

Synthesis and reactivity of alkynyl niobocene complexes

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Abstract

The synthesis of alkynyl containing niobocene complexes with differing auxiliary ligands is described. The niobium(III) derivatives of the general formula $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CR})(\text{L})]$ where L is either carbonyl, phosphine, phosphite, or isocyanide, were prepared by the reaction of the bis(alkynyl)magnesium reagent with the corresponding chloro-niobocene precursor. In a similar manner the niobium(V) imido compounds, of the general formula, $[\text{Nb}(=\text{NR}')(\eta^5\text{-C}_5\text{H}_4\text{R}'')_2(\text{C}\equiv\text{CR})]$, were prepared. The characterization of these complexes is discussed. The reactivity of the alkynyl compounds towards oxidation and protonation has been studied.

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1. Introduction

The chemistry of d-block transition metals with alkynyl [1], vinylidene [2], and alkyne [3] ligands have been well documented with the main focus being on the late transition elements. Early transition metal alkynyl chemistry has centred on the group 4 elements titanium and zirconium. The reactivity studies have been concentrated on 'tweezer complexes' and the formation by coordination to the unsaturated alkynyl C–C triple bonds of late transition metals to give hetero early-late dinuclear compounds. Lang et al. have recently published an extensive review in this field [4]. Despite this abundance of group 4 metal alkynyl complexes, little work has been carried out into the reactivity taking place (i.e. protonation) directly at the C–C triple bond and coupled with the limited redox chemistry of the group 4 compounds means that they cannot be directly

compared with our reactivity studies of group 5 metal alkynyl complexes, discussed in this paper.

During the past few years several families of alkyne niobocene complexes have been reported by our group [5]. Following from this work, we have expanded our research into the synthesis and reactivity of alkynyl containing niobocene complexes and in this paper we present a review of our work in this field [6]. In addition, we include the synthesis and characterization of some previously unpublished alkynyl niobocene complexes.

2. Results and discussion

2.1. Synthesis of alkynyl niobocene complexes

The reaction of the Grignard reagent $\text{BrMg}(\text{C}\equiv\text{CMe})$ with $[\text{Nb}(=\text{NBu}^1)(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}]$ gave the alkynyl complex $[\text{Nb}(=\text{NBu}^1)(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}\equiv\text{CMe})]$ (**1**) as the unique product (Eq. (1)). However, this was the only case in which the reaction yielded the desired alkynyl product and when this substitution reaction was repeated with

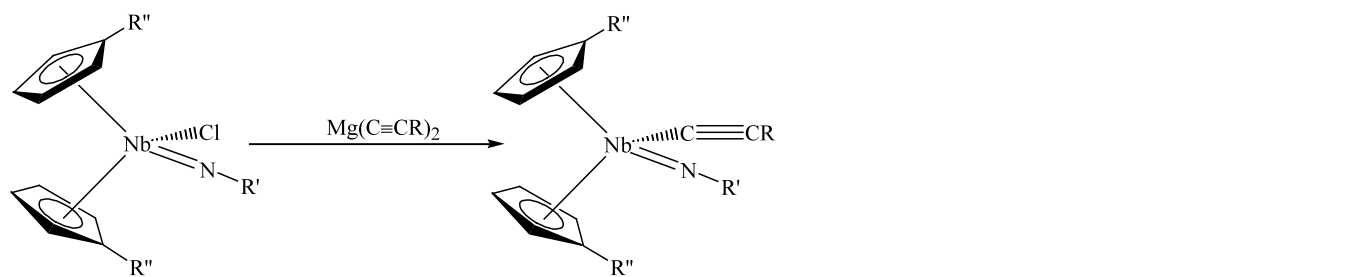
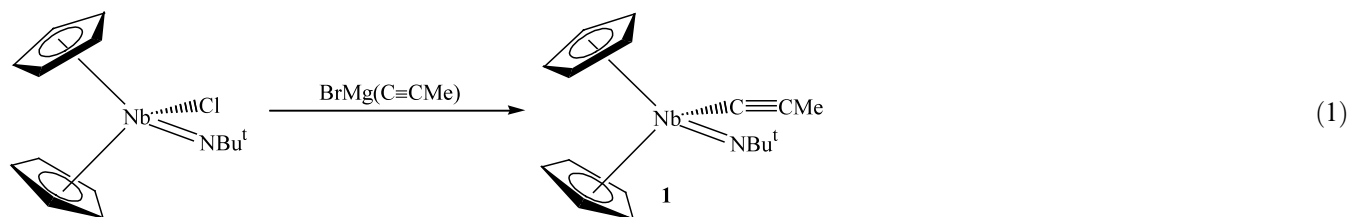
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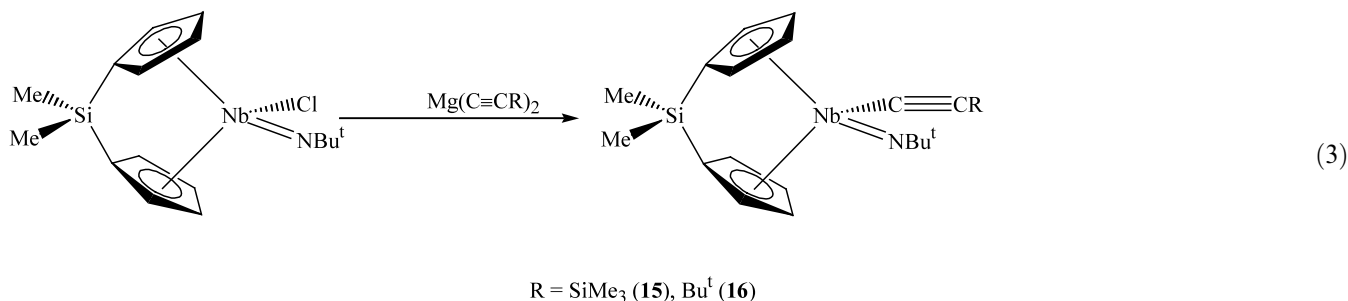
other starting niobocene chloride complexes, and with a variety of Grignard alkynyl reagents the reaction proved to be unsuccessful. However, good results were obtained when bis-alkynyl magnesium derivatives, $\text{Mg}(\text{C}\equiv\text{CR})_2$, were used in this process. The magnesium bis-alkynyl compounds are normally more reactive than their Grignard counterparts and in the synthesis of the alkynyl derivatives this factor is critical to avoid contamination of the desired product with unreacted starting material. We have observed that when the reactions were carried out in refluxing THF the process did not always go to completion and a mixture of both starting material and the corresponding alkynyl-containing complex was isolated. This is probably due to the partial deactivation of $\text{Mg}(\text{C}\equiv\text{CR})_2$ caused by THF coordination. This problem was overcome by conducting all the reactions in a non-coordinating solvent, such as toluene. In this solvent, the corresponding reactions at 100 °C afford the alkynyl complexes, $[\text{Nb}(=$

