Hydrogenolysis of I also occurs at a slow rate in toluene/THF, a mixed-solvent system which often gives enhanced reactivity for hydrogenolysis. After 3 weeks under hydrogen, approximately one-third of the starting I is left with the $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}^-$ product.

The formation of the trimer $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}^-$ rather than the monomer $(C_5H_5)_2YH_2^-$[35] is consistent with other organolanthanide and organoyttrium chemistry we have studied. Trimeric $Ln_3(\mu_3\text{-}H)$ complexes are often the favored products in hydride-forming reactions in which alkali metal salts are present.[35,45,46]

Complex I reacts with H_2 at a rate slower than that observed for terminal alkyl complexes such as $(C_5H_5)_2Ln(t\text{-}C_4H_9)(THF)$,[19] IV, $(C_5H_5)_2Ln(CH_3)(THF)$,[20,45] V, and $(C_5Me_5)_2Th(CH_2SiMe_3)_2$,[47] II. The slowness of the reaction could be understood if, in solution, the Li cation becomes associated with the CH_2SiMe_3 ligands, making them effectively bridging alkyls. If lithium association is not responsible for the reduced reactivity to hydrogenolysis, an alternative basis for the slow reactivity of I vs. complexes such as II, IV, and V is the negative charge on I.[48] Further studies are needed to establish if this is a general principle of organometallic reactivity for metals of this type.

Acknowledgment. For support of this research, we thank the Division of Basic Energy Sciences of the Department of Energy. We also thank the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E) and Dr. Timothy P. Hanusa for help with crystallographic details.

Registry No. I, 97879-10-2; $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(DME)_2\}$, 97879-11-3; $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}^-$, 90762-80-4; $[(C_5H_5)_2yCl]_2$, 79948-35-9; YCl_3, 10361-92-9; $LiCH_2Si(CH_3)_3$, 1822-00-0.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Diene Derivatives of (η^6-Toluene)Ni(C_6F_5)$_2$. The Crystal and Molecular Structures of (η^4-Norbornadiene)Ni(C_6F_5)$_2$ and (η^4-1,5-Cyclooctadiene)Ni(C_6F_5)$_2$

Marc W. Eyring[1] and Lewis J. Radonovich*

*Department of Chemistry, University of North Dakota, Box 7185 University Station,
Grand Forks, North Dakota 58202*

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In order to study the effect of replacing the π-arene ligand in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$ with a diene, the structures of $(\eta^4\text{-}C_7H_8)Ni(C_6F_5)_2$ and $(\eta^4\text{-}C_8H_{12})Ni(C_6F_5)_2$ were determined. $(\eta^4\text{-}C_7H_8)Ni(C_6F_5)_2$ crystallizes in space group $P\bar{1}$ with 2 molecules per unit cell and lattice constants of $a = 10.733(4)$ Å, $b = 10.773(4)$ Å, $c = 9.154(4)$ Å, $\alpha = 113.66(7)°$, $\beta = 95.12(4)°$ and $\gamma = 60.82(2)°$. $(\eta^4\text{-}C_8H_{12})Ni(C_6F_5)_2$ crystallizes in space group $C2/c$ with 4 molecules per unit cell and lattice constants of $a = 18.755(3)$ Å, $b = 8.003(1)$ Å, $c = 13.698(3)$ Å and $\beta = 118.99(1)°$. If the midpoint of the olefin double bonds is taken as the point of attachment to the nickel, then the coordination sphere in both complexes is approximately square planar. Comparison of the bond parameters in these structures to those observed in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$ suggests that the Ni–C_6F_5 bond length is quite sensitive to small changes in the degree of π-back-bonding. A feasible mechanism for small amounts of π-back-bonding is presented.

Introduction

During the past eight years several examples of (π-arene)ML_2 complexes, where M = Fe, Co, and Ni, have been established by X-ray crystallography.[2-8] These structural studies have provided a good deal of insight into the bonding involved in these complexes. Moreover, molecular orbital calculations by T.A. Albright[5] have provided a model to rationalize the structural and chemical observations. Accordingly, the occupancy of the highest occupied molecular orbital (HOMO), which is antibonding with respect to the π-arene ligand, can account for the distortions of the π-arene from planarity and the M–arene bond distances. Thus far it appears that even the lability of the π-arene is related to the nature of this HOMO. Unfortunately, the number of complexes of this type that can be prepared is still quite limited. However, extensive synthetic work aimed at expanding the scope of π-arene complexes is currently ongoing in our laboratory as well as K.J. Klabunde's.

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(η^6-Toluene)Ni(C_6F_5)$_2$[4] is one of the most interesting complexes of this type for several reasons. First, a small but significant "boat" type deformation is observed for the π-arene ligand in this 18 electron complex. Secondly, the π-arene ligand is very labile at, or below, room temperature. Consequently, this complex has a rich chemistry.[3,9] The π-arene is readily displaced by a variety of molecules including norbornadiene (NBD) and 1,5-cyclooctadiene (COD). In a sense, (π-toluene)Ni(C_6F_5)$_2$ can be viewed as though it were attempting to approach η^4-attachment of the arene, although it is certainly much closer to a η^6 attachment. In order to assess the effects of replacing the π-toluene ligand with a diene we have determined the structures of (η^4-NBD)Ni(C_6F_5)$_2$ (**1**) and (η^4-COD)Ni(C_6F_5)$_2$ (**2**). Both structures were done at low temperatures in order to obtain the most reliable bond parameters.

Experimental Section

Both compounds were prepared by R. Gastinger and K. Klabunde as described previously.[3] Orange crystals of **1** and yellow crystals of **2** were wedged inside glass capillaries under an N_2 atmosphere. Crystal data on the two compounds is given below.

