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New coupling reactions for the construction of carbon-rich C$_7$ bridged di-ruthenium complexes

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Dedicated to E.O. Fischer on the occasion of his 85th birthday

Abstract

This microreview summarizes our work on new reactions to obtain ruthenium(II) binuclear species with seven conjugated carbon atoms between the remote metals in very mild conditions via C–C bond formation. (i) The treatment of *trans*-[Cl(dppe)$_2$Ru–C≡C–C≡C–SiMe$_3$] with [Fe(C$_5$H$_5$)$_2$]PF$_6$ leads to an unprecedented metal-assisted [2+2] coupling reaction between C$^\gamma$≡C$^\delta$ bonds to produce *trans*-[Cl(dppe)$_2$Ru–C≡C–C̲=̲C̲H̲C(CH$_2$)=C=C=Ru(dppe)$_2$Cl]PF$_6$ including a cyclobutenyl bridge. (ii) Addition of a cationic allenylidene *trans*-[ClRu(dppe)$_2$(=C=C=C(CH$_2$R^1)R^2)]BF$_4$ (R^1 = H, CH$_3$; R^2 = CH$_3$, Ph) on the C$_\gamma$≡C$_\delta$ bond of the diyne *trans*-[Cl(dppe)$_2$Ru–C≡C–C≡C–H] leads to ruthenium bimetallic complexes *trans*-[Cl(dppe)$_2$Ru–C≡C–C(CH$_3$)=C(R^1)–C(R^2)=C=C=Ru(dppe)$_2$Cl]BF$_4$ containing a planar delocalized "W"-shaped C$_7$ bridge with tunable pendant groups. These complexes display attractive redox and optical properties with a highly delocalized charge over the conjugated carbon atoms. The crystal structures of *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)–C(H)=C(CH$_3$)–C≡C–Ru(dppe)$_2$Cl]BF$_4$ and of the annealated complex were solved.
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1. Introduction

Carbon-rich metal complexes with an extended π-conjugated bridge have gained importance as potential applications in the emerging field of molecular-scale electronic devices [1] as key component for liquid crystals [2], metal-containing polymers [3], supramolecular architectures [4], molecular switches [5], NLO active [6] or luminescent [7] materials, and in particular for the building of molecular wires constituted of bimetallic complexes allowing through bridge exchange of electron between the remote metals [8–17]. The literature is now extensive for complexes with an even

number of conjugated carbon atoms spanning two metal fragments of various structures such as L$_n$MC$_x$ML$_n$ [8,11] or L$_n$M(CH)$_x$ML$_n$ [12]. By contrast, only a limited number of complexes with an odd numbered carbon linear or cyclic bridge have been obtained considering the variety of available metallic fragments. Few bridges with one, three, and five [13–15] carbons capped with two metal moieties have been described, and only one example of a seven carbon bridged bimetallic complex has been reported by Hartbaum and Fischer [16] via a coupling reaction between a dimethylamino(hexatriynyl)carbene complex and [ClRu(CO)$_2$Cp] (Scheme 1).

The limited number of well-defined synthetic processes limits the construction of odd carbon systems from small to nanoscale devices. The most general process involves the building of three carbon bridges and the regioselective [2+2] cycloaddition between the C=C bond of a vinylidene [M]=C=CHR and the C$_\alpha$≡C$_\beta$

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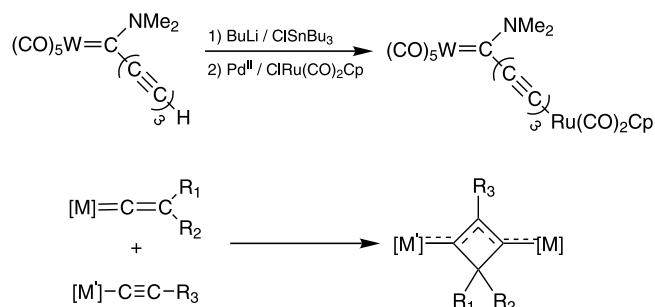
Scheme 1. Binuclear systems with an odd numbered carbon-rich bridge.

bond of a metal acetylide [M]–C≡C–R. This reaction affords rigid four-membered cyclic bridges with a delocalized C_3 path between metals (Scheme 1). Interestingly, when the reaction was applied to an allenylidene [M=C=C=CR$_1$R$_2$] complex [13b] or a diyne [M–C≡C–C≡C–R] complex [13c], a similar C_3-conjugated path is formed with an exocyclic double or triple bond. These reactions show that the C_α≡C_β bond is generally the most activated toward [2+2] cycloaddition, but at the same time is inhibiting the access to higher odd numbered carbon-rich bridges.

The interest to control the building of longer linearly oriented carbon-rich bridged bimetallic compounds for electronic communication and optical properties recently led us to discover two novel methodologies of C–C bond formation to obtain a new class of carbon-rich homobimetallic complexes with seven conjugated carbon atoms between remote metals and a charge highly delocalized over the extended conjugated structure [9,10]. The first one consists in an unprecedented radical-promoted [2+2] coupling reaction occurring on the C_γ≡C_δ bond of a 1,3-diynylmetal derivative [Ru]–C≡C–C≡CR to lead to a novel complex [Ru]$^+$=C=C=C–CH=C(CH$_2$)–C≡C–[Ru] [9] including a carbon-rich annelated C_8H_3 bridge, and involving a butatrienylidene intermediate. The second method describes the coupling between an allenylidene [Ru]$^+$=C=C=C(CH$_2$R$_1$)R$_2$ and a metal diyne to provide "W"-shaped complexes [Ru]–C≡C–C(CH$_3$)=C(R^1)–C(R^2)=C=C=[Ru]$^+$ with pendant groups on the conjugated bridging ligand [10]. The present account summarizes our work on these seven conjugated carbon bridged bimetallic compounds which display attractive redox and optical properties.

2. New binuclear ruthenium with a C_7 bridge based on a radical-promoted metal diyne coupling reaction

Transition metal complexes are useful to stabilize the otherwise highly reactive (C=)$_n$CR$_2$ species which behave as strong electron-withdrawing ligands and to achieve metal cumulenylidenes [M]=(C)$_n$=CR$_1$R$_2$ [18–20]. The chemistry of metal complexes containing

alkynyl and higher poly-ynyl ligands is also now well established and the metal acetylide linkage has proven to be useful to obtain carbon-rich complexes [21]. For the access to carbon-rich linearly oriented transition metal complexes, such as metal-capped molecular wires or oligomers ([M]–(C≡C)$_n$–)$_m$–[M], the ruthenium fragment [RuCl(dppe)$_2$]$^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) appeared to be a model of choice. Indeed, this moiety appears to stabilize carbon-rich species such as cumulenylidenes *trans*-[Cl(dppe)$_2$Ru=(C)$_n$=CR$_1$R$_2$]$^+$ and acetylides *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_n$–R] for steric and electronic reasons [19,20,22]. Furthermore, a Ru(II)-containing bis(acetylide) bridge has been found to enhance the ground-state electronic communication between terminal ferrocenyl groups [23].

