392 *Organometallics* **2001,** *20,* 392−400

Synthesis and Structural and Chemical Features of Formimidoyl-Functionalized Lithium Cyclopentadienides

Klaus Kunz, Gerhard Erker,* Gerald Kehr, and Roland Fröhlich[†]

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40,
D-48149 Münster, Germany

Received August 29, 2000

Treatment of 6-dimethylaminofulvene (**1**) with lithium anilide (**2a**) yields lithium [(*N*-phenylformimidoyl)cyclopentadienide], **3a**, by an anilide addition/dimethylamine elimination reaction sequence. Similar treatment of **1** with the reagents Li[HNAr] [Ar = *p*-tolyl (**2b**), −2,6-dimethylphenyl (**2c**), or −2,6-diisopropylphenyl (**2d**)] gave the corresponding Li[C_5H_4-CH=NAr] products **3b**, **3c**, and **3d** in good yields (80−90% isolated) as THF adducts. Crystallization from THF gave **3d**·3THF, which was characterized by X-ray diffraction. It contains monomeric units in the solid state. The lithium atom is coordinated to the imino nitrogen atom and to three THF molecules in a tetrahedral arrangement. The C_5H_4 unit shows some residual bond alternation. In crystalline **3d** it exhibits no contact to the alkali metal. The structural features of **3d** can be described by a resonance hybrid of mesomeric structures of iminium-cyclopentadienide (i.e., $C_5H_4CH{=}N(Li{\cdot}3THF)Ar$, **3A**) and of fulvenoide character (i.e., $C_5H_4{=}CHN(Li{\cdot}3THF)Ar$, **3B**). The structure of **3c**·3THF in the solid state is analogous. Complex **3a** crystallizes with 1 equiv of THF. It exhibits a cyclodimeric structure (**3a**·THF)$_2$ in the crystal, where each Li atom is η^5-Cp- and κN-coordinated to two different $C_5H_4CH{=}NPh^-$ ligands. The electrostatic nature of the Li−C and Li−N interactions results in very similar structural features of the $C_5H_4CH{=}NAr^-$ ligands in the complexes **3a, 3c**, and **3d**. The solution structures of these systems were characterized by temperature-dependent ^1H and ^7Li NMR spectra. The reagents **3a** and **3d** were employed in the synthesis of the respective bis[1,1′-(*N*-aryl)formimidoyl]ferrocenes **4a** and **4d** (both isolated in ca. 80% yield). The complexes **4a** and **4b** were characterized by X-ray crystal structure analyses.

Introduction

(Cyclopentadienyl)metal compounds that bear organic functional groups bonded to their Cp ligands are of considerable importance.[1] The attachment of such substituents at the CpML$_n$ frameworks of late transition metal complexes is well established.[2] It is much more difficult to introduce such Cp-bonded functionalities at the respective complexes derived from the oxophilic early metals or main group metals.[3−5] There are a number of examples known where a selective introduction of organic functionalities was achieved at the stage of the alkali metal cyclopentadienides,[6,7] but often such routes lead to complications, e.g., caused by multiple incorporation of electrophilic reagents.[8]

In addition, functionalized alkali metal cyclopentadienides may show an interesting structural dichotomy. The highly electrostatic nature of the carbanion−alkali metal bond makes contacts of such metals to either the Cp moiety or the electronegative heteroatoms of the peripheral substituents feasible (see Chart 1).[9]

---

* Corresponding author. E-mail: erker@uni-muenster.de.

[†] X-ray crystal structure analyses

(1) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; Wiley-VCH: Weinheim, 1995. *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Haltermann, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1 and 2, and references therein.

(2) (a) Woodward, R. B.; Rosenblum, M.; Whiting, M. C. *J. Am. Chem. Soc.* **1952**, *74*, 3458−3459. Rosenblum, M.; Woodward, R. B. *J. Am. Chem. Soc.* **1958**, *80*, 5443−5449. (b) Rosenblum, M. *The Chemistry of the Iron Group Metallocenes*; Wiley: New York, 1965; Part I. *Comprehensive Organometallic Chemistry II*, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon/Elsevier Science: Oxford, 1995; Vol. 7.

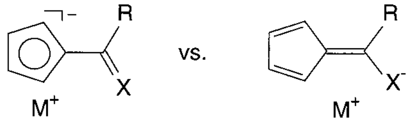
(3) Oberhoff, M.; Duda, L.; Karl, J.; Mohr, R.; Erker, G.; Fröhlich, R.; Grehl, M. *Organometallics* **1996**, *15*, 4005−4011. Knüppel, S.; Erker, G.; Fröhlich, R. *Angew. Chem.* **1999**, *111*, 2048−2051; *Angew. Chem., Int. Ed.* **1999**, *38*, 1923−1926. Knüppel, S.; Fröhlich, R.; Erker, G. *J. Organomet. Chem.* **1999**, *586*, 218−222; **2000**, *595*, 307−312. Kunz, D.; Erker, G.; Fröhlich, R.; Kehr, G. *Eur. J. Inorg. Chem.* **2000**, 409−416. Pflug, J.; Erker, G.; Kehr, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2000**, 1795−1801.

(4) (a) Foster, P.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1997**, *527*, 71−74. van der Zeijden, A. A. H.; Mattheis, C.; Fröhlich, R.; Zippel, F. *Inorg. Chem.* **1997**, *36*, 4444−4450. Gielms, E. E. C. G.; Tiesnitsch, J. Y.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 1652−1654. (b) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 4153−4161. Beckhaus, R.; Oster, J.; Ganter, B.; Englert, U. *Organometallics* **1997**, *16*, 3902−3909. Blais, M. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 3775−3783. Galakhov, M.; Gómez-Sal, P.; Martin, A.; Mena, M.; Yélamos, C. *Eur. J. Inorg. Chem.* **1998**, 1319−1325. (c) Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449−5456. Pflug, J.; Bertuleit, A.; Kehr, G.; Fröhlich, R.; Erker, G.; *Organometallics* **1999**, *18*, 3818−3826. Bosch, B. E.; Brümmer, I.; Kunz, K.; Erker, G.; Fröhlich, R.; Kotila, S. *Organometallics* **2000**, *19*, 1255−1261. Knüppel, S.; Fauré, J.-L.; Erker, G.; Kehr, G.; Nissinen, M.; Fröhlich, R. *Organometallics* **2000**, *19*, 1262−1268.

(5) Reviews: Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1−21. Jutzi, P.; Dahlhaus, *J. Coord. Chem. Res.* **1994**, *137*, 179−199. Okuda, J. *Comments Inorg. Chem.* **1994**, *16*, 185−205. Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 663−674.

10.1021/om000753u CCC: $20.00
Publication on Web 01/05/2001

Chart 1



In subsequent transmetalation reactions attachment of either the Cp anion moiety or the heteroatom has been observed with a few of such reagents, depending on the nature of the transition metal reagent used and the reaction conditions involved.[8] In this article we will describe the preparation of a small series of imino-substituted lithium cyclopentadienides and characterize their remarkable structural properties.

Results and Discussion

Preparation and Structural Characterization of the Lithium [(*N*-Arylformimidoyl)cyclopentadienides]. The functionalized cyclopentadienides described and used in this study were all prepared starting from 6-dimethylaminofulvene (**1**). This in turn was readily prepared according to Hafner et al. by the reaction of O-methylated dimethylformamide with an alkali metal cyclopentadienide.[10] The fulvene **1** was treated with lithium anilide Li[HNPh] (**2a**) in THF solution at room temperature. The reaction proceeds by the addition of the anilide nucleophile to the fulvene C6 carbon atom followed by dimethylamine elimination. The reaction was complete after ca. 2 h, and the product lithium [(*N*-phenylformimidoyl)cyclopentadienide] (**3a**) was isolated as a tetrahydrofuran adduct in ca. 90% yield. The analogous (*N*-*p*-tolylformimidoyl)Cp anion equivalent (**3b**) was prepared similarly by treatment of the fulvene with Li[HN-*p*-tolyl] (**2b**) and isolated in a similarly high yield.

The reaction of 6-dimethylaminofulvene (**1**) with lithium (*N*-2,6-dimethylphenylamide) (**2c**, prepared by deprotonation of 2,6-dimethylaniline with LDA in THF) gave **3c** (85% isolated), and the corresponding lithium [(*N*-2,6-diisopropylphenylformimidoyl)cyclopentadienide] product **3d** was obtained (81% isolated) by treatment of **1** with the reagent **2d** (see Scheme 1).

