

Synthesis of a water-soluble carbene complex and its use as catalyst for the synthesis of 2,3-dimethylfuran

İsmail Özdemir ^{a,*}, Beyhan Yiğit ^a, Bekir Çetinkaya ^b, Dinçer Ülkü ^c,
M. Nawaz Tahir ^c, Cengiz Arıcı ^c

^a Department of Chemistry, İnönü University, 44069 Malatya, Turkey

^b Department of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey

^c Department of Engineering Physics, Hacettepe University, 06532 Beytepe, Ankara, Turkey

Received 26 February 2001; received in revised form 30 April 2001; accepted 30 April 2001

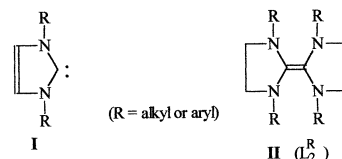
Abstract

1,1',3,3'-Tetrakis(*p*-dimethylaminobenzyl)-2,2'-biimidazolidinylidene, L_2^R ($R = CH_2C_6H_4NMe_2$ -*p*) which contains four peripheral NMe_2 substituents, was obtained from 4-dimethylaminobenzaldehyde by a three-step reaction sequence, and was used for the preparation of imidazolidin-2-ylidene Ru(II) and Rh(I) complexes **1** and **2**. Etherial HCl readily protonates the NMe_2 functionality on the carbene ligand of **1** to give the corresponding salt, **1'**; whereas the reaction of **2** with HCl gave a hygroscopic and ill-defined rhodium species. In aqueous solution the salt **1'** is an efficient and active catalyst for intramolecular cyclisation of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran. The catalyst **1'** could be recovered by simple phase separation and the catalytic reaction was maintained for five different runs. All of the new compounds were characterised by elemental analyses, IR and NMR spectroscopy and the molecular structure of **1** was determined by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Water-soluble carbene complex; Recyclable catalyst; Crystal structures

1. Introduction

The stable 1,3-diorganylimidazol-2-ylidenes, **I**, and their coordination chemistry has recently aroused great interest [1–6]. These crystalline carbenes show no tendency to dimerise [5]. In sharp contrast, 4,5-dihydroimidazol-2-ylidenes containing an unhindered R group [2,7] readily dimerise to give tetraaminoethene derivative, **II** (L_2^R), which behave as carbene precursors under relatively mild conditions. The first isolated transition metal imidazolidin-2-ylidene complex was synthesised by Lappert in 1971 via cleavage of C=C bond by $[PtCl_2(PEt_3)_2]$ [8]. Subsequently this reaction was extended to other tetraaminoalkenes and electrophilic organometallic substrates [9,10].



The renaissance of metal complexes of *N*-heterocyclic carbenes began after their use as alternatives for phosphine complexes used in homogeneous catalysis [1,11]. Examples of such reactions include the Heck olefination of haloarenes [12], the asymmetric hydrosilylation of acetophenone [13,14], hydrogenation [15], hydroformylation [12], metathesis [2,3] and cyclopropanation [16] of alkenes. In a catalytic reaction (*Z*)-3-methylpent-2-en-4-yn-1-ol was converted into 2,3-dimethylfuran in very high yield [17]. The nature of the *N*-substituents of the carbene ligand have a pronounced effect upon the catalytic activity of the complexes [16,17].

Biphasic catalysis, consisting of a water phase which contains a catalytic species and a non-miscible organic phase, continues to attract interest in view of industrial applications [18,19]. For this purpose a number of

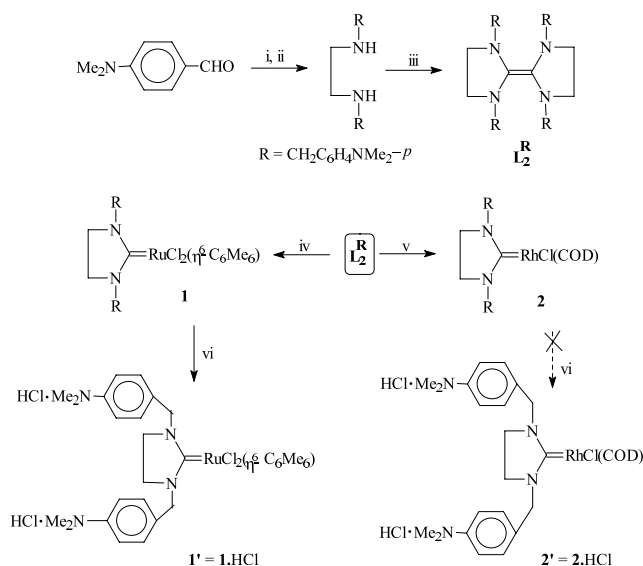
* Corresponding author. Fax: +90-232-341-0037.

