DALTON
FULL PAPER

Formation and structural properties of 1,1′,2,2′-tetra(*tert*-butylcarbamoyl)-ferrocene and -ruthenocene †

Katrin Klaß, Roland Fröhlich and Gerhard Erker *

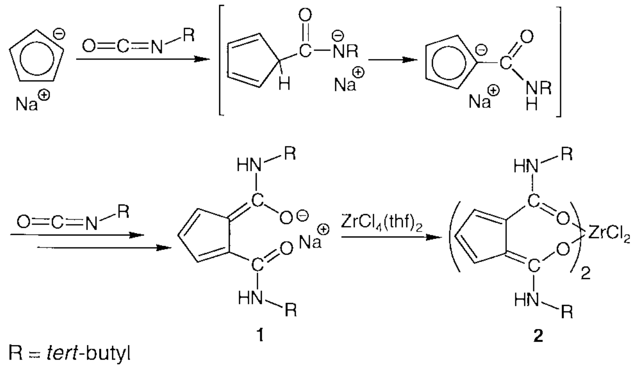
Organisch-Chemisches Institut der Universität Münster, Corrensstr. 40, D-48149 Münster, Germany. E-mail: erker@uni-muenster.de, fax: +49(251)83 36503

Received 12th August 1999, Accepted 28th October 1999

Sodium cyclopentadienide adds two molar equivalents of *tert*-butylisocyanate to yield the 1,2-bis(*N*-*tert*-butylcarbamoyl)cyclopentadienide reagent **1**. This reacts with $RuCl_2(PPh_3)_4$ **3** in a 2 : 1 stoichiometry to yield the metallocene $[\eta^5\text{-}C_5H_3(CONHCMe_3)_2]_2Ru$ **5**. Complex **5** was characterized by an X-ray crystal structure analysis. It shows a near to eclipsed C_2-symmetric metallocene conformation with the carboxamide substituents pairwise connected by intramolecular hydrogen bridges between –CONHR groups attached to different Cp ligands. The intermediate of the substitution reaction sequence, the complex $[\eta^5\text{-}C_5H_3(CONHCMe_3)_2]RuCl(PPh_3)_2$ **4**, was also isolated and characterized by X-ray diffraction. Treatment of **1** with $FeCl_2$ (2 : 1) yields 1,1′,2,2′-tetra(*N*-*tert*-butylcarbamoyl)ferrocene **6**. The X-ray crystal structure analysis of **6** features a staggered C_i metallocene conformation.

Introduction

1,2-Disubstituted acyl- or carboxylate-substituted metallocenes are not easy to synthesize selectively by means of electrophilic aromatic substitution[1] or related arene substitution reactions at the intact metallocene nucleus.[2] Therefore, other pathways that introduce the required substituent pattern at the stage of the ligand synthesis, prior to its attachment to the transition metal, are of value for this synthetic target.[3] We have recently shown[4] that the two-fold addition of an alkylisocyanate to cyclopentadienide directly leads to the selective formation of a 1,2-carboxamide-substituted cyclopentadienyl anion reagent.[5] Thus treatment of CpNa with two molar equivalents of *tert*-butylisocyanate resulted in the formation of **1**. Its subsequent reaction with Group 4 metal halides did not, however, lead to the formation of the respective $\eta^5\text{-}C_5H_3(CONHR)_2$ metal complexes.[6] The formation of strong metal to oxygen bonds[7] was found to be favored, resulting *e.g.* in the clean synthesis of the respective $[\kappa^2\text{-}O,O\text{-}C_5H_3(CONHR)_2]$Zr-chelate complexes (*i.e.* **2** from **1** and $ZrCl_4$)[4,5] (see Scheme 1).

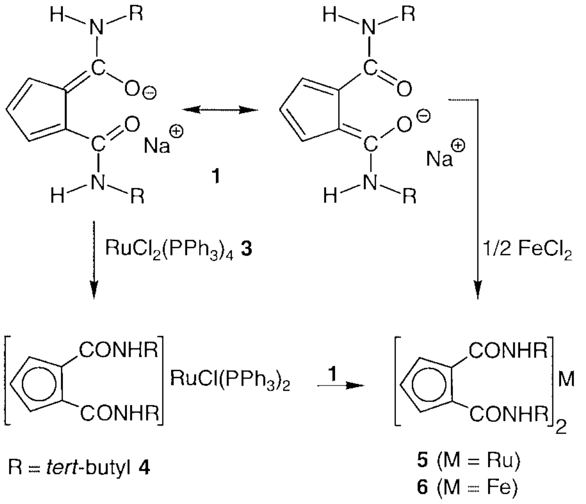


Scheme 1 Synthesis and reactions of the ligand system **1**.