Scheme 1

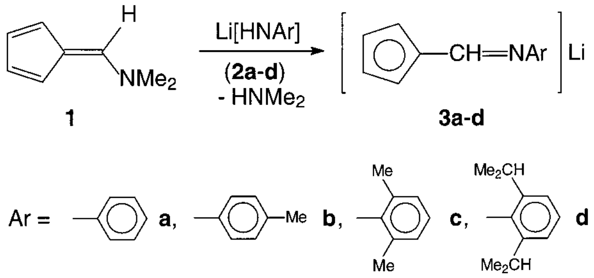


Table 1. Comparison of Characteristic Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) between the Lithium [(*N*-Arylformimidoyl)cyclopentadienes] 3a, 3c, and 3d

	3a[a]	3c	3d
Li−N7	2.077(4)	2.018(4)	2.006(3)
Li−O21	1.936(4)	1.957(5)	1.931(3)
Li−O31		1.940(4)	1.934(3)
Li−O41		1.944(4)	1.987(3)
O−Li−O(av)		108.1(2)	104.6(1)
O−Li−N(av)	107.0(2)	110.6(2)	114.0(1)
N7−C8	1.418(3)	1.421(3)	1.429(2)
N7−C6	1.295(3)	1.309(3)	1.308(2)
C1−C6−N7	125.7(2)	134.1(2)	134.1(1)
C6−N7−C8	117.8(2)	120.1(2)	120.8(1)
C8−N7−Li	119.6(2)	123.1(2)	121.7(1)
C6−N7−Li	117.1(2)	116.8(2)	117.3(1)
C1−C6	1.419(3)	1.402(3)	1.404(2)
C1−C2	1.429(3)	1.419(3)	1.434(2)
C2−C3	1.383(4)	1.369(3)	1.378(2)
C3−C4	1.420(4)	1.411(4)	1.417(3)
C4−C5	1.380(4)	1.361(3)	1.365(3)
C1−C5	1.421(3)	1.417(3)	1.434(2)
C9−C8−N7−C6	151.8(2)	82.9(3)	−96.8(2)
C1−C6−N7−C8	5.9(2)	0.9(4)	−0.3(2)
C2−C1−C6−N7	−8.5(2)	−0.9(5)	−0.4(3)

[a] Average values of the two independent pairs.

Single crystals of **3d**, which were suited for an X-ray crystal structure analysis, were obtained from a concentrated solution in tetrahydrofuran upon cooling to −20 °C. In the crystal the lithium compound **3d** contains discrete monomers. The lithium atom is tetrahedrally coordinated by three tetrahydrofuran molecules (average Li−O distance 1.951(3) Å, for details see Table 1) and the nitrogen atom of the imino substituent. The nitrogen center is trigonally planar coordinated. The five-membered ring of the $C_5H_4{-}CH{=}N{-}Ar$ ligand is oriented away from the lithium atom and has no contact to it (see Figure 1). The carbaldimino unit is Z-configurated: the C_5H_4 moiety bonded at C6 and the bulky aryl substituent at nitrogen are oriented toward the same side of the formal C=N double bond. The substituents at the central C6−N7 vector are oriented in a single plane with dihedral angles C1−C6−N7−C8 being −0.3(2)° and C1−C6−N7−Li amounting to 174.7(2)°. The plane of the 2,6-diisopropylphenyl substituent is arranged normal to the Cp-CH=N plane (dihedral angles C9−C8−N7−C6 −96.8(2)° and C9−C8−N7−Li 88.5(2)°). The C6−N7−C8 angle is in the expected range at 120.8(1)°, whereas the adjacent N7−C6−C1 angle is markedly increased at 134.1(1)°.[11] A considerable bond alternation is observed inside the $C_5H_4{-}CH{=}N{-}$ subunit,[12] with the C2−C3 and C4−C5 bonds in the five-membered ring retaining some of the double-bond

---

(6) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196−1198. Macomber, D. W.; Hart, W. P.; Rausch, M. D.; Pittmann, C. U., Jr.; Priester, R. D., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 884−886. Macomber, D. W.; Rausch, M. D. J. *Organomet. Chem.* **1983**, *258*, 331−341. Arthurs, M.; Al-Daffaee, H. K.; Haslop, J.; Kubal, G.; Pearson, M. D.; Thatcher, P.; Curzon, E. *J. Chem. Soc., Dalton Trans.* **1987**, 2615−2619. Bitterwolf, T. E.; Hubler, T. L.; Rheingold, A. L. J. *Organomet. Chem.* **1992**, *431*, 199−214. Jones, S. S.; Rausch, M. D.; Bitterwolf, T. E. J. *Organomet. Chem.* **1993**, *450*, 27−31. Blais, M. S.; Rausch, M. D. *Organometallics* **1994**, *13*, 3557−3563. Blanalt, S.; Salmain, M.; Malézienx, B.; Jaonen, G. *Tetrahedron Lett.* **1996**, *37*, 6561−6564. Top, S.; Kaloun, E. B.; Jaouen, G. *J. Am. Chem. Soc.* **2000**, *122*, 736−737. Flores, J. C.; Hernández, R.; Royo, P.; Butt, A.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2000**, *593−594*, 202−210.

(7) Review: Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1−55.

(8) Etkin, N.; Ong, C. M.; Stephan, D. W. *Organometallics* **1998**, *17*, 3656−3660. Klass, K.; Duda, L.; Kleigrewe, N.; Erker, G.; Fröhlich, R.; Wegelius, E. *Eur. J. Inorg. Chem.* **1999**, 11−19. Klass, K.; Fröhlich, R.; Erker, G. *J. Chem. Soc., Dalton Trans.* **1999**, 4457−4461.

(9) Rogers, R. D.; Atwood, J. L.; Rausch, M. D.; Macomber, D. W.; Hart, W. P. *J. Organomet. Chem.* **1982**, *238*, 79−85.

(10) Hafner, K.; Schultz, G.; Wagner, K. *Liebigs Ann. Chem.* **1964**, *678*, 39−53. Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Org. Synth.* **1967**, *47*, 52−54.

(11) Könemann, M.; Erker, G.; Fröhlich, R.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1997**, *119*, 11155−11164.

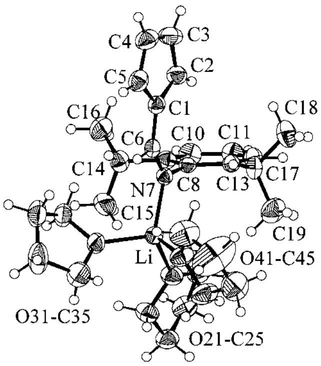


Figure 1. Molecular structure of **3d**.

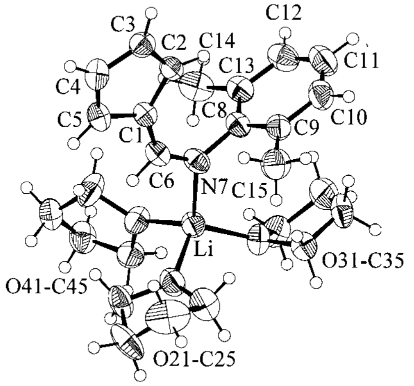


Figure 2. View of the molecular structure of **3c**.

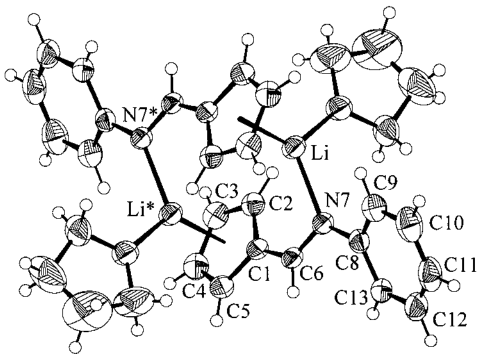
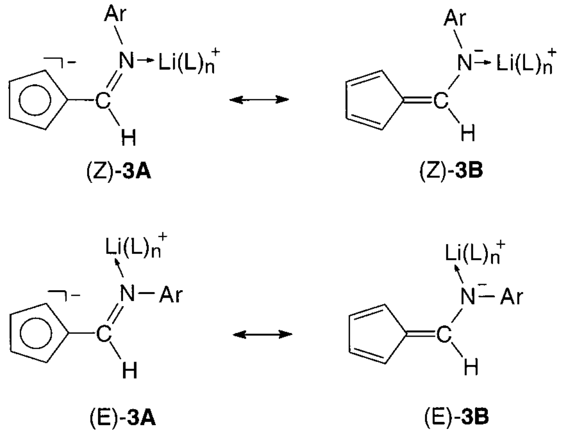


Figure 3. Molecular structure of **3a** in the crystal.

character of their fulvene precursor (at 1.378(2) and 1.365(3) Å), whereas the C3−C4, C1−C2, C1−C5, and also the C1−C6 bonds are markedly longer (see Table 1). The C6−N7 distance is 1.308(2) Å, which indicates a considerable C=N double-bond character of the Li-attached imine functionality. It appears that the organic core of the lithium compound **3d** is best described by a resonance hybrid of "iminium-cyclopentadienide" structure (**3A**) and a N-metalated fulvenoid system (**3B**, see Scheme 2).

