

Priority Communication

N-heterocyclic carbenes: novel ruthenium–alkylidene complexes

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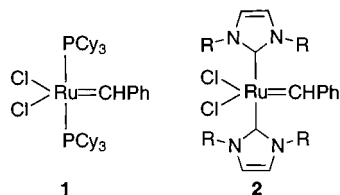
Abstract

Ruthenium-based catalysts for olefin metathesis have attained enormous attention during the past years. Recently we have shown that the application of *N*-heterocyclic carbenes extends and complements the ubiquitous phosphanes. We now report on new members of our family of ruthenium-based catalysts for olefin metathesis. The synthesis of novel mixed carbene/phosphane- and homo- and heterobimetallic rutheniumalkylidene complexes is presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: *N*-heterocyclic carbenes; Ruthenium; Homogeneous catalysis; Olefin metathesis

1. Introduction

During the last years *N*-heterocyclic carbenes (NHC) [1–3] have been well established as alternative ligands in homogenous catalysis [4–7]. In contrast to the corresponding phosphane complexes, their high dissociation energy makes these ligands promising for chiral modifications and catalyst immobilisation. Recently, we published a novel class of complexes **2** containing NHC as well as Schrock-type carbenes [8].



2a: R = Cyclohexyl
2b: R = (*R*)-Phenylethyl
2c: R = (*R*)-Naphthylethyl

These compounds prove to be highly active catalysts for all kinds of olefin metathesis reactions and smoothly combine the advantages of ruthenium–alkylidene complexes [RuCl₂(=CHR)(PR'₃)₂] **1** developed by

Grubbs et al. [9,10] with the unique properties of NHCs.

Herein, we report on the synthesis of novel mixed NHC/phosphane as well as homo- and heterobimetallic ruthenium-alkylidene complexes.

2. Experimental

All reactions were performed with standard Schlenk techniques in an oxygen-free nitrogen atmosphere. Solvents were dried by standard methods and distilled under N₂. NMR spectra were recorded on a Jeol JNM GX 400 instrument. Elemental analyses were performed in the microanalytical laboratory of our institute.

 2.1. General procedure for complexes **3**

A solution of 1.0 mmol of **1** in 100 ml of THF was treated with a solution of the appropriate 1,3-dialkylimidazolin-2-ylidene (1.2 mmol) in 20 ml of THF at –78°C. The reaction mixture was slowly warmed to room temperature. The solution was filtered and the solvent removed. The complex was dissolved in 2 ml of toluene at room temperature. Upon addition of pentane (20 ml) and cooling to –78°C, a solid was precipitated which was separated from the mother-liquid, dissolved in 2 ml of toluene and reprecipitated with pentane at –78°C.

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2.1.1. Complex **3a**

Yield: 80%; $C_{40}H_{63}Cl_2N_2PRu$: Calc. C 61.99, H 8.20, N 3.62; Found C 61.11; H 8.29; N 3.59. 1H -NMR (CD_2Cl_2): δ = 20.30 (1H, d, $^3J_{PH} = 7.4$ Hz, Ru=CH), 8.33 (2H, d, $^3J_{HH} = 7.4$ Hz, *o*-H of C_6H_5), 7.62 (1H, t, $^3J_{HH} = 7.4$ Hz, *p*-H of C_6H_5), 7.33 (2H, t, $^3J_{HH} = 7.4$ Hz, *m*-H of C_6H_5), 7.11 (1H, s, NCH), 6.92 (1H, s, NCH), 5.97 (1H, m, CH of NC_6H_{11}), 3.36 (1H, m, CH of NC_6H_{11}), 2.42 (3H, m, CH of PCy_3), 1.90–0.89 (50H, all m, CH_2 of NC_6H_{11} and PCy_3). ^{13}C -NMR (CD_2Cl_2): δ = 298.7 (Ru=CH), 181.2 (d, $J_{PC} = 88$ Hz, NCN), 152.5 (*ipso*-C of C_6H_5), 130.8, 129.8, and 129.2 (*o*-C, *m*-C, and *p*-C of C_6H_5), 118.9 and 118.0 (NCH), 59.5 and 57.7 (CH of NC_6H_{11}) 33.2 (d, $J_{PC} = 17$ Hz, *ipso*-C of PCy_3), 29.9 (s, *m*-C of PCy_3), 26.8 (d, $J_{PC} = 3.7$ Hz, *o*-C of PCy_3), 25.4 (s, *p*-C of PCy_3) 34.9, 33.3, 33.1, 28.2, 28.1, and 25.7 (CH_2 of NC_6H_{11}). ^{31}P -NMR (CD_2Cl_2): δ = 28.2.

