ELSEVIER

Journal of Organometallic Chemistry 548 (1997) 309–313

Journal of Organometallic Chemistry

Short communication

Electrocatalytic process in the reduction of $\{Nb[\eta^5\text{-}C_5H_4(SiMe_3)]_2(Cl)(NHPh)\}BF_4$

Z. Modarres Tehrani [a], D. Lucas [a], Y. Mugnier [a,*], A. Antiñolo [b], A. Otero [b], M. Fajardo [c], A. Garces [c], C. Lopez-Mardomingo [c]

[a] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, associé au CNRS (UMR 5632), Faculté des Sciences, 6, Boulevard Gabriel, 21000 Dijon, France*

[b] *Departamento de Química Inorgánica, Universidad de Castilla-La Mancha, Paseo de la Universidad 4, 13071 Ciudad Real, Spain*

[c] *Departamento de Química Inorgánica y Química Orgánica, Campus Universitario, Universidad de Alcala de Henares, 28871 Alcala de Henares, Spain*

Received 30 May 1997; received in revised form 27 June 1997

Abstract

Protonation of the biscyclopentadienyl imido niobium complex $(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(Cl)(=NPh)$ affords the corresponding cationic amido complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(Cl)(NHPh)]^+$, **1**. Starting from **1**, an interesting amido group elimination reaction has been found to take place, reaction which must be electrochemically induced. © 1997 Elsevier Science S.A.

Keywords: Niobium; Protonation; Imido and amido complex; Electroreduction

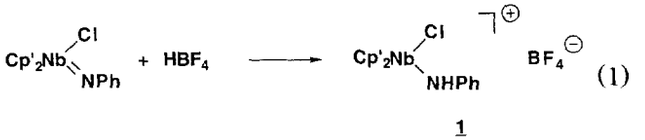
1. Introduction

Transition metal complexes having imido and oxo ligands are of continuing interest in organometallic chemistry [1–3]. An increasing number of early transition metal complexes having two-electron doubly-bonded oxo and imido ligands have been recently reported [4–9] which despite high reactivity and, in some cases, will even activate C–H [5–7].

Recently some of us described the synthesis of the imido niobocene complex $(\eta^5\text{-}C_5H_4SiMe_3)_2Nb(Cl)(=NPh)$ [10]. We now wish to present new features on the reactivity of that complex regarding protonation reaction together with a complete report of the electroreductive behaviour of the resultant cationic amido complex.

2. Results and discussion

Synthesis of the title compound, $[Cp'_2Nb(Cl)(NHPh)]BF_4$ [1], has been realized from protonation of the imido niobocene complex $Cp'_2Nb(Cl)(=NPh)$ (see Section 3). Numerous reactions of imido complexes with electrophiles have been reported where the attacking electrophile is commonly a proton [11–13]. In our case HBF_4 has been used as the proton donor according to the following reaction:



(1)

1

[1] The following abbreviations will be used within the text: THF: tetrahydrofuran; DCM: dichloromethane; TBAHFP: tetrabutylammonium hexafluorophosphate; STPB: sodium tetraphenylborate; Cp': $\eta^5\text{-}C_5H_4SiMe_3$; SCE: saturated calomel electrode; ESR: electron spin resonance; M: mol l^{-1}.

* Corresponding author.

PII S0022-328X(97)00452-X

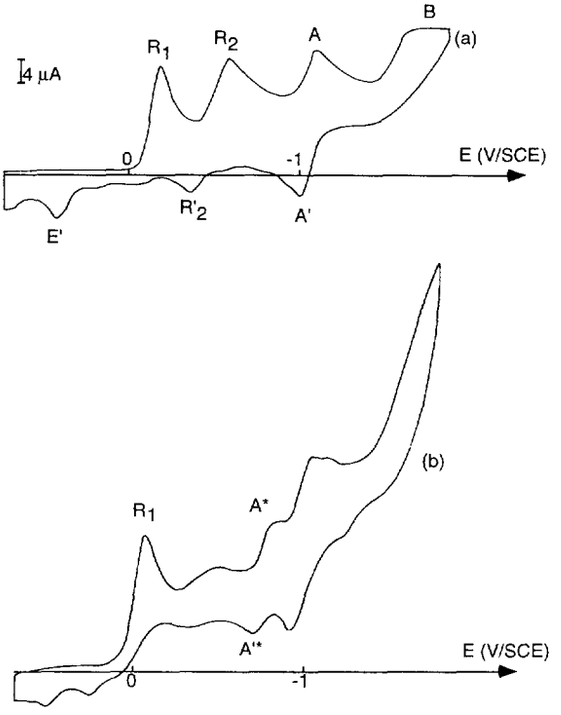
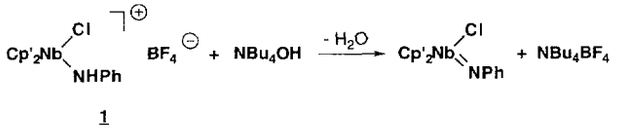