Complex **3c**, single crystals of which were also obtained from THF at −20 °C, exhibits an analogous monomeric structure in the solid state. Again, the planes of the aryl substituent at N7 and the central planar C_5H_4−CH=N(Li)C(8)−core are arranged orthogonal, and there is a similar "soft" bond alternation observed inside the latter, which can be described by a participation of both types of resonance structures (**3A/3B**) as depicted in Scheme 2.

Scheme 2



Crystallization of **3a** from THF gave single crystals that contained only one C_4H_8O donor molecule per Li atom. In the crystal the structure of compound **3a** is dimeric (with two chemically equivalent crystallographically independent dimers in the asymmetric unit). The attachment of the sterically less demanding unsubstituted phenyl substituent at N7 (in contrast to the more bulky 2,6-dimethyl- or 2,6-diisopropylphenyl groups in **3c** and **3d**, respectively) has apparently caused a shifting of the RCH=N(Li)aryl stereochemistry from a *Z*- (in **3c** and **3d**, see above) to an *E*-configuration. The C1−C6−N7−C8 dihedral angle in **3a** amounts to 5.9(2)°, the corresponding C1−C6−N7−Li value now is −27.8(3)°. Again, the aryl group is rotated from the central C_5H_4−CH=N plane (dihedral angle C6−N7−C8−C9 151.8(2)°); the CH=N unit itself is oriented almost coplanar with the adjacent C_5H_4 ring system (dihedral angle C2−C1−C6−N7 −8.5(2)°).

The nitrogen center N7 exhibits a trigonal coordination geometry. As compared to the almost ideal planarity of the ligands around N7 in **3c** and **3d** (see above), the nitrogen atom N7 in **3a** is slightly pyramidalized (sum of bonding angles 354.5°), and there is a marked rotation about the N7−Li vector (dihedral angles C6−N7−Li−Cp(centroid) 79.7°, C6−N7−Li−O21 107.5(2)°) that allows ring closure of the dimeric metallacyclic framework by a—probably electrostatic—(η^5-Cp)Li coordination,[13] characterized by Li−(C1* to C5*) distances ranging between 2.293(5) and 2.522(5) Å.[14] Nevertheless, the (C_5H_4)CH=N(Li)C(8) unit in **3a** shows almost the same bond alternation effect (see Table 1) as was observed for **3c** and **3d**: again the C2−C3 (1.383(4) Å) and C4−C5 (1.380(4) Å) bonds are shorter than their adjacent C1−C2 (1.429(3) Å), C1−C5 (1.421(3) Å), and C3−C4 (1.420(4) Å) linkages. The C1−C6 vector in **3a** is even longer (1.419(3) Å) than the respective bond in

---

(12) See enamine structures for a comparison: Kowalski, D.; Fröhlich, R.; Erker, G. *Z. Naturforsch.* **1996**, *51b*, 1053−1059. Brown, K. L.; Damm, L.; Dunitz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978**, *61*, 3108−3135.

(13) For bridged (Cp−CR_2−NR'_2)Li structural examples see: Kunz, K.; Pflug, J.; Bertuleit, A.; Fröhlich, R.; Wegelius, E.; Erker, G.; Würthwein, E.-U. *Organometallics* **2000**, *19*, 4208−4216.

(14) Reviews: Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1−17; *Pure Appl. Chem.* **1990**, *62*, 1035−1038; **1989**, *61*, 1731−1736; *Adv. Organomet. Chem.* **1986**, *26*, 217−295. Weiss, E. *Angew. Chem.* **1993**, *105*, 1565−1587; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501−1523. Stalke, D. *Angew. Chem.* **1994**, *106*, 2256−2259; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168−2171. Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969−990.

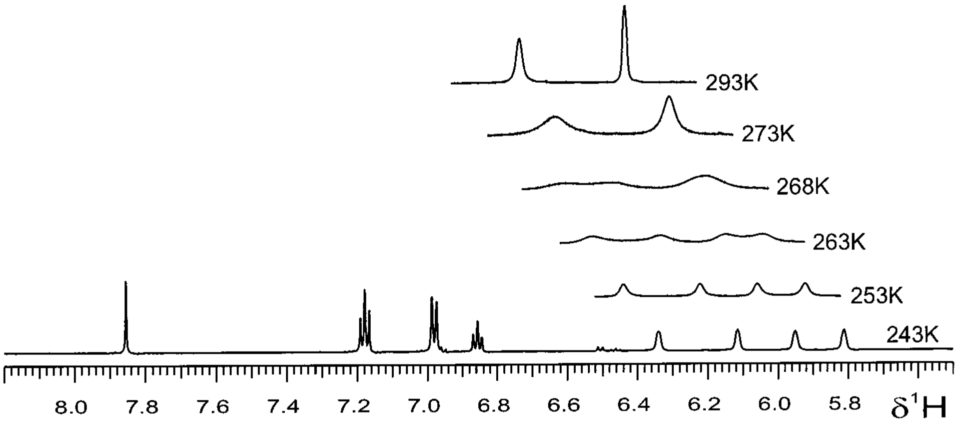
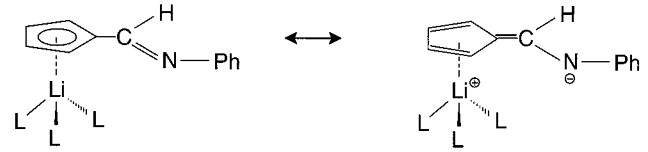


Figure 4. Temperature-dependent ^{1}H NMR (600 MHz) of **3a** in THF-d_8.

3c and **3d**, whereas the C6−N7 double-bond character in **3a** is slightly more pronounced (1.295(3) Å). Overall, the bonding features of the monomeric (C_5H_4)CH═N(Li)Ar subunit in complex **3a** can also be adequately described by assuming a **3A/3B** resonance hybrid, but the cyclopentadienide character in **3a** is slightly more pronounced than in **3c** and **3d**. This may be caused by the electrostatic nature of the $C_5H_4^-/Li^+$ interaction that polarizes negative charge into the Cp ring by Coulombic attraction.[15]

Behavior in Solution and Reactions of the Reagents 3. In THF-d_8 solution complex **3a** shows one single set of NMR signals. At ambient temperature it exhibits two ^{1}H NMR resonances at δ 6.21 and 5.92 corresponding to the symmetry-equivalent pairs of α- and β-methine protons of the C_5H_4-"cyclopentadienide" moiety. Lowering the monitoring temperature rapidly results in broadening of these resonances and then splitting into four separate ^{1}H NMR (600 MHz) "Cp" signals at 6.31, 6.08, 5.91, and 5.77 (at 223 K). This behavior indicates freezing of the rotation about the C1−C6 vector at low temperature on the ^{1}H NMR time scale. From the coalescence behavior a Gibbs activation energy of $\Delta G^{\ddagger}_{\mathrm{rot}}(265\ \mathrm{K}) = 12.2 \pm 0.2$ kcal/mol was deduced[16] for this rotational barrier of **3a**. The ^{7}Li NMR spectrum of the THF-d_8 solution of **3a** shows a single temperature-invariant resonance at δ −0.5 (at 233 MHz), which is typical for a tetrahedral donor ligand stabilized $\mathrm{Li(lig)}_4^+$ species.[17] We thus conclude that complex **3a** in THF-d_8 solution may have retained a −CH═N(Ar)−Li contact and that the cyclodimeric structure observed in the solid state has almost certainly been opened in THF solution, as indicated by the observed rapid rotational process about the Cp−C(6) vector. The presence of the structural type **3A** in solution seems likely for complex **3a** (see Scheme 2). However, the height of the observed rotational barrier probably indicates some residual participation of a fulvenoid component (here (*E*)-**3B**) that is relevant for the adequate description of the structural properties of complex **3a** in THF solution, similar to that in the solid state (see above).

