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# Formation of $\eta^1$-Iminoacyl Compounds by Insertion of Isonitriles in Pentamethylcyclopentadienyl–Tetramethylfulvene Compounds of Titanium and Zirconium. Intramolecular C–H Activation of a Pentamethylcyclopentadienyl Group To Give a Tridentate Ligand with Two Bridged Cyclopentadienyl Rings and a Titanium–Vinyl Bond in the Bridge. Molecular Structure of $[\eta^5{:}\eta^1{:}\eta^5\text{-}C_5Me_4CH_2C(NHXyl){=}CN(Xyl)CH_2C_5Me_4]TiCl$ and $Cp^*[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2C({=}NXyl)C({=}NXyl)]ZrCl$ (Xyl = $2,6\text{-}Me_2C_6H_3$)

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$Cp^*FvMCl$ [$Cp^* = \eta^5\text{-}C_5Me_5$, $Fv = \eta^6\text{-}C_5Me_4CH_2$; M = Ti (**1**), Zr (**2**)] react with $CN(2,6\text{-}Me_2C_6H_3)$ (CNXyl) to give $\eta^1$-iminoacyl complexes $Cp^*[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2C({=}NXyl)]MCl$ [M = Ti (**3**), Zr (**4**)] through insertion of the isonitrile into the $M\text{–}CH_2(Fv)$ bond. Both iminoacyl complexes, **3** and **4**, react with free isonitrile to give a second insertion and coupling of two CNXyl molecules with formation of $Cp^*[\eta^5{:}\eta^1\text{-}C_5Me_4CH_2C({=}NXyl)C({=}NXyl)]MCl$ [M = Ti (**5**), Zr (**6**)]. The molecular structure of **6** shows a typical bent metallocene geometry around zirconium with two coupled isonitrile fragments attached to a cyclopentadienyl ligand and one of them $\eta^1$-bonded through the carbon atom to the metal. Compound **6** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.431$ (2) Å, $b = 16.820$ (5) Å, $c = 16.434$ (3) Å, $\beta = 102.06$ (2)°, $V = 3360$ (1) Å$^3$, and $Z = 4$. The Zr–Cl (2.430 (1) Å) and the Zr–C(iminoacyl) [2.336 (2) Å] bonds are located in the equatorial plane between the cyclopentadienyl ligands [Cl–Zr–C 97.68 (6)°]. Compound **5** rearranges thermally through C–H activation of a methyl substituent on a pentamethylcyclopentadienyl ligand and forms a bis(peralkylcyclopentadienyl)titanium vinyl chloride complex $[\eta^5{:}\eta^1{:}\eta^5\text{-}C_5Me_4CH_2C(NHXyl){=}CN(Xyl)CH_2C_5Me_4]TiCl$ (**7**), in which the cyclopentadienyl ligands are bridged by a $C_3NC$ chain. The bridge itself is bonded to titanium through a regular Ti–C bond, connecting the metal with a C=C fragment of the coupled isonitrile molecules. Crystals of **7** are triclinic, space group $P\bar{1}$, with $a = 8.946$ (1) Å, $b = 13.499$ (3) Å, $c = 16.360$ (3) Å, $\alpha = 102.91$ (1)°, $\beta = 102.81$ (1)°, $\gamma = 108.28$ (1)°, $V = 1735.3$ (6) Å$^3$, and $Z = 2$. The peralkylcyclopentadienyl ligands form a normal bent metallocene, bridged at the front of the wedge by a five-membered chain. The Ti–Cl [2.374 (1) Å] and the Ti–C [2.158 (4) Å] bonds are located in the equatorial plane of the titanocene unit [Cl–Ti–C 97.7 (1)°]. Bridging of the cyclopentadienyl ligands is also found for the zirconium complex **6**, but the main product results from a 1,3-hydrogen shift in the side chain to give a cyclopentadienyl–amide bidentate ligand and formation of $Cp^*[\eta^5{:}\eta^1\text{-}C_5Me_4CH{=}C(CH{=}NXyl)NXyl]ZrCl$ (**8**).

## Introduction

$d^0$ transition metal or lanthanide alkyl complexes react normally with carbon monoxide or isonitriles to give $\eta^2$-acyl or iminoacyl compounds.[1] The high reactivity of the acyl carbon atom as an electrophilic center has been closely related to this coordination mode, and on this basis different mechanisms have been proposed for reactions such as reductive coupling or migration of a coordinated hydride.[2]

We wondered if isonitriles would react with early-transition-metal alkyl complexes to give products in which coordination of the iminoacyl in a $\eta^2$-fashion would be obstructed and if the $\eta^1$-iminoacyl complexes formed in that case would react further with free isonitrile to give diimino species. Fulvene complexes seemed very attractive starting material to us because they can be considered as tucked-in cyclopentadienyl–alkyl complexes.[3] On the other hand, this alkyl group being bonded to the cyclopentadienyl ligand would force the orientation of the iminoacyl group to be with the nitrogen pointing away from the metal center and therefore preventing $\eta^2$-coordination. Formation of $\eta^1$-polyimino ligands has been described for late transition metals to proceed through an insertion process[4] instead of direct attack of the free isonitrile on the iminoacyl carbon proposed for early transition metals.[5]

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(1) (a) Singleton, E.; Oosthuzen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. (b) Durfee, L. D.; Rothwell, I. A. *Chem. Rev.* **1988**, *88*, 1059.

(2) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (c) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56. (d) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467. (e) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffer, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

(3) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, 945.

(4) (a) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 438. (b) Otsuka, S.; Ataka, K. *J. Chem. Soc., Dalton Trans.* **1976**, 327.

(5) (a) Berg, F. J.; Petersen, J. L. *Organometallics* **1989**, *8*, 2461. (b) Chamberlain, L. R.; Durfee, L. D.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.

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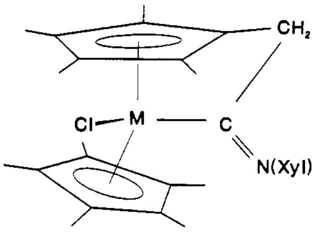

**Figure 1.** Proposed structure for 3 and 4.

## Results and Discussion

Cp*FvMCl [M = Ti (**1**), Zr (**2**)] react instantaneously with CNXyl to give iminoacyl complexes as a result of insertion of the isonitrile into the M–CH$_2$ bond of the fulvene compounds (eq 1). $^1$H NMR spectra or both

$$\mathrm{Cp^*FvMCl} + \mathrm{CNXyl} \rightleftharpoons$$

M = Ti (1), Zr (2)

$$\mathrm{Cp^*[C_5Me_4CH_2\overline{C(NXyl)]M}Cl} \quad (1)$$

M = Ti (3), Zr (4)

complexes, **3** and **4**, prove that the isonitrile has been inserted. The coupling constants of the protons of the methylene group ($^2J_{\mathrm{H-H}}$ = 16.85 Hz for **3** and **4**) are characteristic for coupling of geminal protons in sp$^3$ carbon atoms. The methyl groups of the isonitrile moiety are inequivalent, indicating a very crowded coordination sphere where free rotation of the xylyl group around the N–C bond is prevented. IR spectra show $\nu$(C–N) absorptions at 1574 (**3**) and 1570 cm$^{-1}$ (**4**). Unfortunately, identification of iminoacyl complexes as $\eta^1$ or $\eta^2$ species through IR and NMR data is not possible. For late transition metals, change in the bonding mode from $\eta^1$ to $\eta^2$ is accompanied by an increase of the $\nu$(C–N)[6] values while structurally characterized $\eta^2$-iminoacyl complexes of early transition metals present the $\nu$(C–N) absorption in a very wide range,[7] which makes these data not very useful for identification of the iminoacyl bonding mode. Nevertheless, the special geometric features we have mentioned before make a $\eta^1$ coordination mode in the case of our complexes (Figure 1) very likely. Structural characterization of a derivative (vide infra) confirms our expectation.