2.1. Ruthenium diyne complexes

Few ruthenium poly-yne systems such as [CpRu(PPh$_3$)$_2$–C≡C–C≡C–R] (R = H, SiMe$_3$) [24], [Ru(CO)$_2$(PEt$_3$)$_2$(–C≡C–C≡C–R)$_2$] (R = H, SiMe$_3$) [25], [Cl$_{2-n}$Ru(dppm)$_2$](–C≡C–C≡C–R)$_n$ (R = SiMe$_3$; n = 1, 2) [26], and *trans*-[Cl$_{2-n}$Ru(dppe)$_2$]((C≡C)$_m$–R)$_n$] (R = H, SiMe$_3$; m = 1–4; n = 1, 2) [22a] have been studied. Of interest, here is the mono-diynyl ruthenium complex *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_2$–SiMe$_3$] (**2**) prepared using the classical reaction of preformed polyyne anions Li(C≡C)$_2$SiMe$_3$ with the metal halide complex *cis*-[RuCl$_2$(dppe)$_2$] (**1**) (Scheme 2). This air-stable acetylide is easily further deprotected using Bu$_4$NF to provide the *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_2$–H] (**3**).

Cyclic voltammetry (CV) studies show one oxidation wave for **2** and **3**. Regarding **2**, the oxidation wave ($E°$ = 0.130 V vs. ferrocene) is chemically reversible on the time scale of CV but with ΔE_p = 85 mV, showing that the electron transfer is somewhat slow and suggesting a rearrangement of the structure as the consequence of the electron removal. The single electron of the oxidized species is known to be highly centered on the metal but with a significant ligand character [27]. Then, the oxidized form should correspond to the type Ru$^{+\bullet}$–C≡C–C≡CSiMe$_3$↔Ru$^+$=C=C=C=C$^\bullet$SiMe$_3$ with a significant contribution of the latter cumulenic form.

By contrast, complex **3** shows an irreversible oxidation wave (E_p = 0.135 V vs. ferrocene, v = 100 mV s^{-1}) indicating a high reactivity of the oxidized form. This has to be related to the reaction we observed when the diyne complex **2** is reacted with a strong acid such as HBF$_4$·Et$_2$O. The vinylidene **4** (Scheme 3) is obtained via the cumulene intermediate [**A**] which displays a high electrophilic character on C_γ [22a]. Similar intermediates were proposed with ruthenium diynes such as *trans*-[ClRu(dppe)$_2$–C≡C–C≡C–Ph] [28a] or [CpRu(PPh$_3$)$_2$–C≡C–C≡C–H] [24]. The irreversible chemical behaviour of **3** can be explained by a reaction of the oxidized form due to its cumulenic character with residual water. This
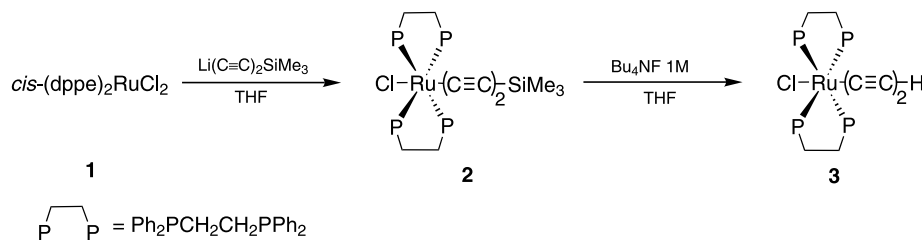
Scheme 2. Syntheses of acetylides **2** and **3**.

suggested an interesting reactivity potential for the acetylides in the oxidized state. This is also true for **2**. Although, the CV behaviour is chemically reversible, microelectrolysis evidenced that the oxidized form is reacting slowly to produce unidentified species.

2.2. Coupling reaction

The reactivity of the chemically oxidized species of **2** was studied, and the most interesting result was observed with the addition of half an equivalent of ferrocenium hexafluorophosphate as oxidant [9]. A [2+2] cycloaddition apparently takes place at the $C_\gamma \equiv C_\delta$ triple bond yielding to dark purple crystals of **5**. The NMR studies are consistent with a highly delocalized structure giving a formal half-positive charge on each ruthenium, intermediate with those sketched in Scheme 4. Indeed, the ^{31}P analysis of **5** shows only one singlet for the eight phosphorus atoms indicating that the two metal sites are equivalent. The ^{13}C analysis shows only five different signals for the symmetric unsaturated bridges linking the two ruthenium atoms. Furthermore, the $Ru-C_\alpha$ resonance at 247.7 ppm (quint, $^2J_{PC} = 14$ Hz) is downfield compared to that of an alkynyl ($\delta = 105.5$ ppm for $[Cl(dppe)_2Ru-C\equiv C-CPh_2H]$) [22c] and upfield to that of an allenylidene complex ($\delta = 308.6$ ppm for $[Cl(dppe)_2Ru=C=C=CPh_2]$) [20a].

The unprecedented observed regioselectivity of the cycloaddition is explained by the steric hindrance of the bulky ruthenium moieties as the $C^\alpha \equiv C^\beta$ bond in the diyne complexes **2** is sterically protected, and only the $C^\gamma \equiv C^\delta$ bond is reactive. Previous studies on ruthenium allenylidenes $[Cl(dppe)_2Ru=C=C=CR_1R_2]$ and acetylides $[Cl(dppe)_2Ru-C\equiv C-R]$ (dppe = 1,2-diphenylphosphinoethane) showed that the bulky ruthenium

$[RuCl(dppe)_2]^+$ moiety prevents nucleophilic attacks to C_α and promotes reactions on C_γ [20,22].

