

Synthesis and catalytic properties of *N*-functionalized carbene complexes of rhodium(I) and ruthenium(II)

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Abstract

Imidazolidin-2-ylidene derivatives of rhodium(I) and ruthenium(II), having 2-methoxyethyl substituent on the *N*-atom, [Rh(L)Cl(PPh₃)₂], [Rh(L)Cl(COD)] or [Ru(L)Cl₂(arene)] (L¹ = $\overline{\text{C}}\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OMe}$ and L² = $\overline{\text{C}}\text{N}(\text{CH}_2\text{CH}_2\text{OMe})\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OMe}$) have been prepared by treatment of [RhCl(PPh₃)₃], [RhCl(COD)]₂ or [RuCl₂(arene)]₂ with the *N*-functionalized electron-rich olefins L¹ = L¹ or L² = L². All of the new carbene rhodium(I) or ruthenium(II) complexes have proved to be effective catalysts for the cyclopropanation reactions of diazoalkane derivatives with styrene and the rhodium(I) precursors lead to the highest catalytic activity.

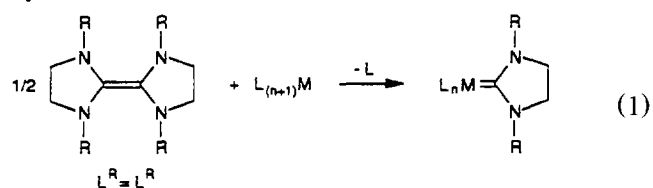
Keywords: Carbene; Imidazole; Ruthenium; Catalysis; Rhodium; Cyclopropanation

1. Introduction

Recent advances in the field of ruthenium carbene chemistry concerns their use as catalyst precursors for selective syntheses such as the formation of cyclopropane derivatives [1], olefin metathesis applied to the olefin ring-forming reactions [2] or to the polymerization of cyclic olefins [3], and the synthesis of furanes from *Z*-hydroxy-enynes [4]. These useful catalytic reactions attract interest for the search of new catalysts with high activity. They have led us to consider the preparation of carbene-metal complexes containing a potential hemilabile carbene ligand: a carbene ligand strongly linked to the metal but with pendant functional groups able to reversibly coordinate the metal.

The coordination chemistry of electron-rich olefins L^R = L^R [5] containing alkyl or aryl R groups has led to the discovery of their role as precursors of a wide range of transition metal carbene complexes of general formula L_nM ← L^R [6] in which L_n represents the sum of all ligands attached to the metal M (Eq. (1)). The synthesis of the olefins L^R = L^R where R is a primary alkyl group, has been accomplished by two general methods: (i) the condensation of *N,N'*-disubstituted

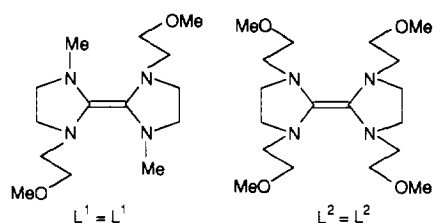
ethylenediamines with CH(OMe)₂NMe₂ [7] and (ii) the reaction of 1,3-dialkylimidazolium salts with sodium hydride [8].



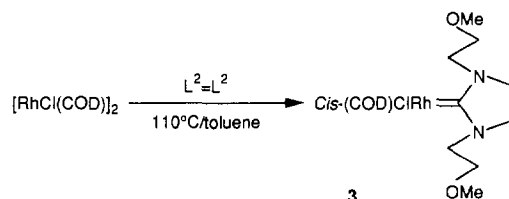
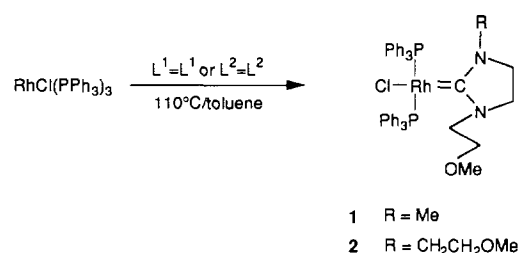
Similarities in chemical behaviour between tertiary phosphines and carbene ligands L^R have long been recognized [9]. On the other hand, the increasing interest in recent years in transition metal complexes of polydentate or functionalized tertiary phosphine suggested the possibility of synthesizing a hybrid carbene-donor ligand. Functionalized electron-rich carbene complexes have received, so far, only limited attention. Hybrid carbene-alkene [10,11] and carbene-phosphine [12,13] ligands have been reported, but until now the carbene and alkoxy functions do not appear to have been associated in the same ligand.