$\text{NBu}^t)(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}\equiv\text{CR})]$ ($\text{R}=\text{SiMe}_3$ (**2**), Bu^t (**3**), CH_2Ph (**4**)), $[\text{Nb}(=\text{NC}_6\text{H}_4\text{Me-4})(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}\equiv\text{CR})]$ ($\text{R}=\text{SiMe}_3$ (**5**), Bu^t (**6**)), $[\text{Nb}(=\text{NBu}^t)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CR})]$ ($\text{R}=\text{SiMe}_3$ (**7**), Bu^t (**8**)), $[\text{Nb}(=\text{NPh})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CR})]$ ($\text{R}=\text{Ph}$ (**9**), Bu^t (**10**)), $[\text{Nb}(=\text{NC}_6\text{H}_4\text{Me-4})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CR})]$ ($\text{R}=\text{SiMe}_3$ (**11**), Bu^t (**12**)), $[\text{Nb}(=\text{NC}_6\text{H}_4\text{OMe-4})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CR})]$ ($\text{R}=\text{SiMe}_3$ (**13**), Bu^t (**14**)), which were obtained, after appropriate work up, as air-sensitive yellow crystalline solids uncontaminated by starting materials (Eq. (2)).

In order to prepare *ansa*-niobocenes containing simultaneously both imido and alkynyl ligands, we have carried out analogous reactions to those described in the preparation of **2–14**. Thus the reactions of the appropriate starting materials with the corresponding $\text{Mg}(\text{C}\equiv\text{CR})_2$ reagents gave rise to the isolation of complexes $[\text{Nb}(=\text{NBu}^t)\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\}(\text{C}\equiv\text{CR})]$ ($\text{R}=\text{SiMe}_3$ (**15**), Bu^t (**16**)), (Eq. (3)).

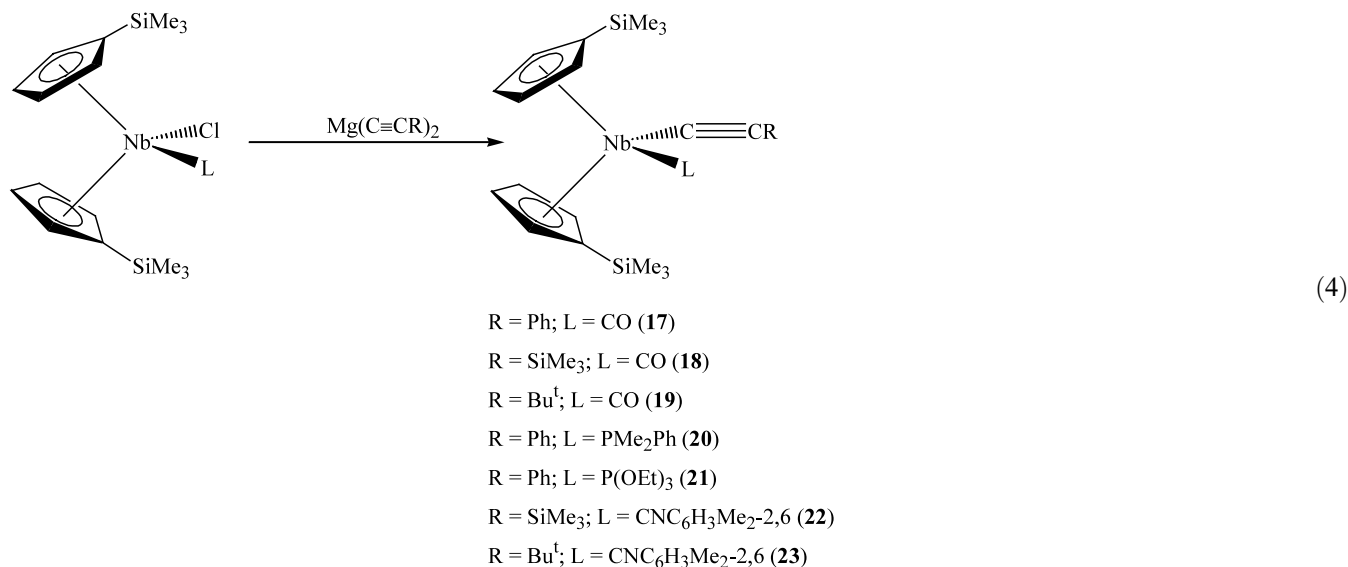


- $\text{R}'' = \text{H}; \text{R}' = \text{Bu}^t; \text{R} = \text{SiMe}_3$ (**2**)
 $\text{R}'' = \text{H}; \text{R}' = \text{Bu}^t; \text{R} = \text{Bu}^t$ (**3**)
 $\text{R}'' = \text{H}; \text{R}' = \text{Bu}^t; \text{R} = \text{CH}_2\text{Ph}$ (**4**)
 $\text{R}'' = \text{H}; \text{R}' = \text{C}_6\text{H}_4\text{Me-4}; \text{R} = \text{SiMe}_3$ (**5**)
 $\text{R}'' = \text{H}; \text{R}' = \text{C}_6\text{H}_4\text{Me-4}; \text{R} = \text{Bu}^t$ (**6**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{Bu}^t; \text{R} = \text{SiMe}_3$ (**7**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{Bu}^t; \text{R} = \text{Bu}^t$ (**8**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{Ph}; \text{R} = \text{Ph}$ (**9**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{Ph}; \text{R} = \text{Bu}^t$ (**10**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{C}_6\text{H}_4\text{Me-4}; \text{R} = \text{SiMe}_3$ (**11**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{C}_6\text{H}_4\text{Me-4}; \text{R} = \text{Bu}^t$ (**12**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{C}_6\text{H}_4\text{OMe-4}; \text{R} = \text{SiMe}_3$ (**13**)
 $\text{R}'' = \text{SiMe}_3; \text{R}' = \text{C}_6\text{H}_4\text{OMe-4}; \text{R} = \text{Bu}^t$ (**14**)