The whole mechanism and the driving force remain unverified but we can anticipate that despite the unfavourable potential, the reaction is likely initiated by an electron transfer between ferrocenium and **2** ($E^\circ = 0.130$ V vs. ferrocene) generating an electrophilic organometallic radical. Further desilylation of 2^+ leads to a radical species of type $Ru^{+\bullet}-C\equiv C-C\equiv CH \leftrightarrow Ru^+ =C=C=C=CH^\bullet$ that can react with another molecule of **2** as half an equivalent of oxidant is necessary. The resulting cyclic radical is desilylated and incorporates hydrogen atoms from the medium. Complex **5** was also obtained when the reaction was performed with the unprotected diyne trans-$[Cl(dppe)_2Ru-C\equiv C-C\equiv C-H]$ as starting material instead of **2**. Thus, spontaneous deprotection occurs in the reaction medium and previous desilylation is not necessary. In that case, a possible mechanism is described in Scheme 5.

3. New binuclear ruthenium with a C_7 bridge based on a metal diyne–metal allenylidene coupling reaction

The first conclusions about the mechanism of the radical-initiated coupling reaction, via a possible metal-lacumulene radical intermediate, gave us impetus to react metal diyne systems with preformed cumulenic species. The isolation of ruthenium butatrienylidene species has not been yet possible because of their high reactivity [19], and this kind of intermediate has been only isolated with a complex of iridium $[Cl(PiPr_3)_2Ir=C=C=C=CPh_2]$ [29]. Therefore, the reaction has been investigated with ruthenium allenylidene and diyne complexes.
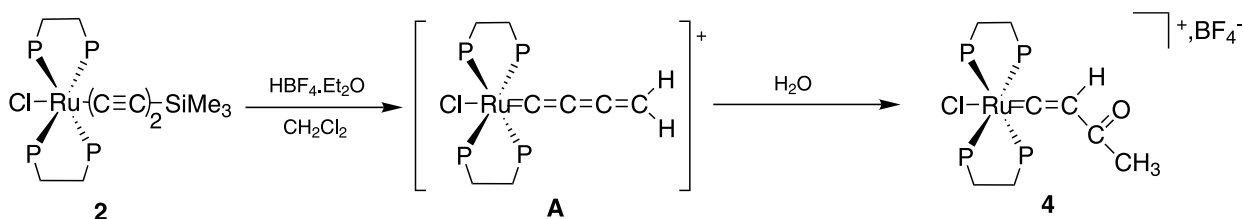
Scheme 3. Evidence for a butatrienylidene intermediate.
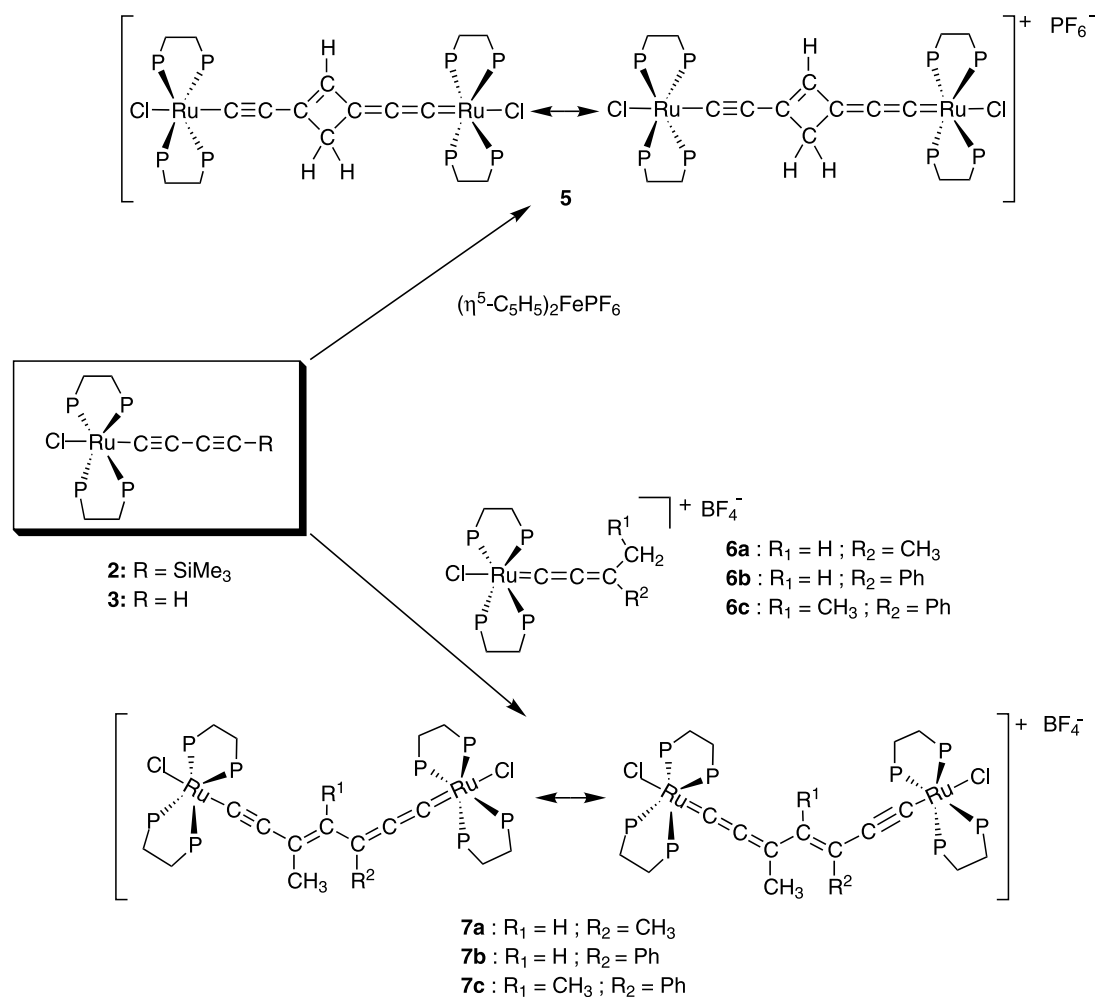
Scheme 4. Binuclear complexes with a seven carbon atom bridge derived from **2** and **3**.
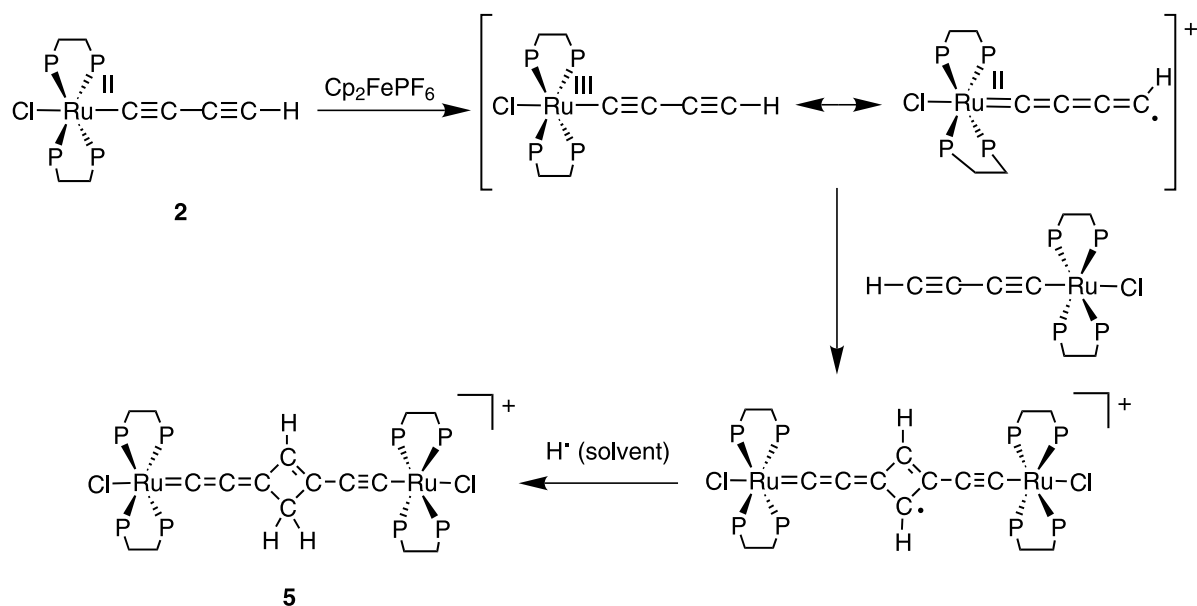
Scheme 5. Proposed mechanism for the formation of **5** starting from **2**.

