Benzimidazole, Benzothiazole and Benzoxazole Ruthenium(II) Complexes; Catalytic Synthesis of 2,3-Dimethylfuran

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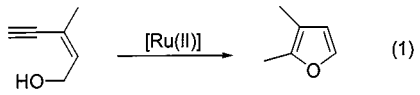
Dedicated to Professor W. P. Fehlhammer for his scientific contribution and on the occasion of his 60th birthday

Keywords: Arene complexes / Ruthenium / Benzimidazole / Benzothiazole / Benzoxazole / Cycloisomerisation

Fourteen ruthenium(II) complexes of the type $[RuCl_2(\eta^6\text{-arene})L]$, (arene = 1,4-$MeC_6H_4Pr^i$ or C_6Me_6; L = benzimidazole derivative in which the NH group is substituted by *N*-alkyl or isoelectronic O or S atoms) have been prepared by cleavage of $[RuCl_2(\eta^6\text{-arene})]_2$ with the *N*-heterocycle L. Their spectroscopic and electrochemical properties are described. The effect of the nature of the benzazole (L) on the catalytic activity of these complexes for the intramolecular cyclization of (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran has also been studied; the benzimidazole complexes were found to be the most active.

Introduction

Transition metal complexes with ligands containing nitrogen-donor atoms have recently shown their potential to successfully promote the catalytic transformation of organic compounds.[1] These discoveries motivate the search for new metal complexes with *N*-coordinated ligands and the evaluation of their catalytic properties. In this context, Rh^I complexes of 1-alkyl-2-imidazoline in which the imidazoline coordinates through the N(3) atom of the ring have already been shown to catalyse the cyclopropanation of styrene with ethyl diazoacetate in good yield.[2] Our contribution to this field has recently started with the syntheses of the 2-imidazoline and 1,4,5,6-tetrahydropyrimidine complexes of Ru^{II} which are capable of catalyzing the intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran (Equation 1) and the observation of the higher efficiency of the tetrahydropyrimidine complexes.[3]



In this paper we report the straightforward preparation of a series of (η^6-arene)ruthenium complexes of *N*-coordinated benzimidazole derivatives in which the NH group is substituted by *N*-alkyl or isoelectronic O or S atoms (Scheme 1). Their spectroscopic and electrochemical properties are described and the influence of the nature of the benzazole ligand L on the catalytic activity of these complexes in the formation of 2,3-dimethylfuran has also been studied.

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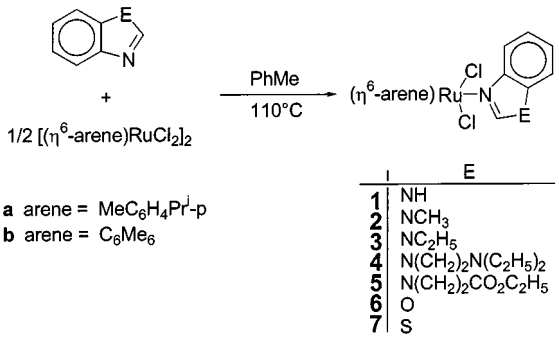

Scheme 1. Synthetic route to benzazole complexes of Ru^{II}

Results and Discussion

The complexes **1**−**7** were prepared in 74−89% yield by simply heating the appropriate benzazole (L) with $[RuCl_2(\eta^6\text{-arene})]_2$ in toluene (Scheme 1). The compounds **1**−**7** were precipitated as red-brown crystalline solids upon cooling the reaction mixture, isolated by filtration and washed with *n*-hexane (see Table 1). The complexes **1**−**7** are perfectly stable in the solid state and show spectroscopic properties indicating that they all are N(3)-bonded. However, the reaction of benzimidazole with $[Ru(H_2O)(NH_3)_5)]^{2+}$, followed by HCl-catalyzed hydrolysis, has been reported to form C(2)-bonded benzimidazole ligand.[4] On the other hand, X-ray crystallographic studies revealed that 2,5-dimethylbenzoxazole, potentially an ambidentate ligand, coordinates to the Pt^{II} centre through the *N*-donor atom.[5] An X-ray structure of cyclopalladated complexes of *N*-acetyl-2-phenyl-benzimidazole has also been described.[6]

