J. Am. Chem. Soc. **1982**, *104*, 2816-2819

Synthesis, Chemistry, and Structure of a New π-Arene Complex of Iron(0), (η^6-Toluene)(2,2′-bipyridine)iron(0). Structural Evidence for Extensive π Back-Bonding to 2,2′-Bipyridine

L. J. Radonovich,*[1a] M. W. Eyring,[1a] T. J. Groshens,[1b] and K. J. Klabunde*[1b]

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

Received September 8, 1981

Abstract: Iron atoms codeposited with excess toluene at −196 °C yielded a brown matrix containing Fe(π-toluene)$_x$. Treatment of this matrix with a limited amount of 2,2′-bipyridine (bpy) yielded (η^6-toluene)Fe(bpy) upon matrix warming. The compound crystallizes in space group *Pnma* with 4 molecules per unit cell and was refined to a residue of 4.1%. The structure was determined from 2910 observed diffractometer data in the range $2\theta \leq 71.0°$ at a stream temperature of −105 ± 2 °C. The structure consists of an iron atom that is bonded to toluene in an η^6 fashion and the two nitrogen atoms of 2,2′-bipyridine in an arrangement of $m(C_s)$ symmetry. An unusually short Fe–N bond distance of 1.902 (1) Å is observed, and distances within the 2,2′-bipyridine ligand deviate from free bipyridine. These structural parameters and supporting IR data provide convincing evidence for a substantial transfer of electron density from the iron atom to the π* orbitals of bipyridine. Chemical reaction studies of (η^6-toluene)Fe(bpy) indicate that the π-arene is not labile and can only be replaced by very strong π-acid ligands such as $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$(dppe).

For several years we have been interested in π-arene complexes of the group 8 transition metals. Our studies are centered around (1) developing an understanding of the bonding, particularly with regard to the lability of the π-arene ligand and nonplanar deformations of the arene carbon framework, and (2) expanding the scope of complexes that are available. Previously, we reported the synthesis, structure determinations, and characterization of some (η^6-arene)ML$_2$ complexes where L = C_6F_5 and M = Co(II) and Ni(II).[2-4] Attempts to produce analogous Fe(II) complexes have not yet been successful. Through a similar procedure, however, we have prepared a π-arene complex of Fe(0) using 2,2′-bipyridine (bpy) as the L$_2$ group. Herein we report this synthesis and the results of an X-ray structure determination of the complex. Comparison to the bonding model proposed from our previous studies[3] provides insight into the interesting and rather unique properties of bipyridine as a σ-bonding ligand and opens up the possibility of preparing additional π-arene complexes of group 8 metals.

Experimental Section

Synthesis. Iron vapor[5,6] (0.756 g, 12.9 mmol) was codeposited at −196 °C with 150 mL of degassed toluene (which had been freshly distilled from benzophenone ketyl). The resultant brown matrix was treated with 1.62 g (10.4 mmol) of bpy dissolved in 25 mL of purified degassed toluene by allowing the solution to flow through a drip tip extending to the bottom of the cold reactor. The mixture was allowed to warm, melt, and with stirring warm to room temperature. At about −30 °C the solution turned from a brown to green color, indicating product formation. The green solution was siphoned out and filtered through a medum-porosity filter frit under N$_2$ flush. The product (η^6-toluene)Fe(bpy) was isolated by removing the excess toluene, redissolving the solid in 150 mL of toluene, and filtering to remove Fe(bpy)$_{2,3}$ compounds. The compound was crystallized by slowly reducing the solution to about 10 mL and decanting the mother liquor. Final yield based on bpy added was 2.1 g or 67% (mp 125 °C dec): ^{1}H NMR (C_6D_6) 2.3 (s, 3), 5.0–5.4 (m, 5), 6.5–7.1 (m, 6), 9.3 (d, 2); IR (cm^{-1}) 742 (vs), 780 (m), 811 (m), 840 (w), 865 (m), 870 (m), 938 (w), 970 (s), 990 (m), 1015 (s), 1025 (m), 1055 (w), 1140 (m), 1154 (m), 1200 (w), 1235 (m), 1260 (m), 1302 (s), 1353 (m), 1376 (m), 1457 (vs), 1515 (s), 1582 (s). Anal. Calcd: C, 66.03; H, 5.43; N, 9.44. Found: C, 67.13; H, 5.30; N, 9.21.