3.1. Allenylidene complexes

A variety of metal allenylidene complexes have been prepared since the breakthrough of Selegue in 1982 [30b]. Following this pioneer reaction, the main route to prepare ruthenium allenylidene consists in the activation of propargylic alcohols in the presence of an in situ-generated or previously isolated 16-electron intermediate $[(dppe)_2RuCl]^+$. Of interest are the ruthenium complexes of type *trans*-$[(dppe)_2(Cl)Ru=C=C=C(CH_2R_1)R_2]BF_4$ obtained with prior isolation of the 16-electron species in the presence of $AgBF_4$ (Scheme 6).
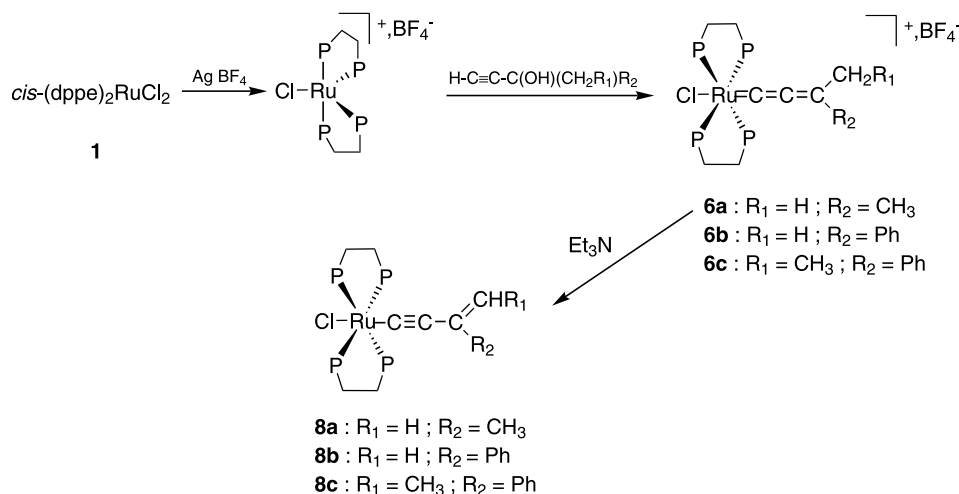
Main characteristic of those allenylidene complexes with a $-CH_2R_1$ group on C_γ is their aptitude to be easily deprotonated into stable ruthenium alkenyl acetylides *trans*-$[(dppe)_2(Cl)Ru-C=C-C(=CHR_1)R_2]$ such as **8a–8c** by action of a weak base (Et_3N) [28]. CV studies show a partially reversible reduction wave for **6b** and for **6c**, and an irreversible one for **6a**, by contrast with *trans*-$[Cl(dppe)_2Ru=C=C=CPh_2]PF_6$. This irreversibility is certainly attributable to the loss of a hydrogen atom in the reduced state.