	(η^4-C_7H_8)Ni(C_6F_5)$_2$	(η^4-C_8H_{12})Ni(C_6F_5)$_2$
space group	$P\bar{1}$	$C2/c$
a, Å	10.733 (4)	18.755 (3)
b, Å	10.773 (4)	8.003 (1)
c, Å	9.154 (4)	13.698 (3)
α, deg	113.66 (7)	90°
β, deg	95.12 (4)	118.99 (1)
γ, deg	60.82 (2)	90°
wavelength, Å	0.709 26	0.709 26
stream temp,[10] °C	−91	−93
Z	2	4
ρ(calcd), g mL	1.92	1.85
cryst size, mm	0.27 × 0.30 × 0.47	0.40 × 0.57 × 0.70

Lattice constants for **1** were determined from 26 reflections in the range of ±(42–48°) in 2θ while those for **2** were determined from 30 reflections in the range of ±(45–58°) in 2θ.

Intensity data were collected on a Picker FACS-1 diffractometer that was fitted with a Syntex LT-1 cooling system. Data on **1** were collected with this system as supplied by Syntex which allows temperature measurements only when the crystal is removed at the beginning and end of the data set. Following this data set, a 3-m Teflon coated iron–constantan thermocouple was inserted into the exit nozzle and connected to an Omega 199 digital readout and recorder in order to provide a continuous monitor of stream temperature. Subsequent experiments revealed that temperature changes as large as 15 °C occurred during the N_2(l) fill cycle of the heat exchanger. Thus, the stream temperature for **1** may have varied by as much as ±8 °C from the −91 °C temperature that was measured. Further modifications to the Syntex LT-1 cooling systems were then made. These modifications plus the continuous stream temperature monitor assured that the −93 °C stream temperature for **2** was maintained to within ±2 °C for the entire data set. Data for both compounds were collected with zirconium-filtered Mo Kα radiation (λ = 0.7107 Å) with a takeoff angle of 2.5°. 2θ scans at the rate of 1°/min were used, and backgrounds were of 20-s duration. Symmetric scans of 1.3° in 2θ were recorded plus an allowance for spectral dispersion. The intensity of three standard reflections, monitored every 100 data, remained statistically constant during data collection. Unique data were collected out to a maximum 2θ of 65.25° (1.6 Cu spheres) in the hemisphere $h,\pm k,\pm l$ for **1** and 63.7° (1.5 Cu spheres) in the quadrant $h,k,\pm l$ for **2**. Absorption corrections were applied to the data on **2** during the final stages of refinement. Transmission factors ranged from 0.76 to 0.82. No absorption corrections were required for **1**.

Intensity data were reduced to a set of $|F_o|$'s by application of Lorentz and polarization corrections (Lp). Standard deviations were calculated according to

$$\sigma_F = [(C + k^2B + (iI)^2)/4|F_o|^2(Lp)^2]^{1/2}$$

where C and B are the count of the scan and backgrounds, k is the ratio of scan to background counting time, and I is the net peak intensity. Values of i were 0.01 for *1* and 0.02 for **2**. Of the 6158 data collected for **1**, some 5601 having $|F_o| > 2\sigma_F$ were judged observed while 2759 from the 3097 collected for **2** satisfied this criterion.

Patterson and Fourier[11] techniques were used to locate all atoms in the two structures. Full-matrix isotropic least-squares refinement[12] was followed by fully anisotropic refinement for all atoms except hydrogens. In order to minimize computer time for **1**, anisotropic refinement was done in two stages ignoring correlations between the two pentafluorophenyl groups. Accordingly, the parameters for the nickel atom, the NBD ligand, and one pentafluorophenyl group were varied in one cycle followed by another cycle varying the other pentafluorophenyl group along with the nickel atom and NBD ligand. Hydrogen coordinates were then obtained from difference syntheses and included in further refinement[13] with fixed thermal parameters of 4 Å^2 for **1** and 5 Å^2 for **2**. After anomalous dispersion corrections[14] were added for nickel, these unit-weighted refinements produced R[15] = 4.5% and R_W = 4.9% for **1** and R = 4.2% and R_W = 5.3% for **2**. Empirical weights ($w = 1/\sigma^2$) were then calculated as described previously[16] and utilized in further refinement. Final refinement of **1** produced R = 4.4% and R_W = 4.6% while **2** produced R = 4.2% and R_W = 6.8%. The error of fit was 1.42 for **1** and 1.71 for **2**. The data to parameter ratios were 19:1 and 17:1 for **1** and **2**, respectively. Final difference syntheses revealed that the largest residual electron densities were 0.63 e/Å for **1** and 0.51 e/Å^3 for **2**. Positional parameters from the final refinements are listed in Tables I and II. Associated anisotropic thermal parameters are listed in Tables III and IV (supplementary Material), and the observed and calculated structure factors are listed in Tables V and VI (supplementary Material).

Results and Discussion

An ORTEP[17] drawing of one molecule of (η^4-NBD)Ni(C_6F_5)$_2$ is shown in Figure 1 with thermal ellipsoids represented at 50% probability. Pertinent bond distances and angles are listed in Table VII and VIII, respectively. The average C–C double bond in the NBD ligand of 1.361 (3) Å displays the normal lengthening associated with complexation to a metal. The corresponding value from an electron diffraction study of free NBD at 77 K is 1.333 Å,[18] and the value found in the low-temperature X-ray structure of (η^4-NBD)PdCl$_2$ is 1.366 (10) Å.[19] A slight lengthening of the C—C single bonds adjacent to the C=C double bonds from 1.522 (6) Å in free NBD[18] to 1.540 (3) Å is also observed. The value observed in (η^4-NBD)PdCl$_2$ is 1.553 (6) Å.[19] This appears to reflect a slight pertur-

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[10] Experiments in our laboratory indicate that the crystal temperature is 9–10 °C warmer than the stream temperature.

