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Redox induced reactions of transition metal π- and σ,π-complexes

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Abstract In this review, redox-induced reactions of π- and σ,π-complexes leading to the selective formation (or cleavage) of C–H, C–C, and C–O bonds have been summarized. To illustrate the synthetic potential of such methodology, the following representative reactions studied in our group are discussed: (1) oxidatively induced hydrogen elimination from "open" cyclic diene and dienyl complexes resulting in formation of "closed" dienyl and arene complexes, respectively; (2) reductive activation of C–H bonds in diene, vinylidene, and carbyne complexes forming new multiple C–C bonds; (3) oxidative dehydro-dimerization of vinylidene complexes into binuclear μ-divinylidene species; and (4) oxidatively induced addition of oxygen nucleophiles to μ-divinylidene complexes affording cyclic μ-dicarbene derivatives.

Keywords Redox induced reactions · Oxidative hydrogen abstraction · Vinylidene complexes · Alkylidyne complexes · Cyclic voltammetry
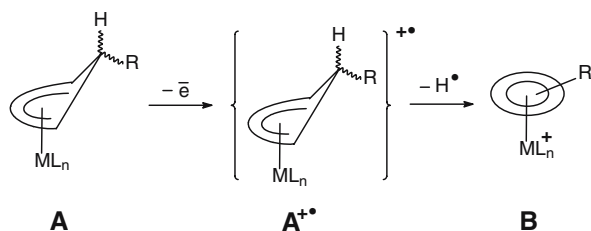
Introduction

Redox activation generally increases the reactivity of transition metal complexes, and therefore, this methodology

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finds an important application in organometallic synthesis. The intermediate formation of more reactive 17-electron (17-e) or 19-electron (19-e) species by electron transfer (ET) can promote reactions that proceed hardly or even do not proceed at all for the starting stable (typically 18-electron [18-e]) compounds. The results obtained in this area were first summarized in the end of the 1980s in several reviews [1–4] and books [5, 6]. Particularly, it was shown that redox activation can increase significantly the rate of key reactions for organometallic chemistry and homogeneous catalysis such as ligand substitution [7–16], migratory insertion [17–20], reductive elimination and oxidative addition [21, 22], structural rearrangments (cis–trans, mer–fac, etc.) [23–26], ligand-to-ligand dimerization [27–34], or dehydrodimerization [35–37]. Oxidatively induced dimerization is especially characteristic of complexes in which π- or σ-ligands do not fully use their coordination abilities; that is, the part of multiple carbon–carbon bonds remains noncoordinated. The representative examples of such dimerization processes were shown for transition metal η^4-cyclooctatetraene [27–29], η^6-fluorenyl [30], σ-alkenyl [31], σ-vinyl [32, 33], and σ-alkynyl [34] complexes. Oxidative ligand-to-ligand dehydrodimerization accompanied by the activation of C–H bonds is less studied and has been found only for η^5-cyclopentadienyl [35–37] and vinylidene complexes [34].

In the present review, the redox-activated processes of C–H bonds formation and cleavage in transition metal π- and σ,π-complexes are considered as well as the oxidatively induced selective formation of C–C (dehydrodimerization of vinylidene complexes) and C–O (nucleophilic addition to μ-divinylidene complexes) bonds. We consider here the results obtained in our group, but all relevant literature data are also covered.

Scheme 1 General scheme of oxidatively induced hydrogen elimination in transition metal "open" π-complexes

Oxidatively induced hydrogen elimination in transition metal complexes with cyclic "open" π-ligands

Oxidatively induced hydrogen atom elimination from the sp^3-hybridized carbon of the "open" π-complex **A** leads to the inclusion of one additional carbon atom into the coordinated polyenyl (or polyene) ligand affording **B** (Scheme 1). Such processes reveal new opportunities for the selective functionalization of coordinated π-ligands.

The reaction proceeds as a sequence of electron removal from the initial 18-e complex **A** and homolytic cleavage of the C–H bond in the intermediate 17-e radical cation **A**$^{+•}$ finally affording new 18-e product **B**. For cyclohexadienyl [38] and cyclohexadiene [39] iron complexes, the oxidative hydrogen elimination proceeds from methylene sp^3-carbon atoms having both C–H$_{exo}$ and C–H$_{endo}$ bonds, and therefore, it was generally supposed to occur for the more sterically accessible C–H$_{exo}$ bond. To clarify the possibility of the alternative reaction pathway via homolysis of the C–H$_{endo}$ bond, we studied the electrochemical and chemical oxidation of two isomeric phenylcyclohexadienyl iron complexes (η^5-PhC$_6$H$_6$)Fe(η^5-C$_5$H$_5$) with *exo-* (**1**) and

endo-orientation (**2**) of phenyl substituent (Scheme 2). Complexes **1** and **2** were prepared according to the literature procedure [40].

The oxidation of **1** and **2** under cyclic voltammetry (CV) conditions proceeds differently [41]. Complex **2** containing the C–H$_{exo}$ bond shows the irreversible one-electron oxidation peak A, and new peaks C$_1$ and C$_2$ of the biphenyl cation **3**$^+$ are observed on the reverse scanning of potential (Fig. 1a). Thus, in this case, the homolytic cleavage of the C-H$_{exo}$ bond in the radical cation **2**$^{+•}$ is fast in the CV time scale and readily yields the product **3**$^+$. Unlike **2**, the complex **1** having the C–H$_{endo}$ bond exhibits the one-electron oxidation peak B with currents ratio $i_p^{ic}/i_p^{ia} = 0.87$ together with low intensity peak C$_1$ of the same product **3**$^+$ on the cathodic branch of the CV (Fig. 1b) revealing less effective transformation **1**$^{+•}$ → **3**$^+$. We found no evidence for the alternative pathway of **1**$^{+•}$ → **3**$^+$ transformation, i.e., the isomerization of the radical cation **1**$^{+•}$ into **4**$^{+•}$ via [1,5]-sigmatropic hydrogen shift followed by "classic" homolysis of the C–H$_{exo}$ bond in **4**$^{+•}$, so we can conclude that the homolysis of the C–H$_{endo}$ bond does proceed with similar results as for the C–H$_{exo}$ bond but more slowly.

Chemical oxidation results for **1** and **2** (AgBF$_4$, CH$_2$Cl$_2$, 20 °C) are consistent with the CV data: In the case of **2**, the reaction proceeds smoothly (10 min, 76%), but oxidation of **1** under the same conditions is slower and less effective (1 h, 35%) [41].

Thus, in 17-e cyclohexadienyl iron radical cations, the homolytic cleavage of the C–H$_{exo}$ bond oriented parallel with the π-electron system proceeds faster than for the C–H$_{endo}$ bond directed to the periphery of the ligand. The transition state for hydrogen elimination is more stabilized by "anchimeric" assistance of the π-ligand for the C–H$_{exo}$ bond than for the C–H$_{endo}$ bond, and this can be the main

Scheme 2 Oxidative hydrogen elimination from iron cyclohexadienyl complexes **1** and **2**
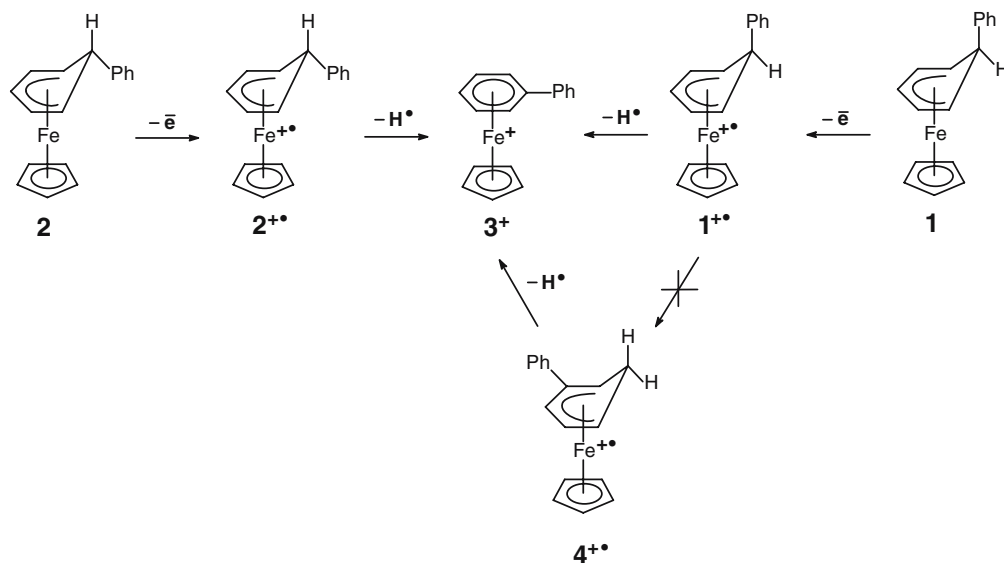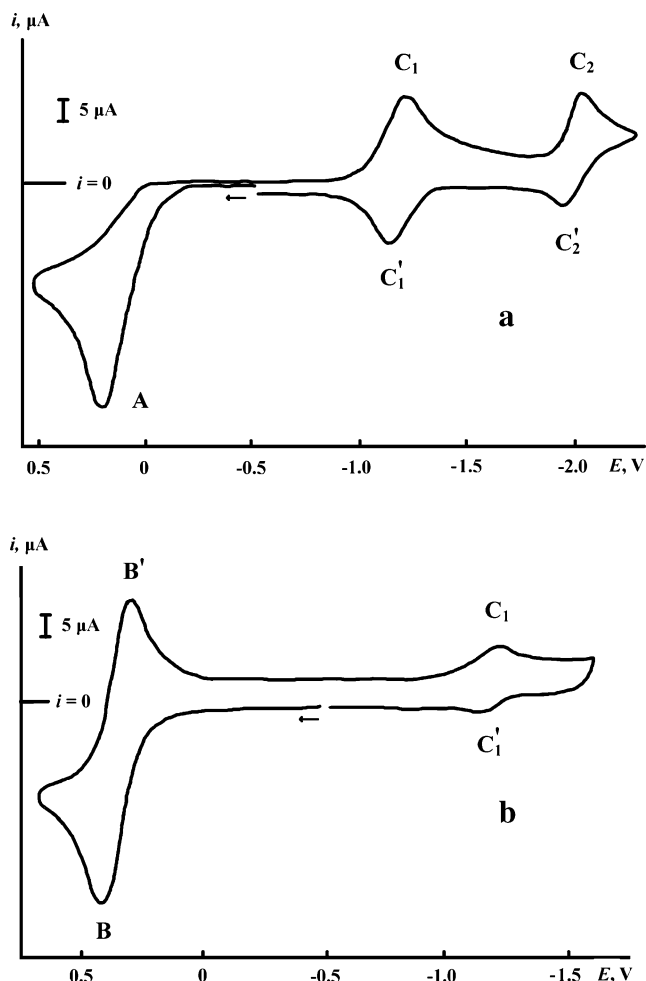
Fig. 1 CVs of iron complexes **1** (**b**, *bottom*) and **2** (**a**, *top*; GC-electrode, CH_2Cl_2, 0.1 M Bu_4NPF_6, 2×10^{-3} M, 200 mV/s, potentials vs SCE)

