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Coordination Chemistry Reviews 248 (2004) 1679–1692

COORDINATION CHEMISTRY REVIEWS

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Redox induced reactions of transition metal vinylidene and related complexes

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Contents

Abstract

In this review redox induced reactions of transition metal vinylidene complexes have been summarized for the first time. Surprisingly there are no reports on metal-centered reactivity of redox-activated vinylidenes so that the prior emphasis is made on ligand-centered reactions (C_β—C_β dimerizations, cleavage, and formation of C_β—H bonds etc.). A discussion of redox activation of related transition metal σ-alkynyl and alkylidyne complexes is limited by the cases wherein transition metal vinylidenes are formed at least as intermediates.

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Keywords: Redox induced reactions; Vinylidene complexes; Alkylidyne complexes; σ-Alkynyl complexes; Cyclic voltammetry

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Abbreviations: Cp, (η^5-C_5H_5); Cp*, (η^5-C_5Me_5); Cp′, (η^5-C_5H_4Me); CPE, controlled potential electrolysis; CV, cyclic voltammetry; dmpe, $Me_2PCH_2CH_2PMe_2$; dppe, $Ph_2PCH_2CH_2PPh_2$; Fc, $(\eta^5$-$C_5H_5)_2Fe^+$; n-e, number of electrons; NP_3, $N(CH_2CH_2PPh_2)_3$; PP_3, $P(CH_2CH_2PPh_2)_3$; SCE, saturated calomel electrode; Tp′, hydridotris(2,5-dimethylpyrazolyl)borate

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doi:10.1016/j.ccr.2004.08.008

1. Introduction

Over the past 15–20 years the chemistry of transition metal vinylidene complexes has been developed into an important area of organometallic chemistry [1]. This was caused by the occurrence of such complexes as key intermediates in catalytic and stoichiometric reactions of alkynes [2] and was mainly concerned with the in-depth study of dimerization and oligomerization of alkynes [2c,d], nucleophilic addition to alkynes [2a], cycloaromatization of conjugated enediynes [2e–g] etc. Compared to this very rich chemistry the redox activation reactions of vinylidene complexes remain far less studied. Nevertheless the application of the redox activation methodology to vinylidene and related complexes should enrich their reactivity since addition of electron to or removal of electron from the most stable complexes promotes reactions that proceed hardly or even do not proceed at all for the starting (typically 18-electron) compounds.

In particular, in redox-activated vinylidene, σ-alkynyl, and alkylidyne complexes a spin density arises at the carbon atoms of the ligands, which allows selective C–C, C–H, and C-heteroatom bond forming and bond cleavage reactions. These reactions of 6–9 group metal vinylidene complexes, i.e. ligand-to-ligand dimerization, nucleophilic addition to C_α atoms, addition and elimination of hydrogen radicals etc. are the specific subject of the present review. Similar reactions of related σ-alkynyl and alkylidyne complexes leading to the formation of corresponding vinylidenes at least as intermediates will also be covered.

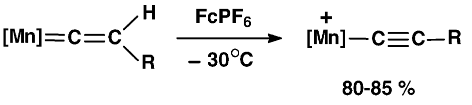
2. Redox induced reactions of transition metals vinylidene complexes

2.1. Oxidative activation of vinylidene complexes

The electronic structure of 17-e radical cation intermediates generated by oxidation of transition metal vinylidene complexes can be represented as a resonance hybrid of metal- and carbon-centered radical forms (Scheme 1). The ratio of these resonance forms strongly depends on the substituent R and ligand environment of the metal atom.

Therefore oxidative activation of 18-e vinylidene complexes can be expected to result in the formation of three types of products (**I–III**, Scheme 1) in accord with the electronic structure of intermediate 17-e species, namely 16-e (**I**) and 17-e (**III**) σ-alkynyl complexes as a result of the homolytic and heterolytic C_β–H bond cleavage (paths (**a**) and (**c**), respectively) and 18-e binuclear complexes **II** (path (**b**)) with bridging μ-butanediylidyne ligands as a result of direct C_β–C_β coupling of the carbon-centered radicals.

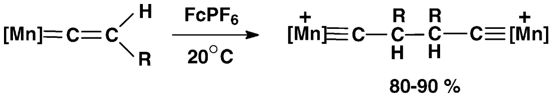
Some examples of dual reactivity (C_β–H bond homolysis and direct C_β–C_β dimerization) for structurally close vinylidene complexes were described [3,4]. In particular, the low temperature oxidation of the electron rich manganese vinylidene compounds in dichloromethane solution was reported by Berke and co-workers [3] to afford cationic σ-alkynyl complexes in a good yield (Eq. (1)).



(1)

[Mn] = Mn(dmpe)Cp'   R = Ph, $SiMe_3$

On the other hand, the oxidation of Cp′(dmpe)Mn=C=CHPh and related compounds at room temperature proceeds via C_β–C_β coupling affording binuclear bis-carbyne complexes (Eq. (2)) [4]. In these cases, the reaction course is controlled by the temperature. It is noteworthy that dimerization of $[Cp'(dmpe)Mn{=}C{=}CHPh]^{+\bullet}$ proceeds stereoselectively with the formation of only a *meso*-form of the bis-carbyne dication. The dimerization energy for the model radical cation $[Cp'(dHpe)Mn{=}C{=}CH_2]^{+\bullet}$ was estimated by DFT method to be −24.2 kcal/mol [4]. The process (**2**) can be realized in an opposite direction. Reduction of binuclear 18-e diylidynes with Cp^*_2Co leads to regeneration of the initial vinylidenes presumably via a C_β–C_β bond cleavage in 19-e intermediates (see also Section 4.2).

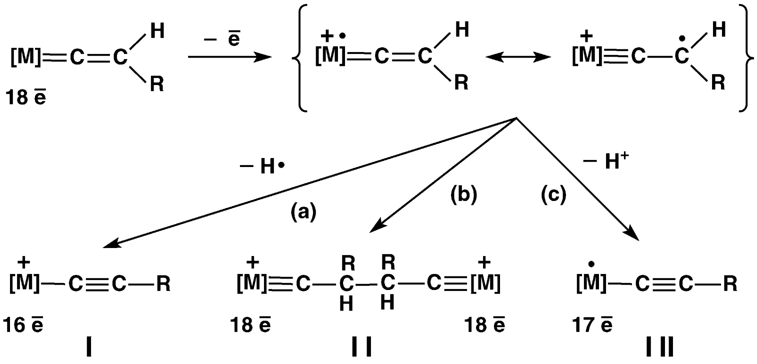


(2)

[Mn] = Mn(dmpe)Cp'   R = Ph, H

It is important to note that reduction of dicationic butane-1,4-diylidyne manganese complexes can proceed also through another pathway with retention of the central C_β–C_β bond and homolysis of the C_β–H bonds in the bis-carbyne moiety as it was found in our studies of oxidation of the manganese phenylvinylidene complexes $(\eta^5\text{-}C_5R_5)(CO)(L)Mn{=}C{=}CHPh$ (R = H, L = PPh_3; R = Me, L = CO) [5b]. CV data and preparative experiments show these compounds to undergo an oxidatively induced dehydrodimerization to bis-vinylidene (2,3-diphenyl-1,3-butadiene-1,4-diylidene) derivatives $(\eta^5\text{-}C_5R_5)(CO)(L)Mn{=}C{=}CPh{-}CPh{=}C{=}Mn(L)(CO)(\eta^5\text{-}C_5R_5)$. However, the reaction pathway depends on the ligand surrounding of the manganese atom (Scheme 2).

For [Mn] = $Mn(CO)_2Cp$ the dehydrodimerization proceeds as a sequence including homolytic cleavage of the C_β–H bond in the 17-e radical cation (**b**), dimerization of resulting 16-e σ-phenylethynyl cation to binuclear 2,3-diphenyl-2-butene-1,4-diylidyne dication (**c**), and two-electron reduction of the latter into the final bis-vinylidene complex (**d**) [5a]. The entire process is fast on the CV time scale. Other examples of the dimerizations of 16-e transition metal σ-alkynyls into corresponding butenediylidynes are discussed in Section 3.1. The redox interconversions of 2-butene-1,4-diylidynes and 1,3-butadiene-1,4-diylidenes are discussed in Section 5.

