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Novel rhodium complexes with ferrocene-based *N*-heterocylic carbenes: Synthesis, structure and catalysis

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Abstract

The synthesis of a chiral *N*-heterocyclic carbene with an oxazolinyl ferrocenyl substituent is reported. The X-ray crystal structure of a rhodium complex reveals the chelating properties of the ligand, and catalysis studies demonstrate the capability of the rhodium complexes to catalyze hydrosilylations of ketones.

Keywords: Carbenes; Catalysis; Ferrocene; Planar chirality; Rhodium

1. Introduction

In recent years, the chemistry of stable *N*-heterocyclic carbenes (NHC) has shown a remarkable growth. After the initial synthesis of transition metal complexes of NHCs by Wanzlick and Öfele [1] and the first isolation of free carbenes by Arduengo [2], the preparation and application of NHCs in catalysis has significantly progressed, and by now this area of organometallic chemistry has become well-established [3]. NHCs have several characteristics, which make them valuable for catalysis. Often, they lead to air-stable compounds, in which the carbene ligands bind more strongly to the metal than in comparable electron-rich phosphine/metal complexes. The powerful σ-donating and weak π-accepting properties of NHCs make the metal centers more electron-rich than in the comparable phosphine complexes. Despite these most interesting properties, only a few examples are known to date directly relating to the application of chiral NHC ligands in asymmetric catalysis [4].

In 2002, we reported the synthesis of the first planar chiral carbenes and metal complexes thereof [5,6]. Recently, this chemistry has been extended and the preparation of another type of planar chiral NHCs having a *pseudo-ortho*-disubstituted [2.2]paracyclophane-based backbone was described [7]. In this context, it was also shown that the application of iridium complexes bearing such [2.2]paracyclophane-based NHCs led to remarkable enantioselectivities in asymmetric hydrogenations of alkenes [7]. With the goal to further improve the catalyst performance, we now intensified those studies and focused our attention on the synthesis of planar chiral NHCs with chelating oxazolinyl ferrocenyl substituents.

2. Results and discussion

The synthetic methodology to generate planar chiral ferrocenes is well established [8]. Most protocols rely on the directed *ortho*-metalation strategy in combination

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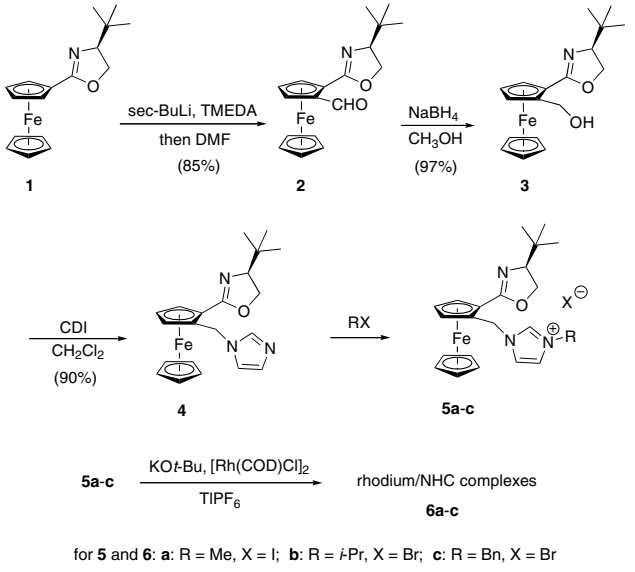
with an achoring group having a stereogenic center [9]. The synthesis of the desired compounds started from the oxazolinylferrocene **1** [10,11]. *ortho*-Functionalization with *sec*-butyl lithium in the presence of TMEDA and trapping of the resulting lithium reagent with DMF afforded aldehyde **2** in 85% yield. Reduction of **2** with sodium borohydride led to 97% yield of the corresponding hydroxymethyl derivative **3**. Reaction of **3** with *N*,*N*-carbonyl diimidazole (CDI) afforded imidazole **4** in 90% yield [12]. As precursors for the stable NHCs, imidazolium salts **5** were prepared by quaternizations of **4** with various alkyl halides. Finally, deprotonation of **5** in THF at ambient temperature using KO*t*-Bu gave the target compounds, which upon treatment with $[Rh(COD)Cl]_2$ led to the formation of air-stable rhodium/NHC complexes **6** (Scheme 1).



