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Communication

Convenient syntheses of novel ruthenium catalysts bearing *N*-heterocyclic carbenes☆

Walter Baratta [a,1], Wolfgang A. Herrmann [b,*], Pierluigi Rigo [a], Jürgen Schwarz [b]

[a] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, via Cotonificio 108, I-33100 Udine, Italy*
[b] *Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*

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Abstract

The 16-electron ruthenium(II) complexes Cp*Ru[C(R)N(H)C=C(H)N(R)]Cl (Cp* = η^5-C_5Me_5; R = Cy (ICy), **1a**; Mes (IMes), **1b**) containing *N*-heterocyclic carbenes are easily accessible in quantitative yields from $[Cp^*Ru(OMe)]_2$ (Me = CH_3) and the corresponding 1,3-diorganylimidazolium chloride by methanol elimination. Compounds **1a–b** can also be prepared in 75–80% yield by treating the commercially available polymeric ruthenium(III) compound $[Cp^*RuCl_2]_n$ with the free 1,3-diorganylimidazolin-2-ylidenes in 1 to 1.5 molar amounts. **1a** reacts with CO, PPh_3, pyridine and ethyl diazoacetate (EDA) affording the 18-electron derivatives Cp*Ru(ICy)(L)Cl (L = CO, **2**; PPh_3, **3**; py, **4**; $CHCO_2Et$, **5**). The mixed dicarbene complex **5** is the first isolable ruthenium cyclopentadienyl species bearing a $CHCO_2Et$ moiety. Compounds **1a–b** catalyze the carbon–carbon coupling of terminal alkynes HC≡CR (R = Ph, $SiMe_3$, ^{t}Bu, *p*-Tol) under mild conditions, with the selectivity strongly depending on the substituent R.

Keywords: Ruthenium; Carbenes; Alkyne coupling; Homogeneous catalysis

1. Introduction

Coordinatively unsaturated ruthenium complexes continue to attract a great deal of interest because of their implications in manifold catalytic transformations involving C–C and C–H bond formation [1]. Free *N*-heterocyclic carbenes, having bulky substituents, have recently been shown to be suitable ligands to afford highly active catalysts with several transition metals [2]. As regard to ruthenium chemistry, the complexes $RuCl_2(L)_2$(=CHPh) (L = imidazolin-2-ylidene, phosphine) have been found to be very efficient catalytic precursors for olefin metathesis [3]. In spite of the vast number of publications on cyclopentadienyl ruthenium complexes of general formula (η^5-C_5R_5)$Ru(L)_2X$ (R = H, Me; L = phosphine, alkene; X = halogen), there are very few reports dealing with their application in catalysis [4]. Recently we have shown that (η^5-C_5H_5)$Ru(PPh_3)_2Cl$ catalyzes the stereoselective formation of *cis*-enediones from α-diazo carbonyl compounds via displacement of one phosphine [5]. Although Cp*Ru(L)X type 16-electron complexes have been isolated using bulky phosphino ligands [6], the employment of sterically demanding *N*-heterocyclic carbenes has not been considered until a very recent communication [3c].

We now describe two simple routes to prepare the highly reactive, coordinatively unsaturated half-sandwich derivatives Cp*Ru[C(R)N(H)C=C(H)N(R)]Cl (R = Cy, **1a**; Mes, **1b**) on a gram scale. Stoichiometric reactions of **1a–b** with several ligands as well as catalytic transformations of alkynes promoted by **1a–b** are reported.

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* Corresponding author.
E-mail addresses: inorg@dstc.uniud.it (W. Baratta), hermann.jom@ch.tum.de (W.A. Herrmann)
[1] Also corresponding author.

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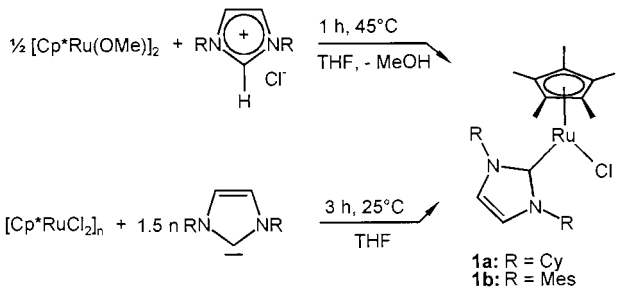
2. Results and discussion

