Synthesis of Enol Esters and Dimerization of Terminal Alkynes Catalyzed by Neutral and Cationic Vinylidene Ruthenium Complexes

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Received 7 January 2003

Abstract: In the current study Ru(II) vinylidene complexes of the general type: $Cl_2Ru\{=C=C(H)R\}(PR'_3)L$ (R = Ph, $SiMe_3$, R′ = Ph, Cyclohexyl (Cy) and L = phosphine or N-heterocyclic carbene) are synthesized and tested for the addition of carboxylic acids to terminal alkynes. A careful choice of the catalytic system, substrate and carboxylic acid gives access to alk-1-en-2-yl esters, alk-1-en-1-yl esters or enyne dimerization products.

Furthermore, an extension was made to synthesize an analogous 14-electron species by treating one of the complexes with $AgBF_4$ and its influence on the catalytic activity and selectivity are investigated.

Key words: enol esters, homogeneous catalysis, NHC-ligands, ruthenium, vinylidene

A great deal of attention has been devoted to the chemistry of transition-metal vinylidene complexes $[M]=C=CR_2$ during the past two decades.[1] One of the most straightforward routes to vinylidene metal complexes arises from the activation of a terminal alkyne to give an η^2-coordinated intermediate followed by either a direct 1,2-hydrogen migration[2a] or an oxidative addition of the alkyne to the metal centre and subsequent 1,3-shift of the hydride to the alkynyl ligand.[2b] It is recently shown that not only terminal alkynes but also silylacetylenes[3a] ($R'CCSiR_3$, R and R′ = Ph, Me), stannylacetylenes[3b] ($R'CCSnR_3$, R and R′ = Ph, Me) and alkylthio or iodoalkynes[3c,d] can be converted in the coordination sphere of transition-metals to the corresponding vinylidene complex. It is now well-established that the stability and properties of such derivatives are a function of both the metal centre and the ancillary ligands.[1] In particular, electron-rich ruthenium(II) complexes such as $RuCl(PPh_3)_n$, $RuH_2Cl_2(P\text{-}iPr_3)_2$, $[RuCl_2(p\text{-cymene})]_2$ and $RuCl(\eta^5\text{-}C_9H_7$ or Cp)L_2 (with L_2 two phosphines, one phosphine and one CO, bitentate phosphine, phospho-enolates) have proven to be appropriate precursors for the preparation of stable vinylidenes.[1]

Ruthenium catalyzed activation of alkynes plays a prominent role in the formation of carbon-hetero-atom or carbon-carbon bonds and has become a key step in a lot of new synthetic methodologies.[4] Since the discovery of the one-step formation of alkenylcarbamates,[5] ruthenium vinylidene species directly generated from terminal alkynes have been recognized as catalytic intermediates in the dimerization of alkynes into enynes[6] or butatrienes,[7] in the cyclization of dienylalkynes or in the coupling of alkynes with allylic alcochols to generate unsaturated carbonyl compounds.[8] In this context we found it reasonable to further explore the catalytic activity of easily accessible ruthenium vinylidenes for this kind of reactions.

The characteristic features of ruthenium (e.g. high electron transferability, low redox potentials, stability of reactive metallic species, low oxophilicity) have paved the way to a broad avenue of catalytic transformations.[9]

A relatively recent development of transition metal mediated catalysis is the application of N-heterocyclic carbenes (NHC) of the imidazole and triazole type as ancillary ligands due to their increased Lewis basicity compared to phosphine ligands in combination with the numerous opportunities for electronic and steric ligand tuning and this provides an ideal platform for catalytic engineering.[10]

