A Toluene Guest in a Poly(heteronuclear) Complex Host of Ferrocenyl−(CH₂)₂-Bridged Bis(pyrazole)

Weiqiang Tan,[†] Zhengkun Yu,*[,†,‡] Wei He,[†] Liandi Wang,[†] Jie Sun,[‡] and Jinzhu Chen[†]

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People's Republic of China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China

Summary: Reactions of ferrocenyl−(CH₂)ₙ-bridged bis(pyrazoles) with nickelocene afforded inter- and intramolecular dimeric poly(heteronuclear) cyclopentadienylnickel(II) complexes from which a novel toluene-embodied guest−host system was obtained by π-interaction. The present paper has demonstrated a new class of potentially useful organometallic building blocks for supramolecular assembly and the first example of a pyrazolato ligand exhibiting a charge transfer type π-interaction.

Pyrazolato ligands have demonstrated rich coordination chemistry due to their diverse coordination modes to metals.[1−4] Pyrazoles and pyrazolato ligands are potentially useful in devising synthetically useful processes in which the presence of a hemiliable ligand is required,[5a,b] as well as in constructing metal architectures for chemical vapor depositon.[5c] Pyrazoles also play a unique role in the design and synthesis of biologically active agents.[6] In particular, incorporation of a ferrocene unit into an organic molecule usually results in unexpected biological activity[7] or electrochemical properties[8] for the newly formed compound. In this aspect, limited work has been directed to the synthesis of ferrocenyl-substituted pyrazoles (Fc-PzH) for construction of bioactive molecules and their functional transition-metal complexes.[8,9] Ferrocene-based mono(pyrazoles), e.g., ferrocenylmethyl pyrazoles,[10] ferrocenylamido pyrazoles,[11] and ferrocenyl−tris(pyrazol-1-yl)borate ligands,[12] have been reported. However, the synthesis of ferrocene-based bis(pyrazoles) remains a challenge due to the synthetic difficulty, and only a few examples have been documented. 1,1′-Bis(1,3-phenyl-eneoxyacetyl−pyrazolyl)ferrocene,[13a] 1,1′-bis{3-(2-pyridyl)pyrazol-5-yl}ferrocene,[13b] Reports of 1,1′-bis{(pyrazol-1-yl)borate}ferrocene,[14] bitopic ferrocenyl-linked bis(pyrazolyl)methane,[15] and 1,1′-bis{(pyrazol-1-yl)methyl}ferrocene and its ansa analogues[16] are the only known publications to date. On the basis of the structural features of ferrocene-based bis(pyrazoles), it can be envisioned that they could be potentially useful as organometallic building blocks for molecular crystal engineering[17] and the construction of functional compounds.[18] During our ongoing studies on transition-metal complexes of pyrazolyl-based N-heterocyclic ligands,[5a,b,19] we have become interested in 1,1′-bis{(pyrazol-4-yl)alkyl}ferrocenes, which may be used as organometallic building blocks. Herein, we report on the synthesis of ferrocenyl−(CH₂)ₙ-bridged bis(pyrazoles) and a novel toluene-containing guest−host system formed by a charge transfer type π-interaction of pyrazolato ligands for the first time.

1,1′-Bis{(1*H*-pyrazol-4-yl)methyl}ferrocenes (**4**) were synthesized by a modified literature procedure starting from ferrocene (**1**) instead of ferrocene-1,1′-dicarboxaldehyde (Scheme

† Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
‡ Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.
(1) For selected recent reviews, see: (a) Oh, M.; Carpenter, G. B.; Sweigart, D. A. *Acc. Chem. Res.* **2004**, *37*, 1–11. (b) Braga, D.; Maini, L.; Polito, M.; Scaccianoce, L.; Cojazzi, G.; Grepioni, F. *Coord. Chem. Rev.* **2001**, *216/217*, 225–248. (c) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375–1406.
(2) Klein, O.; Aguilar-Parrilla, F.; Lopez, J. M.; Jagerovic, N.; Elguero, J.; Limbach, H. H. *J. Am. Chem. Soc.* **2004**, *126*, 11718–11732.
(3) For selected recent papers, see: (a) Trofimenko, S. *Polyhedron* **2004**, *23*, 197–203. (b) Deacon, G. B.; Forsyth, C. M.; Gitlits, A.; Harika, R.; Junk, P. C.; Skelton, B. W.; White, A. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3249–3251. (c) Sadimenko, A. P. *Adv. Heterocycl. Chem.* **2001**, *79*, 115–197.
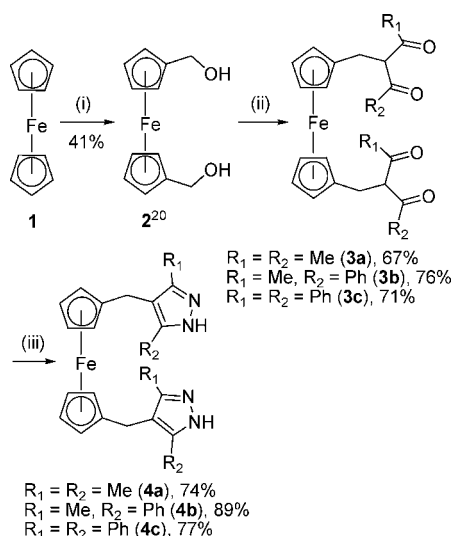(4) Dezelah, C. L., IV; Wiedmann, M. K.; Mizohata, K.; Baird, R. J.; Winter, C. H. *J. Am. Chem. Soc.* **2007**, *129*, 12370–12371.
(5) (a) Zeng, F. L.; Yu, Z. K. *J. Org. Chem.* **2006**, *71*, 5274–5281. (b) Zeng, F. L.; Yu, Z. K. *Organometallics* **2008**, *27*, 2898–2901. (c) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71–80.
(6) Elguero, J. In *Comprehensive Heterocyclic Chemistry II*; Katrizky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon Press: Oxford, U.K., 1996; Vol. 3.
(7) (a) Jaouen, G.; Top, S.; Vessieres, A.; Leclercq, G.; McGlinchey, M. J. *Curr. Med. Chem.* **2004**, *11*, 2505–2517. (b) Togni, A.; Hayashi, T., Eds. *Ferrocenes*; VCH: Weinheim, Germany, 1995.
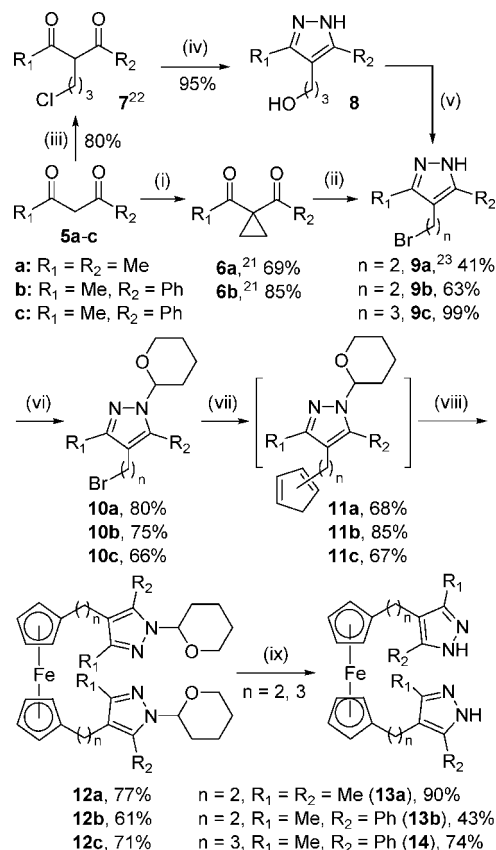(8) Glas, H.; Pleier, A.-K.; Herdtweck, E.; Thiel, W. R. *J. Organomet. Chem.* **2003**, *684*, 376–380.

