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Unexpected Formation and Structural Characterization of a Dinuclear Sodium Half-Sandwich Complex

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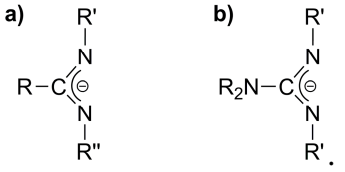
Abstract: Treatment of *N*,*N*′-diisopropylcarbodiimide with sodium cyclopentadienide (NaCp) in a molar ratio of 1:1 in THF solution resulted in formation of the unexpected dinuclear sodium half-sandwich complex $[NaC_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]_2$ (**1**) as colorless crystals in low yield. The newly formed ligand, which belongs to the group of 6-aminofulvene-2-aldiminate ligands, coordinates to sodium in an η^5-coordination mode via the cyclopentadienyl ring. Dimerization occurs through additional chelating $\kappa N,N'$-coordination of the amidine substituents. The NMR data of **1** indicated a slow dimer/monomer equilibrium in solution. A serendipitously isolated hydrolysis product, $\{\mu\text{-}(^i PrNH)_2C{=}O\}_2[NaC_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]_2$ (**2**), contains the new 6-aminofulvene-2-aldiminate ligand in the *N*,*N*′-chelating coordination mode with the cyclopentadiene ring being uncoordinated. In this case, dimerization occurs through the presence of two bridging neutral *N*,*N*′-diisopropylurea ligands. Both compounds have been structurally characterized by single-crystal X-ray diffraction.

Keywords: Sodium; amidinate ligand; cyclopentadienyl; aminofulvene-aldiminate; crystal structure

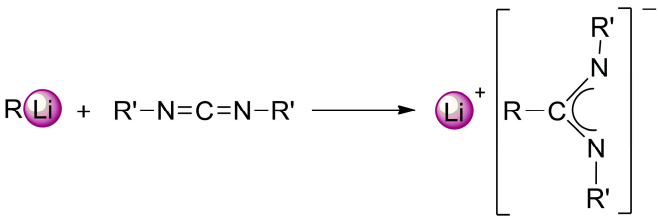
1. Introduction

N,*N*′-Chelating anionic ligands—such as the amidinates, $[RC(NR')_2]^-$, and guanidinates, $[R_2NC(NR')_2]^-$ (Scheme 1)—have become indispensable in various fields of organometallic and coordination chemistry [1–9]. These ligands form well-defined complexes with virtually every metallic element in the periodic system. In main group metal chemistry, bulky amidinate and guanidinate ligands have been successfully employed to stabilize low coordination numbers and uncommon oxidation states [10–12]. Numerous transition metal amidinate and guanidinate complexes have been demonstrated to exhibit high catalytic activity in a variety of organic transformations [2,13–16]. Moreover, alkyl-substituted amidinate and guanidinate complexes of various metals have been established as ALD (atomic layer deposition) and MOCVD (metal–organic chemical vapor deposition) precursors for the deposition of thin films of useful materials, such as metals, metal oxides or metal nitrides, among others [17–19].



Scheme 1. Schematic representation of amidinate anions (**a**) and guanidinate anions (**b**).

Making the amidinate and guanidinate ligands extremely versatile, the substituents at all three atoms of the N–C–N backbone can be varied. A generally applicable synthetic route to lithium amidinate precursors involves the addition of organolithium reagents to *N*,*N*′-disubstituted carbodiimides, as shown in Scheme 2. The substituents R and R′ can be varied in a wide range and, consequently, a large library of amidinate ligands has become available [1–9]. Closely related guanidinate anions can be accessed in a similarly manner by adding lithium diorganoamides, $LiNR_2$, to carbodiimides.

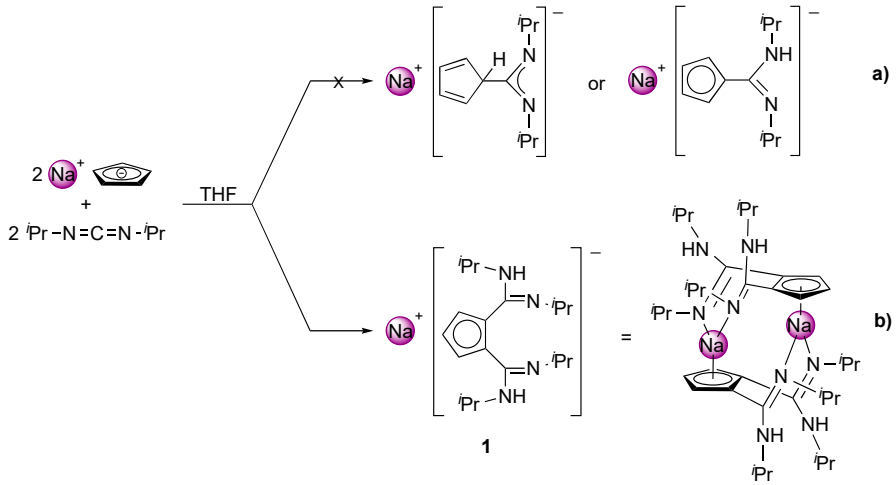


Scheme 2. General synthetic route to lithium amidinates.

