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Articles

New (Carbene)ruthenium−Arene Complexes: Preparation and Uses in Catalytic Synthesis of Furans[†]

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A variety of neutral ruthenium−carbene complexes $RuCl_2$(carbene)(arene) **1** (carbene = $C(NR)C_6H_4(NR)$, R = Me (**a**), Et (**b**); arene = *p*-Me-C_6H_4-^iPr (**1**), $C_6H_3Me_3$ (**2**), C_6Me_6 (**3**)) have been prepared by reaction of $[RuCl_2(arene)]_2$ precursors with the enetetraamines $(RN)C_6H_4(RN)C{=}C(NR)C_6H_4(NR)$ **I** (R = Me) and **II** (R = Et). $Ru{=}C(NCH_2Ph)CH_2CH_2(NCH_2Ph)Cl_2$(*p*-cymene) (**4**) was prepared similarly, whereas the reaction of $[RuCl_2(\text{cycloocta-1,5-diene})]_n$ with **I** led to the formation of the 16-electron neutral complex $RuCl_2[{=}C(NMe)C_6H_4(NMe)]_3$ (**6**). One of them (**3a**) was transformed into the dihydride derivative $RuH_2(C(NMe)C_6H_4NMe)(C_6Me_6)$ (**5**). The cyclic voltammograms of derivatives **1**−**3** show that they are oxidized in the range $E_{1/2}$ = 1.03−1.31 V vs SCE and are more *electrophilic* than the isoelectronic $RuCl_2(PR_3)$(arene) complexes. Derivatives **1a**, **3a**, and **3b** act as efficient catalyst precursors for the *electrophilic* activation of the C≡C bond of (*Z*)-3-methylpent-2-en-4-yn-1-ol to afford 2,3-dimethylfuran in good yield via intramolecular cyclization.

Introduction

During the last few years, the study of ruthenium complexes has revealed their power in promoting novel activation processes and catalytic reactions that have strengthened organic synthesis methodologies. Thus, the activation of terminal alkynes into vinylidene intermediates[1] and the promoted alkene−alkyne coupling[2,3] have led to the discovery of powerful new methods for the synthesis of vinylcarbamates,[4] α,β-unsaturated carbonyl compounds,[5] butatrienes,[6] butenolides,[7] and unsaturated aldehydes.[8]

A promising aspect of ruthenium chemistry deals with the generation of ruthenium carbene species that are expected to be efficient catalyst intermediates for olefin cyclopropanation or metathesis[9] and ring-opening metathesis polymerization of cyclic olefins.[9a,10] For instance, $RuCl_2(PCy_3)$(*p*-cymene) and even $RuCl_2(PPh_3)_3$ on addition of diazoacetic esters generate very efficient catalysts for the polymerization of low-strained cyclic olefins.[10,11] Recently, Grubbs *et al.* have shown that the coordinatively unsaturated carbene complex $Ru{=}CHCH{=}CPh_2(Cl)_2(PCy_3)_2$ is a precursor for the

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(1) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257. (b) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768−2772. (c) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3232−3139. (d) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030−5039.

(2) (a) Mitsudo, T.; Zhang, S.; Nagao, N.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 598−599. (b) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *334*, 157−167. (c) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580−581.

(3) (a) Trost, B. M.; Indolese, A. *J. Am. Chem. Soc.* **1993**, *115*, 4361−4362. (b) Trost, B. M.; Indolese, A. F.; Müller, T. J. J.; Treptow, B. *J. Am. Chem. Soc.* **1995**, *117*, 615−623.

(4) (a) Mahé, R.; Dixneuf, P. H.; Lécolier, S. *Tetrahedron Lett.* **1986**, *27*, 6333−6336. (b) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518−1523. (c) Bruneau, C.; Dixneuf, P. H. *J. Mol. Catal.* **1992**, 1220−1222.

(5) (a) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809−7811. (b) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579−5584.

(6) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.

(7) (a) Trost, B. M.; Müller, T. J. J. *J. Am. Chem. Soc.* **1994**, *116*, 4985−4986. (b) Trost, B. M.; Müller, T. J. J.; Martinez, J. *J. Am. Chem. Soc.* **1995**, *117*, 1888−1889.

(8) Dérien, S.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2551.

(9) (a) Noels, A. F.; Demonceau, A.; Carlier, E.; Hubert, A. J.; Marquez-Silva, R.-L.; Sanchez-Delgado, R. A. *J. Chem. Soc., Chem. Commun.* **1988**, 783−784. (b) Demonceau, A.; Saive, E.; de Froimont, Y.; Noels, A. F.; Hubert, A. J. *Tetrahedron Lett.* **1992**, *33*, 2009−2012. (c) Maas, G.; Werle, T.; Alt, M.; Mayer, D. *Tetrahedron* **1993**, *49*, 881−888. (d) Demonceau, A.; Abreu Dias, E.; Lemoine, C. A.; Stumpf, A. W.; Noels, A. F. *Tetrahedron Lett.* **1995**, *36*, 3519−3522.

(10) Demonceau, A.; Noels, A. F.; Saive, E.; Hubert, A. J. *J. Mol. Catal.* **1992**, *76*, 123−132.

(11) Noels, A. F.; Demonceau, A.; Saive, E. in *Advances in Catalytic Design*., Graziani, M., Rao, C. N. R., Eds.; World Scientific: London, 1992; Vol. 2, pp 73−94.

