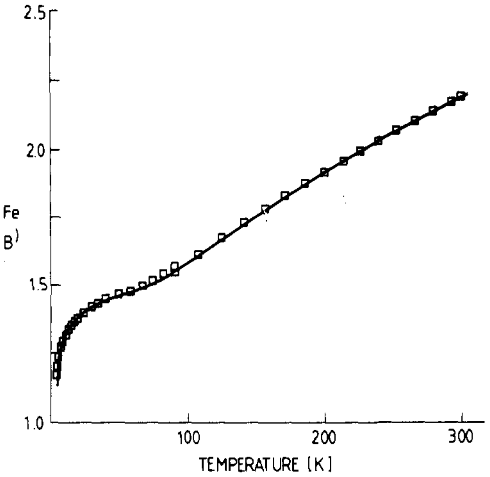


Figure 3. Temperature dependence of the magnetic moment, per Fe, for $[Fe(Pc(2-))]_2O$, sample A. The solid line is the curve computed by using the parameters given in the text, assuming a $^5/_2$–$^5/_2$ dimer and a small percentage of $^5/_2$ monomer.

three samples of I between 4.2 and 300 K were determined. The results for sample A are shown in Figure 3. The plots for samples B and C are very similar in shape but the μ_{Fe} values are a little different in magnitude due, we think, to differing quantities of the high-spin minor species.

These data cannot be explained solely in terms of a simple $^5/_2$–$^5/_2$ coupled system, although the rapid decrease in μ_{eff} between 300 and 70 K shows that such interactions are important. Below 70 K μ_{eff} appears to go through a slight plateau before decreasing very rapidly below 30 K, reaching a value of 1.17 μ_B at 4.2 K. The χ_{Fe}^{-1}/T plot in this low-temperature region is linear with a Curie constant of ca. 4 as expected for a $S = {}^5/_2$ monomer contribution. Given that the Mössbauer spectra also suggest two high-spin Fe(III) complexes are present, one of which is a strongly coupled $S = {}^5/_2$ dimer, the data were analyzed in terms of a mixture of species, viz.

$$\chi_{\text{obsd}} = \rho\chi_1 + (1 - \rho)\chi_2$$

with χ_1 given by the usual $^5/_2$–$^5/_2$ dimer expression[11] and χ_2 by a monomeric high-spin Fe(III) expression. In order to reproduce the observed decrease in μ_{eff} at a very low temperature the effect of zero-field splitting on the monomeric species was considered. Susceptibilities for such a species were calculated by solving the Hamiltonian

$$\mathcal{H} = g\beta\hat{H}\cdot\hat{S} + D[\hat{S}_{z^2} - \tfrac{1}{3}S(S + 1)]$$

By careful variation of the three parameters D, J, and ρ a good fit was obtained with $J = -120 \pm 5$ cm^{-1}, $\rho = 0.063 \pm 0.002$, and $D = 15 \pm 5$ cm^{-1}.

As seen from Figure 3, these parameters successfully reproduce the observed temperature dependence of μ_{eff} over the entire temperature range. The percent monomer impurity calculated from the susceptibility measurements, 6.3%, is significantly lower than that estimated from peak areas in the Mössbauer spectra, ca. 10%. This probably is due to differing Debye–Waller factors in the two complexes.[20] The percent monomer deduced from the $g \sim 6$ ESR line intensity is broadly in agreement with the susceptibility analysis.

Summary

The following points can be made.

(i) Samples of $[Fe(Pc(2-))]_2O$ prepared from PNP[Fe(OH)$_2$(Pc(2-))] consist predominantly of μ-oxo I but invariably contain a small amount of monomeric $S = {}^5/_2$ phthalocyanine iron(III)hydroxo species. Alternative syntheses by Frampton and Silver,[9] using the methods of Ercolani et al.,[4] produce either pure μ-oxo I or mixtures of μ-oxo I plus what appears to be the same monomeric species as obtained here, albeit in higher concentration.[24]

