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Investigations into the reactivity of a molybdenocene formamidinate complex

Joscha Nellesen, Christian Ganter^{*} 

Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

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ABSTRACT

A cationic molybdenocene amidinate complex was investigated in view of its suitability to serve as a precursor for a metalla-N-heterocyclic carbene. Upon deprotonation, an amidinate complex with a cyclopentadiene substituent at the amidinate C atom was identified. This points to the intermediate formation of the sought-after carbene which nucleophilically attacks a Cp ring of the remaining cationic molybdenocene precursor and subsequent fragmentation. In contrast, the nucleophilic attack of standard imidazolylidenes to the cationic molybdenocene amidinate yields stable adducts with a η^4 -cyclopentadiene ligand. The rotational dynamics of this structure has been studied by variable temperature NMR studies. The experimental findings are supported by DFT calculations.

1. Introduction

The chemistry of N-heterocyclic carbenes (NHCs) has been extensively studied over the past couple of decades, with considerable effort directed towards tuning their electronic and steric properties through structural modifications [1–5]. In recent years, a few examples of metal complexes featuring NHC ligands that contain a metal atom within the heterocyclic framework (metalla-N-heterocyclic carbenes, MNHCs) have been reported in the literature [6–15]. Tonks et al. synthesized an example of a free four-membered MNHC featuring a titanocene backbone by reaction of $\text{Cp}_2\text{Ti}(\eta^2\text{-BTMSA})$ (BTMSA: bis(trimethylsilyl)acetylene) with a carbodiimide [16]. Notably, deprotonation of the corresponding cationic formamidinate complex also yielded the free carbene [16], potentially providing a generalizable route to four-membered MNHCs, since amidinate complexes are well established [17,18].

Cyclopentadienyl (Cp) frequently serves as a remarkably inert spectator ligand, although there is a growing number of examples showcasing its non-innocent character [19]. For example, addition reactions of strong nucleophiles such as hydride transfer and organolithium reagents to Cp ligands to generate η^4 -cyclopentadiene frameworks have long been known for cobaltocenium and rhodocenium salts and for cationic iron half-sandwich complexes [20–23]. More recently, Lee et al. reported the synthesis of imidazolium- and pyrrolinium-substituted ferrocene derivatives via the nucleophilic

attack of NHCs or CAACs (CAAC: cyclic alkyl(amino) carbene) on ferrocenium salts [24].

Inspired by the work of Tonks et al., we attempted to synthesize four-membered molybda-N-heterocyclic carbenes by deprotonation of known cationic molybdenocene formamidinate complexes [25]. We found, however, that NHCs attack one of the Cp rings of these cationic complexes forming adducts with a η^4 -cyclopentadiene framework.

2. Results and discussion

The cationic molybdenocene formamidinate complex **1** was prepared using a slightly modified literature procedure [25] reported by Dias et al. (Scheme 1).

The X-ray crystal structure of **1** indicates a delocalization of π -electron density across the N-C-N-framework, resulting in almost identical C1-N1 and C1-N2 bond lengths (Fig. 1). The overall geometrical features are close to those reported by Tonks et al. for a related amidinate complex with a titanocene fragment [16].

The reaction of the precursor **1** with an excess of NaHMDS (3 equivalents) yielded a complex product mixture which we were not able to separate or to isolate a main product from (Scheme 1). Varying the conditions of the deprotonation reaction (order of reagent addition, temperature) did not lead to an improvement. However, analysis of the mixture provided evidence for the presence of the cyclopentadiene-substituted amidinate complex **2**, which apparently was formed via

^{*} Corresponding author.

E-mail address: christian.ganter@uni-duesseldorf.de (C. Ganter).

nucleophilic attack of the *in situ* formed MNHC on a cyclopentadienyl ligand of remaining cationic **1** and subsequent fragmentation (Scheme 1). Compound **2** could be identified in the mass spectrum of the product mixture and its structure was confirmed by X-ray structure analysis of crystals that were grown by layering a dichloromethane solution of the product mixture with *n*-hexane (Fig. 2). The geometrical features within the Mo amidinate fragment are close to those of the parent molecule **1**. Experiments aimed at trapping the intermediately formed MNHC using sulfur, selenium or metal complexes were unsuccessful and yielded mixtures containing **2**. Likewise, resorting to sterically more demanding amidinates with *t*Bu or Dipp substituents at the nitrogen atoms did not result in any improvement as these amidinates did not react with Cp₂MoBr₂. On the other hand, aryl groups with only one ortho-substituent like 2,4-dimethylphenyl provided the amidinate complex analogous to **1**, however the subsequent deprotonation reaction was as unselective as in the case of the phenyl derivative **1**.

