two structures. All results agree within one standard deviation. The electron diffraction study determined the C–H bond distances much more accurately but could not identify any preference for eclipsed or staggered ring conformations in nickelocene in the

Table V. ^{1}H NMR Contact Shift Data for Nickelocenes

Compd	Assignment[a]	$\Delta H/H$,[b] ppm	Integral	Line width at half-height, Hz (at 100 MHz)	A,[c] G	$\varphi_{C_\alpha-H_\beta}$,[h] deg
	Ring H	242[d]		920	−1.24	
 18	Ring H	241[d]	4	880	−1.23	
	Methyl H	−189[d]	3	300	0.96	45
 6a	3,5	+251	2	1250	−1.33	
	4	+269	1	2150	−1.43	
	{1,7	−24.4	2	125	0.13	71 ± 3
	8N,9N}	+0.1	2	250	0.0	
	8X,9X	−95.6	2^e	150	0.51	
	{10A	−21.9	1	60	0.12	
	10S}	+2.1	1	50	−0.01	
 7a	{1,7	+1.6	2	85	−0.01	
	8N,9N	+3.4	2	85	−0.02	90 ± 3
	10N,11N}	+1.7	2	335	−0.01	
	3,4,5	+252	3	720	−1.35	
	{8X,9X	−93.2	2^f	185	0.50	
	10X,11X}	+4.2	2^g	335	−0.02	
 8	7,9	+250	2	835	−1.37	
	8	+238	1	835	−1.30	
	{2S,5S	−312	2	1000	1.71	25 and 131 (±3)
	2A,5A}	−266	2	400	1.45	
		−9.2	1	75	0.05	
	{3,4}	+0.4	2	140	0.00	
		+2.2	1	60	0.01	
 9	Ring H	+249	4	800	−1.30	
	Methine H	−205	1	350	1.07	
	Methyl H	−9.3	6	450	0.05	
 10	Ring H	+261	4	950	−1.38	
	Methine H	−116	1	200	0.61	
	{Methylene and methyl}	+0.4–+2.0	10	70–170	0.00–0.01	

[a] Assignments have been made by specific deuteration where possible, braces enclose tentative assignments which may be reversed (see text). [b] Reported relative to the analogous diamagnetic ferrocene; 40 °C; positive shifts are to high field. [c] $\Delta H/H = -A\bar{g}\beta S(S+1)/3\hbar\gamma_{\mathrm{H}}kT$. [d] From ref 3e; corrected to 40 °C. [e] Decreased to ~2% intensity in **6b**. [f] Decreased to 40 ± 10% intensity in **7b**. [g] Difficult to establish intensity decrease in **7b** due to overlap with other peaks and residual diamagnetic impurities. [h] Dihedral angle between C_α–H_β and cyclopentadienyl p_z axis.

gas phase. The x-ray diffraction study of **6a** clearly shows eclipsed rings in the crystal. This is in contrast to the x-ray-determined staggered ring conformation of ferrocene in the crystal,[13] although an electron diffraction study[14] at 140 °C shows the eclipsed conformation most probable for ferrocene with an estimated ring rotational barrier of only 1.1 kcal/mol. Ring rotational energy barriers have been determined by ^{1}H NMR for nickelocene (1.8 kcal/mol)[15] and for monosubstituted ferrocenes:[16] ethyl, 1.8 kcal/mol; 2-propyl, 3.9 kcal/mol; *tert*-butyl, 4.6 kcal/mol. The molecular structure of crystalline nickelocene has not been determined by x-ray methods. Unit cell parameters have been reported for nickelocene, and nickelocene has been found to be isomorphous with ferrocene.[17-19]

For eclipsed cyclopentadienyl rings in **6a** there are three possible orientations of the coordinated ring substituents with respect to each other: 0° (eclipsed substituents), 72°, or 144°. The observed structure in the crystal has the two ring sub-

Table VI. Structural Data for Nickelocene[12] and **6a**

	Nickelocene	**6a**
Ni–ring, Å	1.828 (0.009)[a]	1.824 (0.003)
Ni–C, Å	2.196 (0.008)	2.167–2.208 (0.003)
C_{ring}–C_{ring}, Å	1.430 (0.003)	1.422 (0.005)
C_{ring}–H, Å	1.083 (0.019)	1.00[b] (0.11)
C_5-(C–H),[c] deg	0.28 (2.90)	3.5 (5.6)

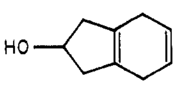
[a] Mean distances; standard deviations in parentheses. [b] X-ray crystallographic C–H bond distances are too short by ~0.13 Å.[9] [c] Angle between the C_5 ring plane and the C–H bond, both displaced away from the nickel.

stituents at 68.1 ± 0.5° (see Figure 2). The 0° conformation is reasonably eliminated on the basis of extensive nonbonded repulsions between the two ligands. The 144° conformation should minimize such intramolecular repulsions, so that intermolecular crystal packing forces must be invoked to explain the observed 68.1 ± 0.5° conformation.

The observed small deviations of the ring hydrogens from the cyclopentadienyl ring plane in **6a** are consistent with the results for both nickelocene[12] and ferrocene.[14] In ferrocene, the ring hydrogens are reported[14] to be displaced toward the iron by 5 ± 3°.

B. Deuterium Labeling. Reduction of dicyclopentadiene, **11**, with D_2 and Pd/C led straightforwardly and quantitatively to 8,9-*exo,exo*-dideuteriotricyclo[5.2.1.0^{2,6}]deca-3-ene, **1b**. The exo orientation of the deuterium atoms was expected[20] and was proved by the Eu(dpm)$_3$ study (Results). Deuteration of diene **14** by a similar procedure eventually gave deuterated tricyclo[5.2.2.0^{2,6}]undeca-2,5-diene, **2b**. This material contained approximately 1.6 deuterium atoms per molecule (mass spectral results). By analogy to **1b**, these deuterium atoms are assumed to be located in the 8,9 exo,exo positions. The reason for hydrogen incorporation (or deuterium loss) in this procedure is unclear.