E-mail address: iozdemir@inonu.edu.tr (İ. Özdemir).

attempts have been made to introduce hydrophilic functional groups on convenient ligands, in particular phosphines [18–21]. Despite their similar catalytic behaviour [11], examples of hydrophilic carbene complexes are rare [22]. The under-representation of hydrophilic carbene complexes may be attributed to difficulties with their preparation. The employment of highly reactive nucleophiles as well as electrophiles at different stages of imidazolidin-2-ylidene metal complex synthesis precludes the presence of many types of functional groups [10]. As a possible system for this endeavour, we have chosen *p*-dimethylaminobenzyl as an *N*-substituent. This is because the presence of the peripheral NMe_2 group is expected to improve water solubility through quaternisation of the NMe_2 group.

2. Results and discussion

The synthesis of the tetraaminoethene L_2^{R} , II ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}p$) was accomplished in a three-step procedure as described in Scheme 1. The Schiff base was synthesised using a method similar to that reported by Billman et al. [23]. The 1,2-disubstituted ethylenediamine was prepared successfully by hydrogenation of the Schiff base over a Pd/C catalyst in dry toluene at 25 °C and 200 psi (13.6 atm) pressure. However, if non-dried solvent, high temperature or high pressure is employed, this leads to the formation of *p*-dimethylaminotoluene. The tetraaminoethene, L_2^{R} , was synthesised in 83% yield by formylation of the NH bonds in an excess of $\text{Me}_2\text{NCH(OMe)}_2$. The compound L_2^{R} , II ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}p$) is relatively air-stable in the



Scheme 1. Synthesis of tetraaminoethene, L_2^{R} , and ruthenium and rhodium complexes. Reagent and conditions: (i) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, EtOH, 25 °C, 4 h; (ii) H_2 , Pd/C, 13.6 atm, PhMe, 25 °C; (iii) $\text{Me}_2\text{NCH(OMe)}_2$, PhMe, 110 °C; (iv) $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)_2]$; (v) $[\text{RhCl(COD)}]_2$, PhMe, 110 °C; (vi) $\text{HCl}_{(\text{g})}$, Et_2O , 25 °C.

solid state and exhibited simple first-order ^1H -NMR spectra at room temperature.

2.1. Neutral carbene complexes

The functional tetraaminoethene L_2^{R} readily reacted with the halogeno-dimers of Ru(II) or Rh(I) to afford $[\text{RuCl}_2(\text{C}_6\text{Me}_6)\text{L}^{\text{R}}]$ (**1**), and $[\text{RhCl(COD)}\text{L}^{\text{R}}]$ (**2**). Each of the complexes **1** and **2** were obtained in high yield as air-stable crystals, which were characterised by elemental analysis and IR, ^1H -NMR and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra. The IR spectra of the complexes showed intense absorption bands at 1614–1616 cm^{-1} assigned to $\nu(\text{CN})$.

The carbene precursor employed in this study potentially has two donor atoms, namely the alkene can bridge across two metal ions via amino nitrogen atoms. However, comparison of the NMR signals from the alkene and coordinated carbene ligands strongly suggested that coordination to ruthenium or rhodium was via the carbon atoms. This was conclusively established by the protonation reactions and by a single crystal X-ray diffraction experiment on $[\text{RuCl}_2(\text{C}_6\text{Me}_6)(\text{L}^{\text{R}})]$ [$\text{L}^{\text{R}} = \text{CN}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}p)\text{CH}_2\text{CH}_2\text{NCH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}p$] (vide infra). All the complexes showed the expected signals due to the coordinated arene/COD and the imidazolidin-2-ylidene in their ^1H -NMR spectra. An AB quartet (doublet of doublets) was observed for the CH_2 protons in the $\text{N-CH}_2\text{Ar}$ substituent in the complexes due to restricted rotation about the M-C_{carb} bond. The ring methylene protons were observed as multiplets.

