

Synthesis via amine elimination and characterization of new heterobimetallic complexes containing the (pentamethylcyclopentadienyl) titanium(IV) moiety

Mikhail Galakhov, Avelino Martín, Miguel Mena*, Carlos Yélamos

Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, 28871 Alcalá de Henares, Spain

Received 19 December 1994

Abstract

Reactions of $[\text{Cp}^* \text{Ti}(\text{NR}_2)_3]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{R} = \text{Me}$ or Et) in a 1:1 ratio with $[\text{CpM}(\text{CO})_3\text{H}]$ ($\text{M} = \text{Mo}$ or W) lead to the formation of the heterobimetallic derivatives $[\text{Cp}^*(\text{R}_2\text{N})_2\text{Ti}(\text{OC})\text{M}(\text{CO})_2\text{Cp}]$ (**1–4**), where the two metals are bridged by a carbonyl group, as is deduced by IR and ^{13}C NMR spectroscopies. Similar reaction of $[\text{Cp}^* \text{Ti}(\text{NMe}_2)_3]$ with $[\text{CpRu}(\text{CO})_2\text{H}]$ gives $[\text{Cp}^*(\text{Me}_2\text{N})_2\text{TiRu}(\text{CO})_2\text{Cp}](\text{5})$ in which a metal–metal bond between the titanium and ruthenium atoms is proposed.

Keywords: Titanium; Ruthenium; Heterobimetallic complexes; Metal–metal bond

1. Introduction

The recent interest in materials termed early and late transition metal heterobimetallic compounds (ELHB) [1] is due to their potential for homogeneous catalytic processes, where the properties of the widely divergent transition metals are combined to perform cooperative activation of small molecules such as carbon monoxide, and their utilization as acceptable models for heterogeneous catalytic systems which display strong metal–support interactions [2]. Most of these heterogeneous catalysts are formed by electron-rich late transition metals supported on high-oxidation-state early transition metal oxides.

A number of synthetic routes to homogeneous EHLBs with metal–metal bonds and/or bridging ligands between metal atoms have been reported. In particular, binuclear elimination reactions in which molecules such as H_2 , alkanes or amines are eliminated, are very successful [1a–c]. We report here the preparation of new heterobimetallic compounds through the reaction of tris(dialkylamide) derivatives of mono(pentamethylcyclopentadienyl)titanium(IV) [3a] with transition-metal hydrides, involving elimination of a secondary amine and formation of a direct metal–metal bond, or a bridging carbonyl group.

2. Results and discussion

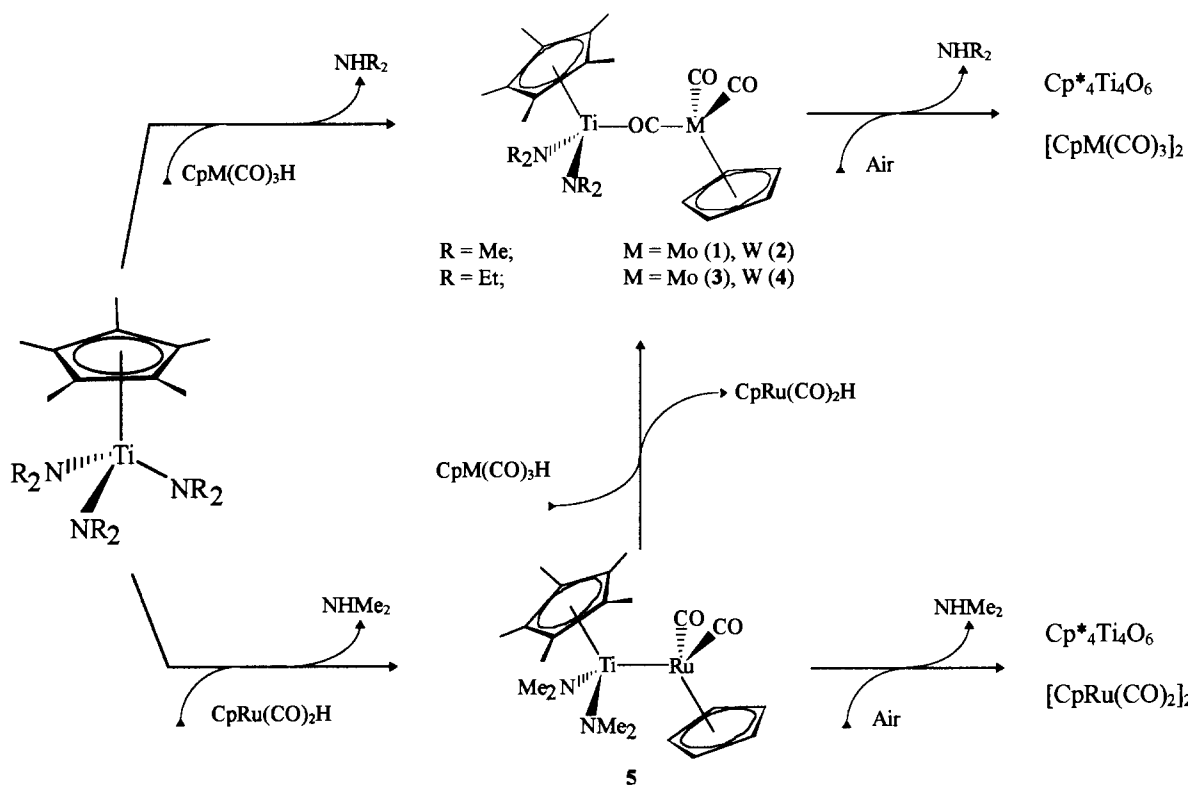
Tris(dialkylamido)(pentamethylcyclopentadienyl)titanium(IV) derivatives react with monocyclopentadienyltricarbonylhydrides of Group 6d metals to afford the corresponding heterobimetallic compounds containing a carbonyl bridge with elimination of 1 equivalent of HNR_2 (see Scheme 1). If two equivalents of $[\text{CpM}(\text{CO})_3\text{H}]$ are used in the same reaction conditions, only monosubstitution is observed and no further changes occur.