Fig. 1. Cyclic voltammogram of **1** ($c = 2$ mM) in THF 0.2 M TBAHFP on carbon disk electrode. (a) at room temperature; (b) at 40°C. Sweep rate: 50 mV s^{-1}. Initial potential: +0.7 V.

The reverse reaction can be readily achieved using a strong base like NBu_4OH:



1

(2)

In THF 0.2 M TBAHFP the cyclic voltammogram of **1** on a carbon disk electrode at room temperature (see Fig. 1a) exhibits four reduction peaks R_1, R_2, A and B ($E_{p,R_1} = -0.11$ V, $E_{p,R_2} = -0.52$ V, $E_{p,A} = -1.02$ V, $E_{p,B} \approx -1.6$ V) on the cathodic scan. Three significant peaks A', R'_2 and E' ($E_{p,A'} = -0.92$ V, $E_{p,R'_2} = -0.28$ V, $E_{p,E'} = +0.5$ V) are seen on the reverse scan when the potential sweep is inverted after peak B; A' and peaks R'_2 and E' are due to species generated along peaks A and R_2, respectively. A and E' are relevant to the reduction and oxidation of the well-known dichloro derivative Cp'_2NbCl_2, **2** [14,15].

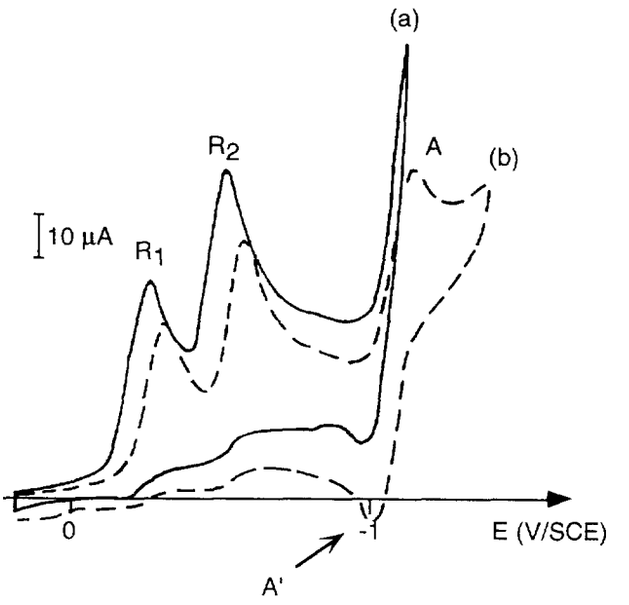


Fig. 2. Cyclic voltammogram of **1** ($c = 2$ mM) in DCM 0.2 M TBAHFP on carbon disk electrode. (a) at room temperature; (b) at −25°C. Sweep rate: 200 mV s^{-1}. Initial potential: +0.2 V.

Changes in the voltammetric profile are observed with the temperature: at 40°C R_2 intensity is significantly reduced as a new reversible system A^*/A'^* ($E_{p,A^*} = -0.83$ V, $E_{p,A'^*} = -0.72$ V) appear which is situated at slightly less negative potentials than A/A' (see Fig. 1b).

In CH_2Cl_2 0.2 M TBAHFP **1** shows the cyclic voltammogram of Fig. 2.; compared to Fig. 1a peaks R_1 and R_2 are reencountered but with no associated anodic peaks on the reverse scan; in the place of peak A a continuously increasing current is registered due to the electrochemically catalysed reduction of the chlorinated solvent as previously mentioned [16]. At low temperature (−25°C) the latter process does not take place and the well-defined reversible system A/A' is observed.

