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The addition of carboxylic acids to 1-alkynes catalysed by a new Ru(II) complex: a very fast route towards the synthesis of enol esters

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Abstract

A new Ru(II) complex (**5**) is synthesised from $RuCl_2(PPh_3)_3$ (**3**) and an N-heterocyclic carbene, 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (**4**). Complex (**5**) catalyses the addition reaction of carboxylic acids to terminal alkynes very fast and quantitatively. The selectivity of the addition to phenylacetylene is dependent on the acidity of the added carboxylic acid. At decreasing pK_a, a change in regioselectivity from Markovnikov to *anti*-Markovnikov addition is observed. The intermolecular attack of acetic acid to aliphatic alkynes and intramolecular addition produces Markovnikov adducts.

Keywords: Alkynes; Ruthenium; Carboxylic acids; Nucleophilic addition; N-heterocyclic carbenes

1. Introduction

A major goal for every synthetic chemist is to achieve high efficiency, which means performing reactions with atom economy and high selectivity [1]. Transition metal complexes, which can be tuned electronically and sterically by variation of the metal/ligand coordination sphere, catalyse a variety of C–C bond formation reactions. A very interesting feature is the ability of transition metal complexes to insert readily into acetylenic C–H bonds. This property derives from both the acidity of the proton and the high coordination ability of the acetylenic linkage. Low valent ruthenium complexes catalyse the addition of carboxylic acids to form alk-en-yl-esters via transient transition metal vinylidenes (Scheme 1) ([2] for enol esters and [3] for enynes).

The regioselectivity for Markovnikov addition has been significantly increased by the use of a variety of Ru-precursors such as $Ru_3(CO)_{12}$ [4], (arene) $RuCl_2(PR_3)$ [5], bis(η^5-cyclooctadienyl)ruthenium/PR_3 without and with addition of maleic anhydride [6]. The first *anti*-Markovnikov *trans*-addition in the presence of the $Ru(Ph_2P(CH_2)_nPPh_2)(\eta^3\text{-}CH_2CMe{=}CH_2)_2$ catalyst was reported by Dixneuf et al. [7]. Enol esters have specific industrial applications as monomers for the production of various polymers and copolymers [8]. They are also useful reagents for carbon–carbon and carbon–heteroatom bond formation via the generation of enolates or acylation reactions [9,10]. The addition of carboxylic acids to the triple bond of the terminal alkyne represents a simple addition reaction with atom economy. The key

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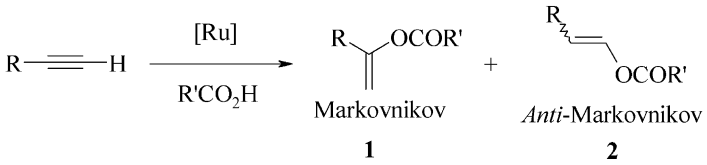


Scheme 1.

step in the formation of enol esters is the formation of a M=C=CHR vinylidene, addition of the carboxylate anion ($R'COO^-$) to yield the M–CH=CR–OCOR′ or M–C(OCOR′)(=CHR) complex, addition of an incoming 1-alkyne generates the M–vinylidene and CH_2=C(–R)(–OCOR′) or RHC=CH(OCOR′) enol ester.

$RuCl_2(PPh_3)_2$ is known to readily react with monosubstituted 1-alkynes to give a stable Ru–vinylidene complex [11]. X-ray analysis revealed the Ru–vinylidene $RuX_2(PPh_3)_2$(=CH=HR) to have a trigonal–bipyrimidal conformation with the two phosphines occupying axial positions. Formation of the vinylidene ligand proceeds by transformation of the η^2-CC coordinated alkyne into the η^2-CH coordinated complex followed by 1,2-hydrogen shift within the acetylene unit.

Tertiary phosphines are frequently used ligands in transition metal chemistry and catalysis. A major disadvantage is that they undergo P–C degradation at higher temperature, which results in deactivation of the catalyst [12,13]. The need for strong nucleophilic ligands that exhibit a stable bond with metals is high. Nucleophilic carbene ligands are ideal mimics for phosphine ligands [14]. In 1995, a new type of heterocyclic carbene (NHC), 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (**4**), which exhibited a marked nucleophilic reactivity, was synthesised [15].

Here we report on the use of the triazol-5-ylidene ligand in combination with $RuCl_2(PPh_3)_3$ for the addition of carboxylic acids on 1-alkynes.