Complexes **1–4** are stable for a long period in the solid state and in solution under an inert atmosphere. However, they are very sensitive to wet air affording $[\text{Cp}_4^* \text{Ti}_4\text{O}_6]$ [4], $[\{\text{CpM}(\text{CO})_3\}_2]$ ($\text{M} = \text{Mo}$ or W) [5a,d] and the corresponding amines, as confirmed by NMR tube scale experiments and IR.

The spectroscopic data of the compounds **1–4** (Table 1 and Section 3) are consistent with the structure depicted in Scheme 1. The IR spectra in the solid state and in toluene solution show two bands between 1942 and 1837 cm^{-1} corresponding to the terminal carbonyl groups bonded to the Group 6d metal, and another band in the range 1600–1550 cm^{-1} assigned to a bridging carbonyl, probably coordinated as isocarbonyl via the oxygen atom to the electron-deficient titanium [1a,6].

The ^1H NMR spectra of **1–4** in C_6D_6 at 298 K reveal one resonance of a Cp^* ligand, other for the Cp

* Corresponding author.



Scheme 1.

group and only one signal due to the NMe_2 fragments in the case of the complexes 1–2, whereas the CH_2 protons of NEt_2 groups for 3 and 4 are diastereotopic. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these compounds show similar features to those found in the ^1H NMR spectra and also indicate the presence of two types of carbonyl

fragments, terminal (upfield signal) and bridging (downfield signal). The ^1H and ^{13}C chemical shifts for the α -carbon atoms of R_2N groups lie in the normal range of terminal dialkylamido-fragments that we have observed for $[\text{Cp}^* \text{MCl}_{3-n}(\text{NR}_2)_n]$ ($n = 1, 2, \text{ or } 3$; $\text{M} = \text{Ti or Zr}$; $\text{R} = \text{Et or Me}$), $[\text{Cp}^* \text{MR}(\text{NMe}_2)_2]$ ($\text{M} = \text{Ti or}$

Table 1
Spectroscopic data for $[\text{Cp}^*(\text{R}_2\text{N})_2\text{Ti}(\text{OC})\text{M}(\text{CO})_2\text{Cp}]$ and 5