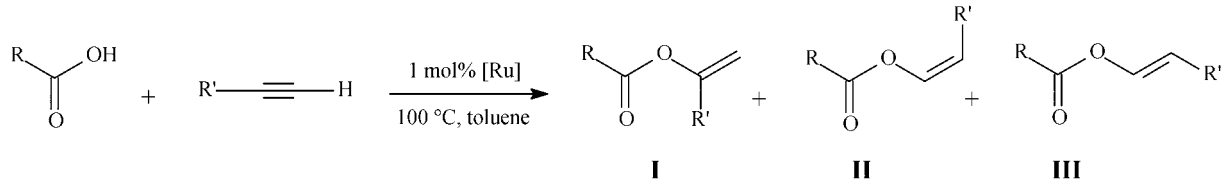
Recently, we have found that the salicylaldiminato Ru vinylidene complexes ($Ru^{II}Cl(PCy_3)(OC_6H_4CH=NR)\{=C=CHR'\}$ (R = 4-Br-2,6-$Me_2C_6H_2$ and R′ = Ph, *t*-But) and $Ru^{II}Cl_2(PCy_3)(L)\{=C=C(H)\text{-}t\text{-But}\}$ (L = PCy_3, N-heterocyclic carbenes) reveal themselves as versatile catalyst for the nucleophilic addition of carboxylic acids to terminal alkynes also referred as vinylation reaction and afford alk-1-en-2-yl esters (**I** also called Markovnikov adduct) or alk-1-en-1-yl esters (**II** and **III** *anti*-Markovnikov adducts) with very good yields and selectivity (Scheme 1).[11,12]

Our experience in this field already showed that in some particular experiments, not the targeted vinylation occurs but rather an alkyne coupling reaction is favoured (Scheme 2).[11,12,17,18] Changing the ligand environment of the metal, using different acids and alkynes or working in aprotic solvents can dramatically alter the observed product distribution.

We now report on the study of a variety of ruthenium vinylidene derivatives of the general type $RuCl_2(PR_3)L(=C=CHR')$ (R = Ph, Cy; R′ = Ph, $SiMe_3$; L = PR_3 or N-heterocyclic carbene) as catalysts for the vinylation of carboxylic acids to terminal alkynes (Figure 1). Furthermore the catalytic potential of the ruthenium complex **4** in vinylation reactions was extended to its cationic 14 electron analogue which is easily gener-

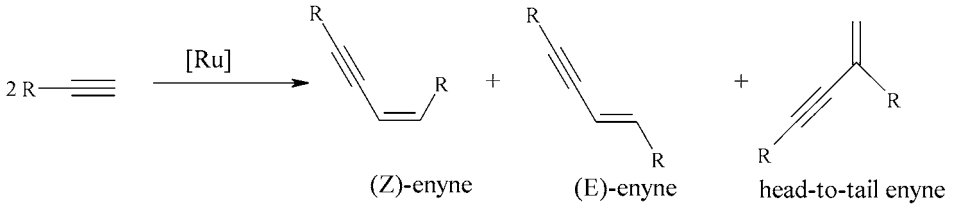
Synlett 2003, No. 3, Print: 19 02 2003.
Art Id.1437-2096,E;2003,0,02,0314,0320,ftx,en;D22103ST.pdf.

ISSN 0936-5214



I **II** **III**

Scheme 1



IV **V** **VI**

Scheme 2

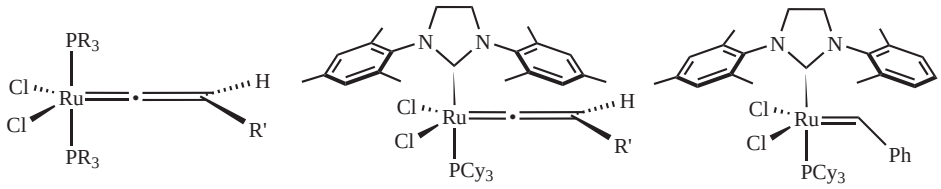
ated in situ by abstracting of a chloride with $AgBF_4$ in toluene.