Compounds **3** and **4** decompose slowly in solution at room temperature to give back respectively **1** and **2**, together with products, which were identified as the result of two consecutive isonitrile insertions. We interpret this result as evidence for the existence of an equilibrium strongly favorable for the insertion product (eq 1). In fact, $^1$H NMR spectra of **3** in C$_6$D$_6$ show, at room temperature, approximately 5% (in molar concentration) of **1** and free isonitrile. As time goes by, growing of the signals corresponding to **1** and a new compound **5** (vide infra) is observed, while signals corresponding to free isonitrile remain present. Extrusion of CO from acyl complexes is well-known,[8] but this type of reaction has not been reported so far for iminoacyl complexes of early transition metals. Extrusion in the cases of **3** and **4** might be related with the $\eta^1$ coordination, which makes the complexes thermodynamically less stable.

**Table I. Selected Spectroscopic Data for the $\eta^1$-Iminoacyl Complexes**

| compd | IR, cm$^{-1}$ $\nu$(C=N) | $^{13}$C NMR, ppm M-*C*NR |
|---|---|---|
| **3** | 1574 (vs) | 193.86 (s) |
| **4** | 1570 (vs) | 202.82 (s) |
| **5** | 1630 (s), 1595 (m), 1560 (vs) | 228.55 (s) |
| **6** | 1620 (s), 1591 (m), 1594 (s) | 233.48 (s) |

**Table II. Selected Bond Distances (Å) and Angles (deg) for 6**

| | | | |
|---|---|---|---|
| | Distances | | |
| Zr(1)–C(22) | 2.336 (2) | Zr(1)–C(12) | 2.565 (2) |
| Zr(1)–Cl(1) | 2.430 (1) | Zr(1)–C(15) | 2.517 (2) |
| Zr(1)–C(5) | 2.572 (2) | Zr(1)–C(2) | 2.523 (2) |
| N(1)–C(22) | 1.281 (3) | C(20)–C(21) | 1.521 (3) |
| N(2)–C(21) | 1.265 (3) | C(21)–C(22) | 1.512 (3) |
| | Angles | | |
| Cl(1)–Zr(1)–C(22) | 97.68 (6) | C(20)–C(21)–C(22) | 112.5 (2) |
| Zr(1)–C(22)–N(1) | 115.9 (2) | C(21)–N(2)–C(23) | 121.4 (2) |
| Zr(1)–C(22)–C(21) | 121.7 (1) | C(22)–N(1)–C(31) | 125.9 (2) |
| N(1)–C(22)–C(21) | 120.8 (2) | | |

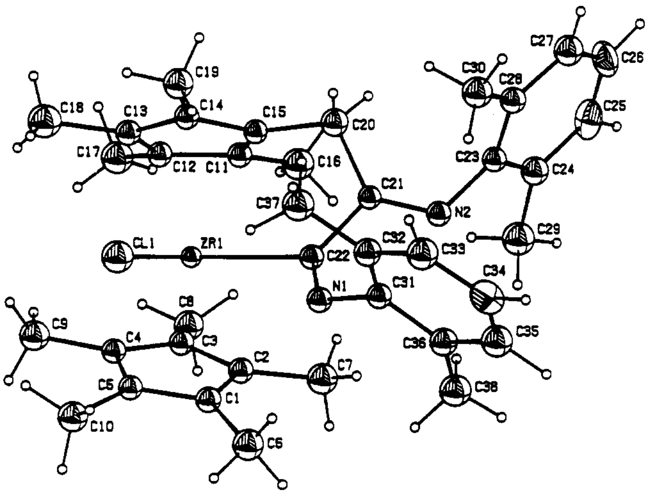

**Figure 2.** ORTEP drawing (50% probability level) of the molecular structure of **6**.

When **1** (**2**) is allowed to react with 2 equiv of CNXyl, complex **5** (**6**) is obtained as the only product (eq 2). Compounds **5** and **6** can also be obtained by reaction of **3** or **4**, respectively, with 1 equiv of CNXyl (eq 3).

$$\mathrm{Cp^*FvMCl} + 2\mathrm{CNXyl} \rightarrow$$

M = Ti (1), Zr (2)

$$\mathrm{Cp^*[C_5Me_4CH_2C({=}NXyl)\overline{C({=}NXyl)]M}Cl} \quad (2)$$

M = Ti (5), Zr (6)

$$\mathbf{3}\ (\mathbf{4}) + \mathrm{CNXyl} \rightarrow \mathbf{5}\ (\mathbf{6}) \qquad (3)$$

$^1$H NMR spectra of both complexes show coupling constants for the protons in the methylene group [15.74 Hz (**5**), 16.50 Hz (**6**)] characteristic for protons bonded to sp$^3$ carbon atoms. Methyl groups in the functionalized Cp* ring are inequivalent, showing four different resonances in each complex. In the same way, four resonances corresponding to the four methyl substituents in the aryl moieties appear, indicating that rotation around the C–N bonds is obstructed. $^{13}$C NMR spectra show two singlets [179.60 and 228.55 ppm (**5**), 179.36 and 233.48 ppm (**6**)], corresponding to the imino (high-field signal) and imino-

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[6] (a) Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41. (b) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L. *Organometallics* **1990**, *9*, 583.

[7] (a) Van Bolhuis, F.; De Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *170*, 299. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556.

[8] (a) Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1974**, *71*, C5. (b) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946. (c) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

**Table III. Selected Bond Distances (Å) and Angles (deg) for 7**

| | | | |
|---|---|---|---|
| Distances | | | |
| Ti(1)-Cl(1) | 2.374 (1) | C(11)-C(20) | 1.373 (6) |
| Ti(1)-C(20) | 2.158 (4) | C(20)-N(2) | 1.422 (5) |
| C(5)-C(10) | 1.492 (6) | N(2)-C(30) | 1.480 (6) |
| C(10)-C(11) | 1.495 (6) | C(30)-C(25) | 1.479 (6) |
| Angles | | | |
| Cl(1)-Ti(1)-C(20) | 97.7 (1) | C(20)-C(11)-C(10) | 118.8 (4) |
| Ti(1)-C(20)-C(11) | 122.4 (3) | C(10)-C(11)-N(1) | 116.5 (4) |
| Ti(1)-C(20)-N(2) | 119.1 (3) | C(11)-C(20)-N(2) | 117.7 (4) |
| C(20)-C(11)-N(1) | 124.7 (4) | | |

acyl (low-field signal) carbon atoms. The shift of the iminoacyl carbon is in the range considered as characteristic for an $\eta^2$ bond,[9] nevertheless the molecular structure of complex 6 proves that nitrogen is not coordinated. This fact invalidates this NMR parameter as conclusive in the assignment of the type of bond present. IR spectra show $\nu$(C-N) vibrations at 1630, 1595, and 1560 cm$^{-1}$ for 5 and 1620, 1591, and 1549 cm$^{-1}$ for 6. (Table I shows selected IR data for the four $\eta^1$-iminoacyl complexes.)

The X-ray crystal structure analysis of 6 reveals a characteristic bent metallocene arrangement of ligands around zirconium (Figure 2). Table II shows a selection of main distances and angles.

Distances from the metal to the ring centers are 2.235 (4) Å for the functionalized cyclopentadienyl group and 2.241 (3) Å for the normal Cp* ring. The angle between the geometrical centers of both rings and the zirconium atom is 137.22 (4)°. These data are in good agreement with those reported for zirconocene complexes.[10] The distance Zr-C(22) is 2.336 (2) Å, considerably longer that those reported for $\eta^2$-iminoacyl zirconium complexes,[11] but within the range of normal Zr-C(alkyl) distances.[12] The dianionic ligand forms a five-membered metallacycle. The orientation of the two aryl groups minimizes steric repulsion between these bulky substituents. Carbon-nitrogen bonds of the imine [C(21)-N(2) = 1.265 (3) Å] and the $\eta^1$-iminoacyl groups [C(22)-N(1) = 1.281 (3) Å] are very similar to and compare well with those found for $\eta^2$-iminoacyl zirconium complexes.[11] The new C-C bonds show distances [C(20)-C(21) = 1.521 (3) and C(21)-C(22) = 1.512 (3) Å] that are normal for single bonds. The distance from the iminoacyl nitrogen to the metal center is 3.117 (2) Å (about 0.9 Å longer that the distances observed in $\eta^2$-iminoacyl zirconium compounds[11]) and rules out a Zr-N bond. The length of the Zr-Cl bond, 2.430 (1) Å, is normal for zirconocene compounds,[13] showing no distortion caused by the bulkiness of the functionalized Cp* ligand.