Here we report the preparation and characterization of novel rhodium(I) and ruthenium(II) complexes which derive from L¹ = L¹ (L¹ = $\overline{\text{C}}\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OMe}$) and L² = L² (L² =

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Scheme 1. Routes to electron-rich olefin-derived monocarbene complexes of rhodium(I) and ruthenium(II). Reagents and conditions: (i) $\text{ClCH}_2\text{CH}_2\text{OMe}$, DMF, 25 °C, 10 h; (ii) NaH or KOBu^t, THF, 25 °C; (iii) $L^1 = L^1$, $[\text{RhCl}(\text{PPh}_3)_3]$, toluene, 110 °C, 2 h; (iv) $L^1 = L^1$, $[\text{RuCl}_2(\text{Me}_2\text{CHC}_6\text{H}_4\text{Me-}p)_2]$, toluene, 110 °C, 2 h; (v) $L^1 = L^1$, $[\text{RuCl}_2(\text{C}_6\text{Me}_6)_2]$, toluene, 110 °C, 2 h; (vi) $L^2 = L^2$, $[\text{RhCl}(\text{COD})_2]$, toluene, 110 °C, 2 h; (vii) $L^2 = L^2$, $[\text{RhCl}(\text{PPh}_3)_3]$, toluene, 110 °C, 2 h; (viii) $L^2 = L^2$, $[\text{RuCl}_2(\text{Me}_2\text{CHC}_6\text{H}_4\text{Me-}p)_2]$, toluene, 110 °C, 2 h; (ix) $L^2 = L^2$, $[\text{RuCl}_2(\text{C}_6\text{Me}_6)_2]$, toluene, 110 °C, 2 h; (x) $\text{BrCH}_2\text{CH}_2\text{Br}$, $\text{MeOCH}_2\text{CH}_2\text{NMe}_2$, ethanol, 76 °C, 8 h; (xi) $[\text{MeOCH}_2\text{CH}_2\text{NHCH}_2]_2$, $\text{CH}(\text{OMe})_2\text{NMe}_2$.



Scheme 2.

$\overline{\text{CN}(\text{CH}_2\text{CH}_2\text{OMe})\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OMe}}$ containing the *N*-2-methoxyethyl substituent (Scheme 1) and their catalytic properties in the cyclopropanation from diazoalkane derivatives and styrene.

2. Results and discussion

2.1. The carbene metal complexes

The precursor $L^1 = L^1$ was prepared from the reaction of 1-methyl-3-(2-methoxyethyl)imidazolium chloride and sodium hydride or potassium *tert*-butoxide [14]. $L^2 = L^2$, with four identical functional *N*-substituents- $\text{CH}_2\text{CH}_2\text{OMe}$, can be made by reacting the acetal $\text{Me}_2\text{NCH}(\text{OMe})_2$ with *N,N'*-bis(2-methoxyethyl)ethylenediamine [14].

The rhodium(I) complexes **1**, **2**, **3** were prepared by PPh_3 displacement from $\text{RhCl}(\text{PPh}_3)_3$ or chloro bridge displacement from $[\text{RhCl}(\text{COD})_2]$ on treatment with $L^1 = L^1$ or $L^2 = L^2$ in toluene at reflux (Scheme 2).

The (arene)ruthenium(II) complexes **4–7** were obtained from $[\text{RuCl}_2(\text{arene})]_2$ (arene: *p*-cymene or hexamethylbenzene) by chloro bridge cleavage but under more drastic conditions than the cleavage by monophosphine leading to the analogous complexes $[\text{RuCl}_2(\text{PR}_3)(\text{arene})]$ [15] (Scheme 3).

A number of $L^R = L^R$ derived carbene-rhodium(I) [16–19] and ruthenium(II) [19–21] species have previously been reported with alkyl and aryl substituents. The introduction of the methoxyethyl group in the new rhodium(I) and ruthenium(II) complexes allows a good solubility of the complexes in hydrocarbon solvents and also to produce air-stable resulting solutions.

