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Synthesis and characterization of asymmetric NHC complexes

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Dedicated to the memory of F. Albert Cotton.

Abstract

New chiral and non-chiral rhodium(I)–NHC complexes were synthesized. The first attempt by deprotonation of an imidazolinium salt with KO*t*Bu and reaction with $[Rh(COD)Cl]_2$ leads to the corresponding rhodium(I) complex. Due to the basic conditions during the reaction a loss of chirality occurs. An alternative transmetallation reaction with a silver(I)–NHC complex yields the desired rhodium(I)–NHC complex under retention of chirality. Both Rh complexes were fully characterized by analytical methods.

Keywords: Carbene complexes; Chirality; Rhodium; Transmetallation

1. Introduction

The first successful synthetic approaches to transition-metal complexes bearing *N*-heterocyclic carbenes (NHCs) as ligands date back to 1968 and have been reported independently by Öfele [1] and Wanzlick and Schönherr [2]. More than 20 years passed before the synthesis of free NHCs was made possible through the pioneering work of Arduengo et al. [3]. Since then free NHCs have been reported in many syntheses and are now recognized as a very important class of ligands for diverse metal complexes [4]. The strong σ-donor electronic properties and striking similarity to electron rich organophosphanes make NHCs versatile spectator ligands [5,6] and have advanced the catalytic application of NHC complexes.

In 1996 the group of Herrmann first reported the use of chiral NHCs as ligands in transition-metal catalyzed asymmetric reactions [7,8]. Examples of the use of chiral NHC ligands in asymmetric synthesis now range from ruthenium complex catalyzed metathesis [9], iridium complex catalyzed hydrogenation [10] to hydrosilylation reactions catalyzed by rhodium compounds [11]. The – so far – most successful example of a chiral monodentate non-chelating NHC liganted complex applied in asymmetric metathesis was published by Grubbs et al. [9]. The high enantiomeric excess obtained (ee = 90%) provides clear evidence for the enormous potential of NHC complexes in enantioselective synthesis.

Recently we reported on several chiral rhodium and iridium complexes with restricted ligand flexibility and their use in catalysis [12]. In contrast to the usually advantageous application of free *N*-heterocyclic carbenes we describe herein a different approach towards asymmetric Rh–imidazolin complexes.

2. Results and discussion

2.1. Synthesis of 1,3-bis[1-phenylethyl]-4,5-di-tert-butylimidazolin-2-ylidene]-[(1,2,5,6-η)-1,5-cyclooctadiene]-chlororhodium(I) 2

Among the various methods for the preparation of transition-metal carbene complexes [4a] the utilization of *in situ* formed free carbenes and the corresponding metal precursors is convenient and generally high-yielding.

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Accordingly, an attempt to generate the desired complex was carried out by deprotonation of the imidazolinium salt with KO*t*Bu and subsequent reaction with $[Rh(COD)Cl]_2$ (Scheme 1). (4*R*,5*R*)-1,3-[(*S*)-1-Phenylethyl]-4,5-di-*tert*-butylimidazolium iodide **1**, which can be synthesized with an enantiomeric purity higher than 95% [13] was chosen for the investigations described here.

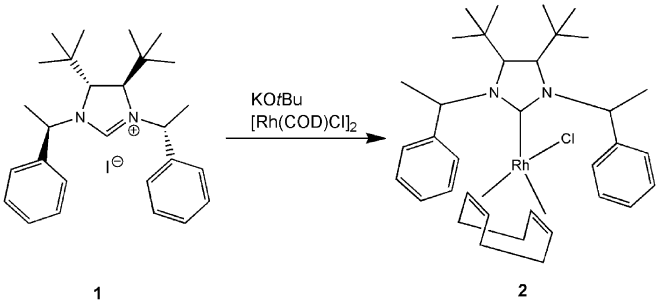
After purification by gradient column chromatography, the complex was characterized by analytical methods. The ^{13}C NMR spectrum of **2** exhibits a signal at 210 ppm with a ^{103}Rh–^{13}C coupling constant of $^{1}J_{Rh,C} = 39$ Hz. This constitutes clear evidence for complex formation. The carbene signal is displayed at lower field when compared to the signal of an unsaturated NHC ligand, which is normally around 180 ppm [12]. Unfortunately, the harsh reaction conditions lead to a loss of chirality, which is evident from polarimeter measurements. Furthermore the deprotonation of the imidazolinium salt **1** at the chiral centers in the side chain was observed by following the generation of the free carbene in the NMR. This additional attack next to the carbene proton leads to the loss of chirality in the NHC ligand.

