The Isocyanate Route to Cyclopentadienyl-Carboxamide- and Cyclopentadienyl-Amino Ester-Substituted Metallocene Complexes

Markus Oberhoff, Lothar Duda, Jörn Karl, Roland Mohr, Gerhard Erker,* Roland Fröhlich, and Matthias Grehl

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

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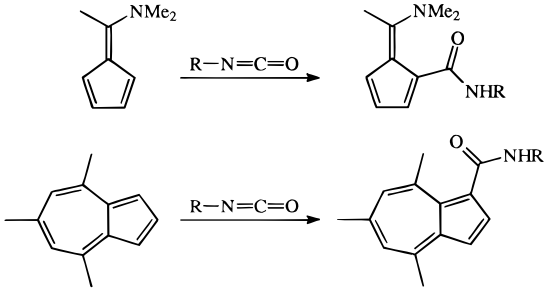
Lithium cyclopentadienide adds to a variety of isocyanates [R−N═C═O, R = *tert*-butyl (**a**), *n*-butyl (**b**), cyclohexyl (**c**), phenyl (**d**), 3-pyridyl (**e**), 2-tetrahydropyranyl (**f**), adamantyl (**g**)] to yield the monocarbamoyl-substituted cyclopentadienides $C_5H_4CONHR^-$ **3** admixed with varying amounts of the respective 1,2-dicarbamoyl-substituted $C_5H_3(CONHR)_2^-$ systems **4** and a corresponding quantity of the $C_5H_5^-$ starting material. Subsequent treatment of these reaction mixtures with anhydrous $FeCl_2$ gave the 1,1′-dicarbamoylferrocenes **6** and the corresponding monocarbamoylferrocenes **5**, which were easily separated by chromatography. The carbamoylferrocenes **5b**, **5c**, and **6d** were characterized by X-ray crystal structure analyses. The (*N*-phenyl- and (*N*-adamantylcarbamoyl)cyclopentadienides were treated with $CpTiCl_3$ to give the carboxamide-substituted titanocene dichloride complexes [$Cp(C_5H_4$-$CONHR)TiCl_2$] **8a** (R = Ph) and **8b** (R = adamantyl), respectively. Complex **8b** was also characterized by X-ray diffraction. The valine ester-derived isocyanate reacts with lithium cyclopentadienide to give the *N*-valinyl-substituted carbamoylcyclopentadienide **3h**. Subsequent treatment with $FeCl_2$ or $FeCl_2$/CpLi, respectively, produces the 1,1′-difunctionalized ferrocene **6h** or the monofunctionalized ferrocene **5h**. Both complexes were characterized by X-ray crystal structure analyses.

Introduction

Functional groups at their Cp rings can change the electronic properties and the range of potential applications of metallocene complexes considerably. This is especially true for the Cp-attached COX functionalities. The presence of acyl- and carboxylic acid-derived functional groups opens novel pathways for chemical modifications of metallocene complexes and their use in organic synthesis and catalysis.[1] In this context, it is of great interest to bind COX functions to the Cp ring systems of electrophilic early transition metal complexes[2] and to attach amino acid-derived side chains to metallocene complexes.[3,4] Both of these synthetic targets cannot be achieved by direct substitution reactions at the organometallic framework.

The COX type functional groups can very easily be introduced at ferrocene and related metallocenes of the late transition metals via electrophilic "aromatic" substitution routes or by using Cp-metalated metallocene systems.[5] Analogously substituted early transition metal metallocene systems do not seem to be available this way;[6] here the COX type substituents must be attached to the Cp−ligand systems before connecting them with the respective metal centers. Rausch et al. have developed such a way of introducing, for example, carboxylate-substituted Cp ring systems. A few examples of $(CpCO_2R)CpMX_2$ and $(CpCO_2R)_2MX_2$ systems of the group 4 metals were prepared by this route, and their structures have been described in the literature.[2]

In 1968, Effenberger et al. described the reaction of activated fulvenoid substrates with isocyanates R−N═C═O that directly led to the respective carboxamide-substituted systems.[7] Both of these reactions



[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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involve as the essential carbon−carbon coupling step the addition of a (substituted) cyclopentadienide anion equivalent to the sp-carbon center of the heterocumulene. Therefore, it was tempting to extend this interesting reaction by adding Cp anions to suitably substituted isocyanates R−N=C=O to produce the carboxamide-substituted cyclopentadienides. We have carried out a number of such reactions and have found it to be a useful synthetic sequence for the preparation of carboxamide-substituted cyclopentadienide−ligand systems and their respective metallocene complexes. Even the respective amino ester-substituted metallocenes can be synthesized in this way. Several typical examples are described in this article.

Results and Discussion

Cyclopentadienyl-Carboxamide-Substituted Metallocenes. *tert*-Butyl isocyanate was treated with cyclopentadienyl anion (with lithium or sodium counteranion) in a 1:1 molar ratio. The reaction was usually started at low temperature (−78 °C) and the reaction mixture allowed to warm to room temperature over a period of several hours before the resulting product mixture was analyzed spectroscopically or used in a subsequent metathetical metal exchange reaction to form the corresponding metallocene systems (see the following). Under these conditions a rapid addition reaction ensues, leading to CC coupling between cyclopentadienide and the heterocumulene sp-carbon center. In view of the pK_a difference between a carboxamido anion and cyclopentadiene, it is likely that a rapid favorable proton transfer subsequently takes place. Consequently, the carboxamido-substituted cyclopentadienide system **3a** is observed to be formed as the major addition product. In the case of Cp^- addition to Me_3CNCO, and in most other cases as well (see the following), the mono-RNHCO-functionalized cyclopentadienide is not the only product obtained. The product **3a** was usually obtained admixed with a substantial quantity of the doubly functionalized product **4a**. The latter is likely to be formed in a subsequent reaction step employing the primarily formed product **3a** as a nucleophile that adds to another RNCO unit. Consequently, some residual unreacted Cp anion makes up the third component of the product mixture. The **3a**:**4a** product ratio is slightly dependent on the actual reaction conditions; usually **3a**:**4a** values were observed ranging between 60:40 and 80:20. Employment of Cp anion and *tert*-butyl isocyanate in a 1:2 ratio led to the sole formation of the bis-adduct **4a**. It may seem surprising that the $CpCONHR^-$ anion that bears an electron-withdrawing substituent exhibits such a high nucleophilicity that it may successfully compete with the unsubstituted cyclopentadienide for the RNCO reagent, but this is probably due to the especially high anion stabilization of the resulting product. The 1,2-$(RNHCO)_2C_5H_3^-$ system is to be regarded as a "fulvenologous" β-dicarbonyl system, exhibiting a highly increased anion stabilization.[8]

The carboxamido-substituted cyclopentadienides were identified by their typical ^{1}H NMR spectra. The monocarboxamido-substituted $(Me_3CNHCO)C_5H_4Li$ product (Li-**3a**) in THF-d_8/benzene-d_6 (1:10) exhibits a *tert*-butyl singlet at δ 1.31, an AA′BB′ pattern of the cyclopentadienyl hydrogens at δ 6.06 and 5.73, and the broad NH resonance at δ 5.80. The 1,2-$(Me_3CNHCO)_2C_5H_3Li$ byproduct (Li-**4a**) shows the ^{1}H NMR signals of the cyclopentadienyl group at δ 6.72 (m, 2H) and 6.39 (m, 1H). The NH resonance is at δ 5.98 (br s, 2H), and the Me_3C signal is at δ 1.30 (s, 18H).