In $Cp_2MX(\eta^2$-iminoacyl) complexes the metallic center is electronically saturated and subsequent isonitrile insertions are suggested to proceed by direct nucleophilic attack of the free isonitrile on the iminoacyl carbon.[5] However, 3 and 4 are 16-e complexes and coordination of the free isonitrile to the metal and posterior insertion is the most likely pathway for formation of 5 and 6, respectively.

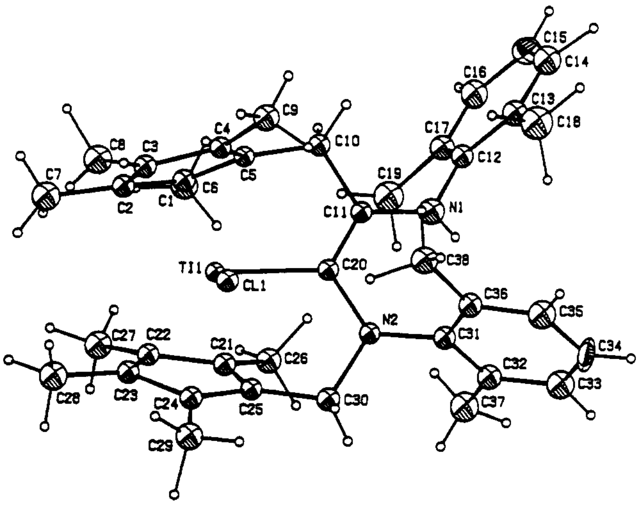

**Figure 3.** ORTEP drawing (50% probability level) of the molecular structure of 7.

When 5 is heated in benzene (or toluene) at about 90 °C, the solution turns green and a green crystalline product 7, with the same elemental composition as 5, can be obtained. Spectroscopic evidence ($^1$H and $^{13}$C NMR, IR) indicates that the Cp* group of 5 has been involved in a reaction to give a compound with two bridged peralkylcyclopentadienyl ligands. The molecular structure of 7 (Figure 3, distances and angles in Table III) reveals what has happened. The compound still can be considered as a $Cp_2Ti(R)Cl$ analogue, with the two cyclopentadienyl ligands bridged at the front of the $Cp_2Ti$ wedge by a five-membered $C_3NC$ chain, which in turn has a carbon atom of a C═C bond linked to titanium, forming a regular Ti—C bond [Ti—C(20) = 2.158 (4) Å]. The distances from titanium to the cyclopentadienyl ring centers [2.083 (2) and 2.101 (2) Å, respectively] and the angle formed by the geometrical center of both rings and titanium [139.5 (1)°] are typical for $Cp^*_2Ti$ derivatives,[14] indicating that the five-atom bridge gives no distortion. The distance Ti—(C(20) is close to other Ti—C(sp$^2$) bonds,[15] and the Ti—Cl distance [2.374 (1) Å] is also as expected.[16] Within the bridge there is a C═C bond [C(20)—C(11) = 1.373 (6) Å], and one of the carbon atoms is $\sigma$-bonded to titanium, thus forming a titanium—vinyl function. The geometry around both nitrogen atoms of the bridge is that of regular sp$^3$ hybridization with N—C distances between 1.397 (6) [N(1)—C(11)] and 1.480 (6) Å [N(2)—C(30)]. The distance N(1)—H(1) [0.80 (4) Å] is also normal.

The $^1$H and $^{13}$C NMR spectra can be fully assigned on the basis of the solid-state structure of 7. The molecule has two different, asymmetric $C_5Me_4CH_2$ groups. Twelve different resonances appear for the twelve inequivalent methyl groups. Both methylene groups show an AB

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[9] (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P. *Organometallics* **1985**, *4*, 1896. (b) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (c) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203. (d) den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509.

[10] (a) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. (b) Schock, L. E.; Brock, C. D.; Marks, T. J. *Organometallics* **1987**, *6*, 232.

[11] (e) Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *2*, 1763. (b) Erker, G.; Korek, U.; Petersen, J. L. *J. Organomet. Chem.* **1988**, *355*, 121.

[12] Hunter, W. E.; Hrncir, D. C.; Vann Bynum, R.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

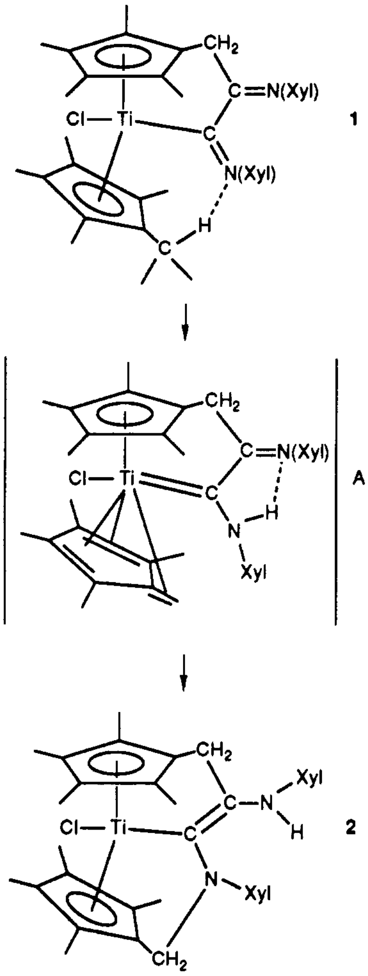
[13] (a) Muir, K. W. *J. Chem. Soc. A* **1971**, 2663. (b) Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *J. Organomet. Chem.* **1974**, *80*, 79. (c) Erker, G.; Frömberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68.

[14] (a) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986**, *5*, 1620. (b) Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 384. (c) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457. (d) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (e) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265.

[15] Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

[16] Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriaty, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51.

Scheme I



pattern in the $^1H$ NMR spectrum with coupling constants characteristic for $sp^3$ C–H bonds. The shift as well as the coupling constant indicates that the low-field AB signal is associated with a $CH_2$–N group and the high-field signal with a $CH_2$–C function. The IR spectrum shows ν(N–H) at 3375 $cm^{-1}$, which indicates that the hydrogen atom is transferred from a Cp* to nitrogen. A broad singlet at 3.93 ppm in the $^1H$ NMR spectrum confirms the presence of an amino proton. $^{13}C$ NMR data are consistent with the structure. A singlet at 227.29 ppm corresponds to a $sp^2$ carbon atom bonded to titanium.

Coupling of isonitrile or carbon monoxide molecules on $d^0$ metal alkyls and posterior rearrangements normally yield compounds containing M–N or M–O bonds,[2c,9b] but here the M–C bond remains. The process observed is reminiscent of the coupling of CO or CO and isonitrile to low-oxidation state Nb or Ta.[17] A possible mechanism for the formation of 7 is given in Scheme I.

The first step is C–H activation in the Cp* ligand, yielding a fulvene complex. In the zirconium compound **6** the distance from the iminoacyl nitrogen, N(1), to the closest hydrogen, H(62), of the Cp* group is 2.32 (3) Å. It is reasonable to assume that in the titanium compound **5** this distance is shorter. In combination with the high nucleophilic character of the nitrogen atom of a $\eta^1$-coordinated iminoacyl this short distance can easily lead to transfer of hydrogen from the Cp* to nitrogen to form an intermediate complex A. C–H activation of Cp* ligands to produce fulvene complexes has been reported for several early transition metals.[18] Subsequent shift of hydrogen to the other nitrogen atom, generation of a carbon–carbon double bond, and coupling with the methylene group of the fulvene in a concerted step will produce 7.