reason for the different reaction rates observed for **1** and **2**. Nevertheless, the oxidative hydrogen elimination involving the C–H_{endo} bond activation as a key step can be promising for organometallic synthesis.

The **A→B** transformations (Scheme 1) can also be performed as electrophilic abstraction of hydride ion with trityl cation. This is characteristic of the less electron-rich cyclohexadienetricarbonyl iron complexes [42, 43]. The electrophilic hydride abstraction for C–H_{endo} bond is unknown. Moreover, this process is sterically blocked even for the C–H_{exo} bond if the substituent is present in the neighboring position of the ligand (**5**, L_3=3 CO, Scheme 3).

However, the more electron-rich iron arenecyclohexadiene complexes (**5**, L_3=C_6H_6, Scheme 3) with the same "unfavorable ligand geometry" react with Ph_3CBF_4 at low temperature to form the target products **6⁺** [38]. The authors believe that this different behavior is caused by the alternative mechanism involving the ET step followed by hydrogen atom abstraction from 17-e **5⁺•** with trityl radical.

These results demonstrate clearly far less sterical sensitivity of the ET pathway compared to the electrophilic hydride abstraction.

Keeping in mind the possible oxidatively induced hydrogen elimination for both *exo*- and *endo*-C–H bonds of polyene ligands, we have applied this methodology to the platinum and palladium η^4-pentamethylcyclopentadiene complexes $[(\eta^4\text{-}C_5Me_5H)M(\eta^5\text{-}C_5R_5)]BF_4$ (**7a⁺** M=Pt, R=H; **7b⁺** M=Pt, R=Me; **7c⁺** M=Pd, R=Me) prepared in our group [44]. By the beginning of this work, the expected products $[(\eta^5\text{-}C_5Me_5)M(\eta^5\text{-}C_5R_5)](BF_4)_2$ (**8a⁺⁺**, M=Pt, R=H; **8b⁺⁺**, M=Pt, R=Me; **8c⁺⁺**, M=Pd, R=Me) remained "unknown metallocenes." Thus, it was a great stimulation for us to choose **7a–c⁺** as the starting compounds for the preparation of **8a–c⁺⁺**.

CV of the platinum diene complex **7b⁺** contains a one-electron oxidation peak at +1.32 V vs the saturated calomel electrode (SCE; Fig. 2, peak A), and a new reduction peak B at −0.60 V of decamethylplatinocene–dication **8b⁺⁺** was observed on the reverse scanning of the potential indicating oxidative hydrogen elimination process fast in the CV time scale (Scheme 4, **a**+**b**) [45].

Complex **8b⁺⁺** was prepared from **7b⁺** using controlled potential electrolysis (GC-electrode, +1.70 V vs SCE, acetone, $NaBF_4$) in 49% yield, and its molecular structure was determined by an X-ray diffractional study [46]. Reduction of **8b⁺⁺** leads to the regeneration of the diene complex **7b⁺** presumably owing to hydrogen radical abstraction from the solvent (tetrahydrofuran [THF],
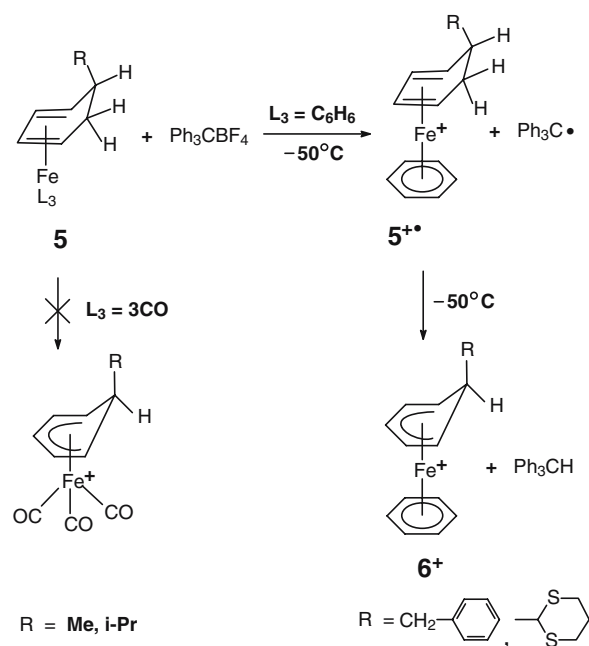
Scheme 3 Electrophilic hydride abstraction vs electron transfer pathway for iron cyclohexadiene complexes **5**
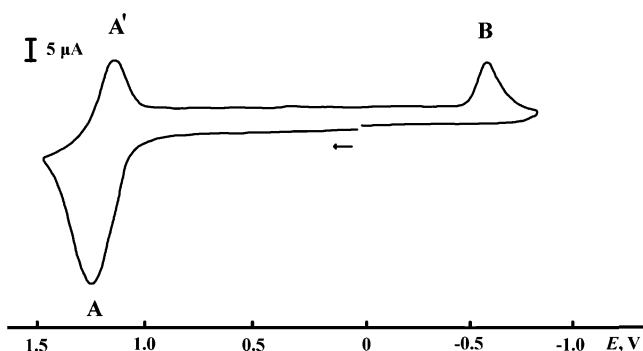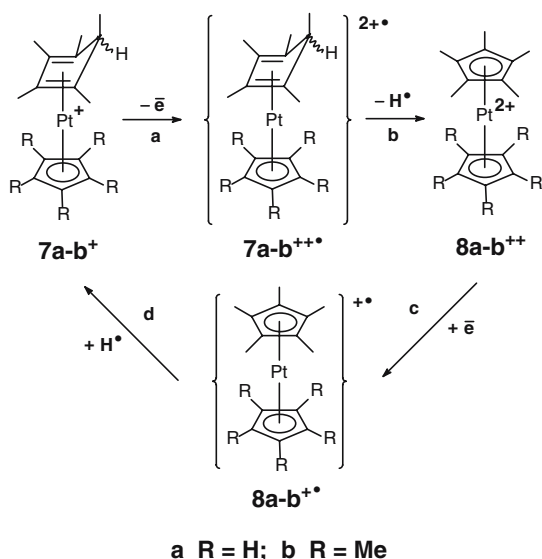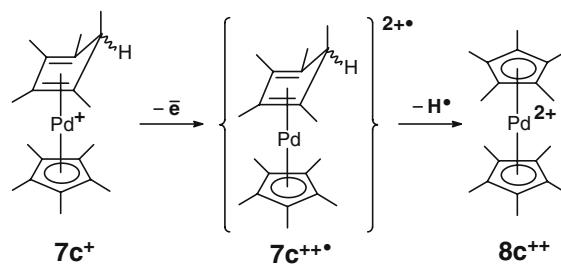
Fig. 2 CV of platinum complex $7b^+$ (GC-electrode, acetone, 0.2 M NaBF$_4$, 2×10^{-3} M, 200 mV/s, potentials vs SCE)

Scheme 5 Preparation of decamethylpalladocene–dication $8c^{++}$

acetone) by 19-e radical cation $8b^{+\bullet}$ (Scheme 4, **c**+**d**). The platinocene–dication $8b^{++}$ can also be prepared by the alternative way through the reaction of binuclear complex [Pt$_2$(η^5-C$_5$Me$_5$)$_2$(μ-Br)$_3$]Br$_3$ with pentamethylcyclopentadiene and AgBF$_4$ (50%) [47], but the method according to Scheme 4 is more convenient because it does not require [Pt$_2$(η^5-C$_5$Me$_5$)$_2$(μ-Br)$_3$]Br$_3$, which is difficult to prepare.