3.2. Metal allenylidene–metal diyne coupling reaction
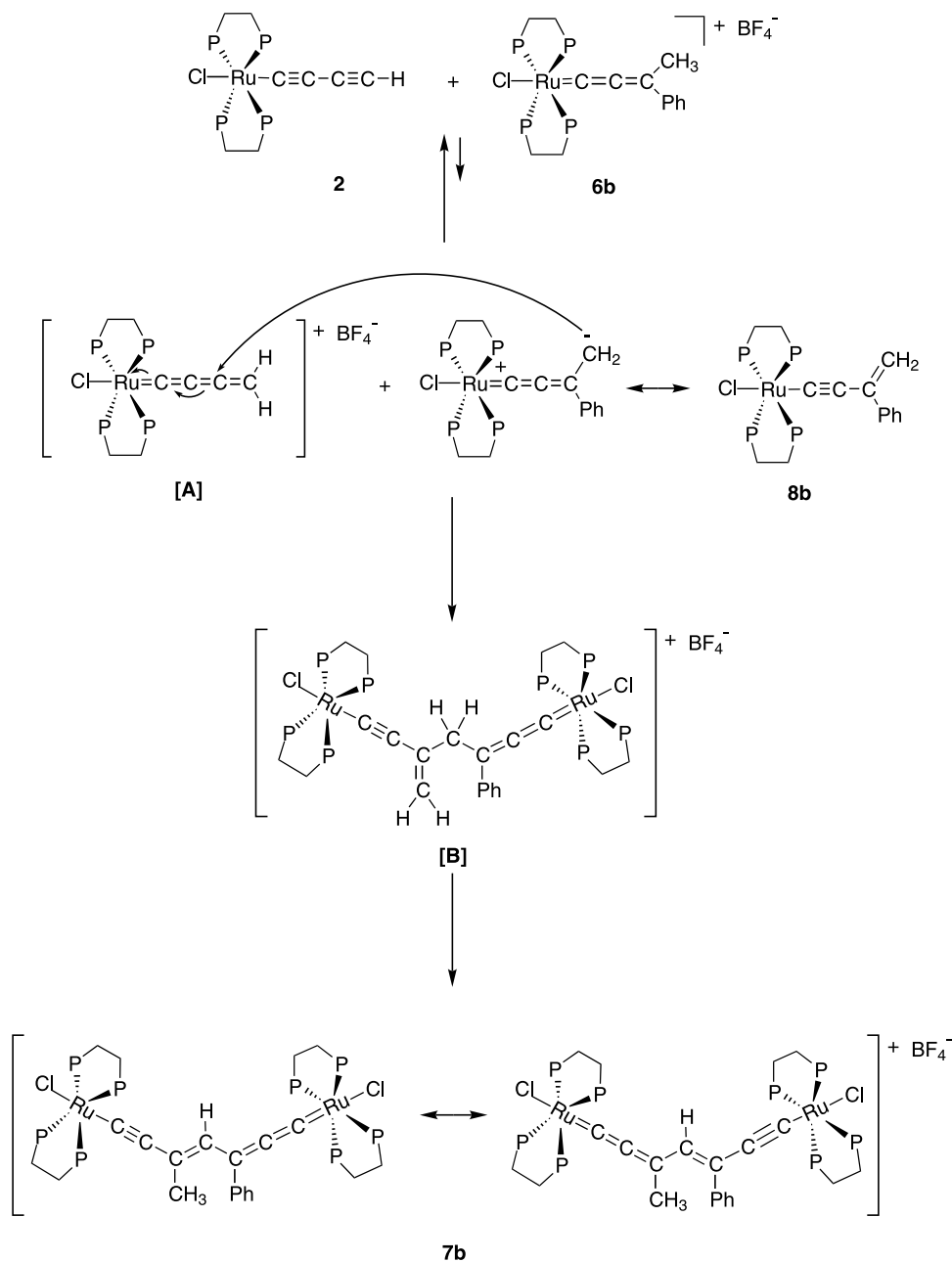
This synthetic route to new ruthenium bimetallic complexes is outlined in Scheme 4. The cationic allenylidene complexes **6a–6c** were reacted, at room temperature, with one equivalent of the neutral diyne compound **3**. A metal-assisted C–C forming reaction took place and stable dark green crystals of **7a–7c** were isolated in good yields (69–75%). These complexes **7a–7c** were also obtained with similar yields when the reaction was performed with the protected diyne **2** as starting material instead of **3**. Thus, spontaneous desilylation of **2** also occurs here in the reaction medium in the presence of the ruthenium allenylidene salt. The FTIR spectra for all compounds present an intense

absorption around 1900 cm^{-1}, characteristic of the cumulenic character of the chain. As observed for **5**, the NMR studies are consistent with a highly delocalized structure giving a formal half-positive charge on each ruthenium fragment. The ^{31}P-NMR analysis shows for **7a** one singlet at 47.1 ppm typical for a symmetrical structure, indicating that the two metal sites are equivalent. The ^{1}H-NMR spectra for **7a** presents a singlet at 5.50 for the proton ($R_1 = H$) on the C_δ of the chain, and a single signal for two methyl groups at 1.35 ppm. Conversely, NMR analyses evidence an unsymmetrical structure for the systems **7b** and **7c**. Indeed, the ^{31}P-NMR spectrum displays two singlets at 43.8 and 49.6 ppm for **7c**. Furthermore, the ^{13}C-NMR spectrum displays seven different signals for the delocalized carbon chain. It is noteworthy that the carbon atom C_α and C'_α resonances for these compounds (**7a**: $\delta = 224$ ppm) are found downfield to that of an alkynyl ($\delta = 105.5$ ppm for $[Cl(dppe)_2Ru-C\equiv C-CPh_2H]$) [22c] and upfield to that of an allenylidene complex ($\delta = 308.6$ ppm for $[Cl(dppe)_2Ru=C=C=CPh_2]$) [20a].

A highly probable mechanism for the reaction is based on the fact that ruthenium allenylidenes with a $-CH_2R_1$ group on C_γ are easily deprotonated into stable ruthenium acetylides (vide infra). This mechanism is depicted in Scheme 7 for **7b**. The first step consists in the transfer of a proton from **6b** to the nucleophilic carbon C_δ of **2** to form an unstable butatrienylidene complex [A] and the acetylide **8b**. A further fast addition of the nucleophilic C_δ of **8** on the electrophilic C_γ of [A] leads to the intermediate [B]. The formation of **7b** would then result from an allylic hydrogen transfer. This hypothesis is supported by ^{31}P-NMR monitoring of the reaction. Two features were observed: (i) at the beginning of the reaction, the apparition of two signals of similar intensity corresponding to the intermediate [B] bearing an enynyl moiety (53.6 ppm) and an allenylidene moiety (43.2 ppm), and a weak intensity signal at 51.2 ppm

6a : $R_1 = H$; $R_2 = CH_3$
6b : $R_1 = H$; $R_2 = Ph$
6c : $R_1 = CH_3$; $R_2 = Ph$

8a : $R_1 = H$; $R_2 = CH_3$
8b : $R_1 = H$; $R_2 = Ph$
8c : $R_1 = CH_3$; $R_2 = Ph$

Scheme 6. Syntheses of allenylidenes **6a–6c**.

Scheme 7. Proposed mechanism for the formation of **7b**.

4. Properties of the seven carbon bridged ruthenium complexes

4.1. Crystal structures

attributed to the transient formation of **8b** and (ii) the gradual disappearance of these peaks and the emergence of two new signals corresponding to the final complex **7b**. It is as well supported by the fact that the reaction does not work with allenylidene complexes such as *trans*-[(dppe)$_2$(Cl)Ru=C=C=CR^{3}Ph]BF$_4$ with R^3 = H, Ph or CH(CH$_3$)$_2$. Hence, two hydrogen atoms on one group on the C$_\gamma$ of the allenylidene are required: one for the proton exchange between **2** and **6b** and another one for the final transfer in [**B**]. Such an intermediate is not observed with R^3 = CH(CH$_3$)$_2$ certainly for steric reasons.