2.1.2. Complex **3b**

Yield: 74%; $C_{44}H_{59}Cl_2N_2PRu$: Calc. C 64.53, H 7.27, N 3.42; Found C 64.58, H 7.34, N 3.44. 1H -NMR (CD_2Cl_2): δ = 20.19 (1H, d, $^3J_{PH} = 4.5$ Hz, Ru=CH), 7.74–7.00 (15H, all m, CH of C_6H_5), 6.83 (1H, m, NCHMePh), 6.73 (1H, s, NCH), 6.70 (1H, s, NCH), 2.52 (1H, m, NCHMePh), 2.44 (3H, m, CH of PCy_3), 2.11 (3H, d, $^3J_{HH} = 6.8$ Hz, NCHMePh), 1.82–1.12 (30H, all m, CH_2 of PCy_3) 1.35 (3H, d, $^3J_{HH} = 6.8$ Hz, NCHMePh). ^{13}C -NMR (CD_2Cl_2): δ = 292.7 (Ru=CH), 183.4 (d, $J_{PC} = 78$ Hz, NCN), 151.8 (*ipso*-C of C_6H_5), 140.1 and 139.5 (*ipso*-C of NCHMePh), 129.5, 128.5, 128.3, 127.9, 127.5, 127.4, 127.2, 126.6, and 126.1 (*o*-C, *m*-C, and *p*-C of C_6H_5) 119.8 and 118.4 (NCH), 57.4 and 56.2 (NCHMePh), 31.3(d, $J_{PC} = 17$ Hz, *ipso*-C of PCy_3), 29.0 (s, *m*-C of PCy_3), 28.9 (s, *m*-C of PCy_3), 27.2 (d, $J_{PC} = 3.7$ Hz, *o*-C of PCy_3), 27.0 (d, $J_{PC} = 3.7$ Hz, *o*-C of PCy_3), 25.8 (s, *p*-C of PCy_3) 21.7 and 20.3 (NCHMePh). ^{31}P -NMR (CD_2Cl_2): δ = 38.1.

2.1.3. Complex **3c**

Yield: 72%; $C_{52}H_{63}Cl_2N_2PRu$: Calc. C 67.95, H 6.91, N 3.05; Found C 68.09, H 7.02, N 3.04. 1H -NMR (CD_2Cl_2): δ = 20.33 (1H, d, $^3J_{HH} = 5.4$ Hz, Ru=CH), 8.88 (2H, d, $^3J_{HH} = 8.0$ Hz, *o*-H of C_6H_5) 7.94–6.96 (17H, all m, CH of C_6H_5), 6.70 (1H, s, NCH), 6.61 (1H, s, NCH), 5.83 (1H, m, NCHMeNaph), 2.59 (1H, m, NCHMeNaph), 2.49 (3H, m, CH of PCy_3), 2.44 (3H, d, $^3J_{HH} = 6.8$ Hz, NCHMeNaph), 1.95–1.01 (30H, all m, CH_2 of PCy_3) 1.54 (3H, d, $^3J_{HH} = 6.8$ Hz, NCHMeNaph). ^{13}C -NMR (CD_2Cl_2): δ = 298.4 (Ru=CH), 184.0 (d, $J_{PC} = 87$ Hz, NCN), 152.3 (*ipso*-C of C_6H_5), 138.3 and 137.6 (*ipso*-C of NCHMeNaph), 134.3 – 122.9 (*o*-C, *m*-C, and *p*-C of C_6H_5 , CHMeNaph) 120.6 and 119.5 (NCH), 56.4 and 55.7 (NCHMeNaph), 32.5(d, $J_{PC} = 17$ Hz, *ipso*-C of PCy_3), 30.1 (s, *m*-C of PCy_3), 30.0 (s, *m*-C of PCy_3), 28.1 (pseudo-t,

$J_{PC} = 7.4$ Hz, *o*-C of PCy_3), 26.8 (s, *p*-C of PCy_3) 24.0 and 22.7 (NCHMeNaph). ^{31}P -NMR (CD_2Cl_2): δ = 31.8.