The nature of the bonding in the benzazole complexes **1**−**7** was readily shown by NMR spectroscopy (Tables 2 and 3). ^{13}C NMR spectroscopy was the most useful tool for structure elucidation. Thus, from our previous experience,[6][7] we expected that *C*-coordination would result in a shift of the carbene carbon nucleus to high frequency i.e. 190−210 ppm, while *N*-coordination would result in a low

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Table 1. Physical measurement of new benzimidazole, benzothiazole and benzoxazole ruthenium complexes **(1−7)**

Compound	M.p. (°C)	Yield (%)	Micro Analysis Found (Calculated) (%)		
			C	H	N
1a	249−250	87	48.02 (48.11)	4.73 (4.75)	6.29 (6.61)
1b	373−374	89	50.71 (50.45)	5.41 (5.35)	6.33 (6.19)
2a	248−249	89	48.98 (49.31)	5.05 (5.06)	6.47 (6.39)
2b	345−346	83	51.41 (51.50)	5.76 (5.62)	5.98 (6.01)
3a	228−229	79	50.12 (50.44)	5.27 (5.35)	6.28 (6.20)
3b	317−318	85	52.25 (52.49)	5.87 (5.88)	6.03 (5.83)
4a	253−254	75	52.38 (52.76)	6.26 (6.36)	7.84 (8.03)
4b	359−361	80	53.99 (54.43)	6.35 (6.77)	7.24 (7.62)
5a	172−173	87	50.08 (50.38)	5.22 (5.38)	5.21 (5.34)
5b	240−241	89	52.34 (52.17)	5.41 (5.84)	4.89 (5.07)
6a	194−195	74	47.69 (48.00)	4.54 (4.51)	3.23 (3.76)
6b	378−378	78	49.92 (50.33)	5.39 (5.12)	3.03 (3.53)
7a	219−220	83	46.21 (46.26)	4.34 (4.34)	3.11 (3.18)
7b	369−370	77	48.15 (48.61)	4.96 (4.94)	2.54 (2.99)

frequency shift towards 160 ppm. The signal pattern for the nitrogen donor ligands and ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode in the 142.6−160.6 ppm range. The ^{1}H NMR spectra of the complexes further supported the assigned structures; the resonances for C(2)−H were observed as sharp singlets in the 7.3−9.7 ppm range. An electrochemical study by cyclic voltammetry showed that these new complexes present one reversible redox wave for the system Ru^{II}/Ru^{III} located in the range 1−1.3V/ECS (Table 4). For the electron releasing C_6Me_6 ligand the redox process takes place at lower potential.

Catalytic Studies

Although various ruthenium catalysts have been reported[3,8,9] for the intramolecular cyclization of (*Z*)-enynols (Equation 1), the search for more efficient catalysts is necessary. Therefore, we evaluated the new ruthenium complexes **1−7** for this reaction. With 1 mol-% of Ru catalyst at 80°C (*Z*)-3-methylpent-2-en-4-yn-1-ol gave moderate to good yields of the cyclization product. These results are summarized in Table 5. They show that the most efficient complexes are **3a** and **5a** (Table 5, entries 7, 12, 13). The best yields were obtained at 80°C for 2−4 h. Comparison of the catalysts containing *p*-cymene (**a** type) and hexa-

Table 2. IR and ^{1}H NMR spectroscopic data for compounds **1−7**[a]