Crystal structures could be resolved for complexes **5** and **7a** (Figs. 1 and 2) confirming the highly delocalized nature of the complexes. They both show very similar features. They are built from two identical bulky ruthenium fragments [RuCl(dppe)$_2$]$^+$ connected by the seven-membered carbon bridge. The Cl–Ru–C–C–C arrangements are almost linear in both structures. The
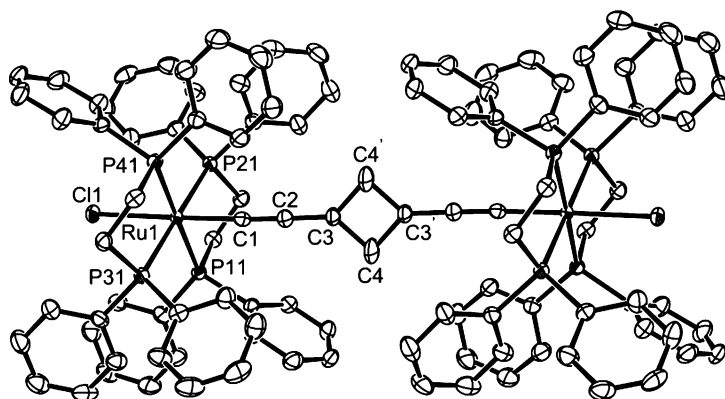
Fig. 1. Molecular structure of **5** (ORTEP view). Selected distances (Å) and angles (°): Ru(1)–C(1), 1.933(3); C(1)–C(2), 1.225(4); C(2)–C(3), 1.372(4); C(3)–C(4), 1.457(5); C(3)–C(4′), 1.459(5); C(1)–Ru(1)–Cl(1), 178.49(9); C(2)–C(1)–Ru(1), 174.4(2); C(1)–C(2)–C(3), 178.3(3); C(2)–C(3)–C(4), 134.2(3); C(3)–C(4)–C(3′), 88.3(3).
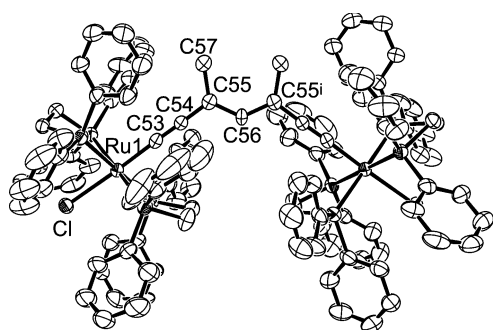

Fig. 2. Molecular structure of **7a** (ORTEP view). Selected distances (Å) and angles (°): Ru(1)–C(53), 1.923(9); C(53)–C(54), 1.218(12); C(54)–C(55), 1.390(13); C(55)–C(56), 1.401(11); C(55)–C(57), 1.528(12); C(53)–Ru(1)–Cl, 177.3(2); C(54)–C(53)–Ru(1), 178.0(8); C(53)–C(54)–C(55), 178.1(11); C(54)–C(55)–C(56), 118.0(9); C(54)–C(55)–C(57), 118.5(8); C(56)–C(55)–C(57), 123.6(9); C(55)–C(56)–C(55)[i], 129.8(13).

Ru(1)–C(53) [1.923(9) Å], C(54)–C(55) [1.390(13) Å] bonds in **7a** and Ru–C(1) [1.933 Å], C(2)–C(3) [1.372 Å] bonds in **5** are significantly shorter than the related single bonds in a ruthenium alkyne system and longer than the corresponding double bonds in a metal allenylidene [30]. On the other hand, the bond lengths C(53)–C(54) [1.218(12) Å] in **7a** and C(1)–C(2) [1.225 Å] in **5** are intermediate between the values found in these mononuclear systems.

In complex **5**, the Cl(1)–Ru(1)-bridge-Ru′(1)–Cl(1)′ arrangement is linear. The four-membered ring is planar giving the maximum orbital overlap across the bridge, and is symmetric as C(3)–C(4) [1.457(5) Å] and C(3)–C(4′) [1.459(5) Å] are identical within experimental errors. In order to account for the inversion center, we should consider the occurrence of a fully delocalized system with a disorder between CH and CH₂.

Considering **7a**, the two ruthenium fragments are connected by an almost planar "W"-shaped C_9H_7 bridge slightly twisted in order to minimize steric repulsions. The different angles and bond lengths

involving C(55) and C(56) show the high sp^2 nature of these carbon atoms, and the extended π-conjugation along the bridge as indicated by the NMR data.

4.2. Electrochemical and optical data

CV was used to investigate the electrochemical behaviour of **5** and **7a**–**7c** (Table 1). All compounds show similar features. They undergo a well-defined reversible one-electron oxidation wave followed by an almost reversible or irreversible second oxidation wave consistent with the doubly oxidized species undergoing following chemical reactions. To a first approximation, these two oxidation steps could be viewed as essentially involving the two Ru^{II}/Ru^{III} couples [22b,27]. The large separation of the processes ($\Delta E° = 650$ mV, $Kc = \exp(\Delta E° F/RT) = 1.27 \times 10^{11}$ for **7b** [8]) is attributable to substantial electronic interaction between the metallic centers and more specifically to a combination of phenomena such as strong electronic coupling, coulombic repulsion, and/or structural distortion through the oxidations. The singly oxidized compounds (mixed valence) should be stable.

These complexes also undergo a well-defined one-electron reduction wave at rather negative potential attributable to the reduction of the unsaturated carbon chain [13b,20b]. Indeed, achieving the reduction of complexes **5** with cobaltocene allows the observation of the radical species **5**[•] which generates an intense and persistent ESR feature at 293 K. The signal without detectable hyperfine structure is located in a characteristic region for organic radicals with $g = 2.009$. Preliminary experiments on **7a**–**7c** lead to the same conclusions. This attribution is also supported by the fact that the reduction potential is highly influenced by the introduction of the phenyl group in **7b** and **7c** in comparison with **7a**.