2. Experimental

2.1. General remarks

All reactions were performed under inert atmosphere using Schlenck techniques. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. GC–MS analysis were performed on a GC (column SPB^{TM}-5 = 30 m × 0.25 mm × 0.25 μm film thickness, carrier gas: He, 100 kPa, detector = FID, gas chromatograph = Varian 4600) and MS (Finnigan MAT ITD). Toluene-d_8 (obtained from Acros), pentane and toluene were dried over Na, dichloromethane is dried over $CaCl_2$, $CDCl_3$ (obtained from Acros, 96.9 at.% D) is dried over molecular sieves. $RuCl_2(PPh_3)_3$ (**3**), 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (**4**), 1-alkynes, 1,7-octadiyne, carboxylic acids, PPh_3 and Cu(I)Cl (obtained from Acros) were used without further purification.

Ru-complex (**5**): To a solution of 0.419 mmol $RuCl_2(PPh_3)_3$ (**3**) in 7 ml dichloromethane is added 0.423 mmol of 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (**4**) in 3 ml CH_2Cl_2. The reaction mixture is stirred overnight at room temperature. A colour change from brown to dark-red occurs. The solution was concentrated to dryness in vacuum and recrystallisation from pentane (−78 °C) gives the $RuCl_2(PPh_3)_2$(triazol-5-ylidene) complex (**5**) in good yield (85%). Complex (**5**): Dark-red solid (85% from (**3**) and (**4**)): [^{1}H] NMR (300 MHz, $CDCl_3$, 25 °C) δ 8.32 (d, 4H, *o*-H of C_6H_5 of PPh_3, J = 9.8 Hz), 7.64 (t, 2H, *p*-H of C_6H_5 of PPh_3), 7.35–6.90 (m, 19H, aromatic H of NHC and *m*-H of C_6H_5 of PPh_3). [^{13}C]–[^{1}H] NMR (75.4 MHz, $CDCl_3$, 25 °C) δ 201.03 (NCRu), 143.67 (*iso*-C of Ph of NHC), 137.56, 132.38, 132.24, 132.10, 128.77, 128.62, 128.31, 115.32 (C of Ph of PPh_3 and NHC); [^{31}P]–[^{1}H] NMR (122 MHz, $CDCl_3$, 25 °C) δ 30.09 (PPh_3).

Vinylation of phenylacetylene catalysed by the complex (**5**): To a solution of complex (**5**) (0.032 mmol) in toluene (3 ml), 100 eq. phenylacetylene (3.2 mmol) and 100 eq. carboxylic acid (3.2 mmol) are added and the reaction mixture is stirred at 110 °C. The reaction is monitored by [^{1}H] NMR and GC–MS.

- Phenylacetylene and acetic acid: *Anti*-Markovnikov *cis* Ph–CH=CH–$OCOCH_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 6.54 (d, $J = 11.3$ Hz, =C*H*$OCOCH_3$), 5.78 (d, $J = 11.3$ Hz, Ph–C*H*=CH), 2.05 (s, OCH_3); GC–MS = $m/z = 162$ (M^+). *Anti*-Markovnikov *trans* Ph–CH=CH–$OCOCH_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 6.91 (d, $J = 16.2$ Hz, =C*H*$OCOCH_3$), 6.25 (d, $J = 16.2$ Hz, Ph–C*H*=CH), 2.05 (s, OCH_3); GC–MS = $m/z = 162$ (M^+). Markovnikov (Ph)($OCOCH_3$)C=CH_2: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 5.31 (s, =CH_2), 4.87 (s, =CH_2), 2.05 (s, OCH_3); GC–MS = $m/z = 162$ (M^+).
- Phenylacetylene and formic acid: *Anti*-Markovnikov *cis* Ph–CH=CH–OCOH: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 9.45 (br s, O*H*), 8.05–7.05 (m, Ph), 6.65 (d, $J = 16.6$ Hz, =C*H*OCOH), 5.67 (d, $J = 16.6$ Hz, Ph–C*H*=CH); GC–MS = $m/z = 148$ (M^+). *Anti*-Markovnikov *trans* Ph–CH=CH–OCOH: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 9.45 (br s, O*H*), 8.05–7.05 (m, Ph), 7.87 (d, $J = 12.2$ Hz, =C*H*OCOH), 6.32 (d, $J = 12.2$ Hz, Ph–C*H*=CH); GC–MS = $m/z = 148$ (M^+). Markovnikov (Ph)(OCOH)C=CH_2: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 9.45 (br s, O*H*), 8.05–7.05 (m, Ph), 5.15 (s, =CH_2), 4.73 (s, =CH_2); GC–MS = $m/z = 148$ (M^+).
- Phenylacetylene and isovaleric acid: *Anti*-Markovnikov *cis* Ph–CH=CH–$OCOCH_2$–CH–$(CH_3)_2$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 6.50 (d, $J = 19.9$ Hz, =C*H*OCOCH_2–CH–$(CH_3)_2$), 5.66 (d, $J = 19.9$ Hz, Ph–C*H*=CH), 2.38 (d, OCH_2), 1.51 (m, C*H*), 1.20 (s, CH_3); GC–MS = $m/z = 204$ (M^+). *Anti*-Markovnikov *trans* Ph–CH=CH–$OCOCH_2$–CH–$(CH_3)_2$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 8.07 (d, $J = 13.2$ Hz, =C*H*$OCOCH_2$–CH–$(CH_3)_2$), 6.36 (d, $J = 13.2$ Hz, Ph–C*H*=CH), 2.38 (d, OCH_2), 1.51 (m, C*H*), 1.20 (s, CH_3); GC–MS = $m/z = 204$ (M^+). Markovnikov (Ph)(OCOCH_2–CH–$(CH_3)_2$)C=CH_2: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 5.32 (s, =CH_2), 5.03 (s, =CH_2), 2.38 (d, OCH_2), 1.51 (m, C*H*), 1.20 (s, CH_3); GC–MS = $m/z = 204$ (M^+).
- Phenylacetylene and trichloroacetic acid: *Anti*-Markovnikov *cis* Ph–CH=CH–$OCOCCl_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 6.46 (d, $J = 11.7$ Hz, =C*H*$OCOCCl_3$), 6.11 (d, $J = 11.7$ Hz, Ph–C*H*=CH); GC–MS = $m/z = 277$ (M^+). *Anti*-Markovnikov *trans* Ph–CH=CHO$COCCl_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 7.00 (d, $J = 8.2$ Hz, =C*H*$OCOCCl_3$), 6.58 (d, $J = 8.2$ Hz, Ph–C*H*=CH); GC–MS = $m/z = 277$ (M^+). Markovnikov (Ph)($OCOCCl_3$)C=CH_2: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 8.05–7.05 (m, Ph), 5.67 (s, =CH_2), 5.55 (s, =CH_2); GC–MS = $m/z = 277$ (M^+).