Exhaustive electrolysis on mercury pool at the potential of −0.2 V and at room temperature in THF results in the consumption of less than 1 F per mol of initial

Table 1
Coulometric data for the electrolysis of **1** on mercury pool (solute concentration: 2–3 mM)

Entry	Solvent/supporting electrolyte	T (°C)	Potential (V versus SCE)	Q (F per mol of **1**)	Electrolysis product colour
1	THF 0.2 M TBAHFP	20	−0.2	0.66	brown
2	THF 0.2 M TBAHFP	40	−0.2	0.2	green
3	DCM 0.2 M TBAHFP	0	−0.4	0.55	orange
4	THF 0.2 M STPB	20	−0.45	0.1	orange

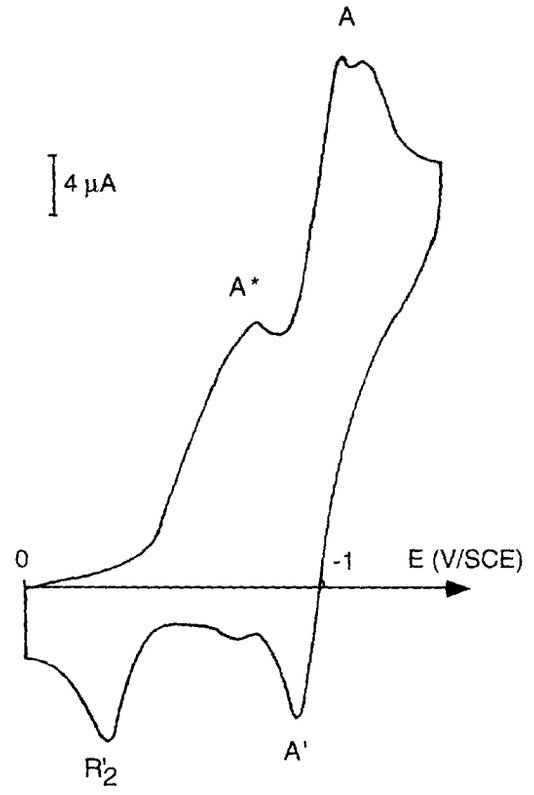


Fig. 3. Cyclic voltammogram of **1** ($c = 2$ mM) in THF 0.2 M TBAHFP on carbon disk electrode after electrolysis on mercury pool at −0.2 V. Sweep rate: 100 mV s^{-1}. Initial potential: +0 V.

complex (see Table 1, entry 1) as the solution colour turns from red to brown. The cyclic voltammogram of the electrolysed solution is depicted on Fig. 3 and exhibits two reduction peaks A^* ($E_{p,A^*} = -0.78$ V) and A and two oxidation peaks A' and R'_2 on the reverse scan. ESR analysis provides a signal which consists in the sum of two well-resolved ten-line spectra (see Fig. 4) corresponding to the presence in solution of two individual paramagnetic niobium (IV) complexes ($g_{iso,+} = 1.995$, $A_{iso,+} = 1.027 \cdot 10^{-2}$ cm^{-1} and $g_{iso,*} = 2.002$, $A_{iso,*} = 1.074 \cdot 10^{-2}$ cm^{-1}). One of the ESR signal components has been clearly attributed to Cp'_2NbCl_2, **2** (marked * on Fig. 4).

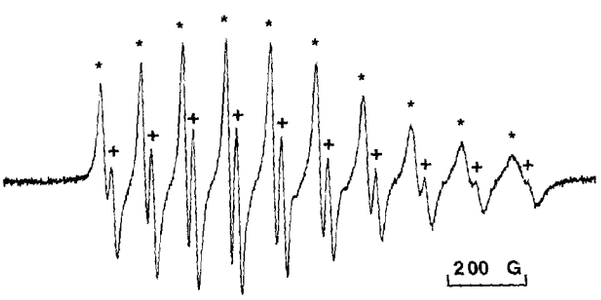


Fig. 4. ESR spectrum of **1** ($c = 2$ mM) after reduction in THF 0.2 M TBAHFP on mercury pool at −0.2 V.

When the electrolysis was carried out at higher temperature (40°C), coulometric consumption dropped to 0.2 F per mol of **1** (see Table 1, entry 2) and **2** was the only species observed by ESR analysis.

As indicated in Table 1 the coulometric consumption is highly dependent on the experimental conditions. However in each case **2** was identified as the major electrolysis product.