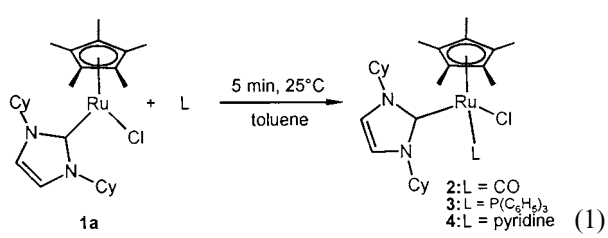
2.1. Preparation and reactivity of *1a–b*

The 16-electron complexes **1a–b** can be easily prepared by two different synthetic pathways. Treatment of a THF solution of the di-μ-methoxo derivative $[Cp^*Ru(OMe)]_2$ [7] with the corresponding 1,3-diorganylimidazolium chloride affords compounds **1a–b,** as a result of methanol elimination. **1a–b** are formed quantitatively, as monitored by NMR, and were isolated in $>85\%$ yields after extraction with diethyl ether (Scheme 1).



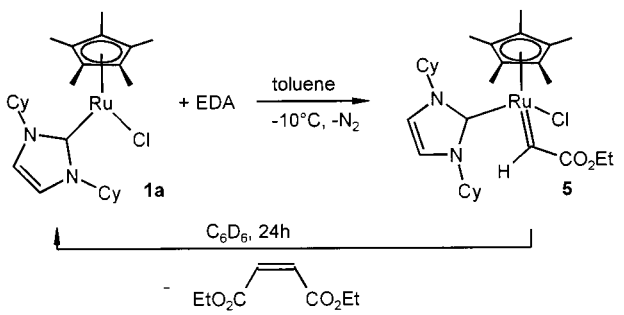
Scheme 1. Syntheses of the coordinatively unsaturated complexes **1a–b** ($Cp^* = \eta^5$-C_5Me_5, Cy = cyclohexyl, Mes = mesityl).

Alternatively, compounds **1a–b** can also be prepared by the reaction of commercially available $[(\eta^5$-$C_5Me_5)RuCl_2]_n$ with 1.5 equivalents of the corresponding free carbenes to give **1a–b** in $>75\%$ yield. In this case, the free carbenes act both as strong coordinating ligands and reducing reagents [8]. The remarkable highfield ^{13}C-NMR resonances of the Cp* ring carbon atoms ($\delta = 73.3$, **1a**; 73.0, **1b**) are similar to those reported for other coordinatively unsaturated half-sandwich ruthenium complexes [3c,6], suggesting that **1a–b** are apparently monomeric in solution. Although complexes **1a–b** exhibit relatively low air sensitivity in the solid state, they are highly soluble in toluene, affording deep blue solutions, which promptly turn brown if air is admitted. According to the coordinative unsaturation of **1a–b**, these compounds promptly react with CO, PPh_3 and pyridine to give quantitatively the corresponding 18-electron complexes Cp*Ru(ICy)(L)Cl (L = CO, **2**; PPh_3, **3**; Py, **4**), which were isolated and fully characterized (Eq. (1)) [9].



(1)

The carbonyl derivative **2** exhibits a ν_{CO} stretching frequency at 1914 cm^{-1} (Nujol). The ^{13}C-NMR spectrum of **2** in C_6D_6 at 70°C reveals signals at δ 298.5 and at 93.5 ppm for the CO and Cp* ligands, respectively. The ^{31}P-NMR spectrum of **3** displays a resonance at 47.6 ppm and in the ^{13}C-NMR spectrum the Cp* ligand appears as a doublet at 84.7 ppm (J(C, P) = 2.0 Hz) at 25°C. The ^{13}C-NMR spectrum of **4** (C_6D_6, 25°C) shows a single resonance for the two N*C*H carbons of the imidazolin-2-ylidene based ring system at δ 117.7, indicating that rotation around the Ru–$C_{carbene}$ bond is relatively fast on the ^{13}C-NMR time scale. By way of contrast, no reaction of **1a** with ethylene (1 atm) and dihydrogen (1 atm) was observed in C_6D_6 at room temperature. In line with our previous findings that $(\eta^5$-$C_5H_5)Ru(PPh_3)(=CHCO_2Et)Cl$ is the key intermediate for the selective carbene transfer reactions from EDA [5], we succeeded in preparing a mixed dicarbene complex, which contains both one electrophilic and one *N*-heterocyclic carbene ligand. Thus, reaction of **1a** in toluene at -10°C with EDA affords the complex $Cp^*Ru(ICy)(=CHCO_2Et)Cl$ (**5**), which was isolated and characterized as an analytically pure compound (Scheme 2).