In a similar manner the niobocene (III) alkynyl complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CR})(\text{L})]$ (R = Ph, L = CO (**17**); R = SiMe₃, L = CO (**18**); R = Bu^t, L = CO (**19**); R = Ph, L = PMe₂Ph (**20**); R = Ph, L = P(OEt)₃ (**21**); R = SiMe₃, L = CNC₆H₃Me_{2-2,6} (**22**); R = Bu^t, L = CNC₆H₃Me_{2-2,6} (**23**)) were prepared (Eq. (4)) (See Section 3 for preparation and characterization of the new compounds **22** and **23**). The contrasting electron effects exerted by the different types of ligands should be the primary factor in the reactivity of the alkynyl complexes.

$[\text{Li}(\text{C}\equiv\text{CH})(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)]$, or Grignard reagents, such as MgCl(C≡CH) in THF, were employed as alternatives, but their reaction with $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{L})]$ under a variety of experimental conditions led to the starting material as the only organometallic product to be isolated from the reaction. To overcome this problem, we sought to desilylate the alkynyl ligand of **18** by reaction with Bu₄NF in THF [7]. However, the complex, $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}\equiv\text{CSiMe}_3)(\text{CO})]$ (**24**), in which the cyclopentadienyl rings have been desilylated, was isolated instead (Eq. (6)). A further desilylation of



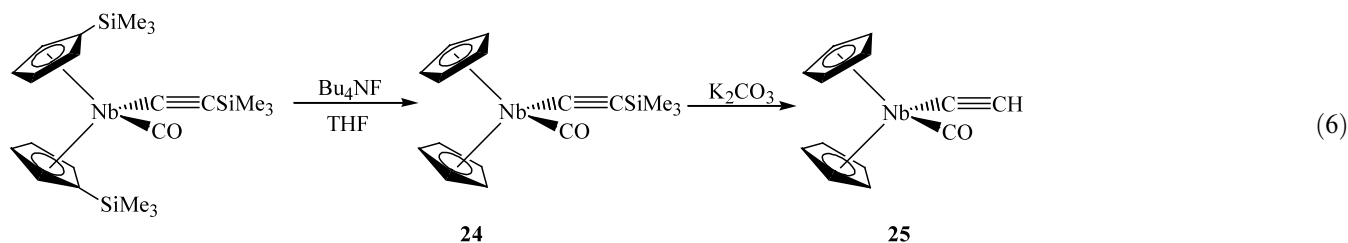
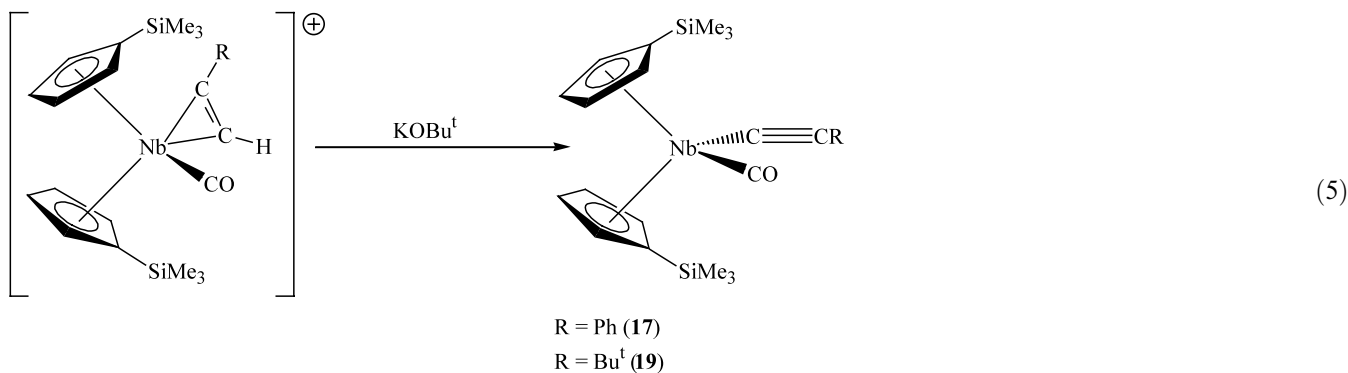
Alternatively the synthesis of the alkynyl compounds **17** and **19** can be achieved by the treatment of the cationic alkyne niobium complexes with KOBu^t (Eq. (5)).

The general procedures described for the preparation of alkynyl niobocene complexes does not, however, allow the synthesis of terminal alkynyl species (R = H), since the preparation of the reagent Mg(C≡CH)₂ is not possible. Different lithium reagents, such as

24 using K₂CO₃ in methanol [8] was successful, giving the terminal alkynyl-containing complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}\equiv\text{CH})(\text{CO})]$ (**25**) (Eq. (6)).