Scheme 1.

The structure **6a** in the solid state was determined by means of X-ray single crystal structure analysis and is shown in Fig. 1. As expected, both fragments of the ligand the carbene as well as the oxazoline coordinate to the metal center leading to a eight-membered chelate. Interestingly, however, and in contrast to structually related rhodium/*N*,*P* ligand complexes [13], the oxazolinyl fragment is rotated with respect to the substituted cyclopentadienyl ring of the ferrocene, which results in a more or less achiral environment at the metal center. With respect to asymmetric catalysis this exposure of the metal to the outer sphere of the complex could, unfortunately, be detrimental, since, for example, a nucleophilic reagent attacking a coordinated substrate could approach from any given direction, and thus, the stereoselectivity would not be high.

In order to test if rhodium/NHC complexes **6a**–**c** show any catalytic activity, their efficiency in the hydrosilylation of acetophenone was investigated [15]. As expected, all complexes were catalytically active giving the reduced product in excellent yield (92–99%; Table 1). Disappointingly, however, none of the complexes showed a significant enantioselectivity (ee $\leqslant$ 6%) neither in etheral nor in chlorinated solvents.

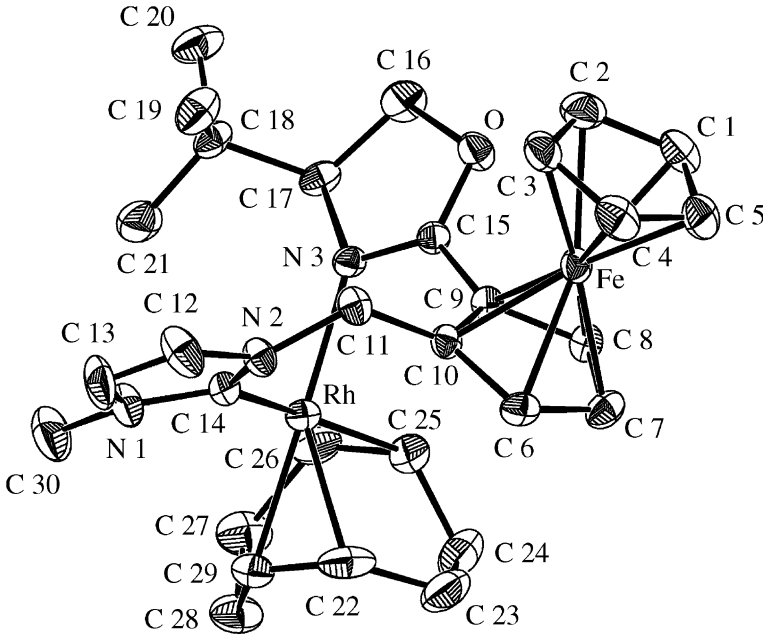
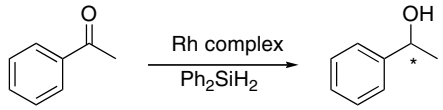


Fig. 1. Ortep plot of the structure of the cation of **6a** in the solid state [14]. Ellipsoids are plotted at the 30% level. Selected bond lengths, bond angles, and dihedral angles: Rh–C14 2.032(4), Rh–C22 2.122(4), Rh–C25 2.222(4), Rh–C26 2.187(4), Rh–C29 2.150(4), Rh–N3 2.140(3), Fe–C_{aver} 2.045(4), N3–C17 1.493(4), N3–C15 1.279(4), C15–O 1.328(4), C16–O 1.477(4), N2–C14 1.372(5), N1–C14 1.348(5), C12–C13 1.324(7), C25–C26 1.345(6), C22–C29 1.402(6) Å; C17–N3–C15 107.5, N1–C14–N2 103.2(2), N3–Rh–C14 92.9(1)°; N3–C15–C9–C10 −54.6(5), C9–C10–C11–N2 94.9(4)°.