Scheme 2. Reactivity of **1a** towards ethyl diazoacetate (EDA).

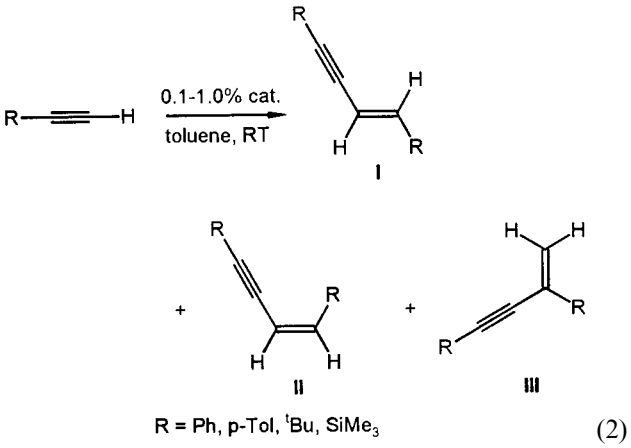
The ^{1}H- and ^{13}C-NMR spectra of **5** show resonances for the Ru=*CH* moiety at δ 16.0 (^{1}H-NMR) and 260.6 ppm (^{13}C-NMR), respectively, while the ring carbon atoms of the Cp* appear at 101.1 ppm. Whereas compound **5** is indefinitely stable in solid state, it slowly reacts in solution (C_6D_6) to give **1a** and 0.5 equiv. of free diethyl maleate within 2 days at room temperature, as a result of a stereoselective carbene degradation process yielding the *cis* olefin only.

2.2. Catalytic alkyne dimerization

The transition metal mediated dimerization of terminal alkynes is of considerable interest because it can lead to a wide variety of organic enyne and oligoacetylene products, that are useful synthetic precursors for organic conducting polymers and other carbon-rich derivatives [4,10]. However, its synthetic application in organic synthesis has been limited due to low selectivity on dimeric products [11]. It has been reported that dimerization of alkynes and coupling reactions of alkynes with alkenes occur in presence of

catalytic amounts of $(\eta^5\text{-}C_5R_5)Ru(L)_nX_m$ (L = phosphine, vinylidene; X = H, Cl) type complexes through dissociation of one ligand [4f–i]. Furthermore, ruthenacyclopentadienes are obtained from acetylene with $(\eta^5\text{-}C_5R_5)Ru(P^iPr_3)Cl$ or PhC≡CH with $(\eta^5\text{-}C_5H_5)Ru(COD)Cl$ as results of stoichiometric carbon–carbon coupling reactions [12]. Therefore our investigation on the catalytic activity of **1a–b** with alkynes was substantially mandated.

When a toluene solution of phenylacetylene is treated with 1 mol% of **1a** under an argon atmosphere at room temperature, quantitative conversion occurs within 5 minutes in a very fast and exothermic reaction to give the dimeric coupling products **I–III**, the derivative **I** being the major product present in solution (Eq. (2)).



(2)

To explore the scope of this catalytic reaction, the dimerization of other terminal alkynes was investigated under similar reaction conditions. Both conversion and selectivity are strongly dependent on the alkyne as well as the *N*-heterocyclic carbene substituents (Table 1).

For $R = SiMe_3$ (**1a**, entry 4) the selectivity is reversed with respect to R = Ph, *p*-Tol and ^{t}Bu (entries 1–3, 5, 6) giving **III** (92%) as the main coupling product and only 8% of **I**. A maximum turn over frequency of 10320 h^{-1} (turn over number = 860) (entry 3) was achieved for phenylacetylene as the most active substrate. By contrast, no catalytic reaction with **1a** or **1b** occurred in the case of primary alkynes such as $PhCH_2C{\equiv}CH$. It is noteworthy that when **1b,** bearing two mesityl substituents, is used instead of **1a,** an inverse selectivity was observed for R = Ph and R = *p*-Tol (entries 7 and 8). In all cases the head-to-tail coupling product **III** is formed with very high selectivity, when complex **1b** is employed. In addition, when catalysts **1a–b** are employed with terminal alkynes bearing electron withdrawing groups, HC≡CCOR (R = OMe, OEt, H) or with internal alkynes $RO_2CC{\equiv}CCO_2R$ (R = Me, Et), the chemoselectivity completely changes and benzene derivatives are obtained in almost quantitative yields. Although the detailed mechanism and the nature of the intermediate species have not been clearly elucidated, it is likely that the carbon–carbon coupling products form via a ruthenacyclopentadiene complex similar to that isolated by Yi and co-workers, from $Cp^*Ru(PPh_3)_2Cl$ and acetylene by displacement of one phosphine [4e].