2.2. Characterization of alkynyl niobocene complexes

1–25 were characterized spectroscopically. IR spectroscopy showed a band, at 2050–2110 cm⁻¹, assigned to the ν(C≡C) of the alkynyl ligand and for the imido



complexes, **1–16**, a band between 1230 and 1300 cm^{-1} characteristic of the terminal imido ligand [9]. In addition the carbonyl containing complexes, **17**, **18**, **24** and **25**, one band was observed in the IR spectra between 1890 and 1950 cm^{-1} corresponding to $\nu(\text{CO})$ and for the isocyanide derivatives **22** and **23** at 2279 and 2034 cm^{-1} , respectively, corresponding to $\nu(\text{C}\equiv\text{N})$. The ^1H NMR spectra of the unsubstituted cyclopentadienyl complexes **1–6** exhibited the expected singlet for the cyclopentadienyl ligand. In addition for **1–3**, **5** and **6** singlets were observed for the alkynyl substituents Me, SiMe₃ or Bu^t and in the case of **4** where R=CH₂Ph a singlet was observed for the CH₂ protons and various multiplets for the phenyl ring. When the trimethylsilyl substituted cyclopentadienyl complexes **7–14** and **17–23** are considered their ^1H NMR spectra are similar to those of their unsubstituted analogues. The C_s symmetry of **7–14** and **17–23** results in the appearance of four multiplets for the C₅ ring protons. In addition, the ^{13}C NMR spectra of all these complexes show two characteristic resonances for the alkynyl C_α and C_β carbons at ca. 110 and 128 ppm, respectively. Furthermore, in the carbonyl and isocyanide containing complexes the resonance of the carbonyl carbon atom appears at ca. 250 ppm and for the isocyanide carbon at ca. 230 ppm.

The molecular structure of [Nb(=NPh)(η⁵-C₅H₄SiMe₃)₂(C≡CPh)] (**9**) was established by X-ray crystal diffraction studies and is the only example of a group 5 alkynyl complex. The molecular structure is shown in Fig. 1. **9** presents a typical bent metallocene structure with two additional ligands. Both cyclopentadienyl rings are η⁵ bonded to the metal with the Cent–Nb–Cent angle of 128.2°. The alkynyl ligand is sigma bonded to the metal as indicated by the C(1)–C(2)

distance of 1.20(1) Å which is typical for a C–C triple bond and the Nb–C(1)–C(2) angle of 177.9(6)° whose linear nature confirms that the C(1) and C(2) atoms are sp hybridized. The Nb–N bond distance of 1.804(5) Å, is at the upper limit for those observed for niobium imido complexes (1.73–1.80 Å) and is indicative of a Nb–N triple bond [10].

The near linear nature of the imide ligand indicates that it acts as a four electron donor and thus the formal electron count of **9** is 20 electrons with the excess 2 electrons probably being located in a non-bonding orbital similar to that proposed by Green et al. for [Mo(=NBu^t)(η⁵-C₅H₅)₂] [11].

2.3. Reactivity of alkynyl niobocene complexes

We have considered the chemical oxidation processes of complexes **17**, **19** and **20** with the ferrocenium salt [FeCp₂][BPh₄] and in the course of these studies, we observed that the nature of the resulting products depended dramatically on the substituent R on the alkynyl ligand, the ancillary ligand L, and the experimental conditions employed (temperature and solvent).

Thus when **17**, **19**, and **20** were reacted with the ferrocenium salt in a 1:1 molar ratio, in CH₂Cl₂ at –30 °C, the reaction gave the radical cationic alkynyl complexes [Nb(η⁵-C₅H₄SiMe₃)₂(C≡CR)(L)]^{•+}[BPh₄][–] (R=Ph, L=CO (**26**); R=Bu^t, L=CO (**27**); R=Ph, L=PMe₂Ph (**28**)) (Eq. (7)). The species **26** and **27** were unstable, giving rise to the corresponding monovinylidene complexes [Nb(η⁵-C₅H₄SiMe₃)₂(=C=CHR)(L)]^{•+}[BPh₄][–] (R=Ph, L=CO (**29**); R=Bu^t, L=CO (**30**)), which result from a hydrogen abstraction from the solvent (Eq. (8)). **29** was isolated as a 1:1 mixture of both the exo and