DFT calculations (B3LYP/aug-cc-pVTZ(-PP)) on the four-membered molybda-NHC **A** featuring methyl groups at both nitrogen atoms indicated a significant increase in energy of the HOMO compared to the corresponding titana-NHC **B** (−4.28 eV to −5.00 eV). The most significant interactions in the plane of the ring were already described by Tonks et al. for their titana-NHC [16]. Importantly, the bonding interaction between an empty Ti *d*-orbital and the N–C σ-bond mixed with the carbon lone pair results in the stabilization of the HOMO of this MNHC, which has both σ(N–C) and π(Ti–N) symmetry while the LUMO has σ(N–C) and π*(Ti–N) symmetry. In the corresponding molybda-NHC **A**, which has two additional valence electrons, the HOMO has σ(N–C) and π*(Mo–N) symmetry and is thus destabilized compared to the HOMO of the titana-NHC **B** (Fig. 3). The latter was found to correspond to the HOMO–2 in **A**, while the HOMO–1 in **A**, which is close in energy (−5.52 eV to −5.12 eV), has a different symmetry and is predominantly localized on the nitrogen atoms. The energies of the unoccupied π* MOs perpendicular to the ring are almost identical (−0.97 eV for **A** and −1.01 eV for **B**).

Inspired by the structure of complex **2** which suggests a nucleophilic addition of the *in situ* formed MNHC to the Cp ring of the cationic amidinate complex, the reactivity of **1** towards nucleophiles was further studied by reacting it with imidazolylidenes. This reaction led to the formation of the stable adducts **3** and **4** featuring an imidazolium-substituted η⁴-cyclopentadiene ligand under concomitant formal reduction of molybdenum from +IV to +II (Scheme 2). Additions of nucleophiles to η⁵-Cp rings have been described for neutral as well as cationic tungstenocene derivatives. Subsequent hydrogen atom transfer from the η⁴-cyclopentadiene intermediates to the W atom under re-establishment of the aromatic η⁵-Cp ligand provided access to tungstenocene derivatives with modified Cp ligands carrying carbon- or heteroatom based substituents [26–28]. We note that in the present case the η⁴-complexes **3** and **4** are stable and show no tendency for rearomatization and hydrogen transfer. DFT calculations (B3LYP/aug-cc-pVDZ(-PP)) on the cationic amidinate complex similar to **1** featuring methyl groups at both nitrogen atoms indicated that the LUMO is mainly located on the Cp ring, in line with the site of nucleophilic attack at this position (Supplementary data).

By slow evaporation of a saturated solution of **4** in tetrahydrofuran, single crystals for an X-ray structure analysis were obtained (Fig. 4).

The cyclopentadiene ring is folded such that the dihedral angle

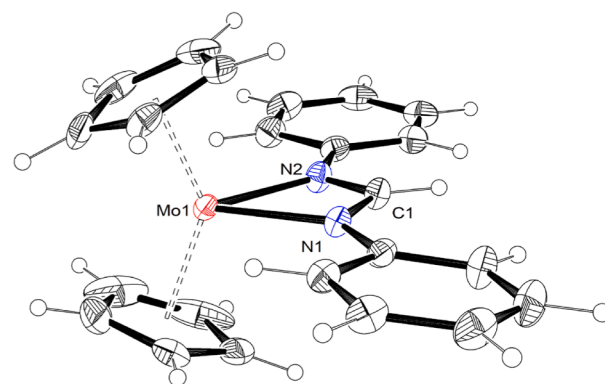


Fig. 1. Molecular structure of complex **1** (ellipsoids drawn for 30 % probability). The PF₆[−] anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–N1 2.141(3), Mo1–N2 2.143(3), N1–C1 1.320(4), N2–C1 1.319(4); N1–Mo1–N2 60.52(11), C1–N1–Mo1 94.9(2), C1–N2–Mo1 94.8(2), N2–C1–N1 109.8(3).