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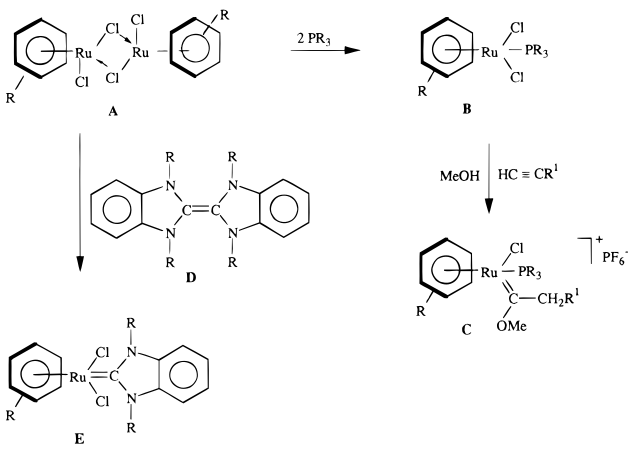
Scheme 1



polymerization of low-strain olefins.[12] Moreover, due to the tolerance of ruthenium catalysts toward a variety of functional groups, these ruthenium-carbene species are finding new applications for organic synthesis.[13,14]

By displacement of the arene ligand of [RuCl$_2$(*p*-cymene)]$_2$ in the presence of an optically active tridentate ligand and N$_2$CHSiMe$_3$, an 18-electron Ru=CHSiMe$_3$ carbene complex[15] has been isolated and shown to catalyze asymmetric cyclopropanation of olefins with N$_2$CHCO$_2$R derivatives. Moreover, a very efficient catalyst for the polymerization of non-strained olefins has just been reported by Noels *et al.*[16] on treatment of RuCl$_2$(PCy$_3$)(*p*-cymene) with N$_2$CHSiMe$_3$ and is consistent with the generation, after displacement of the arene, of a Ru=CHSiMe$_3$ coordinatively unsaturated species containing a bulky PCy$_3$ ligand. In contrast, coordinatively saturated *cationic* Fischer-type (carbene)ruthenium complexes **C**,[1b,17] arising from (arene)ruthenium precursors **A** and **B** (Scheme 1), have been shown to be inactive in catalysis.[18] The efficiency in catalysis and organic synthesis of *neutral* ruthenium−carbene species Ru=CHR generated from (arene)ruthenium(II) precursors[10,15,16] has led us to study the possibility of generating neutral (arene)ruthenium−carbene complexes **E** from the aromatic enetetraamines derivatives **D** (Scheme 1).

Lappert *et al.*[19] have shown that electron-rich olefins closely related to **D** are useful precursors to generate a variety of electron-donating (carbene)metal complexes, and several ruthenium−carbene complexes have been prepared by this method, essentially *via* phosphine displacement from ruthenium−phosphine complexes.[20−22] To our knowledge, no neutral (arene)RuX$_2$(carbene) complexes of type **E** have been prepared so far. The syntheses of enetetraamine derivatives (**D**: R = Me,[23] Et[24]) have been reported recently, and only rhodium-carbene complexes have been prepared from **D**.[23] (Carbene)metal complexes arising from the cleavage of **D** are expected to contain a bulky carbene ligand that, moreover, is a less electron-donating ligand than the related electron-rich carbene $\overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$,[19] due to electron delocalization onto the aromatic rings.

Among the ruthenium(II) complexes the (arene)RuCl$_2$(PR$_3$) derivatives have been shown to be the promoters of many catalytic reactions related to the *electrophilic activation* of alkynes in the synthesis of vinylcarbamates,[4] β-oxopropyl esters,[25] and enol esters.[26] The isoelectronic complexes (arene)RuCl$_2$(=$\overline{\mathrm{C(NR)C_6H_4N}}$R) of type **E**, even if they are not expected to promote olefin metathesis catalysis due to the presence of heteroatoms linked to the carbene carbon, are of interest in providing activation of terminal alkynes. Thus, we have studied the possibility of direct cleavage of the chloro bridges of the binuclear complexes [RuCl$_2$(arene)]$_2$ (**A**) with enetetraamines of type **D** in an attempt to generate (carbene)ruthenium species **E** (Scheme 1).

We now report (i) the detailed preparation of novel neutral (arene)RuCl$_2$(=$\overline{\mathrm{C(NR)C_6H_4N}}$R) complexes of type **E**, (ii) an electrochemical study showing that they cannot be considered as electron-rich ruthenium(II) complexes and (iii) the promotion by these complexes of the efficient catalytic activation of (*Z*)-enynols and a convenient synthesis of furans.

Results and Discussion

Preparation of Complexes. The precursor [RuCl$_2$(*p*-cymene)]$_2$ (**A$_1$**) was reacted with 1 equiv of bis(1,3-dimethylbenzimidazolidine-2-ylidene) (**I**) in toluene at 100 °C for 4 h. The brown complex **1a** was isolated in 93% yield (Scheme 2). Its analytical and spectroscopic data correspond to the addition of only one carbene ligand to the 16-electron ruthenium species [RuCl$_2$(*p*-cymene)]: the *p*-cymene ligand is retained (^{1}H NMR), and the ^{13}C NMR spectrum revealed the presence of the carbene moiety, by the low-field singlet at δ 188.89 ppm for the Ru=C carbon nucleus. Analogously, the carbene complex **1b** was obtained in 88% yield from the reaction of precursor **A$_1$** with the olefin **II** (Scheme 2).

The [(arene)RuCl$_2$]$_2$ precursors containing 1,3,5-trimethylbenzene (**A$_2$**) and hexamethylbenzene (**A$_3$**) are known to lead to a stronger arene−ruthenium bond

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[12] (a) France, M. B.; Paciello, R. A.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4739. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (c) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503−5511. (d) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041.

[13] (a) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857. (b) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801−10802. (c) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020.

[14] Schmalz, H.-G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1833−1836.

[15] Park, S.-B.; Nishiyama, H.; Itoh, Y.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1315−1316.

[16] Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127−1128.