[11] Atomic form factors from Cromer and Mann (Cromer, D. T.; Mann, L. J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321) and A. Zalkin's Fourier program FORDAP were used.

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[15] $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum we(F_o)^2]^{1/2}$.

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Table I. Atomic Coordinates in (η^4-C_7H_8)Ni(C_6F_5)$_2$[a]

atom	10^4x	10^4y	10^4z
Ni	2388.4 (3)	2989.0 (3)	2189.1 (3)
C_1	2658 (2)	1595 (2)	3145 (2)
C_2	1616 (2)	1950 (2)	4255 (2)
C_3	1807 (2)	1017 (2)	5041 (2)
C_4	3095 (2)	−359 (2)	4690 (3)
C_5	4163 (2)	−777 (2)	3574 (3)
C_6	3924 (2)	196 (2)	2821 (3)
C_7	995 (2)	2513 (2)	1023 (2)
C_8	−473 (2)	3548 (2)	1430 (2)
C_9	−1495 (2)	3192 (2)	650 (3)
C_{10}	−1067 (2)	1768 (3)	−615 (3)
C_{11}	381 (2)	701 (2)	−1090 (2)
C_{12}	1373 (2)	1088 (2)	−257 (2)
C_{13}	1808 (2)	5101 (2)	1968 (3)
C_{14}	2540 (2)	5670 (2)	3414 (3)
C_{15}	3250 (2)	4290 (3)	3911 (3)
C_{16}	4324 (2)	3075 (3)	2708 (3)
C_{17}	4311 (2)	3643 (2)	1412 (3)
C_{18}	2873 (2)	3880 (2)	759 (3)
C_{19}	3883 (2)	5359 (3)	2501 (3)
F_2	321 (1)	3258 (1)	4613 (2)
F_3	765 (2)	1409 (2)	6107 (2)
F_4	3293 (2)	−1293 (2)	5419 (2)
F_5	5412 (1)	−2134 (2)	3205 (2)
F_6	5002 (1)	−301 (2)	1706 (2)
F_8	−981 (1)	4981 (1)	2646 (2)
F_9	−2913 (1)	4223 (2)	1134 (2)
F_{10}	−2056 (2)	1412 (2)	−1371 (2)
F_{11}	805 (2)	−702 (2)	−2328 (2)
F_{12}	2776 (1)	−18 (2)	−719 (2)
H_{13}	705 (37)	5675 (40)	1915 (41)
H_{14}	1930 (37)	6743 (41)	4281 (42)
H_{15}	2982 (37)	4345 (40)	5018 (43)
H_{16}	5028 (38)	2061 (41)	2685 (42)
H_{17}	5131 (37)	3003 (40)	563 (43)
H_{18}	2756 (37)	3339 (41)	−322 (43)
$H_{19\text{-}A}$	3579 (37)	6053 (41)	1954 (42)
$H_{19\text{-}B}$	4578 (38)	5423 (40)	3203 (42)

[a] Estimated standard deviations are given in parentheses for the least significant digits.

Table II. Atomic Coordinates in (η^4-C_8H_{12})Ni(C_6F_5)$_2$

atom	10^4x	10^4y	10^4z
Ni	0.0	307.8 (5)	2500.0
C_1	−796 (1)	−1424 (3)	2026 (2)
C_2	−1058 (1)	−2381 (3)	1071 (2)
C_3	−1673 (1)	−3570 (3)	728 (2)
C_4	−2040 (1)	−3847 (3)	1379 (3)
C_5	−1801 (1)	−2931 (3)	2343 (2)
C_6	−1187 (1)	−1756 (3)	2647 (2)
C_7	−909 (1)	2296 (3)	2206 (2)
C_8	−833 (1)	2060 (3)	1273 (2)
C_9	−292 (2)	2972 (4)	929 (2)
C_{10}	504 (2)	3613 (3)	1901 (2)
F_2	−723 (1)	−2156 (3)	399 (1)
F_3	−1917 (1)	−4457 (2)	−220 (2)
F_4	−2631 (1)	−5001 (3)	−1073 (2)
F_5	−2155 (1)	−3214 (3)	2975 (2)
F_6	−981 (1)	−874 (2)	3589 (1)
H_7	−1320 (30)	1663 (62)	2236 (39)
H_8	−1195 (30)	1297 (64)	810 (38)
$H_{9\text{-}A}$	−580 (29)	3852 (66)	438 (39)
$H_{9\text{-}B}$	−217 (29)	2264 (63)	511 (40)
$H_{10\text{-}A}$	433 (32)	4650 (61)	2211 (43)
$H_{10\text{-}B}$	846 (30)	3918 (64)	1558 (40)

bation of the σ-framework of NBD upon complexation.

A computer drawing of one molecule of (η^4COD)Ni(C_6F_5)$_2$ is shown in Figure 2.[17] The molecule resides on a crystallographic twofold rotation axis that passes through the center of the COD ligand and the Ni atom. Double bonds occur between C_7–C_8 and C_7'–C_8', where the prime notation refers to those atoms related by the twofold rotation axis. Bond distances are listed in Table IX, and bond angles are listed in Table X. The observed double bond within the COD ligand is 1.366 (4) Å while the average single bond is 1.513 (4) Å. These are in good agreement with those found in (diphenylacetylene)bis(1,5-cyclooctadiene)nickel[20] of 1.367 (12) and 1.509 (12) Å, for the COD double and single bonds, respectively. The corresponding values found in bis(1,5-cyclooctadiene)nickel(0)[21] of 1.39 and 1.52 Å are also similar.