Several attempts to incorporate deuterium into **3** were unsuccessful. Attempted D_2 reductions of alcohol **17** were



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accompanied by some aromatization and subsequent competition of H_2 with D_2 for the disubstituted double bond.

C. NMR Contact Shifts. Numerical values of the observed isotropic shifts for nickelocene, 1,1'-dimethylnickelocene, and the substituted nickelocenes prepared in this work are presented in Table V. It is assumed that the observed shifts result from Fermi contact interactions, with negligible pseudocontact contribution. Nickelocene itself has been found experimentally to have a quite small magnetic anisotropy together with a sizable zero-field splitting parameter ($g_\parallel = 2.0023$, $g_\perp = 2.06$, $D = 25.6\ \text{cm}^{-1}$).[21] Using these magnetic parameters and the pseudocontact equations of Kurland and McGarvey[22] (which include the zero-field splitting contribution to the metal-centered dipolar shift) we estimate an upper limit of −5 ppm for the dipolar shift of H10S in nickelocene **6a**. This dipolar shift should be the largest observed for any hydrogen in the nickelocene series, because of its proximity to nickel and its angular orientation (~3 Å and 80°). The nickelocene derivatives studied here are very similar to nickelocene in terms of ring hydrogen contact shifts, magnetic susceptibilities, and electronic spectra (see Table V and Experimental Section). Therefore we conclude that pseudocontact shifts are unimportant in all cases.

1. Assignments. Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dien-6-yl)nickel(II), 6a. Assignments of the hydrogen resonances were made by integration, by deuteration, and by comparison with nickelocene (Table V). The nearly complete disappearance of the −95.6-ppm resonance in deuterated **6b** confirms the assignment to hydrogens 8X and 9X. The assignments of the −24.4- and +0.1-ppm resonances unfortunately could not be clarified by deuterium labeling. Numerous approaches to the deuterium labeling of the endo 8,9 positions failed. Assignment of the bridgehead hydrogens (1 and 7) to the −24.4-ppm resonance is however most consistent with the results for all the nickelocenes.

Bis(η^5-tricyclo[5.2.2.0^{2,6}]undeca-2,4-dien-6-yl)nickel(II), 7a. The ^{1}H NMR spectrum of nickelocene **7a** has only one resonance shifted downfield, a peak of integral two at −93.2 ppm. The compound was deuterated to the extent of 1.6 deuterium atoms per ligand in the exo 8,9 positions in an analogous manner to that of **6b**. The NMR of deuterated **7b** shows 40% ± 10% reduction in the intensity of the peak at −93.2 ppm (because of the symmetry of the ligand, the 8,9 and 10,11 positions are equivalent, making possible only a 50% reduction in the peak intensity by total dideuteration of the 8,9 positions). This relates the −93.2-ppm resonance to either 8X,9X or 10X,11X. By analogy to **6a**, we assign the −93.2-ppm resonance to 8X,9X.

The remaining assignments for nickelocenes **8**, **9**, and **10** are straightforward.

2. Spin-Delocalization Mechanisms. Previous studies[3–7] of the ^{1}H and ^{13}C[3g] contact shifts for nickelocene and 1,1'-dimethylnickelocene, **18**, have led to the conclusion that positive unpaired spin density is present mainly in $e_{1g}{}^*$ MO's formed by cyclopentadienyl "out-of-plane" p_z orbitals and nickel d_{xz}, d_{yz} orbitals. The high-field contact shifts for the cyclopentadienyl hydrogens in **6–10** and **18** are nearly identical in each case to the NiCp$_2$ result. In addition the electronic spectra of the compounds are practically invariant. Together, these two sets of observations imply that both the mode and the degree of unpaired electron delocalization to the ligand are nearly the same throughout the series.

By analogy to results with organic π radicals, we observe that the substituent β hydrogens in the rigid nickelocenes **6** and **7** and in the semirigid **8** should have electron–^{1}H hyperfine constants which vary as a function of the dihedral angle φ between the C_α–H_β bond and the adjacent ring-carbon p_z orbital, if the $e_{1g}{}^*$ π-delocalization model is an adequate description. Nickelocenes **9** and **10** were studied in an attempt to observe a possible preferred orientation for the bulky substituent, by means of comparison of the β-hydrogen contact shift to that of 1,1'-dimethylnickelocene.

In the present case, we expect hydrogen nuclei β to a carbon $p\pi$ orbital which contains unpaired spin density to sense that spin density without change in sign, according to eq 5,[23,24]

$$A_\beta = (1/2S)(B_0 + B_2\langle\cos^2\varphi\rangle)\rho^\pi \qquad (5)$$

where A_β is the electron–H_β hyperfine coupling constant, $S = 1$ for all nickelocenes, B_0 and B_2 are empirical parameters, $\langle\cos^2\varphi\rangle$ is conformationally averaged over the range of φ's available, and ρ^π is the $p\pi$ spin density at carbon. Equations similar to (5) have been predicted[23] and followed[24–26] for purely organic π-type free radicals.

The dihedral angles required for eq 5 are listed in Table V, opposite the experimental A_β results. These angles were variously estimated. The free-rotation value (45°) was used for 1,1'-dimethylnickelocene, although small errors would be introduced if the methyl groups are slightly out of plane. For nickelocene **6a**, we used the x-ray determined dihedral angle, and for **7a**, we assumed that the symmetry of the molecule requires a dihedral angle close to 90° (± an estimated 3°). Fortunately, rather complete studies[27] of the structure of cyclohexene are available. These studies have shown that the ground state is a half-chair conformation, with dihedral allylic C–H angles of 25 and 131°. We assume that the six-