High quality crystals were obtained by recrystallization from a 20% toluene/pentane solution under airless conditions. A dark green crystal of the compound having dimensions of 0.60 × 0.50 × 0.47 mm was wedged in a thin-walled capillary under an N$_2$ atmosphere using a glovebag. Preliminary Weisenberg and precession photographs led to the determination of space group *Pnma* (No. 62).[7] Lattice constants determined on a Picker FACS-1 diffractometer, with Mo Kα radiation, at room temperature were *a* = 7.686 (6), *b* = 13.764 (12), and *c* = 12.985 (11) Å. This unit cell with *Z* = 4 provides a calculated density, at ~24 °C, of 1.467 g/mL.

A preliminary data set was collected at room temperature by using a different crystal. Because of the unusual and interesting bond parameters obtained, a final data set was collected at low temperature on the crystal described above. Since the structural details were the same in both determinations, only the results of the low-temperature study will be reported. The Picker diffractometer was fitted with a modified Syntex LT-1 cooling system. A thermocouple inserted in the exit nozzle provided a continuous monitor of N$_2$ gas stream temperature which was maintained at −105 ± 2 °C.[8] Lattice parameters determined at this temperature from the setting angles of 30 reflections were *a* = 7.622 (2), *b* = 13.6854 (4) Å, and *c* = 12.946 (3) Å. Intensity data were collected with Zr-filtered Mo Kα radiation within the range $2\theta \leq 71.00°$. A 2θ scan width of 1.3°, plus an allowance for spectral dispersion, was used, and background counts were of 20-s duration. A set of three standard reflections monitored every 100 data remained stable over the course of data collection. An approximate calculation of absorption effects suggested that the maximum error of F_o was <2%. Thus, no absorption corrections were made.

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

$$\sigma_F = [(C + k^2B + (0.02I)^2)/4|F_o|^2(Lp)^2]^{1/2}$$

where *C* and *B* are the count of the scan and backgrounds, respectively, *k* is the ratio of scan to background counting time, and *I* is the net intensity. Of the 3211 independent data collected, 2910 having $|F_o| >$

---

[1] (a) University of North Dakota. (b) Kansas State University. (c) This work was communicated in part at the Midwest Regional ACS meeting in Lincoln, NB, November, 1980, and the 182nd National Meeting of the American Chemical Society, New York, June 1981. (Inor 132).

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

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

[4] Klabunde, K. J.; Anderson, B. B.; Bader, M.; Radonovich, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1313.

[5] Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* **1979**, *19*, 59.

[6] Klabunde, K. J. "Chemistry of Free Atoms and Particles"; Academic Press: New York, 1980; p 105.

[7] Henry, N. F. M.; Lonsdale, K., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I.

[8] Measurements in our laboratory indicate that the crystal temperature is ~9-10 °C warmer than the N$_2$ stream temperature.

0002-7863/82/1504-2816$01.25/0

Table I. Atomic Coordinates

atom	10^4x	10^4y	10^4z
Fe	2206.2 (4)	2500	167.7 (2)
N	3274.9 (15)	1588.7 (9)	−746.3 (8)
C_1	3246 (2)	589 (1)	−676 (1)
C_2	4030 (2)	−16 (1)	−1379 (1)
C_3	4929 (2)	388 (2)	−2225 (1)
C_4	4988 (2)	1385 (2)	−2321 (1)
C_5	4163 (2)	1982 (1)	−1579 (1)
C_6	−511 (3)	2500	487 (2)
C_7	268 (2)	1618 (1)	823 (1)
C_8	1786 (2)	1618 (1)	1459 (1)
C_9	2557 (3)	2500	1777 (2)
C_{10}	−2110 (3)	2500	−186 (2)
H_1	2738 (41)	303 (33)	−93 (24)
H_2	3906 (39)	−750 (24)	−1272 (22)
H_3	5480 (44)	−14 (21)	−2692 (22)
H_4	5541 (41)	1683 (23)	−2897 (23)
H_7	−272 (39)	1006 (24)	547 (23)
H_8	2373 (38)	1013 (26)	1592 (25)
H_9	3593 (62)	2500	2139 (32)
H_{10}	−3114 (65)	2500	221 (34)
H_{11}	−2055 (39)	1977 (23)	−663 (25)

