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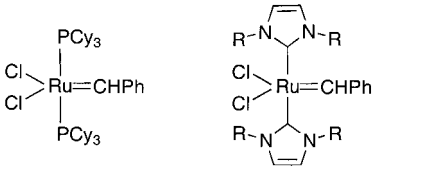
Highly Active Ruthenium Catalysts for Olefin Metathesis: The Synergy of N-Heterocyclic Carbenes and Coordinatively Labile Ligands**

Thomas Weskamp, Florian J. Kohl, Wolfgang Hieringer, Dieter Gleich, and Wolfgang A. Herrmann*

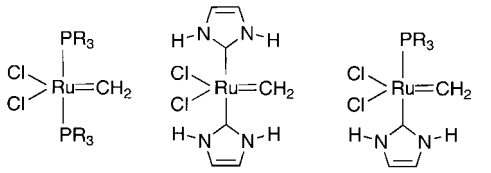
N-Heterocyclic carbenes (NHCs) have been established in homogeneous catalysis to complement and extend the capabilities of the ubiquitous phosphanes.[1, 2] In olefin metathesis[3] ruthenium alkylidene compounds **2**[4] bearing two NHC ligands exhibit a catalytic activity comparable to that of the phosphane system **1**.[5] Herein, we show that it is the combination of NHCs with coordinatively more labile ligands on the ruthenium center that allows NHCs to develop their full potential in this class of catalysts.



1 **2**

2a: R = Isopropyl
2b: R = Cyclohexyl (Cy)

In the catalytic cycle of olefin metathesis the mechanistic scheme for **1** postulates the dissociation of a phosphane ligand as the key step in the dominant reaction pathway.[6] Theoretical investigations of Group 11 transition metal NHC complexes, which suggest a strong metal – NHC bond,[7] raise the question as to whether this mechanism can be transferred to metathesis catalysts of type **2**. To address this problem we calculated the dissociation energies of NHC and phosphanes for ruthenium – alkylidene model compounds (Figure 1) according to Equation (1) by density functional (DFT) methods.[8, 9] The results compiled in Table 1 demonstrate that the ligand dissociation energies ascend in the series $PH_3 < PMe_3 < NHC$.[10a] As a consequence of the higher coordination energy the dicarbene complexes **2** should disfavor a dissociative pathway similar to that of **1**.[6] A mixed NHC/phosphane complex of type **3**, however, reveals a phosphane dissociation energy in the same order of magnitude as **1**. Therefore, **3** should be able to populate the dissociative pathway[6] just as readily as **1**. In contrast to **1**, however, a phosphane-free species **A** is considered as the key intermediate in the catalytic cycle.

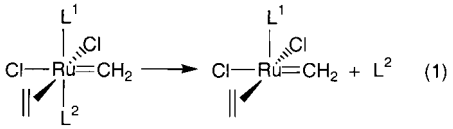


1m: R = H
1n: R = Methyl

2m

3m: R = H
3n: R = Methyl

Figure 1. Model compounds for the calculation of ligand dissociation energies.



(1)

Table 1. Calculated ligand dissociation energies ΔE [kcal mol^{-1}] for the model compounds as depicted in Equation (1).[a]

Model compound	ΔE for PH_3	ΔE for PMe_3	ΔE for NHC
1m ($L^1 = L^2 = PH_3$)	18.2 (19.4)	–	–
1n ($L^1 = L^2 = PMe_3$)	–	27.0 (25.8)	–
2m ($L^1 = L^2 = NHC$)	–	–	45.0 (42.2)
3m ($L^1 = PH_3$, $L^2 = NHC$)	18.7 (15.8)	–	46.9 (49.7)
3n ($L^1 = PMe_3$, $L^2 = NHC$)	–	26.0 (24.9)	42.0 (43.4)

[a] Ligand dissociation energies without ethylene coordination are given in brackets.