(ii) $[Fe(Pc(2-))]_2O$ is a strongly coupled $^5/_2$–$^5/_2$ complex with a J value of -120 cm^{-1}, similar in magnitude to those of other μ-oxo complexes.[11] It provides the best characterized example of the few known high-spin iron(III) phthalocyanines. The Mössbauer parameters, $\delta = 0.37$ mm s^{-1} and $\Delta E = 0.44$ mm s^{-1}, are clearly indicative of $S = {}^5/_2$ Fe^{III} and are quite different from those of $S = {}^1/_2$ and $S = {}^3/_2$ derivatives.[15] Other recently reported μ-oxo complexes of substituted phthalocyanines[21] appear to have the same electronic structure as found here for $[Fe(Pc(2-))]_2O$. The spectral and magnetic properties of μ-oxo I are only compatible with the oxidation state +3 on each Fe. Formulations of the type $H_2[(Fe(Pc(2-)))_2O]$, which involve Fe^{II}, have been suggested by Lukyanets et al.[22] to apply to *tert*-butyl-substituted Pc(2−) μ-oxo species. These compounds have recently been discussed by Hanack et al.[23] A study, of the present type would quickly confirm or deny such proposals.

Acknowledgment. The authors thank Drs. J. R. Pilbrow and J. Cashion (Physics Department, Monash University) and G. Brain for access to ESR and Mössbauer facilities and R. Elliott for measuring electron microprobe scans. K.S.M. acknowledges receipt of grants from the Australian Research Grants Scheme and Monash University Special Research Grants.

Registry No. I, 74353-48-3; Fe^{3+}, 20074-52-6.

---

(20) Haddad, M. S.; Lynch, M. W.; Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 123 and references therein.

(21) Lever, A. B. P.; Licoccia, S.; Ramaswany, B. S. *Inorg. Chim. Acta* **1982**, *64*, L87. These authors reported IR and UV–visible spectra and some magnetic data for two long-chain alkanesulfonamide PcFe^{III} μ-oxo complexes. The results are compatible with $S = {}^5/_2$ Fe(III) centers.

(22) Mekhryakova, N. G.; Bundina, N. I.; Gulina, T. Y.; Kaliya, O. L.; Lukyanets, E. A. *Zh. Obshch. Khim.* **1984**, *54*, 1656.

(23) Metz, J.; Schneider, O.; Hanack, M. *Inorg. Chem.* **1984**, *23*, 1065.

(24) Ercolani et al. are able to consistently obtain a second crystalline form, μ-oxo II, by oxidizing Fe(Pc(2−)) in a solution of isopropylamine and chloronaphthalene. This form has Mössbauer properties different from those of the minor product in this work and from those of μ-oxo 2(b) of Frampton and Silver[9] (Ercolani, C., private communication, June 1985).

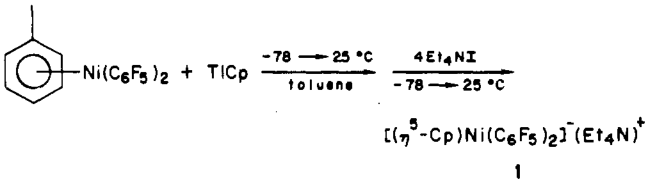
Contribution from the Departments of Chemistry,
Kansas State University, Manhattan, Kansas 66506,
and University of North Dakota,
Grand Forks, North Dakota 58202

The Novel Displacement of a η^6-Arene by η^5-Cyclopentadienide. Synthesis and Structure of $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2][(C_2H_5)_4N]$

Michael M. Brezinski,[†] Kenneth J. Klabunde,*[†]
Stuart K. Janikowski,[‡] and Lewis J. Radonovich*[‡]

Received January 24, 1985

In the course of our continuing investigation of (η^6-arene)MR$_2$ systems,[1] we have discovered a very unusual reaction that has led to the isolation of a new type of organonickel complex. Treatment of (η^6-toluene)bis(pentafluorophenyl)nickel(II) with thallium cyclopentadienide (TlCp) followed by cation exchange with Et$_4$NI resulted in the overall replacement of the η^6-arene by η^5-Cp$^-$:



1

[†] Kansas State University.

[‡] University of North Dakota.