Decamethylpalladocene–dication $8c^{++}$ can be prepared via the ET pathway (Scheme 5). Preparative electrolysis of $7c^+$ under the same conditions as for $7b^+$ was not effective (the yield of $8c^{++}$ was 4–5%), but the chemical oxidation of $7c^+$ with cerium–ammonium nitrate afforded better results (38%). It is noteworthy that in contrast to the platinum analogue $8b^{++}$, there is no alternative synthetic method for the palladium complex $8c^{++}$ [48].

Scheme 4 Synthesis of penta- ($8a^{++}$) and decamethylplatinocene ($8b^{++}$) dications
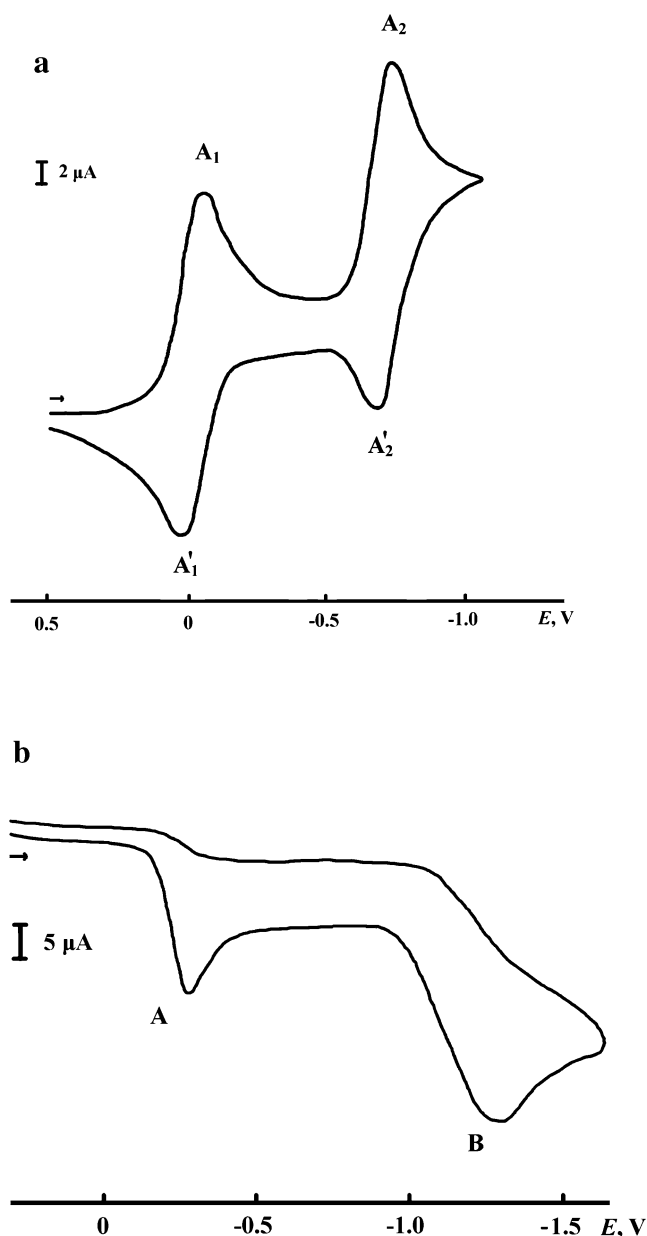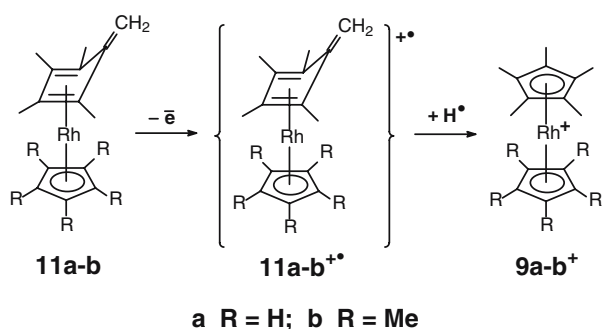

Fig. 3 CVs of dicationic decamethylpalladocene $8c^{++}$ (**a**) and decamethylplatinocene $8b^{++}$ (**b**; GC-electrode, THF, 0.2 M Bu$_4$NPF$_6$, 2×10^{-3} M, 200 mV/s, potentials vs SCE)

Scheme 6 Synthesis of penta- ($9a^+$) and decamethylrhodocene ($9b^+$) cations by fulvene complexes oxidation

Platinocene and palladocene dications show completely different behaviors under CV conditions. Palladium complex $8c^{++}$ exhibits two reversible one-electron reduction peaks A_1 and A_2 (Fig. 3a) indicating the stability of 19- and 20-e palladium sandwiches in the CV time scale [48]. In contrast, the platinum analogue $8b^{++}$ undergoes irreversible one-electron reduction (Fig. 3b, peak A), and new peak B belonging to hydrogen atom abstraction product $7b^+$ is observed on further scanning of the potential. Thus, platinum 19-e radical cation $8b^{+•}$ was shown to be more reactive compared to the corresponding palladium analogue $8c^{+•}$ illustrating the difference between transition metal 19-e complexes of the second and third row.

Penta- and decamethylrhodocene cations $[(\eta^5\text{-}C_5Me_5)Rh(\eta^5\text{-}C_5R_5)]BF_4$ ($9a^+$, R=H; $9b^+$, R=Me) were prepared analogously in good yields (60–80%) by chemical oxidation (THF, $(\eta^5\text{-}C_5H_5)_2FePF_6$, 20 °C) of the corresponding diene complexes $(\eta^4\text{-}C_5Me_5H)Rh(\eta^5\text{-}C_5R_5)$ (**10a**, R=H; **10b**, R=Me) [49]. These complexes can also be obtained by the oxidation of the neutral rhodium fulvene complexes

11a–b (Scheme 6). In the latter case, 17-e rhodium fulvene radical cations $11ab - b^{+•}$ are stabilized by addition of hydrogen atoms from the reaction medium to the methylene carbon atom of the fulvene ligand [49].

Concluding the consideration of oxidatively induced hydrogen elimination processes, we can mention briefly reactions of this type found in our group. The oxidation of the allylcyclohexadienyl ruthenium complex $(\eta^3\text{-}C_3H_5)Ru(PPh_3)(\eta^5\text{-}C_6H_7)$ under CV conditions leads to the formation of the benzene product $[(\eta^3\text{-}C_3H_5)Ru(PPh_3)(\eta^6\text{-}C_6H_6)]^+$ [50]. The analogous reaction for the polycyclic iron complex of cyclohexadienyl type $(\eta^5\text{-}C_5H_5)Fe(1\text{–}3,4a,9a\text{-}\eta^5\text{-}3,4\text{-dihy-dro-9H-fluoren-3-yl})$ afforded the corresponding arene cation $[(\eta^5\text{-}C_5H_5)Fe(1\text{–}4,4a,9a\text{-}\eta^6\text{-}9H\text{-fluorene})]BF_4$ [51].

Reductive activation of C–H bonds in transition metal π-complexes

We have shown that reductive activation can be utilized for the selective homolytic cleavage of the benzyl-type C–H bonds. This process for η^4-pentamethylcyclopentadiene platinum complex $7b^+$ is shown in Scheme 7 [45, 46].

Complex $7b^+$ undergoes an irreversible one-electron reduction at −1.57 V vs SCE (Fig. 4a, peak A), and new oxidation peaks B and C at +0.30 and +0.48 V corresponding to reaction products are observed on the reverse scanning of the potential. Preparative electrolysis of $7b^+$ at −1.80 V vs SCE in THF solution afforded an inseparable mixture of two neutral isomeric complexes that were identified as η^3-allyl (**12**) and σ,π-alkene (**13**) complexes on the basis of nuclear magnetic resonance spectroscopy.

The 19-e radical $7b^•$ undergoes fast homolysis of C–H bonds of the "external" and "internal" methyl groups of the
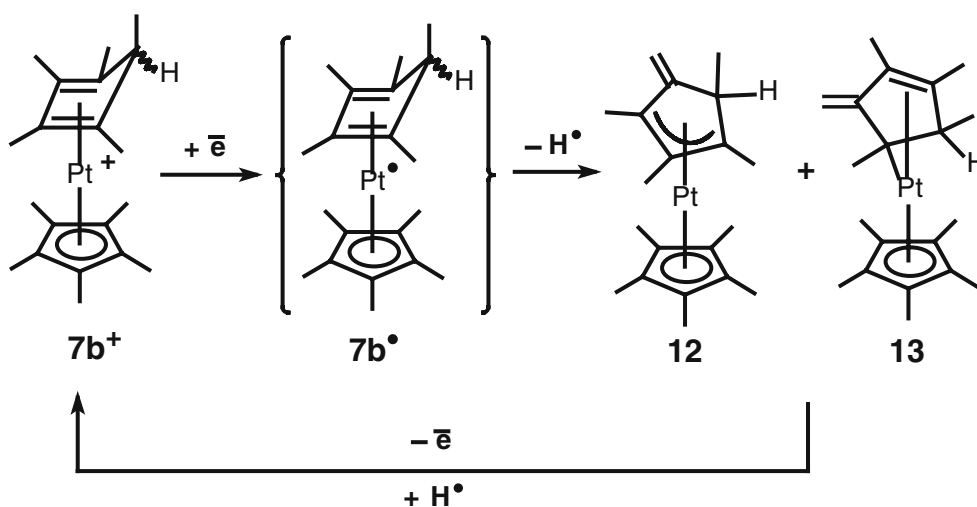
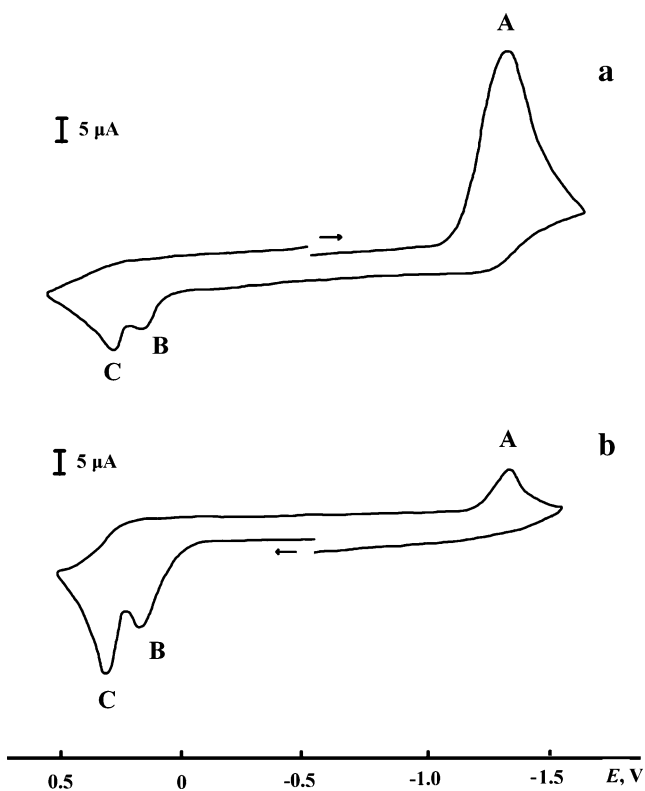**Scheme 7** Reductive activation of platinum diene complex $7b^+$

