



Dalton
Transactions

**Iron(II) Complexes Supported by Pyrazolyl-Substituted
Cyclopentadienyl Ligands: Synthesis and Characterization**

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-COM-01-2022-000199.R1
Article Type:	Communication
Date Submitted by the Author:	15-Feb-2022
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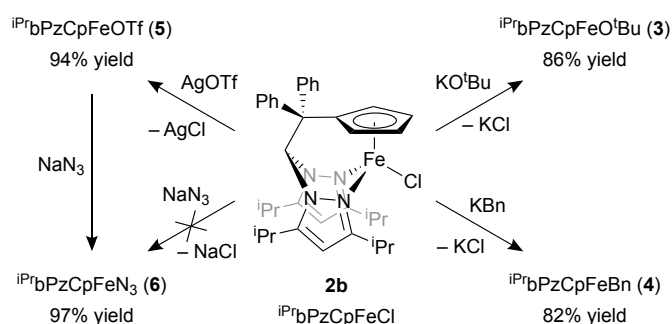
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ligands are coordinated to iron and the cyclopentadienyl group is bound in an η^5 -fashion, consistent with the κ^2 -NN- η^5 -Cp coordination observed for the majority of reported bis(pyrazolyl)cyclopentadienyl metal complexes.^{2,3,6,7} Complex **2a** adopts a pseudo-tetrahedral geometry about the iron center, with an Fe–Cp_{centroid} distance of 2.0293(13) Å that is longer than the Fe–Cp_{centroid} distance in ferrocene (1.6606(11) Å).¹⁵ Coordination of the η^5 -cyclopentadienyl group is relatively symmetrical, with Fe–C bond lengths ranging from 2.338(3) to 2.378(3) Å. Binding to the two pyrazolyl ligands is also fairly uniform, with Fe1–N1 and Fe1–N3 bond lengths of 2.139(2) Å and 2.131(2) Å, respectively.

Complex **2a** is not very soluble in organic solvents, complicating its isolation and characterization. We explored modification of the pyrazolyl groups as a potential solution to this issue, targeting the preparation of the isopropyl-substituted ^{iPr}bPzCpLi(THF) (**1b**, Scheme 1, ^{iPr}bPzCp = 2,2-bis(3,5-di(isopropyl)pyrazol-1-yl)-1,1-diphenylethylcyclopentadienyl). Compound **1b** is prepared in a manner similar to **1a**¹¹ through deprotonation of the bis(pyrazolyl)methane and addition of 6,6-diphenylfulvene (see SI). Reaction of **1b** and FeCl₂ leads to formation of ^{iPr}bPzCpFeCl (**2b**, Scheme 1), which is more soluble in organic solvents such as THF and toluene. As in **2a**, magnetic measurements for **2b** support an *S* = 2 ground state.

Determination of the molecular structure of **2b** confirmed κ^2 -NN- η^5 -Cp coordination of the bis(pyrazolyl)cyclopentadienyl ligand to iron (Figure 1). The Fe–N bond lengths of **2b** are more disparate (2.177(2) Å and 2.138(2) Å) compared to those in **2a** (*vide supra*) and the cyclopentadienyl unit is more canted, with Fe–C bond lengths ranging from 2.286(3) to 2.437(3) Å and an Fe–Cp_{centroid} distance of 2.0390(16) Å. This twisting of the ligand framework in **2b** is such that the longer Fe–N bond couples to the side of the cyclopentadienyl ring that is closer to iron, and is likely in response to the steric bulk of the isopropyl substituents.

We explored the reactivity of ^{iPr}bPzCpFeCl (**2b**) in the presence of a variety of exchange partners (Scheme 2). Reaction of **2b** and potassium *tert*-butoxide (KO^tBu) or benzyl potassium (KBn) in THF at 23 °C overnight leads to the alkoxide and benzyl complexes ^{iPr}bPzCpFeO^tBu (**3**) and ^{iPr}bPzCpFeBn (**4**), respectively, in good yields. On the other hand, no reaction



Scheme 2. Ligand exchange reactivity of **2b**. Reaction conditions: MX (1 equiv), THF, 23 °C, overnight.

occurs on exposure of **2b** to sodium azide (NaN₃). To encourage metathesis reactivity, the chloride ligand of **2b** was exchanged for a more easily displaced trifluoromethanesulfonate (triflate, OTf) group using silver triflate (AgOTf) to give ^{iPr}bPzCpFeOTf (**5**) in 94% yield. Indeed, reaction of **5** and NaN₃ allows access to the iron azide, ^{iPr}bPzCpFeN₃ (**6**), in 97% yield. Complex **6** was exposed to UV light alone and in the presence of triphenylphosphine to facilitate nitrogen atom transfer from a potential, transient iron nitride complex.¹⁶ Unfortunately, both reactions lead to intractable mixtures of unidentified products.