^{13}C -NMR spectra appear to be the most useful spectroscopic probe for structure elucidation. Thus, the $\text{C}_{\text{carbene}}$ resonances in complexes **1** and **2** are found at ca. 205–213 ppm. In each case the downfield chemical shift as well as the structure due to Rh–C coupling ($J = 46.7$ Hz), in complex **2**, served to establish the carbene coordinating mode of L_2^{R} . Values of δ and J are similar to those found for non-functionalised carbene complexes [24].

2.2. Protonations of complexes 1 and 2

The pendant nature of the NMe_2 group in complex **1** is also revealed by the reaction with HCl. Thus, treatment of CH_2Cl_2 solutions of **1** with two equivalents of hydrogen chloride in diethyl ether gave the corresponding red solid **1'** which is soluble in water and stable to air. By comparison, the reaction of **2** with HCl afforded a cream-coloured solid. However, this was determined not to be the analogous product **2'**. This point was strongly evidenced by the ^{13}C -NMR spectrum of the resultant material which did not show the diagnostic $\text{C}_{\text{carbene}}$ doublet in the expected region, indicating the carbene ligand may have been displaced or rearranged. On the other hand, the transformation of the amino

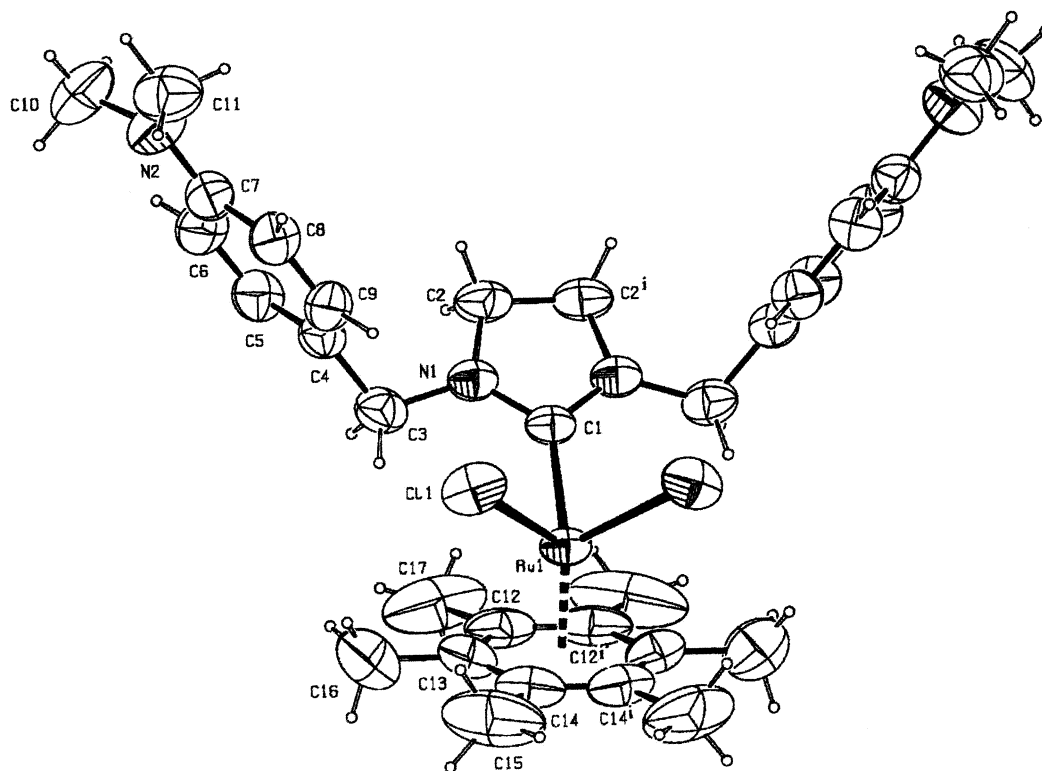


Fig. 1. PLATON drawing of the molecule **1** with the atom-numbering schemes. The displacement ellipsoids are drawn at the %50 probability level. H atoms are shown as small circles with arbitrary radii.

group in complex **1** into a quaternary salt is not accompanied by noticeable changes of the spectroscopic parameters of the carbene fragment. For example, ^{13}C -NMR resonances of the carbene carbon atom shift only slightly ($\Delta\delta = 3$ ppm) in response to the quaternisation. The broad signal observed at 4.3 ppm was assigned to the solvated water in the ^1H -NMR ($\text{DMSO}-d_6$).