[17] Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809−817.

[18] Lavastre, O.; Dixneuf, P. H. *J. Organomet. Chem.* **1995**, *488*, C9-C10.

[19] Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185−214.

[20] Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 837−844.

[21] Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 826−836.

[22] Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. *J. Chem. Soc., Dalton Trans.* **1979**, 1929−1942.

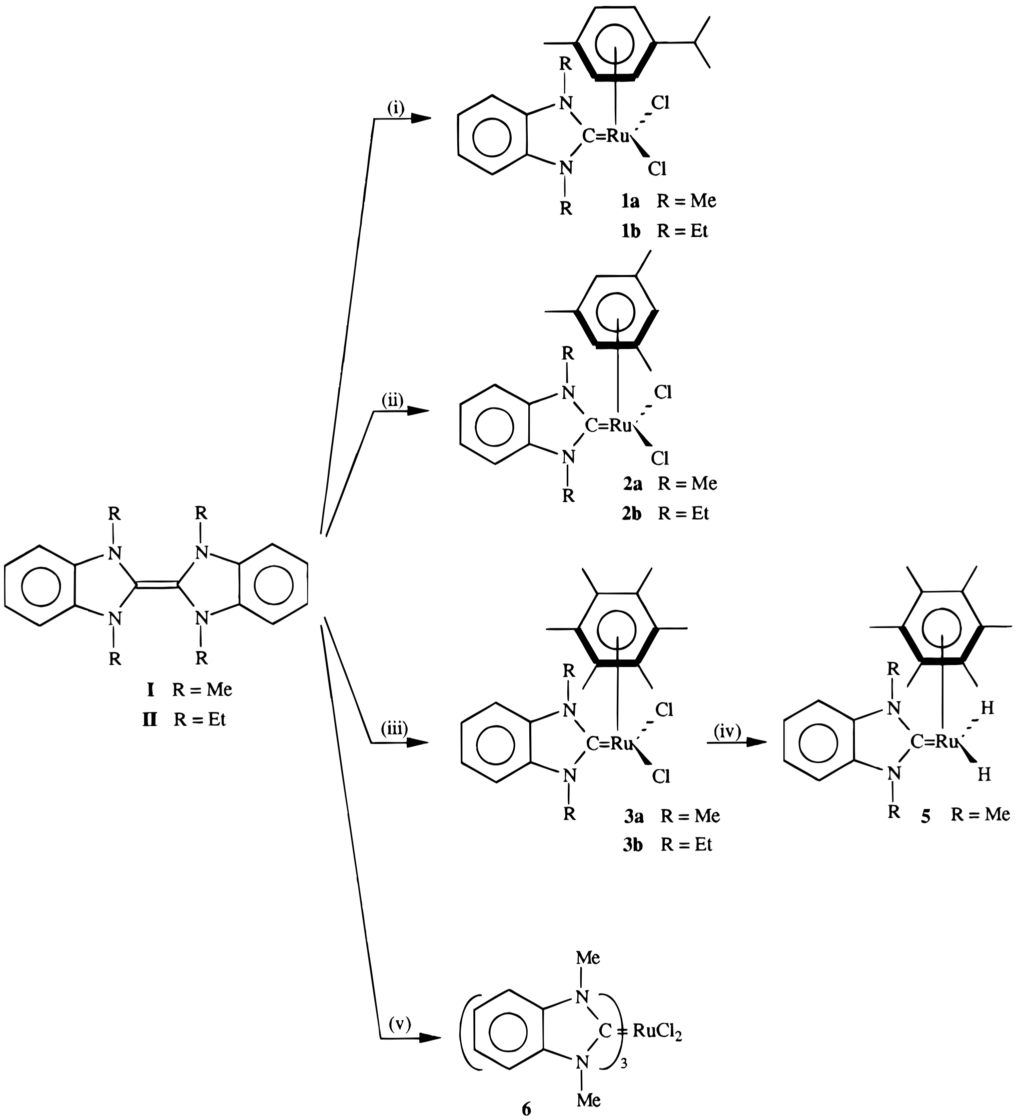
[23] Çetinkaya, E.; Hitchcock, P. B.; Küçükbay, H.; Lappert, M. F.; Al-Juaid, S. *J. Organomet. Chem.* **1994**, *481*, 89−95.

[24] Çetinkaya, B.; Çetinkaya, E.; Küçükbay, H.; Özdemir, I.; Gürbüz, N. Abstracts, 35th IUPAC Congress; Türkish Chem. Soc.: Istanbul, Türkey, 1995; Vol. II, p 1380.

[25] Devanne, D.; Ruppin, C.; Dixneuf, P. H. *J. Org. Chem.* **1988**, *53*, 925−928.

[26] (a) Ruppin, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1986**, *27*, 6323−6324. (b) Bruneau, C.; Neveux, M.; Kabouche, Z.; Ruppin, C.; Dixneuf, P. H. *Synlett* **1991**, 755−763.