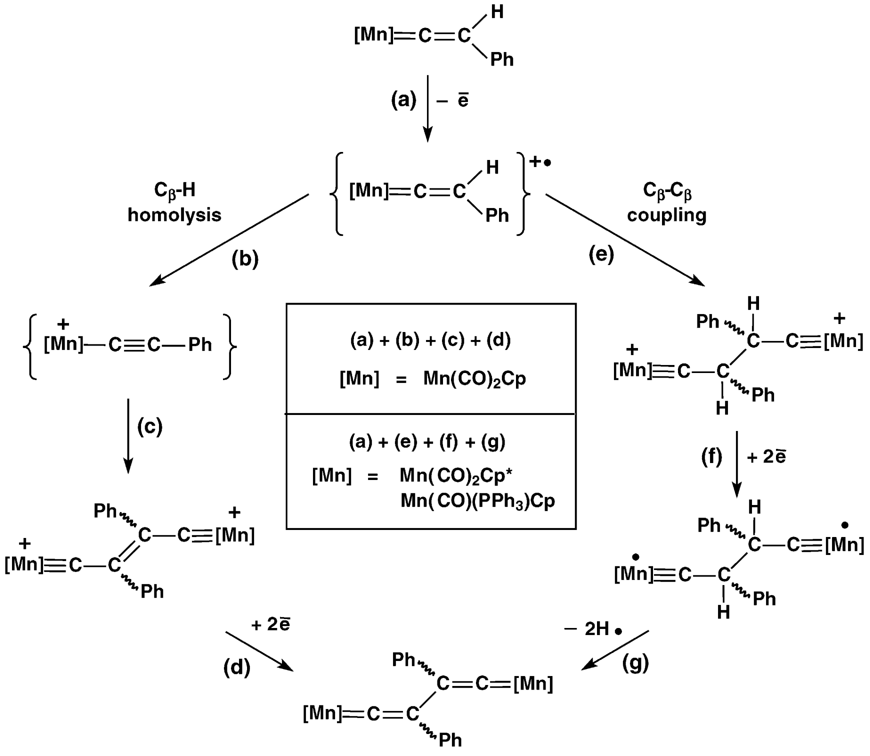


Scheme 1.

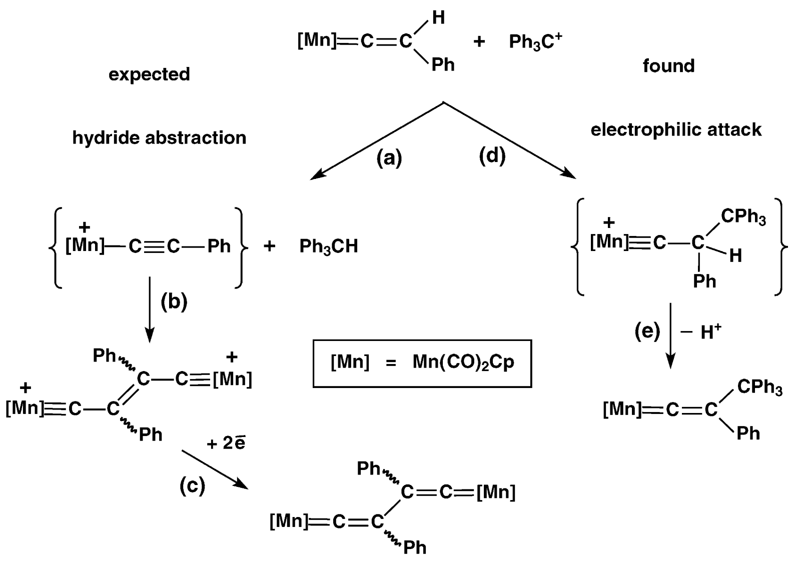
In the case of [Mn] = Mn(L)(CO)(η^5-C_5R_5) (R = Me, L = CO; R = H, L = PPh_3), dehydrodimerization proceeds through the direct C_β–C_β coupling of the 17-e radical cations to 18-e butanediylidyne dimers (**e**), reduction to binuclear 19-e diradicals (**f**), and, finally, homolysis of C_β–H bonds to form bis-vinylidene products (**g**). The last stage (**g**) is slow on the CV time scale (see the Section 4.2, Fig. 1b). It is noteworthy that reduction of 18-e dicationic butanediylidyne derivatives can lead either to C_β–H bonds homolysis (Scheme 2, stage (**g**)) or to C_β–C_β bond cleavage (see the reverse reaction of Eq. (2)) [4]. We have studied the reduction of the mononuclear manganese carbyne complex $[Cp(CO)(PPh_3)Mn{\equiv}C–CH_2Ph]^+$ as a model of stages (**f**) + (**g**) (Scheme 2) and showed that in this case homolytic cleavage of C_β–H bond also takes place to form the corresponding vinylidene complex $Cp(CO)(PPh_3)Mn{=}C{=}CHPh$ (Scheme 17, Section 4.2).

The preparative dehydrodimerization reactions were usually carried out by adding one equivalent of oxidant ($AgBF_4$ or $FcBF_4$) to the solution of the corresponding vinylidene complex in dichloromethane at −40 °C. The reaction mixture was then stirred at –30 to −20 °C to give 2,3-diphenyl-2-butenediylidyne (for $Cp(CO)_2Mn{=}C{=}CHPh$) or 2,3-diphenylbutanediylidyne dications for other vinylidenes; the reaction can be easily monitored by IR-spectroscopy. Addition of a reductant ((η-C_6H_6)$_2$Cr or Et_3N) to the solution of the binuclear bis-carbyne complexes leads to the target bis-vinylidene compounds.

We suppose that the radical cation $[Cp(CO)_2Mn{=}C{=}CHPh]^{+\bullet}$ also undergoes C_β–C_β dimerization (Eq. (3)) but

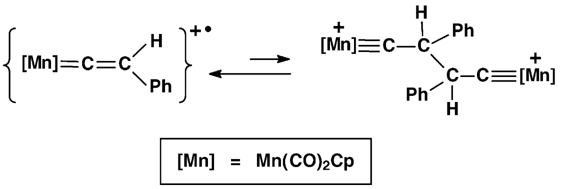


Scheme 2.



Scheme 3.

this equilibrium is strongly shifted to the left owing to instability of the resulting bis-carbyne. Thus, the reaction pathway involving C_β–H bond homolysis in mononuclear 17-e vinylidene radical cation (Scheme 2, (**b**) + (**c**) + (**d**)) becomes feasible.

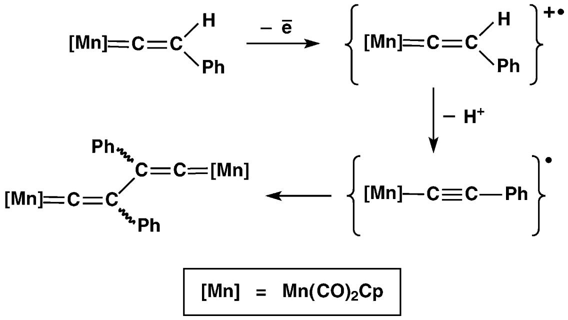


(3)

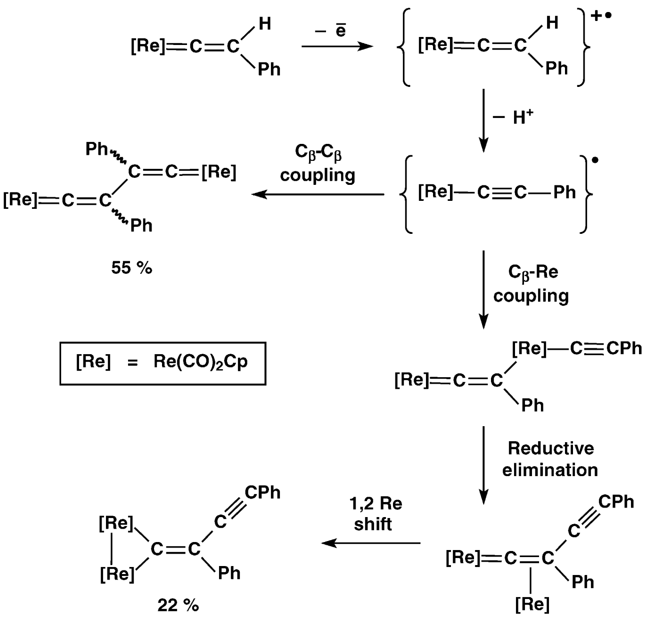
The formation of one of the key intermediates of Scheme 2—$[Cp(CO)_2Mn–C{\equiv}CPh]^+$ from $Cp(CO)_2Mn{=}C{=}CHPh$ as a sequence of one electron oxidation and hydrogen atom loss can formally be considered as hydride abstraction from the initial vinylidene. Therefore we studied the interaction of Ph_3CBF_4 as an abstractor of hydride ion with $Cp(CO)_2Mn{=}C{=}CHPh$ expecting the formation of $[Cp(CO)_2Mn–C{\equiv}CPh]^+$ and its dimerization into $[Cp(CO)_2Mn{\equiv}C–CPh{=}CPh–C{\equiv}Mn(CO)_2Cp]^{2+}$ (Scheme 3, (**a**)–(**c**)). However, a different reaction occured to afford a mononuclear phenyl(trityl)vinylidene complex in 70% yield. The structure of this compound was elucidated by X-ray diffraction [5a]. The electrophilic attack of the trityl cation on the C_β atom followed by deprotonation (Scheme 3, (**d**), (**e**)) is the apparent route for the formation of $Cp(CO)_2Mn{=}C{=}C(CPh_3)Ph$.