Vinylation of 1-monoalkyne and acetic acid catalysed by the complex (**5**): To a solution of complex (**5**) (0.032 mmol) in toluene (3 ml), 100 eq. 1-monoalkyne (3.2 mmol) and 100 eq. acetic acid (3.2 mmol) are added and the reaction mixture is stirred at 110 °C. The reaction is monitored by [^{1}H] NMR and GC–MS.

- 1-Octyne and acetic acid*: Anti*-Markovnikov *cis* CH_3–$(CH_2)_5$–CH=CH–$OCOCH_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 5.37 (d, $J = 11.5$ Hz, =C*H*$OCOCH_3$), 5.24 (d, $J = 11.5$ Hz, CH_3–$(CH_2)_5$C*H*=CH), 2.12 (s, OCH_3), 1.31–1.20 (m, CH_2), 0.87 (t, CH_3); GC–MS = $m/z = 170$ (M^+). *Anti*-Markovnikov *trans* CH_3–$(CH_2)_5$–CH=CH–$OCOCH_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 5.86 (d, $J = 8.2$ Hz, =C*H*$OCOCH_3$), 5.80 (d, $J = 8.2$ Hz, CH_3–$(CH_2)_5$C*H*=CH), 2.12 (s, OCH_3), 1.31–1.20 (m, CH_2), 0.87 (t, CH_3); GC–MS = $m/z = 170$ (M^+). Markovnikov (CH_3–$(CH_2)_5$)($OCOCH_3$)C=CH_2: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 4.78 (s, =CH_2), 4.63 (s, =CH_2), 2.12 (s, OCH_3), 1.31–1.20 (m, CH_2), 0.87 (t, CH_3); GC–MS = $m/z = 170$ (M^+).
- 3,3-Dimethyl-1-butyne and acetic acid: *Anti*-Markovnikov *cis* *t*Bu–CH=CH–$OCOCH_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 6.96 (d, $J = 6.8$ Hz, =C*H*$OCOCH_3$), 4.52 (d, $J = 6.8$ Hz, *t*BuC*H*=CH), 1.84 (s, OCH_3), 1.09 (t, *t*Bu); GC–MS = $m/z = 130$ (M^+). *Anti*-Markovnikov *trans* *t*Bu–CH=CH–$OCOCH_3$: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 7.30 (d, $J = 13.1$ Hz, =C*H*$OCOCH_3$), 5.49 (d, $J = 13.1$ Hz, *t*BuC*H*=CH), 1.84 (s, OCH_3), 1.09 (s, *t*Bu); GC–MS = $m/z = 130$ (M^+). Markovnikov (*t*Bu)($OCOCH_3$)C=CH_2: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 4.81 (s, =CH_2), 4.74 (s, =CH_2), 1.84 (s, OCH_3), 1.09 (t, *t*Bu); GC–MS = $m/z = 130$ (M^+).

