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Imidazolium Cyclopentadienide Salts

Imidazolium Cyclopentadienide Salts and their Use as Cp-Transfer Reagents

Inga-Alexandra Bischoff,[a] Carsten Müller,[a] Volker Huch,[a] Michael Zimmer,[a] and André Schäfer*[a]

Abstract: The reaction of N-heterocyclic carbenes, **1a**–**c**, towards cyclopentadienes, **2a**–**c**, was studied. *N,N′*-diisopropyl-substituted carbene **1a** acts as a Brønsted base and deprotonates cyclopentadiene, **2a**, and isopropylcyclopentadiene, **2b**, to yield the corresponding imidazolium cyclopentadienide salts, **3a**,**b**, whereas there is no reaction towards 1,2,3,4,5-pentamethylcyclopentadiene. Imidazolium cyclopentadienide salts, **3a**,**b**, were characterized in solution by ^{1}H and ^{13}C NMR spectroscopy, as well as in the solid state by single-crystal X-ray diffraction. In addition, it was demonstrated that imidazolium cyclopentadienide salt **3a** can be used as a Cp-transfer reagent in the synthesis of different cyclopentadienyl transition metal complexes.

Introduction

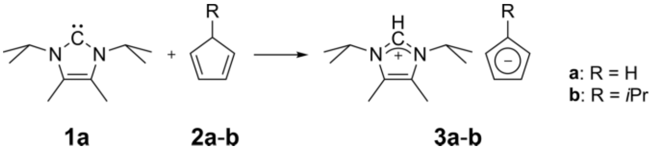
Metallocenes are of tremendous interest for numerous reasons, among others for their application as catalysts,[1] as metal precursors in chemical vapor deposition and pyrolysis techniques,[2] or as bioactive molecules in medical applications.[3]

While some metallocenes, like ferrocene, can be synthesized directly from the corresponding metal element and cyclopentadiene,[4] the far more common route, is to use Cp-transfer reagents like alkali metal cyclopentadienide compounds, usually obtained from the corresponding cyclopentadiene and a suitable metallabase.[5] Hence, the synthesis of metallocenes are often multi step reactions and sometimes suffer from low yields, due to side reactions because of the redox chemistry of the involved metal precursors. Therefore, mild Cp-transfer reagents are of great interest for the preparation of many cyclopentadienyl metal complexes.[6]

Herein, we report on the use an N-heterocyclic carbene, **1a**, as a Brønsted base in the synthesis of imidazolium cyclopentadienide salts, **3a**,**b**, and their application as Cp-transfer reagents in the synthesis of cyclopentadienyl metal complexes.

Results and Discussion

When monomeric cyclopentadienes **2a**,**b** were added to a solution of N-heterocyclic carbene **1a** at 273 K, an immediate Brønsted acid base reaction took place to give the corresponding imidazolium cyclopentadienide salts **3a**,**b** (Scheme 1).

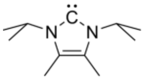


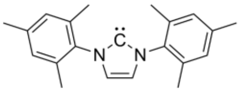
Scheme 1. Reaction N-heterocyclic carbenes **1a** with cyclopentadienes **2a**–**b**.

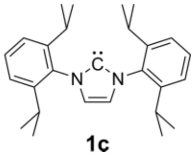
This is in agreement with a pK_a value for N-heterocyclic carbene **1a** of 24 and a pK_a value for cyclopentadiene of 18,[7] and a report of a similar reaction between **1a** and 2,3-benzofluorene.[7a] Furthermore, DFT calculations at the B3LYP-D3/def2-TZVPP level of theory predict the reaction of **1a** with **2a** to be strongly exergonic (ΔG^{298} = 349.2 kJ mol^{-1}).[8,9]

Both the substitution pattern on the N-heterocyclic carbene and on the cyclopentadiene have strong influence on the proton transfer reaction. This is shown by the fact that N-heterocyclic carbene **1a** acts as a potent Brønsted base in the reaction with cyclopentadienes, **2a**, while there is no reaction between **1a** and 1,2,3,4,5-pentamethylcyclopentadiene. This can be attributed to the lower acidity of 1,2,3,4,5-pentamethylcyclopentadiene, compared to cyclopentadiene, **2a**.[10]

Furthermore, more bulky substituted N-heterocyclic carbenes **1b**,**c** do not react with cyclopentadiene, **2a**, at room temperature.