2.3. X-ray crystal structure of $\text{RuCl}_2(\text{C}_6\text{Me}_6)(\text{L}^R)$ (**1**)

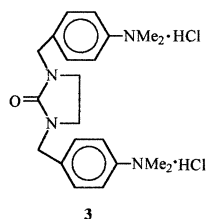
Single crystals of **1** were obtained from a CH_2Cl_2 – Et_2O solution. All diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo}-\text{K}_\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. Least-square refinements of 25 high angle reflections gave the best values for lattice parameters. The data were corrected for Lorentz polarisation and empirical absorption correction via Ψ scans.

The structure was determined by Patterson and Fourier methods [28] and refined by full-matrix least-squares techniques to a conventional R value of 0.038 ($R_w = 0.045$). All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atom positions were taken from difference maps and a riding model was used with $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$. Scattering factors were taken from International Tables for X-ray Crystallography [29]. For data collection, reduction, structure solution and refinement, MOLEN package was used [30].

Crystal data: $[\text{RuCl}_2(\text{C}_6\text{Me}_6)(\text{L}^R)]$, $\text{L}^R = \text{CN}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}p$, $\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}p)$, $M_r = 670.737$, orthorhombic, space group $Pnma$ (No. 62), lattice parameters: $a = 13.559(1)$, $b = 24.988(1)$, $c = 9.610(1)$ Å, $Z = 4$, $V = 3256.1(5)$ Å³, $D_{\text{calc}} = 1.368$ g cm^{-3} , $\mu(\text{Mo}-\text{K}_\alpha) = 0.664$ mm⁻¹, $F(000) = 1400$, $T = 295$ K, orange prisms, crystal dimensions $0.20 \times 0.20 \times 0.25$ mm.

A thermal ellipsoid drawing of compound **1** is shown in Fig. 1. The ruthenium and C1 atoms are located on a mirror plane of the orthorhombic space group so that the whole molecule has a two-fold symmetry with respect to the Ru–C1 bond. If one considers there are three coordination bonds of the ruthenium atom with the electrons of the C_6Me_6 ring, two symmetrical Ru–Cl bonds and one Ru–C1 bond involving the imidazole ring, the coordination around the Ru atom is six-fold, which is in this case distorted octahedrally. The bond lengths Ru–M1 (M1 is the midpoint between C14 and C14a atoms) and Ru–M2 (midpoint between C12 and C13) are 2.140(5) and 2.074(5) Å, respectively (Table 1). As a result of the crystal symmetry, the Ru–M2 and Ru–M2a lengths are equal. The Ru– η bond angles are 60.19 (M1–Ru–M2) and 61.30° (M2–Ru–M2a). On the other side of the coordination sphere, the Ru–Cl [2.4234(12)] and Ru–C1 [2.090(5) Å] bond lengths are considerably different from each other. The Cl–Ru–C1 and Cl–Ru–Cla bond angles are 90.25(1) and 84.78(4)°,

respectively. The dihedral angle between the arene ring and the plane defined by Cl, C1, Cla atoms is 3(1)°. The arene ring is planar with Ru–C distances between 2.090(5) and 2.193(4) Å. Selected geometric parameters are listed in Table 1.



2.4. Catalytic studies

Recently, carbene complexes of Ru(II) have been introduced as catalysts for the activation of (*Z*)-enynols toward their intramolecular cyclisation into furans [17,25,26]. The nature of the *N*-substituents of the carbene ligand have a pronounced effect upon the

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Ru1–Cl1	2.4234(12)	Ru1–C14	2.245(4)
Ru1–C1	2.090(5)	Ru1–M1 ^a	2.140(5)
Ru1–C12	2.193(4)	Ru1–M2 ^a	2.074(5)
Ru1–C13	2.191(5)		
Bond angles			
Cl1–Ru1–C1	90.25(11)	C12–Ru1–C12 ⁱ	37.49(18)
Cl1–Ru1–Cl1 ⁱ	84.78(4)	C12–Ru1–C13 ⁱ	67.81(18)
C1–Ru1–C12	94.20(17)	C13–Ru1–C14	37.34(18)
C1–Ru1–C13	119.96(17)	M1–Ru1–M2	60.19
C1–Ru1–C14	157.24(15)	M2–Ru1–M2 ⁱ	61.30

^a M1 and M2 are the midpoints between C14–C14ⁱ and C12–C13, respectively. Symmetry code: (i) $-x, 1/2+y, -z$.