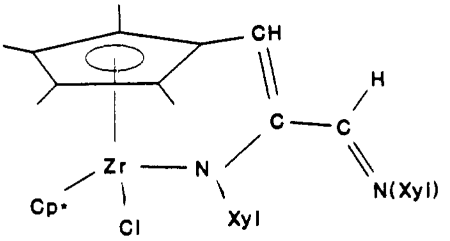


**Figure 4.** Proposed structure for 8.

As mentioned earlier, the distance between the iminoacyl nitrogen and a hydrogen of the Cp* ligand is quite short in **6** and attack of the Cp* group and consequent reactions to form the zirconium analogue of **7** is expected to occur on heating **6**, like **5**, in toluene. This reaction, however, did not take place, and **6** appeared to be stable at 90 °C. The kinetic barrier seems much higher for **6** than for **5**. Heating of **6** in toluene at higher temperatures (>140 °C) gave a mixture of two compounds (NMR analysis). About 15% of the product was identified as an analogue of **7**, indicating that bridging indeed is also possible for zirconium. The main product was synthesized in a separate experiment and identified (IR, NMR, elemental analysis) as $Cp^*[C_5Me_4CH{=}C(CH{=}NXyl)NXyl]ZrCl$, (**8**, Figure 4), where a 1,3-hydrogen shift from the original fulvene methylene group to a carbon atom of the second inserted isonitrile has occurred, with concurrent formation of a Zr–N σ-bond, thus forming a new bidentate peralkylcyclopentadienyl–amide ligand. It is clear that the anticipated ring bridging for zirconium does take place, but other competitive processes at the high temperature needed for conversion make it a less attractive synthetic method than for titanium.

## Conclusions

Tetramethylfulvene complexes Cp*FvMCl (M = Ti, Zr) insert isonitriles in the metal–methylene bond of the fulvene ligand, giving bidentate $\eta^1$-iminoacyl–peralkylcyclopentadienyl ligands. Subsequent isonitrile insertion occurs into the iminoacyl M–C bond and generates a new bidentate $\eta^1$-iminoacyl–cyclopentadienyl ligand with two conjugated C=NR fragments. The $\eta^1$-iminoacyl functionality has a strong nucleophilic nitrogen atom, which can attack a C–H bond of a Cp* ligand to generate, after hydrogen transfer, a tridentate bis(peralkylcyclopentadienyl)carbyl ligand by using the metal as a template. For titanium this represents an excellent method, but for zirconium competitive 1,3-hydrogen shift within the side chain dominates although the bridging reaction does take place as well.

## Experimental Section

All manipulations were carried out under nitrogen by using Schlenk or glovebox techniques. Solvents were distilled from Na/K alloy. $CN(2,6\text{-}Me_2C_6H_3)$ was prepared according to published methods.[19] IR spectra were recorded on a Pye Unicam

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[17] (a) Bianconi, P. A.; Vrtis, R. N.; Rao, C. P.; Williams, I. D.; Engler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968. (b) Vrtis, R. N.; Rao, C. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669. (c) Caraham, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 3230.

[18] (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (b) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (c) den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682.

[19] Shengaki, T.; Takebayashi, M. *Bull. Soc. Chem. Jpn.* **1963**, *36*, 617.

SP3-300 spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on a Varian VXR-300 spectrometer and referenced to residual solvent protons ($^1$H NMR $\delta$ $C_6D_6$ = 7.15 ppm; $^{13}$C NMR $\delta$ $C_6D_6$ = 127.96 ppm). Elemental analyses were carried out at the Micro-Analytical Department of our Laboratory under the supervision of Mr. A. F. Hamminga. Values given are the average of at least two independent determinations.

**Synthesis of Cp*FvTiCl (1).** To Cp*FvTi[20] (0.63 g, 1.99 mmol) in THF (20 mL) was added $PbCl_2$ (0.55 g, 1.98 mmol), and the mixture was stirred at room temperature for 0.5 h. The color changed to green. The solvent was removed under vacuum and the mixture extracted with pentane. After cooling, 1 was isolated as green crystals (0.65 g, 1.84 mmol, 92%). IR (cm$^{-1}$): 3060 (w), 2720 (w), 1070 (w), 1020 (s), 950 (w), 930 (m), 835 (m), 770 (w), 710 (w), 680 (w), 490 (m), 410 (m), 365 (m). Anal. Calcd for $C_{20}H_{29}TiCl$: C, 68.09; H, 8.29; Ti, 13.58; Cl 10.05. Found: C, 67.34; H, 8.18; Ti, 13.35; Cl, 10.12.

**Synthesis of Cp*FvZrCl (2).** $Cp^*_2Zr(CH_2CMe_3)Cl$[21] (3.81 g, 8.13 mmol) was placed in a glass ampule, which was sealed under vacuum and heated in an oven for 1 h at 180 °C. The thermolyzed product was crystallized from pentane to give red crystals of 2 (2.61 g, 6.59 mmol, 81%). IR (cm$^{-1}$): 3040 (w), 2720 (w), 1485 (m), 1420 (m), 1350 (w), 1160 (w), 1070 (w), 1025 (s), 955 (w), 845 (s), 800 (w), 740 (w), 715 (w), 650 (w), 620 (w), 610 (w), 580 (w), 560 (w), 480 (m). Anal. Calcd for $C_{20}H_{29}ZrCl$: C, 60.64; H, 7.38; Cl, 8.95; Zr, 23.03. Found: C, 60.64; H, 7.41; Cl, 8.89; Zr, 23.06.

**Synthesis of Cp*[$\eta^5$:$\eta^1$-$C_5Me_4CH_2C({=}NXyl)$]TiCl (3).** To a solution of 1 (0.30 g, 0.85 mmol) in toluene (10 mL) was added 0.11 g (0.84 mmol) of CNXyl, to give a green precipitate (0.23 g), which, after washing with pentane and drying, was identified as 3. Yield: 56%. IR (cm$^{-1}$): 1574 (vs), 1177 (s), 1088 (m), 1033 (m), 970 (w), 958 (w), 816 (w), 782 (m), 758 (s). $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.42 (s, 3 H), 1.68 (s, 3 H), 1.72 (s, 3 H), 2.03 (s, 15 H), 2.08 (s, 3 H), 2.14 (s, 3 H), 2.43 (s, 3 H), 2.82 (d, 1 H, $^2J_{H-H}$ = 16.85 Hz), 3.33 (d, 1 H, $^2J_{H-H}$ = 16.85 Hz), 7.04 (m, 3 H). $^{13}$C NMR ($C_6D_6$, 75.4 MHz, 20 °C): $\delta$ 10.15 (q, $^1J_{C-H}$ = 126.62 Hz), 11.16 (q, $^1J_{C-H}$ = 126.62 Hz), 11.47 (q, $^1J_{C-H}$ = 126.62 Hz), 12.40 (q, $^1J_{C-H}$ = 126.61 Hz), 15.20 (q, $^1J_{C-H}$ = 127.77 Hz), 18.89 (q, $^1J_{C-H}$ = 125.46 Hz), 19.05 (q, $^1J_{C-H}$ = 126.62 Hz), 32.62 (t, $^1J_{C-H}$ = 131.21 Hz), 113.65 (s), 118.02 (s), 121.59 (s), 122.25 (d, $^1J_{C-H}$ = 158.84 Hz), 123.86 (s), 124.33 (s), 125.71 (s), 126.70 (s), 127.79 (d, $^1J_{C-H}$ = 157.69 Hz), 128.58 (d, $^1J_{C-H}$ = 156.54 Hz), 134.85 (s), 151.85 (s), 193.86 (s). Anal. Calcd for $C_{29}H_{38}NClTi$: C, 72.42; H, 7.33; N, 2.91; Cl, 7.37; Ti, 9.96. Found: C, 71.78; H, 7.89; N, 2.76; Cl, 7.26; Ti, 9.85.