1a


1b


1c

As many cyclopentadienes undergo Diels-Alder dimerization at room temperature, heating of the reaction mixture to promote a proton transfer reaction is not viable. Imidazolium cyclopentadienide salts **3a**,**b** can be isolated as air-sensitive colorless

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[a] *Faculty of Natural Sciences and Technology, Department of Chemistry, Saarland University,*
66123 Saarbrücken, Germany
E-mail: andre.schaefer@uni-saarland.de
https://www.uni-saarland.de/forschung/emmy-noether-chemie

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crystalline solids and can be stored at 248 K under an inert atmosphere for several days. Crystals suitable for single-crystal X-ray diffraction were obtained from THF solutions at 248 K, allowing for a solid state characterization of these species, for the first time.[11] Imidazolium cyclopentadienide salts **3a**,**b** show similar structures in the solid state, which are solvent free crystals with the imidazolium H-atom exhibiting a hydrogen bond to the π-system of the cyclopentadienide anion (Figure 1). Similar structural motives are known for ammonium and phosphonium cyclopentadienide salts.[12]

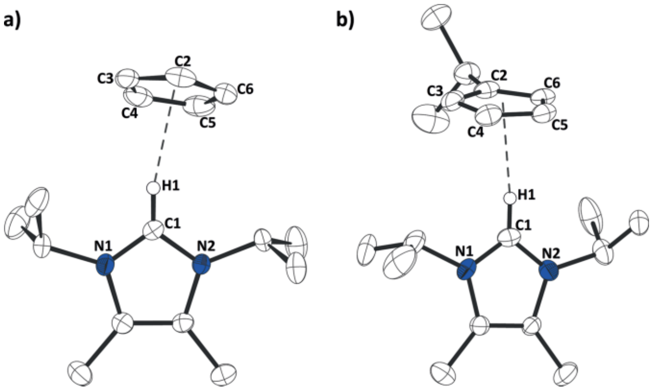
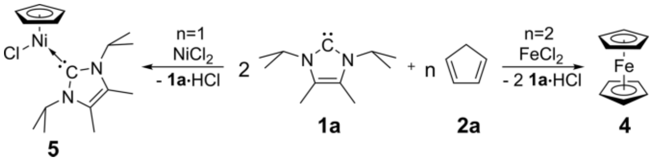


Figure 1. Molecular structure of **3a** (a) and **3b** (b) in the crystal (H-atoms except for imidazolium-H omitted for clarity, thermal ellipsoids set at 50 % probability level).

The (Im)H–Cp^{centroid} bonding distance varies somewhat between **3a** and **3b**, with 238.7–246.8 pm[13] in **3a** and 240.4 pm in **3b**. In both cases, relatively uniform C–C bonding distance within the Cp-moieties are observed (C2–C6: **3a**: 137.6–140.5 pm;[13] **3b**: 139.3–141.5 pm[13]), indicating a conjugated 6π-electron aromatic system. The dihedral angle between the imidazolium ring plane and the cyclopentadienyl ring plane is 67.8–77.3°[13] in case of **3a** and 78.1° in case of **3b**. The structural characteristics of the imidazolium cation in **3a** and **3b** are very similar to the corresponding tetrafluoroborate salt,[14] with N1–C1–N2 angles of 108.5–109.0°[13] (**3a**) / 108.7° (**3b**) and C1–N1/C1–N2 bond length of 132.8–133.6 pm[13] (**3a**) / 132.5–133.0 pm[13] (**3b**).

Even though an isolation of imidazolium cyclopentadienide salts, **3a**,**b**, is possible, it is not required when using them as Cp-transfer reagents in the preparation of transition metal cyclopentadienyl complexes, as they can be generated and used in-situ, in one-pot reaction sequences. (Scheme 2).



Scheme 2. One-pot synthesis of ferrocene, **4**, and cyclopentadienyl nickel chloride-NHC complex **5**.

The one-pot synthesis of ferrocene, **4**, and cyclopentadienyl nickel chloride-NHC complex, **5**, starting from readily available N-heterocyclic carbene **1a**[15] and cyclopentadiene, obtained from commercially available dicyclopentadiene by Retro-Diels-Alder reaction, and metal(II) chloride proceeds at room temperature to give the corresponding metal complex **4** and **5**. The only by-product of the reaction is 1,3-diisopropyl-4,5-dimethylimidazolium chloride, **1a**·HCl, which is easily recovered by filtration and recycled into carbene **1a**, by treatment with a suitable, commercially available base, such as potassium *tert*-butoxide.[16]

When nickel(II) chloride is used as a metal precursor, cyclopentadienylnickel chloride NHC complex **5** is obtained, rather than nickelocene (Figure 2).