Complexes **3**, **4**, **5**, and **6** were characterized by X-ray crystallography (Figure 2). All four compounds exhibit pseudo-tetrahedral geometry at iron with twisting of the ligand scaffold as compared to **2a**. The Fe–N and Fe–Cp_{centroid} distances in *tert*-butoxide and benzyl complexes **3** and **4** are longer compared to chloride complex **2b**, likely due to the steric influence of the ligand. The benzyl group of **4** is coordinated in an η^1 -fashion and is disordered over two positions (73:27%). Though it has the potential to be noncoordinating,¹⁷ the triflate anion in **5** is indeed bound to iron, with an Fe1–O1 length of 2.041(2) Å (average from two crystallographically independent molecules of **5** in the unit cell). Disorder in the position of the distal nitrogen atom in **6** appears to indicate that the azide ligand is bent to some extent (both modeled positions are shown in Figure 2).

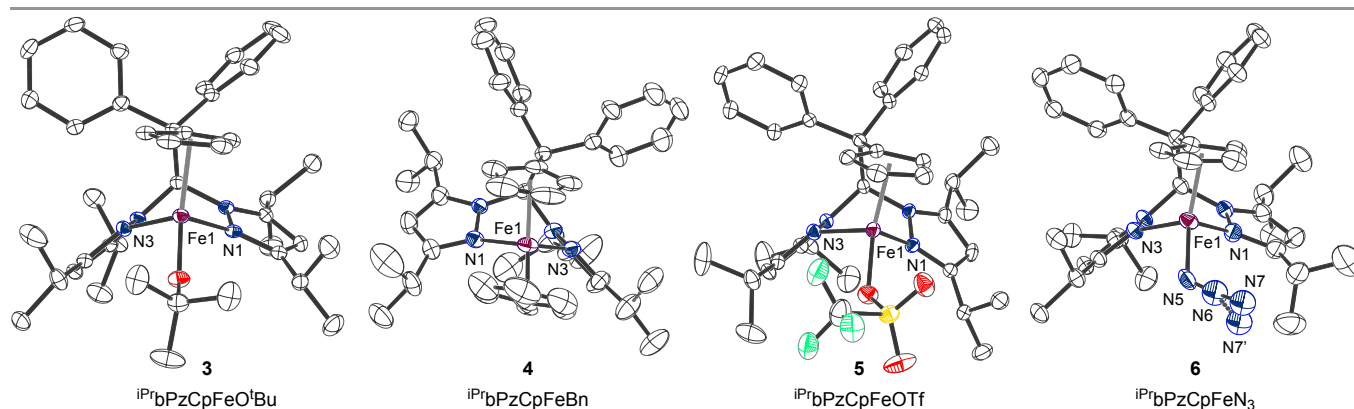
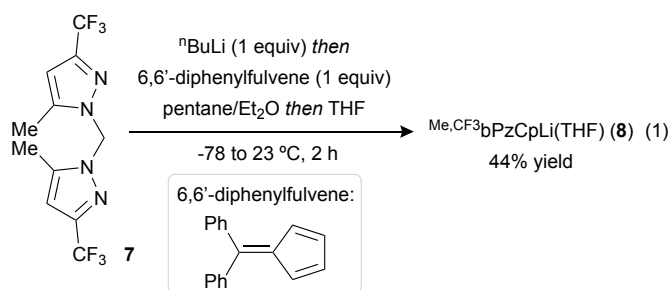