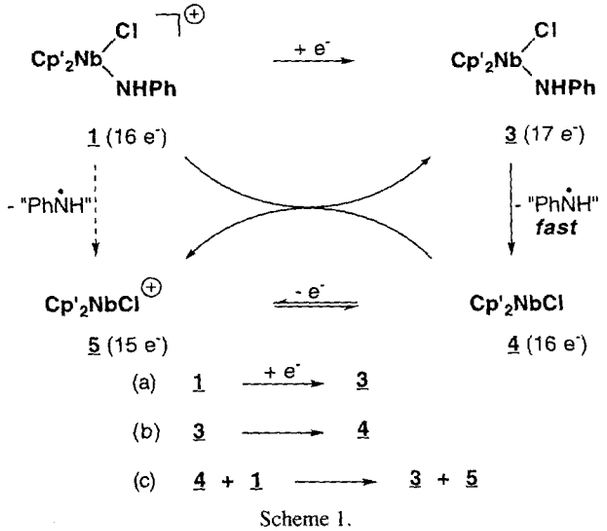
The above results can be rationalized according to Scheme 1.

This type of square scheme was first described by Jacq [17] and is often used to explain ligand exchange reactions in organometallic chemistry [17–36] [37–39]. Our mechanism would refer to the case where the electrocatalytic process is associated with an endergonic cross electron transfer propagation step [40,41].

In Scheme 1, the one-electron reduction of **1** (reaction a) affords the neutral amido niobium (IV) derivative **3** which is very unstable even in the time scale of cyclic voltammetry and rapidly dissociates into the niobium (III) complex Cp'_2NbCl, **4**, through elimination of the organic moiety formulated as 'PhNH·' with a change in the metal oxidation number from +IV to +III (b); **4** is oxidized at the potential of peak R'_2.

4 reduces **1** according to reaction (c) which is driven by the irreversible fast reaction (b).

At the time scale of cyclic voltammetry cationic species **5**, generated from reaction (c), is reduced at the potential of peak R_2. As the system A/A' is seen on Fig. 1a we can suggest that formation of **2** arises from a chloro ligand exchange reaction between electrogenerated Cp'_2NbCl and Cp'_2NbCl^+ formed along reaction (c) as it has been previously mentioned [42]. However, in the time scale of electrolysis $[Cp'_2NbCl]^+$ evolves through Eq. (3) to give Cp'_2NbCl_2, **2**, and transient



Scheme 1.

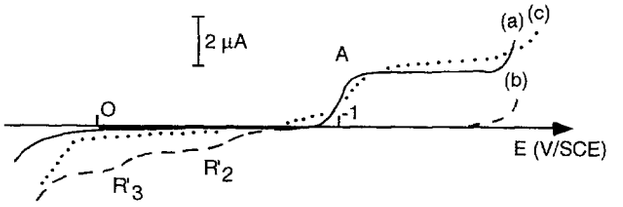


Fig. 5. Polarogram (average current) of **2** ($c = 2.5$ mM) in THF 0.2 M STPB. (a) **2** alone; (b) after reduction on mercury pool at −1 V; (c) immediately after addition of 1 molar equivalent of **1**.

species $[Cp'_2Nb]^{++}$ **6**; indeed the peak R_2 is not found after electrolysis:

$$\underset{\mathbf{5}}{2Cp'_2NbCl^+} \rightarrow \underset{\mathbf{2}}{Cp'_2NbCl_2} + \underset{\mathbf{6}}{Cp'_2Nb^{++}} \quad (3)$$

At room temperature these two paramagnetic species are detected from ESR analysis of the electrolysed solution. Only four dicationic paramagnetic niobocene compounds, $[Cp'_2Nb(L)_2]^{2+}$ [Cp' = η^5-$C_5H_4(SiMe_3)$, L = $P(OMe)_3$ and MeCN] [43] and $[Cp_2Nb(L)]PF_6$ [Cp = η^5-C_5H_5, L = bipyridine or *o*-phenanthroline] [44] and few monocationic analogues [45,46] have previously been reported.

At higher temperature (40°C) the only characteristic signal of Cp'_2NbCl_2 is seen in ESR spectroscopy. Under these experimental conditions and in the absence of suitable ligands, **6** which is probably reduced at the potential of peak A^*, should be very unstable and its decomposition occurs.

The amido radical PhNH · has been previously postulated as an intermediate in the reaction of decomposition of phenyl azide in aliphatic hydrocarbons leading aniline, alkylamine, azobenzene and polymers [47,48]. The first step consists in the formation of a nitrene (singlet or triplet) which offers many reaction possibilities [49,50].