(9) For selected recent papers, see: (a) Xie, Y.-S.; Pan, X.-H.; Zhao, B.-X.; Liu, J.-T.; Shin, D.-S.; Zhang, J.-H.; Zheng, L.-W.; Zhao, J.; Miao, J.-Y. *J. Organomet. Chem.* **2008**, *693*, 1367–1374. (b) Zora, M.; Görmen, M. *J. Organomet. Chem.* **2007**, *692*, 5026–5032. (c) Mochida, T.; Shimizu, F.; Shimizu, H.; Okazawa, K.; Sato, F.; Kuwahara, D. *J. Organomet. Chem.* **2007**, *692*, 1834–1844. (d) Shi, Y.-C.; Sui, C.-X.; Cheng, H.-J.; Zhu, B.-B. *J. Chem. Crystallogr.* **2007**, *37*, 407–413.
(10) (a) Gan, X.-X.; Tan, R.-Y.; Song, H.-B.; Zhao, X.-M.; Tang, L.-F. *J. Coord. Chem.* **2006**, *59*, 783–789. (b) Barranco, E. M.; Gimeno, M. C.; Laguna, A.; Villacampa, M. D. *Inorg. Chim. Acta* **2005**, *358*, 4177–4182. (c) Burckhardt, U.; Baumann, M.; Trabesinger, G.; Gramlich, V.; Togni, A. *Organometallics* **1997**, *16*, 5252–5259.
(11) Liu, Y.-N.; Orlowski, G.; Schatte, G.; Kraatz, H.-B. *Inorg. Chim. Acta* **2005**, *358*, 1151–1161.
(12) (a) Kunz, K.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2007**, *26*, 4663–4672. (b) Guo, S. L.; Peters, F.; de Biani, F. F.; Bats, J. W.; Herdtweck, E.; Zanello, P.; Wagner, M. *Inorg. Chem.* **2001**, *40*, 4928–4936. (c) de Biani, F. F.; Jäkle, F.; Spiegler, M.; Wagner, M.; Zanello, P. *Inorg. Chem.* **1997**, *36*, 2103–2111.
(13) (a) Zhu, M.-J.; Song, X.-K.; Sun, J.; Yan, C.-G. *Chin. J. Struct. Chem.* **2007**, *26*, 505–510. (b) Thiel, W. R.; Priermeier, T.; Fiedler, D. A.; Bond, A. M.; Mattner, M. R. *J. Organomet. Chem.* **1996**, *514*, 137–147.
(14) Ilkhechi, A. H.; Bolte, M.; Lerner, H.-W.; Wagner, M. *J. Organomet. Chem.* **2005**, *690*, 1971–1977.
(15) Reger, D. L.; Brown, K. J.; Gardinier, J. R.; Smith, M. D. *Organometallics* **2003**, *22*, 4973–4983.
(16) Pagel, K.; Werner, A.; Friedrichsen, W. *J. Organomet. Chem.* **1994**, *481*, 109–123.
(17) Braga, D.; Polito, M.; Giaffreda, S. L.; Grepioni, F. *Dalton Trans.* **2005**, 2766–2773.
(18) (a) Li, G.; Song, Y. L.; Hou, H. W.; Li, L. K.; Fan, Y. T.; Zhu, Y.; Meng, X. R.; Mi, L. W. *Inorg. Chem.* **2003**, *42*, 913–920. (b) Sarhan, A. A. O.; Izumi, T. *J. Organomet. Chem.* **2003**, *675*, 1–12.
(19) (a) Sun, X. J.; Yu, Z. K.; Wu, S. Z.; Xiao, W.-J. *Organometallics* **2005**, *24*, 2959–2963. (b) Deng, H. X.; Yu, Z. K.; Dong, J. H.; Wu, S. Z. *Organometallics* **2005**, *24*, 4110–4112.
(20) Carlström, A.-S.; Frejd, T. *J. Org. Chem.* **1990**, *55*, 4175–4180.

Scheme 1. Synthesis of 1,1′-Bis{(1H-pyrazol-4-yl)methyl}ferrocenes (4)[a]

R_1 = R_2 = Me (3a), 67%
R_1 = Me, R_2 = Ph (3b), 76%
R_1 = R_2 = Ph (3c), 71%

R_1 = R_2 = Me (4a), 74%
R_1 = Me, R_2 = Ph (4b), 89%
R_1 = R_2 = Ph (4c), 77%

[a] Legend: (i) n-BuLi, TMEDA, (CH_2O)_n, Et_2O, 23 °C, 24 h; (ii) 1,3-diketone, 40% aqueous HBF_4, 23 °C, 30 min; (iii) 85% aqueous hydrazine, EtOH, reflux, 4 h.

1).[16,20] In a different fashion, 1,1′-bis{n-(1H-pyrazol-4-yl)ethyl or -propyl}ferrocenes (13 and 14) were prepared (Scheme 2). 2-Alkylation of a 1,3-diketone by an organic halide, especially a dihalide, easily leads to dialkylation and other side reactions of its enolized isomer with the alkylating reagent. Thus, different procedures were used to synthesize 4-substituted pyrazole intermediates, i.e., 4-(n-bromo−(CH_2)_n)pyrazoles 9, which was protected by 2-tetrahydropyranyl (THP) before it was further transformed to the cyclopentadienyl-functionalized intermediate 11. Due to its thermal unstability, compound 11 was not further purified and was directly applied in the next step, synthesis of the THP-protected ferrocene-based bis(pyrazole) 12. Acid-catalyzed deprotection of 12 afforded the desired bis(pyrazole) product 13 or 14. All of the ferrocenyl bis(pyrazoles) were fully characterized, including by X-ray single-crystal structural determinations of 13a and 14 (see the Supporting Information). These bis(pyrazoles) exhibit very similar NMR features in solution, and their proton NMR spectra reveal that the ferrocenyl (Fc) and pyrazole moieties are present in a 1:2 molar ratio in a ferrocenyl bispyrazole molecule. The ^{1}H and ^{13}C NMR spectra of 4 and 13 demonstrate one set of resonance signals for their pyrazole groups, suggesting no detectable tautomerism of the pyrazole moieties in solution. However, two different sets of resonance signals were observed for the pyrazole groups in the NMR spectra of 14, revealing 3- and 5-tautomerism of the pyrazole rings in solution.