Table I. Crystal Data for $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2][(C_2H_5)_4N]$

formula	$Ni(C_6F_5)_2(C_5H_5)(N(C_2H_5)_4)$
fw	588.24
space group	$P\bar{1}$
systematic absences	none
a, Å	14.306 (2)
b, Å	8.938 (1)
c, Å	10.599 (2)
α, deg	96.51 (1)
β, deg	106.88 (1)
γ, deg	90.61 (1)
Z	2
d_{calcd}, g/cm³ (23 °C)	1.517 (1)
d_{exptl}, g/cm³ (23 °C)	1.519 (6)
cryst size, mm	0.42 × 0.40 × 0.37
data collcn instrument	Picker FACS-1
orientation ref: no.; range (±2θ), deg	15; $31 \leq 2\theta \leq 39$
temp, °C	23
scan method	2θ
data collcn range, deg	$2 \leq 2\theta \leq 54.86$
data collected	$h,\pm k,\pm l$
no. of unique data; total no. with $F_o > 3\sigma_F$	5871; 4090
no. of params refined	334
μ(Mo Kα), mm⁻¹	0.8479
range of transmission factors	0.83597–0.87281
R	0.054
F_w	0.080
GOF	1.49
largest residual peak, e/Å³	0.49

There are several unusual features about this reaction. To our knowledge this is the first example of the direct replacement of a η^6-arene by Cp^-. Generally, η^6-arene complexes, such as $(\eta^6\text{-arene})Cr(CO)_3$ are attacked on the arene ring by nucleophilic reagents.[2] However, in this case there must be a strong driving force for arene displacement since the reaction takes place with TlCp in toluene upon slow warming from −78 °C. It is a very sensitive reaction, as higher temperatures gave much lower yields. Furthermore, it is quite unusual for TlCp to react with such vigor without the driving force of TlX formation.[3] The extreme lability of these $(\eta^6\text{-arene})MR_2$ complexes (arene exchange is rapid even below room temperature)[1a,c] is apparently an important feature in this displacement reaction.

Table III. Atomic Coordinates for $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2][(C_2H_5)_4N]$

atom	10^4x	10^4y	10^4z
Ni	2036.9 (4)	4539.7 (6)	2140.7 (5)
F_2	2299 (2)	2820 (3)	−490 (3)
F_3	2303 (3)	3847 (4)	−2755 (3)
F_4	2073 (3)	6801 (4)	−3059 (3)
F_5	1785 (2)	8747 (3)	−1041 (3)
F_6	1767 (2)	7767 (3)	1235 (3)
F_8	4167 (2)	4031 (4)	2060 (3)
F_9	5858 (2)	5543 (5)	3399 (4)
F_{10}	5860 (3)	7975 (5)	5186 (5)
F_{11}	4158 (3)	8838 (5)	5629 (4)
F_{12}	2472 (3)	7366 (4)	4289 (3)
C_1	2038 (3)	5243 (4)	510 (3)
C_2	2170 (3)	4325 (5)	−563 (4)
C_3	2176 (3)	4824 (5)	−1744 (4)
C_4	2056 (3)	6302 (5)	−1901 (4)
C_5	1917 (3)	7271 (5)	−885 (4)
C_6	1912 (3)	6735 (4)	284 (4)
C_7	3230 (3)	5611 (4)	3089 (4)
C_8	4123 (3)	5222 (5)	2936 (4)
C_9	5007 (3)	5990 (6)	3623 (5)
C_{10}	5011 (4)	7204 (6)	4517 (5)
C_{11}	4152 (4)	7642 (6)	4731 (5)
C_{12}	3295 (3)	6853 (5)	4023 (4)
C_{13}	1783 (5)	3531 (7)	3684 (5)
C_{14}	1826 (5)	2421 (6)	2773 (7)
C_{15}	1094 (7)	2596 (10)	1627 (6)
C_{16}	604 (4)	3868 (11)	2022 (10)
C_{17}	1037 (5)	4351 (8)	3281 (9)
N_1	0	0	5000
C_{18}	75 (5)	−1147 (9)	2699 (6)
C_{19A}	2 (6)	421 (9)	3577 (8)
C_{19B}	106 (7)	−1537 (9)	4271 (9)
C_{20}	1858 (4)	340 (7)	5905 (6)
C_{21A}	882 (6)	1064 (9)	5215 (9)
C_{21B}	908 (6)	−760 (9)	5611 (8)
N_2	5000	10000	0
C_{22}	3848 (4)	10212 (7)	1477 (6)
C_{23A}	4947 (7)	10358 (12)	1385 (8)
C_{23B}	3949 (6)	9998 (12)	13 (10)
C_{24}	4987 (9)	7203 (8)	341 (11)
C_{25A}	5608 (9)	8894 (13)	944 (11)
C_{25B}	4473 (9)	8399 (12)	−661 (11)