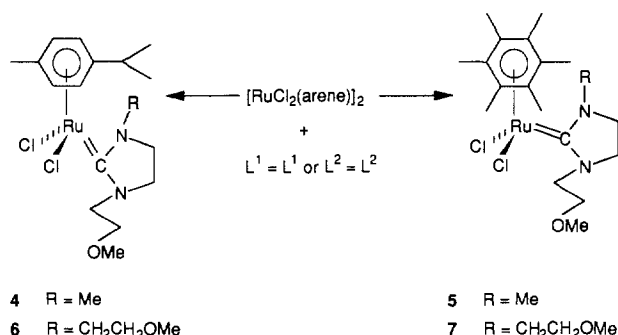
The identity of the compounds has been confirmed by elemental analyses, IR, ¹H, ¹³C, and ³¹P NMR spectroscopy (Tables 1–3). Both rhodium(I) and ruthenium(II) complexes exhibit a characteristic $\nu(\text{CN}_2)$ band

(Table 2) typically at 1490–1525 cm^{-1} (e.g. complex **6** has $\nu(\text{CN}_2)$ at 1492 cm^{-1} which compares well with 1510 cm^{-1} found for the carbene L^R analogue) [16,18].

¹H NMR spectroscopy (Table 2) clearly differentiates (i) the OMe substituents, (ii) the *N*- CH_2CH_2 -OMe protons and (iii) the ring CH_2 protons. All metal- L^2 complexes exhibited first-order ¹H NMR spectra for the *N*-alkyl and ring methylenes, whereas metal- L^1 complexes exhibit AX_2 , A_2B_2 or AA'BB' pattern.

¹³C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}\text{C}_{\text{carb}})$ are in the range 197–214 ppm and are similar to those found for non-functionalized carbene complexes. It is clearly noticeable that $\delta(^{13}\text{C}_{\text{carb}})$ move to higher field upon attachment of the OMe group. Coupling constants $J(^{103}\text{Rh}-^{13}\text{C})$ for the new rhodium complexes (**1**, **2** and **3**) are comparable with those found for carbene rhodium(I) complexes [16,17].

Complexes **1** and **2** have a trans orientation of two PPh_3 ligands on the basis of their ³¹P NMR. Thus, $[\text{RhCl}(L^2)(\text{PPh}_3)_2]$ **2** exhibits a doublet at $\delta = 30.8$ ppm,



Scheme 3.

Table 1
Physical measurement of carbene complexes

Com- pound	M.p. (°C)	Yield (%)	Micro analysis, found (calculated) (%)		
			C	H	N
1	165–166	68	64.1 (63.8)	5.3 (5.3)	3.5 (3.9)
2	79–80	78	44.0 (47.2)	6.6 (6.9)	5.9 (6.5)
3	186–187	82	42.3 (45.5)	5.7 (6.2)	6.6 (6.2)
4	119–120	80	46.4 (46.5)	7.9 (7.7)	11.9 (12.1)
5	244–245	75	63.7 (63.5)	5.6 (5.4)	3.3 (3.4)
6	160–161	69	44.5 (46.3)	6.1 (6.5)	6.4 (5.7)
7	209–210	80	48.4 (48.5)	6.5 (6.9)	5.6 (5.4)

$J(^{103}\text{Rh}-^{31}\text{P}) = 158 \text{ Hz}$ and $[\text{RhCl}(\text{L}^1)(\text{PPh}_3)_2]$ **1** a doublet at $\delta = 30.3 \text{ ppm}$, $J(^{103}\text{Rh}-^{31}\text{P}) = 157 \text{ Hz}$ for the two identical phosphorus nuclei similar to that in related compounds such as *trans*- $[\text{RhCl}(\text{L}^R)(\text{PPh}_3)_2]$ [18].

2.2. Catalytic studies: cyclopropanation of olefins

Rhodium complexes of the type $[\text{RhCl}(\text{L}^R)(\text{COD})]$ and *trans*- $[\text{RhCl}(\text{L}^R)(\text{PPh}_3)_2]$ have been found to be effective hydrosilylation catalysts [22,23]. The temperature applied and the nature of the *N*-substituents of the carbene ligand have a pronounced effect upon the catalytic activity of the complexes [22]. On the other hand, heterofunctional ligands containing a strong and a weak donor group have been found to confer interesting properties to their metal complexes, such as dynamic behaviour via reversible dissociation of the weaker metal-ligand bond resulting in unique catalytic properties [24].