Reactions of the ferrocenyl bis(pyrazoles) with nickelocene in a 1:2 molar ratio were carried out in toluene or CH_2Cl_2 at ambient temperature. Treatment of bis(pyrazoles) 4b and 13a with Cp_2Ni afforded the intermolecular dimeric products 15 (38%) and 16 (80%), respectively (eq 1), while the reaction of bis(pyrazole) 14 with Cp_2Ni gave the intramolecular dimeric product 17 in 82% yield (eq 2). The reactions of other ferrocenyl bis(pyrazoles), i.e., 4a,c and 13b, with Cp_2Ni were also pursued under the same conditions, producing a mixture of complex products from which no identified product was isolated. It has been known that reactions of 4-halo- or 4-methyl-substituted pyrazoles with Cp_2Ni can form dimetallic [CpNi(μ-Pz)]_2, trimetallic [CpNi(μ-Pz)_2]_2Ni, or polymeric [Ni(μ-Pz)_2]_x complexes (Pz = simple substituted pyrazolato) under different

Scheme 2. Synthesis of Ferrocenyl Bis(pyrazoles) 13 and 14[a]

a: R_1 = R_2 = Me
b: R_1 = Me, R_2 = Ph
c: R_1 = Me, R_2 = Ph

n = 2, 9a,[23] 41%
n = 2, 9b, 63%
n = 3, 9c, 99%

10a, 80%
10b, 75%
10c, 66%

11a, 68%
11b, 85%
11c, 67%

12a, 77%
12b, 61%
12c, 71%

n = 2, R_1 = R_2 = Me (13a), 90%
n = 2, R_1 = Me, R_2 = Ph (13b), 43%
n = 3, R_1 = Me, R_2 = Ph (14), 74%

[a] Legend: (i) 1,2-dibromoethane, K_2CO_3, DMSO, 23 °C, 12 h; (ii) NH_2NH_2·H_2O, aqueous NH_4Br (0.02 M), 23 °C, 24 h; (iii) 1,3-bromochloropropane, K_2CO_3, KI, acetone, reflux, 72 h; (iv) NH_2NH_2·H_2O, aqueous HCl, ethanol, reflux, 8 h; (v) PBr_3, 1,2-dichloroethane, reflux, 3 h; (vi) 3,4-dihydro-2H-pyran, p-TsOH, CH_3CN, reflux, 3 h; (vii) NaC_5H_5(THF)_{0.27}, THF, 23 °C, 24 h; (viii) n-BuLi, FeCl_2, THF, 23−60 °C, 16 h; (ix) aqueous HCl, p-TsOH, methanol, 23 °C, 48 h.