The air-stable NHC/phosphane complexes **3a – c** are accessible in excellent yields by adding 1.2 equivalents of the appropriate NHC to a solution of **1** in THF.[11] Low temperature is crucial for the selectivity of the phosphane/NHC substitution reaction. At room temperature the selectivity is

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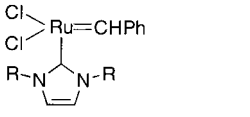
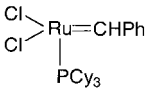


A



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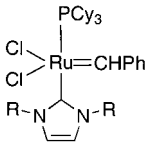


3

3a: R = Cyclohexyl
3b: R = (*R*,*R*)-Phenylethyl
3c: R = (*R*,*R*)-Naphthylethyl

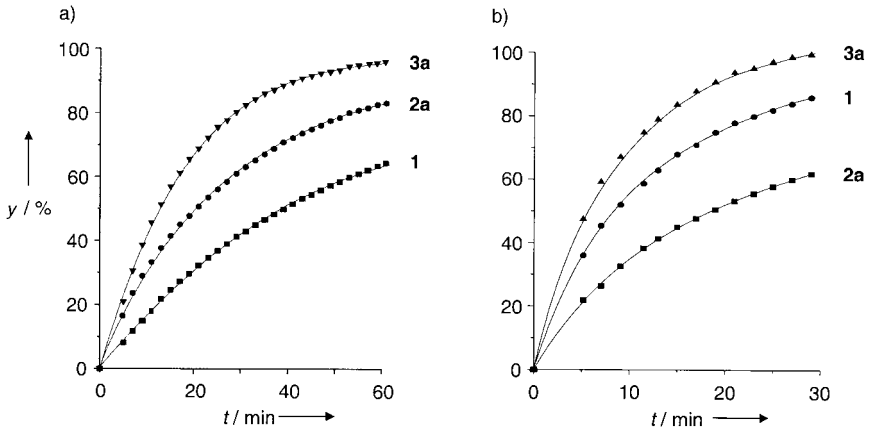
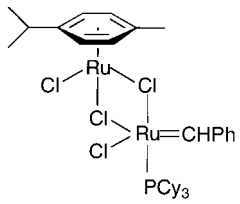


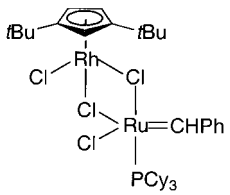
Figure 2. a) ROMP of 1,5-cyclooctadiene (y = yield of the polyoctadienamer). Comparison of catalysts **1**, **2a**, and **3a** as monitored by NMR spectroscopy (T = 25 °C; 1.70 μmol catalyst in 0.55 mL of CD_2Cl_2; [1,5-cyclooctadiene]/[catalyst] = 250:1). b) ROMP of cyclooctene (y = yield of the polyoctenamer). Comparison of catalysts **1**, **2a**, and **3a** as monitored by NMR spectroscopy (T = 25 °C; 2.50 μmol catalyst in 0.50 mL of CD_2Cl_2; [cyclooctene]/[catalyst] = 250:1).

lower and mixtures with significant amounts of the corresponding dicarbene complexes **2** are generated. Even the addition of a large excess of tricyclohexylphosphane to **3** cannot reverse the reaction, which illustrates the stability of the complexes as well as the higher Lewis basicity of NHC with respect to trialkylphosphanes. ROMP-benchmark tests[4, 12] with cyclooctene and 1,5-cyclooctadiene demonstrate a significant increase in the catalytic activity of **3** with respect to **1** and **2** (Figure 2). The activity of **3** gives rise to the assumption that intermediate **A** is more active than its phosphane analogue **B**.

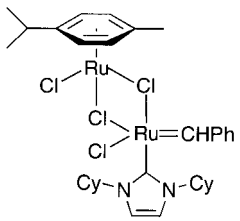
In the next step DFT calculations were performed on a model compound to shed light on the dissociation behavior of the recently published, highly active bimetallic phosphane complexes **4a** and **4b**.[12] Substitution of the phosphane ligand