$3\sigma_F$ were taken as observed and and utilized in the structure determination and refinement. Patterson and Fourier[9] techniques were used to locate all atoms in the asymmetric unit of structure. Full-matrix[10] isotropic refinement was followed by anisotropic refinement for all atoms except hydrogens, which were refined with fixed thermal parameters. Anomalous dispersion corrections were made for the metal atom.[11] Weights ($w = 1/\sigma_2$) were calculated from the equation above. This refinement converged with $R = 0.043$, $R_w = 0.047$, and an error of fit of 2.68.[12] Empirical weights were then calculated as described previously[2] and utilized in further refinement. This final refinement produced $R = 0.041$, $R_w = 0.048$, and an error of fit of 1.30. The data to parameter ratio was 23.9:1. A final difference synthesis revealed the largest residual electron density was 1.06 e/Å^3. This residual was near the iron atom which had a true ρ of 119 e/Å^3. The next highest residual of 0.54 e/Å^3 was in the region between carbon atoms which had true ρ's of 7.80–16.3 e/Å^3. These final atomic coordinates are listed in Table I, and the associated thermal parameters are listed in Table II.

Reaction of (η^6-Toluene)Fe(bpy) with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (dppe). For this study 0.105 g (0.34 mmol) $(C_6H_5CH_3)$Fe(bpy) was dissolved in 20 mL of toluene, and 0.135 g (0.34 mmol) of diphos (freshly sublimed) was added. As the dark green solution was stirred, it slowly turned brown (~2 h). The solution was filtered and the toluene removed under vacuum. IR analysis of the dry solid showed complexed bpy and dppe. ^{1}H NMR in C_6D_6 showed no resonances, indicating that the complex is paramagnetic.

Results and Discussion

Structure and Bonding. A computer drawing of one molecule of the complex is shown in Figure 1 with the thermal ellipsoids represented at 50% probability.[13] The hydrogen atoms have been reduced in size for clarity and are numbered according to the attached carbons. The structure consists of a discrete molecule containing an iron atom that is bonded to toluene in an η^6 fashion and coordinated to the two nitrogen atoms of bpy. The molecular mirror plane containing the iron and bisecting both ligands is also a crystallographic mirror plane. Individual bond distances and angles are listed in Tables III and IV. No unusual intermolecular interactions occur.

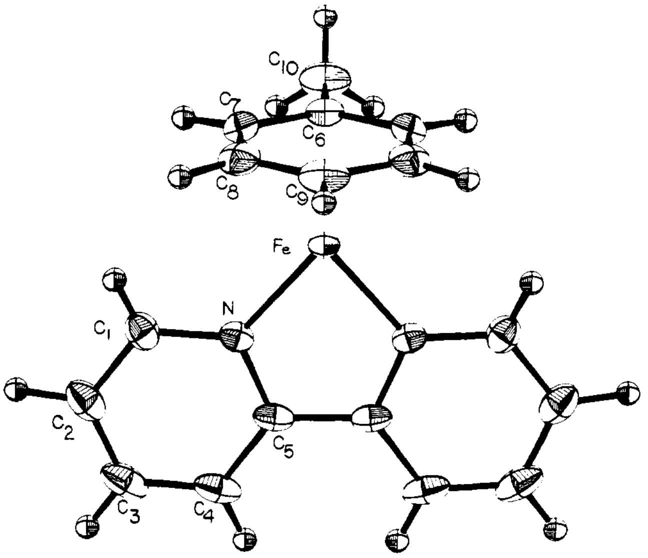


Figure 1. An ORTEP drawing of one molecule of (η^6-toluene)(bpy)Fe^0 at 50% probability. Hydrogen atoms have been deliberately reduced in size for clarity and are numbered according to the attached carbons.

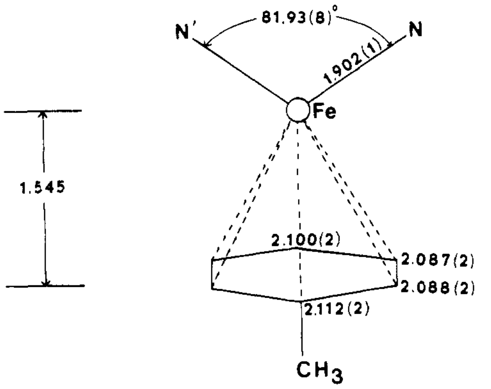


Figure 2. Bond parameters within the coordination sphere of (η^6-toluene)(bpy)Fe^0. Distances are in Å and angles in degrees.