conditions.[24] In our cases, complexes 15−17 are formally dimeric with respect to the coordination mode of the pyrazolatos and NiCp moieties. Variation of the (CH_2)_n linkers and substituents on the pyrazolato rings led to different types of dimeric polynuclear complex products, which can be attributed to the steric impact of the ferrocenyl bis(pyrazoles). Complexes 15−17 were formed as red precipitates during the reaction, and after recrystallization from toluene or toluene/dichloromethane at −20 °C they usually exist as deep red crystals incorporated with the solvent molecules. These complexes exhibit similar NMR features in solution, revealing the presence of NiCp rings and ferrocenyl Cp′ moieties in a 1:1 molar ratio. The ^{1}H NMR resonance signals of the Cp groups in the complexes appear at 5.57−4.92 ppm in CDCl_3, while those of the ferrocenyl Cp′ moieties are shown in the region of 3.99−3.72 ppm, respectively. The proton NMR spectral analyses also reveal that residual dichloromethane was incorporated in the crystals of
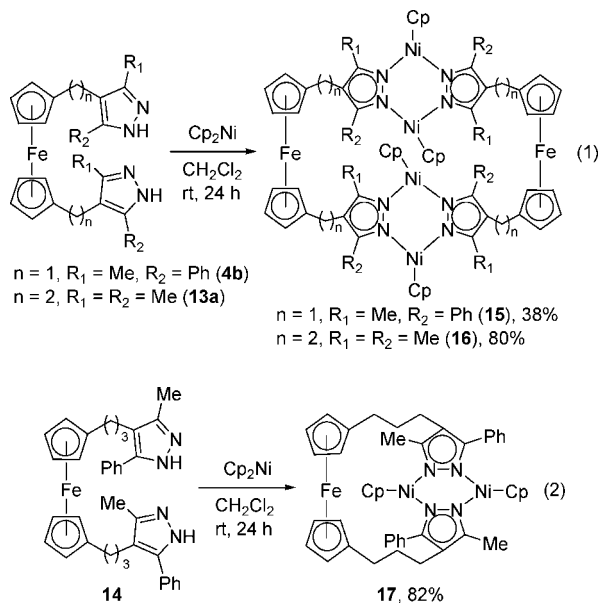
(21) Zefirov, N. S.; Kuznetsova, T. S.; Kozhushkov, S. I.; Surmina, L. S.; Rashchupkina, Z. A. *J. Org. Chem. USSR (Engl. Transl.)* 1983, 19, 474–480.
(22) Meikrantz, S. B.; Smith, M. P.; Xia, X. B.; Natale, N. R. *Synth. Commun.* 1994, 24, 399–407.
(23) Zefirov, N. S.; Kozhushkov, S. I.; Kuznetsova, T. S. *Tetrahedron* 1982, 38, 1693–1697.
(24) (a) Blake, A. B.; Ewing, D. F.; Hamlin, J. E.; Lockyer, J. M. *J. Chem. Soc., Dalton Trans.* 1977, 19, 1897–1901. (b) Rettig, S. J.; Storr, A.; Summers, D. A.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* 1997, 75, 949–958. (c) Storr, A.; Thompon, R. C. *Can. J. Chem.* 1998, 76, 1130–1137.

complex **15**, and toluene coalesced with complexes **16** and **17** in 2:1 and 1:2 molar ratios in their crystals, respectively.[25]

$$n = 1, R_1 = Me, R_2 = Ph (\mathbf{4b})$$
$$n = 2, R_1 = R_2 = Me (\mathbf{13a})$$

$$n = 1, R_1 = Me, R_2 = Ph (\mathbf{15}), 38\%$$
$$n = 2, R_1 = R_2 = Me (\mathbf{16}), 80\%$$
$$(1)$$

14

17, 82%   (2)

Figure 1. Perspective view of complex **15**.