Scheme 3. Proposed Structural Features of 3a in Toluene-d_8 Solution (L is Residual THF and/or an Intermolecular Ph−N═ Interaction)



3C **3D**

Isolated **3a** contains coordinated THF. When such a sample was dissolved in toluene-d_8, it showed a behavior similar to that in THF-d_8 solution, but a temperature-independent ^{7}Li NMR resonance was observed at δ −4.9. This value indicates that in toluene solvent the η^5-Cp−Li interaction is probably retained. This is supported by cryoscopy of **3a**·THF in benzene, which indicated the presence of a dimeric structure in this solvent ($M_{\mathrm{obs}} \approx 450$, calcd for the **3a**·THF dimer: 494). The ^{1}H NMR spectrum (600 MHz) in toluene-d_8 shows four Cp resonances at δ 6.68, 6.57 (2H), and 6.49 at 233 K that show reversible coalescence upon warming. The rotational barrier of **3a** in the noncoordinating solvent toluene-d_8 is identical [$\Delta G^{\ddagger}_{\mathrm{rot}}(260\ \mathrm{K}) = 12.2 \pm 0.2$ kcal/mol) to that in THF-d_8, which probably indicates rapid reversible cleavage of some Li···ligand interaction of the dimer and an equivalent π-contribution of the C1−C6 linkage of **3a** in these two solvents (see Scheme 3).

The spectroscopic behavior of the 2,6-dimethylphenyl-substituted compound **3c** in solution is slightly more complicated. In THF-d_8 solution we have observed the ^{1}H NMR signals of two stereoisomers in ca. 1:1 ratio to which we assign the structures of (*E*)-**3c** and (*Z*)-**3c**. The solid-state structural characterizations of this series of complexes have already shown (see above) that both (*E*)- and (*Z*)-configurated isomers of these compounds are involved. Each of the geometrical isomers of **3c** shows a separate set of 2,6-dimethylphenyl ^{1}H and ^{13}C NMR signals (for details see the Experimental Section) and markedly separated −*CH*═N− NMR signals [δ (^{1}H) 7.66 and 7.42, δ (^{13}C) 162.3 and 157.1]. At 223 K one isomer exhibits a set of four C_5H_4 methine ^{1}H NMR signals at δ 6.34, 5.98, 5.94, and 5.72, which pairwise coalesce upon raising the temperature to a pair of signals at 6.19

---

[15] We thank one of the reviewers for pointing this out to us and for making additional, very useful suggestions.

[16] Green, M. L. H.; Wong, L.-L.; Seela, A. *Organometallics* **1992**, *11*, 2660−2668, and references therein.

[17] Cox, R. H.; Terry, H. W., Jr.; Harrison, L. W. *J. Am. Chem. Soc.* **1971**, *93*, 3297−3298. Cox, R. H.; Terry, H. W., Jr. *J. Magn. Reson.* **1974**, *14*, 317−322. Exner, M. M.; Waack, R.; Steiner, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 7009−7018. Jutzi, P.; Leffers, W.; Pohl, S.; Saak, W. *Chem. Ber.* **1989**, *122*, 1449−1456. Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776−8789. Johnels, D.; Boman, A.; Edlund, U. *Magn. Reson. Chem.* **1998**, *36*, S151−S156.

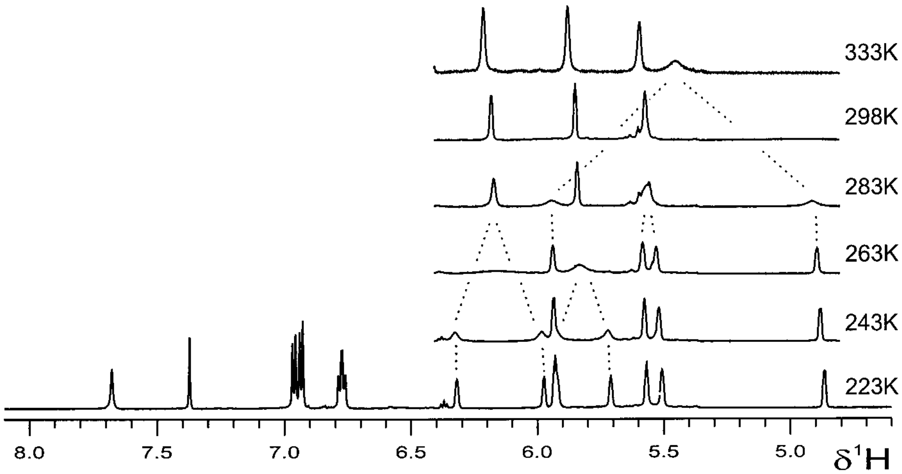


Figure 5. Dynamic ^{1}H NMR spectra of the ca. 1:1 mixture of the (*Z*)-**3c** and (*E*)-**3c** isomers in tetrahydrofuran-d_8.

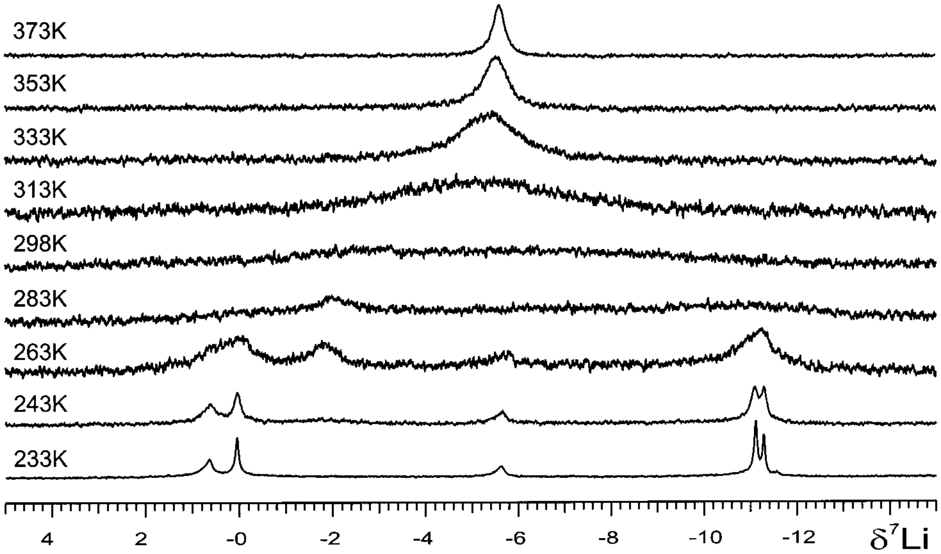


Figure 6. Dynamic ^{7}Li NMR spectra (233 MHz) of **3c**·THF in toluene-d_8 solution (see Schemes 3 and 4 and the text for structural assignments).

and 5.85 (at 298 K), corresponding to a C1−C6 rotational barrier of $\Delta G^{\ddagger}_{\text{rot}}(260\ \text{K}) = 11.7 \pm 0.2$ kcal/mol for this specific isomer. The other isomer of **3c** shows the two pairs of Cp ^{1}H NMR signals at δ 5.94, 4.88/5.58, and 5.51 at 223 K in THF-d_8. These coalesce to two ^{1}H NMR resonances at δ 5.56 and 5.45 [$\Delta G^{\ddagger}_{\text{rot}}(265\ \text{K}) = 12.7 \pm 0.2$ kcal/mol] (see Figure 5 and Scheme 2).

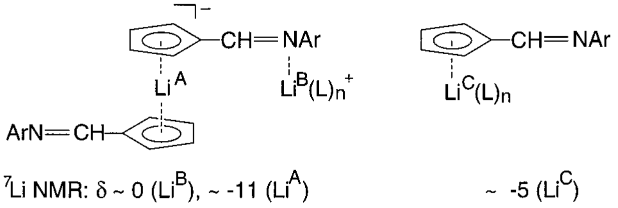
A ^{7}Li NMR resonance of **3c** at ca. δ −1.4 is in accord with a tetrahedral donor stabilized $\text{Li(L}_4)^+$ structure in THF-d_8 solution. The situation got more complicated when the isolated THF adduct of **3c** was dissolved in toluene-d_8. The ^{7}Li NMR spectrum (233 MHz) showed a single resonance at high temperature (373 K) at ca. δ −5.6 that rapidly broadened and split into three sets of signals upon decreasing the temperature (see Figure 6). At 223 K a small ^{7}Li NMR signal remained at δ −5.6, probably indicating a residual amount of a η^5-Cp−Li-type isomer (see Scheme 3) under equilibrium conditions, whereas the majority of complex **3c** in solution was present as lithiocene anion-type structure[14,18,19] (signals of the corresponding (*E*)- and (*Z*)-CH=N−substituted isomers at δ −11.1 and −11.3)[17] complemented with $\text{Li(L}_4)^+$-type counterions (L = residual THF or −CH=*N*− coordination). The $^{7}\text{Li(L}_4)^+$ resonances were found at δ 0.6 and 0.0 (at 223 K) in equal intensity to the high-field ^{7}Li lithiocene signals (see Figure 6). A schematic structural description of the two major structural features that seem to be involved in the solution structural chemistry of **3c** under equilibrium conditions in toluene-d_8 is depicted in Scheme 4. Due to the occurrence of these various structural and isomeric