We expected that metal–oxygen bond formation would probably not be dominant in the related chemistry of late transition metals in combination with the $[C_5H_3(CONHR)_2]^-$ ligand system. This was confirmed by treatment of the reagent **1** with Group 8 metal halides.

Results and discussion

The reagent **1** was prepared as described previously[4] by treatment of sodium cyclopentadienide with two molar equivalents of *tert*-butylisocyanate in tetrahydrofuran at 0 °C. After workup at ambient temperature sodium-1,2-bis(*tert*-butylcarbamoyl)cyclopentadienide **1** was isolated as an off-white solid in 96% yield. It shows characteristic ^1H NMR signals at δ 7.90 (NH), 6.73 (d, 2H) and 6.25 (t, 1H, $^3J_{HH} = 3.6$ Hz, C_5H_3), and at 1.44 (s, *tert*-butyl, CMe_3, in benzene-d_6–THF-d_8, 10 : 1.5). The ^{13}C NMR signals of the C_5H_3-core of **1** appear at δ 116.4 (*ipso*-C), 115.1 and 108.8 (C-2, C-3). The reagent **1** was then reacted with $RuCl_2(PPh_3)_4$ **3** (see Scheme 2).



Scheme 2 Syntheses of the 1,1′,2,2′-tetracarbamoylmetallocenes **5** and **6**.

The reaction required stirring overnight at elevated temperature (40 °C in toluene) to go to completion. Under these conditions both chloride ligands at ruthenium are replaced by the ligand system **1** with formation of sodium chloride. During

---

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4457/

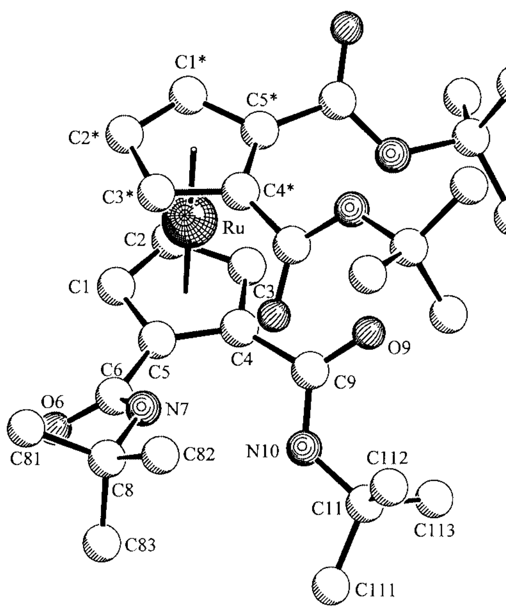


Fig. 1 A view of the molecular structure of **5** (with non-systematic atom numbering scheme). Selected bond lengths (Å) and angles (°): Ru–C4 2.160(6), Ru–C5 2.172(5), Ru–C3 2.172(6), Ru–C1 2.182(5), Ru–C2 2.182(6), C5–C6 1.503(7), C6–O6 1.230(6), C6–N7 1.344(7), N7–C8 1.473(7), C4–C9 1.505(8), C9–O9 1.236(6), C9–N10 1.328(7), N10–C11 1.475(7); C5–C6–O6 118.3(5), C5–C6–N7 117.8(5), O6–C6–N7 123.9(5), C6–N7–C8 125.0(5), C4–C9–O9 120.1(5), C4–C9–N10 114.9(5), O9–C9–N10 124.9(6), C9–N10–C11 126.0(5).

the reaction all four triphenylphosphine ligands are also eliminated from the metal center; they were removed from the reaction mixture during the workup process by washing with pentane. This left a clean product of composition $[C_5H_3(CONHCMe_3)_2]_2Ru$ **5** that was isolated in >60% yield.

In the IR spectrum (KBr) complex **5** exhibits sharp NH bands at $\tilde{\nu} = 3313$ and 3254 cm^{-1} and the typical carboxamide features at $\tilde{\nu} = 1631$ and 1544 cm^{-1} (see for a comparison, **2**: 1585 and 1529 cm^{-1}). In the ^1H NMR spectrum the resonances of the $-CONHC(CH_3)_3$ moiety are found at δ 8.16 (NH) and 1.39 (*tert*-butyl). The C_5H_3 signals show a similar pattern as observed for **2**, but they are found at markedly lower δ values: 5.12 (d) and 4.60 (t, $^3J_{HH} = 2.6$ Hz) (see for a comparison, **2**: 6.43, 6.36). This trend is even more pronounced in the ^{13}C NMR spectrum of **5** [C_5H_3-part: δ 83.0 (*ipso*-C), 79.2, 76.3 (C-2, C-3); see **2** for a comparison: δ 122.7, 114.4, 114.0]. These spectroscopic data already indicated principally different framework structures for the early metal complex **2** and the late transition metal complex **5** of the ligand system **1**. This was confirmed by the X-ray crystal structure analysis of the new complex **5**.