The ferrocenyl bis(pyrazoles) of type **4** (HPzCH$_2$–Fc–CH$_2$PzH) may exist in a syn or anti configuration in the solid state, depending on the substituents on the pyrazole rings.[16] However, $-(CH_2)_2$–Fc–(CH$_2)_2-$ bridged bis(pyrazole) **13a** exists in both syn and anti configurations in the solid state, while the $-(CH_2)_3$–Fc–(CH$_2)_3-$ bridged bis(pyrazole) **14** only exists in an anti configuration (see the Supporting Information). In a unit cell of the single crystals of **13a**, one anti-configuration molecule binds two syn-configuration molecules through the intermolecular N–H···N hydrogen bonds between the pyrazole moieties. Water is coalesced in the single crystals of **14**, and four molecules of the bis(pyrazole) are held together in a unit cell by the hydrogen bonds (N–H···N and O–H···N) formed between the bis(pyrazole) moieties and the incorporated water. Complex **15** exhibits a twisted dimeric structure with the formula {Fc(CH$_2$-3,5-PhMePzNiCp)$_2$}$_2$, in which the pyrazolato moieties demonstrate μ-η^1:η^1 coordination to the nickel atoms and two ferrocene-based bis(pyrazolato) ligands are coordinated to the four NiCp moieties through the pyrazolato nitrogen atoms (Figure 1). The Fe1···Fe1A and Ni1–Ni2 distances in **15** are 11.053 and 3.150 Å, and the Fe1···Ni1, Fe1···Ni2, Fe1A···Ni1, and Fe1A···Ni2 distances are 7.118, 7.038, 7.736, and 7.981 Å, respectively. Three solvent CH$_2$Cl$_2$ molecules coalesce outside the complex coordination cavity. Figure 2 also reveals a dimeric structure for complex **16**. Due to the extended (CH$_2$)$_2$ linkers and coplanarity of the pyrazolato and its two methyl substituents, the dimeric molecule {Fc{(CH$_2$)$_2$-3,5-Me$_2$PzNi-Cp}$_2$}$_2$ (**16**) exhibits a rather symmetrical ring structure (Figure 2c). Unexpectedly, one solvent molecule, i.e., toluene, is
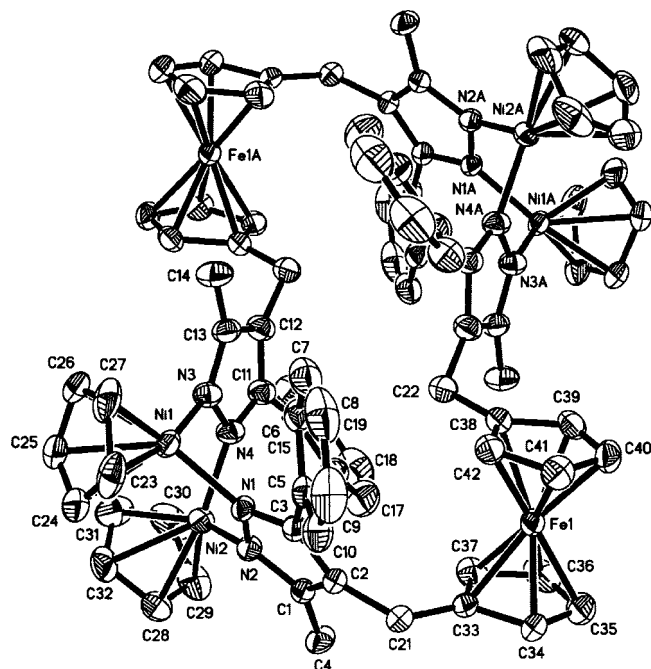
incorporated in the coordination cavity of **16**, and a second toluene molecule coalesces outside the cavity (Figure 2a). Organic solvent molecules (relatively small molecules) can be usually incorporated in the crystals of a target compound via intermolecular van der Waals forces during recrystallization. In general, only polycyclic aromatic molecules can be contained within an organic supramolecular coordination cage.[26] It has been seldom documented for a simple complex coordination cage of type **16** to trap a small aromatic molecule such as an organic solvent molecule like toluene. The Fe1···Fe1A, Fe1···Ni1, and Fe1···Ni2 distances are 13.768, 9.150, and 8.673 Å, respectively, much longer than those in **15**, and the Ni1···Ni2 distance is almost the same as that in **15** (3.160 Å). The pyrazolato ring and its two methyl substituents and the two coordinated nickel atoms are nearly coplanar (Figure 2c; see the Supporting Information). The molecular plane of the incorporated toluene (**A**) is almost parallel to the coplanes Ni1–N2–C13–C12–C11–N1–Ni2 (**B**) and Ni1A–N2A–C13A–C12A–C11A–N1A–Ni2A (**B′**) and perpendicular to the coplanes composed of the other two pyrazolato moieties and their coordinated nickel atoms, respectively. The distances between the incorporated toluene plane (**A**) and its parallel planes **B** and **B′** are ca. 2.8 Å, suggesting an efficient sandwich-type **B–A–B′** π-interaction in the crystals of complex **16**. This structure is attributed to donor–acceptor charge transfer (CT) interactions through the aromatic components (toluene and pyrazolatos). A pyrazolato moiety is electronically equivalent to a cyclopentadienyl group (Cp), and the Ni(II)-coordinated pyrazolato ligands are highly electron deficient due to such a coordination. Thus, the incorporated electron-rich toluene molecule can efficiently form a CT complex with **16** by π-stacking interactions with its two neighboring parallel pyrazolato moieties. The distance between the outside toluene plane and its neighboring pyrazolato plane is longer than 3.0 Å, suggesting no obvious π-interaction between them. Complex **17** exhibits a twisted intramolecular dimeric structure with an incorporated toluene molecule outside the coordination cavity (Figure 3). The Fe1···Ni1, Fe1···Ni2, and Ni1···Ni2 distances are 7.542, 7.546, and 3.165 Å, respectively. Although one more CH$_2$ group is introduced to the linker chain between the ferrocenyl and pyrazolato moiety, the Fe···Ni