Figure 2. Molecular structures of **3**, **4**, **5**, and **6** with ellipsoids drawn at the 50% probability level. Hydrogen atoms, solvent molecules, disorder (except in the azide ligand of **6**), and one of the crystallographically independent molecules in the unit cell of **5** have been removed for clarity. Selected bond distances for **3** (Å): Fe1–N1, 2.210(2); Fe1–N3, 2.189(2); Fe1–Cp_{centroid}, 2.0846(12). For **4** (Å): Fe1–N1, 2.214(3); Fe1–N3, 2.219(3); Fe1–Cp_{centroid}, 2.0731(19). For **5** (Å): Fe1–N1, 2.163(2); Fe1–N3, 2.162(3); Fe1–Cp_{centroid}, 2.0042(15). Selected bond distances (Å) and angles (deg) for **6**: Fe1–N1, 2.133(2); Fe1–N3, 2.143(2); Fe1–Cp_{centroid}, 2.0397(13); N5–N6, 1.136(3); N6–N7, 1.206(5); N6–N7', 1.192(7); N5–N6–N7, 172.4(5); N5–N6–N7', 152.9(9).



We investigated the possibility of accessing a reduced iron species through addition of reducing agents to **2b**. This complex proved resistant to reduction, showing no reactivity in the presence of several reductants including sodium metal and potassium graphite.¹⁸ In an effort to make the iron centre easier to reduce, we aimed to synthesize $\text{Me,Cf}_3\text{bPzCpLi(THF)}$ (**8**, eq 1, $\text{Me,Cf}_3\text{bPzCpLi} = 2,2\text{-bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)-1,1-diphenylethylcyclopentadienyl}$) that contains a bis(pyrazolyl)cyclopentadienyl ligand with electron-withdrawing trifluoromethyl substituents. Preparation of **8** from bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**, eq 1) is accomplished in a manner similar to **1a**¹¹ and **1b** (*vide supra*). However, reaction of electron-deficient **8** and FeCl_2 leads to an intractable mixture of several unidentified products, none of which appear to be the targeted complex.

Given that complexes **2–6** are coordinatively saturated, we explored removal of one pyrazolyl unit as a strategy for opening a coordination site, targeting the synthesis of iPrPzPhCpLi(THF) (**10**, eq 2, $\text{iPrPzPhCp} = 2\text{-}(3,5\text{-di(isopropyl)pyrazol-1-yl)-1,1,2\text{-triphenylethylcyclopentadienyl}$). Deprotonation of 1-benzyl-3,5-diisopropylpyrazole (**9**) and addition of 6,6'-diphenylfulvene affords the lithium salt containing the mono(pyrazolyl)cyclopentadienyl ligand, **10**, in 80% yield (eq 2). Determination of the molecular structure of **10** revealed $\kappa^1\text{-N-}\eta^5\text{-Cp}$ coordination of the iPrPzPhCp ligand to lithium as illustrated in eq 2 (Figure 3, left). Complex **10** adopts a pseudo-trigonal planar geometry at lithium, with N1-Li1-O1 , $\text{N1-Li1-Cp}_{\text{centroid}}$,

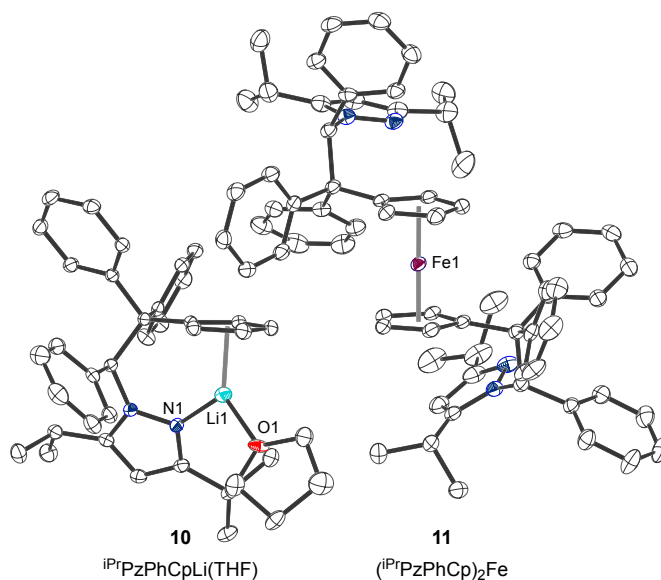
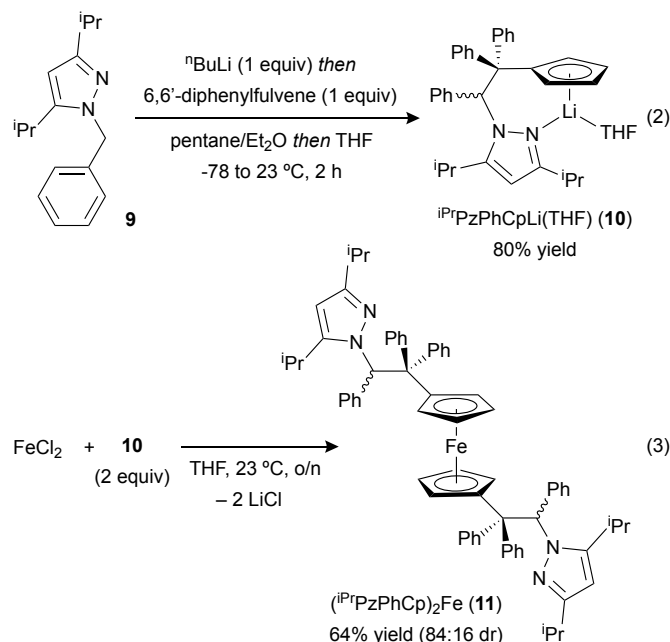