Single crystals of **5** were obtained by slowly concentrating a solution of the product in dichloromethane. The X-ray crystal structure analysis has revealed that a metallocene was formed. The central ruthenium atom is coordinated only to the C_5H_3-core of the $C_5H_3(CONHR)_2$ ligand system. Very different from the situation encountered in the early transition metal complex **2** and its congeners, the carboxamide substituents in **5** are not directly connected to the metal center at all. They solely function as Cp-bonded substituents (Fig. 1).

In the tetra-carboxamide-substituted metallocene both $C_5H_3(CONHR)_2$ rings are η^5-coordinated to ruthenium.[8] The substituted cyclopentadienyl ligands are oriented nearly parallel to each other. The decrease of symmetry introduced by the Cp-substituents and their specific conformational arrangement (see below) has only resulted in a marginal tilting of the η^5-Cp rings:[9] the Ru–C(Cp) distances are between 2.160(6) and 2.182(6) Å.

The conformational arrangement of the substituents at the 1,1′,2,2′-tetra-substituted metallocene framework is noteworthy. In the crystal complex **5** exhibits a chiral C_2-symmetric conformation with a close to eclipsed arrangement of the Cp-rings along the Cp(centroid)–Ru–Cp(centroid) vector.[10] In the projection, two of the $-CONHCMe_3$ substituents eclipse (vectors C4–C9 and C4*–C9*), whereas their adjacent $-CONHCMe_3$ neighbors reside in the lateral ends of the w-shaped projection enforced by the overall C_2-symmetric conformational arrangement (see Fig. 2). The angle between the respective projections of the vectors C5–C6 and C4–C9 amounts to *ca.* 65°, that between the projections of the C5–C6 and C5*–C6* vectors is *ca.* 140°. The carboxamido substituents at each Cp ring are substantially rotated from the cyclopentadienyl plane [dihedral angles C5–C4–C9–O9 −139.7(7)°, C4–C5–C6–O6 −138.7(6)°]. The C(6)=O(6) carbonyl group [and its symmetry equivalent C(6*)=O(6*) counterpart] is oriented toward the "outside" of the metallocene whereas the C(9)=O(9) carbonyl group of the adjacent carboxamido substituent is oriented "inwards". Moreover, the two pairs of $-CONHCMe_3$ substituents are located very close to each other at one sector of the metallocene. This is probably due to intramolecular hydrogen bonding between the C(9)=O(9) carbonyl group and the N(7*)–H hydrogen donor [and their symmetry-equivalent counterparts C(9*)=O(9*) and N(7)–H, see Fig. 3] [N(7*)–H(7*) 0.80(5) Å, H(7*)···O(9) 2.26(6) Å, N(7*)···O(9) 3.030(6) Å, angle N(7*)–H(7*)···O(9) 162(6)°][11] (see Fig. 1 and Fig. 3). Intermolecular hydrogen bonding between N(10)–

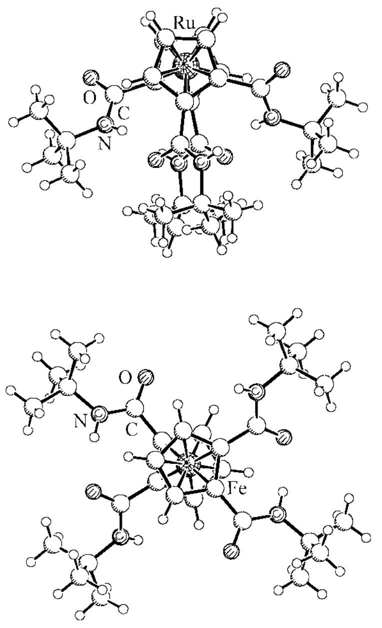
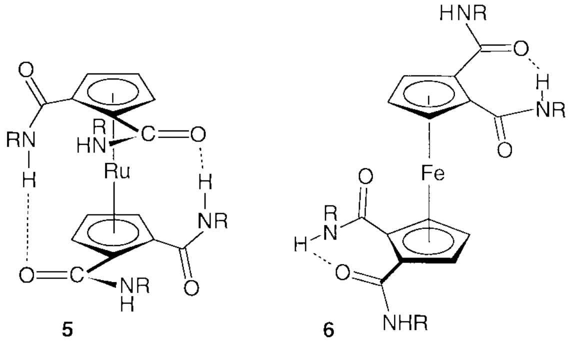


Fig. 2 Comparison of the molecular geometries of **5** (Ru, top) and **6** (Fe, bottom).