2.1.4. Complex **3d**

A solution of 1.0 mmol of $RuCl_2(PPh_3)_2(CHPh)$ in 10 ml of THF was treated with a solution of the appropriate 1,3-dialkyl-imidazolin-2-ylidene (1.2 mmol) in 20 ml of THF at $-78^\circ C$. The reaction mixture was slowly warmed to room temperature. The solution was filtered and the solvent removed. The complex was dissolved in 2 ml of toluene at room temperature. Upon addition of pentane (20 ml, a solid was precipitated which was separated from the mother-liquid, dissolved in 2 ml of toluene and reprecipitated with pentane. Yield: 70%; $C_{36}H_{41}Cl_2N_2PRu$: Calc. C 61.36, H 5.86, N 3.98; Found C 61.12, H 5.55, N 3.62. 1H -NMR (CD_2Cl_2): δ 20.70 (1H, s, Ru=CH), 8.03 (2H, d, $^3J_{HH} = 7.6$ Hz, *o*-H of C_6H_5), 7.50–6.95 (20H, of which 2*m*-H and 1*p*-H of C_6H_5 , 15H of PPh_3 and 2H of NCH), 1.86 (9H, s, $NCMe_3$), 1.45 (9H, s, $NCMe_3$). ^{13}C -NMR (CD_2Cl_2): δ 307.4 (br, Ru=CH), 178.3 (d, $J_{PC} = 86$ Hz, NCN), 151.5 (d, $J_{PC} = 4.5$ Hz, *ipso*-C of C_6H_5), 135.0 (m, *o*-C of PPh_3), 131.9 (m, *ipso*-C of PPh_3), 130.2 (s, *p*-C of PPh_3), 129.5, 128.6 and 128.1 (s, *o*-C, *m*-C and *p*-C of C_6H_5), 128.0 (m, *m*-C of PPh_3), 117.7 and 117.6 (NCH), 58.7 and 58.5 ($NCMe_3$), 30.0 and 29.5 ($NCMe_3$). ^{31}P -NMR (CD_2Cl_2): δ 40.7 (s, PPh_3).

2.2. General procedure for compounds **4a–4d**

A solution of 1.0 mmol of **2a** and **3a**, respectively, in 20 ml of CH_2Cl_2 was treated with a solution of 1.0 mmol $[LMCl_2]_2$ in 10 ml of CH_2Cl_2 and stirred at room temperature. The solution was filtered and the solvent removed.

2.2.1. Compound **4a**

Starting at **3a** and $[(p\text{-cymene})RuCl_2]_2$; reaction time: 2 h; work-up by washing with toluene/pentane (1/2). Yield: 86%; $C_{32}H_{44}Cl_4N_2Ru_2$: Calc. C 48.00, H 5.54, N 3.50; Found C 48.11; H 5.61; N 3.52. 1H -NMR (CD_2Cl_2): δ = 21.14 (1H, s, Ru=CH), 7.89 (2H, d, $^3J_{HH} = 7.8$ Hz, *o*-H of C_6H_5), 7.67 (1H, t, $^3J_{HH} = 7.8$ Hz, *p*-H of C_6H_5), 7.22 (2H, t, $^3J_{HH} = 7.8$ Hz, *m*-H of C_6H_5), 7.09 (1H, s, NCH), 6.65 (1H, s, NCH), 5.70 (1H, m, CH of NC_6H_{11}), 5.53, 5.50, 5.43, and 5.28 (all 1H, d, $^3J_{HH} = 5.7$ Hz, CH of *p*-cymene) 3.05 (1H, m, CH of NC_6H_{11}), 2.85 (1H, m, $CH(CH_3)_2$ of *p*-cymene), 2.34 (3H, s, CH_3 of *p*-cymene), 1.82–0.91 (20H, all m, CH_2 of NC_6H_{11}), 1.41 (3H, d, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$ of *p*-cymene), 1.27 (3H, d, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$ of *p*-cymene). ^{13}C -NMR (CD_2Cl_2): δ = 319.4 (Ru=CH), 165.2 (NCN), 154.0 (*ipso*-C of C_6H_5), 131.4, 130.7, and 128.7 (*o*-C, *m*-C, and *p*-C of C_6H_5), 119.1 and 118.0 (NCH), 101.3, 96.8, 81.3, 80.6, 79.7, and 79.4

(*p*-cymene), 58.9 and 56.7 (CH of NC₆H₁₁), 36.0, 34.9, 31.3, 25.8, 25.4, and 22.3 (CH₂ of NC₆H₁₁), 30.8 (CH(CH₃)₂ of *p*-cymene), 22.2 and 21.9 (CH(CH₃)₂ of *p*-cymene), 18.8 (CH₃ of *p*-cymene).

