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Oxidative dehydrodimerization of manganese vinylidene complexes (η^5-C_5R_5)(CO)(L)Mn=C=CHPh (R = Me, L = CO; R = H, L = PPh_3)[†]

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The oxidative dehydrodimerization of the phenylvinylidene manganese complexes (η^5-C_5R_5)(CO)(L)Mn=C=CHPh (5: R=Me, L=CO; 6: R=H, L=PPh_3) into the corresponding bis-vinylidene compounds (η^5-C_5R_5)(CO)(L)Mn=C=CPh−CPh=C=Mn(CO)(L)(η^5-C_5R_5) (7: R=Me, L=CO; 8: R=H, L=PPh_3) was studied by cyclic voltammetry and chemical experiments. It was found that dehydrodimerization of 5 and 6 proceeds via direct $C_{(\beta)}-C_{(\beta)}$ coupling of the radical cations $5^{+\cdot}$ and $6^{+\cdot}$ to give dicationic bis-carbyne complexes [(η^5-C_5R_5)(CO)(L)Mn≡C−CPhH−CPhH−C≡Mn(CO)(L)(η^5-C_5R_5)]$^{2+}$ (10^{++}: R=Me, L=CO; 11^{++}: R=H, L=PPh_3), which can be converted into bis-vinylidene complexes 7 and 8 respectively by reduction with (η-C_6H_6)$_2$Cr. In this process, binuclear 19-electron bis-carbyne compounds $10^{\cdot\cdot}$ and $11^{\cdot\cdot}$ undergo further transformation into the dimers 7 and 8 via homolysis of $C_{(\beta)}-H$ bonds of the bis-carbyne ligand, thus exhibiting rare examples of reductive activation of C−H bonds in 19-electron transition metal carbyne complexes. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: oxidative dehydrodimerization; vinylidene complexes; carbyne complexes; cyclic voltammetry; redox activation

INTRODUCTION

Oxidatively induced ligand-to-ligand dimerizations and dehydrodimerizations of transition metal σ- and σ, π-complexes have become a common procedure for the selective formation of carbon–carbon bonds. Oxidative dimerizations of neutral 18-electron ($18e^-$) σ-alkenyl- and σ-alkynyl-transition-metal complexes proceed via direct $C_{(\beta)}-C_{(\beta)}$ coupling and lead to dicationic bis-carbene[1,2] and bis-vinylidene complexes[3–6] respectively. In the case of vinylidene complexes, direct $C_{(\beta)}-C_{(\beta)}$ couplings were observed for oxidative dimerizations of anionic vinylidene compounds,[7] whereas dehydrodimerization of the cationic iron vinylidene compound [(η^5-C_5H_5)(dppe)Fe=C=CHMe]$^+$ to the diiron bis-vinylidene ion [(η^5-C_5H_5)(dppe)-Fe=C=CMe−CMe=C=Fe(dppe)(η^5-C_5H_5)]$^{2+}$ proceeds via deprotonation of 17-e radical dications followed by $C_{(\beta)}-C_{(\beta)}$ dimerization of ethynyl radical cations.[8] We have recently shown[9] that oxidative dehydrodimerization of the manganese vinylidene complex (η^5-C_5H_5)(CO)$_2$Mn=C=CHPh (**1**) into bis-vinylidene complex (η^5-C_5H_5)(CO)$_2$Mn=C=CPh−CPh=C=Mn(CO)$_2$(η^5-C_5H_5) (**4**) goes via homolysis of the $C_{(\beta)}-H$ bond in the radical cation $\mathbf{1}^{+\cdot}$ and involves the formally 16-e mononuclear σ-phenylethynyl cation $\mathbf{2}^+$ and the bis-carbyne dication $\mathbf{4}^{++}$ as the key sequential intermediates (see Scheme 1). A similar scheme was also reported for (η^5-C_5H_4Me)(dmpe)Mn=C=CHPh.[5]

In this paper we report on the oxidative dehydrodimerization of manganese vinylidene complexes (η^5-C_5R_5)(CO)(L)Mn=C=CHPh (**5**: R=Me, L=CO; **6**: R=H, L=PPh_3). Despite **5** and **6** having a close similarity to **1**, their dehydrodimerization proceeds according to a different scheme, as will be shown below.