Compound	^1H NMR, δ^a			$^{13}\text{C}\{^1\text{H}\}$ NMR, δ^a					IR ^b $\nu(\text{CO})$
	Cp (s, 5H)	Cp* (s, 15H)	NR_2	CO	C_5Me_5	C_5Me_5	Cp	NR_2	
M = Mo; R = Me (1)	5.29	1.77	2.97 (s, 12H)	244.5 ^c 232.0	123.3	11.1	89.7	46.9	1939 1854 1569 ^c
M = W; R = Me (2)	5.19	1.79	2.97 (s, 12H)	239.1 ^c 222.6	123.1	11.1	88.1	47.0	1902 1848 1569 ^c
M = Mo; R = Et (3)	5.33	1.87	3.60, 3.29, 0.88, 20H, $^2J = 13.8$ Hz $^3J = 6.9$ Hz	244.3 ^c 232.1	123.6	11.6	89.5	47.4 14.8	1942 1859 1591 ^c
M = W; R = Et (4)	5.23	1.89	3.62, 3.29, 0.90, 20H $^2J = 13.5$ Hz $^3J = 6.6$ Hz	238.8 ^c 222.5	123.4	11.7	87.9	47.5 15.0	1934 1850 1586 ^c
$\text{Cp}^*(\text{Me}_2\text{N})_2\text{TiRu}(\text{CO})_2\text{Cp}$ (5)	4.74	1.92	3.06 (s br, 12H)	208.8	121.1	12.4	84.2	47.8 br	1963 1902 ^d
5 in toluene- d_8 at -90°C	4.49	1.90	3.600 (s, 3H) 2.840 (s, 3H) 2.801 (s, 3H) 2.800 (s, 3H)	209.3	120.6	12.4	84.1	52.7 49.9 47.1 41.3	

^a Spectra recorded in benzene- d_6 at 20°C ; δ is relative to the TMS. ^b Stretching frequencies in cm^{-1} ; in toluene solution except where noted.

^c Bridging carbonyl. ^d Hexane solution.

Zr) and $[\text{Cp}^*(\text{Me}_2\text{N})_2\text{M}(\text{O}(\text{Me}_2\text{N})\text{C})\text{M}'(\text{CO})_{n-1}]$ ($n = 6$ or 5 ; $\text{M} = \text{Ti}$ or Zr , $\text{M}' = \text{Cr}$, Mo , W or Fe) [3,7].

The overall spectroscopic data suggest monomeric structures for these complexes confirmed, in the gas phase, by mass spectrometry (Section 3).

When $[\text{Cp}^*(\text{Et}_2\text{N})_2\text{Ti}(\text{OC})\text{Mo}(\text{CO})_2\text{Cp}]$ (**3**) is dissolved in THF, the IR spectrum shows two bands in the carbonyl region at 1898 and 1783 cm^{-1} , characteristic of the free symmetrically solvated $[\text{CpMo}(\text{CO})_3]^-$ [8], and three more at 1938 , 1854 and 1592 cm^{-1} attributable to the undissociated compound. In acetonitrile only two bands, at 1896 and 1775 cm^{-1} , are present and its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CD_3CN solution at 298 K shows only one signal for CO at 236.5 ppm due to the rapid exchange between one bridge and two terminal carbonyl groups.

The reaction of $[\text{Cp}^*\text{Ti}(\text{NMe}_2)_3]$ with $[\text{CpRu}(\text{CO})_2\text{H}]$ (see Scheme 1) gave amine elimination and formation of a direct metal–metal bond between the titanium and the ruthenium atoms, rather than a bridging isocarbonyl group.

Complex **5** is stable both in solution and in the solid state under an inert atmosphere and also below 70°C , but is extremely dioxygen and water sensitive decomposing upon contact with air affording $[\text{Cp}_4^*\text{Ti}_4\text{O}_6]$ [4], $[[\text{CpRu}(\text{CO})_2]_2]$ [5b] and dimethylamine. Compound **5** also reacts with $[\text{CpM}(\text{CO})_3\text{H}]$ ($\text{M} = \text{Mo}$ or W) with cleavage of the metal–metal bond and formation of complexes **1–2** and $[\text{CpRu}(\text{CO})_2\text{H}]$ (see Scheme 1).