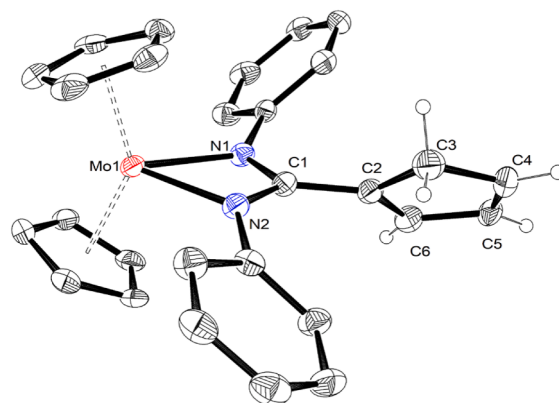
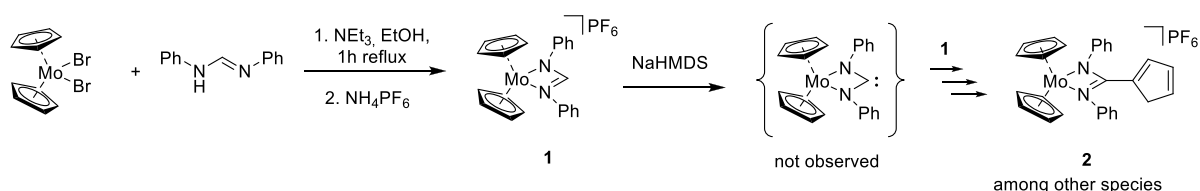


Fig. 2. Molecular structure of complex **2** (ellipsoids drawn for 50 % probability). The PF₆[−] anion and most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–N1 2.132(4), Mo1–N2 2.142(4), N1–C1 1.343(6), N2–C1 1.332(6); N1–Mo1–N2 60.99(15), C1–N1–Mo1 95.4(3), C1–N2–Mo1 95.3(3), N2–C1–N1 108.3(4).

between the C3–C2–C6 plane and the mean diene plane is 31.6°. The substituted cyclopentadiene ligand is twisted relative to the CpMo (amidinate) fragment such that the complex is C₁-symmetric in the crystal. Rotation around the Mo-cyclopentadiene axis should interconvert the enantiomers and thus, the diastereotopic cyclopentadiene protons (2/5 and 3/4 in Scheme 3). In the ¹H NMR spectra of **3** and **4** on a 300 MHz spectrometer at room temperature, the resonances of these protons are strongly broadened.

At −40 °C five resonances attributable to the five inequivalent η⁴-cyclopentadiene protons can be identified in the ¹H NMR spectrum of **3** in acetone-d₆ on a 600 MHz spectrometer. Increasing the temperature leads to a broadening of four of these resonances which are attributed to the two pairs of exchanging protons (H2/5 and 3/4), while the resonance of the non-exchanging proton on the saturated carbon atom (H1)



Scheme 1. Synthesis and reactivity of the molybdenocene formamidinate complex **1**.

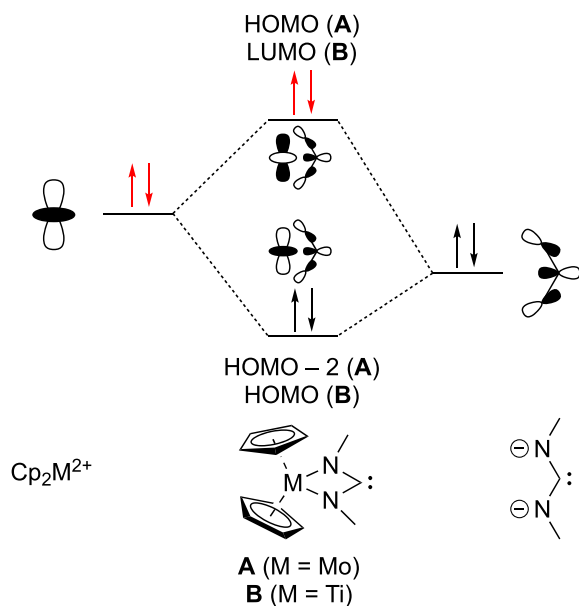


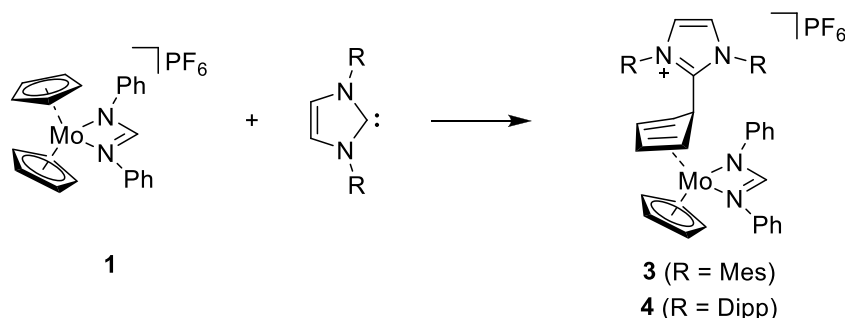
Fig. 3. Schematic molecular orbital diagram showing the in-ring orbital interaction between Ti/Mo and the a_1 -symmetric N-C bonding orbitals (cf. ref. [16]). The additional two electrons present only in the molybdenum complex A are depicted in red.

remains largely unaffected. At 45 °C, two broad resonances for the two pairs of exchanging protons are observed. Likewise, the same observation holds true for the signals of the *o*-Me groups of the two *N*-mesityl substituents: two separated signals (with integrals of 6 protons each) at -40 °C merge into one resonance at 45 °C (Fig 5, the complete set of temperature dependent spectra can be found in the Supplementary data).