The 1,2-$(Me_3CNHCO)_2C_5H_3^-$ system is much less reactive toward metal exchange than the corresponding monocarboxamide-substituted system **3a**. Thus, Na-**4a** was reacted with anhydrous $FeCl_2$ in tetrahydrofuran. It required 2 days of stirring at room temperature to bring this reaction to completion. The product of composition $[1,2\text{-}(Me_3CNHCO)_2C_5H_3]_2Fe$ (**7a**) was isolated (65%). It was characterized spectroscopically (see Experimental Section), but its detailed structural description must await the results of an X-ray crystal structure analysis.

Out of the mixture of **3a**, **4a**, and Cp^- anions, the mono- and unsubstituted cyclopentadienides react much faster with, for example, $FeCl_2$ than their congener **4a**. Iron(II) chloride was added at −10 °C to the reagent mixture produced by treatment of CpLi with Me_3CNCO in a 1:1 molar ratio. The reaction is essentially complete after allowing the mixture to warm to room temperature over several hours with stirring. As expected, a mixture of two organometallic products is obtained. Most of the $(Me_3CNHCO)C_5H_4Li$ reagent is used in the formation of the symmetrically difunctionalized 1,1′-dicarbamoylferrocene derivative $[(Me_3CNHCO)C_5H_4]_2Fe$ (**6a**). However, most of the remaining unreacted CpLi component of the reagent mixture is also used in ferrocene formation, giving rise to a proportional quantity of the "mixed" ferrocene product $[(Me_3CNHCO)C_5H_4]CpFe$ (**5a**). These two products were separated by chromatography. Complex **6a** was isolated in ca. 20% yield, whereas only a very small amount of the **5a** byproduct was obtained, which was just sufficient for characterization.

A variety of differently substituted carbamoylferrocenes were prepared in this way. CpLi was treated with *n*-butyl isocyanate in a 1:1 molar ratio and then reacted with an excess of $FeCl_2$. Chromatographic workup furnished the mono(*n*-butylcarbamoyl)ferrocene complex (**5b**) in 24% yield. A second larger fraction of the corresponding 1,1′-dicarbamoylferrocene complex **6b** was subsequently eluted from the column. However, this product was only isolated admixed with ca. 20% of **5b**. Analogously, the (cyclohexylcarbamoyl)ferrocene complex (**5c**) was obtained and isolated after chromatography. Single crystals of both complexes **5b** and **5c** were obtained, and these products were identified by X-ray crystal structure analyses (for details see the Experimental Section and the supporting information).

The ferrocene framework of **5b** exhibits an eclipsed metallocene conformation in the crystal.[9] The *N*-(*n*-butyl)carboxamide substitutent is oriented in plane with its adjacent Cp ring system. The amide C=O and N−H

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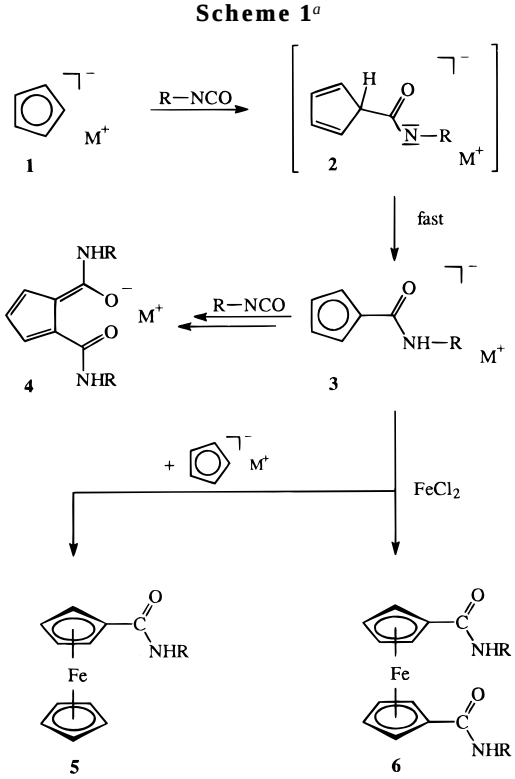
Scheme 1[a]



[a] R = CMe_3 (**a**), *n*-C_4H_9 (**b**), cyclo-C_6H_{11} (**c**), Ph (**d**), 3-pyridyl (**e**), 2-tetrahydropyranyl (**f**).

vectors are E-oriented at the connecting C—N bond. The C—C connection between the functional group and the Cp ring is in the typical range for a $C(sp^2)$—$C(sp^2)$ single bond[10] at 1.476(7) Å. Complex **5c** exhibits a very similar molecular arrangement in the solid state.

Phenyl isocyanate was treated with lithium cyclopentadienide (1:1) in THF and then, without isolation of the intermediate $(PhNHCO)C_5H_4Li$ reagent, reacted with anhydrous $FeCl_2$ at ambient temperature. Soxhlet extraction of the product mixture with ether followed by chromatographic separation (silica gel/ether) and recrystallization gave the 1,1′-bis(phenylcarbamoyl)-ferrocene complex (**6d**) in 25% yield. Single crystals of **6d** were obtained from ether and the complex was characterized by X-ray diffraction (Figure 1).

The view of the structure shows that the ferrocene **6d** has an *N*-phenylcarboxamido substituent bonded to each of the cyclopentadienyl ring systems. The Cp rings are oriented in an eclipsed metallocene conformation, and the PhNHCO substituents are arranged in the closest possible gauche-like orientation.[11] In contrast to the related monocarbamoylferrocenes (**5b**,**c**, see above), the carboxamido planes in **6d** are not located coplanarly with the Cp ring planes, but markedly rotated toward each other. The corresponding dihedral angles amount to 144.3° (C25—C24—C26—O27) and −27.2° (C5—C4—C6—O7), respectively. This deviation from coplanarity of the carboxamide and cyclopentadienyl π-systems is probably due to hydrogen bonding between the carboxamide functions in complex **6d**.[12] In the crystal, **6d** forms two types of hydrogen bonds: an

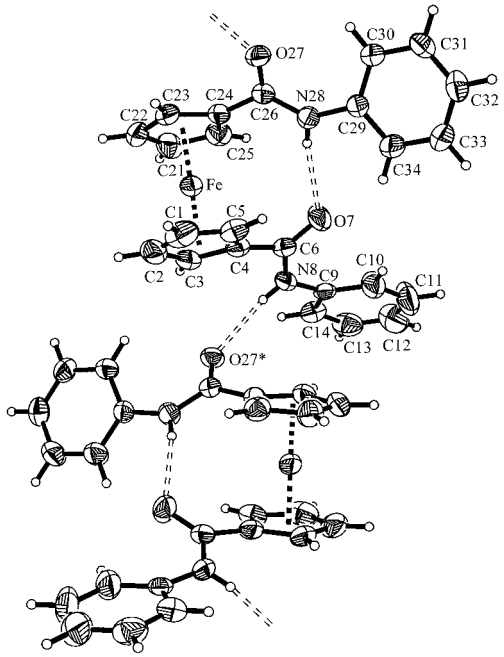


Figure 1. View of the molecular structure and association pattern of **6d** in the solid state (with unsystematical atom numbering scheme). Selected bond lengths (Å) and angles (deg): Fe—C1, 2.046(6); Fe—C2, 2.047(6); Fe—C3, 2.036-(6); Fe—C4, 2.029(5); Fe—C5, 2.025(6); Fe—C21, 2.040(6); Fe—C22, 2.046(6); Fe—C23, 2.039(5); Fe—C24, 2.036(5); Fe—C25, 2.024(6); C4—C6, 1.481(8); C6—O7, 1.236(6); C6—N8, 1.339(7); N8—C9, 1.420(7); C24—C26, 1.477(7); C26—O27, 1.223(6); C26—N28, 1.346(7); N28—C29, 1.422(7); O7—C6—N8, 123.4(5); O7—C6—C4, 121.8(5); N8—C6—C4, 114.8(5); C6—N8—C9, 127.6(5); O27—C26—N28, 124.1(5); O27—C26—C24, 120.3(5); N28—C26—C24, 115.7(5); C26—N28—C29, 126.3(5).