Vinylation of 1,7-octadiyne and acetic acid catalysed by the complex (**5**): To a solution of complex (**5**) (0.032 mmol) in toluene (3 ml), 50 eq. 1,7-octadiyne (1.6 mmol) and 100 eq. acetic acid (3.2 mmol) are added and the reaction mixture is stirred at 110 °C. The reaction is monitored by [^{1}H] NMR and GC–MS. Full and unequivocal analysis by NMR was impossible due to the overlap of signals of the mono- and disubstituted alkyne.

Monosubstituted dialkyne: *Anti*-Markovnikov *cis* CH≡C–$(CH_2)_4$–CH=CH–$OCOCH_3$: GC–MS = m/z = 166 (M^+). *Anti*-Markovnikov *trans* CH≡C–$(CH_2)_4$–CH=CH–$OCOCH_3$: GC–MS = m/z = 166 (M^+). Markovnikov (CH≡C–$(CH_2)_4$–)($OCOCH_3$)C=CH_2: GC–MS = m/z = 166 (M^+).

Disubstituted dialkyne: *Anti*-Markovnikov *cis* CH_3OCO–CH=CH–$(CH_2)_4$–CH=CH–$OCOCH_3$: GC–MS = m/z = 226 (M^+). *Anti*-Markovnikov *trans* CH_3OCO–CH=CH–$(CH_2)_4$–CH=CH–$OCOCH_3$: GC–MS = m/z = 226 (M^+). Markovnikov CH_3OCO–CH=CH–$(CH_2)_4$–CH=CH–$OCOCH_3$: GC–MS = m/z = 226 (M^+). *Anti*-Markovnikov–Markovnikov (CH_3OCO–CH=CH–$(CH_2)_4$–)($OCOCH_3$)C=CH_2: GC–MS = m/z = 226 (M^+).

Vinylation of pentynoic acid catalysed by complex (**5**): To a solution of complex (**5**) (0.032 mmol) in toluene (3 ml), 100 eq. pentynoic acid (3.2 mmol) are added and the reaction mixture is stirred at 110 °C. The reaction is monitored by [^{1}H] NMR and GC–MS.

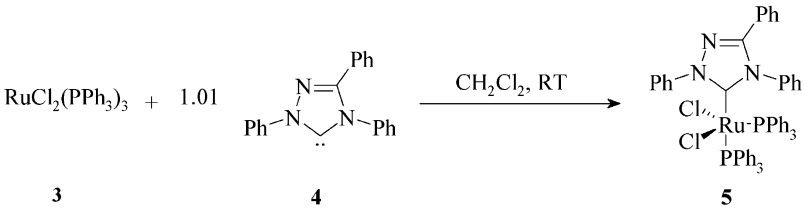
Anti-Markovnikov: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 5.23 (d, J = 5.06 Hz, =C*H*OCO), 5.02 (d, J = 5.06 Hz, C*H*C=CHOCO), 2.32 (t, H_2CCOO), 1.61 (q, CH–CH_2–CH_2); GC–MS = m/z = 98 (M^+). Markovnikov: [^{1}H] NMR (tol-d_8, 300 MHz, 25 °C, ppm) δ 4.63 (s, =C*H*OCO), 3.95 (t, *H*C=CHOCO), 2.49 (t, CH_2CCOO), 1.91 (q, CH_2=C–CH_2–CH_2); GC–MS = m/z = 98 (M^+).

Vinylation of phenylacetylene and acetic acid catalysed by complex (**5**) in the presence of an additive (PPh_3 or Cu(I)Cl): To a solution of complex (**5**) (0.032 mmol) in toluene (3 ml), 100 eq. phenylacetylene (3.2 mmol), 100 eq. carboxylic acid (3.2 mmol) and x mmol of additive are added and the reaction mixture is stirred at 110 °C. The reaction is monitored by [^{1}H] NMR and GC–MS.

3. Results and discussion

Combining the feature of $RuCl_2(PPh_3)_3$ (**3**) to easily generate a stable Ru–vinylidene complex in the presence of a terminal alkyne and the strong donor capacity of the N-heterocyclic carbene, 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (**4**), a new Ru-complex (**5**) is synthesised (Scheme 2).