Fig. 4 CVs of platinum diene complex **7b$^+$** (**a**) and mixture of **12** and **13** (**b**; Hg-electrode, THF, 0.2 M Bu$_4$NPF$_6$, 2×10^{-3} M, 200 mV/s, potentials vs SCE)

diene ligand affording **12** and **13**, respectively. Oxidative activation of the **12**+**13** mixture leads smoothly to the regeneration of the initial **7b$^+$** because of hydrogen atoms addition at the exocyclic methylene fragment in the intermediate 17-e radical cations **12$^{+•}$** and **13$^{+•}$**.

Reductive activation of the fluorene iron complex [(η^5-C$_5$H$_5$)Fe(η^6-C$_{13}$H$_{10}$)](BF$_4$) (**14$^+$**) resulted in the homolysis of the C(9)–H bond in 19-e radical **14$^•$** and led to the formation of the zwitter-ionic η^6-fluorenyl compound (η^5-C$_5$H$_5$)Fe(η^6-C$_{13}$H$_9$) (**15**) (Scheme 8) [52]. This process is fast in the CV time scale, and the chemical reduction of **14$^+$** with sodium amalgam in toluene gives **15** in 70% yield.

In ethereal solvents (THF, 1,2-dimethoxyethane), the reduction of **14$^+$** proceeds differently affording finally the isomeric η^5-fluorenyl complex (η^5-C$_5$H$_5$)Fe(η^5-C$_{13}$H$_9$) (**16**) in low yield (14%) [53]. We suppose that
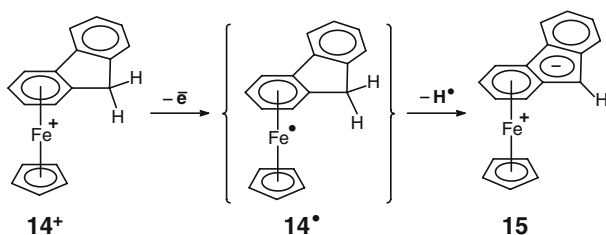
16 is formed mainly because of the inter-ring η^6–η^5 haptotropic interconversion between intermediate radical anions **15$^{-•}$** and **16$^{-•}$**. The regularities of the latter process have been studied in detail by CV [54] and are not considered here.

Thus, along the redox-activated C–H bond homolysis in the "open" π-complexes, the carbon-atom-losing hydrogen becomes coordinated to the metal, and the number of the metal-coordinated carbons increases by one on oxidative activation and decreases by one on reductive activation. Compared to the relevant electrophilic hydride abstraction, the oxidatively induced hydrogen elimination is far less sensitive to steric effects and proceeds with different rates for the *exo-* and *endo*-faced C–H bonds.

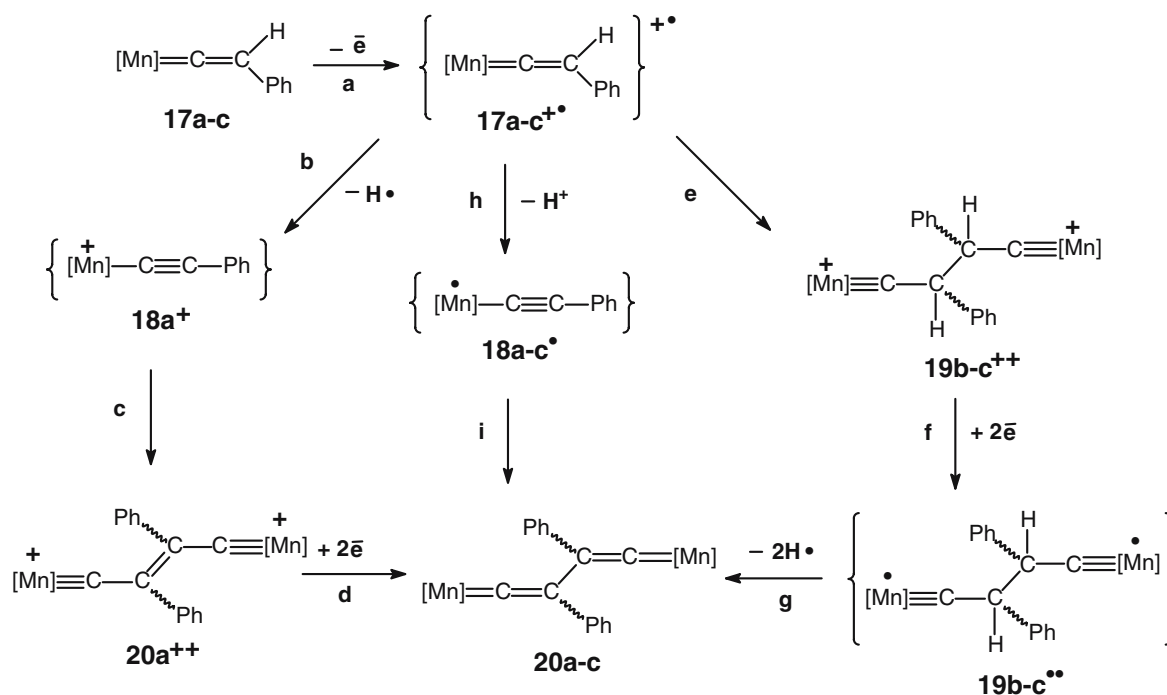## Oxidative dehydrodimerization of manganese and rhenium phenylvinylidene complexes

Over the past two decades, the chemistry of transition metal vinylidene complexes has been developed into an important area of organometallic chemistry because such complexes are key intermediates in catalytic and stoichiometric reactions of terminal alkynes [55–57]. Compared to very rich chemistry of mononuclear 18-e vinylidene complexes, their redox activation reactions remain far less studied.

The oxidative dehydrodimerization represents a good example of successful application of redox activation methodology to transition metal vinylidene complexes (**I**) (Scheme 9).

Reactivity of the resulting binuclear compounds **II** with a bridging 1,3-butadiene-1,4-diylidene (μ-divinylidene) ligands remains practically unexplored, although the presence of two vinylidene functions within the same molecule can give rise to specific reactivity patterns with valuable new applications in organic synthesis. Complexes **II** contain two electrophilic (C$_\alpha$) and two nucleophilic (C$_\beta$) centers making possible concerted or separate participation of the conjugated vinylidene moieties in various addition, cycloaddition, and insertion processes characteristic of mononuclear vinylidene compounds [56, 57]. Moreover, the active sites of the μ-divinylidene ligand can be selectively promoted or blocked using ET. Thus, understanding of the regularities of such processes is of importance for modern organometallic chemistry.