The IR spectrum in hexane solution of **5** shows two bands at 1963 and 1902 cm^{-1} , corresponding to two terminal carbonyl groups and the absence of ν_{CO} absorptions attributable to bridging carbonyl or isocarbonyl suggests a direct Ti–Ru bond. The two carbonyl stretching frequencies (cm^{-1}) are similar to those found for $[(\text{NMe}_2)_3\text{Ti–Ru}(\text{CO})_2(\text{Cp})]$ (1967, 1908) [9], $[(\text{Me}_2\text{N})_2(\text{RO})\text{TiRu}(\text{CO})_2(\text{Cp})]$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, 1969, 1912; Me_2HCO , 1978, 1922) [1c] and $[\text{R}(\text{SiMe}_2\text{NC}_6\text{H}_4\text{CH}_3)_3\text{Ti–Ru}(\text{CO})_2\text{Cp}]$ ($\text{R} = \text{H}$, 1990, 1932; Me , 1988, 1932) [1g] for which the presence of a direct Ti–Ru bond has been unambiguously confirmed by X-ray diffraction studies.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** shows only one signal assignable to the terminal carbonyl groups at

208.8 ppm [10]. Both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5** in C_6D_6 at 298 K show a very broad signal for the methyl groups of the Ti–NMe₂ fragments. However, when a toluene-*d*₈ solution of **5** was cooled to 183 K , the spectra showed four signals for the dimethylamido groups (see Table 1) [11] that might be consequence of the different orientation of the dimethylamido fragments around the Ti–N bonds as shown in Fig. 1.

3. Experimental details

All reactions were carried out under argon using either standard Schlenk techniques or a MBraun glove-box. Hexane, heptane and pentane were heated under reflux over Na/K amalgam, toluene over sodium, and all distilled under argon. $[\text{CpMo}(\text{CO})_3\text{H}]$ and $[\text{CpW}(\text{CO})_3\text{H}]$ were prepared by known procedures [5c] and freshly sublimed before use. $[\text{CpRu}(\text{CO})_2\text{H}]$ [5b] and $[\text{Cp}^*\text{Ti}(\text{NR})_3]$ ($\text{R} = \text{Me}$ or Et) [3a] were obtained by reported procedures.

IR spectra were measured on a Perkin Elmer 883 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Varian Unity-300 and/or Unity-500 Plus spectrometers. Electron impact mass spectra were obtained at 70 eV with a Hewlett-Packard 5890 spectrometer. C, H and N analyses were carried out with a Perkin Elmer 240 B and/or Heraeus CHN-O-Rapid microanalyzer.

3.1. Preparation of $[\text{Cp}^*(\text{Me}_2\text{N})_2\text{Ti}(\mu\text{-OC})\text{Mo}(\text{CO})_2\text{Cp}]$ (**1**)

A solution of 0.45 g (1.83 mmol) of $[\text{CpMo}(\text{CO})_3\text{H}]$ in 20 ml of toluene was added to 0.58 g (1.83 mmol) of $[\text{Cp}^*\text{Ti}(\text{NMe}_2)_3]$ in toluene (50 ml). After stirring at room temperature for 1 h , the dark red solution was filtered. Concentration to ca. 15 ml followed by cooling to -40°C for 24 h afforded red crystals of **1** in 85% yield (0.80 g). IR (KBr, cm^{-1}): 3101m , 2859s , 2772m , 1932vs , 1845vs , 1581vs-br , 1452s , 1379m , 1240m , 1130m , 1043w , 1004m , 941m , 916m , 782m , 654w , 588m , 489m , 432w , 398w . Anal. Found: C, 51.02 ; H, 6.20 ; N, 5.29% . $\text{C}_{22}\text{H}_{32}\text{MoN}_2\text{O}_3\text{Ti}$. Calc. C, 51.18 ; H, 6.25 ; N, 5.43% . MS: m/e [assignment, rel. int. (%): $516\text{ [M}^+, 2]$, $426\text{ [(M-2NHMe}_2)^+, 9]$, $381\text{ [(M-Cp}^+)^+, 5]$.

3.2. Preparation of $[\text{Cp}^*(\text{Me}_2\text{N})_2\text{Ti}(\mu\text{-OC})\text{W}(\text{CO})_2\text{Cp}]$ (**2**)

This was prepared in the same way as **1** from 0.46 g (1.38 mmol) of $[\text{CpW}(\text{CO})_3\text{H}]$ in toluene (20 ml) and 0.43 g (1.36 mmol) of $[\text{Cp}^*\text{Ti}(\text{NMe}_2)_3]$. Yield 92% (0.76 g). IR (KBr, cm^{-1}): 3103m , 2858s , 2771m , 1924vs , 1837vs , 1556vs , 1457s , 1416m , 1377m , 1240m , 1129m , 1043w , 1004w , 941s , 917s , 789m , 653w , 602s ,

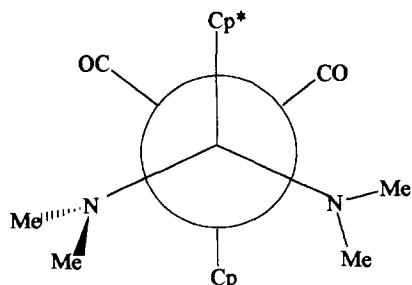


Fig. 1. Newman projection for **5**.