At the outset of the present study, we wondered if it might be possible to directly attach a cyclopentadienyl ring to the amidinate N–C–N backbone by the use of sodium cyclopentadienide, NaCp, as a nucleophile. We now report the outcome of this reaction and the structural characterization of the unexpected product.

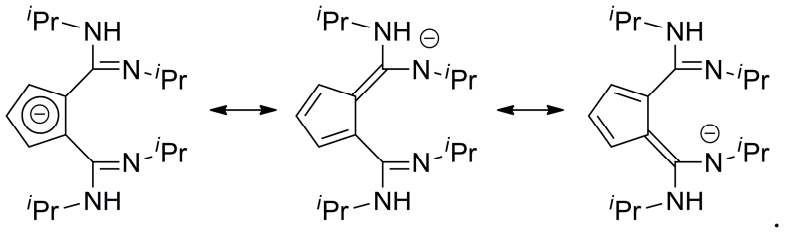
2. Results and Discussion

The reaction of 1 equiv. of sodium cyclopentadienide, NaCp, with *N*,*N*′-diisopropylcarbodiimide was carried out in THF solution at room temperature and resulted in formation of a clear, light-brown solution. Removal of the solvent, followed by extraction with *n*-pentane, provided a yellow solution besides a large amount of insoluble brown material. All attempts to crystallize the latter from diethyl ether or THF failed. Crystallization of the *n*-pentane filtrate at 4 °C afforded colorless, needle-like crystals in low yield. An IR spectrum of the product suggested that the expected simple addition reaction (Scheme 3a) had not taken place, as it showed three bands typical for NH functional groups at ν 3436 m (ν_{as} NH), 3386 m (ν_s NH), 3223 m (ν_s NH). A single-crystal X-ray diffraction study revealed the formation of an unexpected dimeric sodium half-sandwich complex $[NaC_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]_2$ (**1**). As illustrated in Scheme 3b, the bis(amidino)-substituted cyclopentadienyl anion $[C_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]^-$ had formed through double addition of *N*,*N*′-diisopropylcarbodiimide to the cyclopentadienyl ring. With ca. 9% (determined after the crystal structure had been elucidated) the isolated yield of **1** was reproducibly low, although synthetically useful amounts (>1 g) could be easily prepared. Notably and surprisingly, the isolated yield of **1** could not be improved by carrying out the reaction of NaCp with *N*,*N*′-diisopropylcarbodiimide in a 1:2 molar ratio as suggested by the composition of the products. Several experiments using 2 equiv. of $^iPrN{=}C{=}N^iPr$ under different reaction conditions afforded only small amounts of NaCp as the only crystalline material.



Scheme 3. Synthesis of the title compound $[NaC_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]_2$ (**1**).

Colorless, needle-like single crystals of **1** suitable for *X*-ray diffraction were obtained by cooling a solution in *n*-pentane to 4 °C. Figure 1 depicts the molecular structures of **1** along with selected bond lengths and angles, while crystallographic details are listed in the Supplementary Materials. Compound **1** crystallizes in the monoclinic space group $P2_1/n$, with one Na atom and one $[C_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]^-$ ligand in the asymmetric unit. The dimeric molecular structure is completed by inversion symmetry. The ligand in attached to the Na atom in *N*,*N*-chelating fashion via the two non-protonated N atoms (N1, N3), with the bite angle N–Na–N being 91.03(5)°. The two Na–N bonds are virtually identical in length (Na–N1 233.1(2) pm and Na–N3 233.8(2) pm). These values are slightly smaller as compared to those in a previously reported sodium amidinate (Na–N 237.1(3) and 240.7(3) pm; C.N. of Na = 5), which can be attributed to the higher coordination number of sodium in the reference compound [20]. Consequently, it seems like the negative ligand charge is located at the amidine moiety at a significant amount. This is in accordance with amidinocyclopentadienide/aminofulvene-aldiminate mesomerism, as outlined in Scheme 4.



Scheme 4. Resonance forms of the $[C_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]^-$ ligand.