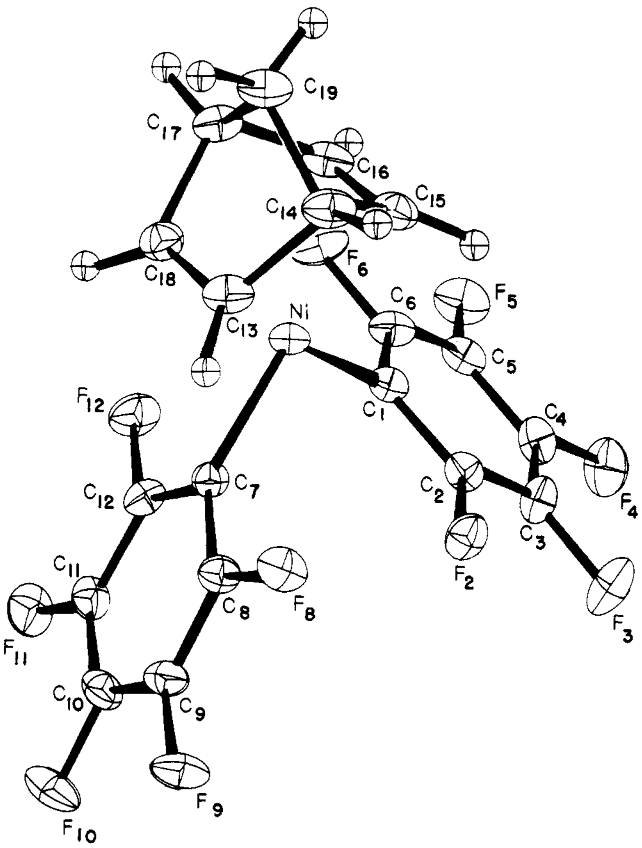

Figure 1. A computer drawing of one molecule of (η^4-NBD)Ni(C_6F_5)$_2$. Thermal ellipsoids are represented at 50% probability and the atomic numbering scheme is displayed. Hydrogen atoms have been deliberately reduced in size for clarity.

Table VII. Bond Distances (Å) in (η^5-C_7H_8)Ni(C_6F_5)$_2$

Coordination Sphere			
Ni–C_1	1.921 (2)	Ni–C_{15}	2.129 (2)
Ni–C_7	1.914 (2)	Ni–C_{16}	2.127 (2)
Ni–C_{13}	2.138 (2)	Ni–C_{18}	2.127 (2)
Within the Ligands			
C_1–C_2	1.380 (3)	C_7–C_8	1.387 (3)
C_1–C_6	1.386 (3)	C_7–C_{12}	1.388 (3)
C_2–C_3	1.387 (3)	C_8–C_9	1.383 (3)
C_3–C_4	1.382 (3)	C_9–C_{10}	1.374 (3)
C_4–C_5	1.378 (3)	C_{10}–C_{11}	1.379 (3)
C_5–C_6	1.388 (3)	C_{11}–C_{12}	1.387 (3)
C_2–F_2	1.351 (2)	C_8–F_8	1.352 (2)
C_3–F_3	1.336 (3)	C_9–F_9	1.350 (2)
C_4–F_4	1.345 (3)	C_{10}–F_{10}	1.344 (2)
C_5–F_5	1.350 (2)	C_{11}–F_{11}	1.350 (3)
C_6–F_6	1.354 (3)	C_{12}–F_{12}	1.351 (2)
C_{13}–C_{14}	1.542 (3)	C_{15}–C_{16}	1.361 (3)
C_{13}–C_{18}	1.361 (3)	C_{16}–C_{17}	1.535 (3)
C_{14}–C_{15}	1.541 (3)	C_{17}–C_{18}	1.542 (3)
C_{14}–C_{19}	1.552 (3)	C_{17}–C_{19}	1.548 (3)
C_{13}–H_{13}	1.04 (3)	C_{17}–H_{17}	0.97 (4)
C_{14}–H_{14}	1.01 (4)	C_{18}–H_{18}	0.96 (4)
C_{15}–H_{15}	1.05 (4)	C_{19}–$H_{19\text{-}A}$	0.97 (4)
C_{16}–H_{16}	0.97 (4)	C_{19}–$H_{19\text{-}B}$	0.95 (4)

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Table VIII. Bond Angles (deg) in (η^4-C_7H_8)Ni(C_6F_5)$_2$