2.2. Synthesis of [(4R,5R)-1,3-bis[(S)-1-phenylethyl]-4,5-di-tert-butylimidazolin-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]iodorhodium(I) 4

An alternative, very mild carbene transfer method was first developed by Wang and Lin [16]. For the transmetallation a silver carbene complex of composition **3** was prepared according to Roland and co-workers [13] (Scheme 2). It was dissolved in excess in CH_2Cl_2 and $[Rh(COD)Cl]_2$ was then added (Scheme 3).

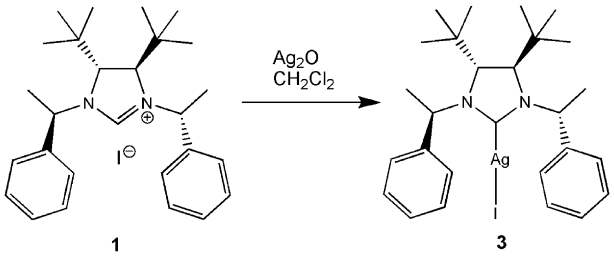
The suspension was stirred for 3 days. The long reaction time can be explained by the steric demand of the carbenes. Hahn and co-workers describe this factor as the limitation of transmetallation reactions [15].

Upon completion, the precipitate was filtered over Celite and the complex was recovered using gradient column chromatography. In a first fraction using CH_2Cl_2 as eluent the starting material was recovered. Additional elutions with THF were used to receive complex **4** as a yellow powder. The successful carbene transfer is confirmed by analytical methods. The most indicative result is shown by a typical carbene carbon signal at 210 ppm in ^{13}C NMR spectroscopy. The ^{103}Rh–^{13}C coupling constant is $^{1}J_{Rh,C} = 39$ Hz. Both results are in good accordance with examples of saturated NHC complexes [12]. Due to the high nucleophilicity of this type of complexes compared to unsaturated NHC complexes a shift of the carbene carbon signal to lower field is usual. The preservation of chirality was determined by polarimetry, showing a rotation angle of −80°.



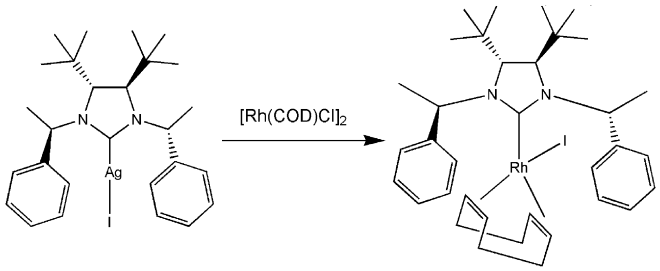
1 2

Scheme 1. Synthesis of the Rh NHC complex.



1 3

Scheme 2. Preparation of Ag(I) complex.



3 4

Scheme 3. Synthesis of the chiral Rh(I) complex **4**.

3. Conclusion

New chiral and non-chiral rhodium NHC complexes were synthesized. The well established method of adding free carbene to $[Rh(COD)Cl]_2$ leads, unfortunately, to a complete loss of chirality in the target complex. In contrast, the alternative transmetallation route preserves chirality. The application of the synthesized complexes in asymmetric catalysis is currently under investigation in our laboratories.

4. Experimental

4.1. General

All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. (4*R*,5*R*)-1,3-[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolium iodide **1**, (4*R*,5*R*)-1,3-bis-[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolin-2-ylidene silver(I) iodide **3** and $[Rh(COD)Cl]_2$ were synthesized as described by previously reported methods [13,14]. All other materials were obtained commercially and used without further purification. All solvents were

dried on an alumina-based solvent purification system. NMR spectra were recorded on a JEOL JMX-GX 400 spectrometer operating at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and on a Bruker AMX 400 operating at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR). The spectra were calibrated to the residual proton of the solvents. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. MS spectra were measured at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer using FAB technique. Optical rotations were measured on a Perkin–Elmer 341. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München.