Additional η^5-coordination of the cyclopentadienyl moiety of the symmetry-related ligand leads to pseudo trigonal-planar coordination of the Na atom (regarding the η^5-Cp moiety as one ligating entity). The Na–centroid(C5) separation is comparatively short at 244.3(1) pm, which can possibly be explained by the low coordination number of sodium (cf. NaCp(DME), NaCp(18-crown-6) and $Na(C_4H_4Me)$(18-crown-6): Na–centroid(C_5-ring) 254(2)–256(2) pm [21] (18-crown-6 = 1,4,6,10,13,16-hexaoxacycooctadecane); $Na[C_3H_3\text{-}1,2\text{-}(COOMe)_2]$: Na–centroid(C5) 253.04(6) pm [22]). Coordination of further ligands, such as THF to sodium, is most likely prevented by the steric bulk of the isopropyl groups. Possibly for the same reason, the N–H hydrogen atoms at N2 and N4 are not involved in hydrogen bonding.

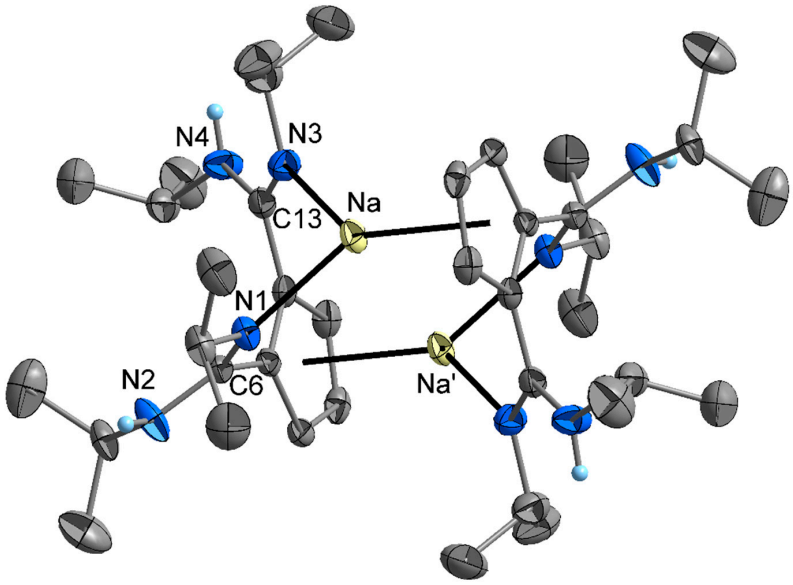
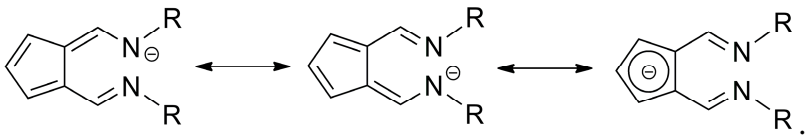


Figure 1. Molecular structure of $[NaC_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]_2$ (**1**) in the crystal. Displacement ellipsoids are drawn at the 50% probability level, H atoms attached to C atoms omitted for clarity. Selected bond lengths (pm) and angles (deg.): Na–N1 233.1(1), Na–N3 233.8(2), Na–C 263.6(2)–278.5(2), Na–centroid(C_5-ring) 244.3(1), N1–Na–N3 91.03(5), N1–C6 129.0(2), N2–C6 136.8(2), N3–C13 128.8(2), N4–C13 137.6(2), N1–C6–N2 123.9(1), N3–C13–N4 124.4(2). Symmetry code: '−x, −y, 2 − z.

In the crystal, the dimeric molecule of **1** possesses inversion symmetry with the center of inversion right between the two Na atoms. According to the ^{1}H and ^{13}C NMR data of **1**, the dimeric structure found in the crystal structure is partly retained in solution. Both the cyclopentadienyl and isopropyl resonance could be assigned. However, the ^{1}H NMR signals are significantly broadened, and in both NMR spectra a doubling of all resonances is observed. This can be interpreted by the presence of a slow equilibrium between the dimer and a (presumably THF-d_8-solvated) monomeric structure in THF-d_8 solution. Copies of the spectra can be found in the Supplementary Material.

With its two amidinate substituents in 1,2-position on the cyclopentadienyl ring, the new ligand in **1** belongs to the group of cyclopentadienyl derivatives called 6-aminofulvene-2-aldiminate (AFA) ligands. The first neutral 6-aminofulvene-2-aldimine (AFAH) compound was first prepared by Hafner et al. in 1963 [23,24]. 6-Aminofulvene-2-aldiminate ligands are ambidentate monoanionic ligands comprising both cyclopentadienyl and diimine donors, as shown in Scheme 5.