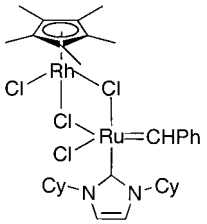
4a



4b

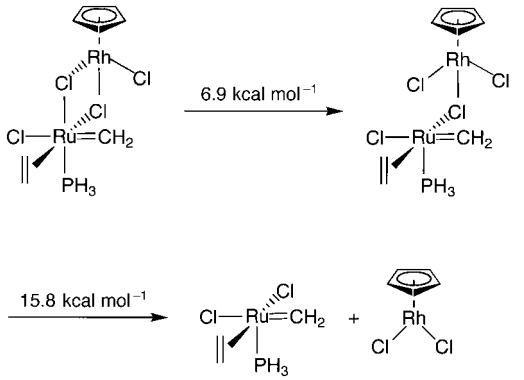


5a



5b

by a NHC makes sense if the metal fragment rather than the phosphane is to be considered decisive for opening up a dissociative pathway in **4**. Therefore, we assume a simplified two-step dissociation mechanism with a sequential heterolytic cleavage of the two chloro bridges [Eq. (2)].[10] The computational results show that liberation of the first coordination site by rupture of the axial chloro bridge is energetically even more favorable than phosphane dissociation. Complete dissociation of the {$CpRhCl_2$} fragment compares with trimethylphosphane dissociation and is furthermore assisted by the exothermic dimerization reaction of {$CpRhCl_2$} to give [{$CpRhCl_2$}]$_2$ (−24.1 kcal mol^{-1}[8]), which renders the overall process thermoneutral (Cp = C_5H_5). On the basis of these results the "ligand" $CpRhCl_2$ is considered as a coordinatively labile fragment,[12] thus favoring a dissociative pathway and making **5a** and **5b** promising catalysts for olefin metathesis.[13]



(2)

Compound **5a** is accessible from **3a** and [{Ru(*p*-cymene)Cl_2}$_2$], which selectively substitutes the phosphane ligand of **3a**, leaving the NHC untouched. In contrast, [{Cp*$RhCl_2$}$_2$] substitutes the NHC moiety as well; thus, **5b** can be synthesized starting from **2b**. The catalyst concept indeed works, as can be seen from a comparison of the bimetallic compounds **5a** and **5b**, NHC/phosphane complex **3a**, dicarbene complex **2a**, and diphosphane complex **1** in ROMP of 1,5-cyclooctadiene (Figure 3). The substrate-specific relative rate constants k_{rel}, approximated by first-order curve fits,[12] illustrate the improvement achieved by the application of more labile coligands within NHC systems. Moreover, the significantly higher rate constants for **5a** (k_{rel} = 13) and **5b** (k_{rel} = 65) with respect to **4a** (k_{rel} = 2.4) and **4b** (k_{rel} = 6)[12] again suggest the higher activity of intermediate **A** relative to **B**.

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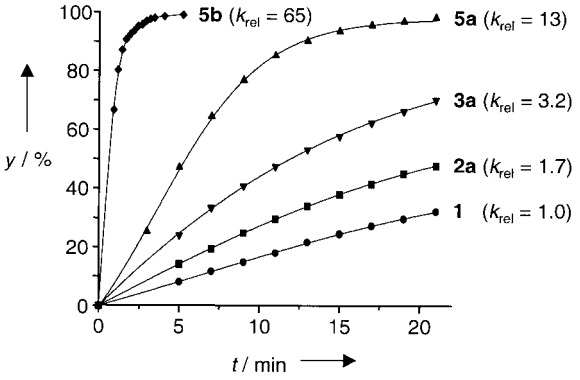

Figure 3. ROMP of 1,5-cyclooctadiene (y = yield of polyoctadienamer). Comparison of catalysts **1a**, **2a, 3a**, **5a**, and **5b** as monitored by NMR spectroscopy (T = 25 °C; 1.70 μmol catalyst in 0.55 mL of CD_2Cl_2; [1,5-cyclooctadiene]/[catalyst] = 250:1).