The activity of the $RuCl_2(PPh_3)_2$(triazol-5-ylidene) complex (**5**) towards the catalytic addition of carboxylic acid on the triple bond of terminal alkynes or vinylation is shown in Tables 1 and 2. In the first set of reactions, phenylacetylene was exposed to different aliphatic carboxylic acids (Table 1). For all reactions, full conversion of the triple bond of arylacetylene was already reached after 30 min (runs 1–4). At decreasing pK_a, a regioselectivity for *anti*-Markovnikov addition is preferred. Formic, acetic and isovaleric acid show no distinctive regioselectivity (runs 1–3). The intermolecular addition of a strong acid, i.e. trichloroacetic acid, on the triple bond proceeds via the attack of the CCl_3COO– group on the external C_1-bond of the aromatic 1-alkyne and thus formation of *anti*-Markovnikov adducts (run 4). The addition of all carboxylic acids leads mainly to the formation of *cis*-adducts. General, Ru(II) complexes catalyse the nucleophilic addition of carboxylic acids with formation of Markovnikov adducts [4–6]. Here, a change in regioselectivity towards the *anti*-Markovnikov addition is shown at low pK_a. Simply altering the acidity of the added acid, provides a reversed regioselectivity.



3 **4** **5**

Scheme 2.

Table 1
Influence of the acidity of the carboxylic acid on the triple bond transformation of phenylacetylene catalysed by $RuCl_2(PPh_3)_2$(triazol-5-ylidene) (**5**)[a]

Run	Acid	pK_a[b]	Time (min)	Total yield (%)[c]	**1** (%)[c]	**2** (*c*:*t*)[c] (%)
1	HCOOH	3.75	30	100	50	50
2	CH_3COOH	4.76	30	100[d]	30	52 (92:8)
3	$(CH_3)_2CH–CH_2–COOH$	4.78	30	100	46	54 (94:6)
4	CCl_3COOH	0.66	30	100	3	97 (89:11)

[a] The reaction mixture was stirred at 110 °C for 30 min.
[b] [16].
[c] Yield and selectivity as determined by [^{1}H] NMR and GC–MS.
[d] Next to enol esters, dimeric products (18% of total yield) are formed with a head-to-tail/tail-to-tail (22/78) selectivity.

Table 2
Addition of carboxylic acid on to terminal alkynes catalysed by $RuCl_2(PPh_3)_2$(triazol-5-ylidene) (**5**)

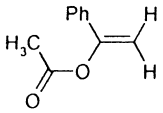
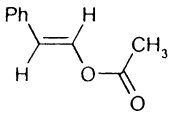
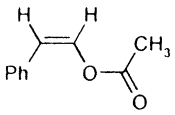
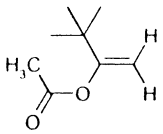
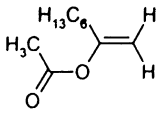
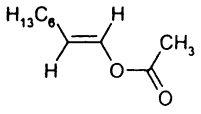
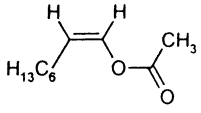
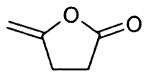
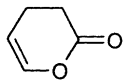
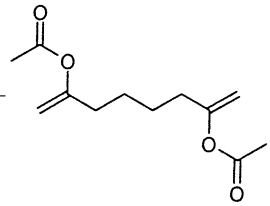
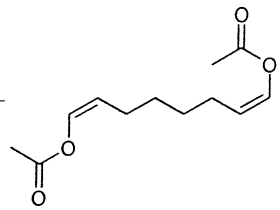
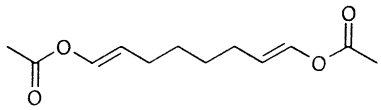
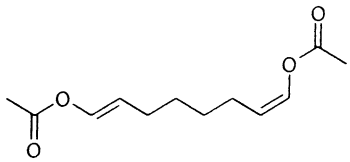
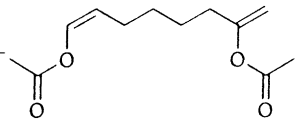
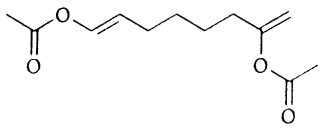
Run	Alkyne	Acid	Time (min)	Product	Yield (%)[a]	Selectivity (%)[a]
5[b,c]	Phenylacetylene	Acetic acid	30		30	
					4	8
					48	92
6[b]	*t*-Butylacetylene	Acetic acid	30		100	
7[b]	1-Octyne	Acetic acid	30		80	
					4	20
					16	80

Table 2 (*Continued*)

Run	Alkyne	Acid	Time (min)	Product	Yield (%)[a]	Selectivity (%)[a]
8[b]	Pentynoic acid		30		73	
					27	
9[b]	1,7-Octadiyne	Acetic acid	30	Markovnikov–Markovnikov 	34	
				Anti-Markovnikov–*anti*-Markovnikov 	23	88
					3	12
					0	0
				Anti-Markovnikov–Markovnikov 	36	90
					4	10

[a] Yield and selectivity as determined by [^{1}H] NMR and GC–MS.
[b] The reaction mixture was stirred at 110 °C for 30 min.
[c] Next to enol esters, dimeric products (18% of total yield) are formed with a head-to-tail/tail-to-tail (22/78) selectivity.