4.2. Synthesis of [1,3-bis(1-phenylethyl)-4,5-di-tert-butylimidazolin-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]-chlororhodium(I) **2**

To a suspension of (4*R*,5*R*)-1,3-[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolium iodide (232 mg, 0.45 mmol) in 5 mL THF a solution of KO*t*Bu (51 mg, 0.45 mmol) in 4 mL THF was added. The suspension was stirred for 30 min at room temperature. A solution of $[Rh(COD)Cl]_2$ (84 mg, 0.16 mmol) in 5 mL of toluene was added to the carbene solution. The mixture was heated for 3 h at 80 °C. After cooling to room temperature the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and filtered over Celite. Purification of the complex was carried out by gradient column chromatography over silica gel. Elution with CH_2Cl_2 gave a $[Rh(COD)Cl]_2$ fraction and subsequent elution with THF yielded complex **2** as a yellow solid after drying under reduced pressure. Yield: 102 mg, 0.16 mmol, 68%. Anal. Calc. for $C_{36}H_{55}ClN_2Rh \cdot 1.3CH_2Cl_2$: C, 58.59; H, 7.59; N, 3.66. Found: C, 58.17; H, 7.07; N, 3.92%. ^{1}H NMR ($CDCl_3$, δ (ppm)): 1.37 (s, 18H, C(CH_3)$_3$), 1.72–1.76 (m, 4H, COD–CH_2), 1.99 (d, 6H, *J* 6.8 Hz, CH_3–CH–N), 2.48–2.52 (m, 4H, COD–CH_2), 3.36 (s, 2H, NC*H*), 4.01 (m, 2H, COD–C*H*), 4.12 (q, 2H, *J* 6.3 Hz, CH_3–C*H*–N), 4.24 (m, 2H, COD–C*H*), 7.12–7.36 (m, 10H, *Ph*). ^{13}C NMR ($CDCl_3$, δ (ppm)): 26.6, 28.2, 30.4, 30.9, 34.2, 35.7, 63.9, 67.9, 70.6, 78.8, 127.9, 128.8, 151.5, 209,9. IR (KBr): ν_{max}/cm^{-1} 2962, 2872, 2828, 1743, 1467, 1261, 1099, 1024, 960, 864, 801, 696, 486. MS (CI) *m*/*z* (%): 654.9 (1, M^+), 545.0 (3, [M^+−COD]), 543.0 (9, [M^+−(COD + 2H)]), 431.1 (100, [M^+−(COD + 2*t*Bu)]), 381.3 (42, [M^+−(COD + Me + Cl + 2*t*Bu)]), 285.2 (77, [M^+−(COD + Cl + 2*t*Bu + Me + Bz + 5H)]).

4.3. Synthesis of [(4R,5R)-1,3-bis[(S)-1-phenylethyl]-4,5-di-tert-butylimidazolin-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]iodorhodium(I) **4**

To a solution of (4*R*,5*R*)-1,3-bis-[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolin-2-ylidene silver(I) iodide **3** (927 mg, 1.48 mmol) in 25 mL CH_2Cl_2, $[Rh(COD)Cl]_2$ (250 mg, 0.51 mmol) was added. The mixture was stirred for 3 days at room temperature. The silver precipitate was removed by filtration over Celite. Purification of the complex was carried out by gradient column chromatography over silica gel. Elution with CH_2Cl_2 gave a $[Rh(COD)Cl]_2$ fraction and subsequent elution with THF yielded compound **4** as a yellow solid after drying under reduced pressure. Yield: 124 mg, 0.19 mmol, 13%; $[\alpha]_D^{20} = -80$ (*c* 0.025, THF). Anal. Calc. for $C_{36}H_{55}IN_2Rh \cdot 1.4CH_2Cl_2$: C, 51.96; H, 6.74; N, 3.24. Found: C, 51.67; H, 6.36; N, 3.92%. ^{1}H NMR ($CDCl_3$, δ (ppm)): 1.72–1.76 (m, 4H, COD–CH_2), 1.42 (s, 18H, C(CH_3)$_3$), 2.06 (d, 6H, *J* 7.2 Hz, CH_3–CH–N), 2.48–2.51 (m, 4H, COD–CH_2), 3.44 (s, 2H, NC*H*), 3.98 (m, 2H, COD–C*H*), 4.11 (q, 2H, *J* 6.3 Hz, CH_3–C*H*–N), 4.24 (m, 2H, COD–C*H*), 7.20–7.39 (m, 10H, *Ph*). ^{13}C NMR ($CDCl_3$, δ (ppm)): 26.7, 28.2, 30.3, 30.9, 34.2, 35.8, 63.9, 67.9, 70.6, 78.8, 127.9, 128.8, 151.5, 210,0. IR (KBr): ν_{max}/cm^{-1} 2962, 2872, 2828, 1743, 1467, 1261, 1099, 1024, 960, 864, 801, 696, 486. MS (CI) *m*/*z* (%): 494.9 (36, [M^+−(COD + I)]), 492.9 (57, [M^+−(COD + I + 2H)]), 435.4 (13, [M^+−(COD + I + 2H + *t*Bu)]), 381.4 (67, [M^+−(COD + I + 2*t*Bu)]), 187.3 (100, [M^+−(COD + I + 2*t*Bu + Rh + Bz)]).