In summary, employment of the easily accessible $[Cp^*Ru(OMe)]_2$ and the corresponding imidazolium chloride salts offers a general entry into the chemistry of this new class of ruthenium cyclopentadienyl complexes. Sterically demanding 1,3-disubstituted *N*-heterocyclic carbenes as strong σ- and π-donors stabilize the 16-electron coordinatively unsaturated species by preventing dimerization or solvent coordination. Complexes **1a–b** represent one of the most active catalyst systems for alkyne dimerization reported to date. The application of these highly reactive compounds in other carbon–carbon forming processes and carbene transfer reactions from diazo compounds are currently under investigation.

3. Experimental

All reactions were carried out with dried solvents under an argon atmosphere using standard Schlenk

Table 1
Catalytic dimerization of terminal alkynes

Entry	Catalyst (mol%)	R	Time	Product ratio **I**:**II**:**III**	Conversion [a] (%)
1	**1a** (1.0)	Ph	5 min	76:16:8	100
2	**1a** (0.5)	Ph	5 min	76:16:8	100
3	**1a** (0.1)	Ph	5 min	76:16:8	86
4	**1a** (1.0)	$SiMe_3$	2 h	8:0:92	100
5	**1a** (1.0)	^{t}Bu	10 min	90:0:10	100
6	**1a** (1.0)	*p*-Tol	5 min	44:38:18	100
7	**1b** (1.0)	Ph	2 h	0:10:90	95
8	**1b** (1.0)	*p*-Tol	2 h	0:4:96	95
9	**1b** (1.0)	$SiMe_3$	24 h	0:0:100	22

[a] Product yields were determined by GC–MS using diethylene glycol-*n*-butylether as an internal standard.

techniques. The ruthenium complex $[Cp^*Ru(OMe)]_2$ [13], 1,3-diorganylimidazolium chlorides and free 1,3-diorganylimidazolin-2-ylidenes were prepared according to the literature procedures [14]. $[Cp^*RuCl_2]_n$ and the other chemicals were purchased from Aldrich and used without further purification. The NMR spectra were recorded on a Bruker AC 200 instrument; the ^1H and ^{13}C chemical shifts, in ppm, are relative to TMS, while H_3PO_4 is used for ^{31}P. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using the CI (isobutane) technique. All elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.

3.1. Synthesis of Cp*Ru[C(Cy)N(H)C=C(H)N(Cy)]Cl (1a)

3.1.1. Method 1

A suspension of $[Cp^*Ru(OMe)]_2$ (1.00 g, 1.87 mmol) and 1,3-dicyclohexylimidazolium chloride (1.26 g, 4.67 mmol) in THF (20 ml) was stirred at 45°C for 1 h. THF was removed in vacuo and the product was extracted with 30 ml of diethyl ether. Further purification could be achieved by recrystallization from hot diethyl ether.

Yield: 1.64 g (3.25 mmol, 87%); ^1H-NMR (200.1 MHz, C_6D_6, 25°C): δ 6.51 (s, 2H, NC*H*), 4.39 (br, 2H, C*H* of NCy), 2.13–0.72 (br, 20H, CH_2 of NCy), 1.65 (s, 15H, C_5Me_5). ^{13}C-NMR (50.3 MHz, C_6D_6, 25°C): δ 196.6 (N*C*N), 116.9 (N*C*H), 73.4 (C_5Me_5), 59.5 (N*C*H of NCy), 34.8, 34.0, 26.3, 26.0 and 25.7 (CH_2 of NCy), 11.8 (C_5Me_5). Found: C, 59.84; H, 7.69; N, 5.71. Anal. Calc. for $C_{55}H_{39}N_2ClRu$ (504.12): C, 59.56; H, 7.80; N, 5.56.

3.1.2. Method 2

A suspension of $[Cp^*RuCl_2]_n$ (300 mg, 0.98 mmol) in THF (6 ml) was treated with a solution of 1,3-dicyclohexylimidazolin-2-ylidene (1.46 mmol) in THF (0.70 ml) and stirred at room temperature for 3 h, during this time the reaction mixture turned deep blue from being initially brown. The product was worked up as described in method 1. Yield: 375 mg (0.74 mmol, 76%).