The exchange rate constants for the dynamic process in the temperature range between -40 °C and +40 °C in 10 °C increments were determined by simulating the resonances of a pair of exchanging protons using the TopSpin software package 4.4.0 (Bruker BioSpin). Evaluation of the Eyring plot resulted in an activation free energy barrier of $\Delta^\ddagger G^0 = 12.6$ kcal/mol (Supplementary data).

DFT calculations (B3LYP/aug-cc-pVDZ(-PP)) were carried out to optimize the geometry and to find the transition state for the ligand rotation. In the optimized geometry of a simplified molecule featuring methyl groups instead of aryl groups at the amidinate and imidazolium nitrogen atoms, the η^4 -cyclopentadiene ligand is twisted relative to the MoCp(amidinate) fragment with a similar angle as in the molecular structure of **4** in the crystal.

The calculated free energy barrier for the rotation of the η^4 -cyclopentadiene ligand in the simplified system was found to be 11.4 kcal/mol and is thus in good agreement with the experimentally obtained value.



Scheme 2. Synthesis of the adducts **3** and **4**.

3. Conclusion

Attempts to synthesize a four-membered molybda-NHC by deprotonation of the cationic molybdenocene formamidinate complex **1** yielded a product mixture due to the nucleophilic attack of the intermediately formed MNHC on a cyclopentadienyl ligand of **1** and subsequent fragmentation.

The nucleophilic addition of imidazolylidenes to **1** resulted in the formation of the stable adducts **3** and **4** featuring a η^4 -cyclopentadiene framework. The hindered rotation of the cyclopentadiene ligand leads to a broadening of resonances in the NMR spectra at room temperature.

4. Experimental

All reactions were performed in a nitrogen-atmosphere using standard Schlenk techniques. Solvents were dried and degassed prior to use.

NMR spectra were recorded on a Bruker Avance III 300 and a Bruker Avance III 600. ¹H and ¹³C{¹H} NMR spectra are referenced to the chemical shifts of residual undeuterated solvent. Mass spectra were recorded on a UHR-QTOF maxis 4G. Elemental analyses were recorded on an Elementar Vario microcube. X-ray crystal structure data were collected on a Rigaku XtaLAB Synergy-S or a Bruker APEX Duo CCD diffractometer. Reagents such as Cp₂MoBr₂ [29], *N,N'*-diphenylformamidinate [30] and IMes [31] were synthesized according to literature procedures. Other reagents were purchased commercially and used without further purification.

Synthesis of Compound 1: This compound was synthesized using a slightly modified literature procedure [25]. A suspension of 300 mg Cp₂MoBr₂ (0.777 mmol, 1 eq), 229 mg *N,N'*-diphenylformamidinate (1.17 mmol, 1.5 eq) and 1 mL triethylamine in 20 mL ethanol was heated under reflux for 1 h. An excess of NH₄PF₆ (2.5 eq) was added to the resulting orange solution, after which the solvent was evaporated under reduced pressure. The residue was taken up in 20 mL dichloromethane and the solution was washed with 0.1 M NaOH solution (2 × 10 mL) and water (10 mL). The dichloromethane solution was dried over MgSO₄. After concentration of the solution under reduced pressure, an orange solid was precipitated by adding 40 mL diethylether. The supernatant was removed *via* syringe and the precipitate was dried *in vacuo* to give **1** as an orange solid (354 mg, 0.622 mmol, 80 %). Single crystals for an X-ray structure analysis were obtained by slow evaporation of a saturated solution of **1** in acetone. ¹H NMR ((CD₃)₂CO, 300 MHz): δ 9.71 (s, 1H, N(CH)₂N), 7.33 – 7.24 (m, 4H, *m*-Ph), 7.10 – 7.05 (m, 2H, *p*-Ph), 7.05 – 7.01 (m, 4H, *o*-Ph), 6.06 (s, 10H, Cp) ppm. ¹³C{¹H} NMR ((CD₃)₂CO, 75 MHz): δ 167.6 (s, N(CH)₂N), 145.3 (s, *ipso*-pH), 129.9 (s, *m*-Ph), 124.6 (s, *p*-Ph), 118.8 (s, *o*-Ph), 100.2 (s, Cp) ppm. MS (ESI): *m/z* 423 [M]⁺. Anal.: % calcd. for C₂₃H₂₁MoN₂PF₆: C 48.78, H 3.74, N 4.95, found: C 48.99, H 3.94, N 5.03.