These electrochemical experiments show that the four bimetallic complexes are harder to oxidize than an

Table 1
CV [a] and UV–vis data for complexes **5** and **7a**–**7c**

	E^o_{red} (V) [b]	E^o_{ox1} (V) [b]	E^o_{ox2} (V)	λ_{max} (nm)	ε (mol^{-1} l cm^{-1}) [c]
5	−1.48	0.42	0.91 [d]	633	141000
7a	−1.38	0.31	0.99 [d]	730	122000
7b	−1.24	0.32	0.97 [e]	746	98000
7c	−1.25	0.23	1.06 [d]	764	109000

[a] Sample: 1 mM Bu$_4$NPF$_6$ (0.1 M) in CH$_2$Cl$_2$; v = 100 mV s^{-1}; potential are reported in volt vs. ferrocene as an internal standard.
[b] Reversible redox processes $\Delta E_p \approx 60$ mV, $I_{pc}/I_{pa} \approx 1$.
[c] In CH$_2$Cl$_2$.
[d] Peak potential of an irreversible process.
[e] Partially reversible peak $\Delta E_p \approx 95$ mV, $I_{pc}/I_{pa} < 1$.

acetylide complex such as **2** ($E^\circ = 0.130$ V vs. ferrocene) and harder to reduce than an allenylidene complex such as [ClRu(dppe)$_2$(=C=C=CPh$_2$)]PF$_6$ ($E^\circ = -1.03$ V vs. ferrocene). This is still consistent with a highly delocalized structure giving a formal half-positive charge on each ruthenium. Nevertheless, all the potential variations remain difficult to rationalize in details so far.

The UV–vis spectra were recorded from CH$_2$Cl$_2$ solutions. Each complex displays a strong charge transfer band with a large extinction coefficient (Table 1). Clearly, the λ_{max} values are influenced by the nature of the bridge. These observations are in agreement with those of the C$_5$ "V"-shaped compound [CpRu(PPh$_3$)$_2$=C=C=CH–C≡C–Ru(PPh$_3$)$_2$Cp]BF$_4$ that shows an intense band at lower wavelength (λ_{max} = 600 nm, ε = 72 000 mol^{-1} l cm^{-1}), as the conjugated path is shorter [15]. It is worth to note that the optical band gaps roughly correlate to the electrochemical band gaps indicative of the metal to ligand charge transfer (MLCT) nature of the transitions for all complexes. For example, **7a** displays an optical band gap of 1.70 eV and $\Delta E^\circ = 1.69$ V. Furthermore, for the complex **5**, the significant red shift (100 nm, 0.25 eV) matches the observed difference in the electrochemical band gap of 0.21 eV ($\Delta E^\circ = 1.90$ V).

Thus, these results evidence that a structural variation in the C$_7$ bridge strongly influence the electrochemical and optical properties. Especially important is the replacement of two methyl groups by a "bridging CH$_2$" unit. The "W"-shaped systems present the highest conjugation and this could be related to the absence of cycle constraint in the delocalized path. These observations support the necessity to tune a general system to find the best physical properties.

5. Conclusion

In conclusion, we have developed two novel easy methods to prepare bimetallic complexes containing unprecedented carbon-rich bridges, starting from simple precursors in very mild conditions. These unique annealated and "W"-shaped C$_7$ bridge arrangements display remarkable stabilities, interesting spectroscopic, redox, and structural properties. Arrangements with a rigid spacer that affords restricted conformational mobility between structural subunit are promising to reach valuable models for new functionalized one-dimensional molecular wires.

References

[1] (a) J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives (Chapter 8), VCH, Weinheim, 1995 (Chapter 8);
(b) R. Loyd Carroll, C.B. Gorman, Angew. Chem. Int. Ed. 41 (2002) 4379.
[2] S.A. Hudson, P.M. Maitlis, Chem. Rev. 93 (1993) 861.
[3] (a) I. Manners, Chem. Rev. 99 (1999) 1515;
(b) N. Matsumi, Y. Chujo, O. Lavastre, P.H. Dixneuf, Organometallics 20 (2001) 2423;
(c) K. Onitsuka, Y. Harada, F. Takei, S. Takahashi, Chem. Commun. (1998) 643.;
(d) J.L. Lewis, P.R. Raithby, W.-Y. Wong, J. Organomet. Chem. 556 (1998) 219.
[4] (a) P.J. Stang, Chem. Eur. J. 4 (1998) 19;
(b) P.J. Stang, B. Olenyuk, Acc. Chem. Res. 30 (1997) 502.
[5] J.-L. Fillaut, M. Price, A.L. Johnson, J. Perruchon, Chem. Commun. (2001) 739.
[6] (a) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 43 (1999) 349;
(b) S.K. Hurst, M.G. Humphrey, T. Isoshima, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, B.L. Davies, Organometallics 21 (2002) 2024;
(c) T. Weyland, I. Ledoux, S. Brasselet, J. Zyss, C. Lapinte, Organometallics 19 (2000) 5235;
(d) A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, T. Wada, H. Sasabe, A. Persoons, J. Am. Chem. Soc. 121 (1999) 1405;
(e) K. Senechal, O. Maury, H. Le Bozec, I. Ledoux, J. Zyss, J. Am. Chem. Soc. 124 (2002) 4560.

[7] (a) V.W.-W. Yam, R.P.-L. Tang, K.M.-C. Wong, K.-K. Cheung, Organometallics 20 (2001) 4476;
(b) V.W.-W. Yam, K.M.-C. Wong, N.J. Zhu, J. Am. Chem. Soc. 124 (2002) 6506;
(c) O. Lavastre, I. Illitchev, G. Jegou, P.H. Dixneuf, J. Am. Chem. Soc. 124 (2002) 5278.

[8] F. Paul, C. Lapinte, Coord. Chem. Rev. 178–180 (1998) 431.

[9] S. Rigaut, L. Le Pichon, J.-C. Daran, D. Touchard, P.H. Dixneuf, Chem. Commun. (2001) 1206.

[10] S. Rigaut, J. Massue, D. Touchard, J.-L. Fillaut, S. Golhen, P.H. Dixneuf, Angew. Chem. Int. Ed. 41 (2002) 4513.

[11] (a) F. Paul, W.E. Meyer, L. Toupet, H. Jiao, J.A. Gladysz, C. Lapinte, J. Am. Chem. Soc. 122 (2000) 9405;
(b) R. Ziessel, M. Hissler, A. El-Gayhouri, A. Harriman, Coord. Chem. Rev. 178–180 (1998) 1251;
(c) P.F.H. Schab, M.D. Levin, J. Michl, Chem. Rev. 99 (1999) 1863;
(d) J.G. Rubio, M. Laubender, H. Werner, Organometallics 19 (2000) 1365;
(e) R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, J. Am. Chem. Soc. 122 (2000) 810;
(f) F.J. Fernandez, O. Blacque, M. Alfonso, H. Berke, Chem. Commun. (2000) 1266.;
(g) M.I. Bruce, P.J. Low, K. Costuas, J.-F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. 122 (2000) 1949;
(h) P. Siemen, U. Gubler, C. Bosshard, P. Günter, F. Diederich, Chemistry 7 (2001) 1333;
(i) D.B. Werz, R. Gleiter, F. Rominger, Organometallics 22 (2003) 843;
(j) W. Lu, H.-F. Xiang, N. Zhu, C.-M. Che, Organometallics 21 (2002) 2343;

For selected representative examples in various fields see

[12] (a) S.H. Liu, H. Xia, T.B. Wen, Z. Zhou, G. Jia, Organometallics 22 (2003) 737;
(b) X. Niu, L. Gopal, M.P. Masingale, D.A. Braden, B.S. Hudson, M.B. Sponsler, Organometallics 19 (2000) 649.