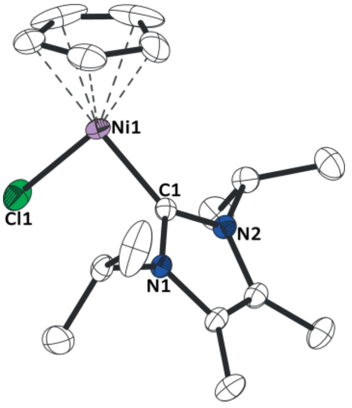


Figure 2. Molecular structure of **5** in the crystal (H-atoms omitted for clarity, thermal ellipsoids set at 50 % probability level).

This is in agreement with the fact that cyclopentadienylnickel chloride NHC complexes of this kind can be obtained by treatment of nickelocene with imidazolium chlorides.[16a] The herein described route, however, presents a more convenient access to these complexes, which is of interest with regards to their catalytic applications.[16b] The nickel atom in **5** exhibits a trigonal planar coordination (sum of angles = 359.8°) with an η^5 bonded cyclopentadienyl substituent and a Ni–C^{NHC} bond of 188.6 pm, which is in line with related complexes of this kind.[16] Interestingly, complex **5** exhibits a very downfield shifted resonances for the methine protons of the isopropyl groups of the NHC moiety in the ^{1}H NMR spectrum (δ^1H = 7.31), compared to **1a** (δ^1H = 4.00). In the solid-state structure, these methine protons can be observed pointing towards the nickel atom with Ni–H distance of 264.1 pm and 271.4 pm, C–H bond lengths of 94.1 pm and 96.7 pm and C–H-Ni angles of 120.7° and 123.5°. However, the C–H bond lengths are actually a bit shorter than in **1a** (100 pm) and there is no lowering of the $^{1}J^{1}{}_{H\text{-}}{}^{13}{}_{C}$ coupling constant. In fact, a coupling constant of $^{1}J^{1}{}_{H\text{-}}{}^{13}{}_{C}$ = 140 Hz for the methylylidene groups in **5** is detected, which is slightly larger than what is observed in **1a** ($^{1}J^{1}{}_{H\text{-}}{}^{13}{}_{C}$ = 135 Hz). This is further supported by DFT calculations at the M06-L/IGLO-III(C,H,Cl,N);def2-TZVPP(Ni)//B3LYP-D3/def2-TZVPP[9] level of theory, suggesting coupling constants of $^{1}J^{1}{}_{H\text{-}}{}^{13}{}_{C}$ = 168 Hz (**1a**), 165 Hz (**5**), which is in qualitative agreement with the experimental observation that there is no significant difference in the $^{1}J^{1}{}_{H\text{-}}{}^{13}{}_{C}$ coupling constant in **1a** and **5**. This suggests that the interaction is mostly electrostatic in nature (anagostic interaction).

Conclusions

The reaction of different N-heterocyclic carbenes **1a**–**c** towards cyclopentadiene and of N-heterocyclic carbene **1a** towards variably substituted cyclopentadienes, **2a**,**b** and 1,2,3,4,5-pentamethylcyclopentadiene, was explored. N-heterocyclic carbene **1a** was shown to react rapidly with cyclopentadienes, **2a**,**b**, in proton transfer Brønsted acid base reactions, to give imidazolium cyclopentadienide salts **3a**,**b**. These species can be isolated and stored as stable crystalline solids and were characterized in solution and in the solid state but may also be generated in-situ when used as Cp-transfer reagents in the synthesis of metallocenes and metallocene derivatives, such as **4** and **5**.

Experimental Section

N-heterocyclic carbenes **1a**–**c** and 6,6-dimethylfulvene were prepared according to literature known procedures.[15,17–19] All manipulations were carried out under an argon inert gas atmosphere (argon 5.0), using either Schlenk line techniques or a glovebox. Dicyclopentadiene (90 %) was cracked and distilled freshly prior to use.

NMR spectra were recorded on Bruker Avance III 300 and Bruker Avance III 400 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced using the solvent signals (δ $^1H(C_6HD_5)$ = 7.16; (δ $^1H(C_6D_5CHD_2)$ = 2.09; δ $^{13}C(C_6D_6)$ = 128.06; δ $^{13}C(C_6D_5CD_3)$ = 20.43). Elemental analyses were performed on an Elementar vario micro cube.