intramolecular one between H28 and O7 (calculated separation = 2.181 Å) and an intermolecular hydrogen bond (2.131 Å = calculated distance between H8 and O27*). The combination of these two weak interactions leads to a characteristic association pattern of **6d** molecules in the solid state. A view of the resulting suprastructure is given in Figure 1.

The isocyanate addition route may offer advantages over the classical electrophilic ferrocene substitution routes when carboxamides are attached that contain acid-labile or basic functional groups in the side chain. This was demonstrated by two selected examples. 3-Pyridyl isocyanate was treated with CpLi and then with $FeCl_2$. Workup and chromatographic separation gave the *N*-(*m*-pyridyl)carboxamide-substituted ferrocenes **5e** and **6e** in 22% and 8% yields, respectively. The analogous reaction sequence was also carried out starting from 2-tetrahydropyranylisocyanate. The *N*-(2-tetrahydropyranyl)carboxamide-substituted ferrocenes **5f** and **6f** were isolated in 54% and 21% yields, respectively.

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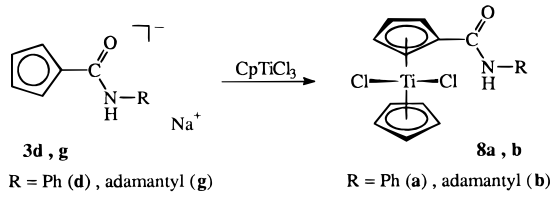
Our new method has turned out to also be suited to prepare cyclopentadienyl-carboxamide-containing bent metallocene complexes of the early transition metals. This is illustrated by the synthesis of two representative examples originating from the chemistry of titanocenes. Sodium (*N*-phenylcarbamoyl)cyclopentadienide was generated by the addition of CpNa to phenyl isocyanate. The resulting reagent was then allowed to react with (cyclopentadienyl)titanium trichloride[13] for several hours at 50 °C in toluene solution. Sodium chloride was removed by filtration and the resulting organometallic product twice recrystallized from dichloromethane. The product [(*N*-phenylcarbamoyl)cyclopentadienyl](cyclopentadienyl)titanium dichloride (**8a**) was isolated as a red solid (mp 155 °C) in 38% yield. The product shows very characteristic NMR spectra [^{1}H NMR in THF-d_8 δ 9.22 (br s, 1H, NH), 6.68 (s, 5H, Cp), 7.38 and 6.68 (AA′BB′, 2H each, C_5H_4); ^{13}C NMR in THF-d_8 δ 160.8 (*C*ONH)]. The IR $\tilde{\nu}$ (NH) band is observed at 3453 cm^{-1}.

In a related experiment, we have reacted adamantyl isocyanate with CpNa in a 1:1 molar ratio. This leads to a ca. 10:3 mixture of the products of 1- and 2-fold addition. Again, the fulvenoid bis-addition product seems to be the much higher stabilized anion system that is much less reactive toward transition metal electrophiles than the monocarbamoylcyclopentadienide. Consequently, the reaction of the 10:3 mixture with $CpTiCl_3$ leads to a product mixture from which pure [(*N*-adamantylcarbamoyl)cyclopentadienyl]$CpTiCl_2$ (**8b**) was isolated in close to 30% yield. Single crystals of **8b** suited for an X-ray crystal structure analysis were obtained from toluene.



Complex **8b** attains a typical bent metallocene conformation in the solid state. The carboxamido substituent is arranged coplanarly with the attached Cp ring. The $RNHCO^-$ group is oriented toward the lateral sector of the bent metallocene wedge. In this arrangement, the amido oxygen atom points toward the narrow back side of the bent metallocene, whereas the NH group is oriented in the direction of the open front side of the bent metallocene wedge. In this orientation the very bulky adamantyl group probably experiences the least steric interference with the other groups present in complex **8b**. Consequently, the bonding parameters around the titanium center are as typically observed in many other group 4 metallocene dihalide complexes.[14]

Amino Ester-Derived Systems. On the basis of the observation that Cp anion equivalents may be added to some simple alkyl or aryl isocyanates to yield the (*N*-hydrocarbylcarbamoyl)cyclopentadienides, a route to Cp−ligand systems bearing amino ester-derived side chains was developed. We have treated valine methyl ester hydrochloride (**9**) with excess diphosgene to yield

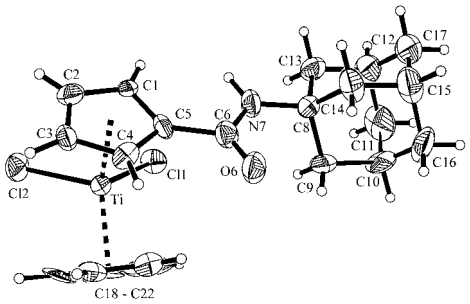
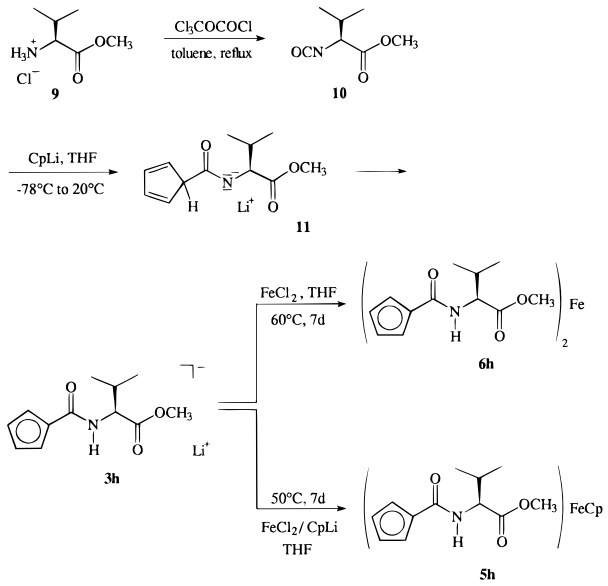


Figure 2. Projection of the molecular geometry of **8b** (with unsystematical atom numbering scheme). Selected bond lengths (Å) and angles (deg): Ti−Cl1, 2.356(3); Ti−Cl2, 2.345(3); Ti−C1, 2.429(9); Ti−C2, 2.418(10); Ti−C3, 2.348(10); Ti−C4, 2.364(9); Ti−C5, 2.380(9); Ti−C18, 2.343(13); Ti−C19, 2.382(12); Ti−C20, 2.350(11); Ti−C21, 2.351(11); Ti−C22, 2.325(12); C5−C6, 1.481(14); C6−O6, 1.235(12); C6−N7, 1.348(13); N7−C8, 1.472(13); O6−C6−N7, 124.7(10); O6−C6−C5, 119.6(10); N7−C6−C5, 115.7(9); C6−N7−C8, 126.0(9); Cl2−Ti−Cl1, 95.69(11).