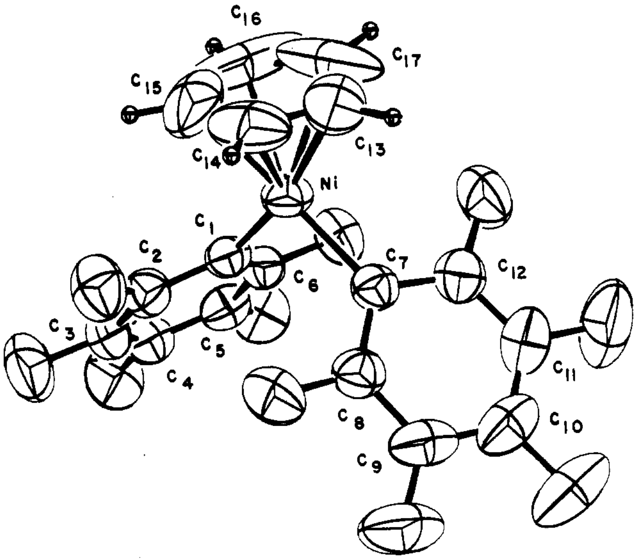


Figure 1. Computer drawing of the $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2]^-$ ion as it exists in crystals of the $[(C_2H_5)_4N]^+$ salt. Anisotropic ellipsoids are represented at 50% probability, and the atomic numbering scheme is displayed. Hydrogen atoms have been deliberately reduced in size for clarity.

An X-ray structure determination was carried out on a translucent, yellow-green crystal of **1** that was obtained by crystallization from a THF/pentane solution. Crystallographic data and other basic information pertaining to the data collection are summarized in Table I. Patterson and Fourier techniques[4] were used to locate all non-hydrogen atoms, which were refined anisotropically. Methylene carbon atoms of the $[(C_2H_5)_4N]^+$ cation were observed to undergo a two-way conformational disorder consistent with the $\bar{1}$ symmetry required for the cation. Atomic coordinates for the Cp hydrogen atoms were calculated at a distance of 0.95 Å from their respective carbon atoms and were included in the final refinement with thermal parameters of 9 Å² at fixed positions. Neutral-atom scattering factors,[4] empirical weighting,[5] and absorption corrections[6] were incorporated in the final refinement,[7] which converged with $R = 5.4$ and $R_w = 8.0$. The atomic coordinates and thermal parameters from

---

(1) (a) Gastinger, R. G.; Anderson, B. B.; Klabunde, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 4959. (b) Brezinski, M. M.; Klabunde, K. J. *Organometallics* **1983**, *2*, 1116. (c) Radonovich, L. J.; Klabunde, K. J.; Behrens, C. B.; McCollor, D. P.; Anderson, B. B. *Inorg. Chem.* **1980**, *19*, 1221.

(2) Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207.

(3) We have observed the same ¹H NMR spectrum for the thallous salt. Unfortunately the material is always contaminated with toluene and has resisted crystallization.

(4) Zalkin's Fourier program FORDAP was used. Neutral atom scattering factors were taken from: Cromer, D. T.; Mann, J. L. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321. Anomalous dispersion corrections for Ni and F were from: Cromer, D. T.; Liberman, P. J. *J. Chem. Phys.* **1979**, *53*, 1891.

(5) Radonovich, L. J.; Klabunde, K. J.; Behrens, C. B.; McCollor, D. P.; Anderson, B. B. *Inorg. Chem.* **1980**, *19*, 1221.

(6) The absorption correction contained in the program DIFFDATA by B. Lee was used.

this refinement are listed in Tables III and IV,[13] respectively. A final difference synthesis revealed that the largest residual electron density of 0.49 e/Å^3 was in the region close to a disordered ethyl carbon.