C_1NiC_7	88.3 (1)	$C_{17}C_{16}H_{16}$	125 (2)
$C_1C_2C_3$	123.5 (2)	$C_{16}C_{17}H_{17}$	118 (2)
$C_2C_3C_4$	119.1 (2)	$C_{18}C_{17}H_{17}$	113 (2)
$C_3C_4C_5$	119.6 (2)	$C_3C_4F_4$	120.0 (2)
$C_4C_5C_6$	119.2 (2)	$C_5C_4F_4$	120.3 (2)
$C_5C_6C_1$	123.3 (2)	$C_4C_5F_5$	119.8 (2)
$C_6C_1C_2$	115.2 (2)	$C_6C_5F_5$	121.0 (2)
$C_7C_8C_9$	123.0 (2)	$C_5C_6F_6$	116.3 (2)
$C_8C_9C_{10}$	119.8 (2)	$C_1C_6F_6$	120.5 (2)
$C_9C_{10}C_{11}$	119.7 (2)	$C_7C_8F_8$	120.8 (2)
$C_{10}C_{11}C_{12}$	118.8 (2)	$C_9C_8F_8$	116.1 (2)
$C_{11}C_{12}C_7$	123.6 (2)	$C_8C_9F_9$	120.6 (2)
$C_{12}C_7C_8$	115.0 (2)	$C_{10}C_9F_9$	119.6 (2)
$C_1C_2F_2$	120.0 (2)	$C_9C_{10}F_{10}$	120.0 (2)
$C_3C_2F_2$	116.5 (2)	$C_{11}C_{10}F_{10}$	120.3 (2)
$C_2C_3F_3$	121.4 (2)	$C_{10}C_{11}F_{11}$	119.8 (2)
$C_4C_3F_3$	119.5 (2)	$C_{12}C_{11}F_{11}$	121.3 (2)
$C_{13}C_{14}C_{15}$	102.2 (2)	$C_{11}C_{12}F_{12}$	116.8 (2)
$C_{14}C_{15}C_{16}$	107.0 (2)	$C_7C_{12}F_{12}$	119.6 (2)
$C_{15}C_{16}C_{17}$	107.0 (2)	$C_{13}C_{14}C_{19}$	99.5 (2)
$C_{16}C_{17}C_{18}$	102.9 (2)	$C_{15}C_{14}C_{19}$	99.4 (2)
$C_{17}C_{18}C_{13}$	106.6 (2)	$C_{16}C_{17}C_{19}$	99.5 (2)
$C_{18}C_{13}C_{14}$	107.2 (2)	$C_{18}C_{17}C_{19}$	99.9 (2)
$C_{14}C_{13}H_{13}$	124 (2)	$C_{14}C_{19}C_{17}$	93.6 (2)
$C_{18}C_{13}H_{13}$	128 (2)	$C_{17}C_{18}H_{18}$	126 (2)
$C_{19}C_{14}H_{14}$	118 (2)	$C_{13}C_{18}H_{18}$	127 (2)
$C_{19}C_{17}H_{17}$	120 (2)	$C_{14}C_{19}H_{19\text{-}A}$	109 (2)
$C_{13}C_{14}H_{14}$	117 (2)	$C_{14}C_{19}H_{19\text{-}B}$	111 (2)
$C_{15}C_{14}H_{14}$	118 (2)	$C_{17}C_{19}H_{19\text{-}A}$	116 (2)
$C_{14}C_{15}H_{15}$	125 (2)	$C_{17}C_{19}H_{19\text{-}B}$	111 (2)
$C_{16}H_{15}H_{15}$	128 (2)	$H_{19\text{-}A}C_{19}H_{19\text{-}B}$	114 (3)
$C_{15}C_{16}H_{16}$	128 (2)		

Table IX. Bond Distances (Å) in (η^4-C_8H_{12})Ni(C_6F_5)$_2$[a]

	Coordination Sphere		
Ni–C_1	1.906 (2)	Ni–C_8	2.165 (2)
Ni–C_7	2.221 (2)		
	Within the Ligands		
C_1–C_2	1.384 (3)	C_2–F_2	1.356 (3)
C_2–C_3	1.390 (3)	C_3–F_3	1.350 (3)
C_3–C_4	1.382 (4)	C_3–F_4	1.344 (3)
C_4–C_5	1.381 (4)	C_5–F_5	1.341 (3)
C_5–C_6	1.386 (3)	C_6–F_6	1.352 (3)
C_7–C_8	1.366 (4)	C_8–H_8	0.90 (5)
C_8–C_9	1.498 (3)	C_9–$H_{9\text{-}A}$	0.94 (5)
C_9–C_{10}	1.530 (4)	C_9–$H_{9\text{-}B}$	0.87 (5)
C_7–C_{10}'	1.511 (4)	C_{10}–$H_{10\text{-}A}$	0.97 (5)
C_7–H_7	0.94 (5)	C_{10}–$H_{10\text{-}B}$	0.99 (5)

[a] Prime notation indicates those atoms related by the twofold symmetry axis.

Table X. Bond Angles (deg) in (η^4-C_8H_8)Ni(C_6F_5)$_2$[a]

C_1NiC_1'	86.7 (1)	$C_{10}C_9H_{9\text{-}B}$	113 (3)
$C_1C_2C_3$	123.8 (2)	$C_2C_3F_3$	121.6 (3)
$C_2C_3C_4$	118.8 (2)	$C_4C_3F_3$	119.6 (2)
$C_3C_4C_5$	119.9 (2)	$C_3C_4F_4$	120.1 (3)
$C_4C_5C_6$	119.0 (2)	$C_5C_4F_4$	120.0 (3)
$C_5C_6C_1$	123.6 (2)	$C_4C_5F_5$	119.7 (2)
$C_6C_1C_2$	114.9 (2)	$C_6C_5F_5$	121.3 (3)
$C_1C_2F_2$	119.9 (2)	$C_5C_6F_6$	116.9 (2)
$C_3C_2F_2$	116.3 (2)	$C_1C_6F_6$	119.5 (2)
$C_{10}'C_7C_8$	127.9 (2)	$C_8C_9C_{10}$	114.5 (2)
$C_7C_8C_9$	128.3 (2)	$C_9C_{10}C_7'$	111.5 (2)
$C_{10}'C_7H_7$	116 (3)	$C_9C_{10}H_{10\text{-}A}$	112 (3)
$C_8C_7H_7$	115 (3)	$C_9C_{10}H_{10\text{-}B}$	105 (3)
$C_7C_8H_8$	111 (3)	$C_7'C_{10}H_{10\text{-}A}$	113 (3)
$C_9C_8H_8$	120 (3)	$C_7'C_{10}H_{10\text{-}B}$	112 (2)
$C_8C_9H_{9\text{-}A}$	110 (3)	$H_{9\text{-}A}C_9H_{9\text{-}B}$	104 (4)
$C_8C_9H_{9\text{-}B}$	104 (3)	$H_{10\text{-}A}C_{10}H_{10\text{-}B}$	105 (4)
$C_{10}C_9H_{9\text{-}A}$	111 (3)		

[a] Prime notation refers to those atoms related by the twofold rotation axis.