Scheme 2



the corresponding isocyanate (**10**).[15] Subsequent reaction of **10** with lithium cyclopentadienide proceeded cleanly to give the *N*-CH(CHMe$_2$)CO$_2$Me-substituted carbamoylcyclopentadienide system **3h**. Again, it must be assumed that **11** is formed as a primary product in this addition reaction. Due to the pronounced pK_a differences between the CpH and carboxamide moieties, proton transfer occurs rapidly to yield **3h**. The reagent **3h**·0.5THF was isolated and characterized spectroscopically .

Anhydrous $FeCl_2$ was treated with the valine ester-derived carbamoyl cyclopentadienide **3h** in a 1:2 molar ratio in THF at 60 °C for 1 week to give the corresponding 1,1′-dicarbamoyl-substituted ferrocene **6h**, which was isolated in >80% yield. Complex **6h** was characterized spectroscopically (see Experimental Section) and by an X-ray crystal structure analysis (see Figure 3). In the solid state, the substituted ferrocene derivative exhibits an eclipsed metallocene conformation with the valine ester-substituted carboxamide substituents oriented in the closest gauche-like positions. The carboxamide π-systems are both arranged in plane with their

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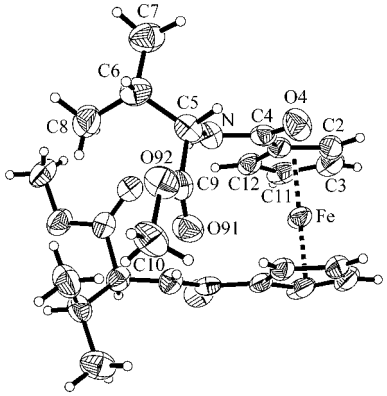

Figure 3. View of the molecular geometry of **6h** (with unsystematical atom numbering scheme). Selected bond lengths (Å) and angles (deg): Fe−C1 2.026(3); Fe−C2, 2.045(4); Fe−C11, 2.036(4); Fe−C3, 2.046(4); Fe−C12, 2.042(4); C1−C4, 1.488(5); C4−O4, 1.222(4); C4−N, 1.354-(4); N−C5, 1.448(5); C11−C1−C2, 107.9(3); C11−C1−C4, 129.6(3); C2−C1−C4, 122.2(3); O4−C4−N, 122.4(3); O4−C4−C1, 120.9(3); N−C4−C1, 116.7(3); C4−N−C5, 120.1-(3); θ C4−N−C5−C9, −91.5(4).

adjacent cyclopentadienyl ring systems. The overall molecular geometry is C_2-symmetric. Thus, the carboxamide C═O vectors are pointing to opposite directions normal to the Cp−Fe−Cp axis.

Treatment of the isocyanate **10** with excess LiCp followed by the reaction with $FeCl_2$ gave, as usual, a mixture of the monofunctionalized ferrocene **5h** and the difunctionalized product **6h**. They were separated chromatographically. Complex **5h** was also characterized by an X-ray crystal structure analysis. Again, the carboxamido substituent is oriented in plane with the attached Cp ring. The structural data are very similar to those of complex **6h** (for details see the Experimental Section and the supporting information).

Conclusions

We conclude that a variety of carboxamido-substituted cyclopentadienides, including the respective amino ester-derived systems, can be generated by Cp anion addition to the corresponding isocyanates. The amide anion **2** formed in the first step is rapidly converted to the corresponding $(RNHCO)C_5H_4^-$ reagent **3** by proton transfer. A certain problem in this reaction scheme is the rapid subsequent additional isocyanate addition to give the fulvenoid bis-adducts **4**. However, it seems that the metallocene formation is not severely hampered by the presence of the additional reagent **4** because of its reduced nucleophilicity. This side reaction during the formation of the $(RNHCO)C_5H_4^-$ reagent in many cases makes it inevitable that a contamination with residual unsubstituted Cp anion will occur. In the following treatment with the transition metal halide, this results in the formation of a proportional quantity of the "mixed" $[(RNHCO)C_5H_4]CpM$ product in addition to the $[(RNHCO)C_5H_4]_2M$ main product. In the case of the ferrocenes, these two final products can often be separated quite easily by chromatography.

An advantage of this new route is the possibility to introduce carboxamido substituents carrying acid-labile and also basic groups bonded to the amido nitrogen. In addition, our novel route can be used to synthesize CpCONHR-substituted early transition metal metallocenes that cannnot be made by electrophilic substitution routes starting from the simple unsubstituted parent bent metallocene complexes. We expect that group 4 metallocenes exhibiting highly functionalized perimeters will become available by variations of this route, e.g., employing the isocyanates of oligopeptides as reagents. Such systems would be interesting candidates for developing novel electrophilic metallocene catalysts. Work directed at opening synthetic entries to such systems is currently being carried out in our laboratory.

Experimental Section

Most reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. Alkyl and aryl isocyanates employed in this study were commercially available. Details of experimental conditions and instruments used for spectroscopic and physical product characterization are as previously described by us in the literature.[16]

Reaction of Lithium Cyclopentadienide with *tert*-Butyl Isocyanate. A solution of 2.00 g (20.2 mmol) of Me_3-CNCO in 50 mL of tetrahydrofuran was added dropwise at −30 °C to a solution of 1.45 g (20.1 mmol) of CpLi in 50 mL of THF. The dark red colored reaction mixture was allowed to warm to room temperature overnight. Solvent was then removed in vacuo, and the solid residue was washed twice with pentane (30 mL). The resulting product mixture (3.0 g) consists of **3a**, **4a**, and CpLi in a 62:22:16 ratio. Complex **3a** was characterized spectroscopically: ^{1}H NMR (THF-d_8) δ 5.93 and 5.53 (m, 2H each, C_5H_4), 5.82 (br s, 1H, NH), 1.37 (s, 9H, CMe_3). In a separate experiment, 6.34 g (64.0 mmol) of Me_3-CNCO was added to 1.68 g (23.4 mmol) of CpLi in 50 mL of THF at room temperature. The mixture was stirred overnight, the solvent removed in vacuo, and the residue washed twice with pentane. Drying in vacuo at room temperature gave 8.4 g of **4a**·0.8THF, mp 133 °C (DSC). The residual THF could be removed at 130 °C in vacuo. IR (KBr): $\tilde{\nu} = 3446$ cm^{-1}, 3402 (NH), 1565, 1500 (CONH). ^{1}H NMR (benzene-d_6/THF-d_8, 10:1): δ 6.72 (d, $^3J = 3.6$ Hz, 2H), 6.39 (t, $^3J = 3.6$ Hz, 1H, C_5H_3), 5.98 (br s, 2H, NH), 1.30 (s, 18H, CMe_3), THF signals at 3.55 (2H) and 1.43 (2H). ^{13}C NMR (THF-d_8): δ 171.9 (*C*ONH), 116.1 (ipso-C, Cp), 115.8, 108.2 (*C*H of Cp), 50.6 and 29.7 (CMe_3). Anal. Calcd for $C_{15}H_{24}LiN_2O_2$·$0.8C_4H_8O$ (329.0): C, 66.65; H, 9.04; N, 8.54. Found: C, 66.41; H, 8.94; N, 8.40.