Scheme 8 Reductive activation of iron fluorene complex **14**
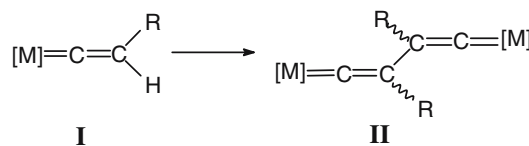
Scheme 9 General scheme for the oxidative dehydrodimerization of vinylidene complexes

a $[Mn] = (\eta^5\text{-}C_5H_5)(CO)_2Mn$;   **b** $[Mn] = (\eta^5\text{-}C_5Me_5)(CO)_2Mn$;   **c** $[Mn] = (\eta^5\text{-}C_5H_5)(CO)(PPh_3)Mn$

Scheme 10 Possible routes for oxidative dehydrodimerization of manganese vinylidene complexes

During the last few years, we have studied in detail oxidatively induced dehydrodimerization of manganese and rhenium phenylvinylidene complexes $(\eta^5\text{-}C_5R_5)(CO)(L)$ M=C=C(H)Ph (**17a–d, 17a** M=Mn, R=H, L=CO; **17b**, M=Mn, R=Me, L=CO; **17c**, M=Mn, R=H, L=PPh$_3$; **17d**, M=Re, R=H, L=CO) [58–60]. This reaction have been shown to be the effective method for μ-divinylidene

complexes **20a–d** preparation (55–90%) and can proceed through three possible routes (Scheme 10) differing by the type of transformation of the primary oxidation product— 17-e radical cation **17$^{+\bullet}$**. The preparative reactions for manganese complexes **17a–c** were usually carried out by adding one equivalent of an oxidant (AgBF$_4$ or $(\eta^5\text{-}C_5H_5)_2FeBF_4$) to the solution of the corresponding

Fig. 5 CVs of vinylidene complex **17a** (**a**) and μ-divinylidene complex **20a** (**b**; GC-electrode, CH$_2$Cl$_2$, 0.1 M Bu$_4$NPF$_6$, 2× 10^{-3} M, 200 mV/s, potentials vs SCE)
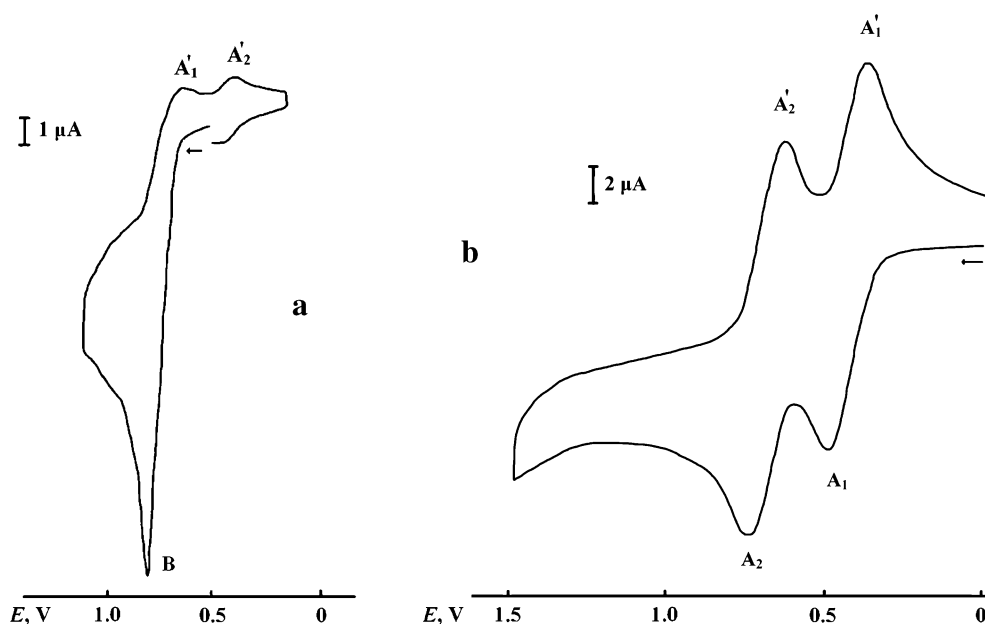
vinylidene complex **17** in CH_2Cl_2 solution at −40 °C. The reaction mixture was then stirred at −30 to −20 °C to give binuclear cations **20a^{++}** or **19b–c^{++}** followed by addition of a reductant ((η-C$_6$H$_6$)$_2$Cr or Et$_3$N) leading to the target μ-divinylidene compounds **20a–c**.

The oxidative dehydrodimerization process is fast in the CV time scale, but the reaction pathway depends on the ligand surrounding of the manganese atom. In the case of **17a** [58], the reaction proceeds as a sequence of steps including homolytic cleavage of the C_β–H bond in the 17-e radical cation **17a$^{+\bullet}$** (**b**), dimerization of the resulting 16-e σ-phenylethynyl cation **18a$^+$** to the binuclear 2-butene-1,4-diylidyne dication **20a^{++}** (**c**), and finally, two-electron reduction of the latter into the μ-divinylidene product **20a**. The electrochemical oxidation of **17a** under CV conditions shows clear evidence for the proposed reaction scheme (Fig. 5): New reduction peaks A$_1'$ and A$_2'$ appearing on the reverse scanning of potential (Fig. 5a) coincide exactly with the reduction peaks of the authentic binuclear μ-dicarbyne dication **20a^{++}** (Fig. 5b). A single example is known for the key steps (**b**) and (**c**) for related manganese complex (η^5-C$_5$H$_5$)(dmpe)Mn=C=C(H)Ph [61].

For more electron-rich manganese vinylidene complexes **17b–c** [59], the oxidative dehydrodimerization proceeds via a different pathway: The intermediate 17-e radical cations **17b − c$^{+\bullet}$** undergo direct $C_\beta − C_\beta$ coupling into the 18-e μ-butane-1,4-diylidyne complexes **19b–c^{++}** (Scheme 10, **a+e**). Two-electron reduction of the latter leads to the corresponding

19-e,19-e diradicals **19b − c$^{\bullet\bullet}$** and finally to the formation of **20b–c** via homolytic scission of the $C_\beta − H$ bonds (**f+g**). Reaction steps **a+e** can be easily observed under CV conditions (Fig. 6), thus confirming the direct dimerization pathway. The final homolysis stage (**g**) is slow in the CV time scale but readily proceeds on cobaltocene or (η-C$_6$H$_6$)$_2$Cr reduction. The reduction of the model mononuclear carbyne complex [(η^5-C$_5$H$_5$)(CO)(PPh$_3$)Mn≡C–CH$_2$Ph]$^+$ (**21$^+$**) was also shown to proceed as a homolytic cleavage of the $C_\beta − H$ bond to form the corresponding vinylidene complex **17c** (Scheme 13). The similar oxidative dimerization of manganese vinylidene complexes containing chelate phosphine (Scheme 10, **a+e**) (η^5-C$_5$H$_4$Me)(dmpe)Mn=C=C(H)R (R=H, Ph) leads to the stereoselective formation (pure *meso*-form for R=Ph) of the μ-dicarbyne dications [(η^5-C$_5$H$_4$Me)(dmpe)Mn=C–C(H)R–C(H)R–C=Mn(dmpe)(η^5-C$_5$H$_4$Me)](BF$_4$)$_2$ (**22^{++}**) [62]. The dimerization energy for the model [($\eta^5 − C_5H_5$)(H$_2PCH_2CH_2PH_2$)Mn = C = CH$_2$]$^{+\bullet}$ was estimated by density functional theory calculations to be −101.4 kJ/mol. Unlike **19b–c^{++}** discussed above, the reduction of the binuclear 18-e complex **22^{++}** with Cp*$_2$Co leads to the $C_\beta − C_\beta$ (not $C_\beta − H$) bond cleavage in 19-e intermediates **22$^{\bullet\bullet}$** and regeneration of the initial vinylidenes (η^5-C$_5$H$_4$Me)(dmpe)Mn=C=C(H)R. The oxidative dimerization of the generated in situ anionic vinylidene complexes of molybdenum and tungsten according to pathway **a+e** can also be mentioned [63, 64].

Fig. 6 CVs of vinylidene complex **17c** (**a**) and μ-dicarbyne complex **19c^{++}** (**b**; GC-electrode, CH_2Cl_2, 0.1 M Bu$_4$NPF$_6$, 2×10^{-3} M, 200 mV/s, potentials vs SCE)
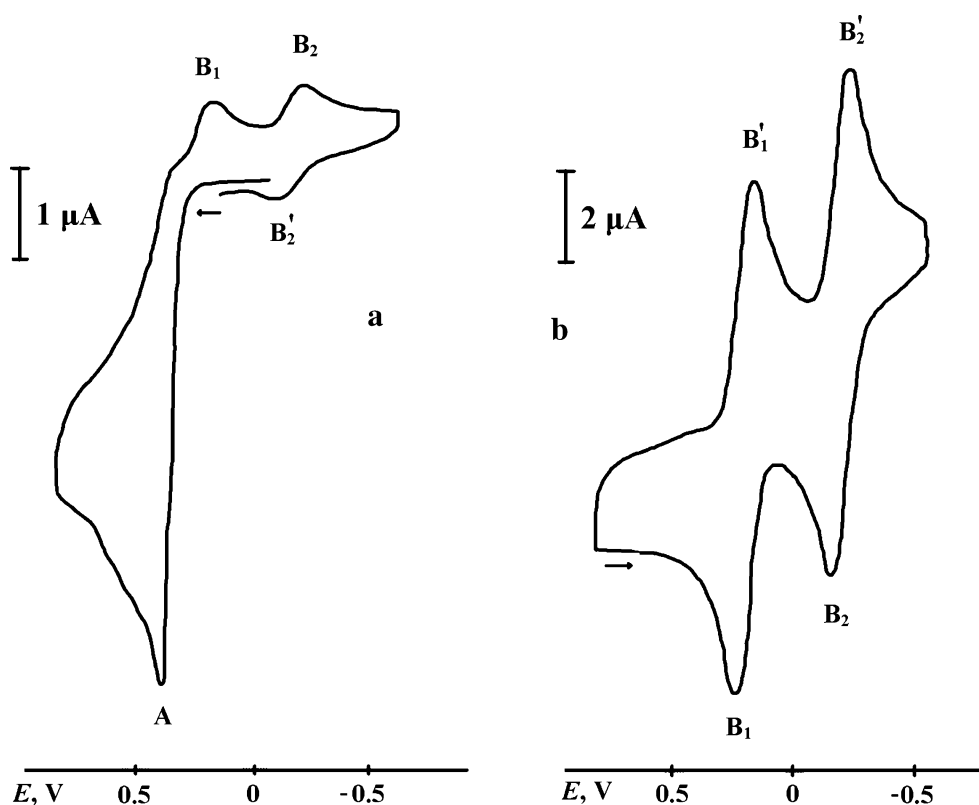
The totally different reaction pathways for structurally similar vinylidene complexes can be explained by low stability of the binuclear μ-butane-1,4-diylidyne complex $19a^{++}$ in the case of [M]=Mn(CO)$_2$(η^5-C$_5$H$_5$). We suppose that the radical cation $[(\eta^5-C_5H_5)(CO)_2Mn=C=C(H)Ph]^{+\bullet}$ $17a^{+\bullet}$ also can undergo $C_\beta-C_\beta$ dimerization (Scheme 10, path e) but this equilibrium is strongly shifted to the left owing to instability of the resulting $19a^{++}$. Thus, the reaction pathway involving the $C_\beta-H$ bond homolysis in mononuclear 17-e vinylidene radical cation $17a^{+\bullet}$ ((a)+(b)+(c)) becomes preferable.