Ruthenium vinylidene complexes (**1** and **3**) can be easily prepared from commercial available terminal alkynes and ruthenium sources and are well-described in literature.[13] The corresponding silyl homologues (**2** and **4**) are obtained by a procedure described in the literature.[14] Complexes **5**–**7** are prepared in a convenient way by the in situ deprotonation of the commercial available imidazolium tetrafluoroborate salt with *t*-BuOK combined with a substitution of a phosphine ligand in the vinylidene or alkylidene complex.[15,16]

In a first set of experiments a vinylation of phenylacetylene with a divergent spectrum of acids was targeted. Therefore, catalysts **1**–**7** were exposed to phenylacetylene and the results are summarized in Table 1. The observed product distribution strongly depends from the used acid and catalyst. From these results it is clearly seen that the bisphosphine systems give mainly access to dimerization products whereas the systems bearing one N-heterocyclic carbene accomplish the expected vinylation.

Reaction of formic acid with phenylacetylene afforded preferentially (*Z*)-alk-1-en-1-yl esters with the phenylvinylidene systems **1** and **3** (Mark/*anti*-Mark = 0.23 and 0.17) and rather alk-1-en-2-yl esters with the other catalysts (Mark/*anti*-Mark>2). A slight increase in yield is observed when the triphenylphosphine ligand is changed by a more bulky cyclohexylphosphine, however the effect is more pronounced with the silylvinylidene system. On the other hand if the ruthenium centre bears one tricylohexylphosphine and one dihydroimidazol-2-ylidene entity, the yields decrease significantly. Indeed a total yield of 86% is reached with catalyst **6** whereas with the bisphosphine analogue 95% yield was found. From Table 1 it is also seen that the vinylidene function is necessary to create an active system as the yields with catalysts **7** are much lower compared to the vinylidene congener **5** (40% vs 69%).

When weaker acids such as acetic acid or isovaleric acid are used, the contribution of the vinylation reaction is dramatically lowered and mainly dimerization products are found in the reaction mixture. This effect is spectacular for catalysts **1** where respectively 60% and 91% of the product distribution for acetic and isovaleric acid consist of dimerization product [(*Z*)-enyne]. An analogous tendency is observed for catalyst **2** where respectively 65% and 86% of the reaction products consist of the (*Z*)-enyne.



1 R = Ph, R' = Ph
2 R = Ph, R' = $SiMe_3$
3 R = Cy, R' = Ph
4 R = Cy, R' = $SiMe_3$

5 R = Cy, R' = Ph
6 R = Cy, R' = $SiMe_3$

7

Figure 1

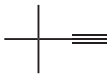
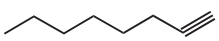
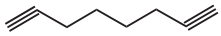
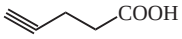
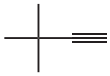
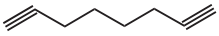
Table 1 Vinylation of Phenylacetylene Using Catalysts **1**–**4**[a]

Cat.	Acid	Yield (%)[b]	**I** (%)[b]	**II** (%)[b]	**III** (%)[b]	(*Z*)-Enyne (%)[b]	(*E*)-Enyne (%)[b]	Head-to-tail Enyne (%)[b]
1	HCOOH	89	18	66	10	6	0	0
1	CH_3COOH	88	17	5	11	60	2	5
1	$(CH_3)_2CCOOH$	93	0	0	0	91	4	5
1	C_6H_5COOH	58	8	0	0	78	14	0
2	HCOOH	80	34	16	7	33	6	4
2	CH_3COOH	84	16	18	3	65	8	0
2	$(CH_3)_2CCOOH$	89	4	5	0	86	3	2
2	C_6H_5COOH	61	9	48	5	34	2	2
3	HCOOH	92	10	76	4	2	4	4
3	CH_3COOH	95	55	6	3	28	0	8
3	$(CH_3)_2CCOOH$	91	38	7	1	39	15	0
3	C_6H_5COOH	70	26	30	5	23	5	11
4	HCOOH	95	64	3	1	6	26	0
4	CH_3COOH	94	78	11	0	4	7	0
4	$(CH_3)_2CCOOH$	98	5	3	2	80	9	1
4	C_6H_5COOH	97	15	57	2	20	6	0
5	HCOOH	69	56	13	15	10	2	4
5	CH_3COOH	66	70	26	0	4	0	0
5	$(CH_3)_2CCOOH$	70	63	20	7	5	5	0
5	C_6H_5COOH	50	31	25	11	23	10	0
6	HCOOH	86	68	32	0	0	0	0
6	CH_3COOH	85	75	24	1	0	0	0
6	$(CH_3)_2CCOOH$	84	77	20	3	0	0	0
6	C_6H_5COOH	90	80	16	4	0	0	0
7	HCOOH	40	79	20	1	0	0	0
7	CH_3COOH	15	64	15	21	0	0	0
7	$(CH_3)_2CCOOH$	70	80	10	8	2	0	0
7	C_6H_5COOH	50	85	6	4	5	0	0