The η^6-toluene ligand is planar, with the maximum deviation of 0.005 Å and an average deviation of 0.003 Å. Because of reduced thermal motion in a low-temperature structure determination, the present study should provide more accurate bond parameters for a π-complexed toluene than previous room-temperature studies of π-arene ML_2 complexes.[2] The ring C–C distances in particular should be slightly longer. Accordingly, the average C–C bond distance is 1.413 (8) Å compared to the 1.391 (9) Å distance observed in $(\eta^6\text{-}C_6H_5CH_3)(C_6F_5)_2Co^{II}$ and the 1.387 (8) Å distance observed i n $(\eta^6\text{-}C_6H_5CH_3)(C_6F_5)_2Ni^{II}$.[2] A slight elongation of ~0.08 Å relative to a regular benzene hexagon is observed along the C_6–C_9 axis, but no compression of the C_7–C_7' and C_8–C_8' distance is observed.[8] This elongation is expected for toluene[2] and accounts for the slightly longer bonds from Fe to C_6 and C_9 in Figure 2. The orientation of the metal and two σ-bonded atoms is generally the same as that observed in other (π-arene)ML_2 moieties.[2] The Fe atom is approximately on the perpendicular line through the ring center and is a distance of 1.545 Å from the toluene mean plane. The interplanar angle between the plane containing N, Fe, and N' and the toluene plane is 89.0°.

Individual pyridine ring fragments within the bpy ligand are planar, with a maximum deviation of 0.002 Å. The bpy ligand as a whole is folded slightly along this plane with an angle between planes of two ring fragments of 2.3°. A comparison of bond distances observed for bpy in the free molecule[14] and several complexes[15-17] is listed in Table V. The corresponding C_5–C_5'

---

(9) Atomic form factors from Cromer and Mann (Cromer, D. T., Mann, J. L. *Acta Crystallogr., Sect A* **1968**, *24*, 321) and A. Zalkin's Fourier program FORDAP were used.

(10) Busing, W. R.; Martin, K. O.; Levy, H. A., Oak Ridge National Laboratory: Oak Ridge, TN, 1962, Report ORNL-TM-305. The function minimized was $w(|F_o| - |F_c|)^2$.

(11) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

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

(13) Johnson, D. K. "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

(14) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 4945.

(15) Depaoli, M. A.; Frühauf, H. W.; Grevels, F. W.; Von Gustorf, E. A. K.; Riemer, W. *J. Organomet. Chem.* **1977**, *136*, 219.

(16) Hoberg, H.; Gotz, V.; Krüger, C. *J. Organomet. Chem.* **1979**, *169*, 219.

Table II. Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{23}	B_{12}	B_{13}	B_{23}	isotropic equivalent[b]
Fe	1.351 (9)	1.758 (9)	1.110 (8)	0.0	0.056 (7)	0.0	1.38
N	1.60 (3)	2.09 (3)	1.43 (3)	0.05 (3)	−0.06 (3)	−0.27 (3)	1.67
C_1	2.30 (5)	2.13 (5)	2.27 (5)	0.11 (4)	−0.22 (4)	−0.41 (4)	2.20
C_2	2.46 (6)	2.71 (6)	3.23 (6)	0.42 (5)	−0.31 (5)	−1.18 (5)	2.60
C_3	2.17 (5)	3.99 (8)	2.88 (6)	0.50 (5)	−0.12 (5)	−1.76 (6)	2.60
C_4	1.69 (4)	4.11 (8)	1.92 (5)	0.17 (5)	0.17 (4)	−0.97 (5)	2.26
C_5	1.30 (4)	2.99 (5)	1.39 (4)	0.03 (4)	−0.04 (3)	−0.27 (4)	1.75
C_6	1.48 (6)	2.60 (7)	1.67 (6)	0.0	0.22 (5)	0.0	1.85
C_7	2.06 (5)	2.23 (5)	2.10 (5)	−0.24 (4)	0.48 (4)	0.17 (4)	2.07
C_8	2.45 (5)	3.10 (6)	1.79 (4)	0.42 (5)	0.39 (4)	0.90 (4)	2.23
C_9	2.23 (8)	4.43 (11)	1.23 (6)	0.0	−0.11 (5)	0.0	2.30
C_{10}	1.77 (7)	4.89 (14)	2.80 (9)	0.0	−0.21 (7)	0.0	2.89