All oxidative activations of the vinylidene complexes discussed above were performed in the absence of an added base. The probability of the deprotonation of primary oxidation products $17a-c^{+\bullet}$ giving σ-alkynyl radicals $18a-c^\bullet$ increases considerably in the presence of a base. For example, the μ-divinylidene complex $20a$ can be prepared more conveniently by room temperature oxidation of $17a$ with (η^5-C$_5$H$_5$)$_2$FeBF$_4$ in the presence of Et$_3$N [58]. Under these conditions, two competitive reaction pathways are possible: a $C_\beta-H$ homolysis (Scheme 10, a–d) and deprotonation (Scheme 10, h+i), where the latter is supposed to be predominated.

The presence of a base has a more distinctive effect on the oxidative dehydrodimerization of the rhenium phenylvinylidene complex (η^5-C$_5$H$_5$)(CO)$_2$Re=C=C(H)Ph (**17d**). Our attempts to perform this reaction as for manganese compounds (according to Scheme 10, a–d or a, e–g) in the absence of a base were unsuccessful because of gradual decomposition of the primary oxidation product $17d^{+\bullet}$. At the same time, the treatment of **17d** and Et$_3$N with one equivalent of (η^5-C$_5$H$_5$)$_2$FeBF$_4$ at room temperature afforded the expected μ-divinylidene product **20d** accompanied by a binuclear complex with a bridging phenyl(phenylethynyl)vinylidene ligand **23** (ratio 2.5:1; Scheme 11). The structure of the byproduct **23** was determined by X-ray diffraction [60].

We believe that under these conditions, the reaction proceeds along Scheme 11 via deprotonation of the radical cation $17d^{+\bullet}$ with triethylamine. The target μ-divinylidene complex **20d** is formed by $C_\beta-C_\beta$ dimerization of the intermediate radical $18d^\bullet$. In our opinion, the minor reaction product **23** is a result of $Re-C_\beta$ coupling followed by reductive elimination and 1,2-shift of the metal moiety. Such carbon–metal coupling for 17-e σ-alkynyl transition metal complexes was found for the first time by our group. Evidently, the analogous 17-e manganese radicals $18a-c^\bullet$
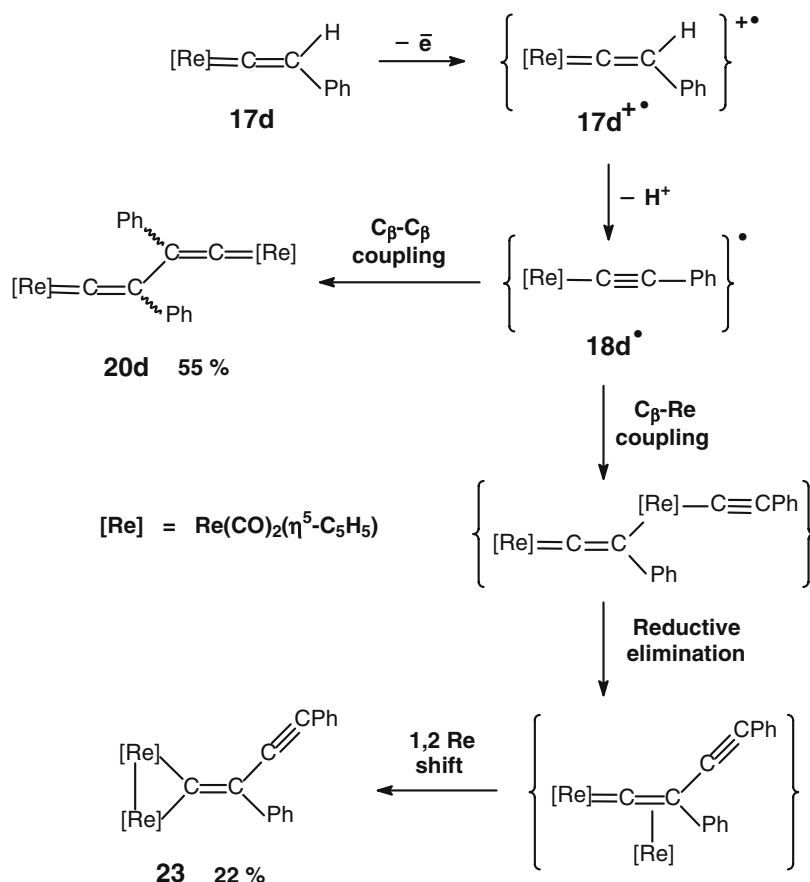
Scheme 11 Oxidative dehydrodimerization of rhenium vinylidene complex **17d**
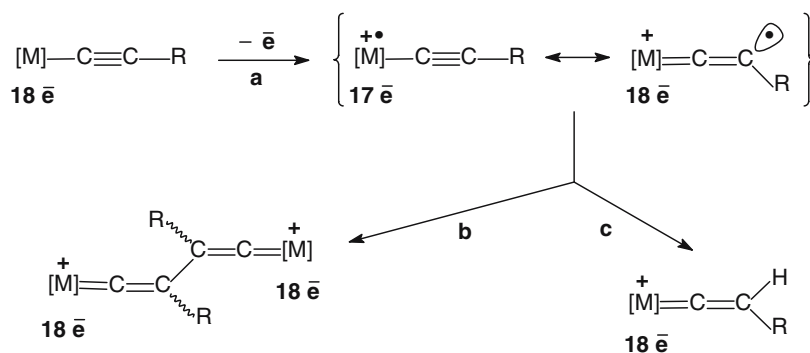
Scheme 12 Oxidative dimerization of transition metal σ-alkynyl complexes

undergo no $Mn - C_\beta$ couplings because the formation of the coupling intermediates with four-legged piano stool geometry is sterically nonaccessible.

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 a base owing to increased acidity of the $C_\beta - H$ bond and afforded 17-e σ-alkynyl radical cations. The clearest example of this process was reported by Bianchini et al. [65, 66]. Oxidative deprotonation of the 18-e cationic complex $[(NP_3)Rh=C=C(H)Ph]^+$ proceeds along an electron transfer–chemical reaction–electron transfer mechanism as spontaneous deprotonation of the primary oxidation product $[(NP_3)Rh = C = CHPh]^{2+\bullet}$ into the 17-e radical cation $[(NP_3)Rh - C = CPh]^{+\bullet}$, which immediately loses one electron at the potential used and affords the final dication $[(NP_3)Rh–C\equiv CPh]^{2+} NP_3=N(CH_2CH_2PPh_2)_3$. Unlike manganese, 16-e σ-alkynyl complex $[(NP_3)Rh–C\equiv CPh]^{2+}$ is unreactive towards dimerization to the corresponding 2-butene-1,4-diylidynes. Oxidative deprotonation of $[(NP_3)Rh=C=CHCOOEt]^+$ proceeds in the same manner [65, 66]. The similar process of consecutive oxidative deprotonation and oxidation of the 17-e intermediate

into the 16-e derivative was found for the isocyanide rhenium compound trans-$Cl(dppe)_2Re=C=NH$, which can be considered as an aza-analogue of the vinylidene complex [67, 68].

The oxidation of cationic iron vinylidene complex $[(\eta^5-C_5H_5)(dppe)Fe=C=C(H)Me]^+$ with an excess of iodosobenzene leads to the formation of the binuclear μ-divinylidene dimer $[(\eta^5-C_5H_5)(dppe)Fe=C=C(Me)–C(Me)=C=Fe(dppe)(\eta^5-C_5H_5)](PF_6)_2$ in 77% yield, the reaction being the first example of oxidative dehydrodimerization of vinylidene complexes [69]. The authors believe that the reaction scheme involves deprotonation of a radical dication intermediate $[(\eta^5 - C_5H_5)(dppe)Fe = C = C(H)Me]^{2+\bullet}$ and dimerization of the resulting σ-propynyl radical cation $[(\eta^5 - C_5H_5)(dppe)Fe - C \equiv CMe]^{+\bullet}$ into the dicationic μ-divinylidene complex. The related sequence of the oxidative deprotonation and σ-alkynyl radicals dimerization was reported by Beddoes et al. [70] for $[(\eta-C_7H_7)(dppe)Mo=C=C(H)Ph]BF_4$.