The favorable features of our novel NHC systems are not limited to the benchmark tests mentioned above. For example, as a result of its rapid initialization **5a** facilitates living ROMP of substrates such as 2,3-bis(carbomethoxy)norbornadiene (M_n = 187 kg mol^{-1}; PDI = 1.1; 41 % *cis*), which has not yet been achieved with other ruthenium systems.[14] Furthermore, **3** and **5a** exhibit excellent performance in the synthesis of tetra-substituted cycloalkenes by ring-closing metathesis.[11b, 15] Since these products are not accessible with **1** they used to be a domain of Schrock's more active, but also significantly more sensitive, molybdenum catalyst.[16]

The synergy of NHC and coordinatively labile ligands allows for the synthesis of catalysts for olefin metathesis that combine high catalytic activity with excellent stability even against air and moisture. This concept also proves successful in catalytic processes other than metathesis, such as palladium-catalyzed coupling reactions.[17]

Experimental Section

3 (general procedure): A solution of **1** (1.0 mmol) in THF (100 mL) was treated with a solution of the appropriate 1,3-dialkylimidazolin-2-ylidene (1.2 mmol) in THF (20 mL) at −78 °C and was slowly warmed to room temperature. The solution was filtered and the solvent removed. The complex was dissolved in toluene (2 mL) and precipitated at −78 °C by adding pentane (20 mL). This procedure was repeated twice. **3a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 20.30 (1 H, d, $^3J_{PH}$ = 7.4 Hz, Ru=CH); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 298.7 (Ru=CH), 181.2 (d, J_{PC} = 88 Hz, NCN); ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ = 28.2. Yield: 80 %; elemental analysis calcd for $C_{40}H_{63}Cl_2N_2PRu$: C 61.99, H 8.20, N 3.62; found: C 61.11, H 8.29, N 3.59. **3b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 20.19 (1 H, d, $^3J_{PH}$ = 4.5 Hz, Ru=CH); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 292.7 (Ru=CH), 183.4 (d, J_{PC} = 78 Hz, NCN); ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ = 38.1. Yield: 74 %; elemental analysis calcd for $C_{44}H_{59}Cl_2N_2PRu$: C 64.53, H 7.27, N 3.42; found: C 64.58, H 7.34, N 3.44. **3c**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 20.33 (1 H, d, $^3J_{HH}$ = 5.4 Hz, Ru=CH); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 298.4 (Ru=CH), 184.0 (d, J_{PC} = 87 Hz, NCN); ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ = 31.8. Yield: 72 %; elemental analysis calcd for $C_{52}H_{63}Cl_2N_2PRu$: C 67.95, H 6.91, N 3.05; found: C 68.09, H 7.02, N 3.04.

5 (general procedure): A solution of **2b** (1.0 mmol) or **3a** (1.0 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of [{Ru(*p*-cymene)Cl_2}$_2$] (1.0 mmol) or [{Cp*RhCl_2}$_2$] (1.0 mmol), respectively, in CH_2Cl_2 (10 mL) and stirred at room temperature. The solution was filtered and the solvent removed. **5a**: Starting from **3a**; work-up by washing with toluene/pentane (1/2). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 21.14 (1 H, s, Ru=CH); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 319.4 (Ru=CH), 165.2 (NCN). Yield: 86 %; elemental analysis calcd for $C_{32}H_{44}Cl_4N_2Ru_2$: C 48.00, H 5.54, N 3.50; found: C 48.11, H 5.61, N 3.52. **5b**: Starting from **2b**; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 21.20 (1 H, s, Ru=CH); ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 319.3 (Ru=CH), 164.4 (NCN). Yield: quantitative conversion after 20 min; 21 % after work-up by flash chromatography. Elemental analysis calcd for $C_{32}H_{45}Cl_4N_2RhRu$: C 47.88, H 5.65, N 3.49; found: C 47.99, H 5.70, N 3.45. The crude product may be used for catalysis without any detectable influence on activity.

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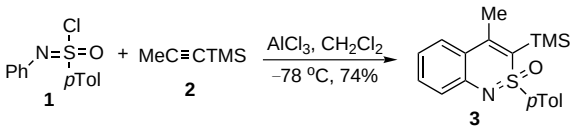
A One-Pot, One-Operation [3+3] Annulation Approach to Benzothiazines**

Michael Harmata* and Neville Pavri

Some time ago we introduced the Lewis acid mediated reaction of *N*-aryl sulfonimidoyl chlorides with alkynes as a means of accessing 2,1-benzothiazines.[1] For example, the reaction of **1** (pTol = p-$H_3CC_6H_4$) with 1-trimethylsilyl-1-propyne (**2**, TMS = Me_3Si) in the presence of $AlCl_3$ afforded benzothiazine **3** regioselectively and in good yield [Eq. (1)].