Table 1
Hydrosilylation of acetophenone catalyzed by Rh/NHC complex **6**[a]



Entry	Complex	Solvent	Temperature	Yield (%)[b]	ee (%)[c]
1	**6a**	THF	r.t.	99	0
2	**6a**	THF	0 °C	97	2
3	**6a**	ether	0 °C	97	3
4	**6a**	CH_2Cl_2	0 °C	92	0
5	**6b**	ether	0 °C	95	6
6	**6c**	ether	0 °C	94	0

[a] For details, see Section 4.
[b] After column chromatography.
[c] Determined by GC using a chiral column.

3. Conclusion

Novel planar chiral imidazolium salts containing an oxazolinyl ferrocenyl backbone have been synthesized. They served as starting materials for chiral rhodium/carbene complexes, which showed high catalytic activity in the hydrosilylation of acetophenone. The lack of enantioselectivity was expected from structural details, which were revealed by an X-ray crystal structure analysis of one of the rhodium/NHC complexes. Work on improving the ligand scaffold taking into account the results of this investigation is currently in progress and will be reported in due course.

4. Experimental

4.1. General

^1H and ^{13}C NMR (300 and 75 MHz, respectively) spectra were recorded in $CDCl_3$ at 25 °C using TMS as an internal standard. Chemical shifts are given in ppm and spin–spin coupling constants, J, are given in Hz. Optical rotation was measured with a 341 automatic polarimeter. Mass spectra were measured using EI ionization mode. IR spectra were taken on a FTIR instrument and are reported in cm^{-1}. All experiments, which were sensitive to moisture or air were carried out under argon atmosphere using standard Schlenk techniques. Commercial reagents were used as received without further purification unless otherwise noted. Tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl and dichloromethane from calcium hydride before use.

4.2. Preparation of (S,S)-(4,5-dihydro-4-tert-butyl-2-oxazoyl)-2-aldehyde ferrocene (2)

To the solution of ferrocenyl oxazoline (0.95 g, 3.05 mmol) and TMEDA (0.58 mL) in THF (40 mL) was added dropwise *n*-BuLi (2.4 mL of a 1.6 M solution in hexane, 3.8 mmol) at −78 °C. The reaction mixture was stirred at this temperature for 2 h, and then DMF (0.25 mL, 3.2 mmol) was added. The reaction mixture was stirred overnight and the temperature was allowed to warm to room temperature. The reaction was quenched with saturated $NaHCO_3$ solution (10 mL). The mixture was extracted with diethyl ether, and the organic phase was separated, washed with brine, and dried over $MgSO_4$. After removal of the solvent, the product was purified by column chromatography (silica gel). Elution with pentane–ethyl acetate (10:1) afforded **2** as a brown solid (0.87 g, 85%). M.p. 78–81 °C. $[\alpha]_D^{20} = -561.2$ (c 0.725, $CHCl_3$). IR (KBr): 3451, 3079, 2955, 2900, 2863, 1669, 1477, 1423, 1383, 1360, 1291, 1241, 1157, 1000, 950, 829, 760, 590, 513 cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ 10.75 (s, 1H), 5.10 (dd, $J = 1.48$, 2.47, 1H), 5.01–4.99 (m, 1H), 4.73 (dt, $J = 0.56$, 2.72, 1H), 4.31–4.18 (m, 6H), 3.99–3.93 (m, 2H), 1.00 (s, 9H). ^{13}C NMR δ 195.2, 163.6, 78.7, 76.4, 74.8, 73.1, 70.2, 70.1, 69.9, 68.2, 33.7, 25.9. EIMS m/z (relative intensity): 339 (M^+). Anal. Calc. for $C_{18}H_{21}FeNO_2$: C, 63.73; H, 6.24; N, 4.13. Found: C, 63.46; H, 5.97; N, 4.01%.