Single crystal X-ray diffraction analysis were carried out at low temperatures on a Bruker AXS X8 Apex CCD diffractometer operating with graphite monochromated Mo-K_α radiation. Structure solution and refinement were performed using SHELX.[20]

CCDC 1885159 (for **3a**), 1885160 (for **3b**), and 1885161 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

All DFT-calculations were performed using the Gaussian 09, Revision D.01 package of programs.[9]

Isopropylcyclopentadiene (2b):

Isopropylcyclopentadiene, **2b**, was prepared by a modified literature procedure.[21] To a solution of $LiAlH_4$ (3.75 g, 98.9 mmol) in THF at 273 K was added 6,6-dimethylfulvene (10.0 g, 11.4 mL, 94.2 mmol). After stirring for 10 min, 25 mL of methanol were added slowly, and the reaction mixture was stirred for 1.5 h at 273 K. 2 M aqueous hydrochloric acid (47.1 mL, 94.2 mmol) was added and the mixture was stirred for an additional 30 min at 273 K. Diethyl ether was added and the aqueous phase was extracted three times with diethyl ether. The organic layers were combined, washed with saturated aqueous $NaHCO_3$ solution, dried with $MgSO_4$ and the solvent was removed under reduced pressure.

If necessary, **2b** can be purified by lithiation and subsequent hydrolysis.

Yield: 5:98 g, 58 %.

^{1}H NMR (400.13 MHz, 300.0 K, C_6D_6) δ = 1.04 (d, J = 7 Hz, 2 H, CH_3), 1.11 (d, J = 7 Hz, 4 H, CH_3), 2.49–2.61 (m, 1 H, CH), 2.69–2.83 (m, 2 H, CH_2), 5.90–6.51 (m, 3 H, Cp-H).

1,3-Diisopropyl-4,5-dimethyl-imidazolium cyclopentadienide salts 3a–b: To a solution of **1a** (300 mg, 1.7 mmol) in THF was added the corresponding cyclopentadiene **2a**,**b** (**2a**: 110 mg, 1.7 mmol; **2b**: 180 mg, 1.7 mmol) at 273 K. The solution was warmed to room temperature and stirred overnight. Evaporation of all volatiles in vacuo gave imidazolium cyclopentadienide salts, **3a**,**b**, as colorless to beige solids. Recrystallization from THF at 248 K afforded crystals suitable for single-crystal X-ray diffraction analysis.

Yield: **3a**: 245 mg, 60 %; **3b**: 241 mg, 50 %.

3a: ^{1}H-NMR (400.13 MHz, 296.9 K, C_6D_6) δ = 1.18 (d, J = 6 Hz, 12 H, CH_3), 1.54 (s, 6 H, CH_3), 4.50 (sept, J = 7 Hz, 2 H, CH), 6.17 (s, 1 H, Im-H), 6.44 (s, 5 H, Cp-H); $^{13}C\{^1H\}$-NMR (100.61 MHz, 296.8 K, C_6D_6) δ = 8.6 (CH_3), 21.7 (CH_3), 51.1 (CH), 104.8 (Cp), 125.9 (C=C), 137.7 (Im-C). Elemental analysis: calculated: C: 78.31 %, H: 10.27 %, N: 11.42 %; found C: 78.11 %, H: 10.08 %, N: 11.40 %.

3b:[8] ^{1}H-NMR (300.13 MHz, 239.8 K, $C_6D_5CD_3$) δ = 1.29 (br s, 18 H, CH_3), 1.48 (br s, 6 H, CH_3), 1.69 (d, J = 7 Hz, 6 H, CH_3), 3.46 (sept, J = 7 Hz, 1 H, CH), 4.45 (br s, 3 H, CH & Im-H), 6.26 (m, 4 H, Cp-H); ^{1}H-NMR (300.13 MHz, 293.1 K, $C_6D_5CD_3$) δ = 1.05 (d, J = 7 Hz, 3 H, CH_3), 1.11 (d, J = 7 Hz, 3 H, CH_3), 1.40 (d, J = 7 Hz, 18 H, CH_3), 1.65 (s, 6 H, CH_3), 2.48–2.60 (m, 1 H, CH), 2.67–2.75 (m, 2 H, CH_2), 4.09 (m, 2 H, CH), 5.89–6.48 (m, 3 H, Cp-H); $^{13}C\{^1H\}$-NMR (75.48 MHz, 240.1 K, $C_6D_5CD_3$) δ = 8.4 (CH_3), 27.1 (CH_3), 30.3 (CH_3), 102.0 (Cp), 103.5 (Cp). Elemental analysis: calculated: C: 79.11 %, H: 11.18 %, N: 9.71 %; found C: 77.07 %, H: 10.68 %, N: 9.97 %.