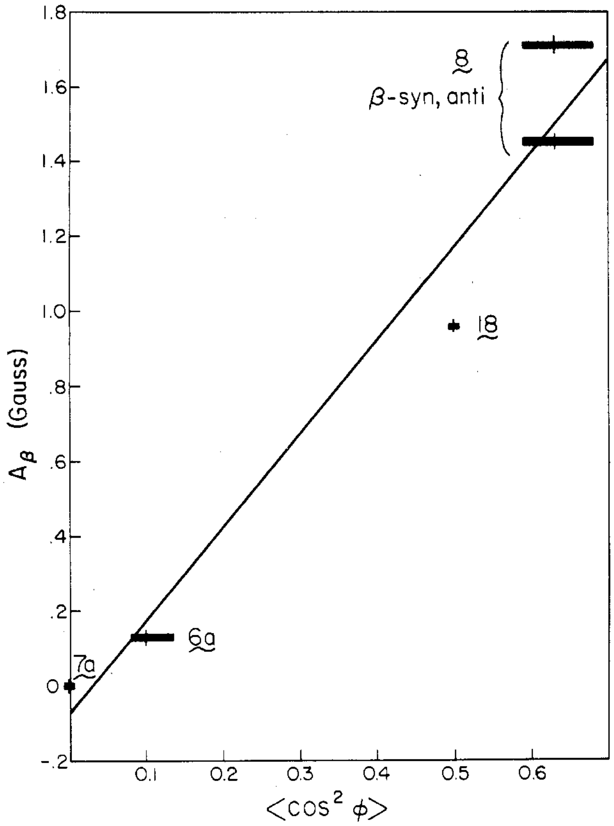


Figure 3. Dependence of A_β on $\langle\cos^2\varphi\rangle$ for substituted nickelocenes. See text for values of constants in eq 5.

membered rings in **8a** are also in the more stable half-chair conformation, and we have utilized the cyclohexene results for the C_α–H_β dihedral angles. Because of conformational averaging between half-chair forms, a given β hydrogen has an averaged dihedral angle and we have therefore averaged $\cos^2$ 25° and $\cos^2$ 131° for use in eq 5.

A graph of A_β vs. $\langle\cos^2\varphi\rangle$ is presented in Figure 3. We have assumed ±3° uncertainties in all φ's except for **18**. The line drawn in Figure 3 is the least-squares line (correlation coefficient 0.98). The results therefore show that the H_β contact shifts are angularly dependent. The observed $\langle\cos^2\varphi\rangle$ dependence of the H_β contact shifts is accounted for by the postulated hyperconjugative interaction of the C–H_β bond with the $e_{1g}{}^*$ π MO, which has most of the unpaired spin density. Similar angular dependencies have been predicted[23] and observed[24-26] for organic π radicals. It therefore seems quite clear that direct π-type delocalization to H_β is strongly dominant in these systems. In fact the near-zero intercept (Figure 3) shows no important σ contribution to the H_β contact shifts.

The extent of spin transfer from the nickel to the cyclopentadienyl π system may be evaluated approximately using the McConnell relation,[28] eq 6. Using the value of $Q = -29.9$

$$A_\alpha = (1/2S)Q\rho^\pi \qquad (6)$$

G for the cyclopentadienyl radical[29] and the observed value of -1.33 ± 0.07 G for the average value of A_α (ring hydrogens) for all the nickelocenes, ρ^π is estimated to be 0.09. Thus the π spin density on each ring is ~0.45, which indicates the appreciable covalency of the nickelocenes.

Insertion of $\rho^\pi = 0.09$ into eq 5 gives $B_0 = 1.7$ G and $B_2 = +55$ G [intercept $= B_0\rho^\pi/2 = -0.078$ ($s = 0.14$), slope $= B_2\rho^\pi/2 = 2.49$ ($s = 0.30$)]. The deviation of B_0 from zero is not significant. The B_2 term is in reasonable agreement with previous results.[24-26] The ρ^π value derived from eq 6 must be considered somewhat uncertain, since utilization of eq 6 assumes that the π–σ exchange is the only important contributor to A_α. The extended Hückel calculations of Rettig and Drago[6] suggested that there might be a positive contribution to A_α from σ delocalization. This has not, however, been experimentally verified.

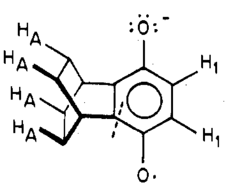
Nickelocene **8** is presumed to undergo rapid interconversions between half-chair forms[27] at the temperature of ^{1}H NMR measurement (40 °C). In a static low-energy form of **8**, which we presume has each ring in a "half-chair" form as in cyclohexene, there are two β hydrogens anti to Ni (H_{2A}, H_{5A}) and two β hydrogens syn to Ni (H_{2S}, H_{5S}) in each ring. Our observation of two low-field resonances in **8** (−266 and −312 ppm) suggests separate averaging of the anti and syn environments. It is interesting to speculate concerning the ~50-ppm difference in resonance position for the anti and syn hydrogens in **8**. We observed above that the substituent α carbons in bis(isodicyclopentadienyl)nickel are bent away from the nickel atom. The deviation from the cyclopentadienyl ring plane is approximately 7° in that case. A similar geometric distortion in **8** would presumably increase the overlap of H_{2A} and H_{5A} with the half-filled $e_{1g}{}^*$ π MO's, because H_{2A} and H_{5A} would necessarily move closer to the cyclopentadienyl ring. The opposite effect would be observed with H_{2S} and H_{5S}. The differing overlaps of the syn and anti hydrogens with $e_{1g}{}^*$ could then lead to the ~50-ppm difference in contact shift. In addition, we would expect an "electronic" distortion in the $e_{1g}{}^*$ molecular orbital, such that the unpaired spin density would be more "concentrated" near nickel on the syn side and more available for sharing anti to nickel. The "electronic" distortion would therefore reinforce the effects of the geometric distortion.[30]