Attempted Synthesis of the free Carbene

A solution of 40 mg **1** (0.0705 mmol, 1 eq) in THF was cooled to -78 °C. NaHMDS in THF (3 eq) was added by syringe and the resulting mixture was allowed to warm slowly to room temperature overnight.

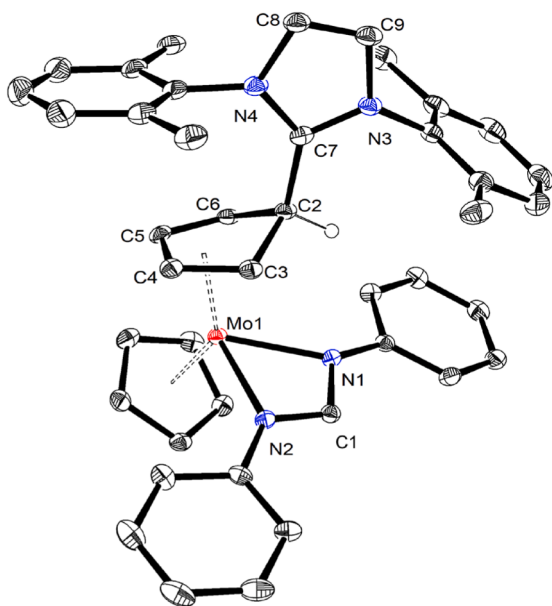


Fig. 4. Molecular structure of complex **4** (ellipsoids drawn for 50 % probability). The methyl groups of the *i*Pr-groups, the PF₆-anion and all hydrogen atoms except C2-H are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1-N1 2.186(2), Mo1-N2 2.175(2), N1-C1 1.325(4), N2-C1 1.324(4); N2-Mo1-N1 59.82(9), C1-N1-Mo1 94.35(17), C1-N2-Mo1 94.87(17), N2-C1-N1 110.3(2).

The solvent was removed under reduced pressure, the residue was taken up in CDCl₃, the suspension was transferred into an NMR tube and centrifuged. Upon standing for a couple of days, some crystals of **2** were formed which were analysed by X-ray diffraction.

Synthesis of Compound 3: 30 mg **1** (0.0529 mmol, 1 eq) and 17.7 mg IMes (0.0582 mmol, 1.1 eq) were dissolved in 2 mL tetrahydrofuran. The orange solution was stirred for 30 mins at room temperature and the solvent was subsequently removed under reduced pressure. The residue was washed with diethylether and dried *in vacuo* to yield **3** as an orange solid (44.7 mg, 0.0513 mmol, 97 %). The resonances of the exchanging cyclopentadiene nuclei are not visible in the NMR spectra at room temperature due to line broadening. ¹H NMR (THF-d₈, 300 MHz): δ 9.24 (s, 1H, N(CH)N), 7.50 (s, 2H, CH_{Imidazol.}), 7.21 – 7.10 (m, 4H, m-Ph), 6.97 (s, 4H, Mes), 6.93 – 6.83 (m, 6H, *o/p*-Ph), 4.82 (s, 5H, Cp), 4.15 (m, 1H, H1), 2.33 (s, 6H, *p*-Me), 2.00 (s, 12H, *o*-Me) ppm. ¹H NMR ((CD₃)₂CO, 600 MHz, 233 K): δ 9.41 (s, 1H, N(CH)N), 7.77 (s, 2H (reduced by H/D exchange with solvent), CH_{Imidazol.}), 7.25 – 7.19 (m, 2H, m-Ph), 7.18 – 7.13 (m, 2H, m-Ph), 7.05 (s, 2H, Mes), 7.03 – 6.99 (m, 3H, *o/p*-pH), 6.95 (s, 2H, Mes), 6.91 – 6.85 (m, 3H, *o/p*-Ph), 5.26 (brs, 1H, H3/H4), 4.91 (s, 5H, Cp), 4.12 (brs, 1H, H1), 3.51 (brs, 1H, H4/H3), 2.78 (brs, 1H, H2/H5), 2.33 (s, 6H, *p*-Me), 2.02 (s, 6H, *o*-Me), 1.98 (s, 6H, *o*-Me), 1.83 (brs, 1H, H5/H2) ppm. ¹³C{¹H} NMR (THF-d₈, 75 MHz): δ 159.5 (s, N(CH)N), 149.8 (s, NCN_{Imidazol.}), 146.7 (s, Ar), 141.8 (s, Ar), 135.6 (s, Ar), 132.7 (s, Ar), 130.7 (s, Ar), 129.8 (s, Ar), 124.6 (s, CH_{Imidazol.}), 122.8 (s, Ar), 118.6 (s, Ar), 92.7 (s, Cp), 45.8 (s, Cyclopentadiene (C1)), 21.5 (s, *p*-Me), 17.9 (s, *o*-Me) ppm. Anal.: % calcd. for

C₄₄H₄₅MoN₄PF₆: C 60.69, H 5.21, N 6.43, found: C 60.30, H 5.48, N 6.10.