[a] The catalyst (0.04 mmol) was dissolved in toluene (1 mL) and subsequently added through a septum to the solution of alkyne (4 mmol), dodecane (250 μL, internal standard) and carboxylic acid (4.4 mmol) in toluene (3 mL). The reaction mixture was heated at 110 °C for 5 h. The reaction was monitored by withdrawing samples at timed intervals from the reaction mixture and analyzed by Raman, NMR and GC-MS.
[b] Total conversion of the alkyne was determined by quantitative Raman analysis ($\nu_{C\equiv C}$) using calibration curves. The yields of enol esters and dimerization products are determined with GC-MS and ^{1}H NMR-spectroscopy and these data are confirmed by literature.[8,17] The reaction products were identified by comparison of the reaction products with the spectral data of authentic samples. Authentic samples were isolated from concentrated reaction mixtures by silica gel chromatography.

A rather mixed product distribution is obtained with the cyclohexylphosphine systems **3** where a vinylation/dimerization ratio of 1.7 and 0.85 is obtained for acetic acid and isovaleric acid with preferential Markovnikov adduct (55% and 38%) and (*Z*)-enyne (28% and 39%). Relatively more vinylation is observed with system **4** (vin./dim. = 8, 78% Markovnikov) for acetic acid while for isovaleric acid almost exclusively dimerization (vin./

Table 2 Vinylation of Different Alkynes with Acetic Acid[a]

Cat.	Alkyne	Yield (%)[b]	**I** (%)[b]	**II** (%)[b]	**III** (%)[b]	(*Z*)-Enyne (%)[b]	(*E*)-Enyne (%)[b]	Head-to-tail Enyne (%)[b]
4		90	88	10	2	–	–	–
4		55	67	9	4	20	–	–
4		71	81	11	8	–	–	–
4		90	100	–	–	–	–	–
6		81	90	8	2	–	–	–
6		40	74	16	3	7	–	–
6		48	86	6	8	–	–	–
6		84	100	–	–	–	–	–

[a] Condtions: Identical as Table 1.
[b] Total conversion of the alkyne was determined by quantitative Raman analysis ($\nu_{C\equiv C}$) using calibration curves. The yields of enol esters and dimerization products are determined with GC-MS and ^{1}H NMR-spectroscopy and these data are confirmed by literature.[8,17] The reaction products were identified by comparison of the reaction products with the spectral data of authentic samples. Authentic samples were isolated from concentrated reaction mixtures by silica gel chromatography.

dim = 0.1, 80% (*Z*)-enyne) occurred. With catalysts **5**–**7** the enol-ester formation is the main reaction and a preference for the Markovnikov products is observed even in the case with acetic acid and isovaleric acid (e.g. catalyst **6** give 77% and 80% Markovnikov for these two acids).

With benzoic acid as acid source the obtained products strongly depend on the used catalyst. With catalyst **1** particularly the (*Z*)-enyne is obtained (78%) while with the other catalysts the vinylation reaction is favoured with rather poor selectivities for systems **3** and **4** [(max 57% (*Z*)-alk-1-en-1-yl ester for catalyst **4**] and quite good selectivities for system **5**–**7** (max 85% alk-1-en-2-yl ester with catalyst **7**).