**Synthesis of Cp*[$\eta^5$:$\eta^1$-$C_5Me_4CH_2C({=}NXyl)$]ZrCl (4).** To a solution of 2 (0.21 g, 0.53 mmol) in 5 mL of toluene was slowly added a solution of CNXyl (0.07 g, 0.53 mmol) in 3 mL of toluene. After the mixture was stirred at room temperature for 1 h, the solvent was evaporated to about 1 mL and 4 mL of pentane was slowly added. Solvents were removed by filtration and the bright orange microcrystalline compound was dried under vacuum and identified as 4 (0.18 g, 64%). IR (cm$^{-1}$): 1570 (vs), 1248 (w), 1219 (w), 1177 (s), 1088 (m), 1026 (m), 964 (m), 808 (m), 774 (m), 758 (s), 704 (w), 671 (w), 407 (m). $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.61 (s, 3 H), 1.70 (s, 3 H), 1.86 (s, 3 H), 2.04 (s, 15 H), 2.16 (s, 3 H), 2.18 (s, 3 H), 2.32 (s, 3 H), 3.01 (d, $^2J_{H-H}$ = 16.85 Hz, 1 H), 3.39 (d, $^2J_{H-H}$ = 16.85 Hz, 1 H), 7.09 (m, 3 H). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.4 MHz, 20 °C): $\delta$ 10.30 (s), 10.51 (s), 11.49 (s), 12.01 (s), 13.33 (s), 18.88 (s), 18.92 (s), 33.52 (s), 114.91 (s), 116.09 (s), 119.31 (s), 121.92 (s), 122.26 (s), 122.39 (s), 123.83 (s), 126.07 (s), 127.34 (s), 128.53 (s), 128.65 (s), 153.52 (s), 202.82 (s). Anal. Calcd for $C_{29}H_{38}NClZr$: C, 66.06; H, 7.26; N, 2.66; Cl, 6.72. Found: C, 65.94; H, 7.25; N, 2.73; Cl, 6.95.

**Synthesis of Cp*[$\eta^5$:$\eta^1$-$C_5Me_4CH_2C({=}NXyl)C({=}NXyl)$]TiCl (5).** A solution of 1 (0.54 g, 1.53 mmol) and CNXyl (0.40 g, 3.05 mmol) in 15 mL of toluene was heated at 55 °C during 8 h. The solution was then cooled to room temperature, and the solvent was partially evaporated under vacuum. Slow condensation of pentane into the toluene solution gave 0.68 g of red crystals, which were identified as 5. Yield: 72%. IR (cm$^{-1}$): 3070 (w), 1630 (s), 1595 (m), 1560 (vs), 1200 (m), 1180 (m), 1168 (w), 1092 (m), 1023 (m), 928 (m), 900 (m), 823 (w), 780 (s), 770 (s), 420 (s). $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.26 (s, 3 H), 1.36 (s, 3 H), 1.49 (s, 3 H), 1.64 (s, 3 H), 2.01 (s, 15 H), 2.18 (s, 3 H), 2.22 (s, 3 H), 2.31 (s, 3 H), 2.58 (s, 3 H), 2.69 (d, 1 H, $^2J_{H-H}$ = 15.74 Hz), 2.84 (d, 1 H, $^2J_{H-H}$ = 15.74 Hz), 6.84 (m, 4 H), 6.93 (m, 2 H). $^{13}$C NMR ($C_6D_6$, 75.4 MHz, 2 °C): $\delta$ 10.25 (q, $^1J_{C-H}$ = 126.69 Hz), 11.67 (q, $^1J_{C-H}$ = 126.69 Hz), 11.72 (q, $^1J_{C-H}$ = 126.69 Hz), 12.92 (q, $^1J_{C-H}$ = 126.69 Hz), 13.91 (q, $^1J_{C-H}$ = 126.70 Hz), 17.16 (q, $^1J_{C-H}$ = 126.70 Hz), 19.00 (q, $^1J_{C-H}$ = 126.70 Hz), 20.65 (q, $^1J_{C-H}$ = 124.68 Hz), 21.37 (q, $^1J_{C-H}$ = 126.70 Hz), 26.41 (dd, $^1J_{C-H}$ = 126.69, 128.71 Hz), 115.94 (s), 121.72 (d, $^1J_{C-H}$ = 158.87 Hz), 121.85 (s), 123.11 (s), 123.64 (d, $^1J_{C-H}$ = 158.87 Hz), 124.31 (s), 126.04 (s), 126.23 (s), 126.49 (s), 127.16 (s), 127.51 (d, $^1J_{C-H}$ = 160.89 Hz), 128.07 (d, $^1J_{C-H}$ = 154.85 Hz), 128.49 (s), 128.63 (d, $^1J_{C-H}$ = 158.87 Hz), 128.76 (s), 128.84 (d, $^1J_{C-H}$ = 156.86 Hz), 147.24 (s), 154.09 (s), 179.60 (s), 228.55 (s). Anal. Calcd for $C_{38}H_{47}N_2ClTi$: C, 74.19; H, 7.70; N, 4.55; Cl, 5.76; Ti, 7.78. Found: C, 74.30; H, 7.71; N, 4.30; Cl, 5.70; Ti, 7.78.

**Synthesis of Cp*[$\eta^5$:$\eta^1$-$C_5Me_4CH_2C({=}NXyl)C({=}NXyl)$]ZrCl (6).** A solution of 2 (0.35 g, 0.88 mmol) and CNXyl (0.23 g, 1.76 mmol) in 10 mL of toluene was stirred for 3 h at room temperature. The solvent was partially evaporated under vacuum, and after slow condensation of pentane and posterior filtration, 0.38 g of 6 was isolated. Yield: 66%. IR (cm$^{-1}$): 1620 (s), 1591 (m), 1549 (s), 1377 (s), 1194 (m), 1171 (m), 1090 (m), 1028 (m), 928 (m), 762 (s). $^1$H NMR ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.36 (s, 3 H), 1.48 (s, 3 H), 1.66 (s, 3 H), 1.70 (s, 3 H), 1.98 (s, 15 H), 2.04 (s, 3 H), 2.17 (s, 3 H), 2.27 (s, 3 H), 2.36 (s, 3 H), 2.72 (d, $^2J_{H-H}$ = 16.5 Hz, 1 H), 2.86 (d, $^2J_{H-H}$ = 16.5 Hz, 1 H), 6.86 (m, 6 H). $^{13}$C NMR ($C_6D_6$, 75.4 MHz, 20 °C): $\delta$ 10.24 (q, $^1J_{C-H}$ = 127.19 Hz), 11.08 (q, $^1J_{C-H}$ = 127.19 Hz), 11.67 (q, $^1J_{C-H}$ = 127.19 Hz), 12.11 (q, $^1J_{C-H}$ = 127.19 Hz), 12.64 (q, $^1J_{C-H}$ = 127.19 Hz), 17.19 (q, $^1J_{C-H}$ = 121.21 Hz), 18.81 (q, $^1J_{C-H}$ = 122.70 Hz), 20.33 (q, $^1J_{C-H}$ = 125.69 Hz), 20.62 (q, $^1J_{C-H}$ = 127.19 Hz), 27.24 (dd, $^1J_{C-H}$ = 127.19, 131.68 Hz), 113.08 (s), 118.97 (s), 120.40 (s), 122.31 (d, $^1J_{C-H}$ = 158.61 Hz), 122.39 (s), 123.52 (d, $^1J_{C-H}$ = 160.13 Hz), 123.75 (s), 124.09 (s), 124.53 (s), 127.53 (s), 127.64 (d, $^1J_{C-H}$ = 161.11 Hz), 127.78 (d, $^1J_{C-H}$ = 155.62 Hz), 127.86 (s), 128.12 (d, $^1J_{C-H}$ = 160.11 Hz), 128.65 (s), 128.77 (d, $^1J_{C-H}$ = 157.11 Hz), 147.6 (s), 153.19 (s), 179.36 (s), 233.48 (s). Anal. Calcd for $C_{38}H_{47}N_2ClZr$: C, 69.32; H, 7.19; Cl, 5.38. Found: C, 69.46; H, 7.25; Cl, 5.48.