One-pot synthesis of ferrocene 4:

To a solution of **1a** (171 mg, 1.0 mmol) and $FeCl_2$ (60 mg, 0.5 mmol) in THF was added **2a** (63 mg, 1.0 mmol) via syringe at 273 K. After stirring overnight and gradual warming to room temperature, all volatiles were removed in vacuo and the solid residue was extracted with hexane. After evaporation of the solvent, the corresponding metal complex was obtained as a crystalline solid.

Yield: 118 mg, 67 %.

^{1}H-NMR (400.13 MHz,296.0 K, $CDCl_3$) δ = 4.14 (s).

The hexane-insoluble residue of the reaction with iron(II) chloride was shown to be 1,3-diisopropyl-4,5-dimethylimidazolium chloride, **1a**·HCl, by ^{1}H NMR spectroscopy.

1a·HCl: ^{1}H-NMR (400.13 MHz, 296.2 K, $CDCl_3$) δ = 1.68 (brs, 12 H, *i*Pr-CH_3), 2.24 (brs, 6 H, CH_3), 4.51 (br s, 2 H, *i*Pr-CH), 10.79 (br s, 1 H, Im-H).

One-pot synthesis of cyclopentadienyl nickel chloride-NHC complex 5:

To a solution of **1a** (557 mg, 3.1 mmol) and $NiCl_2$ (200 mg, 1.5 mmol) in THF was added one equivalent of **2a** (102 mg, 1.5 mmol) via syringe at room temperature. After stirring for 3 h, another equivalent of **2a** was added. After stirring overnight, all volatiles were removed in vacuo and the solid residue was washed with hexane and subsequently extracted with toluene. After evaporation of all volatiles, **5** was obtained as a crystalline purple solid.

Yield: 110 mg, 21 %.

^{1}H-NMR (300.13 MHz, 296.0 K, C_6D_6) δ = 1.18 (d, J = 7 Hz, 6 H, *i*Pr-CH_3), 1.42 (d, J = 7 Hz, 6 H, *i*Pr-CH_3), 1.60 (s, 6H, CH_3), 5.27 (s, 5 H, Cp), 7.27 (sept, J = 7 Hz, 2 H, *i*Pr-CH); $^{13}C\{^1H\}$-NMR (100.62 MHz, 298.0 K, C_6D_6) δ = 9.9 (CH_3), 21.8 (CH_3), 21.9 (CH_3), 55.3 (*i*Pr-CH), 91.8 (Cp), 126.7 (C=C), 158.0 (Carbene-C). Elemental analysis: calculated: C: 56.60 %, H: 7.42 %, N: 8.25 %; found C: 57.33 %, H: 8.08 %, N: 8.67 %.

Acknowledgments

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Keywords: Imidazolium salts · Cyclopentadienyl ligands · Carbene ligands · Metallocenes · Cp-transfer reagents

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[8] Solutions of **3b** in C_6D_6 show rather complicated ^1H and ^{13}C NMR spectra at room temperature, presumably due to an equilibrium between **1a** + **2b** and **3b**, as indicated by VT-NMR spectroscopy. At temperatures below 243 K, **3b** can be observed as the predominate species in solution, while **1a** and **2b** can be observed as predominate species at temperatures above 313 K. See supporting information for ^1H NMR spectra at 239.8 K and 293.1 K.

[9] DFT calculations were carried out using the Gaussian 09 - Revision D.01 package of programs. See supporting information for optimized geometries, references.

[10] ^1H and ^{13}C NMR spectroscopy at room temperature suggest there is no reaction between **3c** and carbenes **1a** and its N,N′-dimethyl-substituted derivative. Attempts to synthesize decamethylferrocene in a similar manner to **4** failed.

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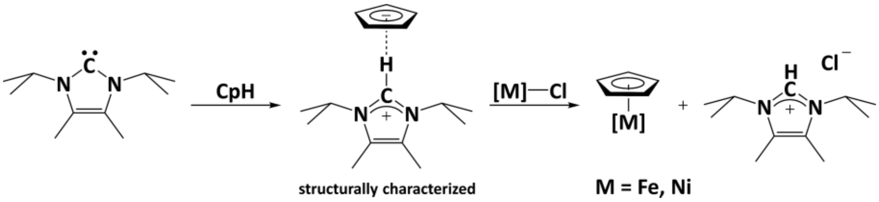

Different imidazolium cyclopentadienide salts were synthesized and structurally characterized. Furthermore, their use as Cp-transfer reagents in the synthesis of transition metal cyclopentadienyl complexes was demonstrated.

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