(25) (a) Crystal data for **15**·3CH$_2$Cl$_2$: C$_{88}$H$_{79}$Cl$_6$Fe$_2$N$_8$Ni$_4$, monoclinic, *P*2$_1$/*n*, *a* = 12.7273(7) Å, *b* = 18.5978(9) Å, *c* = 17.2650(9) Å, $\alpha = \gamma = 90°$, $\beta = 90.6440(10)°$, *V* = 4086.4(4) Å^3, *Z* = 2, *T* = 293(2) K, D_{calcd} = 1.469 g cm^{-3}, *R*(*F*) = 5.79% for 4856 observed reflections (2.62 $\leq 2\theta \leq$ 51.00°). (b) Crystal data for **16**·2PhMe: C$_{82}$H$_{92}$Fe$_2$N$_8$Ni$_4$, triclinic, *P*$\bar{1}$, *a* = 10.9417(8) Å, *b* = 11.8878(9) Å, *c* = 14.2357(11) Å, $\alpha = 79.2390(10)°$, $\beta = 83.8729(10)°$, $\gamma = 89.668(2)°$, *V* = 1808.5(2) Å^3, *Z* = 1, *T* = 293(2) K, D_{calcd} = 1.410 g cm^{-3}, *R*(*F*) = 4.55% for 4502 observed reflections (4.12 $\leq 2\theta \leq$ 54.00°). (c) Crystal data for **17**·0.5PhMe: C$_{49, 50}$H$_{54}$FeN$_4$Ni$_2$, triclinic, *P*$\bar{1}$, *a* = 10.5506(9) Å, *b* = 11.7665(10) Å, *c* = 18.0307(16) Å, $\alpha = 72.868(2)°$, $\beta = 81.398(2)°$, $\gamma = 76.811(2)°$, *V* = 2074.5(3) Å^3, *Z* = 2, *T* = 293(2) K, D_{calcd} = 1.406 g cm^{-3}, *R*(*F*) = 3.90% for 5918 observed reflections (3.70 $\leq 2\theta \leq$ 54.00°).
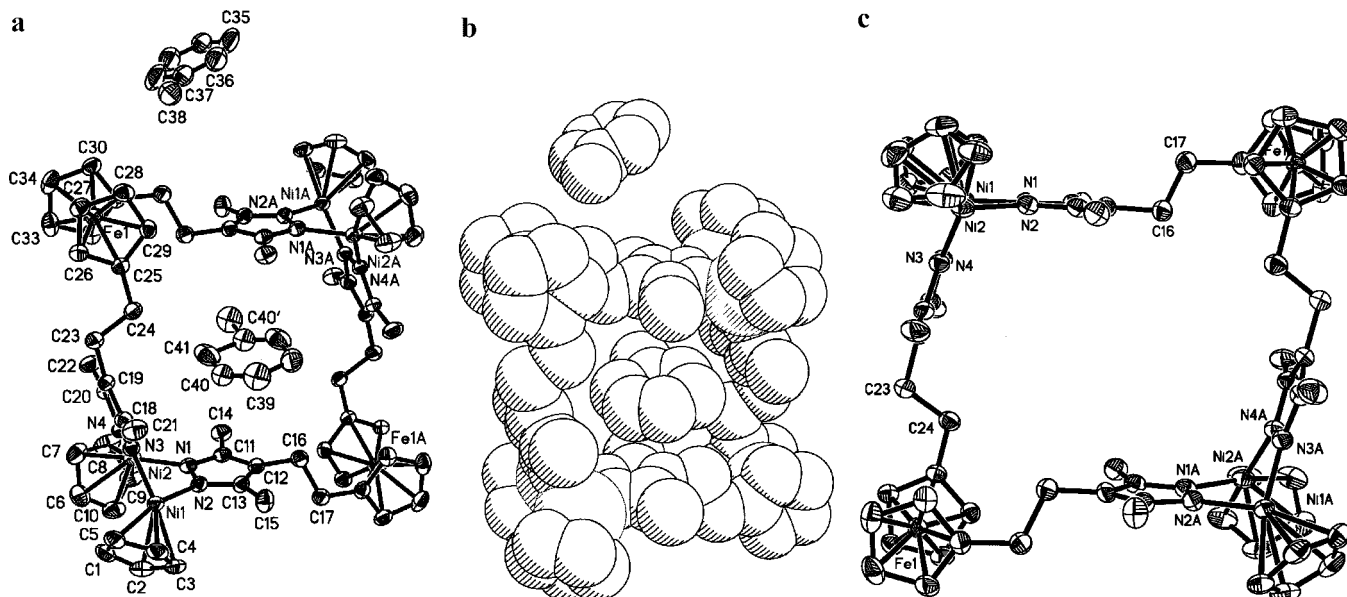
Figure 2. Perspective views of complex **16**: (a) view with incorporated toluene molecules; (b) view showing π-stacking; (c) view without the solvent molecules.
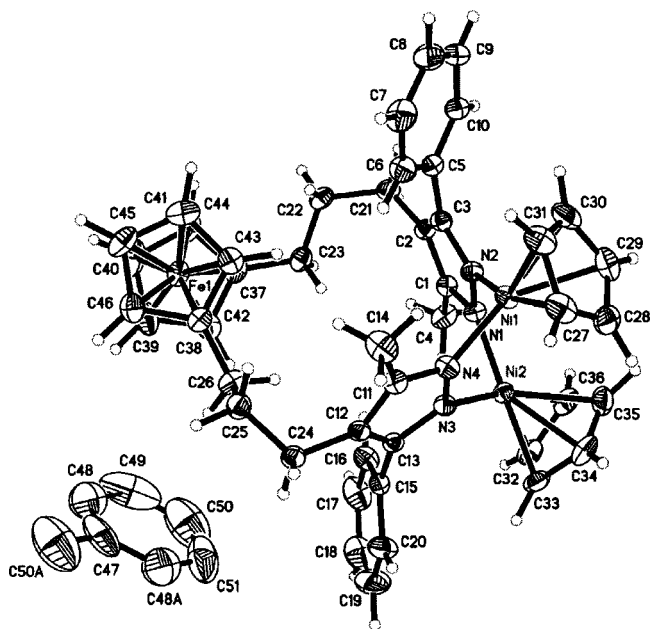