Compound	ν (CN) cm^{-1}	C(2)−*H*	Others
1a	1489	8.0 (s)	2.0 N*H*; 6.61−6.99 (m) C_6H_4; 5.3 and 5.5 (d, *J* 6 Hz)) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 1.2 (d, *J* 7 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.0 (s) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.8 (sept. *J* 7) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]
1b	1484	7.8 (s)	2.0 N*H*; 5.5−5.8 C_6H_4; 1.5 (s) $C_6(CH_3)_6$
2a	1610	8.4 (s)	3.7 (s) CH_3; 7.3−7.9 C_6H_4; 5.3 and 5.5 (d, *J* 6 Hz)) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 1.2 (d, *J* 7 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.1 (s) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.8 (sept. *J* 7) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]
2b	1608	8.2 (s)	3.8 (s) CH_3; 7.3−8.0 (m) C_6H_4; 2.0 (s) $C_6(CH_3)_6$
3a	1610	8.4 (s)	4.1 (q, *J* 7 Hz) CH_2CH_3; 1.4 (t, *J* 7 Hz) CH_2CH_3; 7.2−8.0 (m) C_6H_4; 5.3 and 5.5 (d, *J* 6 Hz)) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 1.2 (d, *J* 7 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.1 (s) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.8 (sept. *J* 7) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]
3b	1611	8.1 (s)	4.1 (q, *J* 7 Hz) CH_2CH_3; 1.4 (t, *J* 7 Hz) CH_2CH_3; 7.2−7.4 (m) C_6H_4; 1.9 (s) $C_6(CH_3)_6$
4a	1513	8.5 (s)	4.1 (t, *J* 6 Hz) $CH_2CH_2N(CH_2CH_3)_2$; 2.8 (t, *J* 6 Hz) $CH_2CH_2N(CH_2CH_3)_2$; 2.7 (q, *J* 6 Hz) $CH_2CH_2N(CH_2CH_3)_2$; 1.0 (t, *J* 7 Hz) $CH_2CH_2N(CH_2CH_3)_2$; 7.3−8.1 (m) C_6H_4; 5.4 and 5.6 (d, *J* 6 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 1.3 (d, *J* 7 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.1 (s) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 3.0 (sept. *J* 7) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]
4b	1490	7.3 (s)	1.8 (qu *J* 6 Hz) $NCH_2CH_2CH_2N$; 4.2 (s) $CH_2C_6H_5$; 7.1−7.3 (m) $CH_2C_6H_5$; 2.0 (s) $C_6(CH_3)_6$
5a	1508	8.3 (s)	2.7 and 4.2 (t, *J* 7 Hz) $CH_2CH_2COOCH_2CH_3$; 4.0 (q, *J* 6 Hz) $CH_2CH_2COOCH_2CH_3$; 1.2 (q, *J* 6 Hz) $CH_2CH_2COOCH_2CH_3$; 6.7−8.1 (m) C_6H_4; 5.3 and 5.5 (d, *J* 6 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 1.2 (d, *J* 7 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.1 (s) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.0 (sept. *J* 7) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]
5b	1506	8.0 (s)	2.6 and 4.0 (t, *J* 7 Hz) $CH_2CH_2COOCH_2CH_3$; 3.9 (q, *J* 6 Hz) $CH_2CH_2COOCH_2CH_3$; 1.1 (q, *J* 6 Hz) $CH_2CH_2COOCH_2CH_3$; 7.1−7.9 (m) C_6H_4; 1.9 (s) $C_6(CH_3)_6$
6a	1471	8.7(s)	7.4−8.0 (m) C_6H_4; 5.4 and 5.5 (d, *J* 6 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 1.2 (d, *J* 7 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.1 (s) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.9 (sept. *J* 7) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]
6b	1502	8.9 (s)	7.2−7.9 (m) C_6H_4; 2.0 (s) $C_6(CH_3)_6$
7a	1413	9.7 (s)	7.5−8.7 (m) C_6H_4; 5.4 and 5.6 (d, *J* 6 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 1.2 (d, *J* 7 Hz) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.0 (s) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 2.8 (sept. *J* 7) [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]
7b	1413	9.2 (s)	7.4 and 8.4 (m) C_6H_4; 1.9 (s) $C_6(CH_3)_6$

s: singlet, d: doublet, t: triplet, q: quadruplet, qu: quintet, sept: septet, chemical shifts referenced to residual solvent $CDCl_3$.