All oxidative activations of the vinylidene complexes discussed above were performed in the absence of added base. The probability of the deprotonation of primary oxidation products (17-e vinylidene radical cations) increases considerably in the presence of base. This bisvinylidene $Cp(CO)_2Mn{=}C{=}CPh–CPh{=}C{=}Mn(CO)_2Cp$ can be prepared more conveniently by room temperature oxidation of $Cp(CO)_2Mn{=}C{=}CHPh$ with $FcBF_4$ in the presence of Et_3N [5a]. Under these conditions two competitive reaction pathways are possible: either a C_β–H homolysis route (Scheme 2, (**a**)–(**d**)), or deprotonation of the 17-e radical cation and recombination of resulting 17-e σ-phenylethynyl radicals (Scheme 4).

Addition of base has a more distinctive effect on the oxidative dehydrodimerization of the phenylvinylidene rhenium complex $Cp(CO)_2Re{=}C{=}CHPh$. Our attempts to perform this reaction as for manganese compounds (in line with Scheme 2 (**a**)–(**d**) or (**a**), (**e**)–(**g**)) in the absence of base were unsuccessful because of the gradual decomposition of the primary oxidation product $[Cp(CO)_2Re{=}C{=}CHPh]^{+\bullet}$. At the same time treatment of the dichloromethame solution of $Cp(CO)_2Re{=}C{=}CHPh$ and Et_3N with one equivalent of $FcBF_4$ at room temperature afforded the expected μ-divinylidene product $Cp(CO)_2Re{=}C{=}CPh–CPh{=}C{=}Re(CO)_2Cp$ accompanied by a binuclear complex with a bridging phenyl(phenylethynyl)vinylidene ligand $[Cp(CO)_2Re]_2$ (μ_2-$C{=}CPh(C{\equiv}CPh)$) (ratio 2.5:1). The



Scheme 4.

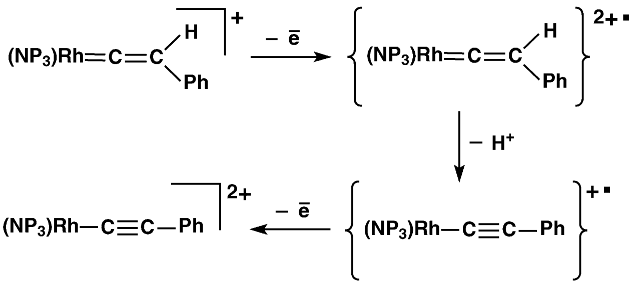


Scheme 5.

structure of the byproduct was determined by X-ray diffraction [6].

We believe that the reaction under these conditions proceeds along the Scheme 5 via deprotonation of the radical cation $[Cp(CO)_2Re{=}C{=}CHPh]^{+\bullet}$ with triethylamine. The target μ-divinylidene complex is formed by C_β–C_β dimerization of intermediate $[Cp(CO)_2Re{-}C{\equiv}CPh]^\bullet$. The minor reaction product, in our opinion, is a result of Re–C_β coupling of radicals followed by reductive elimination and 1,2-shift of the metal site. Such carbon-metal couplings for 17-e σ-alkynyl transition metal complexes were not yet described. Evidently, the analogous 17-e manganese radicals undergo no Mn-C_β coupling, because the formation of the coupling intermediate with four-legged piano stool geometry is sterically non-accessible.

In general, the oxidative activation of cationic vinylidene complexes leads to radical dications as primary products. Deprotonation of such species is often observed even in the absence of base owing to increased acidity of C_β–H bond and afforded 17-e σ-alkynyl radical cations. The clearest example of this process was reported by Bianchini et al. [7]. Oxidative deprotonation of the 18-e cationic complex $[(NP_3)Rh{=}C{=}CHPh]^+$ proceeds along an “electron-chemistry-electron” mechanism (Scheme 6) as was shown by CV and CPE. The primary oxidation product $[(NP_3)Rh{=}C{=}CHPh]^{2+\bullet}$ undergoes spontaneous deprotonation into the 17-e radical cation $[(NP_3)Rh{-}C{\equiv}CPh]^{\bullet+}$ which immediately loses one electron at the potential used and affords the final dication. Unlike other 16-e σ-alkynyl complexes (see Section 3.1) $[(NP_3)Rh{-}C{\equiv}CPh]^{2+}$ is unreactive towards dimerization to corresponding 2-butene-1,4-diylidynes. Oxidative deprotonation for $[(NP_3)Rh{=}C{=}CHCOOEt]^+$ proceeds in the same manner [7].

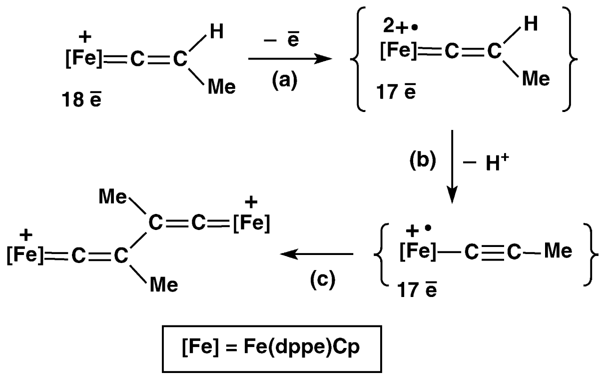


Scheme 6.

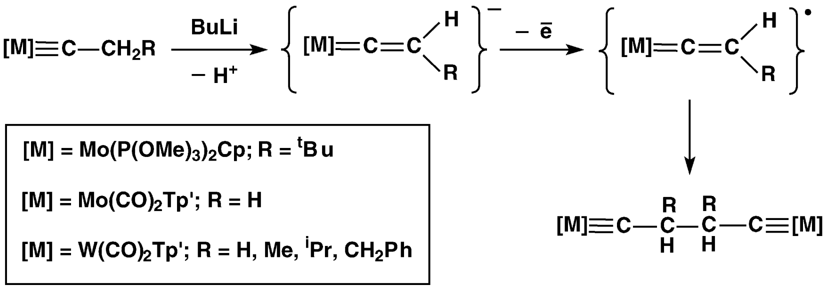
The similar process of consecutive oxidative deprotonation and oxidation of the 17-e intermediate into a 16-e derivative was found for the isocyanide rhenium compound *trans*-$Cl(dppe)_2Re{=}C{=}NH$ which can be considered as aza-analogue of vinylidene complex [8].

The first known example of dehydrodimerization of vinylidene complexes was found by Iyer and Selegue [9]. The cationic propenylidene iron complex was oxidized with an excess of iodosobenzene in acetonitrile solution at room temperature. The binuclear μ-divinylidene dimer was isolated in 77% yield from this reaction (Scheme 7). The authors believe that the reaction scheme involves deprotonation of a radical dication intermediate and dimerization of resulting σ-propynyl radical cation into the dicationic μ-divinylidene complex (Stages (**b**) and (**c**)). The analogous reaction was carried out for $[Cp(dppe)Fe{=}C{=}CHPh]PF_6$ using copper(II) acetate in methanol. However, all efforts by the authors to oxidize complex Cp(dppe)Fe–C≡CMe into the μ-divinylidene dimer using Cu(II), Ag(I) salts, or anodic oxidation failed. This fact indicates some discrepancy with the proposed reaction scheme. Dimerizations of 17-e σ-alkynyl complexes into bis-vinylidene compounds are discussed in detail in Section 3.1.

Whiteley and co-workers have noted [10] that oxidation of the cationic vinylidene complex $[(\eta\text{-}C_7H_7)(dppe)Mo{=}C{=}CHPh]BF_4$ with copper(II) acetate leads to deprotonation resulting in the stable σ-phenylethynyl radical cation $[(\eta\text{-}C_7H_7)(dppe)Mo{-}C{\equiv}CPh]BF_4$. Its dimerization is considered in Section 3.1.



Scheme 7.



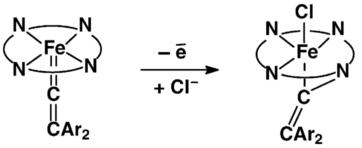
Scheme 8.

Oxidative dehydrodimerization of dianionic [(*meso*-octamethylporphyrinogen)Ru=C=CH$_2$]$^{2-}$ into [(*meso*-octamethylporphyrinogen)Ru=C=CH–CH=C=Ru(*meso*-octamethylporphyrinogen)]$^{4-}$ in 85% yield was carried out by Floriani et al. using phenyl azide as an oxidant [11].