4.3. Preparation of (S,S)-(4,5-dihydro-4-tert-butyl-2-oxazoyl)-2-methanol ferrocene (3)

To the solution of **2** (0.6 g, 1.77 mmol) in methanol (15 mL) was added portionwise $NaBH_4$ (80 mg, 2.1 mmol) at room temperature, resulting in the evolution of hydrogen. After stirring for 2 h, the reaction was quenched with water (10 mL). The solution was extracted with CH_2Cl_2, the organic phase was separated and dried over $MgSO_4$. After removal of the solvent, the product was purified by column chromatography (silica gel). Elution with pentane–ethyl acetate (5:1) afforded **3** as a brown solid (0.59 g, 97%). M.p. 122–124 °C. $[\alpha]_D^{20} = -150.8$ (c 0.95, $CHCl_3$). IR (KBr): 3314, 3088, 2964, 2864, 1646, 1475, 1360, 1305, 1269, 1205, 1159, 1077, 999, 945, 831, 742 cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ 6.46 (s, 1H), 4.68 (d, $J = 13.13$ Hz, 1H), 4.59 (dd, $J = 1.38$, 2.47, 1H), 4.40–4.20 (m, 4H), 4.19 (s, 5H), 3.91 (dd, $J = 2.47$, 10.16, 2H), 1.00 (s, 9H). ^{13}C NMR δ 167.4, 89.3, 75.4, 71.9, 70.3, 69.9, 69.3, 68.9, 68.1, 59.8, 33.5, 26.1. EIMS m/z (relative intensity): 341 (M^+). Anal. Calc. for $C_{18}H_{21}FeNO_2$: C, 63.36; H, 6.79; N, 4.10. Found: C, 63.35; H, 6.76; N, 4.04%.

4.4. Preparation of (S,S)-(4,5-dihydro-4-tert-butyl-2-oxazoyl)-2-methyl imidazole ferrocene (4)

A solution of **3** (30 mg, 0.09 mmol) and 1,1′-carbonyl diimidazole (20 mg; 0.12 mmol) was refluxed for 3 h in CH_2Cl_2 (10 mL). After cooling to ambient temperature the solvent was removed. The product was purified by

chromatography (silica gel). Elution with ethyl acetate afforded **4** as a brown solid (31.6 mg, 90%). M.p. 65–66 °C. $[\alpha]_D^{20} = -113.9$ (*c* 0.8, $CHCl_3$). IR (KBr): 3100, 2953, 2868, 1652, 1500, 1479, 1423, 1355, 1303, 1271, 1220, 1150, 1105, 1074, 1006, 953, 905, 818, 732 cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ 7.11 (b, 2H), 7.00 (b, 1H), 5.67 (d, $J = 14.3$ Hz, 1H), 5.01 (d, $J = 13.6$ Hz, 1H), 4.70 (s, 1H), 4.33 (d, $J = 13.9$ Hz, 2H), 4.27–4.12 (m, 7H), 3.99–3.92 (m, 1H),1.00 (s, 9H). ^{13}C NMR δ 164.2, 137.3, 128.4, 119.3, 83.8, 76.3, 71.6, 70.6, 70.2, 69.7, 69.2, 67.8, 45.5, 33.5, 26.1. EIMS *m*/*z* (relative intensity): 392 (M^+). Anal. Calc. for $C_{21}H_{25}FeN_3O{\cdot}H_2O$: C, 61.62; H, 6.65; N, 10.27. Found: C, 61.71; H, 6.30; N, 10.35%.

4.5. Preparation of (S,S)-(4,5-dihydro-4-tert-butyl-2-oxazoyl)-2-methyl imidazolium ferrocenes (**5a**–**c**)

A solution of **4** (210 mg, 0.54 mmol) and 2 equiv. of the alkyl halide in CH_3CN (10 mL) was heated to 40 °C for 24 h. The solvent was evaporated and the crude product was used in the next reaction without further purification.

4.6. General procedure for the preparation of the rhodium complexes

At ambient temperature K*t*-OBu (1.2 equiv.) was added to a solution of the imidazolium salt **5** (0.2 mmol) in THF (2.5 mL). After stirring for 30 min $[Rh(COD)Cl]_2$ (50 mg, 0.1 mmol) was added. The reaction mixture was stirred at room temperature for 24 h and then the solvent was removed. The residue was purified by column chromatography (silica gel, ethyl acetate:pentane = 1:5). After the removal of the solvents, the product was dissolved in THF (4 mL), and $TlPF_6$ (60 mg, 0.16 mmol) was added. Immediately the formation of a white precipitate was observed. After 20 min, the solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, methanol:dichloromethane = 1:6).