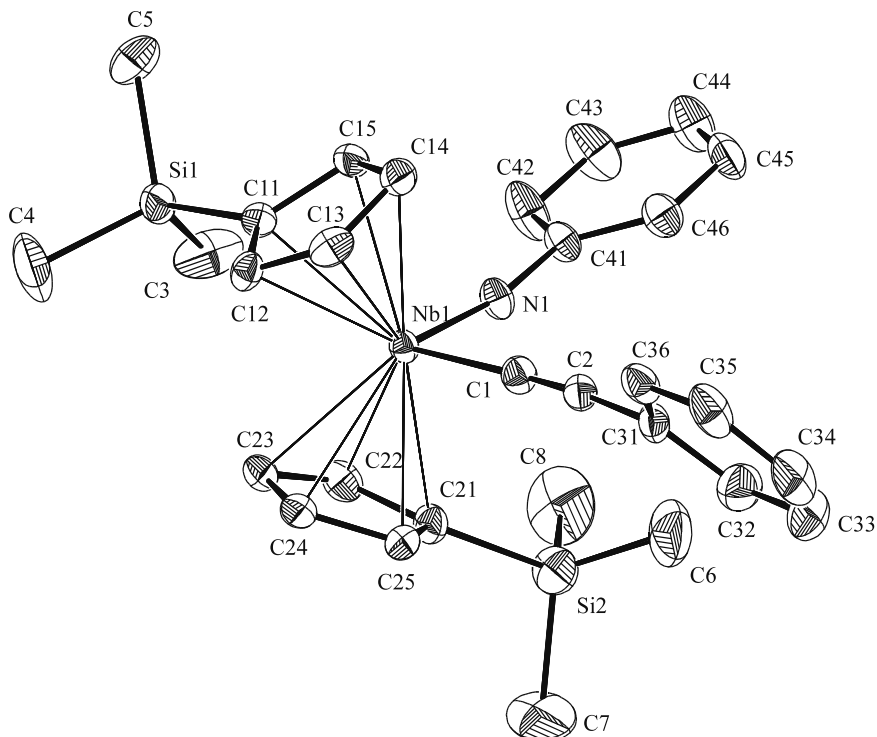


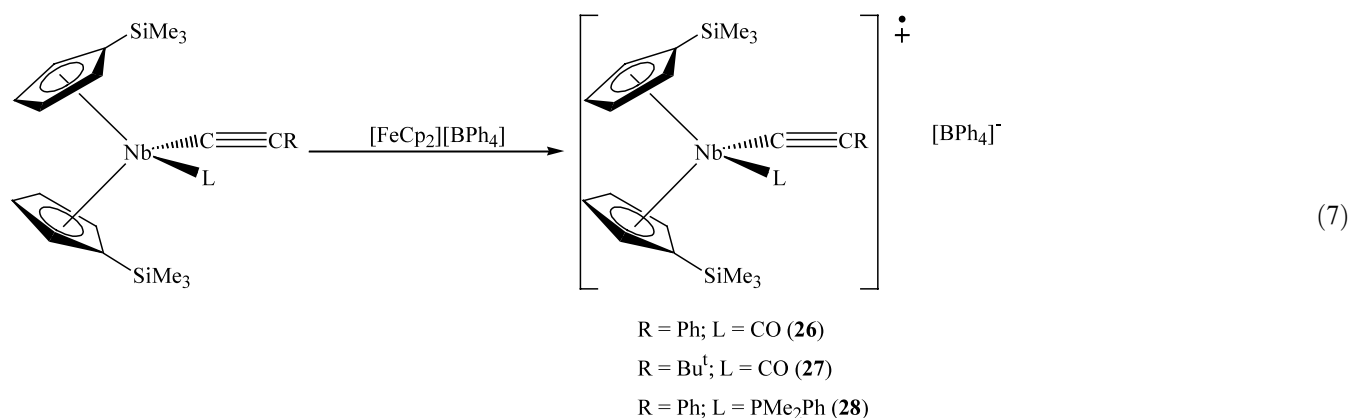
Fig. 1. Molecular structure of $[\text{Nb}(=\text{NPh})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CPh})]$ (**9**).

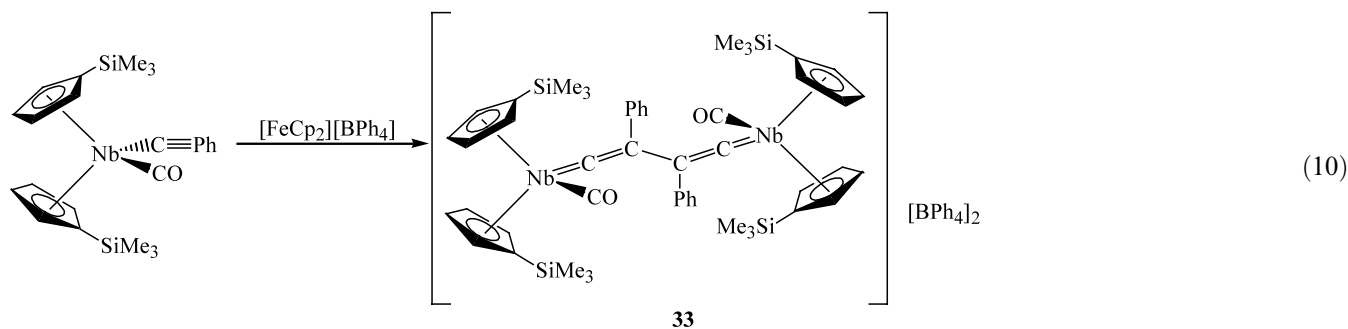
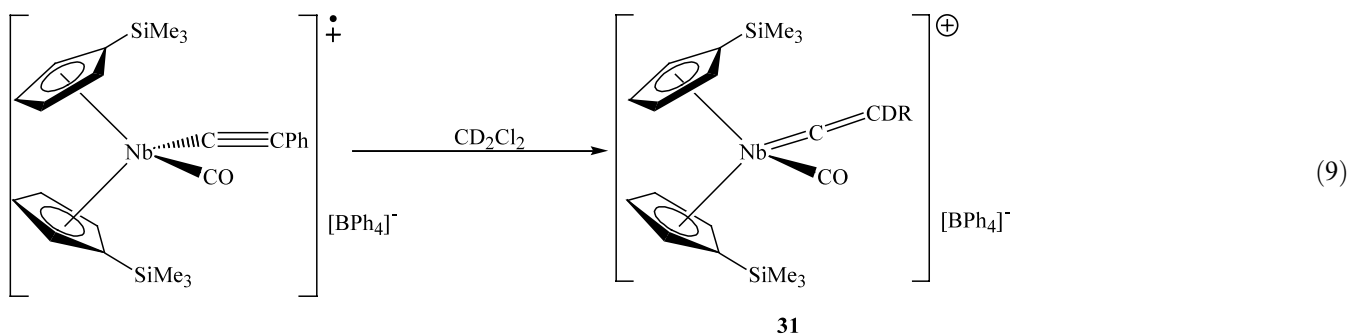
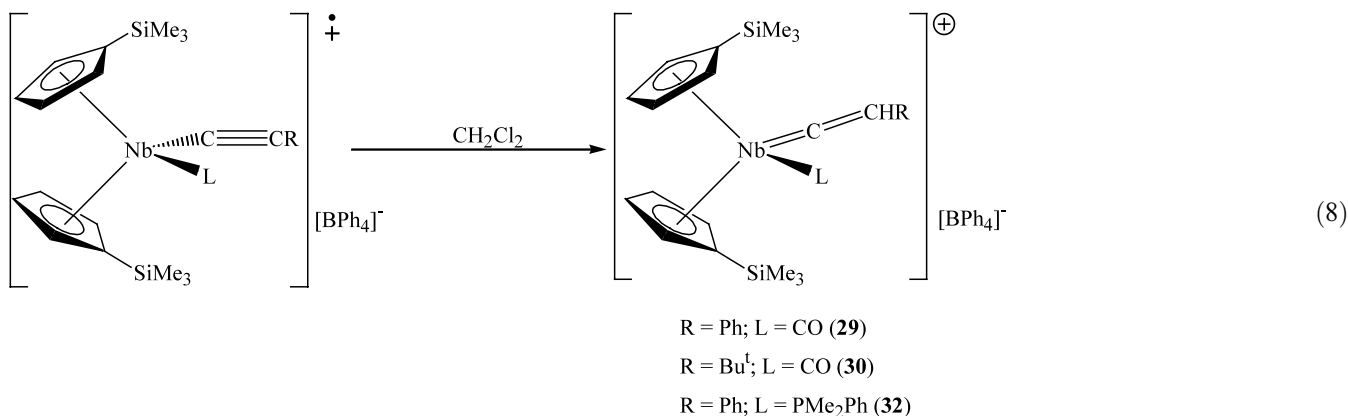
endo isomers and **30** as a single isomer. To confirm this abstraction process, the oxidation of **17** was carried out in dry CD_2Cl_2 at -40°C and the deuterated complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(=\text{C}=\text{CDPh})(\text{CO})][\text{BPh}_4]$ (**31**) (Eq. (9)) was isolated (as established by a ^2H NMR spectroscopy), proving that the solvent is the source of the H^\bullet (or D^\bullet) radical.