Oxidative activation of the anionic vinylidene complexes have been studied in the groups of Green and Templeton [12]. The initial vinylidene compounds were prepared in situ by treatment of the corresponding carbyne complexes with a strong base (Scheme 8). The oxidation of the vinylidene anions occurs under mild conditions using FcBF$_4$ [12a,b], copper salts [12b], iodine, and even nitrobenzene [12a]. The resulting vinylidene radicals undergo C$_\beta$–C$_\beta$ dimerization to form neutral binuclear compounds with bridging butane-1,4-dicarbyne ligands. The yields of dimerization products are lower if a bulky substituent is present at the C$_\beta$ atom. Under the conditions used no products of metal-metal coupling characteristic for 17-e metal carbonyl radicals were observed.

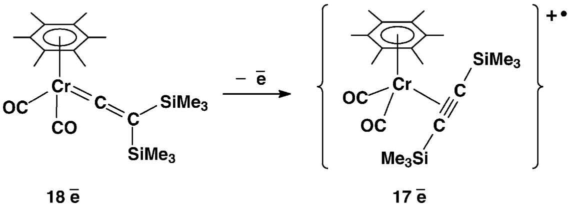
The order of the central C–C bond can be increased to 2 and even to 3 by deprotonation/oxidation sequences (Scheme 9) [12a]. Oxidation of dianionic μ-1,3-butadiene-1,4-diylidene complexes affords the corresponding 2-butene-1,4-diylidyne derivatives (Stage (**b**)) and similar reactions of 1,2,3-butatriene-1,4-diylidene dianions lead to 2-butyne-1,4-diylidyne complexes (Stage (**d**)).

An unusual oxidatively induced C–N coupling in di(4-chlorophenyl)vinylidene iron complex (Eq. (4)) was reported by Lange and Mansuy [13]. The product formation can be regarded as insertion of vinylidene moiety into the Fe–N bond accompanied by coordination of chloride.



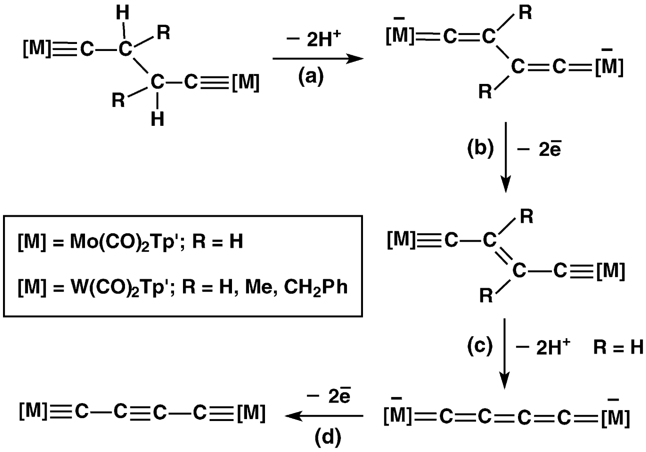
(4)

Oxidative activation of the vinylidene complexes results in C–H and C–C bonds formation or cleavage reactions in all cases considered above. An unusual example of oxidatively induced vinylidene–acetylene rearrangement was reported by Connelly et al. [14], Eq. (5).



(5)

A neutral 18-e alkyne compound can be prepared by reduction of 17-e alkyne radical cation but this complex is unstable and undergoes acetylene–vinylidene isomerization. Thus, a position of the tautomeric acetylene–vinylidene equilibrium is strongly dependent on the electronic configuration (d^5 versus d^6) of the metal atom.

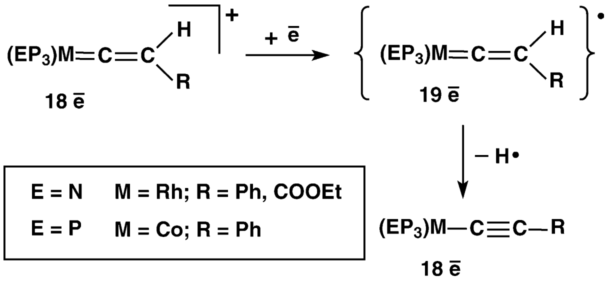


Scheme 9.

2.2. Reductive activation of vinylidene complexes

These processes have been much less studied compared to oxidatively induced reactions of vinylidene complexes. However, few examples of reductive activation of 18-e complexes of cobalt and rhodium have been reported by Bianchini et al. [7,15] (Scheme 10). The intermediate 19-e vinylidene complexes eliminate rapidly the hydrogen atom from the C$_\beta$ position to form 18-e σ-alkynyls and molecular hydrogen, which was detected by gas chromatography. These transformations are fast on the CV time scale and were performed on a preparative scale using CPE.

The formation of a new 18-e complex obviously provides the thermodynamic feasibility of such reactions. The fast reductive activation of the C$_\beta$–H bond is caused by two reasons: «anchimeric assistance» by the multiple M–C$_\alpha$ bond



Scheme 10.

to hydrogen atom elimination and small structural changes accompanying this transformation (the metal atom retains its coordination geometry during the reaction and only the hybridization of C_β atom is changed). Related processes of reductive activation of the C_β–H bond in alkylidyne complexes are discussed in Section 4.2.

The unusual example of reductive activation of the C_β–C_β bond in ruthenium μ-divinylidene [(*meso*-octamethylporphyrinogen)Ru=C=CH–CH=C=Ru(*meso*-octamethylporphyrinogen)]$^{4-}$ was found by Floriani et al. [11]. The reduction of the complex with sodium naphthalenide leads to $\{(\mu\text{-}N_2)[(\textit{meso}\text{-octamethylporphyrinogen})RuC{\equiv}CH]_2\}^{6-}$ as a result of homolytic cleavage of the C_β–C_β bond and dinitrogen coordination. This process can be realized in the reverse direction by the treatment with two equivalents of $FcBPh_4$.

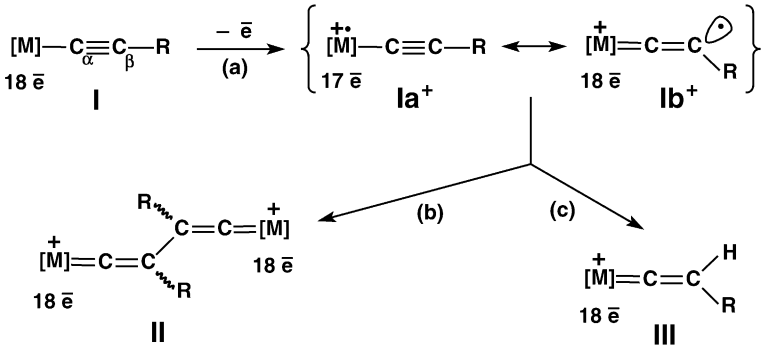
3. Redox induced reactions of σ-alkynyl complexes of transition metals

3.1. Oxidative activation of σ-alkynyl complexes

The electronic structure of 17-e σ-alkynyl compounds can be described as a resonance hybrid of the metal- (**Ia**$^+$) and carbon-centered (**Ib**$^+$) forms (Scheme 11). Accordingly, either ligand-to-ligand C_β–C_β dimerization into the corresponding bis-vinylidenes **II** (Path (**b**)) or hydrogen radical abstraction from the solvent or from the added hydrogen source (Path (**c**)) can be expected to proceed. The known examples of these processes are given in the Table 1.

The structural changes induced by electron removal can evidently be revealed by comparing the molecular geometries of molybdenum σ-phenylethynyls $[(\eta\text{-}C_7H_7)(dppe)MoC{\equiv}CPh]^{n+}$ (n = 0, 1). A contribution of the carbon-centered resonance structure becomes apparent on shortening the Mo–C_α distance from 2.139 Å (n = 0) to 2.068 Å (n = 1) [16]. IR spectroscopy data show the shift of $\nu_{C\equiv C}$ from 2045 cm^{-1} (n = 0) to 2032 cm^{-1} (n = 1), also confirming a contribution of the structure **Ib**$^+$ [17]. At the same time ESR spectroscopy data provide the evidence for significant localization of spin density on the metal and phosphorous atoms and not on the alkynyl ligand [17]. In contrast to the above molybdenum complexes electron removal from 17-e iron complex $(PP_3)FeC{\equiv}CPh$ leads to the considerable structural changes only in PP_3 ligand leaving Fe-alkynyl fragment practically unchanged [18]. The complex $[(\eta\text{-}C_7H_7)(dppe)MoC{\equiv}CPh]^{+\bullet}$ is stable on the CV time scale and slowly dimerizes on prolonged stirring in THF solution (20 °C, 24 h) [10,19]. The dimerization of $[(\eta\text{-}C_7H_7)(dppe)MoC{\equiv}C^nBu]^{+\bullet}$ (CH_2Cl_2, 20 °C, 15 min) proceeds much faster. At the same time $[(\eta\text{-}C_7H_7)(dppe)MoC{\equiv}C^tBu]^{+\bullet}$ bearing a sterically demanding substituent at the C_β atom does not dimerize even after prolonged stirring. Instead, the cationic vinylidene $[(\eta\text{-}C_7H_7)(dppe)MoC{\equiv}CHPh]^+$ is formed presumably by hydrogen abstraction from the reaction medium [19] (Scheme 11, Path (**c**)).