2.2.2. Compound 4b

Starting at **2a** and [(*p*-cymene)OsCl₂]₂ reaction time: 3 h; work-up by flash chromatography. Yield: 32%; C₃₂H₄₄Cl₄N₂OsRu: Calc. C 43.14, H 4.98, N 3.15; Found C 43.31; H 5.11; N 3.13. ¹H-NMR (CD₂Cl₂): δ = 21.21 (1H, s, Ru=CH), 7.91 (2H, d, ³J_{HH} = 6.4 Hz, *o*-H of C₆H₅), 7.72 (1H, t, ³J_{HH} = 6.4 Hz, *p*-H of C₆H₅), 7.24 (2H, t, ³J_{HH} = 6.4 Hz, *m*-H of C₆H₅), 7.04 (1H, s, NCH), 6.69 (1H, s, NCH), 5.70 (1H, m, CH of NC₆H₁₁), 6.08 (1H, d, ³J_{HH} = 5.9 Hz, CH of *p*-cymene), 5.95 (1H, d, ³J_{HH} = 5.9 Hz, CH of *p*-cymene), 5.75 (2H, app t, ³J_{HH} = 5.9 Hz, CH of *p*-cymene), 3.07 (1H, m, CH of NC₆H₁₁), 2.83 (1H, m, CH(CH₃)₂ of *p*-cymene), 2.34 (3H, s, CH₃ of *p*-cymene), 1.90–0.85 (20H, all m, CH₂ of NC₆H₁₁), 1.39 (3H, d, ³J_{HH} = 6.8 Hz, CH(CH₃)₂ of *p*-cymene), 1.33 (3H, d, ³J_{HH} = 6.8 Hz, CH(CH₃)₂ of *p*-cymene). ¹³C-NMR (CD₂Cl₂): δ = 319.7 (Ru=CH), 165.0 (NCN), 153.9 (*ipso*-C of C₆H₅), 131.2, 130.7, and 128.6 (*o*-C, *m*-C, and *p*-C of C₆H₅), 119.3 and 118.1 (NCH), 96.5, 91.5, 71.6, 71.4, 70.4, and 69.7 (*p*-cymene), 58.8 and 56.5 (CH of NC₆H₁₁), 35.8, 35.3, 31.2, 25.9, 25.2, and 22.7 (CH₂ of NC₆H₁₁), 31.2 (CH(CH₃)₂ of *p*-cymene), 22.2 and 22.1 (CH(CH₃)₂ of *p*-cymene), 18.7 (CH₃ of *p*-cymene).

2.2.3. Compound 4c

Starting at **2a** and [Cp*^{Rh}Cl₂]₂; reaction time: 20 min; work-up by flash chromatography. Yield: 21%; C₃₂H₄₅Cl₄N₂RhRu: Calc. C 47.88, H 5.65, N 3.49; Found C 47.99, H 5.70, N 3.45. ¹H-NMR (CD₂Cl₂): δ = 21.20 (1H, s, Ru=CH), 7.95 (2H, d, ³J_{HH} = 7.2 Hz, *o*-H of C₆H₅), 7.67 (1H, t, ³J_{HH} = 7.2 Hz, *p*-H of C₆H₅), 7.25 (2H, t, ³J_{HH} = 7.2 Hz, *m*-H of C₆H₅), 7.09 (1H, s, NCH), 6.68 (1H, s, NCH), 6.57 (1H, m, CH of NC₆H₁₁), 2.97 (1H, m, CH of NC₆H₁₁), 1.85–0.86 (20H, all m, CH₂ of NC₆H₁₁), 1.74 (15H, s, CH₃ of Cp*). ¹³C-NMR (CD₂Cl₂): δ = 319.3 (Ru=CH), 164.4 (NCN), 153.5 (*ipso*-C of C₆H₅), 131.2, 130.4, and 128.7 (*o*-C, *m*-C, and *p*-C of C₆H₅), 118.9 and 118.3 (NCH), 94.3 (d, J_{RhC} = 7.5 Hz, CCH₃ of Cp*), 58.3 and 56.4 (CH of NC₆H₁₁), 35.2, 34.1, 33.3, 25.8, 22.4, 21.2 (CH₂ of NC₆H₁₁), 9.31 (CH₃ of Cp*).

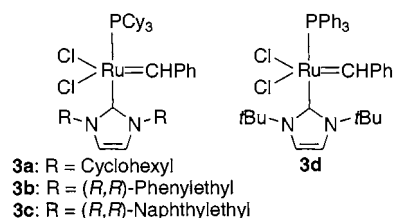
2.2.4. Compound 4d

Starting at **2a** and [Cp*^{Ir}Cl₂]₂; reaction time: 1.5 h; work-up by flash chromatography. Yield: 25%; C₃₂H₄₅Cl₄N₂IrRu: Calc. C 43.05, H 5.08, N 3.14; Found C 43.19, H 5.13, N 3.05. ¹H-NMR (CD₂Cl₂): δ = 21.22 (1H, s, Ru=CH), 7.99 (2H, d, ³J_{HH} = 7.3 Hz, *o*-H of C₆H₅), 7.69 (1H, t, ³J_{HH} = 7.3 Hz, *p*-H of C₆H₅), 7.28 (2H, t, ³J_{HH} = 7.3 Hz, *m*-H of C₆H₅), 7.04