Compound **28**, however, was stable under these experimental conditions and was isolated as a deep red crystalline material after appropriate workup. Solutions of **28** in CH_2Cl_2 evolve slowly at room temperature to give, after several weeks, the monovinylidene complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(=\text{C}=\text{CHPh})(\text{PMe}_2\text{Ph})][\text{BPh}_4]$ (**32**)

(Eq. (8)). Some related mononuclear vinylidene tantalocene and niobocene complexes have previously been described [6c,12].

However, when the oxidation of **17** was carried out in THF at room temperature, an alternative product, the divinylidene complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{CO})\text{Nb}=\text{C}=\text{C}(\text{Ph})(\text{Ph})\text{C}=\text{C}=\text{Nb}(\text{CO})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2][\text{BPh}_4]_2$ (**33**) was obtained (Eq. (10)). Surprisingly, the formation of the corresponding divinylidene species from compounds **19** and **20** has never been observed, even though the oxidation has been attempted under a wide variety of conditions. The formation of the divinylidene species **33** can be envisaged as being the result of a ligand–ligand





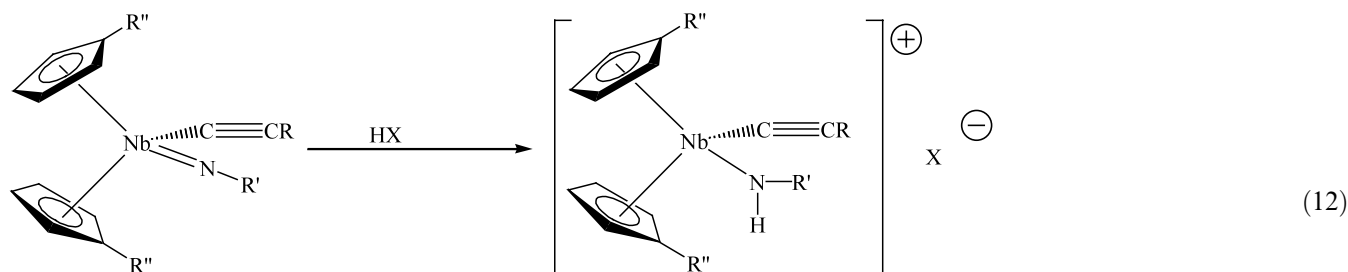
coupling reaction from the radical cationic alkyne species **26** instead of the alternative process of hydrogen atom abstraction. The chemistry of 17-electron organometallic radicals is well-documented, and their often characteristic chemical properties continue to be reported [13]. It is well-known that several organometallic radicals tend to dimerize and that dimerization through the metal centre is most often observed. Nevertheless, the ligand–ligand coupling could be favoured if the metal centre is sterically protected and if one of the ligands possesses a π -system to enable the delocalization of the spin density. Thus, Lapinte and co-workers have demonstrated that the iron–ethynyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{C}\equiv\text{CH})(\text{dppe})]$ reacts with $[\text{FeCp}_2][\text{PF}_6]$ to give a divynylidene complex through a ligand–ligand coupling step [14]. However, they observed that the analogous substituted alkyne complexes $[\text{Fe}(\eta^5\text{-$

$\text{C}_5\text{Me}_5)_2(\text{C}\equiv\text{CR})(\text{dppe})]$ ($R = \text{Ph}, \text{Bu}^t$) did not undergo dimerization or hydrogen atom abstraction, and the 17-electron radical cationic alkyne complexes $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{C}\equiv\text{CR})(\text{dppe})]^+[\text{PF}_6]^-$ could be isolated as air-stable solids. The low reactivity of these complexes was explained on the basis of the steric hindrance of the substituent attached to the alkyne carbon atom [15]. In our case, the 17-electron radical species **26** and **27** were unstable, and this could be due to the fact that the substituents on the alkyne group did not provide sufficient steric protection to prevent the transformation to the corresponding vinylidene complexes **4**. This process of hydrogen atom abstraction has been established in the evolution of several organometallic radicals [16].

Furthermore, complexes **29**, **30** and **32** could alternatively be prepared by the protonation with HBF_4 of

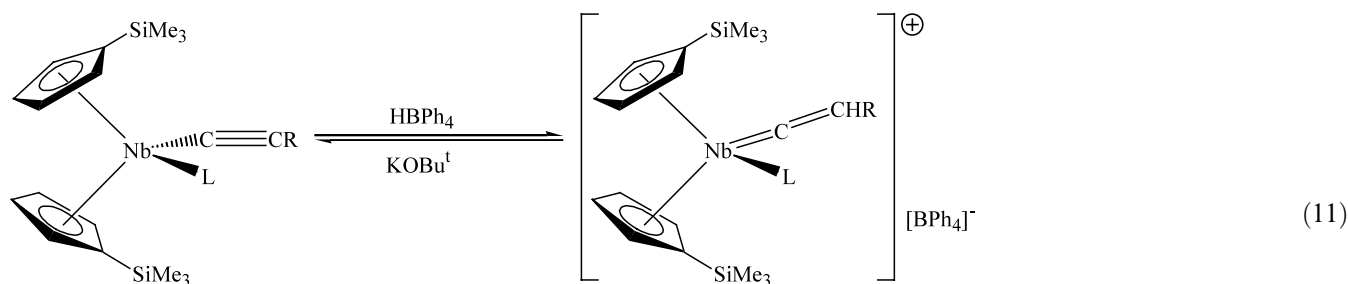
complexes **17**, **19** and **20**, respectively (Eq. (11)). This protonation reaction is reversible, and treatment of **29**, **30** or **32** with KOBU^t quantitatively gives **17**, **19** or **20**, respectively (Eq. (11)).