[a] In Å^2. Estimated standard deviations are given in parentheses for the least significant digits. $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$, where β_{ij} are unitless parameters used in refinement in form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Isotropic thermal parameters of the hydrogens were fixed at 5.0 Å^2. [b] Isotropic equivalent = $4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Bond Distances[a]

	Within the Ligands		
$N-C_1$	1.371 (2)	C_5-C_5'	1.417 (3)
C_1-C_2	1.368 (2)	C_1-H_1	0.93 (4)
C_2-C_3	1.406 (3)	C_2-H_2	1.02 (3)
C_3-C_4	1.370 (3)	C_3-H_3	0.92 (3)
C_4-C_5	1.409 (2)	C_4-H_4	0.95 (3)
C_5-N	1.383 (2)		
C_6-C_7	1.414 (2)	C_8-H_8	0.96 (3)
C_7-C_8	1.421 (2)	C_9-H_9	0.92 (5)
C_8-C_9	1.404 (2)	$C_{10}-H_{10}$	0.93 (5)
C_6-C_{10}	1.499 (3)	$C_{10}-H_{11}$	0.95 (5)
C_7-H_7	1.00 (3)		
	Coordination Sphere		
$Fe-C_6$	2.112 (2)	$Fe-C_9$	2.100 (2)
$Fe-C_7$	2.088 (2)	Fe-N	1.902 (1)
$Fe-C_8$	2.087 (2)		

[a] In Å. Prime notation is used for the atom related by the minor plane.

Table IV. Bond Angles[a]

C_5-N-C_1	116.6 (1)	$C_7-C_8-C_9$	120.7 (2)
$N-C_1-C_2$	123.6 (2)	$C_8-C_9-C_8'$	118.6 (2)
$C_1-C_2-C_3$	119.5 (2)	N-Fe-N′	81.93 (8)
$C_2-C_3-C_4$	118.6 (2)	$Fe-N-C_5$	116.1 (1)
$C_3-C_4-C_5$	120.1 (2)	$N-C_5-C_5'$	112.92 (8)
C_4-C_5-N	121.6 (2)	C_6-Fe-C_9	86.00 (9)
$C_7-C_6-C_7'$	117.3 (2)	C_7-Fe-C_8'	84.31 (7)
$C_6-C_7-C_8$	121.3 (2)	C_8-Fe-C_7'	84.31 (7)

inter-ring distance is 1.50 Å[14] in free bpy and normally remains within 0.04 Å of this value in typical complexes.[15-17] In (η^6-$C_6H_5CH_3$)(bpy)Fe^0, however, this distance is considerably shorter at 1.417 (3) Å and is approaching a typical aromatic value. Also, the average C–N distance appears slightly longer while the average C–C distance is similar to typical bpy bond parameters.

The Fe–N bond distance of 1.902 (1) Å is one of the shortest Fe–N distances reported. It is considerably shorter than the Fe–N_{bpy} distances of 1.977 (3) and 1.979 (3) Å distances reported in (diethyl muconate)(2,2′-bipyridine)carbonyliron(II),[15] which are close to the value anticipated for iron(II) with six monodentate nitrogen ligands,[17] and is as short as the average Fe–N_{DMG} distance of 1.905 (6) Å reported in the low-spin complex bis(dimethylglyoximato)bis(imidazole)iron(II).[18] The 5-membered chelate ring formed at the iron atom shows a small deviation from planarity, amounting to a displacement of the iron atom by 0.06 Å from the plane defined by N, C_5, C_5', and N′.

This extremely short Fe–N distance and the short C_5–C_5' distance provide convincing evidence for a substantial transfer of electron density from the iron atom into the π^* orbitals of bpy. The observed planarity of the η^6-toluene ligand is also consistent with this conclusion. On the basis of our previously proposed model for the bonding in π-arene ML_2 complexes,[3] a small distortion of the ring carbon atoms from planarity is expected for an 18-electron system when π backing-bonding into the π^* orbital ($2b_1$) is not exceptional. Extensive π back-bonding, however, would abate the ring puckering, due to mixing of the $2b_1$ orbital of ML_2 with the b_1 HOMO of the complex, and a planar arene should result.