Table 2
Catalytic synthesis of 2,3-dimethylfuran, at 80 °C

Catalyst	Time (h)	Yield (%) ^{a,b}
1	1	40
1	3	94 (84)
2	1	30
2	2	93 (82)
1'	1	94 (84)
1'	3	95 (85)
1' ^c	1	93
1' ^d	1	93
3	3	— ^e

^a Determined by GC.

^b Isolated yield, after distillation, given in parentheses.

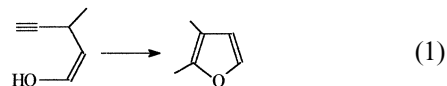
^c Fourth run.

^d Fifth run.

^e Not detected.

catalytic activity of the complexes [23]. Hence, we have investigated the catalytic activity of both the neutral and cationic complexes.

Thus, (*Z*)-3-methylpent-2-en-4-yn-1-ol (10 mmol) was added to 0.1 mmol of the complexes **1** and **2** and the mixture was stirred at 80 °C in an oil bath for 1–3 h (Eq. (1)).



The quaternary salt, **1'**, was tested as a catalyst in biphasic media since it was stable and soluble in water. The results are compiled in Table 2.

The salt **1'** was the most promising candidate. However, the neutral species, although active, were found to be somewhat less effective. The catalyst **1'** was recycled via aqueous work-up and used repeatedly with little detriment to rate or yield. The results afforded by **1'** from five successive cyclisations are shown in Table 2. To confirm that the metal has a key role in this intramolecular cyclisation catalyzed by the quaternary salt **1'**, the urea derivative **3** was synthesised [27] and its reactivity was examined under the same conditions. With this salt, **3**, the reaction did not proceed and the starting (*Z*)-3-methylpent-2-en-4-yn-1-ol was recovered unchanged (last entry in Table 2).

3. Conclusion

Novel $-NMe_2$ functionalised imidazolidin-2-ylidene metal complexes, **1** and **2**, are accessible from appropriately *N*-substituted tetraaminoalkene, L_2^R . Etherial HCl readily protonates the nitrogen atoms of the $-NMe_2$ functionality on the carbene ligand of **1** to yield the corresponding quaternary salt **1'**. In contrast, treatment of **2** with HCl did not give the expected salt **2'**. The salt **1'** is water soluble and a more active catalyst than the neutral complexes **1** and **2** for the conversion of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran. The catalytic activity of the recovered salt **1'** from the catalytic reaction was maintained for at least five different runs. Easy and quantitative recovery of the catalyst in active form from organic reaction products by simple phase separation is the obvious advantage. The use of similar salts as catalyst in other reactions such as hydrogenation and hydroformylation is in progress in our laboratory.

4. Experimental

All reactions were performed using Schlenk-type flasks under Ar and standard high vacuum-line tech-

niques. Solvents were analytical grade and distilled under Ar from sodium benzophenone (toluene, Et₂O), sodium–potassium (pentane, THF), P₂O₅ (dichloromethane). IR spectra were recorded in the 4000–400 cm^{−1} region on a Pye Unicam spectrometer. Samples were prepared as KBr discs. NMR spectra were recorded at 297 K on a Bruker AC300P FT spectrometer operating at 300.13 MHz (¹H), 75.47 MHz (¹³C). Gas chromatography (GC) analyses were performed with a Hewlett Packard instrument using a 25 m × 0.32 mm OV1 capillary column in conjunction with a flame ionisation detector. Elemental analyses were performed by the Middle East Technical University, Ankara. Commercial reagents were used as supplied and other reagents were prepared by literature methods: RuCl₂(C₆Me₆)₂ [31], [{Rh(–Cl)(cod)}₂] [32].