**Synthesis of [$\eta^5$:$\eta^1$:$\eta^5$-$C_5Me_4CH_2C(NHXyl){=}CN(Xyl)$-$CH_2C_5Me_4$]TiCl (7).** An ampule containing 0.66 g (1.07 mmol) of 5 in 10 mL of benzene was heated at 90 °C during 14 h. Afterwards, pentane was slowly condensed onto the benzene solution. Green crystals were obtained and identified as 7. Yield: 0.42 g (0.64 mmol, 60%). IR (cm$^{-1}$): 3375 (s), 1519 (vs), 1324 (m), 1259 (s), 1233 (s), 1207 (m), 1162 (w), 1142 (w), 1103 (w), 1035 (w), 1012 (w), 765 (s), 687 (s), 459 (m). $^1$H NMR of 7 ($C_6D_6$, 300 MHz, 20 °C): $\delta$ 1.50 (s, 3 H), 1.70 (s, 3 H), 1.77 (s, 3 H), 1.78 (s, 3 H), 1.79 (s, 3 H), 1.94 (s, 3 H), 2.04 (s, 3 H), 2.22 (s, 3 H), 2.29 (s, 3 H), 2.42 (s, 3 H), 2.43 (s, 3 H), 2.49 (s, 3 H), 2.81 (d, 1 H, $^2J_{H-H}$ = 17.58 Hz), 3.12 (d, 1 H, $^2J_{H-H}$ = 17.58 Hz), 3.93 (s, 1 H), 4.19 (d, 1 H, $^2J_{H-H}$ = 11.72 Hz), 4.37 (d, 1 H, $^2J_{H-H}$ = 11.72 Hz), 6.83 (m, 4 H), 6.91 (m, 1 H), 6.99 (m, 1 H). $^{13}$C NMR ($C_6D_6$, 75.4 MHz, 20 °C): $\delta$ 9.65 (q, $^1J_{C-H}$ = 126.33 Hz), 10.49 (q, $^1J_{C-H}$ = 126.33 Hz), 11.24 (q, $^1J_{C-H}$ = 126.33 Hz), 11.52 (q, $^1J_{C-H}$ = 126.34 Hz), 12.54 (q, $^1J_{C-H}$ = 126.33 Hz), 13.13 (q, $^1J_{C-H}$ = 126.33 Hz), 13.58 (q, $^1J_{C-H}$ = 126.34 hz), 15.9 (q, $^1J_{C-H}$ = 127.73 Hz), 18.24 (q, $^1J_{C-H}$ = 126.33 Hz), 18.67 (q, $^1J_{C-H}$ = 126.33), 20.22 (q, $^1J_{C-H}$ = 126.33 Hz), 21.13 (q, $^1J_{C-H}$ = 127.74 Hz), 30.04 (dd, $^1J_{C-H}$ = 126.33, 127.74 Hz), 50.37 (t, $^1J_{C-H}$ = 136.16 Hz), 112.19 (s), 115.28 (s), 116.60 (s), 117.91 (s), 118.57 (s), 121.37 (s), 123.01 (s), 125.23 (d, $^1J_{C-H}$ = 160.02 Hz), 125.4 (d, $^1J_{C-H}$ = 158.62 Hz), 125.55 (s), 127.37 (s), 127.80 (d, $^1J_{C-H}$ = 157.21 Hz), 128.44 (d, $^1J_{C-H}$ = 157.21 Hz), 128.62 (s), 128.94 (d, $^1J_{C-H}$ = 155.82 Hz), 129.21 (s), 129.8 (d, $^1J_{C-H}$ = 160.02 Hz), 134.72 (s), 135.53 (s), 137.79 (s), 138.24 (s), 149.11 (s), 149.52 (s), 227.29 (s). Anal. Calcd for $C_{38}H_{47}N_2ClTi$: C, 74.19; H, 7.70; N, 4.55; Cl, 5.76; Ti, 7.78. Found: C, 74.27; H, 7.74; N, 4.51; Cl, 5.72; Ti, 7.80. When 7 is crystallized from hot, concentrated

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(20) Pattiasina, J. W.; Hissink, C. E.; De Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 7758.

(21) $Cp^*_2Zr(CH_2CMe_3)Cl$ was made from $Cp^*_2ZrCl_2$ and $Me_3CCH_2Li$ in THF: Pattiasian, J. W. Doctoral Thesis, Groningen University, Groningen, The Netherlands, 1988.

**Table IV. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms (Esd's in Parentheses) for 6**

| atom | $x$ | $y$ | $z$ | $U_{eq}$, Å$^{2\,a}$ |
|---|---|---|---|---|
| Zr(1) | 0.12756 (2) | 0.23815 (1) | 0.07522 (1) | 0.0129 (1) |
| Cl(1) | 0.31323 (5) | 0.18911 (4) | 0.12647 (4) | 0.0314 (2) |
| N(1) | 0.1193 (1) | 0.2204 (1) | 0.2626 (1) | 0.0189 (6) |
| N(2) | -0.1125 (1) | 0.1675 (1) | 0.2316 (1) | 0.0183 (6) |
| C(1) | 0.1657 (2) | 0.3738 (1) | 0.1474 (1) | 0.0195 (7) |
| C(2) | 0.0569 (2) | 0.3753 (1) | 0.0979 (1) | 0.0195 (7) |
| C(3) | 0.0644 (2) | 0.3725 (1) | 0.0129 (1) | 0.0196 (7) |
| C(4) | 0.1775 (2) | 0.3653 (1) | 0.0098 (1) | 0.0177 (7) |
| C(5) | 0.2397 (2) | 0.3678 (1) | 0.0929 (1) | 0.0178 (7) |
| C(6) | 0.1980 (3) | 0.3874 (2) | 0.2394 (2) | 0.0301 (9) |
| C(7) | -0.0471 (2) | 0.3903 (2) | 0.1288 (2) | 0.0290 (9) |
| C(8) | -0.0277 (2) | 0.3935 (2) | -0.0585 (2) | 0.0268 (8) |
| C(9) | 0.2272 (2) | 0.3676 (2) | -0.0662 (2) | 0.0272 (9) |
| C(10) | 0.3626 (2) | 0.3730 (2) | 0.1180 (2) | 0.0276 (8) |
| C(11) | -0.0445 (2) | 0.1779 (1) | -0.0130 (1) | 0.0185 (7) |
| C(12) | 0.0305 (2) | 0.1853 (1) | -0.0677 (1) | 0.0196 (7) |
| C(13) | 0.1209 (2) | 0.1344 (1) | -0.0383 (1) | 0.0196 (7) |
| C(14) | 0.1013 (2) | 0.0929 (1) | 0.0324 (1) | 0.0188 (7) |
| C(15) | -0.0003 (2) | 0.1207 (1) | 0.0477 (1) | 0.0173 (7) |
| C(16) | -0.1593 (2) | 0.2111 (2) | -0.0249 (2) | 0.0300 (8) |
| C(17) | 0.0079 (3) | 0.2237 (2) | -0.1522 (2) | 0.0318 (9) |
| C(18) | 0.2165 (2) | 0.1212 (2) | -0.0797 (2) | 0.034 (1) |
| C(19) | 0.1700 (2) | 0.0265 (2) | 0.0770 (2) | 0.0283 (8) |
| C(20) | -0.0554 (2) | 0.0934 (1) | 0.1160 (2) | 0.0236 (8) |
| C(21) | -0.0448 (2) | 0.1547 (1) | 0.1853 (1) | 0.0163 (6) |
| C(22) | 0.0562 (2) | 0.2063 (1) | 0.1918 (1) | 0.0173 (7) |
| C(23) | -0.2091 (2) | 0.1213 (1) | 0.2250 (1) | 0.0183 (7) |
| C(24) | -0.3105 (2) | 0.1604 (2) | 0.1989 (1) | 0.0244 (8) |
| C(25) | -0.4064 (2) | 0.1171 (2) | 0.1924 (2) | 0.0340 (9) |
| C(26) | -0.4043 (2) | 0.0374 (2) | 0.2133 (2) | 0.036 (1) |
| C(27) | -0.3043 (2) | 0.0005 (2) | 0.2432 (2) | 0.0286 (9) |
| C(28) | -0.2057 (2) | 0.0415 (1) | 0.2501 (1) | 0.0205 (7) |
| C(29) | -0.3120 (2) | 0.2478 (2) | 0.1798 (2) | 0.0333 (9) |
| C(30) | -0.0989 (2) | 0.0013 (2) | 0.2885 (2) | 0.0289 (9) |
| C(31) | 0.1062 (2) | 0.1891 (1) | 0.3408 (1) | 0.0189 (7) |
| C(32) | 0.1624 (2) | 0.1188 (1) | 0.3679 (1) | 0.0234 (7) |
| C(33) | 0.1603 (2) | 0.0911 (2) | 0.4482 (2) | 0.0308 (8) |
| C(34) | 0.1048 (2) | 0.1319 (2) | 0.4993 (2) | 0.0348 (9) |
| C(35) | 0.0513 (2) | 0.2023 (2) | 0.4717 (2) | 0.0308 (8) |
| C(36) | 0.0517 (2) | 0.2325 (2) | 0.3932 (1) | 0.0234 (7) |
| C(37) | 0.2216 (2) | 0.0744 (2) | 0.3120 (2) | 0.0302 (8) |
| C(38) | -0.0055 (2) | 0.3093 (2) | 0.3657 (2) | 0.0298 (9) |