The contact shifts for 1,1'-dimethyl- and 1,1'-diisopropylnickelocene (**18** and **9**, respectively) are nearly the same, indicating that both the methyl and the isopropyl groups undergo free rotation about the C_{ring}–CR_3 bond ($\langle\cos^2\varphi\rangle = 0.5$).[31] In addition the temperature dependencies of the β-hydrogen shifts in both **9** and **18** are normal (linear $\Delta\nu$ vs. $1/T$, $T\Delta\nu$ independent of temperature). In contrast to the results for **9** and **18**, the more crowded nickelocene **10** not only has an anomalously small methine isotropic shift but also shows abnormal dependence of the methine isotropic shift on temperature ($T(\Delta\nu_{\text{methine}})$ decreases with temperature; $\Delta\nu$ vs. $1/T$ intercept at −56 ppm at $T = \infty$). Exactly the same behavior has been observed by Knorr and co-workers[32] in a series of paramagnetic nickel complexes having alkyl substituents attached to a π system containing unpaired spin density. We attribute the anomalous results for **10** to hindered rotation of the $-CH(CH_2CH_3)_2$ group, with a potential minimum occurring when the methine hydrogen is near the plane of the cyclopentadienyl ring ($\cos^2\varphi \simeq 0$). Knorr and co-workers[32] found a rotational barrier of 4.5 ± 0.3 kcal/mol and an equilibrium methine conformation of 83 ± 3° in the nickel complex with the $-CH(CH_2CH_3)_2$ substituent. Although we have not analyzed our results in as much detail as the Knorr work, the general behavior of the two systems is clearly comparable. It is interesting however that we observe no anomalous effects with the diisopropylnickelocene **9**, where Knorr and co-workers[32] observed that the $-CH(CH_3)_2$ and $-CH(CH_2CH_3)_2$ groups had similar steric requirements. In the latter cases the substituents are appended to a six-membered ring, while in our case the ring is of course five-membered.

The 0.61-G coupling constant observed for the methine hydrogen in **10** corresponds to $\langle\cos^2\varphi\rangle$ of ca. 0.3. Such reduced values of $\langle\cos^2\varphi\rangle$ have also been observed in purely organic π radicals with alkyl substituents,[26,33] and in those cases also hindered rotation with a potential minimum near

$\varphi = 0^\circ$ has accounted nicely for the results.

It has been observed previously that in some cases when a carbon pπ orbital contains unpaired spin density, a fraction of that spin density is transferred to a nucleus three or more bonds remote from the first. This spin transfer is most effective when the pπ orbital and the remote nucleus are in a "W arrangement", for example, as in **19**[25] and **20**.[34] In both **19** and **20**, neither bridgehead nor syn couplings were observed by electron spin resonance, and many other examples of the remote coupling were noted.[25,34,35] In both nickelocenes **6a** and **7a** there are hydrogen atoms which are "remote" and which lie in the "W arrangement" with the cyclopentadienyl pπ orbitals, as shown. In both cases a pair of remote hydrogens is strongly coupled (8X,9X in **6a** and 8X,9X in **7a** by analogy), and these hydrogens are seen to lie on the W path. In **6a**, the geminal 8N,9N hydrogens are not significantly contact shifted, nor are the 8N,11N geminal hydrogens in **7a**. The hydrogen–electron interaction is therefore highly stereospecific, as has been observed for the semidiones[34] and semiquinones.[25] In the previous electron spin resonance investigations of "W arrangement" couplings,[25,34] both spin delocalization and spin polarization mechanisms were discussed. Those investigations and interpretations were hampered by the inability to determine the sign of the hyperfine constant by means of the electron spin resonance experiments performed. In nickelocenes **6a** and **7a** the sign of the spin density on H_{8X} and H_{9X} is the same as the cyclopentadienyl π spin density (both positive), and the most straightforward interpretation is that the cyclopentadienyl spin density is delocalized into the C–$H_{8X \text{ or } 9X}$ bonding orbital. This type of "homohyperconjugative" electron–hydrogen hyperfine coupling was proposed by Russell, Holland, and Chang in their work on rigid semidione radicals.[34] In that case the expected positive hyperfine constant could not be verified by ESR.



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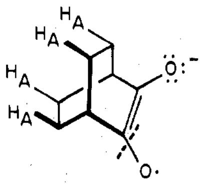
$|A_{H_1}| = 2.78$ G (2H)
$|A_{H_A}| = 0.45$ G (4H)



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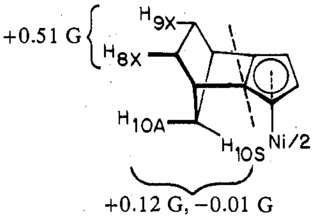
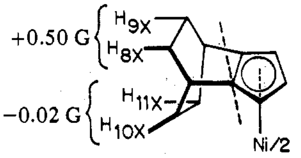
$|A_{H_A}| = 2.09$ G (4H)



6a



7a

In nickelocene **6a**, one of the unit area resonances has a coupling constant of +0.12 G. This could be due to the "W arrangement", as with $H_{8X,9X}$, or alternatively H_{10S} could be shifted to low field by direct interaction with nickel $e_{1g}{}^*$ half-filled orbitals (the crystallographic Ni–H_{10S} distance is 3.12 Å). In nickelocene **7a**, only one pair of hydrogens ($H_{8X,9X}$ or $H_{10X,11X}$) is strongly coupled to the electron spin, although both pairs satisfy the "W arrangement". We suggest that the $e_{1g}{}^*$ cyclopentadienyl π orbitals are distorted inward on the face toward nickel and outward on the opposite face. This would seem to have the effect of maximizing the W coupling to $H_{8X,9X}$, while minimizing the coupling to $H_{10X,11X}$. In addition, the expected geometric distortion of the ligand substituent in **7a** (α carbons displaced away from nickel) would favor $H_{8X,9X}$ coupling to the electron spin and would diminish $H_{10X,11X}$ coupling. These are the same distortions mentioned above in discussing the β-hydrogen shifts of **8**. It is however surprising that no significant shift is observed for $H_{10X,11X}$.