493s, 430w, 399m. Anal. Found: C, 43.66; H, 5.31; N, 4.52%. $C_{22}H_{32}N_2O_3TiW$ Calc. C, 43.73; H, 5.34; N, 4.64%. MS: m/e [assignment, rel. int.(%)]: 604 [M^+ , 1], 495 [($M-Cp-NMe_2$) $^+$, 3], 333 [($CpW(CO)_3$) $^+$, 3], 305 [($CpW(CO)_2$) $^+$, 16].

3.3. Preparation of [$Cp^*(Et_2N)_2Ti(\mu-OC)Mo(CO)_2Cp$] (3)

0.42 g (1.71 mmol) of [$CpMo(CO)_3H$] in 20 ml of toluene were added to a stirred solution of 0.68 g (1.70 mmol) of [$Cp^*Ti(NEt_2)_3$] in 30 ml of hexane. After 12 h at room temperature, the volatiles were removed in vacuo. The dark red oil was washed with ca. 30 ml of cold pentane and dried in vacuo to give 0.80 g (82% yield) of **3**. IR (KBr, cm^{-1}): 3107w, 2968s, 2925s, 2859s, 1937vs, 1857vs, 1589vs, 1445s, 1373m, 1344m, 1184m, 1134m, 1084m, 1059w, 996s, 881m, 861m, 783m, 663w, 587s, 487s, 427w, 394w. Anal. Found: C, 54.49; H, 7.03; N, 4.81%. $C_{26}H_{40}MoN_2O_3Ti$ Calc. C, 54.55; H, 7.04; N, 4.89%. MS: m/e [assignment, rel. int.(%)]: 572 [M^+ , 1].

3.4. Preparation of [$Cp^*(Et_2N)_2Ti(\mu-OC)W(CO)_2Cp$] (4)

The method used to prepare **3** was followed using 0.40 g (1.20 mmol) of [$CpW(CO)_3H$] and 0.48 g (1.20 mmol) of [$Cp^*Ti(NEt_2)_3$]. Red solid of **4** was obtained in 87% yield (0.69 g). IR (KBr, cm^{-1}): 3112w, 2967s, 2914s, 2857s, 1931vs, 1847vs, 1584vs, 1440s, 1377m, 1344w, 1185m, 1135m, 1086w, 1059m, 1044w, 1000s, 881m, 865m, 789s, 663m, 590s, 492s, 422m, 390w. Anal. Found: C, 47.16; H, 6.09; N, 4.24%. $C_{26}H_{40}N_2O_3TiW$ Calc. C, 47.29; H, 6.11; N, 4.24%.

3.5. Preparation of [$Cp^*(Me_2N)_2TiRu(CO)_2Cp$] (5)

A heptane solution of 1.73 mmol of [$CpRu(CO)_2H$] (prepared from 0.36 g of $Ru_3(CO)_{12}$ and 4 ml of freshly distilled cyclopentadiene) was slowly added to 0.54 g (1.71 mmol) of [$Cp^*Ti(NMe_2)_3$] in hexane. After stirring for 12 h, the yellow solution was reduced to dryness, extracted with hexane (25 ml) and the resulting red solution filtered. Cooling the solution to $-40^\circ C$ for 24 h afforded 0.44 g (52% yield) of red **5**. IR (KBr, cm^{-1}): 3047m, 2965s, 2905s, 2852s, 2765s, 1951vs, 1885vs, 1486w, 1446m, 1414m, 1375m, 1235m, 1119m, 1039m, 1010w, 933s, 789s, 734m, 562s, 506m, 403m. Anal. Found: C, 50.89; H, 6.47; N, 5.42%. $C_{21}H_{32}N_2O_2RuTi$ calc. C, 51.12; H, 6.54; N, 5.68%. MS: m/e [assignment, rel. int. (%): 493 [M^+ , 1], 448 [($M-NHMe_2$) $^+$, 1].