(*N*-*tert*-Butylcarbamoyl)ferrocene (5a) and 1,1′-Bis(*N*-*tert*-butylcarbamoyl)ferrocene (6a). CpLi (600 mg, 8.33 mmol) was reacted with 0.95 mL (822 mg, 8.29 mmol) of *tert*-butyl isocyanate in 50 mL of THF as described earlier and then treated with 634 mg (5.00 mmol) of anhydrous $FeCl_2$. Solvent was removed and the residue extracted with dichloromethane. The CH_2Cl_2 solvent was removed and the product chromatographed with ether on silica gel to give a trace amount of **5a** and **6a** (170 mg, 12%) as an orange-colored solid. **5a**: mp 202 °C (dec). ^{1}H NMR ($CDCl_3$): δ 5.4 (br s, 1H, NH), 4.58 and 4.28 (m, each 2H, C_5H_4), 4.17 (s, 5H, Cp), 1.42 (s, 9H, CMe_3). **6a**: mp 109 °C (DSC), 237 °C (dec). HRMS: calcd 384.1500, found 384.1509. IR (KBr): $\tilde{\nu} = 3334$ cm^{-1} (NH), 1631 and 1537 (CONH). ^{1}H NMR ($CDCl_3$): δ 6.36 (br s, 2H, NH), 4.42 and 4.32 (m, each 4H, C_5H_4), 1.46 (s, 18H, CMe_3). ^{13}C NMR ($CDCl_3$): δ 169.2 (*C*ONH), 79.3 (ipso-C of Cp), 70.6 and 70.4 (*C*H of Cp), 51.3 and 28.9 (CMe_3). Anal. Calcd for $C_{20}H_{28}N_2O_2$-Fe (384.3): C, 62.51; H, 7.34. Found: C, 61.82; H, 7.45.

Preparation of the (*N*-*n*-Butylcarbamoyl)ferrocene Complexes 5b and 6b. CpLi (738 mg, 1.02 mmol) was treated with 1.03 g (1.04 mmol) of *n*-butyl isocyanate in 100 mL of THF (12 h), 490 mg (3.87 mmol) of $FeCl_2$ was added, and the mixture stirred for 24 h at room temperature. Solvent was removed in vacuo. Washing with pentane and then toluene gave 1.57 g of the crude reaction product. Of this

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product, 510 mg was chromatographed with ether on silica gel to give 71 mg (24%) of **5b** and 70 mg of **6b** that contained ca. 20% **5b**. **5b**: mp 146 °C. IR (KBr): $\tilde{\nu}$ = 3296 cm^{-1} (NH), 1622 and 1539 (CONH). ^{1}H NMR ($CDCl_3$): δ 5.76 (br s, 1H, NH), 4.64 and 4.29 (m, each 2H, C_5H_4), 4.19 (s, 5H, Cp), 3.35 (m, 2H), 1.53 (m, 2H), 1.38 (m, 2H), 0.92 (br t, 3H, *n*-butyl). ^{13}C NMR ($CDCl_3$): δ 169.0 (*C*ONH), 69.2 and 67.0 (*C*H of C_5H_4), 68.7 (Cp), 38.3, 31.1, 19.1, 12.8 (*n*-butyl). Anal. Calcd for $C_{15}H_{19}NOFe$ (285.2): C, 63.18; H, 6.72. Found: C, 62.84; H, 6.68. X-ray crystal structure analysis: single crystals from $CDCl_3$; formula, $C_{15}H_{19}NOFe$; M = 285.16 g mol^{-1}; orthorhombic space group *Pbca* (No. 61); cell constants a = 9.870(2) Å, b = 10.154(2) Å, c = 26.612(5) Å, V = 2667.1(9) Å^3; T = −50 °C, crystal size 0.3 × 0.2 × 0.05 mm; Z = 8; ρ_{calcd} = 1.420 g cm^{-3}; λ = 0.710 73 Å; [sin θ/λ]$_{max}$ = 0.62 Å^{-1}; μ = 11.2 cm^{-1}; 2714 reflections collected ($+h$, $-k$, $-l$), 2713 independent and 1589 observed reflections; 167 refined parameters, R = 0.049, wR^2= 0.119. Programs used: SHELX 86, SHELX 93, XP. **6b**: ^{1}H NMR ($CDCl_3$) δ 6.75 (br s, 2H, NH), 4.46 and 4.34 (m, each 4H, C_5H_4), 3.39 (m, 4H), 1.61 (m, 4H), 1.41 (m, 4H), 0.96 (br t, 6H, *n*-butyl).

(*N*-Cyclohexylcarbamoyl)ferrocene (5c). CpLi (3.19 g, 44.3 mmol) was reacted with 5.43 mL (5.32 g, 42.5 mmol) of cyclohexyl isocyanate in 50 mL of THF (−78 °C to ambient temperature, 24 h) and then treated with 2.24 g (17.7 mmol) of $FeCl_2$ in 20 mL of THF. The resulting crude product was Soxhlet extracted with ether for 4 days, and the resulting extract was chromatographed with ethyl acetate/ether (2:1) on silica gel to yield 265 mg (4.8%) of **5c**. IR (KBr): ν = 3296 cm^{-1} (NH), 1623 and 1538 (CONH). ^{1}H NMR ($CDCl_3$): δ 5.48 (br s, 1H, NH), 4.64 and 4.32 (m, each 2H, C_5H_4), 4.19 (s, 5H, Cp), 3.92 (br m, 1H), 1.99 (m, 2H), 1.79−1.15 (m, 8H, cyclohexyl). Anal. Calcd for $C_{17}H_{21}NOFe$ (311.2): C, 65.61; H, 6.80; N, 4.50. Found: C, 65.91; H, 7.22; N, 4.64. X-ray crystal structure analysis: single crystals from $CDCl_3$; formula, $C_{17}H_{21}NOFe$; M = 311.20 g mol^{-1}; orthorhombic space group $P2_12_12_1$ (No. 19); cell constants a = 9.722(1) Å, b = 10.159(1) Å, c = 29.952(2) Å, V = 2958.2(5) Å^3; T = −50 °C; crystal size 0.6 × 0.3 × 0.05 mm; Z = 8; ρ_{calcd} = 1.397 g cm^{-3}; λ = 0.710 73 Å; [sin θ/λ]$_{max}$ = 0.62 Å^{-1}; μ = 10.1 cm^{-1}; 3419 reflections collected ($-h$, $+k$, $-l$), 3419 independent and 2582 observed reflections; 369 refined parameters, R = 0.051, wR^2 = 0.139.