Scheme 2[a]



[a] Reagents and conditions: (i) $[RuCl_2(p\text{-}MeC_6H_4CH(Me)_2)]_2$ (**A**$_1$), 4 h, 100 °C; (ii) $[RuCl_2(C_6H_3Me_3)]_2$ (**A**$_2$), 5 h, 100 °C; (iii) $[RuCl_2(C_6Me_6)]_2$ (**A**$_3$), 4 h, 100 °C; (iv) $NaBH_4$, 10 h, room temperature; (v) $[RuCl_2(COD)]_n$, 4 h, 100 °C.

than does *p*-cymene in the cationic (carbene)ruthenium complexes $[(arene)Ru(PR_3)(Cl)(=C(OMe)CH_2R)]^+PF_6^-$ (**C**)[27] originating from the direct activation of terminal alkynes. Thus, both olefins **I** and **II** were reacted in toluene at 100 °C with 1 equiv of $[RuCl_2(\eta^6\text{-}C_6H_3Me_3)]_2$ (**A**$_2$) and $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ (**A**$_3$) successively. The brown, stable (carbene)ruthenium complexes **2a** (96%), **2b** (95%), **3a** (96%), and **3b** (79%) were obtained. Each of these complexes retains the arene ligand and contains one carbene ligand (R = Me) (**a**) or (R = Et) (**b**), as shown by ^1H NMR. The ^{13}C NMR shows the typical low-field signal (singlet) for such a (carbene)metal complex as in the two corresponding rhodium derivatives[23] (δ (ppm): 196.0 (**2a**), 195.0 (**2b**), 195.5 (**3a**), 194.0 (**3b**)) without a noticeable influence of the nature of the arene ligand.

Although complexes **1**−**3** have a formal symmetry plan, the (NCH_2CH_3) methylene protons of the carbene ligand of derivatives **b** are nonequivalent in ^1H NMR, showing that the privileged position of the carbene ligand deviates from this symmetry plan. The carbene is likely to adopt an orthogonal position to the ruthenium−arene axis, as observed in the X-ray diffraction structure of the cationic carbene complex $[(\eta^6\text{-}C_6Me_6)Ru{=}C(OMe)CH{=}CPh_2(Cl)(PMe_3)]PF_6$.[17]

The above synthesis of neutral (carbene)ruthenium complexes **1**−**3** shows that it is possible to cleave the chloro bridges of precursors **A**, not only with phosphorus derivatives or two-electron-donating ligands, but also with the olefins **I** and **II** that are cleaved, although under more drastic conditions (100 °C/4 h). It constitutes a new way to generate *neutral* (arene)ruthenium(II)−carbene derivatives **E** and contrasts with that of the cationic carbene complexes **C** (Scheme 1).

To examine whether this transformation **A** → **E** was restricted to the 1,2-substituted aryl olefins **I** and **II**, the precursor **A**$_1$ was reacted with 1 equiv of the more electron-rich bis(1,3-dibenzylimidazolidine-2-ylidene) (**III**) in toluene at 90 °C for 4 h. The brown complex **4** was isolated in 87% yield (eq 1). Its NMR spectra showed the presence of one arene and one carbene ligand, with the typical singlet in ^{13}C NMR for the Ru=C carbon nucleus at lower field (δ 208.3 ppm) than for the analogous complexes **1**−**3** (δ 194−196 ppm).

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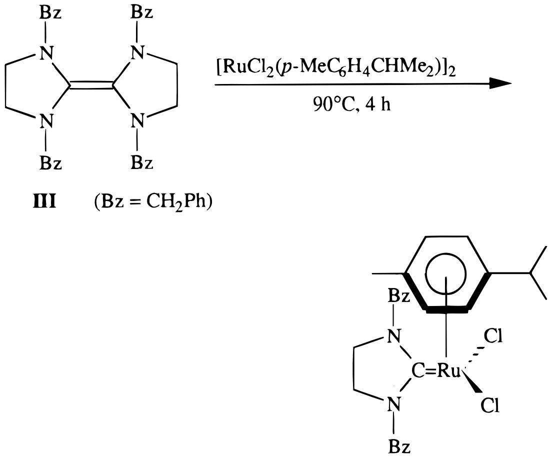
(27) Devanne, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1990**, *390*, 371−378.



III (Bz = CH_2Ph)

4

(1)

Fischer-type carbene ligands have been shown to insert into a *cis*-hydrido-metal bond to generate an η^2-coordinated alkyl ligand,[28] and the subsequent coordination of the ligand heteroatom led to the formation of a stable 18-electron derivative. To study the behavior of the carbene ligand in complexes **1**–**3** toward ruthenium hydrides, complex **3a** was reacted with an excess of $NaBH_4$ in dry ethanol. After 10 h at room temperature the light yellow, unstable complex **5** was isolated in 72% yield. The infrared spectrum indicated two Ru–H absorptions at ν 1924 and 1885 cm^{-1} (KBr), and in ^1H NMR (300 MHz) a signal (2 H) at δ −9.71 ppm was consistent with the formation of a dihydridoruthenium carbene complex ($(C_6H_6)RuH_2(PPh_3)$: δ (Ru–H) −10.70 ppm, ν(Ru–H) 1963, 1932 cm^{-1}).[29] The ^1H NMR shows only one singlet for the NMe groups and rules out the coordination of one nitrogen atom. This transformation **3a** → **5** indicates that the carbene ligand of **3a** stabilizes the dihydrido intermediates rather than leads to (carbene) carbon insertion into the Ru–H bond.

During the formation of complexes **1**–**3** the fixation of a second *neutral* carbene ligand was never observed, whereas from the same precursors **A**, phosphorus derivatives easily undergo coordination of two PR_3 ligands in $[(arene)Ru(PR_3)_2Cl]X$ complexes and mixed bis(carbene)ruthenium–arene derivatives were already obtained *via* an indirect route.[30]

In order to coordinate several carbene ligands to the ruthenium(II) site, $[RuCl_2(COD)]_n$,[31] which is known to easily release the cyclooctadiene ligand, was reacted with a large excess of the functional alkene **I** in toluene. A yellow precipitate, identified as $RuCl_2(=C(NMe)C_6H_4NMe)_3$ (**6**), was isolated in 98% yield (Scheme 2). The coordination of three carbene ligands to the $RuCl_2$ moiety was shown by the presence of one ^{13}C signal at δ 195.5 ppm (Ru=C) and one at δ 34.3 ppm (NMe). This synthesis of the formal 16-electron ruthenium complex **6**, isoelectronic with $RuCl_2(PPh_3)_3$ which appears to be a key catalyst precursor, may have also a potential for catalysis.