Table 3. ^{1}C NMR spectroscopic data for compounds **1−7**[a]

Compound	*C*2	Others
1a	142.6	109.6, 113.4, 115.4, 122.9, 132.3, 138.8 C_6H_4; 81.1 81.7, 97.6, 102.3 [$(CH_3)_2CHC_6H_4(CH_3)$-*p*]; 22.1 [($CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 19.1 [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 30.3 [$(CH_3)_2C$ HC_6H_4 (CH_3)-*p*]
1b	142.7	110.1, 112.9, 117.4, 122.9, 133.1, 137.4 C_6H_4; 90.7 $C_6(CH_3)_6$; 17.6 $C_6(CH_3)_6$
2a	145.7	32.3 CH_3; 110.9, 120.9, 123.9 124.5 134.8 142.7 C_6H_4; 81.5, 83.3, 98.1, 103.1 [$(CH_3)_2CHC_6H_4(CH_3)$-*p*]; 22.7 [($CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 18.9 [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 31.1 [$(CH_3)_2C$ HC_6H_4 (CH_3)-*p*]
2b	145.6	31.8 CH_3; 110.2, 121.3, 122.9, 123.9, 134.5 C_6H_4; 16.3 $C_6(CH_3)_6$; 90.9 $C_6(CH_3)_6$
3a	144.1	15.2, 41.1 CH_2CH_3; 111.0, 120.5, 123.4, 124.0, 133.5, 142.6 C_6H_4; 81.2, 82.9, 97.7, 102.5 [$(CH_3)_2CHC_6H_4(CH_3)$-*p*]; 22.4 [($CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 18.6 [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 30.7 [$(CH_3)_2C$ $HC_6H_4(CH_3)$-*p*]
3b	144.5	15.3, 40.1 CH_2CH_3; 110.6, 121.2, 122.7, 123.8, 133.5, 141.0 C_6H_4; 15.3 $C_6(CH_3)_6$; 90.8 $C_6(CH_3)_6$,
4a	145.6	47.1 $CH_2CH_2NCH_2CH_3$; 10.9, 51.3 $CH_2CH_2N(CH_2CH_3)_2$; 111.0, 120.5, 123.4, 124.2, 133.4, 142.2 C_6H_4; 81.1, 82.9, 97.6, 102.7 [$(CH_3)_2CHC_6H_4(CH_3)$-*p*]; 22.4 [($CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 18.5 [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 30.7 [$(CH_3)_2C$ $HC_6H_4(CH_3)$-*p*]
4b	145.4	46.9 $CH_2CH_2NCH_2CH_3$; 11.0, 51.1 $CH_2CH_2N(CH_2CH_3)_2$; 109.1, 120.2, 122.9, 124.2, 133.6, 142.6 C_6H_4; 15.6 $C_6(CH_3)_6$; 90.5 $C_6(CH_3)_6$,
5a	145.5	41.1, 60.9 $CH_2CH_2CO_2CH_2CH_3$; 14.1, 33.5 $CH_2CH_2CO_2CH_2CH_3$; 170.6 $CH_2CH_2CO_2CH_2CH_3$; 111.1, 120.4, 123.3, 132.9, 142.1, C_6H_4, 81.1, 82.9, 97.5, 102.5 [$(CH_3)_2CHC_6H_4(CH_3)$-*p*]; 22.3 [($CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 18.4 [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 30.4 [$(CH_3)_2C$ $HC_6H_4(CH_3)$-*p*]
5b	146.1	40.8, 60.9 $CH_2CH_2CO_2CH_2CH_3$; 14.1, 33.5 $CH_2CH_2CO_2CH_2CH_3$; 170.7 $CH_2CH_2CO_2CH_2CH_3$; 111.0, 120.9, 122.6, 124.1, 140.5, C_6H_4; 15.8 $C_6(CH_3)_6$; 90.8 $C_6(CH_3)_6$
6a	156.0	111.9, 121.0, 125.9, 126.9, 150.0 C_6H_4; 81.1, 82.9, 97.9, 103.1 [$(CH_3)_2CHC_6H_4(CH_3)$-*p*]; 22.3 [($CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 18.6 [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 30.8 [$(CH_3)_2C$ $HC_6H_4(CH_3)$-*p*]
6b	156.1	112.0, 121.1, 125.3, 127.2, 149.8 C_6H_4; 15.6 $C_6(CH_3)_6$; 90.5 $C_6(CH_3)_6$
7a	160.4	97.6, 122.9, 125.6, 126.9, 127.5 C_6H_4; 81.9, 83.6, 98.4, 103.3 [$(CH_3)_2CHC_6H_4(CH_3)$-*p*]; 22.7 [($CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 18.8 [$(CH_3)_2CHC_6H_4$ (CH_3)-*p*]; 31.1 [$(CH_3)_2C$ $HC_6H_4(CH_3)$-*p*]
7b	160.6	97.8, 123.0, 125.5, 126.8, 128.1 C_6H_4; 15.6 $C_6(CH_3)_6$; 90.6 $C_6(CH_3)_6$