4.1. Synthesis of complexes **1** and **2**

A solution of 1,1',3,3'-tetrakis(*p*-dimethylaminobenzyl)-2,2'-biimidazolidinylidene (0.86 g, 1.23 mmol) in toluene (15 cm³) was added to [RuCl₂(η⁶-C₆Me₆)₂] (0.864 g, 0.99 mmol), and then the mixture was heated for 2 h under reflux. The brown product was precipitated. The product **1**, was filtered, washed with *n*-hexane (2 × 15 cm³), and dried in vacuum. Recrystallisation from CH₂Cl₂ (7 cm³)–Et₂O (14 cm³) at –20 °C, gave brown crystals of **1**. M.p. 242–243 (decomp); 0.81 g, 91% yield. ¹H-NMR (δ, CDCl₃): 2.07 [s, 18H, C₆(CH₃)₆], 2.89 [s, 12H, N(CH₃)₂], 3.19–3.24, 3.32–3.37 (m, 4H, NCH₂CH₂N), 4.16, 5.61 (dd, *J* = 13.8 Hz, 4H, CH₂C₆H₄NMe₂), 6.65 (d, *J* = 8.7 Hz, 4H, C₆H₄–NMe₂), 7.34 (d, *J* = 8.7 Hz, 4H, C₆H₄–NMe₂). ¹³C{H}-NMR (δ, CDCl₃): 14.0 (C₆(CH₃)₆), 38.8 [N(CH₃)₂], 46.7 (NCH₂CH₂N), 53.0 (CH₂C₆H₄NMe₂), 92.3 [C₆(CH₃)₆], 110.6, 122.9, 128.1, 148.3 (C₆H₄CH₂), 207.5 (C-2-Im). Anal. Found: C, 58.64; H, 5.37; N, 8.06. Calc. for C₃₃H₄₆N₄Cl₂Ru: C, 59.01; H, 6.91; N, 8.35%.

Compound **2** was prepared in the same way as **1** from 1,1',3,3'-tetrakis(*p*-dimethylaminobenzyl)-2,2'-biimidazolidinylidene (0.43 g, 0.76 mmol) and [{Rh(μ-Cl)(cod)}₂] (0.38 g, 0.76 mmol) to give yellow crystals of **2**. M.p. 191–192 °C; 0.61 g, 77% yield. ¹H-NMR (δ, CDCl₃): 1.92–1.94, 2.33–2.35 [m, 8H, CH₂ (COD)], 2.92 [s, 12 H, N(CH₃)₂], 3.20–3.23 (m, 4H, NCH₂CH₂N), 3.51–3.52, 5.01–5.02 [s, 4H, CH=CH (COD)], 5.19, 5.35 (dd, *J* = 14.4 Hz, 4H, CH₂C₆H₄NMe₂), 6.71 (d, *J* = 8.6 Hz, 4H, C₆H₄), 7.31 (d, *J* = 8.6 Hz, 4H, CH₂C₆H₄NMe₂). ¹³C{H}-NMR (δ, CDCl₃): 28.7, 32.9 [CH₂ (COD)], 40.6 [N(CH₃)₂], 47.7 (NCH₂CH₂N), 54.4 (CH₂C₆H₄NMe₂), 68.3 [d, *J* = 15.4 Hz, CH=CH (COD)], 98.8 [d, *J* = 6.5 Hz, CH=CH (COD)], 112.6, 124.0, 129.3, 150.2 (C₆H₄NMe₂), 213.2 (d, *J* = 47.0 Hz, C-2 Im). Anal. Found: C, 59.77; H,

6.92; N, 9.62. Calc. for C₂₉H₄₀N₄ClRh: C, 59.16; H, 6.37; N, 9.48%.