Conclusion

The contact-shifted ^{1}H NMR spectra of nickelocene, 1,1'-dimethylnickelocene, and all of the substituted nickelocenes reported in this work can be explained by direct delocalization of positive spin density from the nickel $e_{1g}{}^*$ orbital to the cyclopentadienyl π system as first proposed by Levy and Orgel.[4] McConnell-type π–σ exchange places negative spin density at the α nuclei, resulting in shifts to higher field. Hyperconjugative spin transfer places positive spin density on the β nuclei in proportion to $\langle \cos^2 \varphi \rangle$, resulting in shifts to lower field. The near-zero shift at $\varphi = 90^\circ$ indicates that σ delocalization is not important in nickelocene. The "W arrangement" allows delocalization of positive spin density to γ hydrogens, again resulting in shifts to lower field.

The results reported here imply that the angular dependencies of ^{1}H contact shifts may be utilized as probes of electronic structure and stereochemistry in organometallics, in much the same way that many organic radicals have been studied. This raises the possibility of extension of this work to the paramagnetic arene and cyclooctatetraenyl complexes.

Experimental Section

A. Apparatus and Techniques. Microanalyses for C, H, and Cl were performed by Chemalytics, Inc., Tempe, Ariz. Melting points were taken on a Uni-Melt Thomas-Hoover capillary melting point apparatus and are uncorrected. The ir spectra were obtained on a Perkin-Elmer Model 621 grating spectrophotometer using 1-mm KBr cells. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU6D high-resolution mass spectrometer. Visible and near-infrared spectra were obtained on a Cary 14 spectrometer in 5-mm quartz window cells.

^{1}H NMR spectra were obtained on Varian A-60D or HA-100 spectrometers, the latter being equipped with an external Hewlett-Packard/Moseley Model 7000A X-Y recorder. Isotropic shifts were measured relative to residual signals of the solvent, perdeuterated toluene or benzene, and were calibrated using the solvent side bands. Integration was performed either by cutting out and weighing the peaks or by determining the peak area by height × width at half-height. Integrals were reproducible within 10% and are reported to the nearest integer. Line widths were measured at half-height using side-band calibration. Chemical shifts are reported in ppm relative to tetramethylsilane (δ) for diamagnetic compounds. For the paramagnetic metallocenes, resonances are reported in ppm relative to the corresponding resonance in the diamagnetic ferrocene analogue (i.e., as contact shifts, positive shifts in ppm are to high field of the reference). Variable-temperature studies were performed on the HA-100 using a Varian V-4343 variable-temperature controller. Probe temperatures were measured either with a copper–constantan thermocouple or with methanol (<40 °C) or ethylene glycol (>40 °C). The two methods agreed within ±0.5 °C. Magnetic susceptibilities were measured by the Evans method.[36] Measurements in a variety of solvents (cyclohexane, benzene, or *p*-dioxane) and for a wide concentration range (0.05–1.0 M) generally agreed within ±0.05 BM.

Data for the crystal structure were collected on a Picker x-ray diffractometer, automated with a PDP-8 Digital computer and teletype, and using a Mo K$\bar{\alpha}$ x-ray source. Data analysis for the crystal structure was carried out on an IBM 360/50 computer and for the lanthanide-induced shift (LIS) experiment a Hewlett-Packard 3000 computer was used.

Gas–liquid chromatography (GLC) was performed on a Varian Aerograph A90P3 instrument with the following columns: (A) 10 ft × $^1/_4$ in. SE30 on Chromosorb W (acid washed (AW), dimethylchlorosilane (DMCS) treated), (B) 6 ft × $^1/_4$ in. Apiezon L on Chromosorb W (AW, DMCS), (C) 10 ft × $^1/_4$ in. Apiezon L on Chromosorb W (AW, DMCS). Preparative GLC was performed on a Hewlett-Packard F & M Model 775 instrument using a 5 ft × $^3/_4$

in. 20% Apiezon L on Chromosorb P (AW).

Oxygen- or water-sensitive materials were handled and stored in a Vacuum/Atmospheres Dri-Train HE-373-BI drybox. Solvents are Mallinckrodt reagent grade and were degassed by bubbling N_2 through a freshly opened, serum-capped bottle for 30 min (hexane, cyclohexane, carbon disulfide, benzene, toluene) or by distillation from $LiAlH_4$ (dioxane, ether, tetrahydrofuran, dimethoxyethane) or barium oxide (pyridine) under nitrogen.

B. Synthesis. 1. Organic Compounds. Tricyclo[5.2.1.$0^{2,6}$]deca-2,5-diene (**1a** or isodicyclopentadiene) was synthesized from dicyclopentadiene by a literature method.[37] Bicyclo[4.3.0]nona-1(6),7-diene, **3**, was synthesized from the spirononadiene precursor, **16**, also by a literature method.[38]

8,9-*exo,exo*-Dideuteriotricyclo[5.2.1.$0^{2,6}$]deca-3-ene, 12b. Dicyclopentadiene (distilled, fraction collected at 72 °C (20–22 Torr)), 64.8 g (0.49 mol), was dissolved in 130 ml of absolute ethanol in a Parr Shaker bottle, and 203 mg of 5% Pd on powdered charcoal was added. The bottle was placed on the Parr Shaker, evacuated, and pressurized to 45 psi of D_2 (Bio-Rad). The bottle was agitated for 45 min at which time the pressure had dropped to 0. The bottle was vented, the solution was filtered through Celite (Johns-Manville), and the solvent was removed (crude yield 100%). The material was purified for analysis on GLC column B (112 °C, 100 cm^3/min). NMR (in $CDCl_3$): 1.35 (broad singlet, 2 H—reduced by 2 H from undeuterated **12a**), 1.50 (broad singlet, 2 H), 2.1–2.4 (multiplet, 4 H), 2.4–2.9 (multiplet, 1 H), 2.9–3.3 (multiplet, 1 H), 5.65 (broad singlet, 2 H). Mass spectral analysis showed that the sample was 90% d_2, 8% d_1, and 2% d_0.

Anal. Calcd for $C_{10}H_{12}D_2$: C, 88.16; H + D, 11.84 (total weight percent H + D). Found: C, 88.29; H + D, 11.89.