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

**Table V. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms (Esd's in Parentheses) for 7**

| atom | $x$ | $y$ | $z$ | $U_{eq}$, Å$^{2\,a}$ |
|---|---|---|---|---|
| | | Residue 1 | | |
| Ti(1) | 0.16260 (9) | 0.21354 (6) | 0.30673 (5) | 0.0119 (2) |
| Cl(1) | 0.3537 (1) | 0.14163 (8) | 0.26361 (7) | 0.0164 (3) |
| N(1) | 0.2137 (5) | 0.5060 (3) | 0.2156 (2) | 0.022 (1) |
| N(2) | 0.0904 (4) | 0.2755 (3) | 0.1343 (2) | 0.014 (1) |
| C(1) | 0.1729 (5) | 0.3433 (3) | 0.4338 (3) | 0.016 (1) |
| C(2) | 0.2129 (5) | 0.2619 (3) | 0.4651 (3) | 0.017 (1) |
| C(3) | 0.3653 (5) | 0.2635 (3) | 0.4530 (3) | 0.017 (1) |
| C(4) | 0.4207 (5) | 0.3470 (3) | 0.4147 (3) | 0.015 (1) |
| C(5) | 0.3035 (5) | 0.3961 (3) | 0.4027 (3) | 0.014 (1) |
| C(6) | 0.0369 (5) | 0.3834 (4) | 0.4448 (3) | 0.024 (2) |
| C(7) | 0.1324 (6) | 0.1999 (4) | 0.5196 (3) | 0.028 (2) |
| C(8) | 0.4579 (5) | 0.1972 (4) | 0.4827 (3) | 0.027 (2) |
| C(9) | 0.5823 (5) | 0.3840 (3) | 0.3957 (3) | 0.022 (2) |
| C(10) | 0.3119 (5) | 0.4844 (3) | 0.3609 (3) | 0.016 (1) |
| C(11) | 0.2266 (5) | 0.4337 (3) | 0.2635 (3) | 0.014 (1) |
| C(12) | 0.2534 (5) | 0.6209 (3) | 0.2530 (3) | 0.018 (1) |
| C(13) | 0.3852 (5) | 0.6970 (3) | 0.2460 (3) | 0.021 (2) |
| C(14) | 0.4278 (6) | 0.8089 (4) | 0.2785 (3) | 0.028 (2) |
| C(15) | 0.3241 (6) | 0.8448 (4) | 0.3175 (3) | 0.029 (2) |
| C(16) | 0.1861 (6) | 0.7681 (4) | 0.3241 (3) | 0.027 (2) |
| C(17) | 0.1457 (5) | 0.6564 (3) | 0.2914 (3) | 0.020 (2) |
| C(18) | 0.5090 (6) | 0.6588 (4) | 0.2047 (4) | 0.35 (2) |
| C(19) | -0.0137 (6) | 0.5747 (4) | 0.2924 (3) | 0.032 (2) |
| C(20) | 0.1703 (5) | 0.3216 (3) | 0.2271 (3) | 0.014 (1) |
| C(21) | -0.1260 (5) | 0.1632 (3) | 0.2300 (3) | 0.016 (1) |
| C(22) | -0.1307 (5) | 0.1113 (3) | 0.2958 (3) | 0.015 (1) |
| C(23) | -0.0537 (5) | 0.0338 (3) | 0.2799 (3) | 0.016 (1) |
| C(24) | -0.0123 (5) | 0.0323 (3) | 0.2009 (3) | 0.016 (1) |
| C(25) | -0.0476 (5) | 0.1163 (3) | 0.1721 (3) | 0.015 (1) |
| C(26) | -0.2105 (5) | 0.2410 (3) | 0.2129 (3) | 0.20 (1) |
| C(27) | -0.2328 (5) | 0.1166 (4) | 0.3559 (3) | 0.024 (2) |
| C(28) | -0.0441 (6) | -0.0476 (4) | 0.3287 (3) | 0.027 (2) |
| C(29) | 0.0364 (5) | -0.0540 (3) | 0.1517 (3) | 0.023 (2) |
| C(30) | -0.0039 (5) | 0.1551 (3) | 0.0996 (3) | 0.017 (1) |
| C(31) | 0.1439 (5) | 0.3192 (3) | 0.0687 (3) | 0.017 (1) |
| C(32) | 0.0271 (5) | 0.3355 (3) | 0.0043 (3) | 0.020 (2) |
| C(33) | 0.0760 (6) | 0.3712 (4) | -0.0628 (3) | 0.027 (2) |
| C(34) | 0.2352 (6) | 0.3916 (4) | -0.0665 (3) | 0.031 (2) |
| C(35) | 0.3500 (6) | 0.3787 (4) | -0.0026 (3) | 0.027 (2) |
| C(36) | 0.3081 (5) | 0.3424 (3) | 0.0662 (3) | 0.020 (2) |
| C(37) | -0.1429 (6) | 0.3198 (4) | 0.0097 (3) | 0.030 (2) |
| C(38) | 0.4381 (5) | 0.3315 (4) | 0.1358 (3) | 0.024 (2) |
| | | Residue 2[b] | | |
| C(39) | 0.42637 | 0.02019 | 0.04617 | 0.05060 |
| C(40) | 0.38459 | 0.08231 | -0.00425 | 0.04970 |
| C(41) | 0.43857 | 0.08852 | -0.07589 | 0.02700 |
| C(42) | 0.53433 | 0.03251 | -0.09713 | 0.04900 |
| C(43) | 0.57622 | -0.02962 | -0.04662 | 0.03960 |
| C(44) | 0.52223 | -0.03583 | 0.02503 | 0.04320 |

[a] $U$(eq) = one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] For the benzene with a site occupancy factor of 0.5.

benzene the solvate $7{\cdot}(C_6H_6)_{0.5}$ is obtained.