(*N*-Phenylcarbamoyl)ferrocene (5d). The reaction mixture obtained by treatment of 83 mg (1.15 mmol) of CpLi and 87.7 mL (96.1 mg, 0.81 mmol) of phenyl isocyanate in 30 mL of THF at 0 °C (24 h) was added to 72 mg (0.57 mmol) of anhydrous $FeCl_2$ and stirred for 3 days at 50 °C. The suspension was concentrated in vacuo to a volume of 10 mL and then filtered. The yellow crude product (166 mg) was chromatographed on a short silica gel column with ether/ethyl acetate (10:1, plus 1% of dimethylethylamine) to give, as the first fraction, 72 mg (41%) of **5d** as a yellow amorphous solid, mp 208 °C (DSC). HRMS: calcd 305.0503, found 305.0495. IR (KBr): $\tilde{\nu}$ = 3294 cm^{-1} (NH), 1643 and 1596 (CONH). ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 2H, Ph), 7.30 (m, 3H, Ph and NH), 7.10 (m, 1H, Ph), 4.76 (m, 2H), 4.40 (m, 2H, C_5H_4R), 4.24 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 168.6 (*C*ONH), 138.1 (ipso-C of Ph), 129.1, 124.0, 119.8 (Ph), 70.9 and 68.3 (C_5H_4R), 69.9 (Cp), ipso-C of C_5H_4R not observed. Anal. Calcd for $C_{17}H_{15}NOFe$ (305.2): C, 66.91; H, 4.95; N, 4.59. Found: C, 66.43; H, 5.05; N, 4.71.

1,1′-Bis(*N*-phenylcarbamoyl)ferrocene (6d). CpLi (1.00 g, 13.9 mmol) was reacted with 1.55 mL (1.69 g, 14.2 mmol) of phenyl isocyanate and then treated with 1.00 g (7.89 mmol) of $FeCl_2$ in THF as described earlier. The crude product was Soxhlet extracted with ether, and the extracted product was chromatographed with ether on silica gel to yield 750 mg (25%) of **6d** as an orange red solid, mp 152 °C. IR (KBr): $\tilde{\nu}$ = 3446 cm^{-1}, 3207 (NH), 1645 and 1595 (CONH). ^{1}H NMR ($CDCl_3$): δ 8.72 (br s, 2H, NH), 7.78 (m, 4H), 7.36 (m, 4H), 7.13 (2H, Ph), 4.64 and 4.49 (m, each 4H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ 169.0 (*C*ONH), 138.4 (ipso-C of Ph), 128.4, 124.2, 120.0 (Ph), 79.3 (ipso-C of C_5H_4R), 71.4, 71.2 (*C*H of Cp). X-ray crystal structure analysis: single crystals from $CDCl_3$; formula $C_{24}H_{20}N_2O_2Fe{\cdot}CDCl_3$; M = 543.64 g mol^{-1}; monoclinic space group $P2_1/n$ (No. 14); cell constants a = 9.281(2) Å, b = 14.956-(3) Å, c = 17.540(4) Å, β = 93.52(3)°, V = 2430.1(9) Å^3; T = 20 °C; crystal size 0.5 × 0.3 × 0.1 mm; Z = 4; ρ_{calcd} = 1.486 g cm^{-3}; λ = 0.710 73 Å; [sin θ/λ]$_{max}$ = 0.63 Å^{-1}; μ = 9.8 cm^{-1}; 4842 reflections collected ($-h$, $+k$, $\pm l$), 4561 independent and 3159 observed reflections; 305 refined parameters, R = 0.076, wR^2 = 0.159.

Preparation of the *N*-(3-Pyridyl)carbamoylferrocenes 5e and 6e. 3-Pyridyl isocyanate (400 mg, 3.33 mmol) was treated with 240 mg (330 mmol) of CpLi and then with 220 mg (1.74 mmol) of $FeCl_2$ in THF analogously as described earlier. After removal of the solvent, the crude product was purified by filtration over a short silica gel column with dichloromethane/methanol (10:1). The products were then separated by preparative thick-layer chromatography with dichloromethane/methanol (100:1, then 10:1) on silica gel to yield 110 mg (22%) of **5e** and 60 mg (8%) of **6e**, the latter after additional recrystallization from toluene. **5e**: mp 185 °C. IR (KBr): $\tilde{\nu}$ = 3302 cm^{-1} (NH), 1644 and 1534 (CONH). ^{1}H NMR (THF-d_8): δ 8.75 (br s, 1H, NH), 8.71 (m, 1H), 8.26 (m, 1H), 8.22 (m, 1H), 7.21 (m, 1H, pyridyl; pyridyl coupling constants (PANIC) $^3J_{4,5}$ = 4.7 Hz, $^3J_{5,6}$ = 8.3 Hz, $^4J_{4,6}$ = 1.5 Hz, $^4J_{2,6}$ = 2.5 Hz, $^4J_{2,4}$ = 0.5 Hz, $^5J_{2,5}$ = 0.3 Hz), 4.91 (m, 2H), 4.39 (m, 2H, C_5H_4R), 4.20 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 169.5 (*C*ONH), 135.9 (ipso-C, pyridyl), 144.6, 141.0, 127.3, 124.3 (*C*H of pyridyl), 77.2 (ipso-C of C_5H_4R), 71.2 and 68.5 (*C*H of C_5H_4R), 70.0 (Cp). **6e**: IR (KBr): $\tilde{\nu}$ = 3335 cm^{-1} (NH), 1645 and 1535 (CONH). ^{1}H NMR (THF-d_8): δ 9.53 (br s, 2H, NH), 8.89 (m, 2H), 8.29 (m, 2H), 8.26 (m, 2H), 7.23 (m, 2H, pyridyl), 4.78 and 4.50 (m, each 4H, C_5H_4). ^{13}C NMR (THF-d_8): δ 169.6 (*C*ONH), 137.2 (ipso-C of pyridyl), 145.3, 142.6, 127.1, 124.0 (*C*H of pyridyl), 80.0 (ipso-C of C_5H_4R), 72.2 and 72.0 (*C*H of C_5H_4R). Anal. Calcd for $C_{16}H_{14}N_2OFe$ (306.2): C, 62.77; H, 4.61; N, 9.15. Found: C, 62.62; H, 4.46; N, 9.28.

Preparation of the *N*-(2-Tetrahydropyranyl)carbamoylferrocene Complexes 5f and 6f. CpLi (770 mg, 10.7 mmol) was reacted with 1.26 mL (1.37 g, 10.8 mmol) of 2-tetrahydropyranyl isocyanate in THF and then treated with 800 mg (6.31 mmol) of anhydrous $FeCl_2$ as described earlier. The crude product was filtered over a short silica gel column with dichloromethane/methanol (10:1) and then chromatographed (thick-layer chromatography) with dichloromethane/methanol (100:1; several times developed) on silica gel to yield 900 mg (54%) of **5f** and 500 mg (21%) of **6f**. **5f**: mp 196 °C. IR (KBr): $\tilde{\nu}$ = 3306 cm^{-1} (NH), 1644 and 1534 (CONH). ^{1}H NMR ($CDCl_3$): δ 6.04 (br d, 1H, NH), 5.22 (m, 1H, THP 2-H), 4.71 (m, 1H), 4.63 (m, 1H), 4.33 (m, 2H, C_5H_4R), 4.22 (s, 5H, Cp), 3.99 (br d, 1H), 3.65 (m, 1H, THP 6-H/6-H′), 1.88−1.51 (m, 6H, THP CH_2). ^{13}C NMR ($CDCl_3$): δ 169.8 (*C*ONH), 78.0 (THP C2), 75.3 (ipso-C of C_5H_4R), 70.6 (double intensity), 68.6 and 67.9 (*C*H of C_5H_4R), 69.9 (Cp), 67.5 (THP C6), 32.0 (THP C3), 25.1 and 23.0 (THP *C*H$_2$). Anal. Calcd for $C_{16}H_{19}NO_2Fe$ (313.2): C, 61.36; H, 6.11; N, 4.47. Found: C, 61.11; H, 6.32; N, 4.54. **6f**: IR (KBr): $\tilde{\nu}$ = 3334 cm^{-1} (NH), 1647 and 1534 (CONH). ^{1}H NMR ($CDCl_3$): δ 6.98 (br d, 2H, NH), 5.41 (m, 2H, THP 2-H), 4.84 (m, 2H), 4.52 (m, 2H), 4.37 (m, 2H), 4.31 (m, 2H, C_5H_4R), 4.08 (br d, 2H), 3.73 (m, 2H, THP 6-H/6-H′), 1.96−1.57 (m, 12H, THP CH_2). ^{13}C NMR ($CDCl_3$): δ 169.6 (*C*ONH), 78.6 (THP C2), 75.6 (ipso-C of C_5H_4R), 72.3, 72.1, 71.6, 70.9 (*C*H of C_5H_4R), 67.9 (THP C6), 30.7 (THP C3), 25.2 and 23.2 (THP CH_2).