Synthesis of Compound 4: 50 mg **1** (0.0883 mmol, 1 eq) and 41 mg IDipp (0.106 mmol, 1.2 eq) were dissolved in 5 mL tetrahydrofuran. The orange solution was stirred for 30 mins at room temperature and the solvent was subsequently removed under reduced pressure. The residue was washed with diethylether and dried *in vacuo* to yield **4** as an orange solid (80.1 mg, 0.0839 mmol, 95 %). Single crystals for an X-ray structure analysis were obtained by slow evaporation of a saturated solution of **4** in tetrahydrofuran. The resonances of the exchanging cyclopentadiene nuclei are not visible in the NMR spectra at room temperature due to line broadening. ¹H NMR (THF-d₈, 300 MHz): δ 9.30 (s, 1H, N(CH)N), 7.72 (s, 2H, CH_{Imidazol.}), 7.54 – 7.42 (m, 2H, *p*-Dipp), 7.35 – 7.30 (m, 4H, m-Dipp), 7.14 – 7.03 (m, 4H, m-Ph), 6.91 – 6.76 (m, 6H, *o/p*-Ph), 4.84 (s, 5H, Cp), 4.30 (m, 1H, H1), 2.40 (hept, ³J_{HH} = 6.8 Hz, 4H, *i*Pr), 1.24 (d, ³J_{HH} = 6.8 Hz, 12H, Me), 1.14 (d, ³J_{HH} = 6.8 Hz, 12H, Me) ppm. ¹³C{¹H} NMR (THF-d₈, 75 MHz): δ 159.7 (s, N(CH)N), 150.4 (s, NCN_{Imidazol.}), 146.6 (s, Ar), 145.8 (s, Ar), 133.1 (s, Ar), 132.1 (s, Ar), 129.9 (s, Ar), 125.9 (s, CH_{Imidazol.}), 125.7 (s, Ar), 123.7 (s, Ar), 118.6 (s, Ar), 93.0 (s, Cp), 46.3 (s, Cyclopentadiene (C1)), 30.4 (s, *i*Pr), 25.8 (s, Me), 22.6 (s, *o*-Me) ppm.

CRediT authorship contribution statement

Joscha Nellesen: Writing – original draft, Investigation, Funding acquisition, Data curation. **Christian Ganter:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

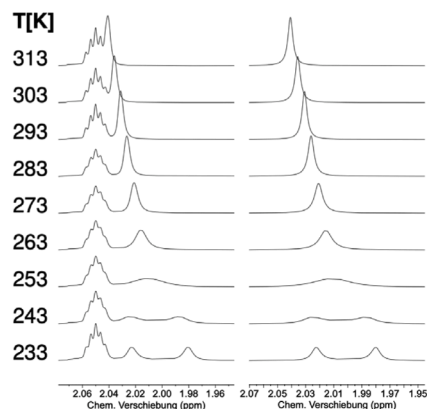
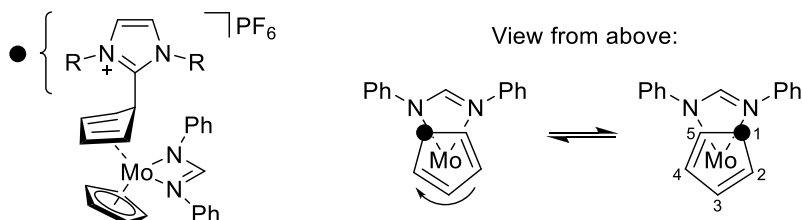


Fig. 5. Section of ¹H NMR spectra of compound **3** in acetone-d₆ between 233 and 313 K (left) and simulated spectra (right) for resonances of exchanging *o*-Me-protons of the two N-mesityl groups.



Scheme 3. Schematic representation of the rotation around the Mo-cyclopentadiene axis. The imidazolium substituent is represented by a filled circle.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2025.123556](https://doi.org/10.1016/j.jorganchem.2025.123556).

Data availability

Data will be made available on request.