**Synthesis of $Cp^*[\eta^5{:}\eta^1\text{-}C_5Me_4CH{=}C(CH{=}NXyl)\overline{NXyl]\text{-}}$ZrCl (8).** An ampule, sealed under vacuum, containing 0.65 g (0.99 mmol) 6 and 20 mL of toluene was kept at 140 °C for 14 h. The solution was cooled to room temperature, and the solvent was removed in vacuum. The residue was extracted with pentane and the solution cooled to -30 °C. Compound 8 separated and was isolated. Yield: 0.35 g (54%). IR (cm$^{-1}$): 1635 (s), 1610 (s), 1595 (s), 1280 (s), 1260 (w), 1200 (vs), 1155 (w), 1110 (m), 960 (m), 880 (m), 860 (m), 770 (s), 745 (w), 740 (w), 525 (w). $^1$H NMR (90 MHz, $C_6D_6$): $\delta$ 1.53 (s, 15 H), 1.68 (s, 3 H), 1.82 (s, 3 H), 1.98 (s, 6 H), 2.04 (s, 3 H), 2.29 (s, 3 H), 2.30 (s, 3 H), 2.36 (s, 3 H), 6.27 (s, 1 H), 6.84 (m, 6 H), 7.03 (s, 1 H). $^{13}$C NMR (75.4 MHz, $C_6D_6$, 20 °C): $\delta$ 10.05 (q, $^1J_{C-H}$ = 127.07 Hz), 10.42 (q, $^1J_{C-H}$ = 127.07 Hz), 11.33 (q, $^1J_{C-H}$ = 127.08 Hz), 12.50 (q, $^1J_{C-H}$ = 127.08 Hz), 13.70 (q, $^1J_{C-H}$ = 128.46 Hz), 18.26 (q, $^1J_{C-H}$ = 127.07 Hz), 20.89 (q, $^1J_{C-H}$ = 125.69 Hz), 21.71 (q, $^1J_{C-H}$ = 125.69 Hz), 101.22 (d, $^1J_{C-H}$ = 167.13 Hz), 118.57 (s), 120.09 (s), 121.5 (s), 122.5 (d, $^1J_{C-H}$ = 157.67 Hz), 123.57 (d, $^1J_{C-H}$ = 158.84 Hz), 125.26 (d, $^1J_{C-H}$ = 158.84 Hz), 127.15 (d, $^1J_{C-H}$ = 158.84 Hz), 128.60 (d, $^1J_{C-H}$ = 158.84 Hz), 128.86 (s), 129.22 (s), 134.72 (s), 137.50 (s), 138.18 (s), 139.04 (s), 151.22 (s), 159.52 (d, $^1J_{C-H}$ = 161.61 Hz), 166.87 (s). Anal. Calcd for $C_{38}H_{47}N_2ClZr$: C, 69.32; H, 7.19; N, 4.25. Found: C, 69.57; H, 7.46; N, 4.12.

**Structure Determination of 6 and 7.** Crystals for this study were selected and glued on a glass fiber in a drybox, transferred to the goniostat, cooled to 130 K by using an on-line liquid nitrogen cooling system, and mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Precise lattice parameters and their standard deviations were derived from the angular settings of 22 reflections in the range 13.46° < $\theta$ < 16.62° for 6 and 11.85° < $\theta$ < 19.17° for 7. Selected data on the structure determination are given in Tables IV and V. The structures were solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[22] For 6 positional and anisotropic thermal parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (XTAL[19]), minimizing the function $Q = \sum_h[w(|F_o| - |F_c|)^2]$. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms. The crystal exhibited some secondary extinction for which the $F_o$ values were corrected by refinement of an empirical isotropic extinction parameter.[23] Weights were introduced in the final refinement cycles. Final refinement on $F$ by full-matrix least-squares tech-

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(22) Sheldrick, G. M. *SHELXS86, Program for crystal structure solution*; University of Göttingen: Federal Republic of Germany, 1986.

(23) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

Table VI. Crystal Data for 6 and 7

| compd | 6 | 7 |
|---|---|---|
| empirical formula | $C_{38}H_{47}ZrClN_2$ | $C_{38}H_{47}TiClN_2(C_6H_6)_{0.5}$ |
| mol wt | 658.48 | 654.19 |
| cryst syst | monoclinic | triclinic |
| space group | $P2_1/n$ | $P\bar{1}$ |
| $a$, Å | 12.431 (2) | 8.946 (1) |
| $b$, Å | 16.820 (5) | 13.499 (3) |
| $c$, Å | 16.434 (3) | 16.360 (3) |
| $\alpha$, deg | | 102.91 (1) |
| $\beta$, deg | 102.06 (2) | 102.81 (1) |
| $\gamma$, deg | | 108.28 (1) |
| $V$, Å$^3$ | 3360 (1) | 1735.3 (6) |
| $Z$ | 4 | 2 |
| $F(000)$, electrons | 1384 | 698 |
| $d_{calc}$, g·cm$^{-3}$ | 1.301 | 1.252 |
| $\mu$(Mo K$\bar{\alpha}$), cm$^{-1}$ | 4.3 | 3.5 |
| approx cryst dimens, mm | 0.12 × 0.35 × 0.38 | 0.05 × 0.07 × 0.37 |
| $\lambda$(Mo K$\bar{\alpha}$ radiation), Å | 0.71073 | 0.71073 |
| monochromator | graphite | graphite |
| $\theta$ range (min, max), deg | 1.21, 25.0 | 1.21, 25.0 |
| $\omega/2\theta$ scan, deg | $\Delta\omega = 1.05 + 0.35 \tan\theta$ | $\Delta\omega = 0.75 + 0.35 \tan\theta$ |
| X-ray exposure time, h | 151.2 | 134.8 |
| total no. of data | 6810 | 6808 |
| no. of unique data | 5901 | 6100 |
| no. of obsd data ($I \geq 2.5\sigma(I)$) | 5012 | 4156 |
| no. of refined params | 568 | 568 |
| final agreement factors: | | |
| $R_F = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$ | 0.031 | 0.052 |
| $R_w = [\sum(w(\lvert F_o\rvert - \lvert F_c\rvert)^2)/\sum w\lvert F_o\rvert^2]^{1/2}$ | 0.039 | 0.051 |
| weighting scheme | $1/\sigma^2(F)$ | $1/\sigma^2(F)$ |
| max (shift/$\sigma$) final cycle | 0.353 | 0.548 |
| av (shift/$\sigma$) final cycle | 0.012 | 0.012 |

niques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged to a conventional $R_F$ factor of 0.031 ($R_w$ = 0.039). A final difference Fourier map did not show residual peaks outside the range ±0.67 e/Å$^3$. For 7 all the non-hydrogen positions and the heavily disordered benzene solvate molecule could be located, but the disordered benzene molecule parameters were not well behaved during the refinement. The benzene molecule is disordered over an inversion center. Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of all the nonsolvate hydrogen atoms. The coordinates for the carbon and hydrogen atoms of the benzene molecule were ultimately calculated by fitting the observed peaks to an idealized benzene structure (C–H = 1.38 and C–H = 0.98 Å, respectively) and a site occupancy factor of 0.5 for all the atom positions, due to the disorder. Refinement of the benzene solvate as a rigid body with anisotropic temperature factors for the carbon atoms and one common for the hydrogen atoms did not refine well and so the benzene solvate was ultimately included in the structure factor calculations but not refined. Following the inclusion of the benzene, the remainder of the structure refined smoothly. Weights were introduced in the final refinement cycles. Refinement on $F$ by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged at $R_F$ = 0.052 ($R_w$ = 0.051). A final difference Fourier map did not show unusual features (−0.59 and +0.78 e/Å$^3$, respectively), except one peak with an electron density of 1.80 e/Å$^3$ in the vicinity of the disordered benzene. Scattering factors were taken from Cromer and Mann.[24] Anomalous dispersion factors are those given by Cromer and Liberman.[25] All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL[26] and EUCLID[27] (calculation of geometric data).

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**Supplementary Material Available:** Tables of thermal parameters, atomic coordinates and isotropic displacement parameters, bond distances, and angles and torsion angles for 6 and 7 (26 pages); listings of observed and calculated structure factors for 6 and 7 (47 pages). Ordering information is given on any current masthead page.

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(24) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(25) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(26) Hall, S. R.; Stewart, J. M. *XTAL2.6 User's Manual.* University of Western Australia, Perth, Australia, and University of Maryland: College Park, MD, 1989.

(27) Spek, A. L. The Euclid Package. In *Computational Crystallography*; Sayre, D., Ed.; Oxford University Press (Clarendon): London/New York, 1982; p 528.