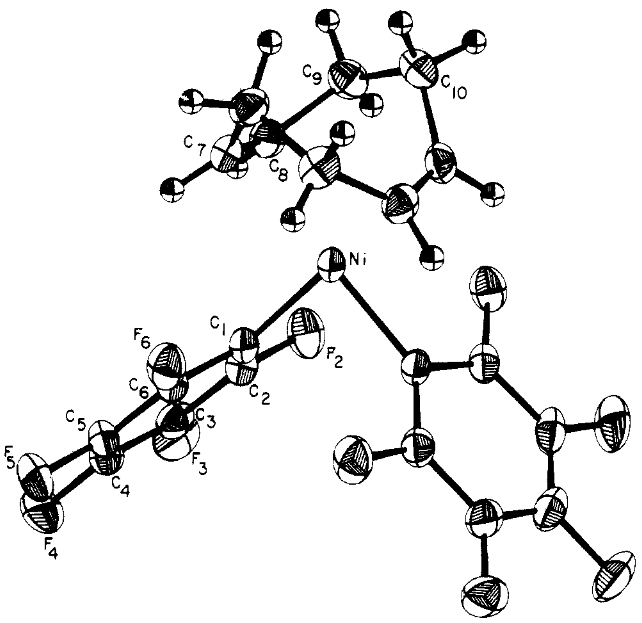

Figure 2. A computer drawing of one molecule of (η^4-COD)-Ni(C_6F_5)$_2$. Thermal ellipsoids are represented at 50% probability and the atomic numbering scheme is displayed. Hydrogen atoms have been deliberately reduced in size for clarity.

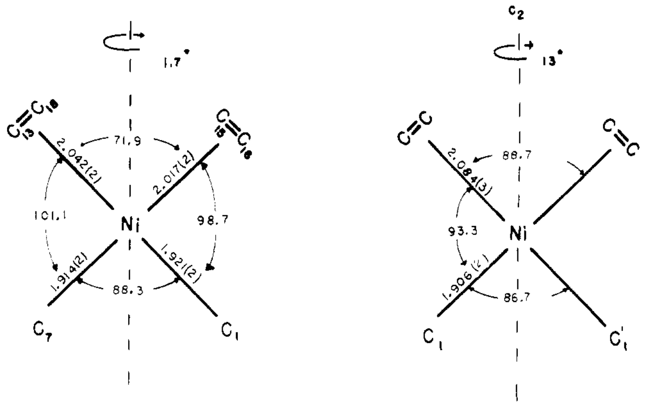

Figure 3. Bond parameters within the coordination sphere of (a) (η^6-NBD)Ni(C_6F_5)$_2$ and (b) (η^4-COD)Ni(C_6F_5)$_2$.

The observed parameters for the pentafluorophenyl ligands in the two structures are remarkably consistent. The six-carbon rings are planar within experimental error with the average deviation being 0.005 Å in 1 and 0.003 Å in 2 and the maximum deviation being 0.009 Å in 1 and 0.004 Å in 2. The average C–C and C–F distances are 1.383 (3) and 1.348 (2) Å, respectively, in 1 and 1.386 (3) and 1.349 (3) Å, respectively, in 2. These distances are also in close agreement to the C–C = 1.374 (7) Å and C–F 1.347 (6) Å values found in the room-temperature structure determination of (η^6-toluene)Ni(C_6F_5)$_2$.[4] Normally one expects small increases in bond lengths for structures done at low temperature due to a reduction in the thermal parameters. It, therefore, appears that the effects of thermal motion are minimal when comparing the results of the present study to other π-arene complexes of Ni(C_6F_5)$_2$ that we have previously studied at room temperature.

Bond parameters within the two coordination spheres are shown in Figure 3. Taking the midpoint of the C=C double bonds as the point of attachment to the Ni atom, both coordination spheres are approximately square pla-

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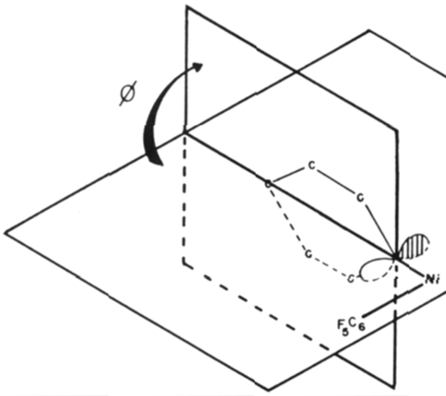
Table XI. Comparison of Ni–C_6F_5 Bonds in C_π–Ni(C_6F_5)$_2$ Complexes Having Approximate C_{2v} Symmetry for the Ni(C_6F_5)$_2$ Moiety[a,b]



	(η^6-toluene)Ni(C_6F_5)$_2$	(η^6-mesitylene)-Ni(C_6F_5)$_2$	(η^4-COD)Ni(C_6F_5)$_2$	[(η^5-C_5H_5)Ni(C_6F_5)$_2$]$^-$	(η^4-NBD)Ni(C_6F_5)$_2$
Ni–C_6F_5, Å	1.891 (4)	1.894 (3)	1.902 (4)	1.900 (3)	1.917 (2)
ϕ, deg	89	86	83	69	72
ref	3	4		24	