The asymmetric unit of structure contains a discrete anion of $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2]^-$ and half of two $[(C_2H_5)_4N]^+$ cations that reside on crystallographically independent centers of inversion with disordered methylene carbon atoms. The anion, depicted in Figure 1,[8] consists of a nickel atom that is σ-bonded to two C_6F_5 ligands and π-bonded to C_5H_5 in η^5 fashion. This arrangement has quasi $m(C_s)$ symmetry with the quasi mirror plane containing the Ni, C_1, C_7, and C_{13} atoms and bisecting the C_{15}–C_{16} bond. The plane of the C_5H_5 ring is within 1° of being perpendicular to the Ni, C_1, C_7 plane and the C_1NiC_7 bond angle is 92.7 (1)°. The average Ni–C_6F_5 bond distance of 1.900 (3) Å is 0.009 Å longer than the corresponding distance in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$.[1c] Bond distances and angles are compiled in Tables V[13] and VI,[13] respectively. Other bond parameters within the planar C_6F_5 ligands are within experimental error equivalent to those in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$.[1c]

The average Ni–C_{Cp} distance is 2.108 (4) Å; the five distances are not equivalent due to a nonplanar deformation of the $\eta^5\text{-}C_5H_5$ ring. This deformation can be described as a displacement of C_{13} from the plane containing C_{14}, C_{15}, C_{16}, and C_{17} by 0.070 (5) Å toward the Ni atom, resulting in a fold angle (about the line between C_{14} and C_{17}) of 5.5°. Alternatively, if the plane defined by C_{13}, C_{15}, and C_{16} is taken as the reference plane, then C_{14} and C_{17} are 0.049 (4) and 0.040 (5) Å, respectively, out of the plane away from the Ni atom.[7] The results of mean-planes calculations are given in Table VII.[13] This second description is comparable to that used to describe the nonplanar deformation in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$,[1c] which can be explained by electronic factors.[9] Interestingly, a similar deformation has been observed in $(\eta^5\text{-}C_5H_5)Ni(GeCl_3)(PPh_3)$,[10] while the C_5H_5 ring in $(\eta^5\text{-}C_5H_5)Ni(C_6F_5)(PPh_3)$[11] is planar.

The product $[(\eta^5\text{-}Cp)Ni(C_6F_5)_2][Et_4N]$, which is isoelectronic with the starting arene complex, represents a new class of cyclopentadienylnickel(II) organometallics. No $[(\eta^5\text{-}Cp)Ni(R)_2]^-$ complexes have been reported. Actually $(\eta^5\text{-}Cp)Ni$ anions are rare, the most notable being $[CpNi(CO)]^-$, which is unstable and is generally trapped at low temperature by nucleophilic displacement of halide from various RX compounds.[12]

A typical preparative reaction is now described. All manipulations were carried out under a nitrogen atmosphere in dry, deoxygenated solvents. When a toluene solution (30 mL) of $(\eta^6\text{-toluene})Ni(C_6F_5)_2$ (0.5 g, 1 mmol) held at −78 °C was treated with 1 equiv of solid TlCp (0.275 g, 1 mmol) followed by warming, the mixture became homogeneous between −10 and 0 °C with a color change from red-brown to green. The mixture was stirred for 3 h at room temperature. Recooling to −78 °C and addition of a 4-fold excess of Et_4NI crystals followed again by slow warming to room temperature resulted in a light green supernate and a green solid. The supernate was removed and discarded. The solid was washed twice with 10-mL portions of toluene and twice with 20-mL portions of Et_2O and was then extracted with THF and filtered. After concentration of the ethereal solution, analytically pure product was obtained by vapor diffusion of pentane into the THF solution. Alternatively, evaporation of the THF, dissolution in a 15:85 (v/v) mixture of CH_2Cl_2/Et_2O followed by cooling also produced the pure salt. The product $[CpNi(C_6F_5)_2][Et_4N]$ is a yellow-green air-stable solid, soluble in CH_2Cl_2, THF, CH_3CN, and acetone, slightly soluble in Et_2O, and insoluble in petroleum ether and water. The complex is decomposed by $CHCl_3$. Yields were 60–80%. Mp: 149.5 °C (uncor).

^{1}H NMR (400 MHz, acetone-d_6, Me_4Si reference): δ(Cp) 5.16 (S, 5 H), (CH_2) 3.51 (q, 8 H, $^3J_{HH}$ = 7.0 Hz), δ(CH_3) 1.4 (tt, 12 H, $^3J_{NH}$ = 1.5 Hz, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ(Cp) 89.6, δ(CH_2) 53.1, δ(CH_3) 7.7. IR (cm^{-1}, KBr pellet): 3050 w, 1690 vw, 1615 vw, 1500 vs, 1455 vs, 1360 m, 1280 w, 1180 m, 1055 vs, 1010 m, 960 vs, 860 w, 690 vs. Anal. Calcd: C, 51.0; H, 4.31; N, 2.35. Found: C, 51.5; H, 4.30; N, 2.58.