species $[\text{Nb}(\text{NHBu}^t)(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}\equiv\text{CSiMe}_3)]^+$ (**34**) and $[\text{Nb}(\text{NHPh})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CPh})]^+$ (**35**). The complexes were isolated as red crystalline very air-sensitive solids after appropriate work-up. **34**–**35** were character-



$\text{R} = \text{SiMe}_3$; $\text{R}' = \text{Bu}^t$; $\text{R}'' = \text{H}$; $\text{X} = \text{CF}_3\text{COO}$ (**34**)

$\text{R} = \text{Ph}$; $\text{R}' = \text{Ph}$; $\text{R}'' = \text{SiMe}_3$; $\text{X} = \text{BF}_4$ (**35**)



$\text{R} = \text{Ph}$; $\text{L} = \text{CO}$ (**17**)

$\text{R} = \text{Bu}^t$; $\text{L} = \text{CO}$ (**19**)

$\text{R} = \text{Ph}$; $\text{L} = \text{PMe}_2\text{Ph}$ (**20**)

$\text{R} = \text{Ph}$; $\text{L} = \text{CO}$ (**29**)

$\text{R} = \text{Bu}^t$; $\text{L} = \text{CO}$ (**30**)

$\text{R} = \text{Ph}$; $\text{L} = \text{PMe}_2\text{Ph}$ (**32**)

The reactivity of the alkynyl imido complexes **1**–**16** with the protic reagents CF_3COOH and HBF_4 has been studied. Protonation of these complexes may occur at the alkynyl and/or the imido moiety as observed previously in complexes containing only one of these ligands [6a,17]. In nearly all cases the final product could not be identified due probably to the evolution of the desired protonated species although a residual broad signal, that may correspond to its N–H proton, was observed in the ^1H NMR spectrum indicating that amide-containing species may have initially been formed. However, in the reactions of **2** and **9** with CF_3COOH and HBF_4 , respectively, the protonated compounds could be isolated (Eq. (12)). It was found that in these imido/alkynyl complexes protonation takes place preferentially at the nitrogen atom of the imido group leading to the formation of the cationic amide

ized by IR and ^1H NMR spectroscopy. Bands at 2090 cm^{-1} for **34** and 2071 cm^{-1} for **35**, assigned to the $\nu(\text{C}\equiv\text{C})$ of the alkynyl ligand, were observed in the IR spectra. Broad signals at 8.55 ppm for **34** and 8.22 ppm for **35**, due to the proton bonded to the nitrogen atom, were also observed in the ^1H NMR spectra. In addition in **34** the signal due to the Bu^t group (1.45 ppm) is shifted downfield with respect to the signal observed in the parent complex (1.01 ppm) thus reflecting the change from imide to amide of the nitrogen containing ligand. The normally greater Bronsted basicity of the imido ligand relative to the alkynyl ligand may explain the selective nature of the protonation reaction of these alkynyl–imido niobocene complexes.

In conclusion we present the first general synthetic procedure for (σ -alkynyl) niobocene complexes. These complexes have been oxidized, and we have observed

that the nature of the resulting products, radical alkynyl, vinylidene, or divinylidene species depend on the substituent R, on the alkynyl ligand, the nature of the ancillary ligand L, and the experimental conditions. In addition protonation processes of the alkynyl niobocene imido complexes indicate that the reaction takes place preferentially at the imido group, giving rise to the corresponding amido complexes.

3. Experimental

3.1. Materials and procedures

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. The synthesis and detailed characterization data of the compounds **1–16**, **34–35** [6b], **17** [6c], **18–21** and **24–33** [6a] can be found in our previous publications. IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. ^1H and ^{13}C spectra were recorded on a Varian FT-300 spectrometer and referenced to the residual deuteriated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer.

3.2. Synthesis of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CSiMe}_3)(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})]$ (**22**)

Toluene (50 ml) was added to a mixture of $\text{Mg}(\text{C}\equiv\text{CSiMe}_3)_2$ (0.24 g, 1.10 mmol) and $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})]$ (0.41 g, 0.77 mmol). The mixture was stirred at 100 °C for 7 h. Solvent was removed in vacuo and the remaining green oil extracted in hexane (50 ml). A green solid was obtained by concentrating (5 ml) and cooling (–30 °C) the solution (0.45 g, 85%). IR (Nujol mull): ν_{CN} 2034 cm^{-1} ; $\nu_{\text{C}\equiv\text{C}}$ 2279 cm^{-1} . ^1H NMR (300 MHz, C_6D_6): δ 0.23 (s, 18H, SiMe_3), 0.30 (s, 9H, $\text{C}\equiv\text{CSiMe}_3$), 2.37 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 4.77, 5.01, 5.15, 5.45 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C_6D_6): δ 1.1 (SiMe_3), 1.9 ($\text{C}\equiv\text{CSiMe}_3$), 20.0 ($\text{C}_6\text{H}_3\text{Me}_2$), 94.0, 97.5, 99.1, 103.1 (C_5H_4), 91.6 ($\text{C}\equiv\text{CNb}$), 128.8 ($\text{C}\equiv\text{CNb}$), 126–132 ($\text{C}_6\text{H}_3\text{Me}_2$). Anal. Calc. for $\text{C}_{30}\text{H}_{28}\text{NNbSi}_3$: C, 60.47; H, 7.44; N, 2.35. Found C, 60.28; H, 7.36; N, 2.33.