All other successful dimerizations of 17-e alkynyls proceed similarly, i.e. 17-e alkynyl generated by oxidation of electron rich precursor should have the life-time enough to ensure dimerization. If the dimerization is blocked by the presence of a bulky substituent at the acetylide moiety the hydrogen abstraction becomes the prevailing reaction (Scheme 11, (**c**)). Sometimes the reaction course is strongly determined by reaction conditions. For example, the radical cation $[Cp^*(dppe)FeC{\equiv}CH]^{+\bullet}$ dimerizes below −50 °C, but undergoes hydrogen abstraction at room temperature [20]. The opposite phenomenon was found by Otero and co-workers for 17-e niobium σ-alkynyl radical cation $[(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)NbC{\equiv}CPh]^{+\bullet}$ [21].



Scheme 11.

Table 1
Transformations of 17-e σ-alkynyl complexes

[M]	R	Reaction pathway	Reference
$(\eta^5{-}C_5H_4SiMe_3)_2(CO)Nb$	Ph	**b** (at 20 °C), **c** (at −30 °C)	[21]
$(\eta^5{-}C_5H_4SiMe_3)_2(CO)Nb$	^{t}Bu	**c**	[21]
$(\eta^5{-}C_5H_4SiMe_3)_2(PPhMe_2)Nb$	Ph	**c**	[21]
$(\eta{-}C_7H_7)$(dppe)Mo	Ph, ^{n}Bu	**b**	[19]
	^{t}Bu	**c**	
Cp*(dppe)Fe	H	**b** (at −80 °C), **c** (at 20 °C)	[20]
$Cp(P(OMe)_3)_2Ru$	Ph	**b**	[24]
$Cp(PPh_3)_2Ru$	Ph	**b**	[22]
trans-Cl(dppe)$_2$Ru	CH_3, ^{i}Pr, $CHPh_2$	**c** (increasing reactivity CH_3 < ^{i}Pr < $CHPh_2$)	[27]

In this case, the hydrogen atom abstraction occurs at −30 °C whereas the C_β–C_β coupling takes place at room temperature. The solvent identity can also be of decisive importance. Bruce et al. showed the reaction of $Cp(PPh_3)_2RuC{\equiv}CPh$ with $AgPF_6$ in toluene to yield the complex $\{[Cp(PPh_3)_2RuC{\equiv}CPh]_2Ag\}PF_6$ (75% for the reagents ratio 2:1) wherein the silver atom is coordinated to carbon-carbon triple bonds. However, the addition of dichloromethane to the complex readily affords the dimerization product $[Cp(PPh_3)_2Ru{=}C{=}CPh{-}CPh{=}C{=}Ru(PPh_3)_2Cp]^{2+}$ in 82% yield (for the reagents ratio 1:1) [22].

Two another bis-vinylidene complexes $\{[P(OMe)_3]_2(CO)_2Fe{=}C{=}C(CHO_2(CH_2)_3){-}C(CHO_2(CH_2)_3){=}C{=}Fe(CO)_2[P(OMe)_3]_2\}$ [23] and $\{Cp[P(OMe)_3]_2Ru{=}C{=}CPh{-}CPh{=}C{=}Ru[P(OMe)_3]_2Cp\}_2(BF_4, PF_6)_2$ [24] were obtained in low yields (3–5%). Presumably they also arise from dimerization of corresponding 17-e σ-alkynyl complexes. In the case of the iron complex, an oxidative activation of the C_γ–H bond should also proceed before the dimerization step.

An unusual C_β–C_β coupling was found by Otero and co-workers [25], Scheme 12. Oxidation of the 17-e π-alkyne complex proceeds as a multistep process involving oxidative addition across the carbon–carbon bond of the alkyne in the 16-e complex (**b**) followed by the loss of methoxy group (**c**) to give μ-divinylidene complex in 70% yield.

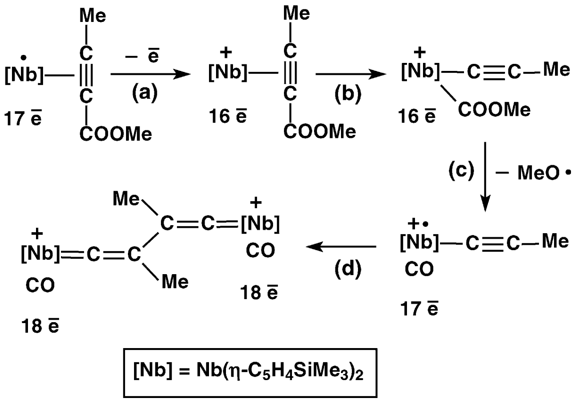
The authors assume C_β–C_β coupling in the intermediate 17-e σ-alkynyl complex to be the key step directly responsible for the formation of the reaction product (**d**). It is noteworthy that the reaction proceeds only at room temperature in concentrated solution whereas oxidation of the starting alkyne complex by $FcBPh_4$ at 20 °C in a tenfold diluted solution yields the expected 16-e alkyne complex as the only product (Step (**a**)).

At the same time there are a great deal of 17-e σ-alkynyl radical cations which are closely related by their structure to those which undergo dimerization according to Scheme 11 (**b**) but, nevertheless, undergo neither dimerization nor hydrogen abstraction [10,26]. One can assume that these processes are very slow owing to low spin density at the C_β atom of the alkynyl ligand.

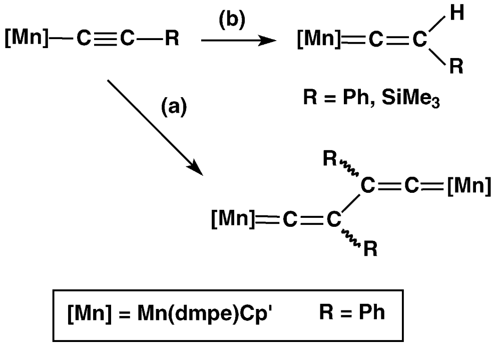
The neutral 17-e phenylethynyl manganese radical was reported by Berke et al. [3] to undergo slow coupling (C_6H_6, 20 °C, 6 weeks), Scheme 13, (**a**)). Only a moderate yield of the bis-vinylidene was achieved (35%); addition of hydrogen radical to the C_β atom affording the mononuclear vinylidene (Path (**b**)) also took place. The latter pathway becomes a prevailing in the presence of hydrogen donors. For R = $SiMe_3$ a path (**b**) is a sole pathway under either conditions.

An outcome of the oxidative activation of σ-alkynyl ruthenium complexes strongly depends on the identity of a substituent at the C_γ atom [27] (Scheme 14).

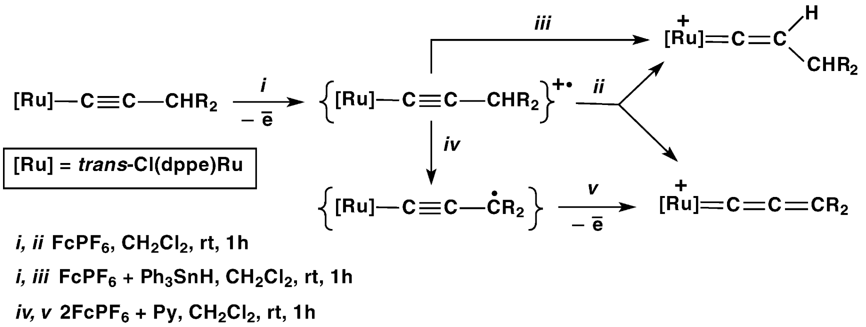
For R = Ph the 17-e radical cation undergoes disproportionation to give an equimolar mixture of cationic vinylidene



Scheme 12.



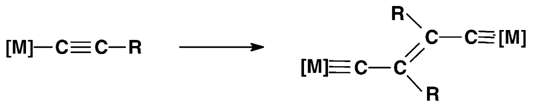
Scheme 13.



Scheme 14.

and allenylidene complexes (***i*** + ***ii***). For R = H, Me this process is considerably slower (under the same conditions conversions were 5 and 15%, respectively). This is presumably caused by the lower spin density at the C_β atom. In the presence of hydrogen donors the mononuclear vinylidenes are again the sole products (path ***i*** + ***iii***). The allenylidene complex was prepared by treating the starting σ-alkynyl with two equivalents of oxidant in the presence of base. In the authors' opinion the reaction proceeds in this case by deprotonation of the radical cation at the C_γ position followed by oxidation of the intermediate radical by the second equivalent of oxidant (***i***+***iv***+***v***).

Some 16-e σ-alkynyl complexes are also able to undergo C_β–C_β dimerization to afford corresponding 2-butene-1,4-diylidynes (Eq. (6)).