Dixneuf described a similar influence on the regioselectivity by modification of the chelating phosphine ligand coordinated on the Ru-centre [7].

In the second set of experiments, different aliphatic and aromatic alkynes are treated with acetic acid (Table 2). All alkynes are converted quantitatively within 30 min. The intermolecular addition of acetic acid on the aromatic alkyne, phenylacetylene, is moderately selective for the formation of *cis anti*-Markovnikov products (48%, run 5). The addition on

Table 3
Vinylation reaction catalysed by **5**: Influence of the phosphine ligand

Run	Additive	Total yield (%)[a]	Vinylation (%)[b]	**1**:**2** (*c*/*t*)[a]	Dimerisation (%)[a]
10[b]	No	100	82	36:64 (92/8)	18
11[b]	1 eq. PPh_3	61	30	4:96 (43/57)	70
12[b]	5 eq. PPh_3	41	38	4:96 (75/25)	62
13[b]	Cu(I)Cl	100	90	2:98 (73/27)	10

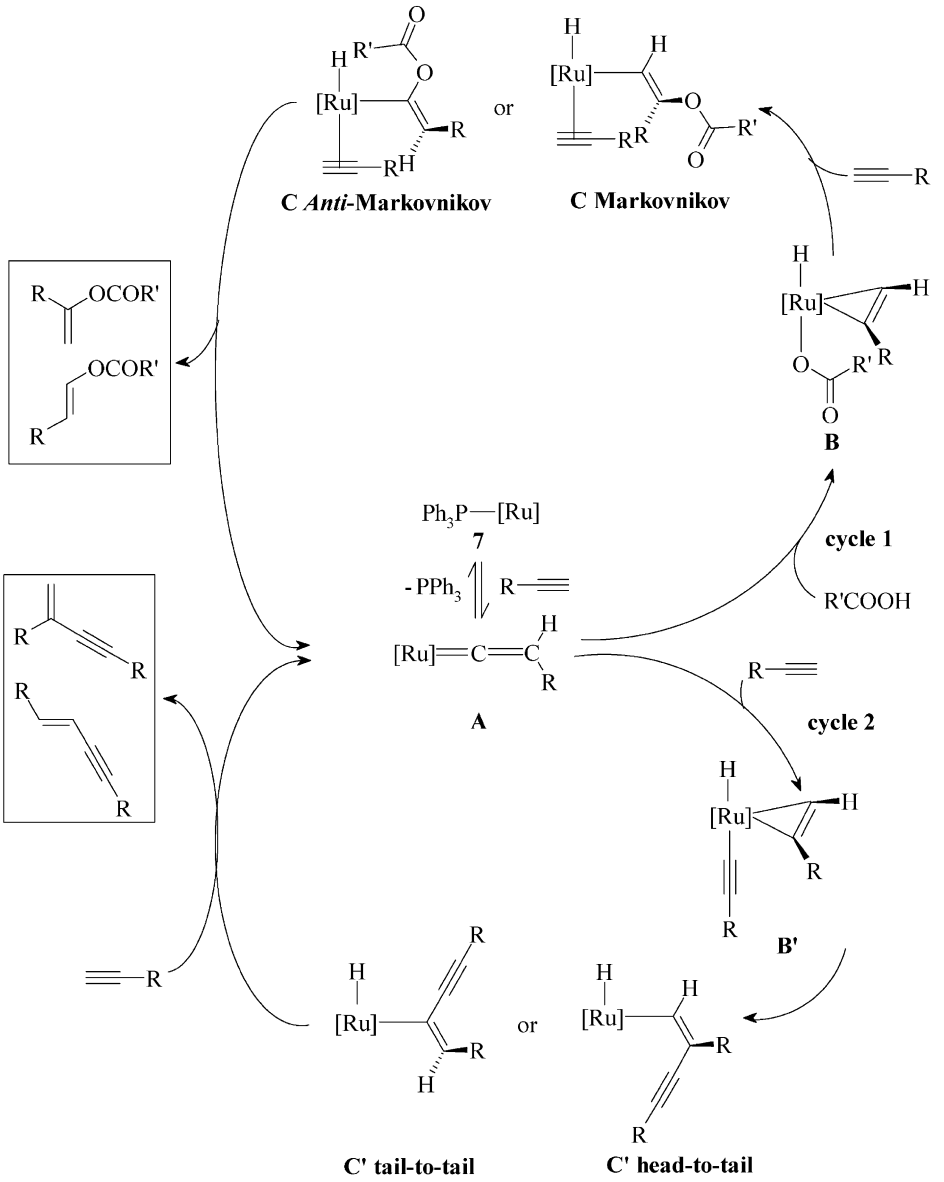
[a] Yield and selectivity as determined by [^{1}H] NMR and GC–MS.
[b] The reaction mixture was stirred at 110 °C for 30 min.