Figure 3. Molecular structures of **10** and **11** with ellipsoids drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and disorder have been removed for clarity. Selected bond distances (Å) and angles (deg) for **10**: Li1-N1 , 2.070(3); Li1-O1 , 2.038(12); $\text{Li1-Cp}_{\text{centroid}}$, 1.907(3); N1-Li1-O1 , 111.9(4); $\text{N1-Li1-Cp}_{\text{centroid}}$, 122.37(10); $\text{O1-Li1-Cp}_{\text{centroid}}$, 125.5(4). For **11**: $\text{Fe1-Cp}_{\text{centroid}}$, 1.6588(12); $\text{Fe1-Cp}_{\text{centroid}}$, 1.6576(12).

and $\text{O1-Li1-Cp}_{\text{centroid}}$ bond angles that sum to 359.8 degrees. The single Li-N bond in **10** is shorter than the two Li-N bonds in **1a** (2.070(3) Å versus 2.37(1) Å and 2.13(1) Å).¹¹

Addition of one equivalent of **10** to FeCl_2 leads to two new diamagnetic species as observed by ^1H NMR spectroscopy. NMR data for these compounds are consistent with the ferrocene complex $(\text{iPrPzPhCp})_2\text{Fe}$ (**11**, eq 3) that exists as a mixture of diastereomers due to the stereogenicity of the tertiary carbon in the backbone of the iPrPzPhCp ligand. Given the 2:1 ratio of ligand/iron in **11**, the amount of **10** added was increased to two equivalents, leading to a higher yield (64%, 84:16 mixture of diastereomers, eq 3). Analysis by X-ray crystallography confirmed the structure of **11** in which the cyclopentadienyl groups of two iPrPzPhCp ligands coordinate to iron, each in an η^5 -fashion, while the pyrazolyl units are unbound (Figure 3, right).

Conclusion

Several iron complexes supported by pyrazolyl-substituted cyclopentadienyl ligands were synthesized and characterized. Isopropyl substitution in the bis(pyrazolyl)cyclopentadienyl ligand increased the solubility of the iron(II) chloride complex that allowed access to the *tert*-butoxide, benzyl, triflate, and azide derivatives through ligand exchange. An electron deficient analogue containing trifluoromethyl groups was also prepared, but did not lead to the targeted coordination complex. The lithium salt of a mono(pyrazolyl)cyclopentadienyl ligand was synthesized and analysed by X-ray crystallography. Complexation of this ligand in a 2:1 ratio compared to iron afforded a substituted ferrocene derivative. In addition to demonstrating coordination of this important heteroscorpionate scaffold to iron, we expect the new

pyrazolyl-substituted cyclopentadienyl ligands disclosed in this work to be useful in other applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank Saint Louis University for instrumentation and financial support. We are grateful to the National Science Foundation for providing funding to purchase the Venture-Duo diffractometer used for X-ray crystallography (MRI, CHE-1827756).