In another experiment, catalysts **4** and **6** were tested for the vinylation reaction of acetic acid to different alkynes and the results are depicted in Table 2. These results clearly indicate that the outcome of a vinylation reaction strongly depends on the used alkyne. Both catalysts give access to Markovnikov products with *tert*-butylacetylene as alkyne source in high yields (81 and 90%) and selectivity (Mark/*an*ti-Mark>7). With the terminal alkyne, 1-octyne, the yields are lower but again a preference for the alk-1-en-2-yl ester is found. Almost no dimerization products are observed for these two alkynes.

From Table 2 it also follows that after reaction of acetic acid with 1,7-octadiyne, a preference for the (geminal, geminal)dienol diester (Markovnikov adduct) synthesis is observed for both catalysts and small percentages (*E*,*E*) and (*Z*,*Z*) dienol diesters and no traces dimerization products are detected with GC-MS. The alkynyl acid, 4-pentynoic acid, gave after internal vinylation exclusively the γ-methylene-γ-butyrolactone in excellent yields for both catalysts (90 and 84%).

When the complexes **1**–**7** are exposed to a solution of phenylacetylene in toluene (100 equiv) one expects that a dimerization reaction should occur. The results of these experiments are depicted in Table 3.

Table 3 Dimerization of Phenylacetylene Using Catalysts **1**–**7**[a]

Cat.	Yield (%)[c]	(*Z*)-Enyne (%)[c]	(*E*)-Enyne (%)[c]	Head-to-tail Enyne (%)[c]
1	39	20	70	10
2	40	32	49	19
3	56	27	50	23
4	46	24	55	21
5	37	87	13	0
6	40	100	0	0
7	10	80	17	3

[a] The catalyst (0.04 mmol) was dissolved in toluene (1 mL) and subsequently added through a septum to the solution of alkyne (4 mmol) and dodecane (250 μL, internal standard) in toluene (3 mL).
[b] The reaction mixture was heated at 110 °C for 5 h.
[c] Total conversion of the alkyne was determined as previous described (Table 1).

From Table 3 it follows that all the tested catalysts are moderate active for the dimerization of phenylacetylene. In the observed product distribution a preference for the

(*E*)-enyne is found with the systems **1**–**4** and a preference for the (*Z*)-enyne is seen for the systems **5**–**7**.

Since it is known from our previous reported results that abstracting a chloride in neutral vinylidene complexes which involves the generation of a cationic species, has an advantageous effect on the catalytic activity, our best system was treated with $AgBF_4$ (**4**) and tested for the vinylation and dimerization reaction.[12] Before the reaction starts, 0.04 mmol catalyst has been stirring with $AgBF_4$ at room temperature in a glass vessel for 30 minutes. After this period a precipitation of AgCl is observed and the alkyne and acid are subsequently added. The results are summarized in Table 4.

During the monitoring of the reaction we saw that the disappearance of the alkyne proceeds much faster than with the neutral complex. After a reaction time of 2.5 hours almost a total conversion was obtained. A preference for the vinylation reaction was established with vin./dim. ratio's ranging from 6.7 (isovaleric acid), 9 (formic acid) to 100% (acetic acid) and corresponding Mark/*anti*-Mark ratio's from 0.5 (isovaleric acid), 5 (formic acid) and 32 (acetic acid). The reaction of formic acid with 1,7-octadiyne leads almost exclusively to the (geminal, geminal) dienol diester. The dimerization of phenylacetylene reaches 65% conversion with the cationic system and an almost equal amount of (*E*)- and (*Z*)-enyne. A probably explanation for the increased activity is that the cationic complex is more attractive for a nucleophilic attack of an carboxylic acid.[12]

Kinetic data clearly demonstrate that the relative activity for the reaction of benzoic acid with phenylacetylene increase in the following order: $2<6<4<4^+$ as is indicated by the relative trend in initial TOF: **4**: 44 h^{-1}, **6**: 62 h^{-1}, **4**, 72 h^{-1}, $\mathbf{4}^+$: 106 h^{-1}.