The oxidative activation of σ-alkynyl complexes reveals the alternative widely used method for synthesis of the cationic μ-divinylidene complexes (Scheme 12) [34, 69]. The key step of this process (**b**) is the coupling of reactive 17-e σ-alkynyl radicals at the C_β atoms.
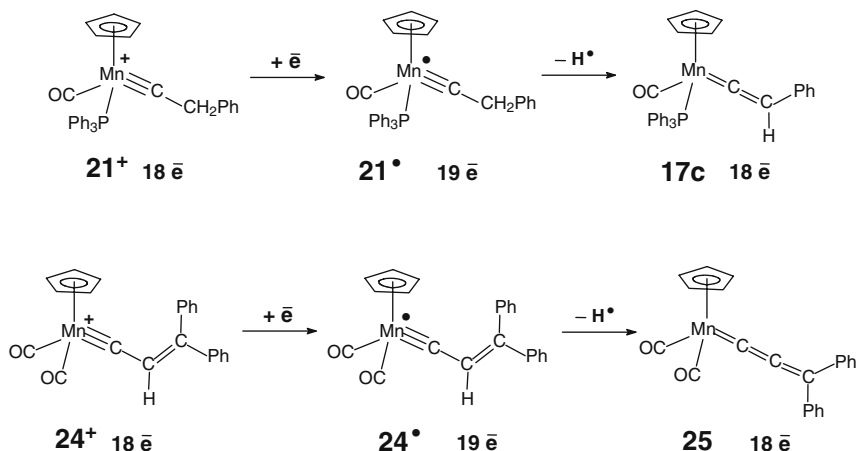
Scheme 13 Activation of the $C_\beta - H$ in 19-e manganese carbyne radicals **21$^\bullet$** and **24$^\bullet$**

The competitive hydrogen abstraction process (c) proceeds instead of dimerization for complexes containing bulky substituents (R=t–Bu, SiMe$_3$ etc.) [61, 70–73]. However, sometimes, the reaction pathways (b or c) can be totally controlled by temperature or the solvent used. For example, the complex $[(\eta^5 - C_5Me_5)(dppe)Fe - C \equiv CH]^{+\bullet}$ undergoes dimerization (b) and hydrogen abstraction (c) at −70 and 20 °C, respectively [71], whereas for 17-e niobium radical $[(\eta^5 - C_5H_4SiMe_3)_2(CO)NbC = CPh]^{+\bullet}$, the hydrogen atom abstraction occurs at −30 °,C and the $C_\beta - C_\beta$ coupling takes place at room temperature [72].

Reductive activation of C–H bonds in vinylidene and alkylidene complexes

In the previous section, we mentioned that the binuclear 19-e, 19-e μ-dicarbyne diradicals $19b - c^{\bullet\bullet}$ undergo the $C_\beta - H$ homolysis affording μ-divinylidene complexes 20b–c (Scheme 10, g). Such processes are extremely rare. It was only pointed out by Lemos and Pombeiro [74] that the reduction of benzylcarbyne cation [trans-(dppe)$_2$(Cl)Re≡C–CH$_2$Ph]$^+$ led to the corresponding phenylvinylidene complex trans-(dppe)$_2$(Cl)Re=C=C(H)Ph, and the process was fast in the CV time scale. For modeling the step (g), we studied in detail the reduction of mononuclear cationic manganese complexes [(η^5-C$_5$H$_5$)(CO)(Ph$_3$P)Mn$^+$≡C–CH$_2$Ph]BF$_4$ (21$^+$) and [(η^5–C$_5$H$_5$)(CO)$_2$Mn$^+$≡C–CH=CPh$_2$]BF$_4$ (24$^+$) (Scheme 13). Both compounds can be prepared easily by the protonation of neutral metallocumulene species 17c and (η^5-C$_5$H$_5$)(CO)$_2$Mn=C=C=CPh$_2$ (25) [75, 76].

Complex 21$^+$ under CV conditions displays an irreversible one-electron reduction peak A (Fig. 7), and new oxidation peak B corresponding to the authentic vinylidene complex 17c is observed on the reverse scanning of potential revealing the $C_\beta - H$ homolysis process fast in the CV time scale.

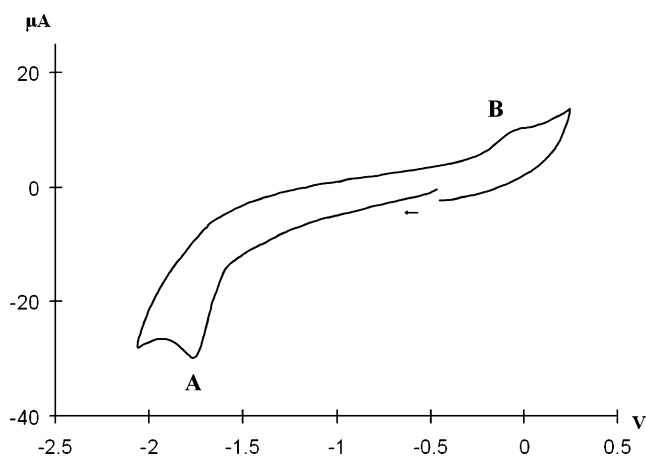Fig. 7 CV of manganese benzylcarbyne complex 21$^+$ (GC-electrode, CH$_2$Cl$_2$, 0.1 M Bu$_4$NPF$_6$, 2×10^{-3} M, 200 mV/s, potentials vs Fc)
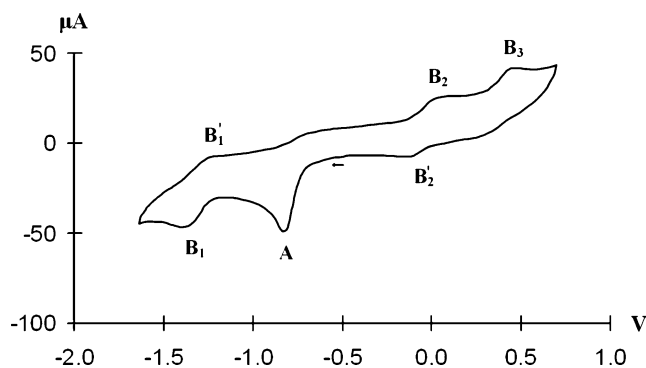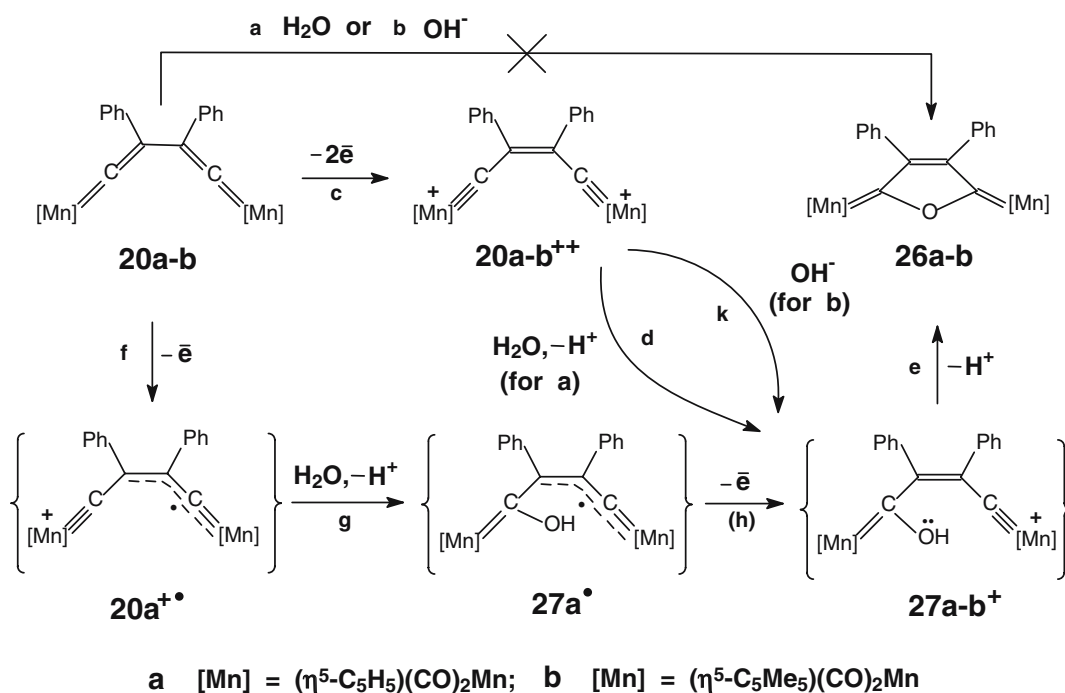

Fig. 8 CV of manganese vinylcarbyne complex 24$^+$ (GC-electrode, CH$_2$Cl$_2$, 0.1 M Bu$_4$NPF$_6$, 2×10^{-3} M, 200 mV/s, potentials vs Fc)

CV behavior of the vinylcarbyne complex 24$^+$ is quite similar: irreversible one-electron reduction (Fig. 8, peak A) followed by reduction peak B$_1$ and oxidation peaks B$_2$ and B$_3$ of the allenylidene complex 25. However, CV experiments using high scan rates revealed the different $C_\beta - H$ homolysis rates in 19-e radicals 21$^\bullet$ and 24$^\bullet$. The reduction peak for 21$^+$ is completely irreversible even at 100 V/s, whereas the reduction peak of 24$^+$ at 10 V/s has the anodic response of 50% i_p^a / i_p^c ratio and becomes completely reversible at 100 V/s showing slower hydrogen elimination process. We suppose that the greater stability of 24$^\bullet$ compared to 21$^\bullet$ is caused by lesser electron density on the metal atom and the delocalization of the unpaired electron at the C_γ atom and phenyl substituents of the ligand.