References

- 1 A. Otero, J. Fernández-Baeza, A. Lara-Sánchez and L. F. Sánchez-Barba, *Coord. Chem. Rev.*, 2013, **257**, 1806–1868.
- 2 a) A. Otero, J. Fernández-Baeza, A. Lara-Sánchez, A. Antiñolo, J. Tejada, E. Martínez-Caballero, I. Márquez-Segovia, I. López-Solera, L. F. Sánchez-Barba and C. Alonso-Moreno, *Inorg. Chem.*, 2008, **47**, 4996–5005. b) A. Otero, J. Fernández-Baeza, A. Antiñolo, A. Lara-Sánchez, E. Martínez-Caballero, J. Tejada, L. F. Sánchez-Barba, C. Alonso-Moreno and I. López-Solera, *Organometallics*, 2008, **27**, 976–983. c) I. Márquez-Segovia, A. Lara-Sánchez, A. Otero, J. Fernández-Baeza, J. A. Castro-Osma, L. F. Sánchez-Barba and A. M. Rodríguez, *Dalton Trans.*, 2014, **43**, 9586–9595. d) J. Martínez, J. Fernández-Baeza, L. F. Sánchez-Barba, J. A. Castro-Osma, A. Lara-Sánchez and A. Otero, *ChemSusChem*, 2017, **10**, 2886–2890.
- 3 A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejada, A. Lara-Sánchez, L. F. Sánchez-Barba, M. Sánchez-Molina, C. Bo and M. Urbano-Cuadrado, *Inorg. Chim. Acta*, 2009, **362**, 2909–2914.
- 4 X. Zhang, X. Liu, H. Song and L. Tang, *Chin. J. Chem.*, 2011, **29**, 2702–2706.
- 5 E. Roa, V. Salazar, D. Mendoza-Espinosa, M. Paneque, A. Rodríguez-Diéguez, A. M. Rodríguez, J. Tejada, J. A. Castro-Osma, A. Otero and A. Lara-Sánchez, *Inorg. Chem.*, 2018, **58**, 900–908.
- 6 a) A. Garcés, L. F. Sánchez-Barba, C. Alonso-Moreno, M. Fajardo, J. Fernández-Baeza, A. Otero, A. Lara-Sánchez, I. López-Solera and A. M. Rodríguez, *Inorg. Chem.*, 2010, **49**, 2859–2871. b) M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez, J. Martínez-Ferrer, S. Sobrino and A. M. Rodríguez, *Organometallics*, 2015, **34**, 3196–3208.
- 7 A. Otero, A. Lara-Sánchez, C. Nájera, J. Fernández-Baeza, I. Márquez-Segovia, J. A. Castro-Osma, J. Martínez, L. F. Sánchez-Barba and A. M. Rodríguez, *Organometallics*, 2012, **31**, 2244–2255.
- 8 C. A. Richards, N. P. Rath, and J. M. Neely, *Organometallics*, 2021, **40**, 2945.
- 9 European Medicines Agency, Committee for Human Medical Products. ICH guideline Q3D on elemental impurities, March 28, 2019; https://www.ema.europa.eu/en/documents/-scientific-guideline/international-conference-harmonisation-technical-requirements-registration-pharmaceuticals-human-use_en-32.pdf (accessed February 11, 2022).
- 10 L. Tan and Y. Chi-lung, *Int. Geol. Rev.* 1970, **12**, 778–786.
- 11 A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejada, A. Lara-Sánchez, L. Sánchez-Barba, A. M. Rodríguez and M. A. Maestro, *J. Am. Chem. Soc.*, 2004, **126**, 1330–1331.
- 12 The μ_{eff} of **2a** determined by the Evans method was 4.5 μ_{B} (see SI). This value is lower than that expected for an $S = 2$ species (4.9 μ_{B} , spin-only), possibly due to the poor solubility of **2a** in the NMR solvent.
- 13 G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.*, 1952, **74**, 2125–2126.
- 14 L. Reger, C. A. Little, A. L. Rheingold, M. Lam, L. M. Liable-Sands, B. Rhagitan, T. Concolino, A. Mohan, G. J. Long, V. Briois and F. Grandjean, *Inorg. Chem.*, 2001, **40**, 1508–1520.
- 15 J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Crystallogr.*, 1956, **9**, 373–375.
- 16 J. M. Smith and D. Subedi, *Dalton Trans.*, 2011, **41**, 1423–1429.
- 17 A study of anion coordinating ability found the triflate anion to be coordinated in 31% of the 5,009 transition metal complexes evaluated. See: R. Díaz-Torres and S. Alvarez, *Dalton Trans.*, 2011, **40**, 10742–10750.
- 18 Attempts to reduce the triflate complex **5** with potassium graphite were also unsuccessful.