5

6

R = *tert*-butyl

Fig. 3 Metallocene conformations and intramolecular hydrogen bonding pattern of **5** and **6** found in the solid state.

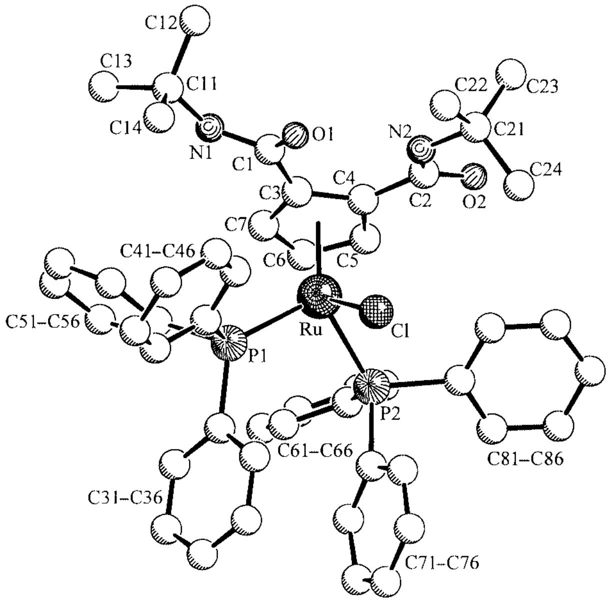


Fig. 4 A view of the molecular structure of **4**.

H and O(6**) then results in the formation of supramolecular strands of **5** in the crystal [N(10)–H(10) 0.81(5) Å, H(10) · · · O(6**) 2.23(6) Å, N(10) · · · O(6**) 2.943(6) Å, angle N(10)–H(10) · · · O(6**) 148(6)°].

Chloride substitution at the $RuCl_2(PPh_3)_4$ starting material **3** and triphenylphosphine elimination takes place sequentially upon treatment with the $[C_5H_3(CONHCMe_3)_2^-]$ reagent. A likely intermediate of the overall reaction sequence could be observed and isolated by the reaction between **3** and **2** in a 1 : 1 stoichiometry. After a reaction time of 14 h at 40 °C in toluene an almost quantitative conversion to the ruthenium half-sandwich complex $[\eta^5\text{-}C_5H_3(CONHCMe_3)_2]RuCl(PPh_3)_2$ **4** (see Scheme 2) was monitored, and this product was isolated in *ca.* 90% yield. Complex **4** shows the presence of two remaining PPh_3 ligands at ruthenium (^{31}P NMR: δ 38.7 in benzene-d_6), and it exhibits the typical ^{1}H and ^{13}C NMR resonances of the $\eta^5\text{-}C_5H_3(CONHR)_2$ ligand system [^{1}H NMR: δ 8.80 (NH), 4.14 and 3.83 (C_5H_3); ^{13}C NMR: δ 94.8, 81.0, 80.9 (C_5H_3), both in toluene-d_8].

The X-ray crystal structure analysis reveals the presence of a three-legged piano-stool structure of the half-sandwich complex **4** (Fig. 4). The $C_5H_3(CONHR)_2$ ligand is η^5-coordinated to ruthenium. Both carboxamide functionalities are arranged almost coplanar with the Cp-ring system. The unsaturated functional groups appear to be in π-conjugation with the adjacent Cp-π-system. The coplanar conformational arrangement of the carboxamido groups is supported, or probably even dominated by intramolecular hydrogen bonding between the CONHR moieties [C(1)=O(1) · · · H–N(2) interaction, see Fig. 4]. Due to disorder problems of cocrystallized solvent details of the crystal structure of **4** will not be discussed.

The reaction of $[C_5H_3(CONHCMe_3)_2]Na$ **1** with $FeCl_2$ produced the corresponding 1,1′,2,2′-tetracarbamoyl-ferrocene system **6** (Scheme 2 and Fig. 5). In this case we did not observe or isolate a mono-cyclopentadienyl iron intermediate corresponding to the Ru-system **4**. Single crystals of the ferrocene **6** were obtained from dichloromethane by slow evaporation of the solvent at ambient temperature.