With the aim of proving reaction c, we have carried out the following experiment: **4** has been electrogenerated from one-electron reduction of **2** in THF 0.2 M $NaBPh_4$ as supporting electrolyte [51]. In polarography **4** exhibits two oxidation waves R'_2 and R'_3 (Fig. 5b). The addition of cationic species **1** in equivalent amount causes R'_2 and R'_3 to disappear and reduction wave A to appear (Fig. 5c) indicating that Cp'_2NbCl_2, **2**, is effectively formed (also verified from ESR).

3. Experimental details

3.1. Preparation of $(\eta^5$-$C_5H_4SiMe_3)_2NbCl(NHPh)^+$-$BF_4^-$, 1

To a solution of 0.50 g (1.00 mmol) of $(C_5H_4SiMe_3)_2NbCl(NPh)$ in 50 ml of diethyl ether, 0.18 ml (1.08 mmol) of $HBF_4 \cdot OEt_2$ 6 M was added dropwise at 0°C until complete precipitation of the title compound. Yield: 69%.

^{1}H NMR (CD_3CN, 300 MHz): d 0.23 (s, 18H, $SiMe_3$), 6.90 (4H), 7.11 (4H)(m, $C_5H_4SiMe_3$), 7.20 (d, 2H), 7.30 (m, 1H), 7.49 (7, 2H)(phenyl ring), 12.79 (broad, 1H, NHC_6H_5)

Acknowledgements

The authors acknowledge financial support from Direccíon General de Investigación Científica y Tecnica (DGICyT). (Grant No. PB92-0715) of Spain, from Electricité de France (EDF—Club Electrochimie Organique de France) and Conseil Régional de Bourgogne. We thank M. Compain for her technical assistance.

References

[1] W.A. Nugent, J.M. Mayer, Metal–ligand Multipled Bonds, Wiley, New York, 1988.
[2] W.A. Nugent, B.L. Haymore, Coord. Chem. Rev. 31 (1980) 123.
[3] D.E. Wigley, Prog. Inorg. Chem. 42 (1994) 239.
[4] G. Parkin, J.E. Bercaw, J. Am. Chem. Soc. 111 (1989) 391.
[5] C.C. Cummins, S.M. Baxter, P.T. Wolczanski, J. Am. Chem. Soc. 110 (1988) 8731.
[6] P.J. Walsh, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 110 (1988) 8729.
[7] C.C. Cummins, C.P. Schaller, G.D. Van Duyne, P.T. Wolczanski, A.W.E. Chan, R. Hoffmann, J. Am. Chem. Soc. 113 (1991) 2985.
[8] C.P. Schaller, P.T. Wolczanski, Inorg. Chem. 32 (1993) 131.
[9] R.S. Huber, T.C. Baldwin, D.E. Wigley, Organometallics 12 (1993) 91.
[10] A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. Lopez-Mardomingo, A. Martin-Alonso, A. Otero, J. Chem. Soc., Dalton Trans. (1995) 1007.
[11] J.M. Mayer, C.J. Curtis, J.E. Bercaw, J. Am. Chem. Soc. 105 (1983) 2651.
[12] W.A. Herrmann, G. Weichselbaumer, R.A. Paciello, R.A. Fisher, E. Herdweck, J. Okuda, D. Marz, Organometallics 9 (1990) 489.
[13] R. Toreki, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 114 (1992) 3367.
[14] H. Nabaoui, A. Fakhr, Y. Mugnier, A. Antiñolo, M. Fajardo, A. Otero, P. Royo, J. Organomet. Chem. 338 (1988) C17.
[15] A. Antiñolo, M. Fajardo, A. Otero, Y. Mugnier, H. Nabaoui, Y. Mourad, J. Organomet. Chem. 414 (1991) 155.
[16] A. Fakhr, Y. Mugnier, A. Antiñolo, A. Otero, M. Fajardo, J. Organomet. Chem. 346 (1988) C49.
[17] J. Jacq, J. Electroanal. Chem. Interfacial Electrochem. 29 (1971) 191.
[18] R.D. Rieke, H. Kojima, D. Ofele, J. Am. Chem. Soc. 98 (1976) 6735.
[19] G. Pilloni, G. Zotti, C. Corvaja, M. Martelli, J. Electroanal. Chem. Interfacial Electrochem. 91 (1978) 395.
[20] R.A. Rader, D.R. McMillin, Inorg. Chem. 18 (1979) 546.
[21] J. Moraczewski, W.E. Geiger, J. Am. Chem. Soc. 101 (1979) 3407.