References

- [1] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Stable Carbenes, *Chem. Rev.* 100 (2000) 39–91, <https://doi.org/10.1021/cr940472u>.
- [2] L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Lapponnaz, V. César, Synthetic routes to N-heterocyclic carbene precursors, *Chem. Rev.* 111 (2011) 2705–2733, <https://doi.org/10.1021/cr100328e>.
- [3] M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, An overview of N-heterocyclic carbenes, *Nature* 510 (7506) (2014) 485–496, <https://doi.org/10.1038/nature13384>.
- [4] D.J. Nelson, S.P. Nolan, Quantifying and understanding the electronic properties of N-heterocyclic carbenes, *Chem. Soc. Rev.* 42 (2013) 6723–6753, <https://doi.org/10.1039/c3cs60146c>.
- [5] H.V. Huynh, Electronic properties of N-heterocyclic carbenes and their experimental determination, *Chem. Rev.* 118 (2018) 9457–9492, <https://doi.org/10.1021/acs.chemrev.8b00067>.
- [6] J. Ruiz, L. García, B.F. Perandones, M. Vivanco, A Fischer carbene within an Arduengo carbene, *Angew. Chem. Int. Ed.* 50 (2011) 3010–3012, <https://doi.org/10.1002/anie.2011007937>.
- [7] J. Ruiz, L. García, C. Mejuto, M. Vivanco, M.R. Díaz, S. García-Granda, Strong electron-donating metalla-N-heterocyclic carbenes, *Chem. Comm.* 50 (2014) 2129–2132, <https://doi.org/10.1039/c3cc47987k>.
- [8] J. Ruiz, L. García, M. Vivanco, Á. Berros, J.F. Van Der Maelen, Generating and trapping metalla-N-heterocyclic carbenes, *Angew. Chem. Int. Ed.* 54 (2015) 4212–4216, <https://doi.org/10.1002/anie.201411647>.
- [9] A.G. Tskhovrebov, K.V. Luzyanin, F.M. Dolgushin, M.F.C. Guedes Da Silva, J. Pombeiro, V.Y. Kukushkin, Novel reactivity mode of metal diaminocarbenes: palladium(II)-mediated coupling between acyclic diaminocarbenes and isonitriles leading to dinuclear species, *Organometallics* 30 (2011) 3362–3370, <https://doi.org/10.1021/om2002574>.
- [10] H. Brunner, W. Meier, J. Wachter, I. Bernal, E. Raabe, CO-induced, reversible insertion of a terminal imido ligand into an η^1 : η^2 -isocyanide bridge in the dimolybdenum complex $\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-CNPh})\text{Mo}(\text{NPh})\text{Cp}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), *J. Organomet. Chem.* 362 (1989) 95–103, [https://doi.org/10.1016/0022-328X\(89\)85283-0](https://doi.org/10.1016/0022-328X(89)85283-0).
- [11] O. Theilmann, M. Ruhmann, A. Villinger, A. Schulz, W.W. Seidel, K. Kaleta, T. Beweries, P. Arndt, U. Rosenthal, $[\text{Cp}_2\text{Ti}^{\text{III}}(\text{NCy})_2\text{C-Ti}^{\text{III}}\text{Cp}_2]$: a transient titanocene carbene complex? *Angew. Chem. Int. Ed.* 49 (2010) 9282–9285, <https://doi.org/10.1002/anie.201004145>.
- [12] S.P. Green, C. Jones, A. Stasch, Stable magnesium(I) compounds with Mg-Mg bonds, *Science* 318 (2007) 1754–1757, <https://doi.org/10.1126/science.1150856>.
- [13] L. Xiao, W. Chen, L. Shen, L. Liu, Y. Xue, Y. Zhao, X.J. Yang, Reduction of carbodiimides by a dialumane through insertion and cycloaddition, *Chem. Comm.* 56 (2020) 6352–6355, <https://doi.org/10.1039/d0cc02048f>.
- [14] J. Hicks, A. Mansikkamäki, P. Vasko, J.M. Goicoechea, S. Aldridge, A nucleophilic gold complex, *Nat. Chem.* 11 (2019) 237–241, <https://doi.org/10.1038/s41557-018-0198-1>.
- [15] C. McManus, J. Hicks, X. Cui, L. Zhao, G. Frenking, J.M. Goicoechea, S. Aldridge, Coinage metal alumanyl complexes: probing regiochemistry and mechanism in the insertion and reduction of carbon dioxide, *Chem. Sci.* 12 (2021) 13458–13468, <https://doi.org/10.1039/D1SC04676D>.