The X-ray crystal structure analysis of **6** shows the presence of a metallocene structure with two symmetry-equivalent η^5-$C_5H_3(CONHCMe_3)_2$ ligands at the central Fe-atom. The Fe–C(Cp) distances range uniformly between 2.033(2) and 2.052(2) Å. The metallocene conformation in the crystal is staggered with an inversion symmetry. Thus the two pairs of carboxamido-substituents occupy sectors opposite to each other at the metallocene framework. Within each $-CONHCMe_3$ pair there seems to be an intramolecular hydrogen bond interaction (see Fig. 3) [N(22)–H(22) 0.87(2) Å, H(22) · · · O(11) 1.93(2) Å, N(22) · · · O(11) 2.764(2) Å, angle N(22)–H(22) · · · O(11) 162(2)°]. An additional intermolecular close hydrogen bridging contact is observed between N(12)–H(12) [0.84(2) Å] and O(21*) [H(12) · · · O(21**) 2.22(2) Å, N(12) · · · O(21**) 3.047(2) Å, angle N(12)–H(12) · · · O(21**) 168(2)° (see Fig. 5)] that leads to the formation of μ-H bridged chains of molecules of **6** in the solid state.

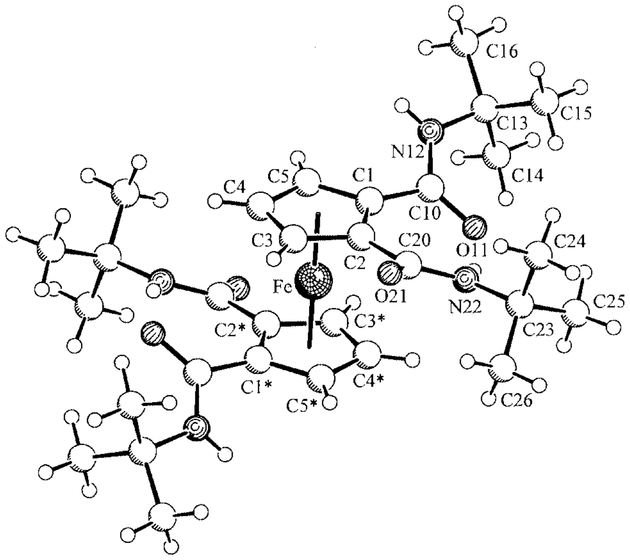


Fig. 5 Molecular structure of **6** (with non-systematic atom numbering scheme). Selected bond lengths (Å) and angles (°): Fe–C1 2.033(2), Fe–C2 2.038(2), Fe–C3 2.043(2), Fe–C5 2.046(2), Fe–C4 2.052(2), C1–C10 1.495(2), C10–O11 1.239(2), C10–N12 1.341(2), N12–C13 1.479(2), C2–C20 1.501(2), C20–O21 1.240(2), C20–N22 1.336(2), N22–C23 1.481(2); C1–C10–O11 121.9(1), C1–C10–N12 114.6(1), O11–C10–N12 123.5(2), C10–N12–C13 124.6(1), C2–C20–O21 118.7(1), C2–C20–N22 116.7(1), O21–C20–N22 124.7(2), C20–N22–C23 125.7(2).

Conclusions

We[6] and others[12] had shown that a single ester or carboxamide substituent at a Cp ligand does not substantially change its coordination behavior toward a Group 4 transition metal: $\eta^5\text{-}C_5H_4X$ coordination is still observed. This situation is drastically changed when two such electron-withdrawing carbonyl substituents are jointly removing electron-density from the Cp ligand core. It was shown that the 1,2-$C_5H_3(COX)_2$-type ligands prefer bonding through their substituent heteroatoms at the oxophilic Group 4 metals.[4,5] Chelate zirconium complexes of these ligands exhibiting the uncomplexed Cp-ring systems were observed. This present study has now revealed that there is a subtle balance for these easily available ligands between κ^2-O,O-chelate and η^5-cyclopentadienyl coordination that may be tipped by a selective choice of the central transition metal. Apparently, the metal–oxygen bond energy in the case of the late transition elements iron and ruthenium is too low to compensate for the π-ligand/metal combination and consequently the conventional metallocene structure is favored in this case.

Our route makes 1,1′,2,2′-tetra-functionalized metallocene systems very readily available. To our knowledge the reactions shown in Scheme 2 represent the first examples of simple synthetic entries to ferrocene and ruthenocene 1,1′,2,2′-tetracarboxamides. Systems, such as **5** and **6**, show an interesting hydrogen-bonding pattern. The resulting close spatial concentration of polar functional groups may lead to an interesting coordination behavior and resulting redox properties which we have begun to investigate in our laboratory.