8,9-*exo,exo*-Dideuteriotricyclo[5.2.1.$0^{2,6}$]deca-4-en-3-ol, 13b. The published procedure for the undeuterated compound was followed.[37] After SeO_2 oxidation of 8,9-*exo,exo*-dideuteriotricyclo[5.2.1.$0^{2,6}$]deca-3-ene, **12b**, the product was purified by distillation to yield an oily white solid which was crystallized twice from hexane to give a 55% yield of white crystalline solid, mp 51.5–52.5 °C. NMR (in $CHCl_3$): 0.8 (broad singlet, 2 H), 1.15 (broad singlet, 2 H), 1.8–2.1 (multiplet, 3 H), 2.65–2.95 (multiplet, 1 H), 4.1 (broad, 1 H), 4.25 (broad, 1 H), 5.45 (broad singlet, 2 H). Assignments of resonances and measurements of J values were assisted by $Eu(dpm)_3$ (Results).

Anal. Calcd for $C_{10}H_{12}D_2O$: C, 78.90; H + D, 10.58 (total weight percent H + D). Found: C, 78.74; H + D, 10.22.

8,9-*exo,exo*-Dideuteriotricyclo[5.2.1.$0^{2,6}$]deca-2,5-diene, 1b. 8,9-*exo,exo*-Dideuteriotricyclo[5.2.1.$0^{2,6}$]deca-4-en-3-ol, **13b** (20.5 g (135 mmol)), was added to 41 g of Al_2O_3 (Woelm activity grade 1) which had been treated with 1% quinoline,[39] in a 100-ml round-bottomed flask. To this was attached a distillation head with thermometer and a vacuum takeoff adapter with a 25-ml receiver flask. The reaction flask was heated with a silicone oil bath and the receiver flask cooled in dry ice. The pressure was lowered to 50 ± 2 Torr and the oil bath was heated slowly to 160 °C over 2 h and then to 175 °C over 1 h. The product distilled over gradually at 97–107 °C. The adapter was rinsed out with ether and added to the contents of the receiver, and the solution was dried over Na_2CO_3 and filtered, and the ether was removed. The yield of colorless liquid was 5.0 g (37 mmol, 27%). NMR (in benzene): δ 1.2–1.9 (multiplets, 4 H), 3.05 (multiplet, 2 H, bridgehead), 3.2 (multiplet, 2 H, doubly allylic), 5.8 (multiplet, 2 H olefinic).

Tricyclo[5.2.2.$0^{2,6}$]undeca-3,8-diene, 14. A 50.4-g (0.63-mol) sample of cyclohexa-1,3-diene and 41.8 g (0.32 mol) of dicyclopentadiene were added to a sealed glass tube 25 cm × 4 cm (o.d.) × 2 mm thick and heated to 180 ± 5 °C in a mineral oil bath for 24 h. Vacuum distillation yielded a fraction boiling at 88–89 °C (18 Torr) [lit.[40] 80.5 °C (20 Torr)] containing 58.0 g (0.40 mol, 63%) 95% pure (GLC). The product was collected for analysis on GLC column A (150 °C, 100 cm^3/min). NMR (in $CDCl_3$): 1.0–1.6 (double doublet, 4 H, $J_1 = 17$ Hz, $J_2 = 10$ Hz), 1.6–2.2 (multiplet, 2 H), 5.4 (broad singlet, 2 H), and 5.9–6.1 (double doublet, 2 H, $J_1 = 5$ Hz, $J_2 = 3$ Hz).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.70; H, 9.90.

Tricyclo[5.2.2.$0^{2,6}$]undeca-3-ene, 15a. Tricyclo[5.2.2.$0^{2,6}$]undeca-3,8-diene, **14** (2.0 g (13.7 mmol)), was dissolved in 25 ml of absolute ethanol in a Parr Shaker bottle, and 18 mg of 5% Pd on C was added. The bottle was placed on the Parr Shaker, evacuated, flushed with H_2 (American Cryogenics), and pressurized to 50 psi. The bottle was agitated for 30 min and then vented. The solution was filtered through Celite, and the solvent was removed (crude yield 66%). The material was purified by GLC on column B (112 °C, 100 cm^3/min) to yield 1.0 g (6.75 mmol, 49%). NMR (in CS_2): 1.1–1.6 (multiplet, 11 H), 2.1–2.5 (multiplet, 2 H), 2.5–2.9 (multiplet, 1 H), 5.3–5.7 (multiplet, 2 H).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.36; H, 10.97.

Tricyclo[5.2.2.$0^{2,6}$]undeca-4-en-3-ol. Tricyclo[5.2.2.$0^{2,6}$]undeca-3-ene, **15a** (8.0 g (54 mmol)), was dissolved in 50 ml of *p*-dioxane and 5 ml of water. A 3.11-g (28-mmol) amount of SeO_2 (Alfa) was added as the solid with stirring over 30 min. The solution was refluxed for 8 h, cooled, filtered through Celite, and poured into 100 ml of water. The aqueous solution was extracted with three 100-ml portions of ether. The extracts were combined, dried over $MgSO_4$, and filtered, and the solvent was removed. The resulting dark oil was bulk distilled at 1 Torr to give a white pasty oil, 5.0 g (30 mmol, 56%). The oil was further purified by crystallization from hexane to give a white solid, mp 52–53 °C NMR (in $CDCl_3$): 1.3–2.0 (11 H), 2.4–3.0 (1 H), 4.55 (1 H), 5.88 (2 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.32; H, 9.79.