Preparation of Bis[1,2-bis(*tert*-butylcarbamoyl)cyclopentadienyl]iron (7). Sodium cyclopentadienide (4.28 g, 48.6 mmol) was dissolved in 100 mL of THF and cooled to −78 °C. *tert*-Butyl isocyanate (11.1 mL, 97.28 mmol) was added dropwise with stirring. The mixture was allowed to warm to room temperature overnight. Solvent was removed in vacuo and the residue washed twice with 40 mL of pentane to give **4a** as a pale yellow powder [quantitative, ^{1}H NMR (THF-d_8): δ 8.13 (br s, 2H, NH), 6.28 (d, ^3J = 3.6 Hz, 2H), 5.59 (t, ^3J = 3.6 Hz, 1H, C_5H_3), 1.37 (s, 18H, CMe_3)]. The sodium salt **4a** thus

prepared was dissolved in 100 mL of THF. $FeCl_2$ (3.08 g, 24.3 mmol) was added. The mixture was stirred for 2 days. Solvent was removed in vacuo, and the residue was extracted with 100 mL of dichloromethane. The extract was washed with water (100 mL). The aqueous phase was extracted twice with 50 mL of dichloromethane, and the combined organic layers were dried over magnesium sulfate. Solvent was removed in vacuo. The residue was washed twice with 100 mL of pentane and then dried in vacuo to yield 9.26 g (65%) of **7**: mp 272 °C. IR (KBr): $\tilde{\nu} = 3267$ cm^{-1}, 3209 (NH), 1645, 1622, 1584 (CONH). ^{1}H NMR ($CDCl_3$): δ 8.52 (br s, 4H, NH), 4.82 (d, $^3J = 1.9$ Hz, 4H), 4.22 (t, $^3J = 1.9$ Hz, 2H, $C_5H_3R_2$), 1.45 (s, 36H, CMe_3). ^{13}C NMR ($CDCl_3$): δ 168.6 (CO), 78.0 (ipso-C of $C_5H_3R_2$), 77.9 (double intensity) and 74.9 (CH of $C_5H_3R_2$), 51.8 and 28.7 (CMe_3). Anal. Calcd for $C_{30}H_{46}N_4O_4Fe$ (582.6): C, 61.85; H, 7.96; N, 9.62. Found: C, 61.56; H, 7.72; N, 9.74.

[(*N*-Phenylcarbamoyl)cyclopentadienyl](cyclopentadienyl)dichlorotitanium (8a). Solid sodium (*N*-phenylcarbamoyl)cyclopentadienide (Na-**3d**) (1.00 g, 4.83 mmol) and 1.10 g (5.01 mmol) of solid $CpTiCl_3$ were mixed in a Schlenk flask, and toluene (50 mL) was slowly added at 0 °C. The mixture was stirred at 50 °C for 20 min and then overnight at room temperature. Solvent was removed in vacuo. The residue was extracted with dichloromethane, and the extract was filtered over silica gel. Solvent was removed in vacuo and the residue recrystallized twice from dichloromethane to yield 704 mg (38%) of **8a**: mp 155 °C (DSC). IR (KBr): $\tilde{\nu} = 3453$ cm^{-1} (NH), 1581 and 1525 (CONH). ^{1}H NMR (THF-d_8): δ 9.22 (br s, 1H, NH), 7.69 (m, 2H), 7.24 (m, 2H), 7.04 (m, 1H, Ph), 7.38 and 6.60 (m, each 2H, C_5H_4R), 6.68 (s, 5H, Cp). ^{13}C NMR (THF-d_8): δ 160.8 (*C*ONH), 139.9 and 120.8 (ipso-C of Ph and C_5H_4R), 129.4, 124.5, 123.6, 122.2, 121.2 (*C*H of Ph and C_5H_4R), 122.7 (Cp).

[(*N*-1-Adamantylcarbamoyl)cyclopentadienyl](cyclopentadienyl)dichlorotitanium (8b). A suspension of 370 mg (1.30 mmol) of a 10:3 mixture of Na-**3g** and Na-**4g** in 20 mL of toluene was mixed with a suspension of $CpTiCl_3$ (281 mg, 1.28 mmol) in 15 mL of toluene at 0 °C. The mixture was allowed to warm to room temperature overnight with stirring. Solvent was removed in vacuo, and the residue was washed with pentane. The solid was extracted with 30 mL of hot toluene and filtered while still hot. The product **8b** crystallizes from the toluene solution upon cooling. The product was collected by filtration to yield 156 mg (28%) of **8b**: mp 156 °C (DSC). IR (KBr): $\tilde{\nu} = 3402$ cm^{-1} (NH), 1660 and 1526 (CONH). ^{1}H NMR (dichloromethane-d_2): δ 6.02 (br s, 1H, NH), 7.01 and 6.63 (m, each 2H, C_5H_4R), 6.47 (s, 5H, Cp), 2.05 (m, 9H), 1.71 (m, 6H, adamantyl). ^{13}C NMR (dichloromethane-d_2): δ 161.4 (CONH), 128.5 and 124.8 (CH of C_5H_4R), 122.1 (Cp), 119.2 (ipso-C of C_5H_4R), 41.8, 36.7, 30.0 (adamantyl), one adamantyl resonance not observed. Anal. Calcd for $C_{21}H_{25}NOCl_2Ti$ (426.2): C, 59.18; H, 5.91; N, 3.29. Found: C, 59.47; H, 6.06; N, 3.70. X-ray crystal structure analysis: single crystals from toluene; formula, $C_{21}H_{25}Cl_2NOTi$; $M = 426.22$ g mol^{-1}; monoclinic space group $P2_1/c$ (No. 14); cell constants $a = 13.446(1)$ Å, $b = 10.937(1)$ Å, $c = 13.308(1)$ Å, $\beta = 92.41(1)°$, $V = 1955.3(3)$ Å^3; $T = -50$ °C; crystal size $0.2 \times 0.15 \times 0.01$ mm; $Z = 4$; $\rho_{calcd} = 1.448$ g cm^{-3}; $\lambda = 0.710\ 73$ Å; $[\sin\theta/\lambda]_{max} = 0.53$ Å^{-1}; $\mu = 7.21$ cm^{-1}; 2518 reflections collected ($+h$, $+k$, $\pm l$), 2397 independent and 1501 observed reflections; 239 refined parameters, $R = 0.068$, $wR^2 = 0.183$.