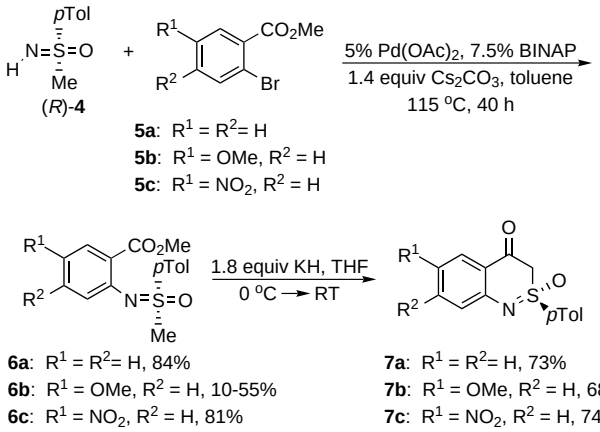
(1)

The reaction proceeded in a Markownikoff fashion and generally afforded good yields of adducts with a variety of alkynes. We extended this reaction to alkenes with equal success[2] and have subsequently demonstrated that the heterocycles produced by either sequence are useful in the preparation of other compounds, including 2-allyl-, 2-alkyl-, and 2-alkenylanilines.[3]

Although benzothiazines such as **3** are chiral the stereochemical lability of sulfonimidoyl chlorides[4] suggested that it would be difficult to prepare enantiomerically pure benzothiazines with the reaction we had introduced, thus limiting the possiblities of exploiting such compounds in asymmetric synthesis as chiral templates, for example.

Advances in the amination of aryl halides, however, indicated that a solution to this problem might be found.[5] In particular, Bolm and Hildebrand reported[6] that NH sulfoximines could be coupled to aryl halides, which suggested to us that it would be possible to devise a one-pot, one-operation synthesis of enantiomerically pure benzothiazines using enantiomerically pure sulfoximines and appropriately substituted aryl halides such as *ortho*-bromobenzaldehydes or benzoate esters.

Our initial studies were conducted with a small number of *ortho*-bromobenzoate esters. The results are summarized in Scheme 1. Formation of a nitrogen – carbon bond was at-



Scheme 1. Two-pot procedure for benzothiazine synthesis. BINAP = 1,1′-binaphthalene-2,2′-diylbis(diphenylphophane).

tempted using (*R*)-**4**[7] and the bromoarene in the presence of 5 mol% of $Pd(OAc)_2$, 7.5 mol% of racemic BINAP, and 1.4 equivalents of cesium carbonate, as described by Bolm and Hildebrand.[6] Although more studies are needed to define substituent effects in this series it is clear that a π donor *para* to the bromine substituent, as in **5b**, is detrimental to the coupling process; adduct **6b** is obtained in only 10% yield. A similar result was obtained by Bolm and Hildebrand with 4-*tert*-butyl bromobenzene.[6] However, the yield of **6b** could be improved to 55% if the catalyst and ligand loading were doubled.

Despite the fact that the coupling occurred under basic conditions, only formation of a nitrogen – carbon bond was observed. Attempts to convert **6a** into **7a** by using sodium methoxide in methanol were unsuccessful. However, stronger bases such as NaH and KH worked well, and we used excess KH in THF to effect this transformation. The benzothiazines **7a** – **c** were prepared in good yield with this procedure (Scheme 1).

We were also able to prepare the cinnamate derivative **8** in 59% yield by using the coupling methodology. Cyclization to the benzothiazine **9** occurred in 70% yield upon treatment with lithium diisopropylamide (LDA) [Eq. (2)]. A single stereoisomer was obtained, and its structure was assigned on the basis of X-ray data.[8]

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