Experimental

Most reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information including a compilation of the instrumentation used for spectroscopic and physical characterization of the compounds, see refs. 4 and 6. $RuCl_2(PPh_3)_4$ **3** was used as purchased, the reagent **1** was prepared as previously described in the literature.[4]

Preparation of [1,2-bis(*N-tert*-butylcarbamoyl)cyclopentadienyl]bis(triphenylphosphine)chlororuthenium 4

A solution containing 500 mg (0.41 mmol) of $RuCl_2(PPh_3)_4$ **3** and 117 mg (0.41 mmol) of the $[C_5H_3(CONHCMe_3)_2]Na$ reagent **1** in 50 mL of toluene was stirred for 14 h at 40 °C. After cooling to room temperature a precipitate was filtered off and the solvent was removed from the clear filtrate *in vacuo*. The resulting light brown solid was stirred in pentane, collected by filtration and washed with pentane (2 × 10 mL) to remove most of the liberated triphenylphosphine. The product was then dried *in vacuo* to yield 340 mg (90%) of **4**, mp 254 °C. A sample was recrystallized from benzene; the obtained microcrystalline material contained 1.5 equiv. of the solvent as analyzed by ^1H NMR. (Found: C, 70.09; H, 6.29; N, 2.57%. $C_{51}H_{53}N_2O_2P_2ClRu\cdot 1.5C_6H_6$ (M 719.9) requires C, 69.19; H, 6.00; N, 2.69%). δ_H(599.9 MHz, toluene-d_8) 8.80 (br s, 2H, NH), 7.52 (m, 12H, *m*-Ph), 6.87 (m, 18H, *o*-, *p*-Ph), 4.14 (br, 2H), 3.83 (br, 1H, C_5H_3), 1.37 (s, 18H, *tert*-butyl). δ_C(150.8 MHz, toluene-d_8): 165.2 (C=O), 138.1 (dd, $^1J_{PC}$, $^3J_{PC} = 21.3$, 20.1 Hz, *ipso*-Ph), 134.8 (pt, $^3J_{PC} = {}^5J_{PC} = 4.8$ Hz, *m*-Ph), 128.4 (d, $^4J_{PC} = 11.9$ Hz, *p*-Ph), 127.6 (pt, $^2J_{PC} = {}^4J_{PC} = 4.4$ Hz, *o*-Ph), 94.8 (*ipso*-C of C_5H_3), 81.0, 80.9 (C_5H_3), 51.6, 28.8 (CMe_3). δ_P(81.0 MHz, benzene-d_6): 38.7, $\nu_{1/2} = 3.1$ Hz. $\delta_{C/H}$ correlation (GHSQC, 150.8/599.9 MHz, toluene-d_8) 134.8/7.52 (*m*-Ph), 128.4/6.87 (*p*-Ph), 127.6/6.87 (*o*-Ph), 81.0/3.83 (C3/3-H of C_5H_3), 80.9/4.14 (C2/2-H of C_5H_3), 28.8 /1.37 (*tert*-butyl). $\delta_{C/H}$ correlation (GHMBC, 150.8/599.9 MHz, toluene-d_8) 165.2/8.80 (C=O), 138.1/7.52 (*ipso*-Ph/*m*-Ph), 134.8/7.52, 6.87 (*m*-Ph/*o*-, *m*-, *p*-Ph), 128.4/7.52 (*p*-Ph/*m*-Ph), 127.6/6.87 (*o*-Ph/*o*-, *p*-Ph), 94.8/4.14, 3.83 (C1/2-H, 3-H of C_5H_3), 81.0/4.14 (C3/2-H of C_5H_3), 80.9/3.83 (C2/3-H of C_5H_3), 51.6/1.37 (*tert*-butyl). X-Ray crystal structure analysis of **4**: $C_{51}H_{53}N_2O_2P_2ClRu\cdot 1/2C_7H_8$, $M = 970.48$, $a = 11.511(1)$, $b = 13.315(1)$, $c = 18.735(1)$ Å, $\alpha = 70.27(1)$, $\beta = 73.87(1)$, $\gamma = 72.15(1)°$, $V = 2523.6(4)$ Å^3, $\mu = 4.68$ cm^{-1}, $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $T =$ 223 K, 6996 reflections collected ($+h$, $\pm k$, $\pm l$), 6601 independent ($R_{int} = 0.066$) and 4263 observed reflections [$I \geq 2\sigma(I)$], $R = 0.086$, $wR^2 = 0.221$, disordered solvent molecule refined with restraints.