Few examples of analogous reductive activation of cationic 18-e vinylidene complexes of cobalt, rhodium, and ruthenium giving hydrogen and σ-alkynyl derivatives have been reported [65, 77, 78]. These transformations are fast on the CV time scale and were performed in a preparative scale using controlled potential electrolysis.
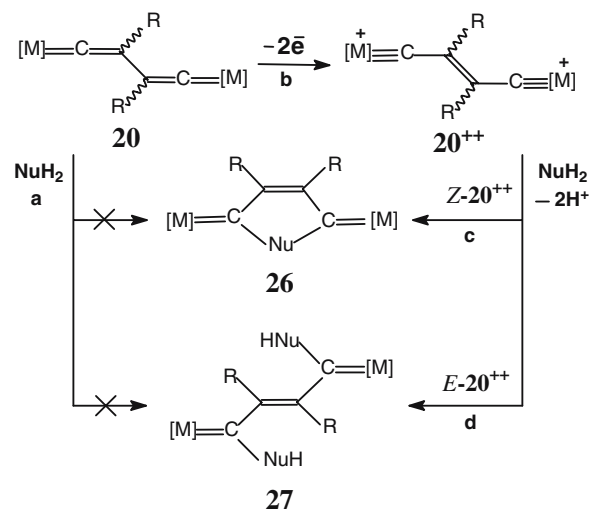
Scheme 14 Oxidative activation of π-divinylidene complexes towards nucleophilic addition

a H_2O or   **b** OH^-

20a-b   **20a-b^{++}**   **26a-b**

20a$^{+\bullet}$ **27a$^{\bullet}$**   **27a-b^{+}**

a   **[Mn] = (η^5-C$_5$H$_5$)(CO)$_2$Mn;**   **b**   **[Mn] = (η^5-C$_5$Me$_5$)(CO)$_2$Mn**

Scheme 15 Oxidatively induced addition of oxygen nucleophiles to manganese π-divinylidene complexes **20a–b**

The formation of a new 18-e complex obviously provides the thermodynamic feasibility of reactions described in this section. The fast reductive activation of the $C_\beta - H$ bond is caused by two reasons: «anchimeric assistance» by the multiple $M - C_\alpha$ bond 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). Easy vinylidene/carbyne or σ-alkynyl/vinylidene interconversion and fast $C_\beta - H$ bond homolysis processes in 19-e radicals producing hydrogen can be applied for the design of new homogeneous catalysts for electrochemical proton reduction.

Oxidatively induced nucleophilic addition to binuclear manganese μ-divinylidene complexes

We began a systematic study of oxidatively induced nucleophilic additions to the C_α atoms in transition metal μ-divinylidene compounds as shown in the general Scheme 14. If these carbon atoms are insufficiently electrophilic to undergo addition of protonic nucleophiles (Scheme 14, **a**), the reaction can be induced by two-electron oxidation of the μ-divinylidenes **20** into dicationic 2-butene-1,4-diylidyne complexes **20^{++}** (Scheme 14, **b**). Both C_α carbons in such compounds are more electrophilic relative to those of the initial complexes **20**, facilitating the formation of nucleophilic addition products **26** or **27**. For diprotonic nucleophiles and isomers of **20^{++}** with a $Z - C_\beta - C_\beta$ central double bond, a
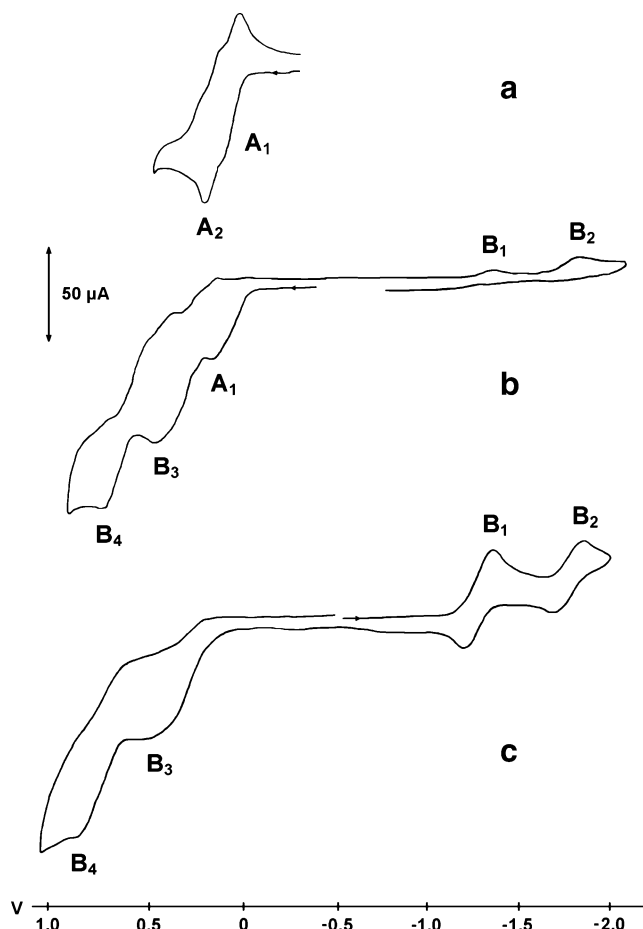

Fig. 9 CVs of μ-divinylidene complex **20a** (**a**); **20a** +H$_2$O(**b**); μ-dicarbene complex **26a** (**c**; THF, GC-electrode, 0.2 M ^{n}Bu$_4$NPF$_6$, sweep rate, 200 mV s^{-1}, potentials vs Fc)

nucleophilic addition (Scheme 14, **c**) is expected to proceed with a cyclization into cycloalkenediylidene complexes **26**. In the case of *E*-isomers of **20**$^{++}$, reactions (**d**) should lead to acyclic binuclear complexes **27** with a bridging 2-butene-1,4-diylidene ligand.

To ensure successful realization of the reaction of the Scheme 14, the reactants **20** and NuH$_2$ should meet the following requirements:

1. The μ-divinylidenes **20** should be inert to NuH$_2$ under conditions of thermal initiation; the reaction should be induced by oxidation of **20** into **20**$^{++}$.
2. The nucleophiles NuH$_2$ should be of limited reducing ability to not remove the target intermediates **20**$^{++}$ from the reaction media by reducing them into the initial **20**.
3. The reaction centers (C$_\alpha$ atoms) of μ-dicarbynes **20**$^{++}$ should be sterically accessible for the attack by nucleophiles NuH$_2$.

We have studied [79] the oxidatively induced addition of oxygen nucleophiles (H$_2$O, OH$^-$) to manganese μ-divinylidene complexes **20a**–**b** and found that cyclized μ-dicarbene products **26a**, **27b** are formed (Scheme 15). Complex **20a** is unreactive towards an excess of water, but the addition of oxidant ((η^5-C$_5$H$_5$)$_2$FeBF$_4$, AgBF$_4$) immediately induces the reaction to afford **26a** in 76–90% yield. CV studies revealed that reaction of **20a** with water starts after the first electron removal and is fast in the CV time scale (Fig. 9).

Under CV conditions, compound **20a** in the THF solution shows two reversible one-electron oxidation peaks A$_1$ and A$_2$ (Fig. 9a). The addition of water to the solution of **20a** in THF changes the CV considerably (Fig. 9b). 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 CV. These peaks coincide in their potentials with those of the reference compound **26a** (Fig. 9c).

CV data and chemical experiments reveal the reaction of **20a** with H$_2$O in THF solution to proceed via stages **f**+**g**+**h**+**e**, (Scheme 15). Therefore, the synthesis of **26a** can be performed as a sequence of two-electron oxidation of **20a** and double nucleophilic attack of oxygen atom to the C$_\alpha$ atoms of the μ-dicarbyne ligand (Scheme 15, **c**+**d**+**e**).

Complex **20b** does not react with water in the presence of an oxidant because of lower electrophilicity and greater shielding of the C$_\alpha$ atoms. However, its doubly oxidized form **20b**$^{++}$ reacts with a stronger nucleophile namely, hydroxide ion, to give **26b** in 15% yield (**c**+**k**+**e**). The molecular structures of **26a** and **26b** were determined by X-ray diffraction [79].

Thus, we have found the first examples of oxidatively induced nucleophilic addition to μ-divinylidene complexes resulting in cyclic products (**b**+**c**). Nevertheless, the regularities of this reaction are still not clear, and further studies are required to reach their full understanding.

Conclusion

In the present review, we have demonstrated that redox activation can be successfully utilized for the selective homolytic cleavage (or formation) of strong C–C and C–H bonds in transition metal π- and σ,π-complexes under mild conditions. The odd-electron metal center promotes strongly such homolytic processes; the latter becoming thermodynamically feasible, if stable 18-e metal configuration is restored in the final products. In particular, C–H bond activation reactions using a redox methodology proceed without a hydrogen radical abstractor added. The reactivity of odd-electron transition metal vinylidenes, carbynes, and σ-alkynyls (ligand-to-ligand dimerizations hydrogen atom abstraction or elimination) mainly exhibits at the C$_\beta$ atom of the ligands, and the metal atoms are not directly involved. Even some nonradical reactions like nucleophilic addition to the C$_\alpha$ atoms in transition metal μ-divinylidenes can also be redox induced.

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