Registry No. $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2]^-[(C_2H_5)_4N]^+$, 97645-18-6; $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$, 66197-14-6; TlCp, 34822-90-7.

Supplementary Material Available: Listings of structure factor amplitudes (Table II), anisotropic thermal parameters (Table IV), bond distances (Table V), bond angles (Table VI), and mean-planes calculations (Table VII) (30 pages). Ordering information is given on any current masthead page.

---

[7] J. J. Park's block-diagonal-refinement program REFINE was used. Because block-diagonal refinement was used, estimated standard deviations were calculated by using only correlations between coordinates and are underestimated.

[8] Johnson, D. K. "ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration", Report ORNL-3974, Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

[9] Radonovich, L. J.; Koch, F. J.; Albright, T. A. *Inorg. Chem.* **1980**, *19*, 3373.

[10] Bell, N. A.; Glocking, F.; McGregor, A.; Schneider, M. L.; Schearer, H. M. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 623–625.

[11] Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1968**, 2970–2976.

[12] Jolly, J. W. In "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Vol. 6, Chapter 37.8, pp 189–228.

[13] Supplementary material.

Contribution from the Departments of Chemistry,
Universität Zürich, CH-8057 Zürich, Switzerland,
Philipps-Universität, D-3550 Marburg, Germany,
and Kansas State University, Manhattan, Kansas 66506

Metal π Complexes of Benzene Derivatives. 22.[1] Ground-State Configuration of $(\eta^6$-Toluene)bis$(\eta^1$-pentafluorophenyl)cobalt(II): An EPR Study

John H. Ammeter,[2a] Christoph Elschenbroich,*[2b]
Thomas J. Groshens,[2c] Kenneth J. Klabunde,[2c]
R. Oskar Kühne,[2a] and Reinhart Möckel[2b]

Received September 19, 1983

The observation[3] that bis(pentafluorophenyl)cobalt(II) produced via cocondensation of cobalt atoms with pentafluorobromobenzene vapor adds a toluene molecule to yield the novel paramagnetic $(\eta^6$-toluene)bis(pentafluorophenyl)cobalt(II) inaugurated the field of (η-arene)ML_2 chemistry, which continues to reveal many interesting aspects structurally[4,5] as well as chemically.[6] One outstanding feature of this new class of π complexes is the facile substitution of η^6-toluene for other arenes. This has been attributed to the weakness of the transition-metal–arene bond and rationalized in terms of the occupation of an antibonding orbital by one or two electrons (M = Co, Ni, respectively).[5] The availability of the isostructural[4] complexes $(\eta^6\text{-tol})Co(\eta^1\text{-}C_6F_5)_2$ and $(\eta^6\text{-tol})Ni(\eta^1\text{-}C_6F_5)_2$ prompted us to engage in a thorough powder and single-crystal EPR investigation, the results of which are reported in the present communication. The principal aim was the identification of the singly occupied MO in complexes of the general formula (arene)ML_2, with $(\eta^6\text{-tol})Co(\eta^1\text{-}C_6F_5)_2$ serving as a representative example.

---

[1] Part 21: Elschenbroich, Ch.; Möckel, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 375.

[2] (a) Universität Zürich. (b) Universität Marburg. (c) Kansas State University.

[3] Anderson, B. B.; Behrens, C. L.; Radonovich, L. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 5390.

[4] Radonovich, L. J.; Klabunde, K. J.; Behrens, C. B.; McCollor, D. P.; Anderson, B. B. *Inorg. Chem.* **1980**, *19*, 1221.

[5] Radonovich, L. J.; Koch, F. J.; Albright, Th. *Inorg. Chem.* **1980**, *19*, 3373.

[6] (a) Klabunde, K. J.; Anderson, B. B.; Bader, M.; Radonovich, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1313. (b) Brezinski, M. M.; Klabunde, K. J. *Organometallics* **1983**, *2*, 1116.

0020-1669/85/1324-3307$01.50/0