[a] Although other complexes are known that contain Ni–C_6F_5 bonds, such as (η^5-C_5H_5)Ni(PPh_3)(C_6F_5),[22] *trans*-(PPh_2Me)$_2$Ni(C_6F_5)(C_6Cl_5),[23] and *trans*-(SC_4H_8)$_2$Ni(C_6F_5)$_2$,[24] *they were excluded from this table because a different geometry is observed.* In each case a better π-acid ligand is present and/or a trans configuration exists. [b] In structures containing more than one independent Ni–C_6F_5 determination the average results are listed.

nar. Accordingly, in the NBD complex the plane containing the two midpoints and the Ni atom is rotated 1.7° from the plane comprised of the Ni atom and two σ-bonded carbons. In the COD complex this rotation is 13° which still is much closer to a square-planar orientation (0° rotation) than tetrahedral (90° rotation). Considered in this fashion, Ni(II) is behaving as a typical d^8 species forming approximately square planar complexes that are diamagnetic.

The Ni–C_π bond lengths in the NBD and COD complex are considerably different. In **1** the four independently determined Ni–C_{NBD} distances are equivalent with the average value being 2.130 (2) Å. The four coordinating carbon atoms (C_{13}, C_{15}, C_{16}, C_{18}) are planar within 0.003 Å, and the perpendicular distance from this plane to the Ni atom is 1.622 Å. In **2** the individual Ni–C_{COD} distances are not equivalent due to a torsional twist of the COD ligand. The Ni–C_8 distance is 2.165 (2) Å while the Ni–C_7 distance is considerably longer at 2.221 (2) Å. Because of this twist the four coordinating atoms (C_7, C_8, C_7', C_8') are not planar. Thus, the average Ni–C_π distance in (η^4-NBD)Ni(C_6F_5)$_2$ is ~0.06 Å shorter than the average in (η^6-toluene)Ni(C_6F_5)$_2$ while the average Ni–C_π distance in (η^4-COD)Ni(C_6F_5)$_2$ is about the same as the η^6-arene complex.

The molecular orbital diagram for a (π-arene)ML_2 complex of C_{2v} symmetry (in the relevant conformation) is shown in Figure 4.[5] A brief description of the parameters used by T. A. Albright in obtaining this diagram is given in the Appendix. For an 18-electron system, such as (η^6-toluene)Ni(C_6F_5)$_2$, the HOMO (b_1) is antibonding with respect to the π-arene ligand and points directly at the ring carbon atoms along the *y* axis. Thus, it is responsible for the ring puckering.[5] When the η^6-arene is replaced with *a diene to form a* square-planar complex, the b_1 antibonding orbital (and associated bonding interaction) would be absent. One would, therefore, expect the π-ligand to move closer to the Ni atom. This is clearly the case in (η^4-NBD)Ni(C_6F_5)$_2$ where ~0.06 Å reduction in the Ni–C_π bonds is observed. However, no reduction is observed in (η^4-COD)Ni(C_6F_5)$_2$ when compared with (η^6-toluene)Ni(C_6F_5)$_2$. Even if the b_1 orbital were to remain populated, one would expect some shortening of the Ni–C_π bonds because the geometry of the NBD and COD ligands require that carbon atoms adjacent to the olefin bonds be bent away from the metal along the *y* axis and thus reduce the antibonding interaction. It also seems unlikely that the relatively long Ni–C_π average bond length of 2.193 (2) Å observed in (η^4-COD)Ni(C_lF_5)$_2$ is due to stereochemical constraints of the COD ligand, because the average length in (COD)$_2$Ni[21] is 2.12 Å.

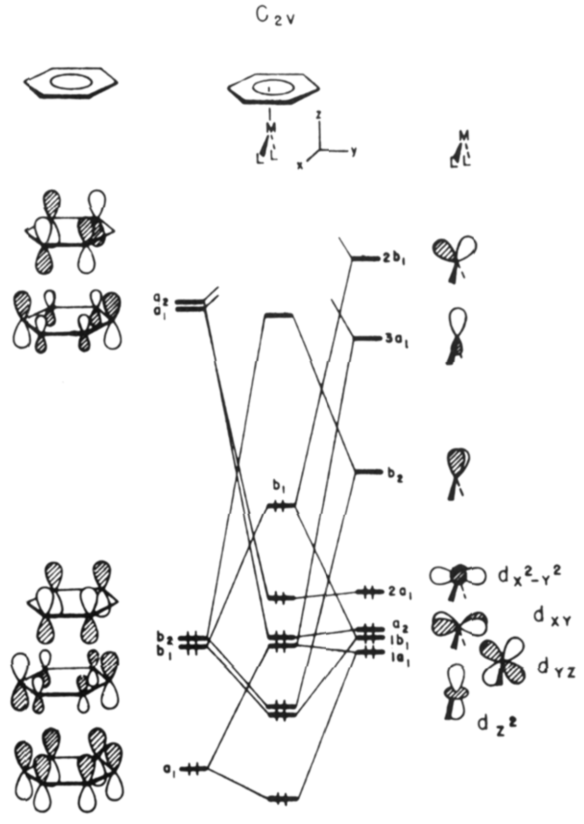


Figure 4. Molecular orbital interaction diagram for a (π-arene)ML_2 complex of C_{2v} symmetry. The electron count displayed is for an 18-electron complex.