3.3. Synthesis of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{C}\equiv\text{CBu}^t)(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})]$ (**22**)

The synthesis of **22** was carried out in an identical manner to that of **21**. $\text{Mg}(\text{C}\equiv\text{CBu}^t)_2$ (0.20 g, 1.07 mmol) and $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})]$ (0.41 g, 0.77 mmol). Yield 0.46 g, 80%. IR (Nujol mull): ν_{CN} 2034 cm^{-1} ; $\nu_{\text{C}\equiv\text{C}}$ 2080 cm^{-1} . ^1H NMR (200 MHz, C_6D_6): δ 0.30 (s, 18H, SiMe_3), 1.38 (s, 9H, $\text{CC}(\text{CH}_3)_3$),

2.37 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 4.80, 5.07, 5.18, 5.49 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C_6D_6): δ 1.9 (SiMe_3), 20.0 ($\text{C}_6\text{H}_3\text{Me}_2$), 33.3 ($\text{CC}(\text{CH}_3)_3$), 33.5 ($\text{C}(\text{CH}_3)_3$), 93.5, 97.2, 99.5, 104.1 (C_5H_4), 91.2 ($\text{C}\equiv\text{CNb}$), 128.8 ($\text{C}\equiv\text{CNb}$), 126–132 ($\text{C}_6\text{H}_3\text{Me}_2$). Anal. Calc. for $\text{C}_{31}\text{H}_{44}\text{NNbSi}_2$: C, 64.22; H, 7.65; N, 2.42. Found C, 64.00; H, 7.59; N, 2.38.

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References

- [1] (a) R. Nast, *Coord. Chem. Rev.* 47 (1982) 89; (b) E. Sappa, A. Tiripicchio, P. Braunstein, *Chem. Rev.* 83 (1983) 203; (c) J. Manna, K.D. Jonh, M.D. Hopkins, *Adv. Organomet. Chem.* (1996) 79.
- [2] (a) M.I. Bruce, A.G. Swincer, *Adv. Organomet. Chem.* 22 (1983) 59; (b) M.I. Bruce, *Chem. Rev.* 91 (1991) 197; (c) A.B. Antonova, A.A. Johanasson, *Russ. Chem. Rev. (Engl. Transl.)* 58 (1989) 693.
- [3] (a) S.D. Ittel, J.A. Ibers, *Adv. Organomet. Chem.* 14 (1976) 33; (b) S. Otsuka, A. Nakamura, *Adv. Organomet. Chem.* 14 (1976) 245.
- [4] H. Lang, D.S.A. George, G. Rheinwald, *Coord. Chem. Rev.* 206–207 (2000) 101.
- [5] (a) A. Antiñolo, P. Gómez-Sal, J.M. Martínez de Ilarduya, A. Otero, P. Royo, S. Martínez-Carrera, S. García-Blanco, *J. Chem. Soc. Dalton Trans.* (1987) 975; (b) A. Antiñolo, M. Fajardo, F. Jalón, C. López-Mardomingo, A. Otero, C. Sanz-Bernabé, *J. Organomet. Chem.* 369 (1989) 187; (c) A. Antiñolo, M. Fajardo, R. Gil-Sanz, C. López-Mardomingo, A. Otero, D. Lucas, H. Chollet, Y. Mugnier, *J. Organomet. Chem.* 481 (1994) 27; (d) A. Antiñolo, M. Martínez-Ripoll, Y. Mugnier, A. Otero, S. Prashar, A.M. Rodríguez, *Organometallics* 15 (1996) 3241; (e) A. Antiñolo, T. Expósito, I. del Hierro, D. Lucas, Y. Mugnier, I. Orive, A. Otero, S. Prashar, *J. Organomet. Chem.* 655 (2002) 63.
- [6] (a) C. García-Yebra, C. López-Mardomingo, M. Fajardo, A. Antiñolo, A. Otero, A. Rodríguez, A. Vallat, D. Lucas, Y. Mugnier, J.J. Carbó, A. Lledós, C. Bo, *Organometallics* 19 (2000) 1749; (b) A. Antiñolo, M. Fajardo, C. López-Mardomingo, I. López-Solera, A. Otero, Y. Pérez, S. Prashar, *Organometallics* 20 (2001) 3132; (c) A. Antiñolo, A. Otero, M. Fajardo, C. García-Yebra, C. López-Mardomingo, A. Martín, P. Gómez-Sal, *Organometallics* 16 (1997) 2601.
- [7] A. Wong, P.C.W. Kang, C.D. Tagge, D.R. Leon, *Organometallics* 9 (1990) 1992.
- [8] W. Weng, T. Bartie, J.A. Gladysz, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2199.

- [9] D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neil, V.C. Gibson, *J. Chem. Soc. Dalton Trans.* (1992) 739.
- [10] A. Antiñolo, M. Fajardo, A. Otero, S. Prashar, *Eur. J. Inorg. Chem.*, (2003) 17.
- [11] J.C. Green, M.L.H. Green, J.T. James, P.C. Konidras, G.H. Maunder, P. Mountford, *J. Chem. Soc. Chem. Commun.* (1992) 1361.
- [12] (a) V.C. Gibson, G. Parkin, J.E. Bercaw, *Organometallics* 10 (1991) 220;
(b) A. Van Asselt, B.J. Burger, V.C. Gibson, J.E. Bercaw, *J. Am. Chem. Soc.* 108 (1986) 5347;
(c) M.C. Fermin, J.W. Bercaw, *J. Am. Chem. Soc.* 115 (1993) 7511.
- [13] I. Kuksis, M.C. Baird, *J. Organomet. Chem.* 527 (1997) 137.
- [14] N. Le Narvor, L. Toupet, C. Lapinte, *J. Am. Chem. Soc.* 117 (1995) 7129.
- [15] N.G. Connelly, M.P. Gamasa, J. Gimeno, C. Lapinte, E. Lastra, J.P. Maher, N. Le Narvor, A.L. Rieger, P.H. Reiger, *J. Chem. Soc. Dalton Trans.* (1993) 2575.
- [16] R.S. Iyer, J.P. Selegue, *J. Am. Chem. Soc.* 109 (1987) 910 (See for example).
- [17] A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martín-Alonso, A. Otero, *J. Chem. Soc. Dalton Trans.* (1995) 1007.