Reaction of Valine Methyl Ester Isocyanate (10) with CpLi: Preparation of 3h and Subsequently 6h. Lithium cyclopentadienide (390 mg, 5.4 mmol) in 30 mL of THF was combined with a solution of 860 mg (5.5 mmol) of methyl (*S*)-2-isocyanato-2-isopropyl acetate (**10**) in 30 mL of THF at −78 °C. The mixture was allowed to warm to ambient temperature overnight. Solvent was removed in vacuo, and the residue was washed with pentane and dried in vacuo to give 1.32 g (91%) of **4**·0.5THF. ^{1}H NMR (benzene-d_6/THF-d_8, 10:1.5): δ 6.49−6.45 (m, 3H, α-C*H* of C_5H_4R and NH, overlapping), 6.20 (m, 2H, β-C*H* of C_5H_4R), 4.68 (dd, $^3J = 8.9$, 6.2 Hz, 1H, NHC*H*), 3.37 (s, 3H, OCH_3), 2.11 (m, 1H), 0.94 (2d, 6H, isopropyl). ^{13}C NMR (benzene-d_6/THF-d_8, 10:1.5): δ 174.0, 169.2 (*C*ONH, *C*O_2Me), 111.6 (ipso-C of C_5H_4R), 110.8, 109.3 (*C*H of C_5H_4R), 58.4 (NH*C*H), 51.5 (OCH_3), 32.4, 19.6, 18.6 (isopropyl). The reagent **3h** thus prepared contains less than 5% of the bis(isocyanate) addition product. This product was treated with 320 mg (2.5 mmol) of $FeCl_2$ in 60 mL of THF at 60 °C for 1 week. Solvent was removed in vacuo and washed with pentane. Chromatographic separation with THF on silica gel gave 1.04 g (83%) of **6h**: mp 168 °C (DSC), $[\alpha]^D_{20} = +115°$ ($c = 0.59$ in CH_2Cl_2). HRMS: calcd 500.1610, found 500.1597. IR (KBr): $\tilde{\nu} = 3395$ cm^{-1} (NH), 1743, 1723 (CO_2Me), 1655, 1529 (CONH). UV (CH_2Cl_2): $\lambda = 256$ nm ($\epsilon = 1730$). ^{1}H NMR ($CDCl_3$): δ 7.48 (d, $^3J = 9.0$ Hz, 2H, NH), 4.83, 4.74, 4.50, 4.35 (m, each 2H, C*H* of C_5H_4R), 4.63 (dd, $^3J = 9.0$, 7.2 Hz, 2H, NHC*H*), 3.78 (s, 6H, OCH_3), 2.16 (m, 2H), 0.98 and 0.97 (each d, $^3J = 6.7$ Hz, each 6H, isopropyl). ^{13}C NMR (benzene-d_6): δ 175.6, 170.3 (*C*ONH and *C*O_2Me), 77.5 (ipso-C of C_5H_4R), 71.9, 71.7, 70.9, 70.7 (*C*H of C_5H_4R), 58.5 (NH*C*H), 51.8 (OCH_3) 30.4, 19.5, 19.2 (isopropyl). Anal. Calcd for $C_{24}H_{32}N_2O_6Fe$ (500.4): C, 57.61; H, 6.45; N, 5.60. Found: C, 57.35; H, 6.21; N, 5.73. X-ray crystal structure analysis: single crystals from CH_2Cl_2; formula, $C_{24}H_{32}N_2O_6Fe$; $M = 500.37$ g mol^{-1}, crystal size $0.5 \times 0.5 \times 0.4$ mm; space group $P4_12_12$ (No. 92); cell parameters $a = b = 11.374(5)$ Å, $c = 18.750(5)$ Å, $V = 2426(2)$ Å^3; $T = -50$ °C; $Z = 4$; $r_{calcd} = 1.370$ g cm^{-1}; $\lambda = 0.710\ 73$ Å; $[(\sin\theta)/\lambda]_{max} = 0.62$ Å^{-1}; $\mu = 6.6$ cm^{-1}; 2780 reflections collected, ($+h$, $+k$, $+l$), 2464 independent and 1795 observed reflections; 156 refined parameters, $R = 0.039$, $R_w^2 = 0.099$.

Preparation of 5h. Lithium cyclopentadienide (136 mg, 1.89 mmol) and 207 mg (1.32 mmol) of **10** were mixed at 0 °C in 40 mL of THF. The reaction mixture was allowed to warm to room temperature and then stirred for 16 h. $FeCl_2$ (115 mg, 0.91 mmol) was added and the mixture was stirred for 1 week at 50 °C. Solvent was removed in vacuo and the product filtered through a short silica gel column with THF (with ca. 1% of triethylamine added). The eluted material (193 mg) was then chromatographed on silica gel with ethyl acetate/ether (1:5, plus 1% of triethylamine) to give 50 mg (16% of **5h**) followed by 108 mg (24%) of **6h**. **5h**: mp 120 °C (DSC); $[\alpha]^D_{20} = -27.2°$ ($c = 0.083$ in CH_2Cl_2). IR (KBr): $\tilde{\nu} = 3321$ cm^{-1} (NH), 1743 (CO_2Me), 1626, 1531 (CONH). ^{1}H NMR ($CDCl_3$): δ 6.14 (br d, $^3J = 8.6$ Hz, 1H, NH), 4.68 (m, 3H, C*H* of C_5H_4R and NHC*H*), 4.35 (m, 2H, C*H* of C_5H_4R), 4.23 (s, 5H, Cp), 2.22 (m, 1H), 0.99 and 0.96 (d, $^3J = 6.9$ Hz, 6H, isopropyl). ^{13}C NMR ($CDCl_3$): δ 172.9 170.3 (*C*ONH and *C*O_2Me), 75.5 (ipso-C of C_5H_4R), 70.5, 68.2 (*C*H of C_5H_4R), 69.7 (Cp), 56.8 (NH*C*H), 52.3 (OCH_3) 31.3, 19.1, 17.9 (isopropyl). Anal. Calcd for $C_{17}H_{21}NO_3Fe$ (343.2): C, 59.49; H, 6.17; N, 4.08. Found: C, 58.88; H, 5.85; N, 4.10. X-ray crystal structure analysis: single crystals from CH_2Cl_2; formula, $C_{17}H_{21}NO_3Fe$; $M = 343.20$ g mol^{-1}, crystal size $0.5 \times 0.4 \times 0.2$ mm; space group $P2_1$ (No. 4); cell parameters $a = 10.084(2)$ Å, $b = 11.182(2)$ Å, $c = 14.364(3)$ Å, $\beta = 92.20(2)°$, $V = 1618.5(5)$ Å^3; $T = -50$ °C; $Z = 4$; $r_{calcd} = 1.408$ g cm^{-3}; $\lambda = 0.710\ 73$ Å; $[(\sin\theta)/\lambda]_{max} = 0.62$ Å^{-1}; $\mu = 9.4$ cm^{-1}; 3644 reflections collected, ($+h$, $+k$, $\pm l$), 3451 independent and 1732 observed reflections; 403 refined parameters, $R = 0.059$, $R_w^2 = 0.113$.

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Supporting Information Available: Details of the X-ray crystal structure determinations of the complexes **5b**, **5c**, **5h**, **6d**, **6h**, and **8b** including tables of bond lengths and angles and positional parameters (47 pages). Ordering information is given on any current masthead page.

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