4.2. Synthesis of the salts **1'**, and **2'**

A solution of the complex **1** (0.52 g, 0.78 mmol) in CH₂Cl₂ (10 cm³) was added to HCl in Et₂O (1.2 M, 1.5 cm³) and stirred for 24 h. A brown precipitate appeared. The product, **1'**, was filtered and then washed with Et₂O (2 × 15 cm³) and dried under vacuum. M.p. 230–231 °C; 96% yield. ¹H-NMR (δ, D₂O): 2.07 [s, 18H, C₆(CH₃)₆], 3.34 [s, 12H, N(CH₃)₂], 3.50–3.55, 3.71–3.77 (m, 4H, NCH₂CH₂N), 4.59, 5.55 (bdd, *J* = 12.5, 4H, CH₂C₆H₄NMe₂), 7.58 (d, *J* = 8.7 Hz, 4H, C₆H₄–NMe₂), 7.64 (d, *J* = 8.7 Hz, 4H, C₆H₄–NMe₂). ¹³C{H}-NMR (δ, D₂O): 15.6 (C₆(CH₃)₆), 47.0 [N(CH₃)₂], 49.4 (NCH₂CH₂N), 54.1 (CH₂C₆H₄NMe₂), 95.2 [C₆(CH₃)₆], 120.8, 130.4, 141.8, (CH₂C₆H₄CH₂–NMe₂), 210.0 (C-2-Im). Selected Ir (KBr disk): ν(N–H), 2350 cm^{−1}. *A*_M (25 °C), 290 Scm² mol^{−1}. Anal. Found: C, 48.81; H, 6.65; N, 6.96. Calc. for C₃₃H₅₄N₄Cl₄O₄Ru: C, 48.71; H, 6.64; N, 6.88%.

Using a similar procedure, a cream-coloured solid was precipitated from **2**. However, it was very hygroscopic and unstable; its ¹³C-NMR spectrum did not show the C_{carbene} doublet in the expected region. Therefore, it was not characterised.

4.3. Catalytic studies

Ruthenium or rhodium catalyst (0.1 mmol) was added to 10 mmol of neat (*Z*)-3-methylpent-2-en-4-yn-1-ol without a solvent. The mixture was stirred in an oil bath at 80 °C for 1–3 h. The conversion of the starting enynol was determined by GC and the pure furan was isolated by distillation under reduced pressure.

In biphasic catalysis a solution of the salt **1'** (0.1 mmol) in H₂O (2.0 ml) and a solution of the enynol (10 mmol) in toluene (2.0 ml) were mixed and heated to 80 °C. The organic phase was analysed by GC. For the second run the organic phase was replaced by a fresh solution of enynol and the procedure was repeated.

5. Supplementary material

Final fractional atomic coordinates, full list of bond lengths, bond angles and displacement parameters (*U*_{ij}) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 156705 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support for this work from the State Planning Organization, DPT (Grant No. 98-DPT-001) is gratefully acknowledged.