3.2. Synthesis of Cp*Ru[C(Mes)N(H)C = C(H)N(Mes)]Cl (1b)

3.2.1. Method 1

A suspension of $[Cp^*Ru(OMe)]_2$ (1.00 g, 1.87 mmol) 1,3-dimesitylimidazolium chloride (1.59 g, 4.67 mmol) in THF (20 ml) was stirred at 45°C for 1 h. THF was removed in vacuo and the product was extracted with 30 ml of diethylether. Further purification could be achieved by recrystallization from hot heptane.

Yield: 1.92 g (3.33 mmol, 89%); ^1H-NMR (200.1 MHz, C_6D_6, 25°C): δ 6.75 (s, 2H, Mes), 6.20 (s, 2H, NCH), 2.27 (br, 12H, o-CH_3 of Mes), 2.12 (s, 6H, p-CH_3 of Mes), 1.23 (s, 15H, C_5Me_5). ^{13}C-NMR (50.3 MHz, C_6D_6, 25°C): δ 200.2 (N*C*N), 138.1, 137.5, 136.9 and 130.3 (4 × Mes), 123.1 (N*C*H), 73.0 (C_5Me_5), 21.0, 20.0 and 19.0 (CH_3 of Mes), 10.8 (C_5Me_5). Found: C, 64.81; H, 6.78; N, 4.93. Anal. Calc. for $C_{31}H_{39}N_2ClRu$ (576.19): C, 64.62; H, 6.82; N, 4.86.

3.2.2. Method 2

A suspension of $[Cp^*RuCl_2]_n$ (300 mg, 0.98 mmol) in THF (6 ml) was treated with a solution of 1,3-dimesitylimidazolin-2-ylidene (1.46 mmol) in THF (0.70 ml) and stirred at room temperature for 3 h, during this time the reaction mixture turned deep blue from being initially brown. The product was worked up as described in method 1. Yields: 443 mg (0.77 mmol, 79%).

3.3. Synthesis of Cp*Ru[C(Cy)N(H)C=C(H)N(Cy)](=CHCO2Et)Cl (5)

A toluene solution (4 ml) of **1a** (200 mg, 0.26 mmol) was cooled at −10°C and treated with EDA (89 mg, 0.78 mmol). After the N_2-evolution stopped, the solvent was removed in vacuo. Pentane (8 ml) was added to the oily residue to give the product as a brown solid. Yield: 112 mg (0.19 mmol, 73%); ^1H-NMR (C_6D_6, 25°C, ppm): δ 16.04 (s, 1H, C*H*CO_2Et), 7.45 (bs, 2H, C*H* of NC_6H_{11}), 6.73 (bs, 2H, NC*H*), 3.67 (q, 2H, CH_2CH_3, $^3J(H, H) = 7.6$ Hz), 1.84–0.73 (br, 23H, CH_2 of NC_6H_{11} and CH_2CH_3), 1.25 (s, 15H, CH_3 of C_5Me_5). ^{13}C-NMR (C_6D_6, 25°C, ppm): δ 260.6 (*C*HCO$_2$Et), 181.7 (*C*O), 171.1 (N*C*N), 119.9 and 118.5 (N*C*H), 101.1 (C_5Me_5), 60.9 and 58.8 (N*C*H of NC_6H_{11}), 59.9 (CH_2CH_3). 35.3, 35.0, 33.8, 33.5, 33.9, 26.3, 26.2, 25.9, 25.5 and 25.1 (CH_2 of NC_6H_{11}), 13.9 (CH_2CH_3), 10.0 (CH_3 of C_5Me_5). Found: C, 59.65; H, 7.73; N, 4.97. Anal. Calc. for $C_{29}H_{45}N_2O_2ClRu$: C, 59.02; H, 7.68; N, 4.75.

3.4. General procedure for dimerization catalysis

The solutions for alkyne dimerization studies were typically prepared as follows: the alkyne (0.1 mmol), internal standard (diethylene glycol-*n*-butylether) and catalyst were added to 3 ml of toluene under an argon atmosphere. The reaction progress was monitored by the removal of a small aliquot of the reaction mixture which was analyzed by GC–MS. After the reaction time (Table 1), the reaction was quenched by exposure of the reaction mixture to air and a small aliquot was taken for GC–MS analysis. Products were identified by comparisons with authentic samples. In addition, the structures of the dimeric products were unequivocally established by spectroscopic methods.

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