Figure 3. Perspective view of complex **17** showing the incorporated toluene molecule.

distances in **17** are shortened by 1.1–1.6 Å as compared to those in **16** due to the twisted structure. Both complexes **15** and **17** demonstrate highly twisted molecular structures because methyl and phenyl substituents are introduced to the pyrazolato rings, resulting in no coplanarity for the pyrazolatos and their associated substituents. Therefore, no solvent toluene molecule can be embodied in their coordination cavities by π-interaction.

In conclusion, reactions of ferrocenyl–$(CH_2)_n$-bridged bis(pyrazoles) with nickelocene can be applied to synthesize complex cavities which may form guest–host complexes by π-interactions. The coplanarity of the pyrazolato moiety and its two associated substituents and the $(CH_2)_n$-linker lengths are crucial to formation of such a guest–host system. The present toluene-containing guest–host system has demonstrated the first example of a pyrazolato ligand exhibiting a charge transfer type π-interaction and the potential application of ferrocene-based $(CH_2)_n$-linked

bis(pyrazoles) as organometallic building blocks in a supramolecular assembly.

Typical Procedure for Synthesis of the Complexes: Synthesis of Complex 16. A mixture of **13a** (200 mg, 0.46 mmol) and nickelocene (176 mg, 0.93 mmol) in 10 mL of CH_2Cl_2 was stirred at ambient temperature for 24 h, forming a dark red solution. All the volatiles were removed under reduced pressure, and the resultant red residue was purified by flash silica gel column chromatography with *n*-hexane/toluene (v/v, 1/1) as the eluent to afford **16** as a red solid (250 mg, 80%). Single crystals suitable for an X-ray crystallographic determination were grown from dichloromethane/toluene (v/v, 1/10) at ambient temperature. Mp: >120 °C dec. ^{1}H NMR (CDCl$_3$, 400 MHz, 23 °C): δ 7.37 and 7.30 (br each, 4:6 H, aromatic CH of 2 × PhMe), 5.57 (s, 20 H, CH of 4 × CpNi), 3.99 and 3.72 (s and br each, 8:8 H, CH of ferrocenyl), 2.47 and 2.42 (br each, 8:8 H, 4 × CH$_2$Pz and 4 × CH$_2$Fc), 2.32 (s, 24 H, 8 × CH$_3$), 2.16 (br, 6 H, CH$_3$ of toluene). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.4 (Cq, C–N of Pz), 137.7 (Cq, *i*-C of PhMe), 129.2, 128.4, and 125.4 (s each, aromatic CH of toluene outside the coordination cavity), 128.7, 127.8, and 124.9 (t each, aromatic CH of toluene inside the coordination cavity), 117.9 (Cq, C4 of Pz), 92.6 (CH of CpNi), 88.8 (Cq, *i*-C of ferrocenyl), 68.5 and 67.3 (CH of ferrocenyl), 30.4 and 25.3 (CH$_2$Pz and CH$_2$Fc), 14.3 (CH$_3$). Anal. Calcd for C$_{68}$H$_{76}$Fe$_2$N$_8$Ni$_4$ · 2PhMe: C, 64.11; H, 6.04; N, 7.29. Found: C, 64.21; H, 5.90; N, 7.22.

Supporting Information Available: Text, tables, figures, and CIF files giving experimental procedures, analytical data, copies of NMR spectra, and X-ray crystallographic data for **13a** and **14**-**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800704A

(26) For selected recent reports, see: (a) Yoshizawa, M.; Nakagawa, J.; Kumazawa, K.; Nagao, M.; Kawano, M.; Ozeki, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1810–1813. (b) Ono, K.; Yoshizawa, M.; Kato, T.; Watanabe, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1803–1806. (c) Yamaguchi, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2067–2069.