A more detailed analysis of the bond parameters within the bpy ligand, shown in Figure 3, provides more insight into the electronic structure of this complex. Consider the C–C distances within the pyridine ring fragment. Although the difference between any individual C–C distance and those observed in free bpy[14] or other typical complexes[15-17] is not large enough to be reliably significant, there is a definite trend that is not present in the other structures containing bpy. Specifically, an alternating pattern of long and short bonds occurs, indicating that some of the delocalization has been destroyed.[19] Although valence bond terminology cannot

Table V. Comparison of Some 2,2′-Bipyridine Bond Parameters[a]

parameter[b]	this work	uncomplexed bpy[c]	(DM)-(bpy)-COFe[d]	(C_2H_5)-(bpy)(IB)-Ni[e]	($C_{10}H_{16}$)-(bpy)Ni[f]
C_5-C_5'	1.417 (3)	1.490 (3)	1.463 (5)	1.469 (9)	1.48 (1)
C-N av	1.377 (2)	1.344 (2)	1.354 (5)	1.353 (9)	1.348 (9)
C-C av	1.388 (3)	1.387 (2)	1.379 (7)	1.373 (11)	1.38 (1)

[a] All distances are in Å. [b] The C_5–C_5' distance refers to the bond between individual pyridine ring fragments. [c] Reference 14. [d] DM = diethylmuconate.[15] [e] IB = *tert*-butyliminoborate.[16] [f] Reference 17.

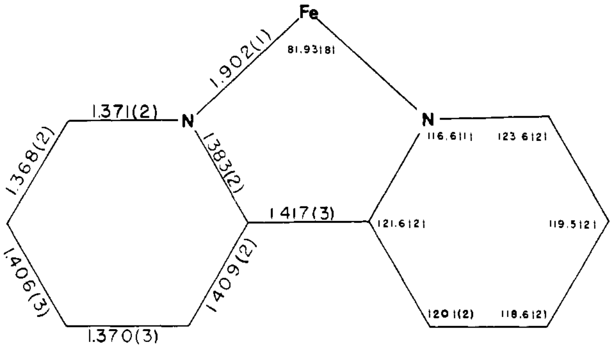


Figure 3. Bond parameters within the bpy ligand in (η^6-toluene)(bpy)Fe^0.

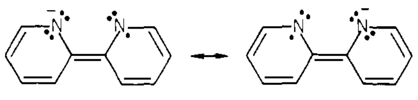
---

(17) Collins, D. M.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2066.

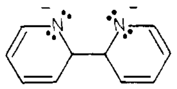
(18) Bowman, K.; Gaughan, A. P.; Dori, Z., *J. Am. Chem. Soc.* **1972**, *94*, 727.

(19) It should be noted that this trend was also present in the room-temperature structure determination. The net difference between the room-temperature and low-temperature parameters was that bonds to the iron increased an average of 0.005 Å while those in the bpy ligand increased an average of 0.007 Å.

adequately represent π back-bonding, resonance forms can be drawn representing the donation of charge from the iron atom to the bpy ligand which are consistent with the observed bond parameters. Accordingly, for a bpy$^-\cdot$ formulation resonance forms i and ii would be important contributors and for a bpy^{2-} formulation resonance form iii would be an important contributor.