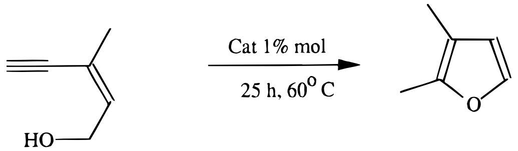
Table 1. Cyclic Voltammetric Data for (Carbene)ruthenium Complexes[a]

compd	$E_{1/2}(Ru^{3+}/Ru^{2+})$, V vs SCE	ΔE_p, mV
1a	1.31	120
1b	1.23	150
2a	1.18	170
2b	1.12	160
3a	1.12	165
3b	1.03	140
4	1.27	125
6	1.50	200
$RuCl_2(PMe_3)(C_6Me_6)$[1b]	0.77	80
$RuCl_2(PPh_3)(C_6Me_6)$[1b]	0.92	70
$RuCl_2(CNBu^t)(C_6Me_6)$[30]	1.06	70

[a] *E* vs SCE; Pt working electrode; 200 mV/s; recorded in CH_2Cl_2 solution with 0.026 M Bu_4NPF_6 as supporting electrolyte.

Electrochemical Studies of Complexes 1–6. The *electrophilicity* concept of ruthenium(II) catalyst precursors has been used to explain selective, mild catalytic transformations of alkynes.[4,26,32] The method of choice to evaluate either the electron deficiency or richness of a metal complex remains the measure of its reversible oxidation potential ($E_{1/2}$) by cyclic voltammetry. In addition, it offers a direct comparison of (arene)$RuCl_2$(carbene) with related derivatives such as (arene)$RuCl_2L$ (L = PR_3,[1b,27] CNR[30]). Complexes **1**–**6** were studied by cyclic voltammetry in CH_2Cl_2 solution with $Bu^n{}_4NPF_6$ as supporting electrolyte. Each of them gives a reversible oxidation process at 200 mV/s. The corresponding data are gathered in Table 1. It shows that (arene)$RuCl_2$(carbene) complexes (**1**–**4**) are oxidized at a much higher potential ($E_{1/2}$ = 1.03–1.31 V (SCE)) than the corresponding phosphine complexes (arene)$RuCl_2(PR_3)$. The electron-donating capability of the arene ligand is reflected in the sequence $Me\text{-}C_6H_4\text{-}Pr^i$ (**1a**) < $C_6H_3Me_3$ (**2a**) < C_6Me_6 (**3a**). The coordinatively unsaturated complex **6** possesses the highest potential of oxidation. The (arene)$RuCl_2$(carbene) derivatives **1**–**3** *a priori* offer a good balance of electron deficiency to provide *electrophilic* activation of alkynes with respect to (arene)$RuCl_2(PR_3)$ complexes.[1b]

Catalytic Synthesis of Furan Derivatives. Whereas ruthenium(II) catalysts allow the *electrophilic* activation of (*E*)-3-methylpent-2-en-4-yn-1-ol (**7**) toward the addition of carboxylates to provide a direct access to a variety of dienes,[33] we have shown that the activation of its *Z* isomer **8** could constitute a way to generate furan derivatives[34] but that catalytic efficiency could be improved. The catalytic activity of the (arene)$RuCl_2$(carbene) derivatives **1**–**3** in the transformation **8** → **9** was thus investigated (eq 2).



8 **9**

(2)

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[28] (a) Le Bozec, H.; Fillaut, J.-L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1182–1185. (b) Osborn, V. A.; Parker, C. A.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1185–1186.

[29] Werner, H.; Kletzin, H. *J. Organomet. Chem.* **1982**, *228*, 289.

[30] Dussel, R.; Pilette, D.; Dixneuf, P. H.; Fehlhammer, W. P. *Organometallics* **1991**, *10*, 3287–3291.

[31] Müller, J.; Fischer, E. O. *J. Organomet. Chem.* **1966**, *5*, 275.

[32] (a) Doucet, H.; Höfer, J.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 850–851. (b) Darcel, C.; Bruneau, C.; Dixneuf, P. H.; Neef, G. *J. Chem. Soc., Chem. Commun.* **1994**, 333–334.

[33] Bruneau, C.; Kabouche, Z.; Neveux, M.; Seiller, B.; Dixneuf, P. H. *Inorg. Chim. Acta* **1994**, *222*, 155–163.

[34] Seiller, B.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 493–494.

Table 2. Catalytic Synthesis of 2,3-Dimethylfuran (9)[a]

catalyst	time (h)	yield (%)[b]
1a	2	45
1a	10	67
1a	25	79
3a	25	75
3b	15	48
3b	25	72
6	25	23

[a] Experimental conditions: 10^{-2} mol of (*Z*)-3-methylpent-2-en-4-yn-1-ol (**8**) and 10^{-4} mol of catalyst **1**, **3**, or **6** without solvent at 60 °C. [b] Yield calculated on distilled products.

The reaction of (*Z*)-3-methylpent-2-en-4-yn-1-ol (**8**; 10 mmol) in the presence of **1a**, **3a**, or **3b** (0.1 mmol) as catalyst precursor, without solvent, led to a complete conversion of the alkyne after 20−25 h at 60 °C and to the quantitative formation of the 2,3-dimethylfuran **9** which was isolated on distillation in 79, 75 and 72% yield, respectively (Table 2). Under these conditions, with 1 mol % of catalyst, **1a** appeared to be the best catalyst. The slightly less electron deficient (carbene)-ruthenium complexes **3a**,**b** show a slightly weaker activity, and the electron-deficient but bulky tris(carbene)ruthenium complex **6** did not show a reasonable activity.