---

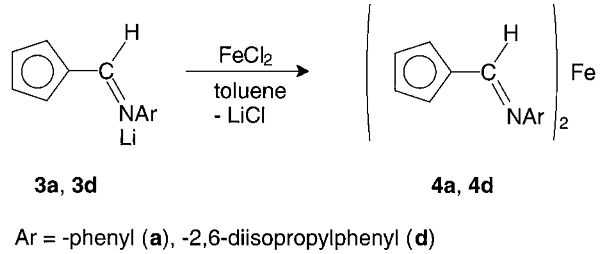
[18] den Besten, R.; Harder, S.; Brandsma, L. *J. Organomet. Chem.* **1990**, *385*, 153−159. Eiermann, M.; Hafner, K. *J. Am. Chem. Soc.* **1992**, *114*, 135−140. Harder, S.; Prosenc, M. H. *Angew. Chem.* **1994**, *106*, 1830−1832; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744−1746. Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Sivik, M. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1994**, *116*, 6466−6467. Hausen, H.-D.; Tödtmann, J.; Weidlein, J. *J. Organomet. Chem.* **1994**, *466*, C1−C4. See for a comparison: Bünder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1−6. Haaland, A.; Lusztyk, J.; Brunvoll, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1975**, *85*, 279−285. Bladauski, D.; Broser, W.; Hecht, H. J.; Rewicki, D.; Dietrich, H. *Chem. Ber.* **1979**, *112*, 1380−1391. See also: Malaba, D.; Chen, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1992**, *11*, 1007−1009. Malaba, D.; Djebli, A.; Chen, L.; Zarate, E. A.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1993**, *12*, 1266−1276. Könemann, M.; Erker, G.; Grehl, M.; Fröhlich, R.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1995**, *117*, 11215−11219.

[19] In principle three diastereomeric lithiocene anions should be formed exhibiting (*Z*,*Z*)-, (*E*,*E*)-, and (*E*,*Z*)-configurated −CH=N(Li)-Ar combinations. However, these configurational combinations are probably not individually resolved in our dynamic ^{7}Li NMR experiment, so that only the two pairs of signals due to (*E*)- and (*Z*)-configurated −CH=N(Li)Ar substituents are observed.[15]

Scheme 4. Schematic Description of the Structural Types and Subunits that are Probably Present in Toluene-d_8 Solutions of 3c·THF



Scheme 5



forms and their interconversion or dynamic equilibration, rather complex ^{1}H and ^{13}C NMR spectral behavior has resulted from **3c**·THF in toluene-d_8 solution, which will not be further discussed.

Only a few 1,1′-bis(formimidoyl)-substituted metallocenes have been known and described so far.[20] This is surprising in view of the great specific importance of both structural moieties, namely, the imino functionality[21] and the metallocene frameworks[1] for ligand design and application in catalysis. We have therefore reacted both the functionalized carbanion equivalents **3a** and **3d** with anhydrous $FeCl_2$ in toluene (at 60 °C) and obtained the respective substituted ferrocenes (**4a** and **4d**) that were each isolated in ca. 80% yield. Single crystals from each complex were obtained from toluene. Both complexes **4a** and **4d** were characterized by X-ray diffraction.

Complex **4d** exhibits the typical ferrocene structure as expected. Both cyclopentadienide ligands are η^5-coordinated, with the Fe−C(Cp) bond lengths being found in a narrow range between 2.031(2) and 2.050(2) Å. The Cp(centroid)−Fe−Cp(centroid) angle in **4d** amounts to 178.1°. The marked bond alternation within the five-membered ring, which was characteristic for the Li reagents **3a**, **3c**, and **3d**, is absent in the corresponding ferrocenes. The C−C distances within the η^5-Cp ligands in **4d** are found in a typical range between 1.411(3) and 1.435(2) Å. The aldimino functional groups are oriented almost coplanar with their attached Cp rings (dihedral angles C2−C1−C6−N7 14.4(3)°, C22−C21−C26−N27 −6.4(3)°, see Figure 7). The C1−C6 (1.458(2) Å) and C21−C26 (1.460(2) Å) bonds in **4d** are longer than the corresponding C1−C6 bonds in the complexes **3** (see Table 1), whereas the adjacent C6−N7 (1.272(2) Å) and C26−N27 (1.273(2) Å) C=N double bonds[22] in **4d** are, consequently, shorter than typically observed in the precursor **3d** and its congeners.

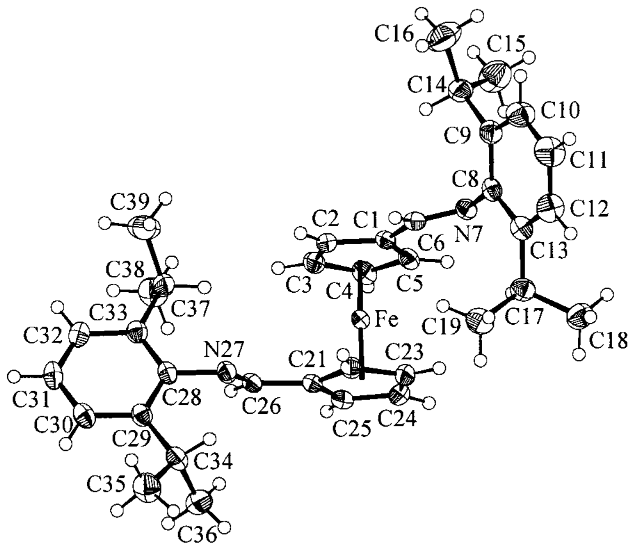


Figure 7. Molecular structure of the 1,1′-bis(N-arylformimidoyl)ferrocene **4d**.

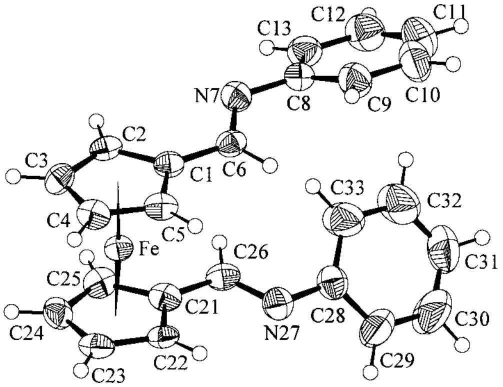


Figure 8. View of the molecular structure of **4a**. Selected bond lengths (Å) and angles (deg) (average values of the three independent molecules found in the crystal): (Fe−C)$_{min}$ 2.029(4), (Fe−C)$_{max}$ 2.061(4), C1−C2 1.426(5), C2−C3 1.406(5), C3−C4 1.415(5), C4−C5 1.405(5), C5−C1 1.422(5), C1−C6 1.449(6), C−N7 1.273(5), N7−C8 1.415(5); C2−C1−C5 107.4(4), C2−C1−C6 127.3(4), C5−C1−C6 125.3(4), C1−C2−C3 107.9(4), C2−C3−C4 108.4(4), C3−C4−C5 108.1(4), C4−C5−C1 108.2(4), C1−C6−N7 121.5(3), C6−N7−C8 119.7(3).

The N-arylformimidoyl substituent in **4d** is (E)-configurated (in contrast to the structurally characterized (Z)-isomer of its precursor **3d**, see above), with the aryl plane being in a close to perpendicular orientation (dihedral angle C6−N7−C8−C9 −87.1(2)°, C26−N27−C28−C29 113.2(2)°). In the crystal, complex **4d** exhibits a staggered metallocene conformation in which the bulky (N-2,6-diisopropylphenyl)formimidoyl substituents at the respective 1,1′-positions are found at a maximum distance from each other.

The related 1,1′-bis(N-phenylformimidoyl)ferrocene, **4a**, exhibits similar structural features (see Figure 8), but shows a notably different metallocene conformation

---

(20) Neuse, E. W.; Rosenberg, H.; Carlen, R. R. *Macromolecules* **1968**, *1*, 424−430. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Organoiron Compounds, Part A, Ferrocene 9; Slawisch, A., Ed. Springer-Verlag: Berlin, 1989; pp 99−104, and references therein.

(21) Jacobson, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, 1993; pp 159−202. Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415. Katsuki, T. *J. Mol. Catal.* **1996**, 87−107. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *111*, 448−468; *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447. Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203.