(6)

$[M] = \overset{+}{M}n(CO)_2Cp$, R = Ph $[M] = \overset{+}{M}n(dmpe)Cp'$, R = Ph	$[M] = Mo(N(CH_2CH_2NSiR_3)_3)$ R = H, $R_3 = Me_3$, Me_2Ph
$[M] = Mo[N(CHMe_2)(3,5\text{-}Me_2C_6H_3)_2]_3$	R = Ph, Me, ^nBu, $(CH_2)_3CN$, $4\text{-}CF_3C_6H_4$, $4\text{-}MeOC_6H_4$

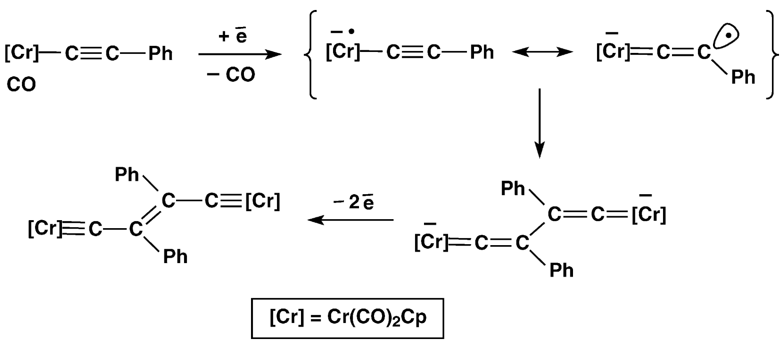
The clearest example of such dimerization was reported in [3]. A dimerization of manganese σ-phenylethynyl $[Cp'(dmpe)Mn\text{-}C{\equiv}CPh]^+$ proceeds slowly (CH_2Cl_2, 20 °C, 6 weeks) to give a low yield of the corresponding enediyne (20%). Such dimerization can be considered as a model for dimerization of $[Cp(CO)_2Mn–C{\equiv}CPh]^+$ the key intermediate in oxidative dehydrodimerization of manganese phenylvinylidene $Cp(CO)_2Mn{=}C{=}CHPh$ (Scheme 2) [5a].

The dimerizations (**6**) can be thought to proceed via C_β-centered radicals arising owing to redistribution of π-electron density along the carbon–carbon and the metal–carbon bonds. Therefore, such dimerization processes can also be expected for σ-alkynyl complexes that are even less electron saturated. The dimerization of formally 10-e and 12-e σ-alkynyl molybdenum complexes can be the examples of such processes [28] (Eq. (6)).

Attention should be paid to the fact that dimerizations of the 17-e σ-alkynyl radical $[Cp'(dmpe)Mn–C{\equiv}CPh]^\bullet$ and 16-e σ-alkynyl cation $[Cp'(dmpe)Mn–C{\equiv}CPh]^+$ proceed at nearly the same rate. Apparently, the charge of the metal atom has no decisive influence on ligand-to-ligand coupling (Scheme 13 and Eq. (6), respectively).

3.2. *Reductive activation of σ-alkynyl complexes*

It was shown by Ustynyuk et al. that C_β–C_β coupling could also be induced by reductive activation of σ-alkynyl complexes. Thus reduction of $Cp(CO)_3Cr–C{\equiv}CPh$ with alkali metals gave the neutral enediyne $Cp(CO)_2$



Scheme 15.

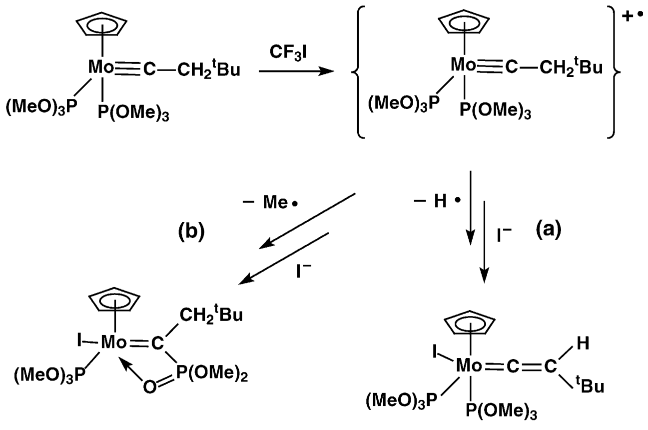
Cr≡C–CPh=CPh–C≡Cr(CO)$_2$Cp in 30% yield (Scheme 15) [29]. The structure of the latter was established by X-ray diffraction [29a]. It was concluded from CV and CPE studies that the addition of electron to the starting phenylethynyl complex caused decarbonylation followed by C$_\beta$–C$_\beta$ dimerization to afford the dianionic bis-vinylidene. The latter intermediate can easily be oxidized into the final product. A limitation of this reaction is instability of the product under conditions of its generation therefore only moderate yields are achievable. Similar transformations of molybdenum and tungsten analogues were found to give even lower yields of the corresponding enediynes [29b]. The other redox induced interconversions of bis-vinylidene and 2-butene-1,4-diylidyne complexes are discussed below in Section 5.

4. Redox induced reactions of transition metal alkylidyne complexes

4.1. Oxidative activation of alkylidyne complexes

Oxidative activation of transition metal alkylidyne complexes remains essentially unexplored. Such an oxidative activation of 18-e alkylidyne complexes can be expected by analogy with vinylidene complexes to undergo homolysis or deprotonation of the C$_\beta$–H bond affording 16-e or 17-e vinylidene complexes, respectively. However, clear examples of such processes were not reported until now. Some examples of C–H bond activation were found by McElwee-White and Torraca [30] on studying the photoinduced electron transfer in alkylidyne complexes of molybdenum and tungsten but we do not discuss them here. Pombeiro et al. reported [31] that alkyl substituted carbyne complexes of rhenium [Re]$^+$≡C–CH$_2$R ([Re] = *trans*-ReCl(dppe)$_2$, R = Ph or ^{t}Bu) oxidized reversibly at +1.60 and +1.56 V, respectively, in acetonitrile (versus SCE) and activation of C–H bond was not observed. Unlike the above alkylidynes the oxidation of the aminocarbyne complex [Re]$^+$≡C–NH$_2$ results in the deprotonation into the corresponding isocyanide [Re]$^+$=C=NH [8]. Electrochemical oxidation of cationic and neutral alkenylcarbyne complexes of tungsten (dppe)(CO)$_2$LW$^+$≡C–CH=C(CH$_2$)$_n$ and (dppe)(CO)$_2$(X)W≡C–CH=C(CH$_2$)$_n$ (n = 4 or 7, L = CO [8c], CH$_3$CN [8d], CNR [8e]; X = Cl, SCN, OCN [8c]; CN [8d]) was studied by CPE. The process is multielectronic and accompanied by the loss of protons, the number of consumed electrons and the amount of protons formed being dependent on the nature of X and L. For example, the CPE of acetonitrile (L = CH$_3$CN) and cyanide (X = CN) complexes proceeds with a consumption of three electrons and accompanied by the loss of three and one protons, respectively [8d]. The authors believe that the deprotonation involves both C$_\beta$–H and C–H bonds of cycloalkanylidene fragment, however attempts to isolate corresponding complexes failed.

An unusual example of iodovinylidene complex formation by the reaction of molybdenum carbyne complex with trifluoromethyliodide was described [32]. The authors presumed that the reaction is a multistep process with electron transfer from the carbyne complex to CF$_3$I in the first step (Scheme 16). The vinylidene ligand is formed through homolysis of the C$_\beta$–H bond in the 17-e carbyne intermediate (Step (**a**)). Nucleophilic addition of iodide ion completes the formation of Cp(P(OMe)$_3$)$_2$(I)Mo=C=CH^{t}Bu.



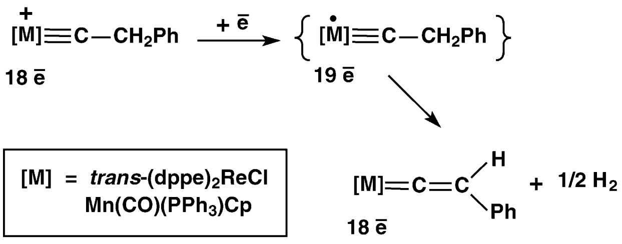
Scheme 16.

The chelate carbene-phosphonate complex Cp(P(OMe)$_3$)(I)Mo=C(PO(OMe)$_2$)CH^{t}Bu is also formed presumably via competitive trimethylphosphite shift from the metal center to the C$_\alpha$ atom followed by an Arbusov like rearrangement.

4.2. Reductive activation of alkylidyne complexes

By analogy with the reductive activation of vinylidene complexes the reduction of 18-e alkylidyne complexes can proceed through homolytic scission of the C$_\beta$–H bond to yield 18-e vinylidene compounds. However, such processes are extremely rare. It was pointed out by Pombeiro [31] that the reduction of benzylcarbyne cation leads to a phenylvinylidene complex (Scheme 17). Hydrogen was detected by gas chromatography. The monoelectronic reduction of 18-e cationic alkenylcarbyne complexes of tungsten (dppe)(CO)$_2$LW$^+$≡C–CH=C(CH$_2$)$_n$ (n = 4 or 7, L = CO [8c], CH$_3$CN [8d], CNR [8e]) was reported to proceed irreversibly but the expected allenylidene complexes (dppe)(CO)$_2$LW=C=C=C(CH$_2$)$_n$ were not detected.