Experimental Section

General Data. All reactions were performed under an argon or dinitrogen atmosphere with use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^{1}H (300.13 and 250 MHz) and ^{13}C (50.289 and 125.8 MHz) NMR spectra were recorded on Gemini-Varian and Bruker AMX-500 and AC300P spectrometers at 297 K and referenced to TMS. Mass spectra were obtained with Varian MAT 711 and Kratos MS902 instruments. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Vernaison.

Cyclic Voltammetry. Conventional electrochemical equipment was used: EGG PAR Model 362 scanning potentiostat with a BD90 X-Y recorder. The working electrode was a stationary platinum-disk electrode of 1-mm diameter. The auxiliary electrode was a platinum electrode, and the reference electrode was an aqueous saturated calomel electrode (SCE). In a typical experiment, 4 × 10^{-5} mol of complex was dissolved, under a dinitrogen atmosphere, in 15 mL of dried dichloromethane containing 0.15 g of pure Bu_4NPF_6 as electrolyte.

The complexes $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$,[35] $[RuCl_2(COD)]_n$,[31] $[RuCl_2(1,3,5\text{-}C_6H_3Me_3)]_2$,[36] and $[RuCl_2(C_6Me_6)]_2$[35] and electron-rich olefins **I**,[23] **II**,[24] and **III**[37] were prepared by literature methods. The commercial (Janssen) (*Z*)-3-methyl-2-penten-4-yn-1-ol was used as received.

Synthesis of $[RuCl_2(L^{Me})(p\text{-}MeC_6H_4CHMe_2)]$ (1a). A solution of bis(1,3-dimethylbenzimidazolidine-2-ylidene) (**I**; 1.4 mmol) in 10 mL of toluene was added to $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$ (1.4 mmol), and the mixture was heated for 4 h at 100 °C. A brown precipitate appeared. The product formed was filtered off from the hot solution, washed with Et_2O, and then dried under vacuum (yield 93%). Mp: 195−196 °C. Anal. Calcd for $C_{19}H_{24}N_2RuCl_2$: C, 50.44; H, 5.31; N, 6.19. Found: C, 50.65; H, 5.38; N, 6.85. Mass (*m/z*): 452 (20, M^+), 417 (40, $[M - 35]^+$). ^{1}H NMR (250 MHz, $CDCl_3$, 297 K, δ in ppm): 7.29−7.25 (m, 4 H, C_6H_4), 5.45 and 5.17 (4 H, MeC_6H_4-, $^3J_{HH}$ = 6 Hz), 4.10 (s, 6 H, NCH_3), 2.96 (sept, 1 H, $CHMe_2$, $^3J_{HH}$ = 7 Hz), 1.99 (s, 3 H, $C_6H_4CH_3$), 1.23 (d, 6 H, $(CH_3)_2CHC_6H_4$, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 297 K, δ in ppm): 188.89 (s, Ru=*C*), 135.40, 122.93, 109.62, and 99.08 (s, C_6H_4), 85.87 (s, MeC_6H_4-), 82.82 (s, MeC_6H_4-), 36.21 (s, NCH_3), 30.58 (s, $-C_6H_4CHMe_2$), 22.28 (s, $-C_6H_4CH_3$), 18.59 (s, $CH(CH_3)_2$).

Synthesis of $[RuCl_2(L^{Et})(p\text{-}MeC_6H_4CHMe_2)]$ (1b). Similar to the above procedure, compound **1b** was synthesized from bis(1,3-diethylbenzimidazolidine-2-ylidene) (**II**; 1.1 mmol) and $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$ (1.1 mmol) (yield 88%). Mp: 215−216 °C. Anal. Calcd for $C_{21}H_{28}N_2RuCl_2$: C, 52.50; H, 5.83; N, 5.83. Found: C, 52.26; H, 5.92; N, 5.84. Mass (*m/z*): 480 (21, M^+), 445 (50, $[M - 35]^+$), 174 (6, $[M - 306]^+$). ^{1}H NMR (250 MHz, $CDCl_3$, 297 K, δ in ppm): 7.40−7.20 (m, 4 H, C_6H_4), 5.40 and 5.10 (4 H, MeC_6H_4-, $^3J_{HH}$ = 6 Hz), 4.90 (2 H_A) and 4.60 (2 H_B) (m, 2 NCH_2Me; the $^2J_{H_AH_B}$ value could not be determined), 2.90 (sept, 1 H, $CHMe_2$, $^3J_{HH}$ = 7 Hz), 1.94 (s, 3 H, $C_6H_4CH_3$), 1.56 (t, 6 H, CH_3CH_2N, $^3J_{HH}$ = 7.9 Hz), 1.21 (d, 6 H, $(CH_3)_2CHC_6H_4$), $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 297 K, δ in ppm): 187.91 (s, Ru=*C*), 134.89, 122.58, 110.54, and 99.11 (s, C_6H_4), 86.29 (s, MeC_6H_4-), 82.77 (s, MeC_6H_4-), 44.68 (s, CH_2Me), 30.48 (s, $-C_6H_4CHMe_2$), 22.35 (s, $CH_3C_6H_4$), 18.43 (s, $-NCH_2CH_3$), 15.86 (s, $CH(CH_3)_2$).