Table XII

orbital	H_{ii}, eV	ξ_1	ξ_2	C_1	C_2
Ni 3d	−12.99	5.75	2.00	0.5682	0.6292
4s	−8.86	2.10			
4p	−4.90	2.10			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
H 1s	−13.60	1.30			

A comparison of Ni–C_6F_5 bond lengths observed in π-complexes of $Ni(C_6F_5)_2$ in which the $Ni(C_6F_5)_2$ moiety has approximate C_{2v} symmetry is given in Table XI. In each case the angle between the two Ni–C_6F_5 bonds is approximately 90° and the plane of the C_π atoms is approximately perpendicular to the plane containing the Ni and two σ-bonded carbons. Although changes in the Ni–C_6F_5 bonds are quite small, in general, there does appear to be a significant increase in going from η^6-toluene to the η^4-NBD complex. It should also be noted that the bond length observed in (π-toluene)$Ni(C_6F_5)_2$ is considerably shorter than "normal" estimates[25] of Ni–C(sp^2) single bonds, suggesting that some multiple bonding to the metal occurs. Indeed, a considerably longer Ni–C_6F_5 bond length of 1.948 (4) Å is observed in *trans*-$(SC_4H_8)_2Ni(C_6F_5)_2$.[24] Also listed in Table XI is the angle ϕ which is defined as the angle of rotation of the pentafluorophenyl six-carbon plane relative to the plane containing the Ni and two σ-bonded carbons. In order to illustrate the potential overlap between the p_π system of C_6F_5 with the Ni orbitals, one p orbital is also depicted in the illustration of Table XI. Accordingly, maximum overlap is expected for ϕ = 0° and ϕ = 90°. This overlap should decrease as ϕ moves away from 0° or 90°.

For the case where ϕ = 0° the p_π orbitals of the L groups would be perpendicular to the plane containing the Ni and two σ-bonded ligands and overlap would occur through orbitals of b_1 symmetry. This corresponds, exactly, to the general case that has been discussed previously[5] in which low-lying b_1 orbitals of a strong π-acceptor (L_2) mix with the b_1 HOMO. The effect is to depopulate the HOMO, thus reducing the antibonding interaction which abates the ring puckering and allows the π-arene to move closer to the metal. This has been exemplified nicely by the structure of (η^6-toluene)Fe(2,2′-bipyridine).[6] Of course, this mechanism of π-back-bonding could not occur in (η^6-toluene)$Ni(C_6F_5)$ because ϕ is close to 90°. When the two L groups are C_6F_5, a ϕ of 0° is precluded due to nonbonded repulsions between F atoms on the two ligands.

For the case of ϕ = 90° the p_π orbitals of C_6F_5 would be in the plane of the Ni and two σ-bonded ligands. Overlap could only occur through metal orbitals of a_1 symmetry. The $d_{x^2-y^2}$ seems to be the likely choice since it is principally nonbonding in an ML_2 fragment. Back π-bonding through this a_1 interaction would serve to increase the stability of the complex but would have no effect on the ring puckering. In (η^6-toluene)$Ni(C_6F_5)_2$ then, it is likely that a small amount of π-back-bonding occurs (much less than that in (η^6-toluene)Fe(2,2′-bipyridine)) through the a_1 orbital which helps to stabilize the complex. The π-arene still feels the repulsion of two antibonding electrons in the b_1 HOMO and is, therefore, readily displaced by dienes. In (η^4-NBD)$Ni(C_6F_5)_2$ the repulsion is diminished and less π-back-bonding to C_6F_5 is required to stabilize the complex. Thus the Ni–C_π bonds shorten while the Ni–C_6F_5 bonds lengthen. It remains unclear why this is not observed in (η^4-COD)$Ni(C_6F_5)_2$ although nonbonded interactions might be responsible. Finally, the data in Table XI indicate that a reasonably good correlation exists between the Ni–C_6F_5 bond lengths and ϕ. As ϕ gets further away from 90° the Ni–C_6F_5 bond lengths increase except for the results in $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2]^-$. In considering this correlation a caveat should be realized. ϕ is simply a measure of the orientational requirements for maximum d_π–p_π overlap. Whether or not this overlap is actually utilized in π-back-bonding depends upon electronic factors in a given complex. Nonetheless, the data do suggest that the Ni–C_6F_5 bond length is quite sensitive to small changes in the extent of π-back-bonding. Moreover, a small amount of π-back-bonding to C_6F_5 through the a_1 orbital provides a feasible explanation for the remarkable stability of (η^6-toluene)$Ni(C_6F_5)_2$.

Packing of the two molecules in the solid state is reasonably tight. In both molecules intermolecular F···H interaction occur that are less than the 2.67-Å value expected for a van der Waals contact distance.[27] In (η^4-NBD)$Ni(C_6F_5)_2$ the shortest is the $F_4\cdots H_{19}{}^{I}$ interaction of 2.47 Å while in (η^6-COD)$Ni(C_6F_5)_2$ the shortest is the $F_6\cdots H_{9B}{}^{II}$ interaction of 2.56 Å, where I = $1 - x, -y, 1 - z$ and II = $x, -y, {}^1/_2 + z$.

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Appendix

Molecular orbital calculations by T. A. Albright were carried out with the extended Hückel method.[28] The metal H_{ii}'s were taken from previous work.[29] The parameters are given in Table XII. The modified Wolfsberg–Helmolz formula was used[30] along with the following bond lengths: C–H = 1.09, C–C = 1.41, and Ni–C = 1.60 Å. Regular bond angles were used for benzene, and the L–Ni–L angle was set at 88°. See ref 5 for further details.

Registry No. 1, 74153-76-7; 2, 74153-75-6; (η^6-toluene)$Ni(C_6F_5)_2$, 66197-14-6; Ni, 7440-02-0.

Supplementary Material Available: Anisotropic thermal parameters (Tables III and IV) as well as structure factor amplitudes (Tables V and VI) (48 pages). Ordering information is given on any current masthead page.

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