4.6.1. (η^4-1,5-Cyclooctadiene)(1-[2-(4,5-dihydro-4-tert-butyl-2-oxazoyl)ferrocenylmethyl]-3-methylimidazolin-2-ylidene)rhodium (I) hexafluorophosphate (**6a**)

M.p. 234–236 °C. $[\alpha]_D^{20} = -217.0$ (*c* 0.75, $CHCl_3$). IR (KBr): 3723, 3430, 2963, 2876, 1802, 1623, 1463, 1156, 1007, 843, 557 cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ 7.52 (d, $J = 1.7$ Hz, 1H), 7.02 (d, $J = 1.7$ Hz, 1H), 6.39 (d, $J = 15.0$ Hz, 1H), 5.05 (d, $J = 15.1$ Hz, 1H), 4.96 (dd, $J = 1.8$ Hz, 2.4 Hz, 1H), 4.90 (m, 1H), 4.62 (t, $J = 2.7$ Hz, 1H), 4.52–4.45 (m, 1H), 4.36–4.20 (m, 3H), 4.15 (s, 5H), 3.98 (s, 3H), 3.78 (dd, $J = 8.41$ Hz, 10.63 Hz, 1H), 3.65–3.62 (m, 1H), 3.41–3.39 (m, 1H), 2.58–2.45 (m, 1H), 2.32–2.19 (m, 2H), 2.18–2.04 (m, 4H), 1.85–1.73 (m, 2H), 1.20 (s, 9H). Anal. Calc. for $C_{30}H_{39}F_6FeN_3OPRh$: C, 47.33; H, 5.16; N, 5.52. Found: C, 46.80; H, 4.88; N, 5.40%.

4.6.2. (η^4-1,5-Cyclooctadiene)(1-[2-(4,5-dihydro-4-tert-butyl-2-oxazoyl)ferroceneylmethyl]-3-isopropyl-imidazolin-2-ylidene)rhodium (I) hexafluorophosphate (**6b**)

M.p. 255–257 °C. $[\alpha]_D^{20} = -249.0$ (*c* 1.0, $CHCl_3$). IR (KBr): 3431, 2926, 2859, 1609, 1462, 1262, 1215, 1103, 1024, 841, 556 cm^{-1}. ^1H NMR (DMSO/TMS) δ 7.70 (b, 1H), 7.44–7.32 (m, 5H), 7.25 (d, $J = 7.2$ Hz, 1H), 6.00 (d, $J = 14.6$ Hz, 1H), 5.76 (d, $J = 5.9$ Hz, 1H), 5.53 (d, $J = 16.0$ Hz, 1H), 4.84 (s, 1H), 4.71 (b, 2H), 4.54 (s, 1H), 4.48–4.46 (m, 1H), 4.38 (s, 2H), 4.31 (s, 5H), 4.29–4.24 (m, 2H), 3.98–3.89 (m, 2H), 3.38 (m, 1H), 2.59–1.91 (m, 8H), 1.05 (s, 9H). Anal. Calc. for $C_{32}H_{43}F_6FeN_3OPRh$: C, 48.69; H, 5.49; N, 5.32. Found: C, 48.31; H, 5.40; N, 5.71%.