(1H, s, NCH), 6.70 (1H, s, NCH), 6.65 (1H, m, CH of NC₆H₁₁), 3.03 (1H, m, CH of NC₆H₁₁), 1.84–0.88 (20H, all m, CH₂ of NC₆H₁₁), 1.70 (15H, s, CH₃ of Cp*). ¹³C-NMR (CD₂Cl₂): δ = 319.9 (Ru=CH), 165.2 (NCN), 153.7 (*ipso*-C of C₆H₅), 131.2, 130.4, and 128.7 (*o*-C, *m*-C, and *p*-C of C₆H₅), 118.5 and 118.0 (NCH), 88.0 (CCH₃ of Cp*), 59.4 and 58.0 (CH of NC₆H₁₁), 36.2, 35.8, 35.3, 26.2, 25.6, 24.2 (CH₂ of NC₆H₁₁), 9.42 (CH₃ of Cp*).

3. Results and discussion

Mixed NHC/phosphane complexes **3a–3c** with any *N*-heterocyclic carbene (NHC) [1,11,12] known from **2** are accessible in excellent yields by adding 1.2 equiv. of the appropriate NHC to a solution of **1** in THF at low temperatures [13].

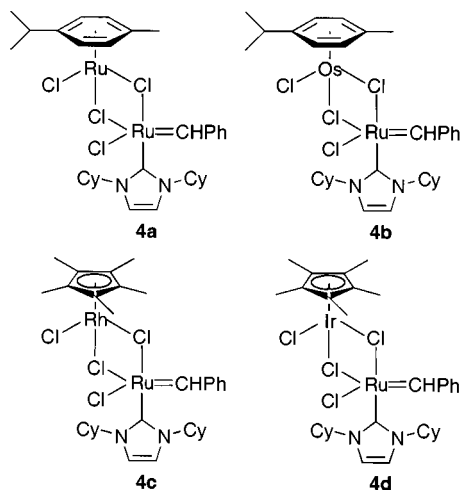


Even chiral derivatives, like **3b** and **3c** are conveniently available. In all cases, low temperature is crucial for the selectivity of the phosphane/NHC substitution. At room temperature selectivity is poor and mixtures with significant amounts of the corresponding dicarbene complexes **2** are generated. It is important to note that adding a large excess of tricyclohexylphosphane to **3a–3c** cannot reverse the reaction, clearly demonstrating the stability of the complexes as well as the stronger Lewis basicity of NHC with respect to trialkylphosphanes.

Mixing **1** and **2a** in stoichiometric amounts affords **3a** in about 15% yield after 12 h. This reaction is even observed in technical grade solvents without the exclusion of air pointing to a bimolecular mechanism for the NHC transfer rather than involvement of a free, dissociated NHC which is unlikely to survive these conditions. In contrast, no rearrangement of **3** to **1** and **2** whatsoever is observed in solution.

In the case of the corresponding triphenylphosphane/NHC complexes the steric bulk of the NHC is even more crucial, e.g. the *tert*-butyl derivative **3d** is obtained in high yields, whereas other NHCs successfully applied for the synthesis of **3a–3c** afford these NHC/PPh₃-complexes in significantly lower yields.

The increased catalytic activity of homo- and hetero-bimetallic ruthenium–phosphane-complexes in ROMP [14] prompted us to synthesise the corresponding NHC complexes **4a–4d**.



The differences in reactivity of the chloro-bridged organometallic precursors gives an interesting insight into the affinity of different metal fragments to NHCs. In the case of $[(p\text{-cymene})\text{RuCl}_2]_2$, **4a** can only be obtained from **3a** as starting material. Selective substitution of the phosphane ligand occurs, whereas the NHC remains untouched. Starting at **2a** reveals no conversion. In contrast, **4b–4d** have to be synthesised from **2a**. Starting at **3a** leads to a mixture of hetero-bimetallic phosphane and NHC complexes. Apparently, the decisive criterion for the reactivity is the different affinity of the NHC to the chloro-bridged compounds, which is illustrated by the reaction times for quantitative conversion: Rh(III) (20 min) > Ir(III) (1.5 h) > Os(II) (3 h) > Ru(II) (no reaction).

First applications of these catalysts in ring-opening metathesis polymerisation (ROMP) and ring-closing metathesis (RCM) show a significantly higher catalytic activity than any complexes of this type known yet. More detailed investigations are in progress.

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