(22) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

in the crystal. The arrangement of the η^5-Cp ligands in the ferrocene **4a** is eclipsed and the C1−C6/C21−C26 vectors that connect the substituents with the Cp rings are also in an eclipsed orientation. The planes of the two phenyl substituents attached at the imino nitrogen atoms of **4a** are rotated toward a perpendicular orientation. This may lead to a weak C−H···arene-π-interaction similar to that observed for benzene in the crystalline state[23,24] and may potentially explain the specific metallocene conformation observed. In the three crystallographically independent molecules of **4a** the intramolecular phenyl(centroid)−phenyl(centroid) distances are found in a range between 4.62 and 4.94 Å [cryst benzene: 5.08 Å (phase 1), 4.63 Å (phase 2)[23]] (details, including the C−H···phenyl(centroid) distances of the individual molecules of **4a** are provided in the Supporting Information).

Conclusions

The NH mono-deprotonated anilines have shown to be well-suited nucleophiles to attack a *tert*-aminofulvene at the C6 position.[25] The introduced *sec*-amino substituent carries a hydrogen atom and therefore allows for a thermodynamically favorable and kinetically feasible HNR_2 elimination with formation of a $-CH{=}NAr$ substituent in an overall anionic [Cp−X]Li system. This procedure has turned out to be a very convenient synthetic route for the preparation of formimidoyl-substituted cyclopentadienide ligand systems. A selected synthetic application of the [CpCH═NR]Li reagents (**3**) has been demonstrated by the synthesis of the 1,1′-bis(*N*-arylformimidoyl)ferrocenes **4**, which may become interesting ligands for the development of new metal catalysts themselves.[26]

The structural features of the lithium (formimidoyl)-cyclopentadienides are very interesting. It was shown by X-ray diffraction that the lithium atom can either be located in the vicinity of the aldimino-nitrogen atom, serving as a two-electron donor ligand in the compound **3c**·3THF or **3d**·3THF, or η^5-attached to the C_5H_4 moiety as found in the dimeric structure (**3a**·THF)$_2$. Very remarkably both these geometrically very different structural types exhibit rather similar structural features of the central $[C_5H_4{-}CH{=}NAr]^-$ moiety. In both complexes a high degree of π-delocalization across the whole ligand system is observed. The structural features can probably be described by a contribution of two mesomeric structures, namely, a substituted cyclopentadienide type $Cp^-{-}CH{=}NAr$ (**3A**) and a fulvenoide type $C_5H_4{=}CH{-}N^-Ar$ (**3B** in Scheme 2). The actual localization of the lithium counterion relative to the ligand framework apparently does not much influence the structural (and probably also the electronic) features of the delocalized $[C_5H_4CHNAr^-]$ system. This is quite different, as it would be expected (and is actually observed in **4**) for a transition metal complex of this ligand system. The fundamental structural differences of the systems **3** and, for example, **4** underline the specific features of such organometallic lithium compounds that originate from the pronouncedly electrostatic nature of the lithium−carbon and lithium−nitrogen bonds.[27]

Experimental Section

All reactions were carried out under an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. NMR spectra were measured using a Bruker AC 200 P or Varian Unity Plus 600 NMR spectrometer (Ξ (^{13}C) = 25.14, (^7Li) = 38.86 MHz). Most assignments were based on a series of 2D NMR experiments. 6-(Dimethylamino)fulvene (**1**) was prepared analogously as described by K. Hafner et al.[10] Lithium anilides **2a**, **2c**, and **2d** were prepared by deprotonation of the aniline derivatives with *n*-butyllithium in pentane.

Preparation of Lithium [(*N*-Phenylformimidoyl)cyclopentadienide] (3a). A solution of 2.45 g (25.0 mmol) of the lithium anilide (**2a**) in 50 mL of THF was added to a solution of 3.00 g (25.0 mmol) of 6-(dimethylamino)fulvene (**1**) in 150 mL of THF at room temperature, and the mixture was stirred for 2 h at ambient temperature. The solvent was then removed in vacuo. Pentane (30 mL) was added 3 × and removed in vacuo to solidify the product. The residue (**3a**) was collected by filtration, washed with pentane (30 mL), and dried in vacuo to yield 5.55 g (91%) of **3a** as a brown powder, containing 1 equiv of THF. ^1H NMR (599.8 MHz, THF-d_8): 298 K δ 7.90 (s, 1H, 6-H), 7.17 (m, 2H), 6.98 (m, 2H), 6.83 (m, 1H) (Ph), 6.21, 5.92 (each br, each 2H, C_5H_4), 3.61, 1.76 (each m, each 4H, THF); 223 K δ 7.90 (s, 1H, 6-H), 7.17 (m, 2H), 6.98 (m, 2H), 6.83 (m, 1H) (Ph), 6.31, 6.08, 5.91, 5.77 (each m, each 1H, C_5H_4), 3.61, 1.76 (m, each 4H, THF). Dynamic NMR spectra: T_c = 268 K, $\Delta\nu$ = 141 Hz (223 K), $\Delta G^{\ddagger}{}_{rot}$(268 K) = 12.2 kcal mol^{-1} (δ 6.31/6.08 coalescence), and T_c = 263 K, $\Delta\nu$ = 82 Hz (223 K), $\Delta G^{\ddagger}{}_{rot}$(263 K) = 12.2 kcal mol^{-1} (δ 5.91/5.77). ^1H NMR (599.8 MHz, toluene-d_8): 298 K δ 8.18 (s, 1H, 6-H), 7.15 (m, 2H), 6.95 (m, 2H), 6.89 (m, 1H) (Ph), 6.51, 6.40 (each m, each 2H, C_5H_4), 3.44, 1.20 (each m, each 4H, THF); 223 K δ 8.20 (s, 1H, 6-H), 7.15 (m, 2H), 6.95 (m, 2H), 6.89 (m, 1H) (Ph), 6.68, 6.49 (each br, each 1H, C_5H_4), 6.57 (br, 2H, C_5H_4), 3.44, 1.20 (each m, each 4H, THF). Dynamic NMR spectra: T_c = 260 K, $\Delta\nu$ = 66 Hz (223 K), $\Delta G^{\ddagger}{}_{rot}$(260 K) = 12.2 ± 0.2 kcal mol^{-1} (δ 6.68/6.57 coalescence) and 256 K, $\Delta\nu$ = 48 Hz (223 K), $\Delta G^{\ddagger}{}_{rot}$(256 K) = 12.2 ± 0.2 kcal mol^{-1} (δ 6.57/6.49). $^{13}C\{^1H\}$ NMR (50.3 MHz, benzene-d_6, 298 K): δ 158.5 (C-6), 155.5 (ipso-C of Ph), 129.1, 121.9, 121.2 (Ph), 120.7 (ipso-C of C_5H_4), 114.4, 112.8 (CH of C_5H_4). $^7Li\{^1H\}$ NMR (232.8 MHz, THF-d_8, 298 K): δ −0.5. $^7Li\{^1H\}$ NMR (232.8 MHz, toluene-d_8, 298 K): δ −4.9. IR (KBr): $\tilde{\nu}$ 3061, 2970, 2879, 1637, 1604, 1557, 1472, 1334, 1276, 1229, 1179, 1050, 917, 892, 861, 756, 690, 646 cm^{-1}. Mp: 85 °C. Anal. Calcd for $C_{16}H_{18}NOLi$ (247.3): C, 77.72; H, 7.34; N, 5.66. Found: C, 78.02; H, 7.44; N, 5.18. Molecular weight determined by cryoscopy in benzene: 0.19

---

(23) Bacon, G. E.; Curry, N. A.; Wilson, S. A. *Proc. R. Soc. London Ser. A* **1964**, *279*, 98−110. Piermarini, G. J.; Mighell, A. D.; Weir, C. E.; Block, S. *Science* **1969**, *165*, 1250−1255.

(24) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768−4774. Chipot, C.; Jaffe, R.; Maigret, B.; Pearman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 11217−11224. Dupont, J.; Suarez, P. A. Z.; De Souza, R. F.; Burrow, R. A.; Kintzinger, J.-P. *Chem. Eur. J.* **2000**, *6*, 2377−2381, and references therein.

(25) For other examples of nucleophilic attack at the fulvene C6 center see e.g.: Ziegler, K.; Schäfer, W. *Liebigs Ann. Chem.* **1934**, *511*, 101−109. Ziegler, K.; Gellert, H.-G.; Martin, H.; Nagel, K.; Schneider, J. *Liebigs Ann. Chem.* **1954**, *589*, 91−121. Sullivan, M. F.; Little, W. F. *J. Organomet. Chem.* **1967**, *8*, 277−285. Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *148*, 35−42.