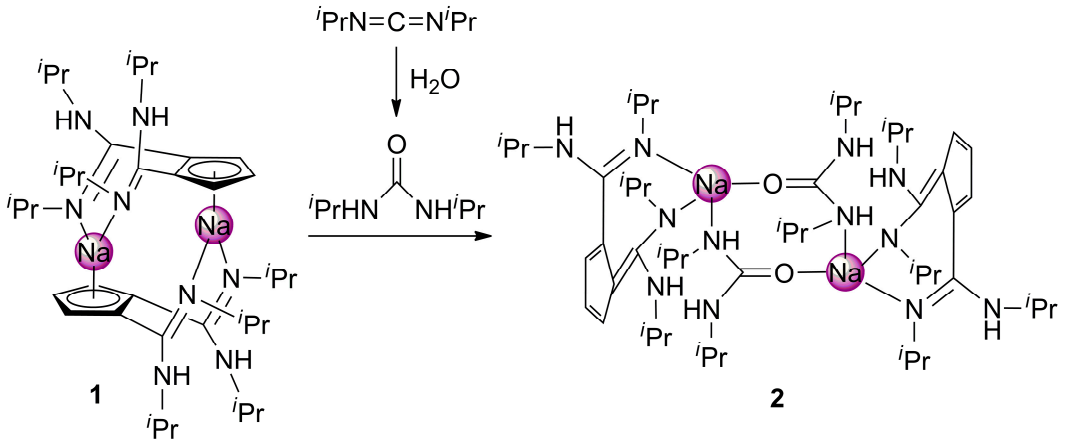


Scheme 5. Resonance forms of 6-aminofulvene-2-aldiminate (AFA) ligands.

As a consequence of this resonance, a 6-aminofulvene-2-aldiminate ligand can coordinate to a metal atom in a chelating mode through the two imine nitrogen donors as a fulvenealdiminate (**A**) or in an η^5-mode as a cyclopentadienyldiimine. Complexes of this ligand system have been reported for some main group metals, as well as first and second row transition metals [25–32]. Closer investigation of the coordination chemistry of 6-aminofulvene-2-aldiminate ligands began in 1998 with the discovery of a straightforward synthesis of the C-phenyl-substituted precursor $C_5H_3[1,2\text{-}C(Ph)NH]_2H$ based on the reaction of magnesocene with benzonitrile. The ligand $C_5H_3[1,2\text{-}C(Ph)NH]_2H$ was successfully employed in a number of complexes with Mg [25], Al, Ga [26]

and Zr [25]. In all these compounds, the 6-aminofulvene-2-aldiminate anion acts as a *N*,*N*′-chelating ligand. The same coordination mode was established for some 6-aminofulvene-2-aldiminate complexes of palladium [27,28], copper [29,30] and zinc [27], while the η^5-coordination mode as a cyclopentadienyldiimine has been found in some AFA complexes of ruthenium [27,31]. Notably, two magnesium complexes of the AFA ligand system bearing cyclohexyl groups at the nitrogen atoms have been reported, in which both coordination modes have been realized [32]. Deprotonation of *N*,*N*′-dicyclohexyl-6-aminofulvene-2-aldimine (HCy_2AFA) with MeLi followed by reaction with MeMgBr afforded the *N*,*N*′-coordinated complex [[1,2-$(CyN{=}CH)_2C_5H_3$-*N*,*N*′]MgMe(THF)] with an uncoordinated cyclopentadienyl ring. In contrast, the direct reaction of HCy_2AFA with MeMgBr resulted in liberation of methane and formation of the binuclear bromide-bridged complex $Mg_2(\mu\text{-Br})[\mu\text{-}\eta^5{:}\kappa N,\kappa N'\text{-}1,2\text{-}(CyN{=}CH)_2C_5H_3][1,2\text{-}(CyN{=}CH)_2C_5H_3\text{-}\kappa N,\kappa N']$ in which one of the Mg centers is ligated both to the η^5-cyclopentadienyl ring of one of the ligands and to both N donor atoms of the other. Thus, this magnesium derivative is the closest structural relative of our sodium complex **1**, although the ligand system in **1** is rather unusual, as it bears additional secondary amino functionalities attached to the imine carbon atoms. It should be noted that the 1:1 addition of *N*-heterocyclic carbenes (NHCs) to carbodiimides has been reported. These reactions proceed in an analogous manner as outlined in Scheme 3a and afford zwitterionic neutral amidinate derivatives. The resulting imidazolium-2-amidinates have also been shown to be promising ligands in coordination chemistry [33–35].