[13] (a) T. Bartik, M.T. Johnson, A.M. Arif, J.A. Gladysz, Organometallics 14 (1995) 889;
(b) H. Fischer, F. Leroux, R. Stumpf, G. Roth, Chem. Ber. 129 (1996) 1475;
(c) F. Leroux, R. Stumph, H. Fischer, Eur. J. Inorg. Chem. (1998) 1225.;
(d) N.Y. Kolokova, V.V. Skripkin, G.G. Alexandrov, Y.T. Struchkov, J. Organomet. Chem. 169 (1979) 293;
(e) W. Weng, J.R. Berenguer, J. Fornies, E. Lalind, F. Martinez, L. Sanchez, B. Serrano, Organometallics 17 (1998) 1640;
(f) R.M. Bullock, J. Am. Chem. Soc. 109 (1987) 8087;
(g) G. Roth, D. Reindl, M. Gockel, C. Troll, H. Fischer, Organometallics 17 (1998) 1393.

[14] (a) T. Bartik, W. Weng, J.A. Ramsden, S. Szafert, S.B. Falloon, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 120 (1998) 11071;
(b) R. Dembinski, S. Szafert, P. Haquette, T. Lis, J.A. Gladysz, Organometallics 18 (1999) 5438;
(c) B. Fuss, M. Dede, B. Weibert, H. Fischer, Organometallics 21 (2002) 4425.

[15] (a) G. Jia, H.P. Xia, W.F. Wu, W.S. Ng, Organometallics 16 (1997) 2940;
(b) H.P. Xia, W.S. Ng, J.S. Ye, X.Y. Li, W.T. Wong, Z. Lin, C.

Yang, G. Jia, Organometallics 18 (1999) 4552;
(c) J.P. Selegue, J. Am. Chem. Soc. 105 (1983) 5921.

[16] C. Hartbaum, H. Fischer, J. Organomet. Chem. 578 (1999) 186.

[17] (a) G. Xu, T. Ren, Organometallics 20 (2001) 2400;
(b) G.-H. Wong, K.T. Lehn, J.-M. Peng, S.-M. Lee, Chem. Commun. (2000) 2259.

[18] (a) M.I. Bruce, Chem. Rev. 98 (1998) 2797;
(b) V. Cadierno, M.P. Gamasa, J. Gimeno, Eur. J. Inorg. Chem. 3 (2001) 571;
(c) H. Werner, R. Wiedemann, M. Laubender, B. Windmüller, P. Steinert, O. Gevert, J. Wolf, J. Am. Chem. Soc. 124 (2002) 6669.

[19] D. Touchard, P.H. Dixneuf, Coord. Chem. Rev. 178–180 (1998) 409.

[20] (a) D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, Organometallics 17 (1998) 3844;
(b) S. Rigaut, O. Maury, D. Touchard, P.H. Dixneuf, Chem. Commun. (2001) 373.;
(c) D. Touchard, P. Haquette, A. Daridor, L. Toupet, P.H. Dixneuf, J. Am. Chem. Soc. 116 (1994) 11157;
(d) S. Guesmi, D. Touchard, P.H. Dixneuf, Chem. Commun. (1996) 2773.

[21] (a) J. Manna, K.D. John, M.D. Hopkins, Adv. Organomet. Chem. 38 (1995) 79;
(b) P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH, Weinheim, 1995.;
(c) P.J. Low, M.I. Bruce, Adv. Organomet. Chem. 48 (2001) 71.

[22] (a) S. Rigaut, J. Perruchon, L. Le Pichon, D. Touchard, P.H. Dixneuf, J. Organomet. Chem. 670 (2003) 37;
(b) S. Rigaut, F. Monnier, F. Mousset, D. Touchard, P.H. Dixneuf, Organometallics 21 (2002) 2657;
(c) D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, Organometallics 16 (1997) 3640.

[23] (a) C. Lebreton, D. Touchard, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, Inorg. Chim. Acta 272 (1998) 188;
(b) Y. Zhu, O. Clot, M.O. Wolf, G.P.A. Yap, J. Am. Chem. Soc. 120 (1998) 1812.

[24] M.I. Bruce, P. Hinterding, E.R.T. Tiekink, B.W. Skelton, A.H. White, J. Organomet. Chem. 450 (1993) 209.

[25] (a) Y. Sun, N.J. Taylor, A.J. Carty, J. Organomet. Chem. 423 (1992) C43;
(b) Y. Sun, N.J. Taylor, A.J. Carty, Organometallics 11 (1992) 4293.

[26] L. Dahlenburg, A. Weiß, M. Bock, A. Zahl, J. Organomet. Chem. 541 (1997) 465.

[27] (a) O.F. Koentjoro, R. Rousseau, P.J. Low, Organometallics 20 (2001) 4502;
(b) R.F. Winter, K.-W. Klinkhammer, S. Zalis, Organometallics 20 (2001) 1317.

[28] (a) P. Haquette, D. Touchard, L. Toupet, P.H. Dixneuf, J. Organomet. Chem. 565 (1998) 63;
(b) D. Touchard, N. Pirio, P.H. Dixneuf, Organometallics 14 (1995) 4920;
(c) S. Rigaut, D. Touchard, P.H. Dixneuf, in press.

[29] K. Ilg, H. Werner, Chem. Eur. J. 8 (2002) 2812.

[30] (a) M. Younus, N.J. Long, P.R. Raithby, J. Lewis, N.A. Page, A.J.P. White, D.J. Williams, M.C.B. Colbert, A.J. Hodge, M.S. Khan, D.G. Parker, J. Organomet. Chem. 578 (1999) 198;
(b) J.P. Selegue, Organometallics 1 (1982) 217.