(26) The systems **3** were used as starting materials for the preparation of homogeneous sp^3-C$_1$-bridged "constrained geometry" Ziegler catalysts: Kunz, K.; Erker, G.; Döring, S.; Fröhlich, R.; Kehr, G. Submitted.

(27) (a) Alexandratos, S.; Streitwieser, A., Jr.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 7959−7962. Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781−4788. Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353−451. Lambert, C.; Schleyer, P. v. R. *Angew. Chem.* **1994**, *106*, 1187−1199; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129−1141. (b) Sapse, A.-M., Schleyer, P. v. R., Eds. *Lithium Chemistry, A Theoretical and Experimental Overview*; Wiley: New York, 1995, and references therein.

g of **3a**·THF in 3.48 g of benzene gave $\Delta T = 0.62$ °C, corresponding to M(found) = 450 [calcd for (**3a**·THF)$_2$: 494].

X-ray crystal structure analysis of 3a: formula $C_{16}H_{18}NOLi$, $M = 247.25$, yellow crystal $0.20 \times 0.20 \times 0.10$ mm, $a = 9.733(1)$ Å, $b = 11.428(1)$ Å, $c = 13.226(1)$ Å, $\alpha = 102.15(1)°$, $\beta = 90.21(1)°$, $\gamma = 94.62(1)°$, $V = 1433.2(2)$ Å^3, $\rho_{calc} = 1.146$ g cm^{-3}, $\mu = 0.70$ cm^{-1}, empirical absorption correction via SORTAV ($0.986 \leq T \leq 0.993$), $Z = 4$, triclinic, space group P1bar (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 10 046 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 6560 independent ($R_{int} = 0.028$) and 4802 observed reflections [$I \geq 2\ \sigma(I)$], 344 refined parameters, $R = 0.076$, $wR_2 = 0.190$, max. residual electron density 0.37 (−0.31) e Å^{-3}, refinement of the positional disorder in the THF molecules did not improve the quality of the analysis, hydrogens calculated and refined as riding atoms.

Preparation of Lithium [(*N*-*p*-Tolylformimidoyl)cyclopentadienide] (3b). Lithium (*p*-tolyl)amide (**2b**) was generated in situ by reacting 535 mg (5.0 mmol) of *p*-tolylamine with 535 mg (5.0 mmol) of lithium diisopropylamide in 50 mL of THF for 1 h. The mixture was then added to a solution of 610 mg (5.0 mmol) of 6-(dimethylamino)fulvene in 100 mL of THF at room temperature. The solvent was removed in vacuo after 12 h reaction time. Pentane (30 mL) was added 3 × and removed in vacuo again to solidify the product (**3b**), which was then collected by filtration, washed with pentane (30 mL), and dried in vacuo to give 1.11 g (91%) of pale brown **3b**, containing 1 equiv of THF. ^{1}H NMR (200.13 MHz, benzene-d_6, 298 K): δ 8.15 (s, 1H, 6-H), 6.94, 6.86 (AA′XX′, 4H, *p*-tolyl), 6.39, 6.27 (each m, each 2H, C_5H_4), 3.47 (m, 4H, THF), 2.15 (s, 3H, *p*-tolyl CH_3), 1.48 (m, 4H, THF). ^{13}C{^{1}H} NMR (50.3 MHz, benzene-d_6, 298 K): δ 159.3 (C6), 152.3 (ipso-C of tolyl), 131.8, 129.8, 121.0 (tolyl), 112.1, 111.5 (C_5H_4), 20.7 (tolyl CH_3). IR (KBr): $\tilde{\nu}$ 3070, 2951, 2914, 2882, 1647, 1616, 1584, 1581, 1515, 1477, 1334, 1296, 1236, 1177, 1061, 819, 750, 650 cm^{-1}. Mp: 78 °C. Anal. Calcd for $C_{17}H_{20}NOLi$ (261.3): C, 78.15; H, 7.72; N, 5.36. Found: C, 78.07; H, 7.52; N, 5.37.

Preparation of Lithium {[(*N*-2,6-Dimethylphenyl)formimidoyl]cyclopentadienide} (3c). A solution of 1.00 g (8.3 mmol) of 6-(dimethylamino)fulvene (**1**) in 100 mL of THF was treated with 1.00 g (8.3 mmol) of lithium 2,6-dimethylphenylamide (**2c**), dissolved in 30 mL of THF, at room temperature. The reaction mixture was stirred for 2 days. The solvent was removed in vacuo to give a dark brown viscous oil. Product **3c** (1.94 g, 85%) was obtained as a red-brown powder after treatment with pentane (2 × 20 mL). ^{1}H NMR (599.8 MHz, THF-d_8, two isomers, ca. 1:1 *E*- and *Z*-**3c**): 298 K δ 7.66, 7.42 (each s, each 1H, 6-H), 6.96, 6.78 (m, 6H, Ph), 6.19 (br, 2H, C_5H_4), 5.85 (br, 2H, C_5H_4), 5.56 (br, 2H, C_5H_4), 5.40 (br, 2H, C_5H_4), 3.62 (m, 8H, THF), 2.28, 2.15 (each s, each 6H, CH_3), 1.79 (m, 8H, THF); 223 K δ 7.65, 7.39 (each s, each 1H, 6-H), 6.96, 6.78 (m, 6H, Ph), 6.34, 5.98, 5.72, 5.58, 5.51, 4.88 (each br, each 1H, C_5H_4), 5.94 (br, 2H, C_5H_4), 3.62 (m, 8H, THF), 2.28, 2.15 (each s, each 6H, CH_3), 1.79 (m, 8H, THF). Dynamic NMR spectra: isomer A T_c = ca. 290 K, $\Delta\nu = 636$ Hz (223 K), $\Delta G^{\ddagger}_{rot}$(298 K) 12.8 ± 0.5 kcal mol^{-1} (δ 5.94/4.88 coalescence) and 268 K, $\Delta\nu = 42$ Hz (223 K), $\Delta G^{\ddagger}_{rot}$(268 K) = 12.7 ± 0.2 kcal mol^{-1} (δ 5.58/5.51); isomer B: $T_c = 263$ K, $\Delta\nu = 216$ Hz (223 K), $\Delta G^{\ddagger}_{rot}$(263 K) = 11.7 ± 0.2 kcal mol^{-1} (δ 6.34/5.98) and 258 K, $\Delta\nu = 144$ Hz (223 K), $\Delta G^{\ddagger}_{rot}$(258 K) = 11.7 ± 0.2 kcal mol^{-1} (δ 5.94/5.72). ^{1}H NMR (599.8 MHz, toluene-d_8, 298 K): δ 8.42, 7.69 (each br, each 1H, 6-H), 6.95−6.65 (m, 6H, Ph), 6.55, 6.24, 5.95 (each br, 8H, C_5H_4), 3.26 (m, 8H, THF), 2.20 (br, 12 H, CH_3), 1.19 (m, 8H, THF). ^{13}C{^{1}H} NMR (50.3 MHz, THF-d_8, 298 K): δ 162.3, 157.1 (C-6), 128.4, 122.4, 122.0, 113.1, 112.7, 106.1, 102.2 (Ph and Cp), 19.3, 18.7 (CH_3). ^{7}Li{^{1}H} NMR (232.8 MHz, THF-d_8, 298 K): δ −1.4. ^{7}Li{^{1}H} NMR (232.8 MHz, toluene-d_8, 223 K): δ 0.6, 0.0, −5.6, −11.1, −11.3. IR (KBr): $\tilde{\nu}$ 3071, 2964, 2877, 1619, 1577, 1465, 1461, 1355, 1285, 1047, 918, 853, 750, 653 cm^{-1}. Mp: 71 °C. Anal. Calcd for $C_{18}H_{22}NOLi$ (275.3): C, 78.53; H, 8.05; N, 5.09. Found: C, 78.30; H, 7.37; N, 5.18.

X-ray crystal structure analysis of 3c: formula $C_{26}H_{38}NO_3Li$, $M = 419.51$, colorless crystal $0.25 \times 0.15 \times 0.10$ mm, $a = 9.479(1)$ Å, $b = 16.927(1)$ Å, $c = 15.531(1)$ Å, $\beta = 93.25(1)°$, $V = 2488.0(3)$ Å^3, $\rho_{calc} = 1.120$ g cm^{-3}, $\mu = 0.71$ cm^{-1}, empirical absorption correction via SORTAV ($0.982 \leq T \leq 0.993$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 20803 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 4370 independent ($R_{int} = 0.143$) and 2626 observed reflections [$I \geq 2\ \sigma(I)$], 357 refined parameters, $R = 0.064$, $wR_2 = 0.138$, max. residual electron density 0.18 (−0.18) e Å^{-3}, positional disorder in the THF groups O21−C25 (0.52(2):0.48(2)) and O31−C35 (0.42(2):0.58(2)), hydrogens calculated and refined as riding atoms.