Preparation of 1,1′,2,2′-tetra(*N-tert*-butylcarbamoyl)ruthenocene 5

A reaction mixture containing 1.00 g (0.82 mmol) of **3** and 938 mg (3.28 mmol) of **1** in 50 mL of toluene was stirred overnight at 40 °C, then cooled to room temperature and filtered. Solvent was removed from the filtrate *in vacuo*. The residue was suspended in pentane with stirring, collected by filtration and washed with pentane (4 × 20 mL) to remove PPh_3. After drying *in vacuo* 330 mg of **5** (64%) was obtained. Mp 237 °C. (Found: C, 60.44; H, 7.50; N, 6.97%. $C_{30}H_{46}N_4O_4Ru\cdot C_7H_8$ (M 719.9) requires C, 61.73; H, 7.56; N, 7.79%). HRMS (ESI): Found $m/z = 651.2454$, ($C_{30}H_{46}N_4O_4Ru + Na^+$) requires 651.2453. IR (KBr): $\tilde{\nu} = 3313$, 3254 (NH), 1631, 1544 (CONH) cm^{-1}. δ_H(200.13 MHz, dichloromethane-d_2) 8.16 (br s, 4H, NH), 5.12 (d, 4H, $^3J = 2.6$ Hz), 4.60 (t, 2H, $^3J = 2.6$ Hz, C_5H_3), 1.39 (s, 36H, *tert*-butyl). δ_C(50.3 MHz, dichloromethane-d_2) 167.7 (C=O), 83.0 (*ipso*-C of C_5H_3), 79.2, 76.3 (C_5H_3), 51.9, 28.8 (*tert*-butyl). X-Ray crystal structure analysis of **5**: $C_{30}H_{46}N_4O_4Ru\cdot C_6H_6$, $M = 705.89$, 0.40 × 0.05 × 0.05 mm, $a = 12.458(4)$, $b = 15.758(3)$, $c = 18.019(2)$ Å, $\beta = 96.61(2)°$, $V = 3513.9(14)$ Å^3, $\mu = 4.89$ cm^{-1}, $Z = 4$, monoclinic, space group $C2/c$ (No. 15), $T = 223$ K, 3194 reflections collected ($\pm h$, $+k$, $-l$), 3090 independent ($R_{int} = 0.085$) and 1799 observed reflections [$I \geq 2\sigma(I)$], $R = 0.056$, $wR^2 = 0.113$.

Preparation of 1,1′,2,2′-tetra(*N-tert*-butylcarbamoyl)ferrocene 6

A mixture of $FeCl_2$ (100 mg, 0.79 mmol) and $[C_5H_3(CONHCMe_3)_2]Na$ **1** (451 mg, 1.58 mmol) was suspended in tetrahydrofuran at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and was then stirred overnight. The solvent was removed *in vacuo* and 20 mL of dichloromethane was added. The precipitate was filtered off and the solvent was removed *in vacuo* from the clear filtrate. The residue was suspended in pentane, isolated on a frit, washed with pentane until the washings were colorless (2 × 10 mL), and dried *in vacuo* to yield 298 mg (66%) of **6**, mp 274 °C. (Found: C, 60.93; H, 7.96; N, 9.44%. $C_{30}H_{46}N_4O_4Fe$ (582.6) requires C, 61.85; H, 7.96; N, 9.62%). HRMS (ESI): Found $m/z = 605.2740$, ($C_{30}H_{46}N_4O_4Fe + Na^+$) requires 605.2766. IR (KBr): $\tilde{\nu} = 3276$, 3072 (NH), 1650, 1644, 1591 (CONH) cm^{-1}. δ_H(200.1 MHz, chloroform-d) 8.49 (br s, 4H, NH), 4.81 (d, 4H, $^3J = 2.7$ Hz), 4.21 (t, 2H, $^3J = 2.7$ Hz, C_5H_3), 1.45 (s, 36H, *tert*-butyl). δ_C(50.3 MHz, chloroform-d) 168.6 (C=O), 77.9, 74.9 (C_5H_3), 51.8, 28.7 (*tert*-butyl), *ipso*-C of C_5H_3 not detected. X-Ray crystal structure analysis of **6**: $C_{30}H_{46}N_4O_4Fe$, $M = 582.56$, $a = 6.793(1)$, $b = 10.902(1)$, $c = 11.208(1)$ Å, $\alpha = 92.05(1)$, $\beta = 99.78(1)$, $\gamma = 107.58(1)°$, $V = 776.4(2)$ Å^3, $\mu = 5.24$ cm^{-1}, $Z = 1$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, 6015 reflections collected ($\pm h$, $\pm k$, $\pm l$), 3538 independent ($R_{int} = 0.022$) and 3309 observed reflections [$I \geq 2\sigma(I)$], $R = 0.036$, $wR^2 = 0.097$. Data sets were collected with Nonius MACH3 or KappaCCD diffractometers, using a rotating anode generator FR591.[13]

CCDC reference number 186/1719.

See http://www.rsc.org/suppdata/dt/1999/4457/ for crystallographic files in .cif format.