Another example of reductive scission of C$_\beta$–H bond was found by our group [6]. The manganese benzylcar-



Scheme 17.

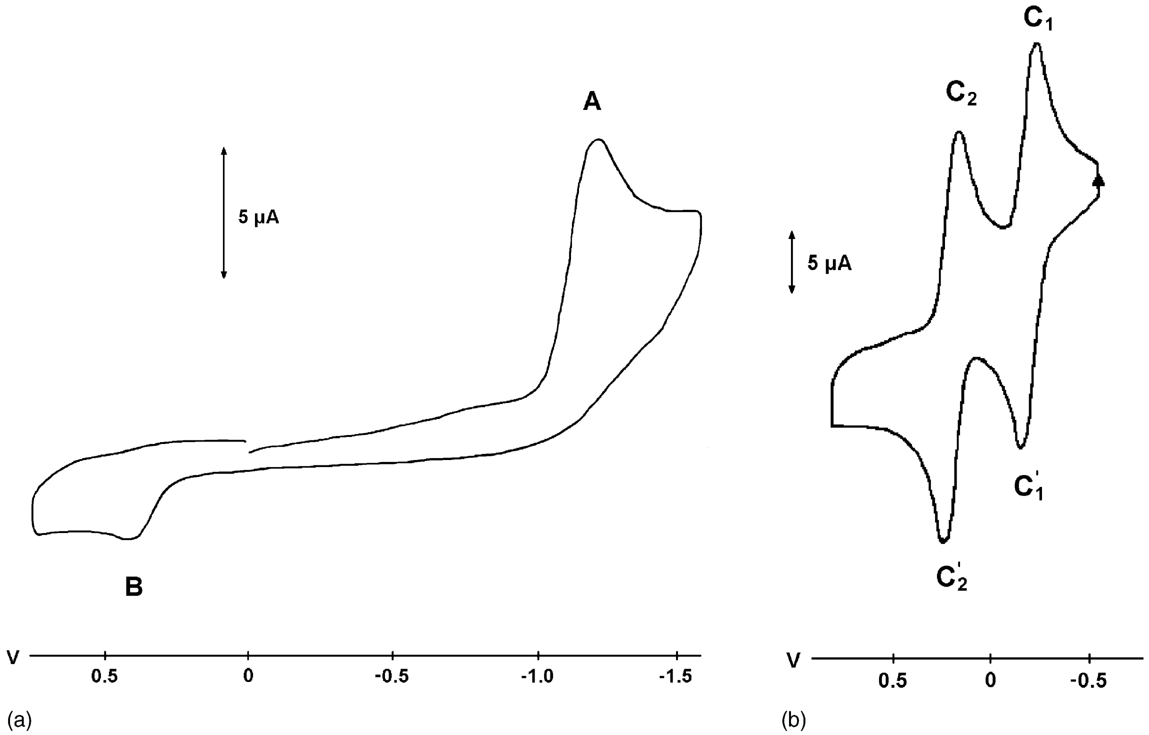
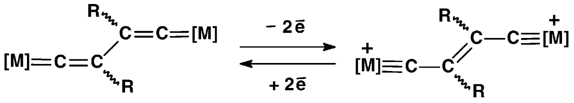


Fig. 1. Cyclic voltammogramm of complexes $[Cp(CO)(Ph_3P)Mn{\equiv}C{-}CH_2Ph]BF_4$ (a), and $[Cp(CO)(Ph_3P)Mn{\equiv}C{-}CHPh{-}CHPh{-}C{\equiv}Mn(CO)(PPh_3)Cp](BF_4)_2$ (b). (CH_2Cl_2, GC-electrode, 0.1 M $^{n}Bu_4NPF_6$, sweep rate 200 mV s^{-1}, potentials vs. SCE).

byne cation $Cp(CO)(Ph_3P)Mn^{+}{\equiv}C{-}CH_2Ph$ undergoes irreversible one-electron reduction at −1.23 V (versus SCE) (Fig. 1a, peak **A**). On the reverse scanning of potential the peak **B** appears at the potential characteristic for the authentic phenylvinylidene complex $Cp(CO)(Ph_3P)Mn{=}C{=}CHPh$. It is interesting to note that related binuclear bis-carbyne complex $[Cp(CO)(Ph_3P)Mn^{+}{\equiv}C{-}CHPh{-}CHPh{-}C{\equiv}Mn^{+}(CO)(PPh_3)Cp](BF_4)_2$ undergoes reversible reduction under CV conditions (Fig. 1b, peaks **C**$_1$, **C**$_2$), though preparative reduction leads to the homolysis of the $C_\beta{-}H$ bonds to form the corresponding bis-vinylidene [5b]. Alternatively, the reduction of related manganese butanediylidyne complexes can proceed through a scission of the $C_\beta{-}C_\beta$ bond and regeneration of mononuclear vinylidene complexes (reverse reaction to Eq. (2)).

5. Oxidatively induced nucleophilic addition to binuclear complexes with a bridging μ-2,3-Ph_2-1,3-butadiene-1,4-diylidene ligand

Redox induced reactions of vinylidene and σ-alkynyl complexes can be successfully used for synthesis of binuclear complexes with bridging μ-divinylidene (1,3-butadiene-1,4-diylidene) and μ-enedicarbyne (2-butene-1,4-diylidyne) ligands, as was shown in the previous sections. The chemistry of such compounds can provide in the future some new opportunities for their use in organic synthesis because, first, two electrophilic C_α and two nucleophilic C_β atoms are present in the molecule and, second, these reaction centers can be selectively activated or blocked using redox reactions. The known examples of redox transformations for bis-vinylidene and bis-carbyne complexes are given in Eq. (7).

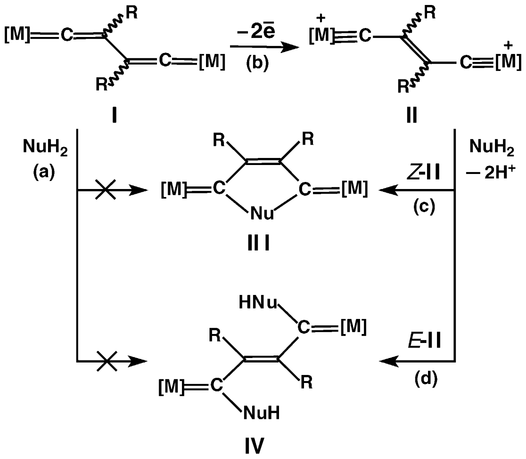


(7)

Ref.	
[11a]	[M] = $\bar{M}o(CO)_2Tp'$; R = H [M] = $\bar{W}(CO)_2Tp'$; R = H, Me, CH_2Ph
[30]	[M] = $Mn(CO)_2Cp$; R = Ph [M] = $Mn(CO)_2Cp^*$; R = Ph
[3]	[M] = $Mn(dmpe)Cp'$; R = Ph

Transition metal μ-2-butene-diylidynes can also be prepared by alternative methods, for instance using alkyne metathesis [33].

We began a systematic study of oxidatively induced nucleophilic additions to the C_α-atoms in transition metal bis-vinylidene compounds as shown in the general Scheme 18. If these carbon atoms are insufficiently electrophilic to undergo addition of protonic nucleophiles (Scheme 18, (**a**)) the reaction can be induced by two-electron oxidation of the bis-vinylidenes **I** into dicationic 2-butene-1,4-diylidyne complexes **II** (Scheme 18, (**b**)). Both C_α carbons in such compounds are more electrophilic relative to those of the initial complexes **I**, facilitating the formation of nucleophilic ad-



Scheme 18.