Preparation of Lithium {[(*N*-2,6-Diisopropylphenyl)formimidoyl]cyclopentadienide} (3d). A solution of 4.52 g (25.0 mmol) of lithium 2,6-diisopropylphenylamide (**2d**) in 100 mL of THF was added to a solution of 3.00 g (25.0 mmol) of 6-(dimethylamino)fulvene (**1**) in 100 mL of THF at room temperature. After 7 days of stirring at ambient temperature the solvent was removed in vacuo, and the oily product was solidified by treatment with pentane (3 × 20 mL). The product was obtained as a brown solid (6.62 g, 81%) as a mixture of *E*- and *Z*-isomers. ^{1}H NMR (599.8 MHz, THF-d_8, 298 K): δ 7.72, 7.57 (each s, each 1H, 6-H); 7.02 (m, 4H), 6.88 (m, 2H) (Ph), 6.20, 5.85, 5.56 (m, 8H, C_5H_4), 3.62 (m, 8H, THF), 3.32, 2.96 (each sept., $^3J = 7.0$ Hz, each 2H, $CH(CH_3)_2$), 2.21, 2.20 (each d, $^3J = 7.0$ Hz, each 12H, $CH(CH_3)_2$), 1.79 (m, 8H, THF). ^{13}C{^{1}H} NMR (150.8 MHz, THF-d_8, 298 K): δ 162.3, 157.1 (C6), 154.1, 151.2 (ipso-C of Ph), 141.9, 141.2, 123.5, 123.3, 123.1, 122.9 (Ph), 119.6, 119.4 (ipso-C of C_5H_4), 112.2 (br, C_5H_4), 28.4, 28.2 ($CH(CH_3)_2$), 24.5, 22.9 ($CH(CH_3)_2$. IR (KBr): $\tilde{\nu}$ 3077, 2961, 2926, 2864, 1637, 1501, 1466, 1453, 1357, 1260, 1178, 1102, 1074, 1054, 1026, 928, 813, 744 cm^{-1}. Mp: 107 °C dec. Anal. Calcd for $C_{22}H_{30}NOLi$ (331.4): C, 79.73; H, 9.12; N, 4.23. Found: C, 79.54; H, 8.21; N, 4.87.

X-ray crystal structure analysis of 3d: formula $C_{30}H_{46}LiNO_3$, $M = 475.62$, yellow crystal $0.25 \times 0.20 \times 0.15$ mm, $a = 17.202(1)$ Å, $b = 9.953(1)$ Å, $c = 17.564(1)$ Å, $\beta = 101.45(1)°$, $V = 2947.3(4)$ Å^3, $\rho_{calc} = 1.072$ g cm^{-3}, $\mu = 0.67$ cm^{-1}, empirical absorption correction via SORTAV ($0.984 \leq T \leq 0.990$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 28585 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 6752 independent ($R_{int} = 0.036$) and 4942 observed reflections [$I \geq 2\ \sigma(I)$], 320 refined parameters, $R = 0.055$, $wR_2 = 0.137$, max. residual electron density 0.38 (−0.32) e Å^{-3}, hydrogens calculated and refined as riding atoms.

1,1′-Bis(*N*-phenylformimidoyl)ferrocene (4a). A mixture of 988 mg (4.0 mmol) of lithium [(*N*-phenylformimidoyl)cyclopentadienide] (**3a**) and 254 mg (2.0 mmol) of iron(II) chloride in 100 mL of toluene was stirred at 60 °C for 2 days. The suspension was then filtered and the solvent removed in vacuo. The red microcrystalline residue was washed with pentane and dried in vacuo to give 646 mg (82%) of product **4a**. ^{1}H NMR (200.13 MHz, benzene-d_6, 298 K): δ 8.14 (s, 2H, 6-H), 7.22−7.07 (m, 10 H, Ph), 4.73, 4.12 (each br, each 4H, C_5H_4). ^{13}C{^{1}H} NMR (50.3 MHz, benzene-d_6, 298 K): δ 159.7 (C6), 153.2 (ipso-C of Ph), 129.4, 125.6, 121.1 (Ph), 82.5 (ipso-C of C_5H_4), 72.1, 70.4 (C_5H_4). IR (KBr): $\tilde{\nu}$ 3065, 2962, 2881, 1620, 1589, 1466, 1261, 1099, 1073, 1021, 813, 801, 766, 737, 692 cm^{-1}. Mp: 96 °C. Anal. Calcd for $C_{24}H_{20}N_2Fe$ (392.3): C, 73.48; H, 5.14; N, 7.14. Found: C, 72.18; H, 5.46; N, 6.66.

X-ray crystal structure analysis of 4a: formula $C_{24}H_{20}N_2Fe$, $M = 392.27$, red crystal $0.30 \times 0.15 \times 0.10$ mm, $a = 41.129(1)$ Å, $b = 93.155(3)$ Å, $c = 5.851(1)$ Å, $V = 22417(4)$ Å^3, $\rho_{calc} = 1.395$ g cm^{-3}, $\mu = 8.17$ cm^{-1}, empirical absorption correction via SORTAV ($0.792 \leq T \leq 0.923$), $Z = 48$, orthorhombic, space group $Fdd2$ (No. 43), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 16 767 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 8756 independent ($R_{int} = 0.030$) and 7362 observed reflections [$I \geq 2\sigma(I)$], 730 refined parameters, $R = 0.042$, $wR_2 = 0.075$, max. residual electron density 0.34 (−0.28) e Å^{-3}, Flack −0.01(1), three nearly identical molecules in the asymmetric unit, hydrogens calculated and refined as riding atoms.

1,1′-Bis[(*N*-2,6-diisopropylphenyl)formimidoyl]ferrocene (4d). A 1.32 g (4.0 mmol) sample of lithium {[(*N*-2,6-diisopropylphenyl)formimidoyl]cyclopentadienide} (**3c**) and 254 mg (2.0 mmol) of iron(II) chloride were suspended in 100 mL of toluene and stirred at 60 °C for 2 days. After filtration through Celite the volatiles were removed in vacuo to give 884 mg (79%) of the red product **4d**. ^{1}H NMR (200.13 MHz, benzene-d_6, 298 K): δ 7.89 (s, 2H, 6-H), 7.16−7.02 (m, 6H, Ph), 4.74, 4.30 (each br, each 4H, C_5H_4), 3.24 (sept., $^3J = 7.0$ Hz, 4H, $CH(CH_3)_2$), 1.22 (d, $^3J = 7.0$ Hz, 24H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (50.3 MHz, benzene-d_6, 298 K): δ 161.2 (C6), 151.1 (ipso-C of Ph), 137.8, 124.4, 122.3 (Ph), 82.0 (ipso-C of C_5H_4), 71.8, 69.7 (C_5H_4), 28.1 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$). IR (KBr): $\tilde{\nu}$ 2967, 2926, 2864, 1639, 1598, 1446, 1391, 1315, 1274, 1240, 1184, 1052, 1026, 841, 806, 765, 730 cm^{-1}. Mp: 130 °C. Anal. Calcd for $C_{36}H_{44}N_2Fe$ (560.6): C, 77.13; H, 7.91; N, 5.00. Found: C, 77.50; H, 5.62; N, 5.29.

X-ray crystal structure analysis of 4d: formula $C_{36}H_{44}N_2Fe \cdot 0.5C_7H_8$, $M = 606.65$, red crystal 0.40 × 0.25 × 0.20 mm, $a = 8.619(1)$ Å, $b = 23.041(1)$ Å, $c = 17.140(1)$ Å, $\beta = 102.72(1)°$, $V = 3320.3(5)$ Å^3, $\rho_{calc} = 1.214$ g cm^{-3}, $\mu = 4.83$ cm^{-1}, empirical absorption correction via SORTAV ($0.830 \leq T \leq 0.910$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 21 935 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.65 Å^{-1}, 7448 independent ($R_{int} = 0.039$) and 5892 observed reflections [$I \geq 2\sigma(I)$], 412 refined parameters, $R = 0.043$, $wR_2 = 0.090$, max. residual electron density 0.28 (−0.38) e Å^{-3}, disordered toluene solvate molecule (occupancy 0.5) refined with constraints, hydrogens calculated and refined as riding atoms.

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37; Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997), SCHAKAL (Keller, E., Universität Freiburg, 1997).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supporting Information Available: Detailed information about the X-ray crystal structure analyses of the compounds **3a**, **3c**, **3d**, **4a**, and **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000753U