Several experiments were performed to apprehend the nature of the active species for the vinylation and dimerization reactions.[18] Addition of 10 equivalents of tricyclohexylphosphine to a mixture of **4** with alkyne and formic acid inhibited the reaction immediately and no vinylation products were observed. On the other hand the addition of a phosphine sponge such as CuCl to a mixture of **4** afforded a quantitative conversion after 3 hours. Therefore we reasoned that the dissociation of a phosphine ligand is crucial in the reaction cycle (Scheme 3).

In conclusion catalysts **1**–**4** are efficient catalysts for the addition of carboxylic acids to activated alkynes. A careful choice of the used acid can preferentially steer the reaction into one direction either a vinylation reaction with mainly Markovnikov adduct or a dimerization reaction with the (*Z*)-enyne as the major product. Complexes **5**–**7** have proven to be efficient catalysts for the vinylation reaction of formic acid, acetic acid, isovaleric acid and benzoic acid to phenylacetylene. Finally a cationic variant of complex **5** was synthesized and has proven to be a more active system then the neutral complexes.

Acknowledgment

T.O. is indebted to the Research founds of Ghent University for a research grant F.V. is indebted to the FWO-Flanders (Fonds voor Wetenschappelijk Onderzoek-Vlaanderen) and to the Research Fund of Ghent University for financial support.

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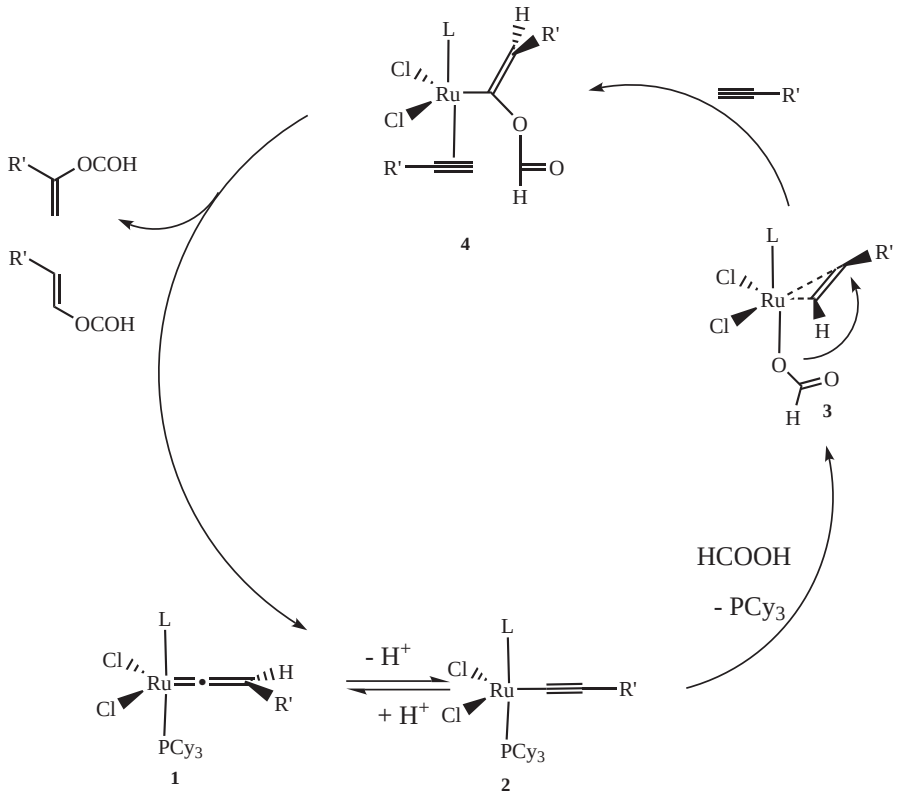
Table 4 Vinylation of Phenylacetylene Using the Cationic Variant of Catalyst **4**[a]