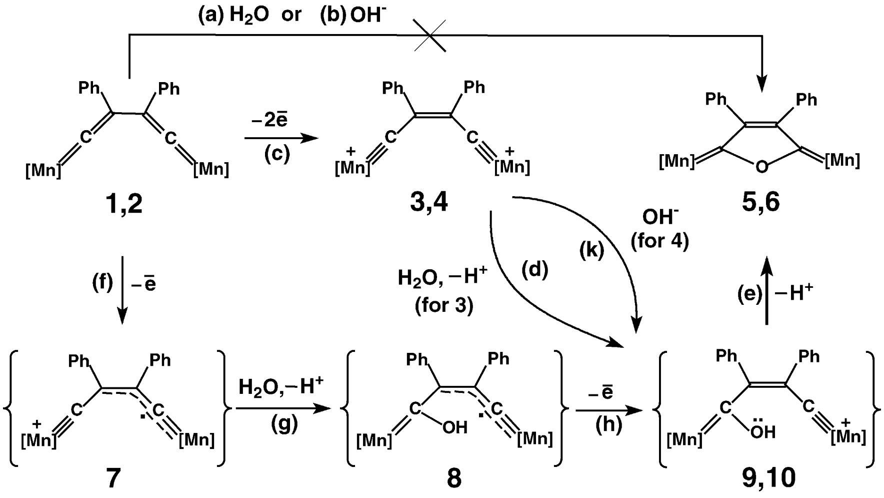
dition products **III** or **IV**. For diprotonic nucleophiles and isomers of **II** with a *Z*–C_β–C_β central double bond, a nucleophilic addition (Scheme 18, (**c**)) is expected to proceed with a cyclization into cycloalkenediylidene complexes **III**. In the case of *E*-isomers of **II** reactions (**d**) should lead to acyclic binuclear complexes **IV** with a bridging 2-butene-1,4-diylidene ligand.

In the context of exploring the reactions of Scheme 18 it is important to know the geometry of the central C_4 moiety in complexes **II**. In the initial bis-vinylidenes **I** the occurrence of s-*cis* or s-*trans* conformations of the central C_4 moiety (torsion angles C_α-C_β-C_β-C_α of 0° and 180°, respectively) is governed by the steric requirements of both R groups and the metal surroundings, this angle being found to be close to 180° in crystallographically studied complexes **I** [9,16,19,21]. Only in two manganese complexes Cp′(dmpe)Mn=C=CPh–CPh=C=Mn(dmpe)Cp′ [3] and Cp*$(CO)_2$Mn=C=CPh–CPh=C=Mn$(CO)_2$Cp* [34] the values of C_α–C_β–C_β–C_α angle are 86.3° and −76.4° respectively. The known conformation of **I** enables the straightforward prediction of the geometry of the C_α–C_β–C_β–C_α moiety in **II**, provided that the oxidation of **I** (i.e. s-*cis*-**I** → *Z*-**II** or s-*trans*-**I** → *E*-**II**) proceeds selectively. However, this assumption need to be experimentally tested especially for the reactions carried out in coordinating solvents.

To ensure successful realization of the reaction of the Scheme 18 the reagents **I** and NuH_2 should meet the following requirements:

1. the bis-vinylidenes **I** should be inert to NuH_2 under conditions of thermal initiation; the reaction should be induced by oxidation of **I** into **II**;
2. the nucleophiles NuH_2 should be of limited reducing ability in order to not remove the target intermediates **II** from the reaction media by reducing them into the initial μ-divinylidenes **I**;
3. the reaction centers (C_α atoms) of bis-carbynes **II** should be sterically accessible for the attack by nucleophiles NuH_2.

We have studied [34] the oxidatively induced addition of oxygen nucleophiles (H_2O, OH^-) to manganese bis-vinylidene complexes (η^5-C_5R_5)$(CO)_2$Mn=C=CPh–CPh=C=Mn$(CO)_2$(η^5-C_5R_5) (**1**, R = H; **2**, R = Me) (Scheme 19). It was shown that cyclized bis-carbene products **5**, **6** are formed and this reaction proceeds via the pathway (**b**) + (**c**), (Scheme 18). Complex **1** is unreactive towards an excess of water but the addition of oxidant ($FcBF_4$, $AgBF_4$)



1,3,5,7,8,9	[Mn] = Mn$(CO)_2$Cp
2,4,6,10	[Mn] = Mn$(CO)_2$Cp*

Scheme 19.

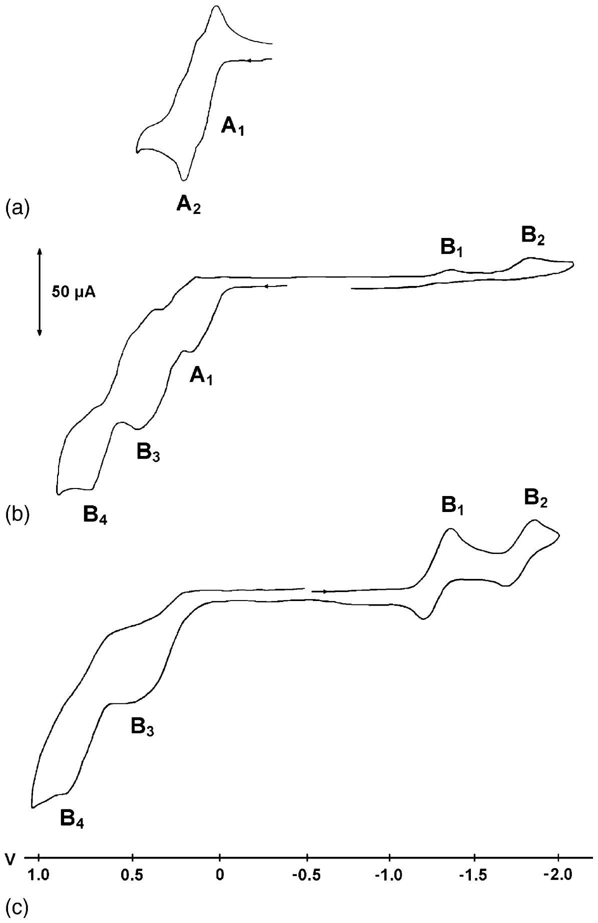


Fig. 2. Cyclic voltammogramm of complexes 1 (a); 1 + H_2O (b); 5 (c). (THF, GC-electrode, 0.2 M $^n Bu_4NPF_6$, sweep rate 200 mV s^{-1}, potentials vs. Fc).

immediately induces the reaction to afford **5** in 76–90% yield. CV studies revealed that reaction of **1** with water starts after the first electron is removed and is fast on the CV time scale (Fig. 2).

Compound **1** in THF solution shows two reversible one-electron oxidation peaks **A**$_1$, **A**$_2$ (Fig. 2a) corresponding to the removal of the first and the second electron, respectively. Addition of water to the solution of **1** in THF changes the cyclic voltammogram considerably (Fig. 2b). Even the first oxidation peak **A**$_1$ becomes irreversible and new reduction peaks **B**$_1$ and **B**$_2$ appear on the cathodic branch of the cyclic voltammogram. These peaks coincide in their potentials with those of reference compound **5** (Fig. 2c).

CV data and chemical experiments reveal the reaction of **1** with H_2O in THF solution to proceed via stages (**f**) + (**g**) + (**h**) + (**e**), (Scheme 19). The synthesis of **5** can also be performed as a sequence of two-electron oxidation of **1** and double nucleophilic attack of oxygen atom on C_α atoms of the bis-carbyne ligand (Scheme 19, (**c**) + (**d**) + (**e**)), if the reaction proceeds in a solvent of low coordination ability like dichloromethane.

Complex **2** does not react with water in the presence of oxidant due to lower electrophilicity and greater shielding of the C_α atoms. However, in a doubly oxidized form it reacts with a stronger nucleophile, namely hydroxide ion, to give **6** in 15% yield (Scheme 19, (**c**) + (**k**) + (**e**)). The molecular structures of **5** and **6** were determined by X-ray diffraction [34].

The reaction sequencies (Scheme 19, (**f**) + (**g**) + (**h**) + (**e**) and (**c**) + (**d**) + (**e**)) are the first examples of oxidatively induced nucleophilic addition to bis-vinylidene complexes resulting in a cyclic products (Scheme 18, (**b**)+(**c**)).

6. Concluding remarks

This review clearly shows that redox activation of transition metal vinylidene and related complexes leads to the appearance of spin density on the ligand so that subsequent reactions (C_β–C_β dimerizations, cleavage and formation of C_β–H bonds etc.) proceed as a rule at the C_β atoms and not at the metal atom as could be expected for example for 17-e complexes [35]. Results of redox initiated reactions are controlled by a delicate balance of a number of factors mainly a charge and a ligand environment of the metal and a steric volume of substituents at C_β atoms. However, some non-radical reactions like nucleophilic addition to the C_α atoms in transition metal bis-vinylidenes can also be redox initiated.

Some reactions of transition metal vinylidene (for example cycloaddition processes) have not yet been neither covered by the redox-activation methodology nor subjected to the quantum-chemical analysis. Nevertheless one can forecast that new redox reactions of transition metal vinylidenes will be developed in a near future including redox catalytic transformations.

Acknowledgements

Authors are grateful to Russian Foundation for Basic Research (Grants No. 99-03-33060, 02-03-33180) and Program of the Presidium of the Russian Academy of Sciences "Directed synthesis of substances with a prescribed properties" (No. 587-03) for support of our study of redox reactions of the transition metal vinylidene and carbyne complexes. We also express deep thanks to our colleagues M.G. Peterleitner for electrochemical studies and A.H. White, V.N. Khrustalev and M.Yu. Antipin for X-ray crystallography studies and stimulative discussions.

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