Acknowledgements

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

References

1 *Gmelin, Handbook of Inorganic and Organometallic Chemistry*, 8th edn., ed. A. Slawisch, *Organoiron Compounds, Part A8* (*Ferrocene*), Springer-Verlag, Berlin, 1986, pp. 323–345; *Part A11* (*Ferrocene*), 1995, pp. 1–33 and references cited therein. See also: A. F. Cunningham, Jr., *Organometallics*, 1994, **13**, 2480.

2 For selected examples see *e.g.* L. Westman and K. L. Rinehart, Jr., *Acta Chem. Scand.*, 1962, **16**, 1199; F. L. Hedberg and H. Rosenberg, *J. Am. Chem. Soc.*, 1973, **95**, 870; M. Tsukazaki, M. Tinkl, A. Roglans, B. J. Chapell, N. J. Taylor and V. Snieckus, *J. Am. Chem. Soc.*, 1996, **118**, 685.

3 (*a*) F. Effenberger, R. Gleiter, L. Heider and R. Niess, *Chem. Ber.*, 1968, **101**, 502; C. E. Wallace, J. P. Selegue and A. Carrillo, *Organometallics*, 1998, **17**, 3390; (*b*) M. I. Bruce, R. C. Wallis, M. L. Williams, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 2183; P. Bickert, B. Hildebrandt and K. Hafner, *Organometallics*, 1984, **3**, 653.

4 K. Klaß, L. Duda, N. Kleigrewe, G. Erker, R. Fröhlich and E. Wegelius, *Eur. J. Inorg. Chem.*, 1999, 11.

5 N. Etkin, C. M. Ong and D. W. Stephan, *Organometallics*, 1998, **17**, 3656.

6 In contrast, the $[C_5H_4{-}CONHR]^-$ ligands add to Zr or Ti centers to form the respective $[\eta^5\text{-}C_5H_4{-}CONHR]$ metal complexes: M. Oberhoff, L. Duda, J. Karl, R. Mohr, G. Erker, R. Fröhlich and M. Grehl, *Organometallics*, 1996, **15**, 4005.

7 J. K. Kochi, in *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978, pp. 237–245; J. A. Connor, *Top. Curr. Chem.*, 1977, **71**, 71.

8 *Ferrocenes: Homogeneous Catalysis*, *Organic Synthesis*, *Materials Science*, ed. A. Togni and T. Hayashi, VCH, Weinheim, 1995 and references cited therein.

9 J. C. Green, *Chem. Soc. Rev.*, 1998, **27**, 263.

10 (*a*) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, 1958, **80**, 5443; A. N. Nesmeyanov, E. V. Leonova, N. S. Kochetkova and A. I. Malkova, *J. Organomet. Chem.*, 1975, **96**, 271; (*b*) P. Seiler and J. D. Dunitz, *Acta Crystallogr*, *Sect. B*, 1979, **35**, 1068, 2020; *Acta Crystallogr.*, *Sect. B*, 1980, **36**, 2946; F. Takusagawa and T. F. Koetzle, *Acta Crystallogr.*, *Sect. B*, 1979, **35**, 1074.

11 G. A. Jeffrey and W. Saenger, in *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991.

12 (*a*) W. P. Hart, D. W. Macomber and M. D. Rausch, *J. Am. Chem. Soc.*, 1980, **102**, 1196; M. D. Rausch, J. F. Lewison and W. P. Hart, *J. Organomet. Chem.*, 1988, **358**, 161; M. Ogasa, D. T. Mallin, D. W. Macomber, M. D. Rausch, R. D. Rogers and A. N. Rollins, *J. Organomet. Chem.*, 1991, **405**, 41; (*b*) Review: D. W. Macomber, W. P. Hart and M. D. Rausch, *Adv. Organomet. Chem.*, 1982, **21**, 1; N. J. Coville, K. E. duPlooy and W. Pickl, *Coord. Chem. Rev.*, 1992, **116**, 1.

13 Programs used. Data collection: EXPRESS: Nonius B.V., 1994. Collect, Nonius B.V., 1998. Data reduction: MolEN: K. Fair, Enraf Nonius B.V., 1990. Denzo-SMN: Z. Otwinowski and W. Minor, in *Methods Enzymol.*, 1997, **276**, 307. Absorption Correction for CCD data: SORTAV: R. H. Blessing, *Acta Crystallogr.*, *Sect. A*, 1995, **51**, 33; *J. Appl. Crystallogr.*, 1997, **30**, 421. Structure Solution: SHELXS-97: G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467. Structure refinement: SHELXL-97: G. M. Sheldrick, Universität Göttingen, 1997. Graphics: SCHAKAL: E. Keller, Universität Freiburg, 1997.

Paper 9/06553I