It has been shown recently that ruthenium-carbene species were catalytically active either in the ring open-

Table 2
IR and ^1H NMR spectroscopic data for compounds 1–7

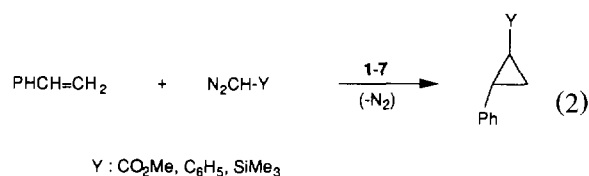
Com- pound	IR ν (NCN) (cm^{-1})	Ring 4,5- C_6H_2	Others
1	1433	2.4 (t, J 6 Hz); 2.7 (t, J 6 Hz)	7.4 (m) $\text{P}(\text{C}_6\text{H}_5)_3$; 3.1 and 3.9 (t, J 6 Hz) $\text{CH}_2\text{CH}_2\text{OCH}_3$; 3.1 (s) $\text{CH}_2\text{CH}_2\text{OCH}_3$;
2	1583	3.5 (t, J 5 Hz)	2.7 (s) CH_3
3	1506	4.2 (m)	2.8 (t, J 5 Hz) $\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_3$; 2.9 (s) $\text{CH}_2\text{CH}_2\text{OCH}_3$; 7.5 (m) $\text{P}(\text{C}_6\text{H}_5)_3$
4	1510	3.6 (m)	3.9 (m) $\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_3$; 3.4 (s) $\text{CH}_2\text{CH}_2\text{OCH}_3$; 2.0 (m) COD C_6H_2 ; 3.3 and 4.7 (s) COD C_6H_2
5	1506	4.3 (q, d, J 3 Hz); 3.9 (t, J 4 Hz)	5.5 and 5.1 (d, J 6 Hz) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 1.3 (d, J 7 Hz) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 2.2 (s) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 2.9 (sept. J 7 Hz) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 3.6 (m) $\text{CH}_2\text{CH}_2\text{OCH}_3$; 3.5 (s) $\text{CH}_2\text{CH}_2\text{OCH}_3$;
6	1492	3.6 (m)	3.4 (s) CH_3
7	1488	3.5 (m)	2.0 (s) $\text{C}_6(\text{CH}_3)_6$; 3.5 (m) $\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_3$; 3.3 (s) $\text{CH}_2\text{CH}_2\text{OCH}_3$; 3.2 (s) C_6H_2
			5.4 and 5.1 (d, J 6 Hz) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 1.3 (d, J 7 Hz) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 2.2 (s) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 3.0 (sept. J 7 Hz) $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 3.5 (m) $\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_3$;
			3.3 (s) $\text{CH}_2\text{CH}_2\text{OCH}_3$
			2.0 (s) $\text{C}_6(\text{CH}_3)_6$; 4.3 and 4.2 (t, J 4 Hz) $\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_3$;
			3.3 (s) $\text{CH}_2\text{CH}_2\text{OCH}_3$

Table 3
 ^{13}C NMR spectroscopic data for compounds 1–7^a

Com- pound	M=C	Ring 4,5- C_6H_2	Others
1		49.4, 49.6	127.0, 129.9, 133.7, 134.9, 136.7 $\text{P}(\text{C}_6\text{H}_5)_3$; 50.4, 58.1, 71.2 $\text{CH}_2\text{CH}_2\text{OCH}_3$
2	198.3 (d, J 47 Hz)	51.7, 51.8	73.1, 74.4 $\text{CH}_2\text{CH}_2\text{OCH}_3$; 60.7 $\text{CH}_2\text{CH}_2\text{OCH}_3$; 130.4, 130.6, 132.9, 136.4 $\text{P}(\text{C}_6\text{H}_5)_3$
3	213.3 (d, J 47 Hz)	51.8, 52.1	72.0, 73.1 $\text{CH}_2\text{CH}_2\text{OCH}_3$; 60.7 $\text{CH}_2\text{CH}_2\text{OCH}_3$; 30.5, 34.6 COD C_6H_2 ;
4	206.5	49.1, 51.9	70.2 and 98.9 (d, J 7 Hz) COD C_6H_2
5	209.7	50.4, 51.4	82.8, 86.4, 99.5, 101.9 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 22.5 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$;
6	207.5	49.6, 52.2	18.8 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 30.6 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$;
7	211.8	52.7, 53.4	51.9, 58.8, 71.6 $\text{CH}_2\text{CH}_2\text{OCH}_3$; 39.6 C_6H_2
			93.9 $\text{C}_6(\text{CH}_3)_6$; 15.4 $\text{C}_6(\text{CH}_3)_6$; 52.3, 74.2 $\text{CH}_2\text{CH}_2\text{OCH}_3$; 39.1 CH_2
			82.5, 86.2, 99.9, 108.7 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 22.7 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$;
			18.4 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$; 30.6 $[(\text{CH}_3)_2\text{CHC}_6\text{H}_4(\text{CH}_3)-p]$;
			50.9, 58.2, 72.3 $\text{CH}_2\text{CH}_2\text{OCH}_3$
			95.9 $\text{C}_6(\text{CH}_3)_6$; 17.3 $\text{C}_6(\text{CH}_3)_6$; 60.5, 76.2 $\text{CH}_2\text{CH}_2\text{OCH}_3$; 22.1 $\text{CH}_2\text{CH}_2\text{OCH}_3$