- [16] E.P. Beaumier, C.P. Gordon, R.P. Harkins, M.E. McGreal, X. Wen, C. Copéret, J. D. Goodpaster, I.A. Tonks, $\text{Cp}_2\text{Ti}(\kappa^2\text{-tBuNCNtBu})$: a complex with an unusual κ^2 coordination mode of a heterocumulene featuring a free carbene, *J. Am. Chem. Soc.* 142 (2020) 8006–8018, <https://doi.org/10.1021/jacs.0c02487>.
- [17] F.T. Edelman, Advances in the coordination chemistry of Amidinate and Guanidinate Ligands, *Advances in Organometallic Chemistry* 57 (2008) 183–352, [https://doi.org/10.1016/S0065-3055\(08\)00003-8](https://doi.org/10.1016/S0065-3055(08)00003-8).
- [18] J. Barker, M. Kilner, The coordination chemistry of the amidine ligand, *Coord. Chem. Rev.* 133 (1994) 219–300, [https://doi.org/10.1016/0010-8545\(94\)80059-6](https://doi.org/10.1016/0010-8545(94)80059-6).
- [19] A. VanderWeide, D.E. Prokopchuk, Cyclopentadienyl ring activation in organometallic chemistry and catalysis, *Nat. Rev. Chem.* 7 (2023) 561–572, <https://doi.org/10.1038/s41570-023-00501-1>.
- [20] M.L.H. Green, L. Pratt, G. Wilkinson, 760. A new type of transition metal-cyclopentadiene compound, *J. Chem. Soc.* (1959) 3753–3767, <https://doi.org/10.1039/JR9590003753>.
- [21] E.O. Fischer, G.E. Herberich, Über Aromatenkomplexe von Metallen, XLIV. Über die reaktivität des Di-cyclopentadienyl-kobalt(III)-Kations, *Chem. Ber.* 94 (1961) 1517–1523, <https://doi.org/10.1002/cber.19610940615>.
- [22] A. Davison, M.L.H. Green, G. Wilkinson, π -Cyclopentadienyl-and cyclopentadienyl-iron carbonyl complexes, *J. Chem. Soc.* 620 (1961) 3172–3177, <https://doi.org/10.1039/JR9610003172>.
- [23] S.G. Davies, M.L.H. Green, D.M.P. Mingos, Nucleophilic addition to organotransition metal cations containing unsaturated hydrocarbon ligands. A survey and interpretation, *Tetrahedron* 34 (1978) 3047–3077, [https://doi.org/10.1016/0040-4020\(78\)87001-X](https://doi.org/10.1016/0040-4020(78)87001-X).
- [24] H. Song, G. Kwon, C. Citek, S. Jeon, K. Kang, E. Lee, Pyrrolinium-substituted persistent zwitterionic ferrocene derivative enabling the application of ferrocene anolyte, *ACS Appl. Mater. Interfaces* 13 (2021) 46558–46565, <https://doi.org/10.1021/acsami.1c11571>.
- [25] A.R. Dias, M.A. Queirós, Amidinato complexes of dicyclopentadienylmolybdenum. Synthesis and redox properties, *J. Organomet. Chem.* 390 (1990) 193–201, [https://doi.org/10.1016/0022-328X\(90\)85031-S](https://doi.org/10.1016/0022-328X(90)85031-S).
- [26] J.P. McNally, D. Glueck, N.J. Cooper, A versatile route to diastereomeric tungstenocene complexes containing chiral metal centers, *J. Am. Chem. Soc.* 110 (1988) 4838–4840, <https://doi.org/10.1021/ja00222a058>.
- [27] T.C. Forschner, N.J. Cooper, Magnesium dihalide promoted addition of Grignard reagents to the cyclopentadienyl rings of tungstenocene dichloride, *J. Am. Chem. Soc.* 111 (1989) 7420–7424, <https://doi.org/10.1021/ja00201a022>.
- [28] S. Rigny, V.I. Bakhmutov, B. Nuber, J.-C. Leblanc, C. Moïse, A new type of heterobimetallic compound containing Tungstenocene: synthesis, reactivity, NMR, and stereochemical studies, *Inorg. Chem.* 35 (1996) 3202–3209, <https://doi.org/10.1021/ic950966p>.
- [29] R.L. Cooper, M.L.H. Green, Some bis- π -cyclopentadienyl halides of molybdenum, Tungsten and Rhenium, *J. Chem. Soc. A* (1967) 1155–1160, <https://doi.org/10.1039/J19670001155>.
- [30] K.M. Kuhn, R.H. Grubbs, A facile preparation of imidazolium chlorides, *Org. Lett.* 10 (2008) 2075–2077, <https://doi.org/10.1021/ol800628a>.
- [31] A.J. Arduengo, H.V. Dias, R.L. Harlow, M. Kline, Electronic stabilization of nucleophilic carbenes, *J. Am. Chem. Soc.* 114 (1992) 5530–5534, <https://doi.org/10.1021/ja00040a007>.