References

- [1] D. Bourissou, O. Guerriet, F.P. Gabbai, G. Bertrand, *Chem. Rev.* 100 (2000) 39.
- [2] (a) A.K. Chatterjee, J.P. Morgan, M. Scholl, R.H. Grubbs, *J. Am. Chem. Soc.* 122 (2000) 3783;
(b) A.K. Chatterjee, R.H. Grubbs, *Org. Lett.* 1 (1999) 1751;
(c) M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, *Org. Lett.* 1 (1999) 953;
(d) M. Scholl, T.M. Tinka, J.P. Morgan, R.H. Grubbs, *Tetrahedron Lett.* 40 (1999) 2247.
- [3] (a) M. Prin, M. Grosche, E. Herdtweck, W.A. Herrmann, *Organometallics* 19 (2000) 1692;
(b) W. Baratta, W.A. Herrmann, P. Rigo, J. Schwarz, *J. Organomet. Chem.* 593 (2000) 489;
(c) L. Ackermann, A. Fürstner, T. Weskamp, F.J. Kohl, W.A. Herrmann, *Tetrahedron Lett.* 40 (1999) 4787;
(d) A. Fürstner, O.R. Thiel, L. Ackermann, H.J. Schanz, S.P. Nolan, *J. Org. Chem.* 65 (2000) 2204.
- [4] (a) J. Hwang, E.D. Stevens, S.P. Nolan, *Organometallics* 19 (2000) 1194;
(b) A. Briot, M. Bujard, V. Gouverneur, S.P. Nolan, C. Mioskowski, *Org. Lett.* 2 (2000) 1517;
(c) C. Zhang, J. Hwang, M.L. Trudell, S.P. Nolan, *J. Org. Chem.* 64 (1999) 3804;
(d) J. Hwang, H.J. Schanz, E.D. Stevens, S.P. Nolan, *Organometallics* 18 (1999) 5375;
(e) J. Hwang, E.D. Stevens, S.P. Nolan, J.L. Petersen, *J. Am. Chem. Soc.* 121 (1999) 2674;
(f) J. Hwang, G. Grasa, S.P. Nolan, *Org. Lett.* 1 (1999) 1307.
- [5] R.E. Dauthwaite, D. Haussinger, M.L.H. Green, P.J. Silcock, P.T. Gomes, A.M. Martins, A.A. Dahapoulos, *Organometallics* 18 (1999) 4584.
- [6] R.W. Alder, M.E. Blake, C. Bortolotti, S. Bufali, C.P. Bulst, E. Linehan, J.M. Oliva, A.G. Orpen, M.J. Quayle, *Chem. Commun.* (1999) 241.
- [7] (a) F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* 5 (1999) 1931;
(b) M.K. Denk, K. Hatano, M. Ma, *Tetrahedron Lett.* 40 (1999) 2057.
- [8] D.J. Cardin, B. Çetinkaya, M.F. Lappert, Lj. Manojlovic Muir, K.W. Muir, *Chem. Commun.* 00 (1971) 400.
- [9] B. Çetinkaya, P. Dixneuf, M.F. Lappert, *J. Chem. Soc. Dalton. Trans.* (1974) 1827.
- [10] M.F. Lappert, *J. Organomet. Chem.* 358 (1988) 185.
- [11] W.A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed.* 36 (1997) 2162.
- [12] (a) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, *Angew. Chem. Int. Ed.* 34 (1995) 2371;
(b) D.S. McGuinness, K.J. Cavell, *Organometallics* 19 (2000) 741.
- [13] (a) J.E. Hill, T.A. Nile, *J. Organomet. Chem.* 137 (1977) 293;
(b) M.F. Lappert, in: A. Müller, E. Diemann (Eds.), *Transition Metal Chemistry*, Verlag Chemie, Weinheim, 1981.
- [14] W.A. Herrmann, L.J. Goossen, C. Köcher, G.R.J. Artus, *Angew. Chem. Int. Ed.* 35 (1996) 2805.
- [15] M.F. Lappert, in: A. Müller, E. Diemann (Eds.), *Transition Metal Chemistry*, Verlag Chemie, Weinheim, 1981.
- [16] B. Çetinkaya, İ. Özdemir, P.H. Dixneuf, *J. Organomet. Chem.* 534 (1997) 153.
- [17] B. Çetinkaya, İ. Özdemir, C. Bruneau, P.H. Dixneuf, *J. Mol. Catal.* 118 (1997) L1.
- [18] W.A. Herrmann, C.W. Kohlpaintner, *Angew. Chem. Int. Ed.* 32 (1993) 1524.
- [19] B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, Verlag Chemie, Weinheim, 1996.
- [20] B. Cornils, E. Wiebus, *Chemtech* 25 (1995) 33.
- [21] G. Papadogianakis, R.A. Sheldon, *New J. Chem.* 20 (1996) 175.
- [22] W.A. Herrmann, L.J. Goossen, M. Spiegler, *J. Organomet. Chem.* 547 (1997) 357.
- [23] J.H. Billman, J.Y. Chen Ho, L.R. Caswell, *J. Org. Chem.* 17 (1952) 1375.
- [24] B. Çetinkaya, P.B. Hitchcock, M.F. Lappert, D.B. Shaw, K. Spyropoulos, N.J.W. Warhurst, *J. Organomet. Chem.* 459 (1993) 311.
- [25] H. Küçükbay, B. Çetinkaya, S. Guesmi, P.H. Dixneuf, *Organometallics* 15 (1996) 2434.
- [26] B. Sielle, C. Bruneau, P.H. Dixneuf, *Tetrahedron* 51 (1995) 13089.
- [27] B. Binbaşıoğlu, İ. Özdemir, B. Çetinkaya, unpublished results.
- [28] A.L. Spek, *PLATON Molecular Geometry Program*, University of Utrecht, Utrecht, The Netherlands.
- [29] *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, vol. IV, 1974.
- [30] C.K. Fair, *MOIEN, An Interactive Intelligent System for Crystal Structure Analysis*, Enraf Nonius, Delft, The Netherlands.
- [31] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, *Inorg. Synth.* 21 (1982) 74.
- [32] J. Chatt, L.M. Venanzi, *J. Chem. Soc.* (1957) 4735.