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References

[1] K. Öfele, J. Organomet. Chem. 12 (1968) P42.
[2] H.W. Wanzlick, H.J. Schönherr, Angew. Chem., Int. Ed. Engl. 7 (1968) 141.
[3] (a) A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361;
(b) A.J. Arduengo, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530.
[4] (a) W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290;
(b) L. Jafarpour, S.P. Nolan, Adv. Organomet. Chem. 46 (2001) 181;
(c) D. Bourrissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39;
(d) W.A. Herrmann, C. Köcher, Angew. Chem., Int. Ed. 36 (1997) 2162;
(e)F. Glorius (Ed.), *N*-Heterocyclic Carbenes in Transition Metal Catalysis (Topics in Organometallic Chemistry), Springer, Berlin, Heidelberg, 2007;
(f)S.P. Nolan (Ed.), *N*-Heterocyclic Carbenes in Synthesis, Wiley-VCH, 2006.
[5] (a) J.E. Hill, T.A. Nile, J. Organomet. Chem. 137 (1977) 293;
(b) M.F. Lappert, R.I.K. Maskell, J. Organomet. Chem. 264 (1984) 217;
(c) M.G. Gardiner, W.A. Herrmann, C.P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239;
(d) A.C. Hillier, H.M. Lee, E.D. Stevens, S.P. Nolan, Organometallics 20 (2001) 4246;
(e) S. Lee, N.A. Beare, J.F. Hartwig, J. Am. Chem. Soc. 123 (2001) 8410;
(f) G.A. Grasa, M.S. Viciu, J.K. Huang, C.M. Zhang, M.L. Trudell, S.P. Nolan, Organometallics 21 (2002) 2866;
(g) R. Jackstell, A. Frish, M. Beller, D. Rottger, M. Malaun,

Bildstein, J. Mol. Catal. A: Chem. 185 (2002) 105;
(h) M. Muehlhofer, T. Strassner, W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1745;
(i) M. Sholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1991) 953.
[6] D.J. Cardin, B. Cetinkaya, P. Dixneuf, M.F. Lappert, Chem. Rev. 72 (1972) 545.
[7] W.A. Herrmann, L.J. Goossen, C. Köcher, G.R.J. Artus, Angew. Chem., Int. Ed. Engl. 35 (1996) 2805.
[8] (a) V. César, S. Bellemin-Laponnaz, L.H. Gade, Chem. Soc. Rev. 33 (2004) 619;
(b) S. Lee, J.F. Hartwig, J. Org. Chem. 66 (2001) 3402;
(c) M.C. Perry, K. Burgess, Tetrahedron: Asymmetry 14 (2003) 951.
[9] T.J. Seiders, D.W. Ward, R.H. Grubbs, Org. Lett. 3 (2001) 3225.
[10] M.C. Perry, X.H. Cui, M.T. Powell, D.R. Hou, J.H. Reibenspies, K. Burgess, J. Am. Chem. Soc. 125 (2003) 113.
[11] J.W. Faller, P.P. Fontaine, Organometallics 25 (2006) 5887.
[12] D. Baskakov, W.A. Herrmann, E. Herdtweck, St. D. Hoffmann, Organometallics 26 (2007) 626.
[13] J. Pytkowicz, S. Roland, P. Mangeney, J. Organomet. Chem. 631 (2001) 157.
[14] D.A. Axelson, Inorg. Synth. 19 (1979) 218.
[15] M. Paas, B. Wibbeling, R. Fröhlich, F.E. Hahn, Eur. J. Inorg. Chem. (2006) 158.
[16] H.M.J. Wang, J.B. Lin, Organometallics 17 (1998) 972.