Acid	Alkyne	Yield (%)[c]	**I** (%)[c]	**II** (%)[c]	**III** (%)[c]	(*Z*)-Enyne (%)[c]	(*E*)-Enyne (%)[c]	Head-to-tail Enyne (%)[c]
HCOOH	Phenylacetylene	97	75	10	5	0	10	0
CH_3COOH		90	97	2	1	0	0	0
$(CH_3)_2CCOOH$		97	20	15	5	60	0	0
C_6H_5COOH		98	30	49	8	13	0	0
HCOOH	1.7-Octadiyne	90	88	10	2	0	0	0
–	phenylacetylene	65	0	0	0	40	56	4

[a] The catalyst (0.04 mmol) was dissolved in toluene (1 mL) and subsequently added through a septum to the solution of alkyne (4 mmol), dodecane (250 μL, internal standard) and carboxylic acid (4.4 mmol) in toluene (3 mL). The reaction mixture was heated at 110 °C for 2.5 h.
[b] Total conversion of the alkyne was determined as previously described (Table 1).



Scheme 3

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(14) **Synthesis of Complexes 2 and 4:** To a suspension of $[RuCl_2(p\text{-cymene})]_2$ (0.72 g, 1.17 mmol) in toluene (45 mL), the phosphine PCy_3 (1.32 g, 4.7 mmol) or PPh_3 (1.23 g, 4.7 mmol) was added and stirred at r.t. The mixture instantly changed into a reddish brown solution. Me_3SiCCH (3.34 mL, 23.5 mmol) was added and the solution was stirred for 1 h at r.t. The solution instantly darkened to a dark red solution. After 1 h the temperature was gradually risen to 60 °C and stirred during one night. The analytical pure compound was obtained (65% yield) after washing the crude product with methanol. $Cl_2Ru\{=C=C(H)SiMe_3\}(PPh_3)_2$(**2**): ^{1}H NMR (299.89 MHz, C_6D_6, 25 °C): δ = 7.82–7.64 and 7.00–6.65 (each m, 30 H, PPh_3), 0.33 (s, 9 H, SiCH_3), 0.01 (dt, $J_{(RuH)}$ = 2.1 Hz, $J_{(PH)}$ = 2.5 Hz, 1 H, =C*H*SiMe_3). ^{13}C NMR (75.41 MHz, C_6D_6, 25 °C): δ = 279.33 (dt, $J_{(RuH)}$ = 57.0 Hz, $J_{(PC)}$ = 15.4 Hz, Ru=*C*=C), 86.45 (dt, $J_{(RuH)}$ = 15.7 Hz, $J_{(PC)}$ = 5.1 Hz, Ru=C=*C*), 150.16 (s, C^1 of PPh), 129.77, 128.00, 126.87 (s, PPh). ^{31}P NMR {^{1}H} (121.40 MHz, C_6D_6, 25 °C, ref. H_3PO_4): δ = 26.3 (s). IR (KBr): ν = 1625 (C=C) cm^{-1}. Anal. Calcd for $C_{41}H_{40}Cl_2P_2SiRu$: C, 61.96; H, 5.07. Found: C, 62.30; H, 5.82. $Cl_2Ru\{=C=C(H)SiMe_3\}(PCy_3)_2$(**4**): ^{1}H NMR (299.89 MH_z, C_6D_6, 25 °C): δ = 2.68–2.59, 2.13–1.97, 1.89–1.64, 1.26–1.16 (each m, 66 H, PCy_3), 0.29 (s, 9 H, SiCH_3), 0.023 (dt, $J_{(RuH)}$ = 1.9 Hz, $J_{(PH)}$ = 2.8 Hz, 1 H, =C*H*SiMe_3). ^{13}C NMR (75.41 MHz, C_6D_6, 25 °C): δ = 274.30 (dt, $J_{(RuH)}$ = 57.2 Hz, $J_{(PC)}$ = 15 Hz, Ru=*C*=C), 81.20 (dt, $J_{(RuH)}$ = 16 Hz, $J_{(PC)}$ = 5 Hz, Ru=C=*C*), 35.46 (pseudo triplet, *J* = 8.7 Hz, C^1 of PCy), 30.14 (s, $C^{3,5}$ of PCy), 27.83 (pseudo triplet, *J* = 4.2 Hz, $C^{2,6}$ of PCy), 26.35 (s, C^4 of Pcy). ^{31}P NMR {^{1}H} (121.40 MHz, C_6D_6, 25 °C, ref. H_3PO_4): δ = 31.50 (s). IR (KBr): ν = 1630 (C=C) cm^{-1}. Anal. Calcd for $C_{41}H_{76}Cl_2P_2SiRu$: C, 59.26; H, 9.58. Found: C, 59.52; H, 10.10.