^a δ ppm relative to Me_4Si in CDCl_3 .

ing cyclic olefin polymerization, in the formation of cyclic olefins from non-conjugated dienes or in cyclopropanation [1–3]. The possibility that in metal carbene complexes **1–7**, the carbene ligand having one or two coordinating $\text{CH}_2\text{CH}_2\text{OMe}$ "arms" plays the role of hemilabile ligands on elimination of PPh_3 or COD from rhodium(I) and arene from ruthenium(II) complexes led us to study their catalytic activity toward the cyclopropanation reaction. Compounds **1–7** have been studied in order to promote the cyclopropanation of styrene with functional diazomethane derivatives $\text{N}_2\text{CHCO}_2\text{Et}$, $\text{N}_2\text{CHC}_6\text{H}_5$ and $\text{N}_2\text{CHSiMe}_3$ (Eq. (2)). The results are summarized in Table 4.



The cyclopropanation using $\text{N}_2\text{CHSiMe}_3$ does not occur (6% yield with **7**) and that with $\text{N}_2\text{CHC}_6\text{H}_5$ gives moderate yields 35–40%. However, the catalytic cyclopropanation involving $\text{N}_2\text{CHCO}_2\text{Et}$, promoted by complexes **1–7**, appears to be effective and with a cis-trans ratio of 1/3 approximately. It is interesting to note that the catalytic activity of these complexes **1–7** is markedly dependent upon temperature. Thus in the case of complex **6** the yield of the cyclopropane at 80 °C after 4 h is 52%, whereas at 60 °C the yield is only 38%. One-arm complexes **4** and **5** appear less efficient than their equivalent two-arm complexes **6** and **7** at 80 °C. The

Table 4
Styrene cyclopropanation reactions by ruthenium(II) and rhodium(I) complexes

N_2CHY	Catalyst	T (°C)	Time (h)	Yield (%) ^a (cis/trans)
$\text{Y} = \text{CO}_2\text{Et}$	1	80	4	71 (25/75)
	2	80	4	69 (25/75)
	3	80	4	91 (24/76)
	4	80	4	26 (24/76)
	5	80	4	44 (24/76)
	6	60	4	38 (18/82)
	6	80	4	52 (18/82)
	7	60	4	34 (33/67)
	7	60	13	44 (27/73)
	7	80	4	54 (25/75)
	7	80	8	56 (25/75)
	7	100	2	58 (22/78)
	7	100	4	59 (23/77)
$\text{Y} = \text{Ph}$	3	80	2	37 (48/52)
	7	80	2	39 (51/49)
$\text{Y} = \text{SiMe}_3$	7	80	2	6

^a Yields measured using gas chromatography, based on diazoalkanes.

Table 5
Cyclic voltammetric data of rhodium(I) and ruthenium(II) complexes^a

Compound	$E_{1/2}$ (V _{SCE})	ΔE_p (mV)
2	0.085	115
3	0.639	147
4	1.122	111
5	0.958	122
6	1.157	67
7	0.989	124

^a E vs. SCE, Pt working electrode, 100 mV s⁻¹. Recorded in CH_2Cl_2 solution 0.05 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte.

rhodium(I) complexes **1**, **2** and **3** are clearly better catalysts than their related ruthenium(II) complexes **6** or **7**, and complex **3** which has a labile COD ligand gives the cyclopropane derivative in 91% yield. The comparison of *para*-cymene (**4**, **6**) and hexamethylbenzene (**5**, **7**) ruthenium(II) complexes shows that the latter, containing the more electron-releasing group, provide a better activity. In order to evaluate the influence of electron-richness of the metal centre we recorded the cyclic voltammograms of the complexes (Table 5).

The cyclic voltammograms show that (i) all complexes can be oxidized reversibly, (ii) the rhodium(I) complexes—the most efficient catalyst precursors—are the most electron-rich complexes, (iii) the C_6Me_6 ruthenium complexes are more electron-rich than their *para*-cymene analogues and (iv) the effect of the L^1 or L^2 ligand does not significantly modify the oxidation potentials (Table 5). It is thus obvious that the electron-richness of catalyst precursors does not alone reflect the catalyst activity.