Synthesis of $[RuCl_2(L^{Me})(C_6H_3Me_3)]_2$ (2a). To a solution of bis(1,3-dimethylbenzimidazolidine-2-ylidene) (**I**; 0.5 mmol) in 10 mL of toluene was added $[RuCl_2(C_6H_3Me_3)]_2$ (0.5 mmol) and the mixture was heated for 5 h at 100 °C. A light brown precipitate appeared. The product was filtered off from the hot solution, washed with Et_2O and then dried under vacuum (yield 96%). Mp: >300 °C dec. Anal. Calcd for $C_{18}H_{22}N_2RuCl_2$: C, 49.31; H, 5.02; N, 6.39. Found: C, 49.68; H, 5.23; N, 6.49. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 297 K, δ in ppm): 7.45−7.25 (m, 4 H, C_6H_4), 4.90 (s, 3 H, $C_6H_3Me_3$), 4.20 (s, 6 H, $-NCH_3$), 2.05 (s, 9 H, $C_6H_3(CH_3)_3$). $^{13}C\{^1H\}$ NMR (50.289 MHz, $CDCl_3$, 297 K, δ in ppm): 196.00 (s, Ru=*C*), 137.74, 123.64, and 111.72 (s, C_6H_4), 107.34 (s, $C_6H_3Me_3$), 82.04 (s, $C_6H_3Me_3$), 38.37 (s, NCH_3), 21.06 (s, $C_6H_3(CH_3)_3$).

Synthesis of $[RuCl_2(L^{Et})(C_6H_3Me_3)]_2$ (2b). Similar to the above procedure, compound **2b**, $[RuCl_2(L^{Et})(C_6H_3Me_3)]_2$, was synthesized from bis(1,3-diethylbenzimidazolidine-2-ylidene) (**II**) and $[RuCl_2(C_6H_3Me_3)]_2$ (yield 95%). Mp: 293−295 °C. Anal. Calcd for $C_{20}H_{26}N_2RuCl_2$: C, 51.50; H, 5.58; N, 6.00. Found: C, 51.65; H, 5.58; N, 6.35. Mass (*m/z*): calcd for $C_{20}H_{26}N_2Cl_2{}^{102}Ru$ 466.056, found 466.052. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 297 K, δ in ppm): 7.45−7.25 (m, 4 H, C_6H_4), 4.90 and 4.35 (dq, 4 H, (2 H_A, 2 H_B), 2 NCH_2Me, $^2J_{H_AH_B}$ = 13.4 Hz, $^3J_{HH}$ = 7 Hz), 4.75 (s, 3 H, $C_6H_3Me_3$), 1.90 (s, 9 H, $C_6H_3(CH_3)_3$), 1.50 (s, 6 H, $-NCH_2CH_3$, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (50.289 MHz, $CDCl_3$, 297 K, δ in ppm): 195.00 (s, Ru=*C*), 137.34, 124.66, and 112.64 (s, C_6H_4), 107.60 (s, $C_6H_3Me_3$), 81.86 (s, $C_6H_3Me_3$), 46.84 (s, CH_2Me), 20.93 (s, $-C_6H_3(CH_3)_3$), 18.21 (s, $-NCH_2CH_3$).

Synthesis of $[RuCl_2(L^{Me})(C_6Me_6)]$ (3a). A solution of bis(1,3-dimethylbenzimidazolidine-2-ylidene) (**I**; 1.0 mmol) in 10 mL of toluene was added to $[RuCl_2(C_6Me_6)]_2$ (1.0 mmol), and the mixture was heated for 4 h at 100 °C. A brown precipitate appeared. The product was filtered off from the hot solution, washed with Et_2O and then dried under vacuum (yield 96%). Mp: 323−325 °C. Anal. Calcd for $C_{21}H_{28}N_2RuCl_2$: C, 52.50; H, 5.83; N, 5.83. Found: C, 52.45; H, 5.77; N, 5.476. Mass (*m/z*): calcd for $C_{21}H_{28}N_2{}^{102}RuCl_2$ 480.067, found 480.071. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 297 K, δ in ppm): 7.35−7.18 (m, 4 H, C_6H_4), 4.00 (s, 6 H, NCH_3), 1.98 (s, 18 H, $C_6(CH_3)_6$). $^{13}C\{^1H\}$ NMR (50.289 MHz, $CDCl_3$, 297 K, δ in ppm): 195.50 (s, Ru=*C*), 137.98, 124.84, and 111.49 (s, C_6H_4), 96.42 (s, C_6Me_6), 37.99 (s, NCH_3), 17.57 (s, $C_6(CH_3)_6$).

Synthesis of $[RuCl_2(L^{Et})(C_6Me_6)]$ (3b). Similar to the above procedure, compound **3b** was synthesized from bis(1,3-diethylbenzimidazolidine-2-ylidene) (**II**; 1.2 mmol) and $[RuCl_2(C_6Me_6)]_2$ (1.2 mmol) and obtained in 79% yield. Mp:

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(35) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74−78.

(36) (a) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233−241.

(37) Winberg, H. E.; Carnahan, J. E.; Coffman, D. D.; Brown, M. *J. Am. Chem. Soc.* **1965**, *87*, 2055.

275−277 °C. Anal. Calcd for $C_{23}H_{32}N_2RuCl_2$: C, 54.33; H, 6.02; N, 5.51. Found: C, 54.39; H, 6.20; N, 5.45. Mass (*m/z*) calcd for $C_{23}H_{32}N_2RuCl_2$ 508.099; found 508.102. ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K, δ in ppm): 7.45−7.18 (m, 4 H, C_6H_4), 4.95 and 4.10 (dq, 4 H, ($2H_A$, $2H_B$), NCH_2Me, $^2J_{H_AH_B} = 12.9$ Hz, $^3J_{HH} = 6.9$ Hz), 1.95 (s, 18 H, $C_6(CH_3)_6$), 1.50 (t, 6 H, CH_3CH_2N, $^3J_{HH} = 6.9$ Hz). $^{13}C\{^1H\}$ NMR (50.289 MHz, $CDCl_3$, 297 K, δ in ppm): 194.00 (s, Ru=C), 137.31, 124.40, and 112.25 (s, C_6H_4), 96.46 (s, C_6Me_6), 46.30 (s, CH_2Me), 18.09 (s, $-NCH_2CH_3$), 17.44 (s, $C_6(CH_3)_6$).