[a] Chemical shifts referenced to residual solvent $CDCl_3$.

Table 4. Cyclic voltammetric data of ruthenium(II) complexes[a]

Compound	$E_{1/2}$ vs. SCE	E_p, mV
1a	1.29	87
3a	1.29	195
3b	1.03	104
4a	1.38	90
4b	1.05	100
5a	1.28	109
5b	1.04	114
6a	1.42	110
6b	1.17	100
7a	1.18	90

[a] *E* versus SCE, Pt working electrode, 100 mV/s. Recorded in CH_2Cl_2 solution 0.05M *n*-Bu_4NPF_6 as supporting electrolyte.

methylbenzene (**b** type) indicates that the presence of the *p*-cymene ligand gives a much better catalyst precursor. This may be due to the higher lability of the *p*-cymene ligand. The nature of the nitrogen ligand also has a strong influence on the catalytic activity as the ruthenium benzimidazole complexes **3** and **5** are the best catalysts and are much more efficient than the benzoxazole or benzothiazole complexes.

In conclusion, the preparation of ruthenium(II)-benzazole (L) complexes (**1−7**) is straightforward from the benzazole ligand and commercially available $[RuCl_2(arene)]_2$. The benzazoles behave as *N*-centered nucleophiles and all the complexes showed moderate to good catalytic activity for the cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethyfuran at 80°C, but (*p*-cymene)$RuCl_2$(benzimidole) appeared to give the best catalyst precursors.

Table 5. Catalytic synthesis of 2,3-dimethylfuran at 80°C

Entry	Catalyst	Time (h)	Yield (%)[a,b]
1	**1a**	2	75
2	**1a**	12	96 (82)[b]
3	**1b**	32	65
4	**1b**	40	79 (69)[b]
5	**2a**	8	83 (75)[b]
6	**2b**	40	84 (73)[b]
7	**3a**	1	90
8	**3a**	4	97 (89)[b]
9	**3b**	24	90 (78)[b]
10	**4a**	14	83 (75)[b]
11	**4b**	25	81 (69)[b]
12	**5a**	2.5	93
13	**5a**	12	98 (87)[b]
14	**5b**	30	90 (78)[b]
15	**6a**	32	83 (73)[b]
16	**6b**	20	81 (69)[b]
17	**7a**	36	76 (65)[b]
18	**7b**	13	81 (70)[b]

[a] Determined by gas chromatography. − [b] Isolated yield after distillation.