At this stage it is not possible to propose the nature of the catalytic species. The generation of metal-carbene species $\text{M}=\text{CHY}$ was expected, but the stoichiometric addition of $\text{N}_2\text{CHCO}_2\text{Et}$ to complex **7** did not allow the isolation of a complex or to observe an intermediate. The reaction even at room temperature only produces diethylfumarate, as shown by vapour gas chromatography, and the compound **7** was recovered unchanged. Thus, in the absence of the alkene the complex only favours the decomposition of the diazoalkane derivative and it is not possible to prove whether the carbene moiety coordinates to the metal as it was previously shown [1].

3. Experimental

All reactions were performed by using Schlenk-type flasks under argon and standard high vacuum-line techniques. Solvents were analytical grade and distilled under argon from sodium benzophenone (toluene, diethyl ether), sodium-potassium (pentane, thf), P_2O_5 (dichloromethane). IR spectra were recorded in the 4000–

400 cm⁻¹ region on a Pye Unicam spectrometer. Samples were prepared as KBr discs or Nujol mulls. NMR spectra were recorded at 297 K on a Bruker AC300P FT spectrometer operating at 300.13 MHz (¹H), 121.50 MHz (³¹P) and 75.47 MHz (¹³C).

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: [RhCl(PPh₃)₃] [25], [RuCl₂(*p*-Me-C₆H₄CHMe₂)₂] [26], [RuCl₂(C₆Me₆)₂] [26]. The synthesis of electron-rich olefins L¹ = L¹ and L² = L² with other *N*-functionalized tetraaminoalkenes will be reported separately [14].

3.1. Synthesis of rhodium(I) complexes 1, 2 and 3

A solution of L¹ = L¹ (0.65 g, 2 mmol) in toluene (15 ml) and [RhCl(PPh₃)₃] (0.35 g, 0.37 mmol) were heated for 2 h under reflux. *n*-Hexane (7 ml) was added to the solution while warm. Upon cooling to room temperature orange crystals of **1** were obtained in 68% yield.

Compound **2** was prepared in the same way as **1** from L² = L² (0.37 g, 0.99 mmol) and [RhCl(PPh₃)₃] (0.626 g, 0.67 mmol) to give yellow crystals of **2** in 78% yield.

Compound **3** was prepared in the same way as **1** from L² = L² (0.25 g, 0.67 mmol) and [RhCl(COD)]₂ (0.33 g, 0.66 mmol) to give yellow crystals of **3** at -15 °C in 82% yield.

3.2. Synthesis of ruthenium(II) complexes 4, 5, 6 and 7

A solution of L¹ = L¹ (0.39 g, 1.37 mmol) in toluene (15 ml) was added to [RuCl₂(*p*-Me₂CHC₆H₄Me)₂] (0.64 g, 1.04 mmol) and the mixture was heated for 2 h under reflux. The resulting solution, on addition of *n*-hexane (15 ml) and cooling to room temperature, gave the orange solid **4**. The product **2**, was filtered, washed with *n*-hexane (2 × 15 ml), dried in vacuum and obtained in 80% yield.

Using a similar procedure, [RuCl₂(C₆Me₆)₂] (0.7 g, 1.04 mmol) and L¹ = L¹ (0.368 g, 1.29 mmol) afforded **5** in 75% yield.

Compound **6** was prepared in the same way as **4** from L² = L² (0.60 g, 1.60 mmol) and [RuCl₂(*p*-Me₂CHC₆H₄Me)₂] (0.658 g, 1.10 mmol) to give the orange solid **6** in 69% yield.

Using a similar procedure as that of **4**, L² = L² (0.415 g, 1.10 mmol) and [RuCl₂(C₆Me₆)₂] (0.618 g, 0.94 mmol) gave the orange crystals of **7** in 80% yield.

3.3. Catalytic reaction conditions

Catalyst (0.009 mmol), styrene (20 mmol, 2.3 ml) were introduced into a Schlenk tube and then ethyl

diazoacetate (1 mmol diluted in 1 ml of styrene) was added. The mixture was stirred in an oil bath at 60–80 °C for 4–13 h.

Phenyldiazomethane was added as 1 mmol diluted in 1 ml styrene and 1 ml CH₂Cl₂. (Trimethylsilyl)diazomethane was added as 1 mmol (2.0 M solution in hexane) diluted in 1 ml styrene.

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