Synthesis of $[RuCl_2(L^{Bz})(p\text{-}MeC_6H_4CHMe_2)]$ (4). A solution of bis(1,3-dibenzylimidazolidine-2-ylidene) (**III**; 0.6 mmol) in 10 mL of toluene was added to $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$ (0.6 mmol), and the mixture was heated for 4 h at 90 °C. A brown precipitate appeared. The product was filtered off from the hot solution, washed with Et_2O, and then dried under vacuum (yield 87%). Mp: 230−232 °C. Anal. Calcd for $C_{27}H_{32}N_2RuCl_2$: C, 58.27; H, 5.76; N, 5.03. Found: C, 58.48; H, 5.91; N, 5.33. Mass (*m/z*): 556 (5, M^+), 350 (94, $[M - 206]^+$), 249 (18, $[M - 307]^+$. ^1H NMR (250 MHz, $CDCl_3$, 297 K, δ in ppm): 7.55−7.26 (m, 10 H, C_6H_5), 5.41 and 5.14 (m, 4 H, MeC_6H_4-, $^3J_{HH} = 6$ Hz), 5.39 and 4.90 (AB system, 4 H, 2 NCH_2Ph, $J_{H_AH_B} = 14.7$ Hz), 3.51 (m, 4 H, NCH_2CH_2N), 2.89 (sept, 1 H, $CHMe_2$, $^3J_{HH} = 7$ Hz), 2.14 (s, 3 H, $-C_6H_4CH_3$), 1.26 (d, 6 H, $(CH_3)_2CHC_6H_4-$), $^3J_{HH} = 7$ Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 297 K, δ ppm): 208.36 (s, Ru=C), 136.96, 128.62, 127.65, and 127.55 (s, C_6H_4), 108.20 (s, MeC_6H_4-), 97.69 (s, MeC_6H_4-), 85.68 (s, MeC_6H_4-), 83.50 (s, MeC_6H_4-), 55.75 (s, NCH_2Ph), 48.81 (s, $-NCH_2CH_2N-$), 30.63 (s, $CHMe_2$), 22.49 (s, $-C_6H_4CH_3$), 18.67 (s, $(CH_3)_2CHC_6H_4-$).

Synthesis of $[RuH_2(L^{Me})(C_6Me_6)]$ (5). A suspension of $[RuCl_2(L^{Me})(C_6Me_6)]$ (0.6 mmol) in 10 mL of dried EtOH was added to $NaBH_4$ (2.5 mmol), and the mixture was stirred at room temperature for 10 h. The color changed progressively from brown to yellow, and the suspension became nearly a solution in this period. The mixture was filtered, and the clear filtrate was then concentrated to *ca.* 5 mL; Et_2O (3 mL) was added, and the solution was cooled to −25 °C to yield the cream-colored compound (yield 72%). The complex **5** is not stable even under an inert atmosphere, and its spectroscopic data had to be immediately obtained. Its elemental analysis could not be determined. Mp: >300 °C. IR (cm^{-1}, KBr): 1924, 1885 (s, Ru−H). ^1H NMR (300 MHz, C_6D_6, 297 K, δ in ppm): 6.93−6.68 (m, 4 H, C_6H_4), 3.70 (s, 6 H, NCH_3), 2.15 (s, 18 H, $C_6(CH_3)_6$), −9.71 (s, 2 H, Ru−H).

Synthesis of $[RuCl_2(L^{Me})_3]$ (6). To a solution of bis(1,3-dimethylbenzimidazolidine-2-ylidene) (**I**; 1.3 mmol) in 20 mL of toluene was added $[RuCl_2(COD)]_n$ (0.43 mmol) and the mixture was heated for 4 h at 100 °C. A yellow precipitate appeared. The product was filtered off from the hot solution, washed with Et_2O and then dried under vacuum (yield: 98%). Mp: 303−305 °C. Anal. Calcd for $C_{27}H_{30}N_6RuCl_2$: C, 53.11; H, 4.92; N, 13.77. Found: C, 54.08; H, 5.01; N, 13.93. Mass (*m/z*): 610 (3, M^+), 575 (65, $[M - 35]^+$), 464(10, $[M - 146]^+$), 140 (35, $[M - 464]^+$). ^1H NMR (250 MHz, $CDCl_3$, 297 K, δ in ppm): 7.26−7.22 (m, 12 H, C_6H_4), 3.63 (s, 18 H, $-NCH_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 297 K, δ in ppm): 195.50 (s, Ru=C), 136.19, 121.63, and 108.53 (s, C_6H_4), 34.33 (s, NCH_3).

Catalytic Synthesis of 2,3-Dimethylfuran (9). In a typical experiment, to 10 mmol of (*Z*)-3-methylpent-2-en-4-yn-1-ol (**8**) was added 0.1 mol of the ruthenium catalyst **1**, **3**, or **6** without additional solvent. The mixture was stirred in an oil bath at 60 °C for 25 h. The mixture was distilled at atmospheric pressure; bp 90−91 °C. Yields are indicated in Table 2. IR (pure, ν): 1605 cm^{-1} (C=C). Mass (*m/z*): calcd for C_6H_8O 96.0572, found 96.0575. ^1H NMR (300.13 MHz, $CDCl_3$, δ in ppm): 7.19 (d, H_5, $^3J_{HH} = 1.8$ Hz), 6.14 (d, H_4), 2.19 (s, Me(3)), 1.94 (s, Me(2)).

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