Experimental Section

General: Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen atmosphere with previously dried solvents and standard Schlenk techniques. The complexes $[RuCl_2(p-MeC_6H_4CHMe_2)]_2$ and $[RuCl_2(C_6Me_6)]_2$ were prepared according to literature methods.[10] 1-Substituted benzimidazoles, used for the synthesis of **2−5**, were prepared from the potassium salt of benzimidazole by following the literature procedure.[11] Infrared spectra were recorded as KBr pellets in the range 4000−400 cm^{-1} on a ATI UNICAM systems 2000 Fourier Transform spectrometer. ^{1}H NMR spectra (300.131 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded on a Bruker AM 300

WB FT spectrometer with δ referenced to residual solvent $CDCl_3$. Microanalyses were performed by the TÜBITAK (Ankara−Turkey) or Service Central D′analyses du Centre National de la Recherche Scientifique (Vernaison-France).

General Procedure for the Preparation of Ruthenium(II) Benzazole Complexes 1−7: A solution of the azole (2.1 mmol) in toluene (20 mL) and $[RuCl_2(p-MeC_6H_4CHMe_2)]_2$ or $[RuCl_2(C_6Me_6)]_2$ (1.0 mmol) were heated for 2 h under reflux. Upon cooling to room temperature, orange crystals of **1−7** were obtained. The crystals were filtered, washed with *n*-hexane (2 × 15 mL) and dried under vacuum. The reported yields are based on $[RuCl_2(\eta^6\text{-arene})]_2$ and relevant physical data are compiled in Tables 1−4.

Catalytic Reaction Conditions: Ruthenium 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 1−32 hours. The conversion of the starting enynol was determined by gas chromatography and the pure furan was isolated by distillation under reduced pressure.

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[1] A. Togni and C. M. Venanzi, *Angew. Chem.* **1994**, *106*, 517; *Angew. Chem. Int. Ed. Eng.* **1994**, *33*, 497; C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1996**, **15**, 3998; C.-P. Lan, L. Cheng, *J. Mol. Catal.* **1993**, *84*, 39; F. Simal, A. Demonceau, A. F. Noels, *Tetrahedron Lett*. **1998**, *39*, 3493; E. Galardon, P. Le Maux, L. Toupet, G. Simonneaux, *Organometallics* **1998**, *17*, 565; S.-B. Park, N. Sakata, H. Nishiyama, *Chem. Eur. J.* **1996**, *2*, 303.
[2] B. Çetinkaya, E. Çetinkaya, P. B. Hitchcock, M. F. Lappert, I. Özdemir, *J. Chem. Soc., Dalton Trans.* **1997**, 1359.
[3] B. Çetinkaya, B. Alici, I. Özdemir, C Bruneau, P. H. Dixneuf, *J. Organomet. Chem.* **1999**, *575*, 187.
[4] R. J. Sundberg, R. F. Bryan, I. F. Taylor, H. Taube, *J. Am. Chem. Soc.* **1974**, *96*, 381.
[5] G. F. Restrepo, C. L. Barnes, M. E. Cadz, E. Olivero, S. D. Huang, *Acta Cryst. C* **1998**, 15.
[6] F. Zamora, S. Luna, P. A. Ochoa, L. A. M.-Cruz, A. Vegas, *J. Organomet. Chem.* **1996**, *522*, 97.
[7] B. Çetinkaya, I. Özdemir, P. H. Dixneuf, *J. Organomet. Chem.* **1997**, *534*, 153.
[8] B. Çetinkaya, I. Özdemir, C. Bruneau, P. H. Dixneuf, *J. Mol. Catal. A* **1997**, *118*, L1; H. Küçükbay, B. Çetinkaya, S. Guesmi, P. H. Dixneuf, *Organometallic,* **1996**, *15*, 2334.
[9] B. Seiller, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.* **1994**, 493; B. Seiller, C. Bruneau, P. H. Dixneuf, *Tetrahedron* **1995**, *51*, 13089.
[10] M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.* **1982**, *21*, 74.
[11] A. F. Pozharskii, A. M. Simanov, *Zh. Obsch. Khim.* **1963**, *33*, 179.

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