When repeating the synthesis of **1**, occasionally small amounts of block-like crystals of a second product first came out upon cooling of the *n*-pentane extract. These were characterized through their IR spectrum as well as single-crystal X-ray diffraction. The IR spectrum showed a characteristic ν C=O band at 1674 cm^{-1}, indicating the formation of a hydrolysis product. This was confirmed by the X-ray crystal structure determination, which revealed the presence of the dinuclear product $\{\mu\text{-}(^i\text{PrNH})_2C{=}O\}_2[NaC_5H_3\{C(NH^i\text{Pr})(=N^i\text{Pr})\}_2\text{-}1,2]_2$ (**2**), as shown in Scheme 6. The complex contains two formula moieties of *N*,*N*′-diisopropylurea, which is the common hydrolysis product of *N*,*N*′-diisopropylcarbodiimide. Even though the crystals of **2** did not allow for full structure refinement, the interatomic connectivity was clearly accessible. Just as in **1**, the $[C_5H_3\{C(NH^i\text{Pr})(=N^i\text{Pr})\}_2\text{-}1,2]^-$ ligand is attached to the Na atom in a *N*,*N*′-chelating mode, but the cyclopentadiene moiety does not contribute to metal coordination. Consequently, in **2**, the ligand can be regarded exclusively as an aminofulvene-aldiminate anion, as illustrated in the middle and the right formula in Scheme 4. Coordinative saturation of sodium is achieved by *N*,*O*-bridging coordination of two symmetry-equivalent $(^i\text{PrNH})_2C{=}O$ moieties, resulting in a distorted tetrahedral environment of the metal atom. The bridging coordination mode of the *N*,*N*′-diisopropylurea ligand leads to a dimeric structure with a centrosymmetric $Na_2O_2C_2N_2$ eight-membered ring as the central motif.



Scheme 6. Proposed formation of the hydrolysis product $\{\mu\text{-}(^i\text{PrNH})_2C{=}O\}_2[NaC_5H_3\{C(NH^i\text{Pr})(=N^i\text{Pr})\}_2\text{-}1,2]_2$ (**2**).

3. Conclusions

The reaction of NaCp with *N*,*N*′-diisopropylcarbodiimide did not result in formation of the expected sodium amidinate with a cyclopentadienyl ring attached to the central carbon atom of the amidinate backbone. Instead, the newly formed ligand $[C_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]^-$ belongs to the group of ambidentate 6-aminofulvene-2-aldiminate ligands, which can coordinate to metal atoms either as *N*,*N*′-fulvenealdiminates or in an η^5-coordination mode as a cyclopentadienyldiimine. However, the anion $[C_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]^-$ differs from all previously reported 6-aminofulvene-2-aldiminates in that the two substituents in 1,2-positions comprise additional secondary amino functionalities, providing another potential donor moiety.

4. Experimental Section

4.1. General Procedures

All reactions were carried out in oven-dried or flame-dried glassware under an inert atmosphere of dry argon, employing standard Schlenk and glovebox techniques. The solvent THF was distilled from sodium/benzophenone under nitrogen atmosphere prior to use. Sodium cyclopentadienide (NaCp) was prepared according to the published method [36]. *N*,*N*′-Diisopropylcarbodiimide was purchased from Sigma-Aldrich (Steinheim, Germany) and used as received. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded in THF-d_8 or toluene-d_8 solution on a Bruker DPX 400 spectrometer (Bruker BioSpin, Rheinstetten, Germany) at 25 °C. IR spectra were measured with a Bruker Vertex 70V spectrometer (Bruker Optics, Rheinstetten, Germany) equipped with a diamond ATR unit between 4000 cm^{-1} and 400 cm^{-1}. Microanalyses (C, H, N) were performed using a LECO CHNS 932 apparatus (LECO Corporation, Saint Joseph, MI, USA).

*4.2. Synthesis of $[NaC_5H_3\{C(NH^iPr)(=N^iPr)\}_2\text{-}1,2]_2$ (**1**)*

In a 250 mL Schlenk flask, sodium cyclopentadienide (3.02 g, 34.4 mmol) was dissolved in THF (40 mL) and *N*,*N*′-diisopropylcarbodiimide (4.37 g, 34.4 mmol) was added to the light-brown solution at r.t. while stirring. After stirring at r.t. for 48 h, the THF was removed in vacuo and the solid residue extracted with *n*-pentane (40 mL). A large amount of amorphous brown solid was separated by filtration and the clear yellow filtrate was concentrated in vacuo to ca. 20 mL. Cooling to 4 °C for a few days afforded colorless, needle-like crystals which were suitable for X-ray diffraction. Yield: 1.05 g (9%). Elemental analysis calcd. for $C_{38}H_{66}N_8Na_2$ (680.98 g·mol^{-1}): C, 67.02%; H, 9.77%; N, 16.45%; found C, 66.25%; H, 9.87%; N, 16.11%.

^{1}H NMR (400.1 MHz, THF-d_8, 23 °C): δ 6.04 (s br, 1H, C*H*–Cp), 5.96 (t, 1H, ^3J = 3 Hz, C*H*–Cp), 5.82 (s br, 1H, C*H*–Cp), 5.69–5.70 (s br, 2H, C*H*–Cp), 5.59 (t, 1H, C*H*–Cp), 4.36 (s br, 4H, N*H*), 3.86–4.18 and 3.63–3.70 (s br, 8H, C*H*$^{i\mathrm{Pr}}$), 0.98–1.11 (m, 48H, C*H*$_3{}^{i\mathrm{Pr}}$) ppm.