Acknowledgements

Financial support from the DGICYT (PB93-0476), the Comunidad Autónoma de Madrid (CAM C198/91) and the Universidad de Alcalá de Henares is gratefully acknowledged.

References and notes

- [1] (a) For a comprehensive review see: D.W. Stephan, *Coord. Chem. Rev.*, 95 (1989) 41; (b) T. Bartik, B. Happ, A. Sorkau, K.-H. Thile and G. Pályi, *Organometallics*, 8 (1989) 558; (c) W.J. Sartain and J.P. Selegue, *Organometallics*, 8 (1989) 2153; (d) C.P. Casey, *J. Organomet. Chem.*, 400 (1990) 205; (e) D.G. Dick and D.W. Stephan, *Organometallics*, 9 (1990) 1910; (f) P. Braunstein, D. Cauzzi, D. Kelly, M. Lanfranchi and A. Tiripicchio, *Inorg. Chem.*, 32 (1993) 3373; (g) S. Friedrich, H. Memmler, L.H. Gade, W.-S. Li and M. McPartlin, *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 676; (h) M. Herberhold and G.-X. Jin, *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 964; (i) J.R. Pinkes, B.D. Steffey, J.C. Vites and A.R. Cutler, *Organometallics*, 13 (1994) 21.
- [2] (a) R.T.K. Backer, S.J. Tauster and J.A. Dumesic, (eds.), *Strong Metal-Support Interactions*, American Chemical Society, Washington, DC, 1986; (b) S.A. Stevenson, J.A. Dumesic, R.T. Baker and E. Ruckenstein, (eds.), *Metal-Support Interactions in Catalysis, Sintering and Redispersion*, van Nostrand-Reinholdt, New York, 1987.
- [3] (a) A. Martín, M. Mena, P.R. Raithby, R. Serrano and C. Yélamos, *J. Organomet. Chem.*, 467 (1994) 79; (b) A.M. Irigoyen, A. Martín, M. Mena, F. Palacios and C. Yélamos, *J. Organomet. Chem.*, in press.
- [4] (a) L.M. Babcock, V.W. Day and W.G. Klemperer, *J. Chem. Soc., Chem. Commun.*, (1987) 858; (b) M.P. Gómez-Sal, M. Mena, P. Royo and R. Serrano, *J. Organomet. Chem.*, 358 (1988) 147.
- [5] (a) G. Brauer (ed.), *Handbuch der Präparativen Anorganischen Chemie*, Vol. III, Ferdinand Enke Verlag, Stuttgart, 1981, pp. 1864, 1875, 1969, and references therein; (d) E.O. Fischer, *Inorganic Synthesis*, Vol. VII, McGraw Hill, 1963, p. 136.
- [6] (a) B. Longato, B.D. Martín, J.R. Norton and O.P. Anderson, *Inorg. Chem.*, 24 (1985) 1389; (b) P.Y. Zheng, T.T. Nadasdi and D.W. Stephan, *Organometallics*, 8 (1989) 1393; (c) D.G. Dick and D.W. Stephan, *Organometallics*, 9 (1990) 1910.
- [7] M. Galakhov, A. Martín, M. Mena, F. Palacios, P.R. Raithby and C. Yélamos, *Organometallics*, 14 (1995) 138.
- [8] (a) J.A. Marsella, J.C. Huffman, K.G. Caulton, B. Longato and J.R. Norton, *J. Am. Chem. Soc.*, 104 (1982) 6360, and references therein; (b) W.J. Sartain and J.P. Selegue, *Organometallics*, 3 (1984) 1922.
- [9] W.J. Sartain and J.P. Selegue, *J. Am. Chem. Soc.*, 107 (1985) 5818.
- [10] B.E. Mann and B.F. Taylor, *^{13}C NMR Data for Organometallic Compounds*, Academic Press, New York, 1981, p. 174.
- [11] The 1H NMR spectra at 183 K gave four slightly broadened resonances at 3.600, 2.840, 2.801 and 2.800 ppm, and the saturation transfer experiments at this temperature showed exchange between the signals at 3.600 and 2.800 ppm, and also between the signals at 2.840 and 2.801 ppm.