the aliphatic monoalkynes gives almost exclusively the Markovnikov adduct in quantitative yield (runs 6–7). This is in agreement with results previously reported, which illustrate that Ru(II) complexes generally produce Makovnikov adducts [4–6]. The intramolecular addition affords the *exo*-cyclic 5-methylene-dihydrofuran-2-one in good yield (73%, run 8). The addition on the dialkyne, 1,7-octadiyne, results in three different types of substitution: Markovnikov–Markovnikov (34%), *anti*-Markovnikov–*anti*-Markovnikov (26%) and Markovnikov–*anti*-Markovnikov (40%) (run 9). For both *anti*-Markovnikov–*anti*-Markovnikov and Markovnikov–*anti*-Markovnikov products nearly all *anti*-Markovnikov additions consist of the *cis*-isomer.

The addition of carboxylic acid on the triple bond of 1-alkynes catalysed by $RuCl_2(PPh_3)_2$(triazol-5-ylidene) proceeds smoothly at 110 °C. Within a 30 min time period, all alkynes are converted into the respective enol esters. To investigate the influence of the reaction temperature on the activity, the reaction between acetic acid and phenylacetylene in the presence of (**5**) is performed at different reaction temperatures and monitored for 90 min. The yield increases from 0 < 25 < 40 < 60 < 80 < 110 °C. At 0, 25 and 40 °C the reaction does not proceed at all. An increase in activity is observed from 60 °C (15%) < 80 °C (39%) < 110 °C (100%). The regio- and stereoselectivity remain the same at decreasing temperature. The optimum temperature, at which the reaction is performed, is 110 °C.

As reported before, the reaction between $RuX_2(PPh_3)_3$ (X = Cl, Br) and *t*-butylacetylene results in the formation of stable Ru–vinylidene complexes of the formula $RuX_2(PPh_3)_2$(=C=CH*t*Bu) [11]. A key step in the generation of the Ru–vinylidene complex is the release of one phosphine ligand from the Ru centre. To investigate if the nature of the active species generated from the $RuCl_2(PPh_3)_2$(triazol-5-ylidene) complex (**5**) is similar to the active species generated from $RuX_2(PPh_3)_3$, the vinylation reaction is performed with an excess of free PPh_3 and with addition of Cu(I)Cl (Table 3). An excess of PPh_3 clearly slows down the vinylation reaction (run 10 versus runs 11 and 12). A change in preference from vinylation to addition of another alkyne or dimerisation is shown. In the presence of an excess phosphine, the intermolecular attack of acetic acid proceeds preferably on the internal C_2 carbon atom and thus formation of *anti*-Markovnikov adducts (runs 11 and 12). Cu(I)Cl is known to act as a phosphine scavenger. Addition of the Cu(I)Cl also yields a quantitative formation of enol esters (run 13) and preference towards the vinylation products with a marked increased regio- and stereoselectivity for the *cis anti*-Markovnikov addition (run 10 versus run 13).

Ab initio molecular orbital calculations performed on the reaction between $RuX_2(PPh_3)_3$ and *t*-butylacetylene led to a very good understanding of the mechanism for the generation of the stable Ru–vinylidene $RuX_2(PPh_3)_2$(=C=CH*t*Bu) [11]. Based on the similar geometry of $RuCl_2(PPh_3)_3$ (**3**) and the $RuCl_2(PPh_3)_2$(triazol-5-ylidene) (**5**) and the outcome of the catalytic performance of the catalyst (**5**), some mechanistic insights can be suggested (Scheme 2). In analogy to $RuX_2(PPh_3)_3$ and the results depicted in Table 3, it is proven that release of a PPh_3 ligand takes place from the metal centre. Addition of a carboxylic acid favours vinylation (cycle 1). The intermolecular attack of the carboxylic acid on aliphatic 1-alkynes is favoured on the internal C_2 carbon atom of the triple bond and thus formation of Markovnikov adducts (C Markovnikov). Arylacetylene shows no regioselectivity at high pK_a.



Scheme 3.

Increasing the acidity of the acid results in a reversed selectivity for the *anti*-Markovnikov with an additional *cis*-stereoselectivity (C *anti*-Markovnikov). The addition of acetic acid to phenylacetylene and addition of an excess of free phosphine partly leads to the side-reaction, the homo-coupling of 1-alkynes or dimerisation (cycle 2) (Scheme 3).