4.6.3. (η^4-1,5-Cyclooctadiene)(1-[2-(4,5-dihydro-4-tert-butyl-2-oxazoyl)ferroceneylmethyl]-3-benzylimidazolin-2-ylidene)rhodium (I) hexafluorophosphate (**6c**)

M.p. 255–257 °C. $[\alpha]_D^{20} = -246.0$ (*c* 0.35, CH_2Cl_2). IR (KBr): 3146, 2988, 2956, 2876, 2832, 1627, 1472, 1398, 1365, 1288, 1246, 1220, 1177, 1161, 1079, 1021, 952, 835, 713 cm^{-1}. ^1H NMR (DMSO/TMS) δ 7.70 (b, 1H), 7.44–7.32 (m, 5H), 7.25 (d, $J = 7.2$ Hz, 1H), 6.00 (d, $J = 14.6$ Hz, 1H), 5.76 (d, $J = 5.9$ Hz, 1H), 5.53 (d, $J = 16.0$ Hz, 1H), 4.84 (s, 1H), 4.71 (b, 2H), 4.54 (s, 1H), 4.48–4.46 (m, 1H), 4.38 (s, 2H), 4.31 (s, 5H), 4.29–4.24 (m, 2H), 3.98–3.89 (m, 2H), 3.38 (m, 1H), 2.59–1.91 (m, 8H), 1.05 (s, 9H). Anal. Calc. for $C_{32}H_{43}F_6FeN_3OPRh$: C, 51.63; H, 5.18; N, 5.02. Found: C, 51.28; H, 5.08; N, 4.96%.

4.7. General procedure for the catalytic hydrosilylation reaction

The catalyst (0.01 mmol) was dissolved in THF (1 mL). After addition of acetophenone (24 mg, 0.5 mmol), the reaction flask was dipped into a thermoregulated bath at 0 °C. Diphenylsilane (56 μL, 0.75 mmol) was then slowly added by syringe. The reaction progress was monitored by TLC. After the disappearance of the ketone methanol (1 mL) was slowly added to the reaction mixture at 0 °C, and stirring was continued for 0.5 h. After gas evolution ceased, 1 M aqueous HCl (1 mL) was added and stirring was continued at room temperature for 1 h. The reaction mixture was diluted with diethyl ether and washed with water. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (silica gel) using petroleum ether–diethyl ether (2:1) as eluent to afford the product as a colorless oil. The enantiomer ratio was determined by GC using a chiral column (cyclodex β-I/P. 2,3,6-trimethyl-β-cyclodextrin, 0.25 mm × 25 m, 100 kPa N_2. column 120 °C, injector 200 °C, split 1:1)

4.8. X-ray crystal structure determination of rhodium/NHC complex **6a** [14]

A suitable crystal ($\sim 0.3 \times 0.3 \times 0.3$ mm) has been obtained at room temperature from CH_2Cl_2/EtOAc. The compound ($C_{30}H_{39}F_6FeN_3OPRh$ $M_r = 761.38$) crystallizes in orthorhombic space group $P2_12_12_1$ (No. 19) with cell dimensions $a = 9.5536(7)$, $b = 14.8609(9)$, and $c = 21.8920(12)$ Å. A cell volume of $V = 3108.1(3)$ Å^3 and $Z = 4$ result in a calculated density of $\rho_{cal} = 1.627$ g cm^{-3}. 15806 reflections have been collected in the $\omega/2\Theta$ mode at $T = 238$ K on a Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα-radiation ($\lambda = 0.71073$ Å). Data collection covered the range $0 \leqslant h \leqslant 12$, $-19 \leqslant k \leqslant 19$, and $-28 \leqslant l \leqslant 28$ up to $\Theta_{max} = 27.97°$. $\mu = 1.114$ mm^{-1}, no absorption correction. The structure has been solved by direct methods as implemented in the Xtal 3.7 suite of crystallographic routines [16] where GENSIN has been used to generate the structure-invariant relationships and CRISP for the tangent direct methods. 6188 observed reflections ($I > 2\sigma(I)$) have been included in the final full-matrix least-squares refinement on F involving 389 parameters and converging at R (R_w) = 0.035 (0.028, $w = 1/[5.0\,\sigma^2(F)]$), $S = 1.031$, and a residual electron density of $-0.55/0.68$ e Å^{-3}. The absolute configuration has been determined using Flack's method. $X_{abs} = -0.024(28)$ [17] for the structure shown in Fig. 1. The hydrogen positions have been calculated in idealized positions. Their Us have been fixed at 1.5 times U of the relevant heavy atom before the final refinement, and no hydrogen parameters have been refined.

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