^{13}C NMR (100.6 MHz, THF-d_8, 23 °C): δ 158.1 (NCN), 113.8 (*C*–Cp), 108.9, 107.9, 107.4, 106.6, 106.1, 105.6 (*C*H–Cp), 46.2, 45.7 (*C*H$^{i\mathrm{Pr}}$), 23.7, 25.5 (*C*H$_3{}^{i\mathrm{Pr}}$) ppm.

IR (ATR): ν 3436m (ν_{as} NH), 3386m (ν_s NH), 3223m (ν_s NH), 3084m (ν CH Cp), 3036m, 2966vs (ν CH$_3$), 2932s (ν CH$_3$), 2869m (ν CH), 2536w, 2224w, 1635vs (ν C=C Cp), 1590vs (ν C=C Cp), 1467s, 1448s, 1382m (δ CH$_3$), 1365m (δ CH$_3$), 1344m, 1310m, 1247m, 1168m, 1127m, 1098m, 1081m, 984w, 963w, 922w, 909w, 868w, 836w, 806w, 720m (δ CH Cp) cm^{-1}.

MS (EI): *m*/*z* (%) 681 (2%) [M$^+$], 318 (100) $[\{(^i\mathrm{PrN})_2\mathrm{C}\}_2\mathrm{Cp}]^+$, 275 (39) $[\{(^i\mathrm{PrN})_2\mathrm{C}\}\mathrm{Cp}\{(^i\mathrm{PrN})\mathrm{CN}\}]^+$, 218 (87%) $[\{(^i\mathrm{PrN})_2\mathrm{C}\}\mathrm{Cp}\{\mathrm{CN}\}]^+$.

Occasionally, when repeating the synthesis of **1**, small amounts of block-like crystals of the hydrolysis product **2** first came out upon cooling of the *n*-pentane extract. These were characterized through their IR spectrum, as well as single-crystal X-ray diffraction.

IR (ATR) of **2**: ν 3436m (ν_{as} NH), 3422m, 3370m (ν_s NH), 3253m (ν_s NH), 3230m, 3080w (ν CH Cp), 3057w (ν CH Cp), 2969m (ν CH_3), 2932m (ν CH_3), 2870m (ν CH), 1674m (ν C=O), 1638m (ν C=C Cp), 1611m (ν C=C Cp), 1591m, 1557m, 1560m, 1489m, 1466m, 1454m, 1446m, 1384m (δ CH_3), 1367m (δ CH_3), 1309m, 1298m, 1246vs, 1207m, 1180m, 1165s, 1130m, 985m, 868w, 807w, 765w, 747w, 723m (δ CH Cp) cm^{-1}.

4.3. X-ray Crystallography

Single crystal X-ray intensity data of **1** and **2** were collected on a STOE IPDS 2T diffractometer (STOE, Darmstadt, Germany) [37] equipped with a 34 cm image plate detector, using graphite-monochromated Mo-K_α radiation, at T = 153(2) K. The structure was solved by direct methods (*SHELXS*-97) [38] and refined by full matrix least-squares methods on F^2 using *SHELXL*-2016/4 [39]. Crystallographic data for compound **1** have been deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number **1030712** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supplementary Materials: The following are available online at http://www.mdpi.com/2304-6740/6/2/47/s1, Crystal data and details on structure refinement of **1**, ^{1}H and ^{13}C NMR spectra of compound **1**.