[22] A.M. Bond, J. Electroanal. Chem. Interfacial Electrochem. 50 (1974) 285.
[23] A.M. Bond, R. Colton, J.J. Jackowski, Inorg. Chem. 14 (1975) 275.
[24] A.M. Bond, R. Colton, M.J. Mc Cormick, Inorg. Chem. 16 (1977) 155.
[25] A.M. Bond, B.S. Grabaric, Z. Grabaric, Inorg. Chem. 17 (1978) 103.
[26] A.M. Bond, D.J. Darensbourg, E. Mocellin, B.J. Stewart, J. Am. Chem. Soc. 103 (1981) 6827.
[27] A.M. Bond, S.W. Carr, R. Colton, Inorg. Chem. 23 (1984) 2343.
[28] A.M. Bond, S.W. Carr, R. Colton, Organometallics 3 (1984) 541.
[29] A.M. Bond, S.W. Carr, J.E. Kavekordes, Inorg. Chem. 25 (1986) 749.
[30] F.L. Wimmer, M.R. Snow, A.M. Bond, Inorg. Chem. 13 (1974) 1617.
[31] A.M. Bond, B.S. Grabarid, J.J. Jackowski, Inorg. Chem. 17 (1978) 2153.
[32] Y. Mugnier, C. Moise, E. Laviron, J. Organomet. Chem. 204 (1981) 61.
[33] Y. Mugnier, C. Moise, E. Laviron, Nouv. J. Chim. 6 (1982) 197.
[34] A. Fakhr, Y. Mugnier, R. Broussier, B. Gautheron, E. Laviron, J. Organomet. Chem. 255 (1983) C8.
[35] A. Vallat, M. Person, L. Roullier, E. Laviron, Inorg. Chem. 26 (1987) 232.
[36] D. Faure, D. Lexa, J.M. Savéant, J. Electroanal. Chem. Interfacial Electrochem. 140 (1982) 265.
[37] D. Lexa, P. Reutien, J.M. Savéant, F. Xu, J. Electroanal. Chem. 191 (1985) 253.
[38] D. Lexa, J.M. Savéant, Acc. Chem. Res. 16 (1983) 235.
[39] J.M. Savéant, Acc. Chem. Res. 13 (1980) 323.
[40] C. Amatore, J.N. Verpeaux, A. Madonik, M.H. Desbuis, D. Astruc, J. Chem. Soc., Chem. Commun. (1988) 200.
[41] A. Da Rold, Y. Mugnier, R. Broussier, B. Gautheron, E. Laviron, J. Organomet. Chem. 369 (1989) C27.
[42] H. Nabaoui, Y. Mugnier, A. Fakhr, E. Laviron, A. Antiñolo, F.A. Jalon, M. Fajardo, A. Otero, J. Organomet. Chem. 375 (1989) 67.
[43] L. Roullier, D. Lucas, Y. Mugnier, A. Antiñolo, M. Fajardo, A. Otero, J. Organomet. Chem. 396 (1990) C12.
[44] M.A.A.F. de C.T. Carrondo, J. Morais, C.C. Romao, L.F. Veiros, XVth Congress and General Assembly of IUG, Bordeaux, 1990
[45] J. Arnolt, T.D. Tilley, A.L. Rheingold, S.J. Geib, Organometallics 6 (1987) 473.
[46] A. Fakhr, Y. Mugnier, R. Broussier, B. Gautheron, J. Organomet. Chem. 375 (1989) 67.
[47] J.H. Hall, J.W. Hill, J.M. Fargher, J. Am. Chem. Soc. 90 (1968) 5313.
[48] J.H. Hall, J.W. Hill, H. Tsai, Tetrahedron Lett. (1965) 2211.
[49] B. Iddon, O. Meth-Cohn, E.F.V. Scriver, H. Suschitzky, P.T. Gallagher, Angew. Chem., Int. Ed. Engl. 18 (1979) 900.
[50] R.A. Aitken, in: A.C. Knipe, W.E. Watts (Eds.), Organic Reaction Mechanism, Wiley, 1990, p. 285.
[51] D. Lucas, Y. Mugnier, A. Antiñolo, M. Fajardo, A. Otero, J. Organomet. Chem. 435 (1992) C3–C7.