i ii

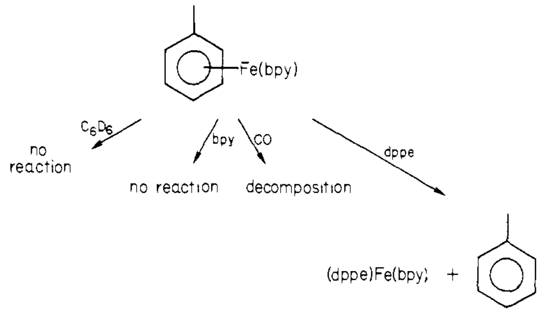


iii

While there has been no evidence presented in the literature for the formation of a bpy^{2-} species in a transition-metal complex, there has been considerable spectroscopic support for the formulation of a bpy$^-\cdot$ species in low oxidation state complexes. Indeed, the very convincing IR work of Nakamoto and coworkers[20] and the UV-vis work of Herzog[21] and Reynolds[22] and their co-workers suggest that neutral $M(bpy)_3$ and $M(bpy)_2$ complexes favor a bpy$^-\cdot$ formulation for some of the transition metals. In accordance with Nakamoto's work,[20] our IR data support the concept of substantial negative charge residing on the bpy ligand. Thus, bands were observed at 1582 and 1515 cm^{-1} that are shifted to lower frequencies than bpy complexes where the ligand is in the normal oxidation state. It is, of course, impossible from the present study to determine the actual magnitude of the charge on the iron atom and bpy ligand. Thus, there are three possible views for the bonding in this formally 18-electron complex. The system may be approaching a bpy$^-\cdot$ formulation and a 17-electron configuration about iron or the system may be approaching a bpy^{2-} formulation and a 16-electron configuration about iron. Finally, a synergistic effect similar to the metal carbonyls could occur in which strong donation though the σ framework of bpy would be reinforced by strong π acceptance, and the system would approach electroneutrality. Molecular orbital calculations on this subject are being done in collaboration with Professor T. A. Albright. Further spectroscopic and structural studies have also been initiated to elucidate more details of the bpy bonding interaction.

The present study does provide the first structural evidence for extensive π back-bonding to a bpy ligand from a first-row transition metal[23] and indicates that the C_5–C_5' inter-ring distance is quite sensitive to the extent of π back-bonding. The existence of the compound also opens up the possibility of preparing additional π-arene complexes of group 8 transition metals.

Scheme I



Chemical Studies

The π-arene ligand in (π-toluene)Fe(bpy) is not exchangeable even at elevated temperatures or in the presence of catalysts such as acetone or acetonitrile. This is in stark contrast to the isoelectronic Ni(II)–π-arene systems we have studied previously.[4] Attempts to displace the π-arene with excess bpy yielded no reaction, with CO led to decomposition, and with dppe led to displacement (Scheme I). Overall these studies indicate that the Fe(0)–π-arene bond is very robust chemically, and only susceptible to displacement by selected strong π-acid ligands. Mechanistic studies of the displacement reaction would be informative.

Conclusions Regarding Bonding

The results of this study serve as a test of the bonding model that we have proposed for (π-arene)$M(L)_2$.[3] In particular, a comparison of these results with those obtained for the isoelectronic (π-toluene)$Ni(C_6F_5)_2$ complex fits nicely with the molecular orbital description. The shortness of the perpendicular Fe–π-toluene distance, which is more than 0.10 Å shorter than in the Ni complex, is quite consistent with extensive π back-bonding to the L_2 ligand. The π back-bonding reduces the antibonding character of the HOMO, allowing the π-arene to move closer to the metal.

Of particular interest is the dramatically reduced lability of the π-arene in (π-toluene)Fe(bpy). It appears from this study that a substantial reduction in the antibonding character of this HOMO greatly reduces the chemical lability of the π-arene ligand. We are vigorously attempting to isolate addition complexes of this type to determine if this antibonding interaction is indeed responsible for the chemical lability of π-arene ligands in (π-arene)$M(L)_2$ complexes.

Acknowledgment. Support of this work from Research Corp. (L.J.R.) and the National Science Foundation (K.J.K.) is acknowledged with gratitude. Acknowledgement is also made to the University of North Dakota for a contribution of computer time.

Registry No. $(C_6H_5CH_3)$Fe(bpy), 81064-03-1; dppe, 1663-45-2.

Supplementary Material Available: A listing of the structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

---

(20) Saito, Y.; Takemoto, J.; Hutchinson, B.; Nakamoto, K. *Inorg. Chem.* **1972**, *11*, 2003.

(21) Koenig, E.; Herzog, S. *J. Inorg. Nucl. Chem.* **1970**, *32*, 585, 601, 613.

(22) Mahon, C.; Reynolds, W. L. *Inorg. Chem.* **1967**, *6*, 1927.

(23) As the final draft of this paper was being typed, the structure of a bpy complex of a second-row transition metal (Mo(II)) was reported in which extensive π back-bonding occurs. The general structural features are the same; see ref 14.