Author Contributions: N.H. performed the experimental work. P.L. carried out the crystal structure determination. L.H. measured the IR and NMR spectra, and S.B. measured the mass spectrum. F.T.E. conceived and supervised the experiments. F.T.E. and P.L. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kissounko, D.A.; Zabalov, M.V.; Brusova, G.P.; Lemenovskii, D.A. Principal trends in the chemistry of amidinate complexes of main-group and transition elements. *Russ. Chem. Rev.* **2006**, *75*, 351–374. [CrossRef]
2. Edelmann, F.T. Advances in the coordination chemistry of amidinate and guanidinate ligands. *Adv. Organomet. Chem.* **2008**, *57*, 183–352.
3. Edelmann, F.T. Lanthanide Amidinates and guanidinates: From laboratory curiosities to efficient homogeneous catalysts and precursors for rare-earth oxide thin films. *Chem. Soc. Rev.* **2009**, *38*, 2253–2268. [CrossRef] [PubMed]
4. Coles, M.P. Bicyclic-guanidines, -guanidinates and -guanidinium salts: Wide ranging applications from a simple family of molecules. *Chem. Commun.* **2009**, *25*, 3659–3676. [CrossRef] [PubMed]
5. Trifonov, A.A. Guanidinate and amidopyridinate rare-earth complexes: Towards highly reactive alkyl and hydrido species. *Coord. Chem. Rev.* **2010**, *254*, 1327–1347. [CrossRef]
6. Mohamed, A.A.; Abdou, H.E., Jr.; Fackler, J.P. Coordination chemistry of gold(II) with amidinate, thiolate and ylide ligands. *Coord. Chem. Rev.* **2010**, *254*, 1253–1259. [CrossRef]
7. Edelmann, F.T. Lanthanide amidinates and guanidinates in catalysis and materials science: A continuing success story. *Chem. Soc. Rev.* **2012**, *41*, 7657–7672. [CrossRef] [PubMed]
8. Edelmann, F.T. Recent progress in the chemistry of metal amidinates and guanidinates: Syntheses, catalysis and materials. *Adv. Organomet. Chem.* **2013**, *61*, 55–374.
9. Zhang, Y.-Y.; Lin, Y.-J.; Shi, X.-C.; Jin, G.-X. Organometallic macrocycles and cages based on bis(amidinate) ligands. *Pure Appl. Chem.* **2014**, *86*, 953–965. [CrossRef]
10. Jones, C. Bulky guanidinates for the stabilization of low oxidation state metallacycles. *Coord. Chem. Rev.* **2010**, *254*, 1273–1289. [CrossRef]
11. Chlupatý, T.; Růžička, A. Hybrid amidinates and guanidinates of main group metals. *Coord. Chem. Rev.* **2016**, *314*, 103–113. [CrossRef]
12. Tacke, R.; Ribbeck, T. Bis(amidinato)- and bis(guanidinato)silylenes and silylenes with one sterically demanding amidinato or guanidinato ligand: Synthesis and reactivity. *Dalton Trans.* **2017**, *46*, 13628–13659. [CrossRef] [PubMed]