Tricyclo[5.2.2.$0^{2,6}$]undeca-2,5-diene, 2a. A 8.2-g (50-mmol) amount of tricyclo[5.2.2.$0^{2,6}$]undeca-4-en-3-ol was added to 30 g of Al_2O_3 (Merck activity grade 1) which had been treated with 1% quinoline, in a 100-ml round-bottomed flask. To this was attached a distillation head with thermometer and a vacuum takeoff adapter with a 25-ml receiver flask. The reaction flask was heated with a silicone oil bath and the receiver flask was cooled in dry ice. The pressure was lowered to 50 ± 2 Torr and the oil bath was heated slowly to 160 °C over 1 h and to 180 °C over 2 h. The product distilled over gradually and then steadily at 125–127 °C. The adapter was rinsed out with ether and added to the contents of the receiver, and the solution was dried over Na_2SO_4. The product was collected on GLC column B (90 °C, 250 cm^3/min) to yield 3.5 g (2.4 mmol, 48%) of a clear liquid. NMR (in $CHCl_3$): 1.6 (8 H, broad singlet), 2.7 (2 H, multiplet), 2.9 (2 H, triplet, $J = 1.5$ Hz), 6.9 (2 H, triplet, $J = 1.5$ Hz).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 89.30; H, 9.63.

8,9-Dideuteriotricyclo[5.2.2.$0^{2,6}$]undeca-2,5-diene, 2b. The predominantly 8,9-dideuterated material was prepared using D_2 in the above procedure giving a 65% crude yield. Mass spectral analysis of a sample purified by collection on GLC column C showed that the sample was 67% d_2, 29% d_1, and 4% d_0.

1-(1-Methylethyl)cyclopenta-1,3-diene, 4. A 24.6-g (0.20-mol) amount of 2-bromopropane was dissolved in 200 ml of THF in a 1-l. three-necked round-bottomed flask fitted with a dropping funnel, a mechanical stirrer, and a reflux condenser and was flushed with nitrogen and cooled with an ice bath. Over a period of 1 h 0.217 mol of NaC_5H_5 in 95 ml of THF (prepared from cyclopentadiene and NaH in THF) was added. The light red solution and white solid which formed were stirred for an additional 30 min at room temperature and were then poured onto 250 ml of low-boiling petroleum ether, and 250 ml of water was added slowly. The layers were separated, and the aqueous layer was extracted with three 200-ml portions of low-boiling petroleum ether. The organic layers were combined and dried overnight with Na_2SO_4. The solution was filtered, the solvent removed, and the residue distilled at 40–41 °C (38 Torr) to yield 3.3 g (30 mmol, 15%) of a clear liquid. NMR (in $CDCl_3$): 0.7 (6 H, doublet, $J = 7$ Hz), 1.9–2.5 (1 H, multiplet), 2.4 (2 H, quintet, $J = 7$ Hz), 5.4–6.1 (3 H, multiplet).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.69; H, 10.77.

1-(1-Ethylpropyl)cyclopenta-1,3-diene, 5. The same procedure was used as described for 1-(1-methylethyl)cyclopenta-1,3-diene. The product was distilled at 80–83 °C (50 Torr) to yield 17 g (0.125 mol, 50%) of a clear liquid. NMR (in $CDCl_3$): 0.8 (6 H, triplet, $J = 6$ Hz), 1.45 (4 H, quintet, $J = 6$ Hz), 2.1 (1 H, multiplet), 2.8 (2 H, doublet, $J = 6$ Hz), 5.8–6.4 (3 H, multiplet).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.43; H, 11.95.

2. Nickelocenes. The general procedure outlined below was used for the synthesis of the substituted nickelocenes. The substituted cyclopentadienes were used as synthesized in the previous section.

In the drybox, a weighed amount of the substituted cyclopentadiene was dissolved in hexane and 1 equiv of *n*-butyllithium (1.3 M in

Table VII. Properties of Nickelocenes

Compd	% yield	Mp or distilln temp, °C (pressure, Torr)	Electronic spectra		Magnetic susceptibility, BM	Anal. %			
						Calcd		Found	
			λ_{max}, nm	ϵ, M^{-1} cm^{-1}		C	H	C	H
$Ni(C_5H_5)_2$		Mp 171–173[a]	692[b,d]	60.3[b]	2.86[c]				
6a	55	Mp 145.0–146.0	677[h]	78	2.83 ± 0.05[g]	74.80	6.92	74.67	7.18
7a	57	Mp 160–162	705[e]	80	2.46 ± 0.3[e]	75.68	7.51	76.03	7.58
8a	79	Bp 100–120 (0.7)	667[f]	86	2.79 ± 0.10[f]	72.77	7.46	72.85	7.46
9	62	Bp 57–130 (0.5)	682[e]	62	2.85 ± 0.10[e]	70.38	8.12	70.34	8.20
10	58	Bp 115–125 (0.65)	687[f]	82	2.80 ± 0.10[f]	72.98	9.09	74.83	8.95

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hexane) was added dropwise at a rate of about 1 ml/min. A white solid formed shortly after the addition. The solution was stirred for 1 h and the white solid was filtered off, washed with a small amount of hexane, and vacuum dried for 4 h. The yields of the lithium salts of the alkyl-substituted cyclopentadienes varied from 77 to 92%. These salts were stored in the drybox until needed.

To prepare the nickelocenes, a weighed portion of the appropriate lithium salt was dissolved in a small amount of THF in the drybox. To this stirred solution was added a slight excess of $NiBr_2$(glyme).[41] The solution immediately turned green and was stirred for 30 min. The solvent was removed by vacuum and the product was extracted from the residue with hexane until the extracts were no longer green. The hexane extracts were combined and filtered, and the solvent was removed by vacuum. The resulting green product was reasonably pure but could be further purified by crystallization from toluene for the solids (**6a**, **b**, **7a**, **b**) or for the liquids (**8**, **9**, **10**) by distillation onto a dry ice–methanol cold finger on which they solidified.

Yields and physical data are listed in Table VII. All of the nickelocenes are oxygen sensitive, changing to yellow-brown in a few minutes for the liquids or in up to several weeks for crystals of **6a**.