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(16) **A Typical Procedure for the Preparation of Complex 6 is as follows.** A solution (0.1 M in THF) of the 4,5-dihydroimidazol-2-ylideen tetrafluoro-borate salt (300 µl) (STREM), a magnetic stirring bar and toluene (1 mL) were added to a glass vessel. *t*-BuOK was added (30 µL 1 M in Et_2O, Aldrich) to the rapidly stirred suspension at r.t., resulting in the immediate dissolution of the salt to form a light yellow solution. After 5 min, a 0.1 M solution of the vinylidene (**3** or **4**, 250 µL) or alkylidene $[Cl_2(PCy_3)_2Ru$ (= CHPh)] complex in toluene were added via cannula. The mixture was heated to 70 °C for 1 h and subsequently cooled

to r.t. Complex **6**: ^{1}H NMR (299.89 MHz, C_6D_6, 25 °C): δ = 7.03–6.96 (br, 2 H, Mes), 6.92–6.86 (br, 2 H, Mes), 3.49 (s, 4 H, imidazolium), 2.44–2.10, 1.99–1.84 (br,18 H, Mes), 2.12 (m, 3 H, C^1 PCy_3), 1.55–1.52, 1.39, 1.02–0.96 (m, 32 H, PCy_3) 0.05 (s, 9 H, SiCH_3), –0.15 (dt, $J_{(RuH)}$ = 1.9 Hz, $J_{(PH)}$ = 2.8 Hz, 1 H, =C*H*SiMe_3). ^{13}C NMR (75.41 MHz, C_6D_6, 25 °C): δ = 267.27 (dt, $J_{(RuH)}$ = 56.8 Hz, $J_{(PC)}$ = 15 Hz, Ru=*C*=C), 194.46 (s, $J_{(CP)}$ = 80 Hz, Ru-CNN), 144.82, 141.00, 137.64, 134.95, 131.93 (all s, Mes), 129.01 (d, $J_{(CH)}$ = 150 Hz, Mes), 128.82 (d, $J_{(CH)}$ = 130Hz, Mes), 71.05 (dt, $J_{(RuH)}$ = 15 Hz, $J_{(PC)}$ = 5.5 Hz, Ru= C=*C*), 31.30 (pseudo triplet, *J* = 9 Hz, C^1 of PCy_3), 29.96 (s, $C^{3,5}$ of PCy), 27.87 (pseudo triplet, *J* = 4 Hz, $C^{2,6}$ of PCy_3), 26.36 (s, C^4 of PCy_3) 21.96, 21.13, 19.54, 18.61 (all s, Mes). ^{31}P NMR {^{1}H} (121.40 MHz, C_6D_6, 25 °C, ref. H_3PO_4): δ = 28.03 (s). IR (KBr): ν = 1634 (C = C) cm^{-1}. Anal. Calcd for $C_{44}H_{69}N_2Cl_2PSiRu$: C, 61.66; H, 8.11; N, 3.27. Found: C, 62.98; H, 9.23; N, 4.03.

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