13. Nagashima, H.; Kondo, H.; Hayashida, T.; Yamaguchi, Y.; Gondo, M.; Masuda, S.; Miyazaki, K.; Matsubara, K.; Kirchner, K. Chemistry of coordinatively unsaturated organoruthenium amidinates as entry to homogeneous catalysis. *Coord. Chem. Rev.* **2003**, *245*, 177–190. [CrossRef]
14. Edelmann, F.T. Homogeneous catalysis using lanthanide amidinates and guanidinates. *Struct. Bond.* **2010**, *137*, 109–163.
15. Collins, S. Polymerization catalysis with transition metal amidinate and related complexes. *Coord. Chem. Rev.* **2011**, *255*, 118–138. [CrossRef]
16. Elkin, T.; Eisen, M.S. Amidinate group 4 complexes in the polymerization of olefins. *Catal. Sci. Technol.* **2015**, *5*, 82–95. [CrossRef]
17. Barry, S.T. Amidinates, guanidinates and iminopyrrolidinates: Understanding precursor thermolysis to design a better ligand. *Coord. Chem. Rev.* **2013**, *257*, 3192–3201. [CrossRef]
18. Devi, A. "Old Chemistries" for new applications: Perspectives for development of precursors for MOCVD and ALD applications. *Coord. Chem. Rev.* **2013**, *257*, 3332–3384. [CrossRef]
19. Koponen, S.E.; Gordon, P.G.; Barry, S.T. Principles of precursor design for vapour deposition methods. *Polyhedron* **2016**, *108*, 59–66. [CrossRef]
20. Lichtenberg, C.; Adelhardt, M.; Wörle, M.; Büttner, T.; Meyer, K.; Grützmacher, H. Mono- and Dinuclear Neutral and Cationic Iron(II) Compounds Supported by an Amidinato-diolefin Ligand: Characterization and Catalytic Application. *Organometallics* **2015**, *34*, 3079–3089. [CrossRef]
21. Cole, M.L.; Jones, C.; Junk, P.C. Ether and crown ether adduct complexes of sodium and potassium cyclopentadienide and methylcyclopentadienide—Molecular structures of $[Na(dme)Cp]_\infty$, $[K(dme)_{0.5}Cp]_\infty$, [Na(15-crown-5)Cp], $[Na(18\text{-crown-6})Cp^{Me}]$ and the "naked Cp^-" complex $[K(15\text{-crown-5})_2][Cp]$. *J. Chem. Soc. Dalton Trans.* **2002**, *6*, 896–905. [CrossRef]
22. Ursillo, S.; Can, D.; N'Dongo, H.W.P.; Schmutz, P.; Spingler, B.; Alberto, R. Cyclopentadienyl Chemistry in Water: Synthesis and Properties of Bifunctionalized $[(\eta^5\text{-}C_5H_3\{COOR\}_2)M(CO)_3]$ (M = Re and ^{99m}Tc) Complexes. *Organometallics* **2014**, *33*, 6945–6952. [CrossRef]
23. Hafner, K.; Vöpel, K.H.; Ploss, G.; König, C. Cyclisch konjugierte 5- und 7-Ringsysteme, I. Synthesen und Reaktionen von Fulvenaldehyden. *Justus Liebigs Ann. Chem.* **1963**, *661*, 52–75. [CrossRef]
24. Hafner, K.; Vöpel, K.H.; Ploss, G.; König, C. 6-(Dimethylamino)fulvene. *Org. Synth.* **1967**, *47*, 52–53.
25. Etkin, N.; Ong, C.M.; Stephan, D.W. Synthesis of 1,2-Cyclopentadienyl Diimine Anions and Their Zirconium Complexes. *Organometallics* **1998**, *17*, 3656–3660. [CrossRef]
26. Ong, C.M.; Stephan, D.W. 1,2-Cyclopentadienyl Diimine−Group 13 Complexes. *Inorg. Chem.* **1999**, *38*, 5189–5191. [CrossRef] [PubMed]
27. Bailey, P.J.; Melchionna, M.; Parsons, S. Ambidentate Character of the 6-Aminofulvene-2-aldiminate Ligand Containing Both Diimine and Cyclopentadienyl Donors. *Organometallics* **2007**, *26*, 128–135. [CrossRef]
28. Bailey, P.J.; Collins, A.; Haack, P.; Parsons, S.; Rahman, M.; Smith, D.; White, F.J. Palladium complexes of 6-aminofulvene-2-aldiminate (AFA) ligands. *Dalton Trans.* **2010**, *39*, 1591–1597. [CrossRef] [PubMed]
29. Willcocks, A.M.; Johnson, A.L.; Raithby, P.R.; Schiffers, S.; Warren, J.E. Bis(*tert*-butyl isocyanide-*κC*) cyclopenta-2,4-dien-1-ylidene}methyl)anilinido-κ^2N,N']copper(I). *Acta Crystallogr. Sect. C* **2011**, *67*, m215–m217. [CrossRef] [PubMed]
30. Willcocks, A.M.; Gilbank, A.; Richards, S.P.; Brayshaw, S.K.; Kingsley, A.J.; Odedra, R.; Johnson, A.L. Synthesis and Structure of 6-Aminofulvene-2-aldiminato Complexes. *Inorg. Chem.* **2011**, *50*, 937–948. [CrossRef] [PubMed]
31. Bailey, P.J.; Rahman, M.; Parsons, S.; Ahzar, M.R.; White, F.J. Metalloligands containing aminofulvene-aldiminate (AFA) ligands and their bimetallic complexes. *Dalton Trans.* **2013**, *42*, 2879–2886. [CrossRef] [PubMed]
32. Bailey, P.J.; Loroño-González, D.; Parsons, S. 6-Aminofulvene-2-aldimine, a novel class of ambidentate cyclopentadienyl/diimine ligand: Synthesis and characterisation of magnesium complexes. *Chem. Commun.* **2003**, *12*, 1426–1427. [CrossRef]
33. Kuhn, N.; Steimann, M.; Weyers, G.; Henkel, G. l,3-Diisopropyl-4,5-dimethylimidazolium-2-*N,N'*-diisopropylamidinat, ein neuartiges Betain. *Z. Naturforsch.* **1999**, *54*, 434–440. [CrossRef]
34. Márquez, A.; Àvila, E.; Urbaneja, C.; Àlvarez, E.; Palma, P.; Cámpora, J. Copper(I) Complexes of Zwitterionic Imidazolium-2-Amidinates, a Promising Class of Electroneutral, Amidinate-Type Ligands. *Inorg. Chem.* **2015**, *54*, 11007–11017. [CrossRef] [PubMed]

35. Baishya, A.; Kumar, L.; Barman, M.K.; Biswal, H.S.; Nembenna, S. *N*-Heterocyclic Carbene–Carbodiimide ("NHC–CDI") Adduct or Zwitterionic-Type Neutral Amidinate-Supported Magnesium(II) and Zinc(II) Complexes. *Inorg. Chem.* **2017**, *56*, 9535–9546. [CrossRef] [PubMed]
36. Hart, W.P.; Shihua, D.; Rausch, M.D. The formation and reactions of (η^5-carboxycyclopentadienyl)dicarbonylcobalt. *J. Organomet. Chem.* **1985**, *282*, 111–121. [CrossRef]
37. Stoe, C. *X-Area and X-Red*; Stoe & Cie GmbH: Darmstadt, Germany, 2002.
38. Sheldrick, G.M. *ShelXS, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.
39. Sheldrick, G.M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8. [CrossRef] [PubMed]