C. Crystal Structure of Bis(η^5-tricyclo[5.2.1.0^{2,6}]deca-2,4-dienyl)nickel(II), 6a. Dark green crystals of **6a** were obtained from toluene by slow evaporation at room temperature under nitrogen. A parallelepiped about 1.0 × 0.8 × 0.2 mm thick was selected for the x-ray study. Precession photographs showed monoclinic symmetry. The crystal was mounted on the diffractometer with systematically absent reflections $h0l$ ($l \neq 2n$) and hkl ($h + k \neq 2n$); confirmed space group $C2/c$. The unit cell constants a = 18.898 (4) Å, b = 7.578 (3) Å, c = 10.967 (4) Å, and β = 109.5 (1)° were determined from a least-squares fit of 12 intense high-angle reflections (λ(Mo Kα_1) 0.709 16 Å). The assumption of four formula units per unit cell gave a density calculated from the x-ray data of 1.44 g/cm^3 compared with 1.42 g/cm^3 obtained by flotation in 3:1 carbon tetrachloride–benzene.

Intensity data were collected in a Picker Model FACS II four-circle diffractometer, using Mo K$\bar{\alpha}$ radiation (λ 0.710 Å). Reflections with 2θ values of 3–55° were collected using the 2θ–θ scan technique with a scan range of 2.0°. Ten-second counts measured at the extremes of each scan were averaged to give the background. Altogether, 1975 independent reflections were collected. Three standard reflections, remeasured every 50 reflections, showed only small statistical fluctuations during the data collection. Reflections with intensity 3σ above background were considered observed, leaving 1621 reflections after data reduction. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by the heavy-atom method using only reflections with $3° \leq 2\theta \leq 45°$. Unitary structure factors were calculated from a Wilson plot of the data from which an origin-removed Patterson map was calculated.[42] The nickel atom was located in position 4e[45] allowing all reflections to be phased. An electron density map was then calculated from which the cyclopentadienyl ring carbons were identified. Two cycles of least-squares refinement yielded a map from which all nonhydrogen atoms could be identified. Two additional cycles of refinement on the coordinates of all nonhydrogen atoms reduced the conventional and weighted disagreement factors $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w F_o{}^2]^{1/2}$ to 0.080 and 0.117, respectively.

At this point the 677 reflections with $45° \leq 2\theta \leq 55°$ were used to refine further the nonhydrogen atom coordinates. These high-angle reflections should suffer less from distortions due to nonspherical distribution of valence electrons around the central atom core, thus giving more accurate positional parameters for the nonhydrogen atoms. Four cycles of refinement of positional and thermal parameters, allowing the nickel and the carbon atoms to vibrate anisotropically, reduced R_1 and R_2 to 0.039 and 0.041, respectively.

A difference Fourier map was calculated using the observed reflections with $3° \leq 2\theta \leq 35°$ and the nickel and carbon atom coordinates calculated from reflections with $45° \leq 2\theta \leq 55°$. All hydrogens were located. Three cycles of refinement of the hydrogen coordinates, again using only reflections with $3° \leq 2\theta \leq 35°$, reduced R_1 and R_2 to 0.073 and 0.093, respectively. Three cycles of refinement of anisotropic temperature factors for nickel and carbon and isotropic temperature factors for hydrogen using all 1621 observed reflections reduced R_1 and R_2 to 0.056 and 0.074, respectively.

No attempt was made to refine all of the atom coordinates using all of the reflection data. Although this procedure might result in lower overall disagreement factors, the resulting atom positions would be shifted slightly in an attempt to compensate for bonding electrons between atoms. Indeed, the hydrogen atom positions determined here are shifted by as much as 0.13 Å toward the carbon to which they are bonded.[9]

D. Lanthanide-Induced Shift (LIS) Study on Tricyclo[5.2.1.0^{2,6}]deca-4-en-3-ol, 13a and 13b. The use of shift reagents in NMR has been reviewed extensively.[43] A 1 M solution of the alcohol or its 8,9-*exo*,*exo*-dideuterio derivative in chloroform containing 10% tetramethylsilane was prepared in an NMR tube and tris(dipivalomethanato)europium(III), Eu(dpm)$_3$, was added gradually as the solid. After each addition, the solution was heated to promote reaction, the sample was thermally equilibrated with the NMR probe, and a spectrum was run. The shifts of each peak were measured with both $CHCl_3$ and TMS as internal references and are precise to ±2 Hz.

Hydrogen and oxygen atom positions were measured from a Dreiding model, assuming the oxygen to be in the exo position, in accord with the known attack of SeO_2 from the least sterically hindered side.[44] This stereochemistry was confirmed by the induced shift of H2 and the observed coupling constants to H2 and H3 (see Results). The lanthanide-induced shifts were calculated using PSEUDO[10] on the Hewlett-Packard 3000 computer. The program allows variation of the Eu–O distance, rotation around the Eu–O and C–O bonds, and evaluation of rotamer populations in up to three rotational minima and uses the crystallographic disagreement factor R_1. For the calculation the oxygen was placed at the origin, the oxygen–carbon bond was the x axis, and the perpendicular to the plane defined by the oxygen, the carbon bonded to oxygen, and the hydrogen bonded to this same carbon was the y axis.

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Registry No. **1b**, 58616-84-5; **2a**, 58569-52-1; **2b**, 58616-85-6; **4**, 35071-66-0; **5**, 58569-53-2; **6a**, 58581-88-7; **7a**, 58569-56-5; **8**, 58569-57-6; **9**, 57197-55-4; **10**, 58569-58-7; **12b**, 58640-66-7; **13a**, 58616-86-7; **13b**, 58640-67-8; **14**, 19574-35-7; **15a**, 58569-50-9; NaC_5H_5, 4984-82-1; Ni(Br)$_2$(glyme), 28923-39-9; 2-bromopropane, 75-26-3; tricyclo[5.2.2.0^{2,6}]undeca-4-en-3-ol, 58569-51-0; dicyclopentadiene, 77-73-6; cyclohexa-1,3-diene, 592-57-4.

Supplementary Material Available: Table of observed and calculated structure factors for nickelocene **6a** (11 pages). Ordering information is given on any current masthead page.

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