4. Conclusion

The new $RuCl_2(PPh_3)_2$(triazol-5-ylidene) complex (**5**) is an excellent precursor for the catalytic transformation of terminal alkynes. The nucleophilic addition of carboxylic acids on the 1-alkynes proceeds very fast and smoothly. Full conversion of the triple bond into

the corresponding enol esters is already reached within a 30 min time period. The addition proceeds mainly on the external C_1-atom of the alkyne and thus resulting in the production of Markovnikov adducts. The regioselectivity is easily tuned by changing the acidity of the acid. At decreasing pK_a, a reversed regioselectivity for the *anti*-Markovnikov addition is preferred.

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References

[1] B. Trost, Angew. Chem. Int. Ed. Engl. 34 (1995) 259–281.
[2] (a) C. Bruneau, P. Dixneuf, J. Chem. Soc., Chem. Commun. 1 (1997) 507;
(b) B. Trost, R. Kulawiec, J. Am. Chem. Soc. 114 (1993) 5579;
(c) P. Dixneuf, C. Bruneau, S. Dérien, Pure Appl. Chem. 70 (1998) 1065;
(d) T. Mitsudo, Y. Hori, Y. Watanabe, J. Org. Chem. 50 (1985) 1566;
(e) C. Ruppin, P. Dixneuf, Tetrahedron Lett. 27 (1986) 6323;
(f) Y. Hori, T. Mitsudo, Y. Watanabe, J. Organomet. Chem. 321 (1987) 397;
(g) C. Bruneau, P. Dixneuf, Acc. Chem. Res. 32 (1999) 311;
(h) T. Opstal, F. Verpoort, Synth. Lett. 6 (2002) 935.
[3] (a) M. Akita, H. Yasuda, A. Nakamura, Bull. Chem. Soc. Jpn. 57 (1984) 480;
(b) A. Echavarren, J. Organomet. Chem. 414 (1991) 393;
(c) C. Bianchini, M. Peruzzini, F. Zanobini, P. Frediani, A. Albinati, J. Am. Chem. Soc. 113 (1991) 5453;
(d) C. Yi, N. Liu, Organometallics 16 (1997) 3910;
(e) C. Yi, N. Liu, Organometallics 17 (1998) 3158;
(f) M. Tenorio, M. Puerta, P. Valerga, Organometallics 19 (2000) 1333;
(g) Y. Nishibayashi, M. Yamanashi, I. Wakiji, M. Hidai, Angew. Chem. Int. Ed. Engl. 39 (2000) 2909.
[4] M. Rotem, Y. Shvo, Organometallics 2 (1983) 1689.
[5] (a) R. Mahé, Y. Sasaki, C. Bruneau, P. Dixneuf, J. Org. Chem. 54 (1989) 1518;
(b) C. Ruppin, P. Dixneuf, Tetrahedron Lett. 27 (1986) 6323;
(c) C. Ruppin, P. Dixneuf, Tetrahedron Lett. 29 (1988) 5365;
(d) H. Katayama, F. Ozawa, Organometallics 17 (1998) 5190;
(e) D. Devanne, C. Ruppin, P. Dixneuf, J. Org. Chem. 53 (1988) 926;
(f) N. Leadbeater, K. Scott, L. Scott, J. Org. Chem. 65 (2000) 3231.
[6] T. Mitsudo, Y. Hori, Y. Yamakawa, Y. Watanabe, Tetrahedron Lett. 27 (1986) 2125.
[7] H. Doucet, B. Martin-Vanca, C. Bruneau, P. Dixneuf, J. Org. Chem. 60 (1995) 724710.
[8] J. Monthéard, M. Camps, G. Seytre, J. Guillet, J. Dubois, Makromol. Chem. 72 (1978) 45.
[9] H. House, D. Crumrine, A. Teranishi, H. Olmstead, J. Am. Chem. Soc. 95 (1973) 3310.
[10] E. Rothman, G. Moore, Tetrahedron Lett. 9 (1969) 2553.
[11] Y. Wakatsuki, N. Koga, H. Yamazaki, K. Morokuma, J. Am. Chem. Soc. 116 (1994) 8105.
[12] L.H. Pignolet, Homogeneous Catalysis with Metal Phosphines, Plenum Press, New York, 1983.
[13] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, Part II, University Science, Mill Valley, CA, 1997.
[14] (a) H. Wanzlick, E. Schikora, Angew. Chem. 72 (1960) 494;
(b) A. Baceiredo, G. Bertrand, J.-P. Majoral, Angew. Chem. Int. Ed. Engl. 23 (1984) 459;
(c) A. Arduengo, R. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
[15] D. Enders, K. Breuer, G. Raabe, J. Runsink, H. Teles, J.-P. Melder, K. Ebel, S. Brode, Angew. Chem. Int. Ed. Engl. 34 (1995) 1021.
[16] A. Martell, R. Smith, Critical Stability Constants, Other Organic Ligands, vol. 3, Plenum Press, New York, 1977, p. 1.