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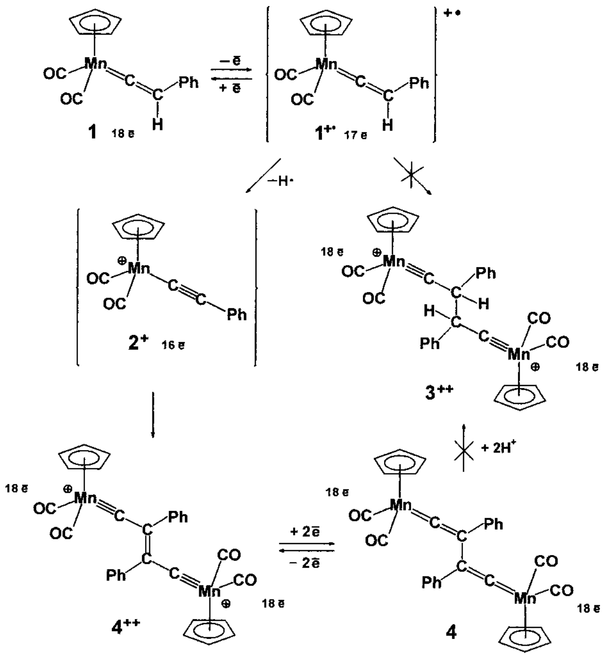
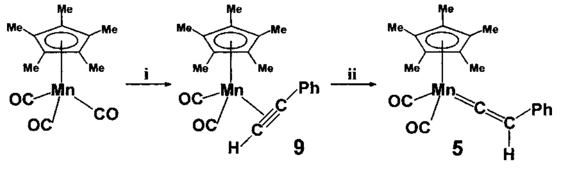


Scheme 1.

RESULTS AND DISCUSSION

The vinylidene complex **5** was prepared in 29% yield by a standard photolytic route in benzene solution (see Scheme 2) and fully characterized by microanalysis and spectroscopic means. The formation of alkyne intermediate **9** was confirmed by the presence of the ν_{CO} 1954, 1890 cm^{-1} and $\nu_{C\equiv C}$ 1820 cm^{-1} bands in the IR spectrum of the reaction mixture, which are very similar to those reported for the structurally similar analogue (η^5-C_5H_5)(CO)$_2$Mn(η^2-PhC≡CH).[10]

Experimentally, dehydrodimerization of **5** to (η^5-C_5Me_5)(CO)$_2$Mn=C=CPh−CPh=C=Mn(CO)$_2$(η^5-C_5Me_5) (**7**) was carried out using a procedure similar to that for **1**,[9] i.e. **5** was oxidized by $AgBF_4$ in dichloromethane at −40°C, the solution was kept at this temperature for 2 h and finally reduced by (η-C_6H_6)$_2$Cr. The target complex **7** was obtained in 40% yield and characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by mass spectrometry. We found that the yield of **7** can be increased to 85–90% if either potassium t-butylate or triethylamine is used in the final reaction step.



i = hν, C_6H_6, 5°C, 2 h.
ii = 20% HMTA, C_6H_6, 65°C, 4 h.

Scheme 2.

Table 1. Redox potentials of complexes **5, 6, 7, 8** and **11**$^{++}$, CV (CH_2Cl_2, 0.1 M Bu_4NPF_6, v = 200 μV s^{-1}, CG-electrode, V *versus* SCE). $E^*_{p,c}$are potentials of peaks obtained by reverse scanning of potential

Compound	$E_{p,a}$ (V)	Peak	n (e$^-$)	$E^*_{p,c}$ (V)	Peak	n (e$^-$)
5	+0.77	C	1	+0.67	D	
				+0.26	E	
6	+0.43	H	1	+0.18	K	
			1	−0.22	L	
7	+0.17	A	1	+0.11	A′	1
	+0.58	B		+0.52	B′	1
8	+0.19	F	1	+0.12	F′	1
	+0.61	G	1	+0.54	G′	1
11^{++}	−0.15	L′	1	−0.23	L	1
	+0.24	K′	1	+0.16	K	1

In order to determine the mechanism of the dehydrodimerization process, we studied the electrochemical behavior of complexes **5** and **7** by cyclic voltammetry in CH_2Cl_2 solution (see Table 1).

Complex **7** displays two one-electron reversible oxidation waves at +0.17 V (peak A) and +0.58 V (peak B) (see Fig. 1). Complex **5** oxidizes irreversibly at +0.77 V (see Fig. 2, peak C). The reverse scanning of potentials revealed new cathodic peaks at +0.67 V and +0.27 V (peaks D and E respectively). These peaks do not coincide with the reduction peaks A′, B′ of **7**$^{++}$.

Thus, **7**$^{++}$ is not an initial product of transformation of **5**$^{+\cdot}$, i.e. dehydrodimerization of **5** proceeds by a different mechanism than that for complex **1** (Scheme 1). We believe

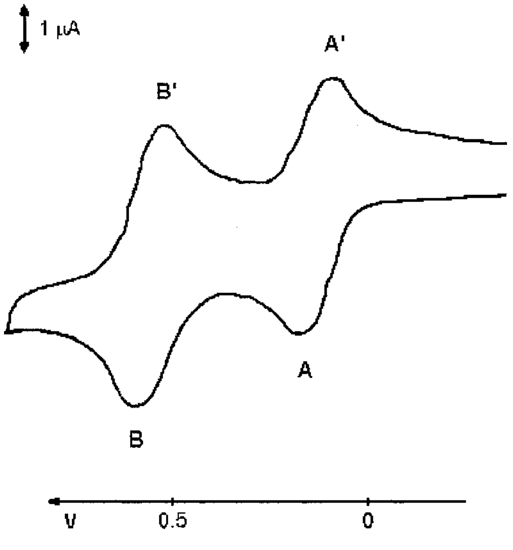


Figure 1. CV of bis-vinylidene complex **7** at 20 °C.

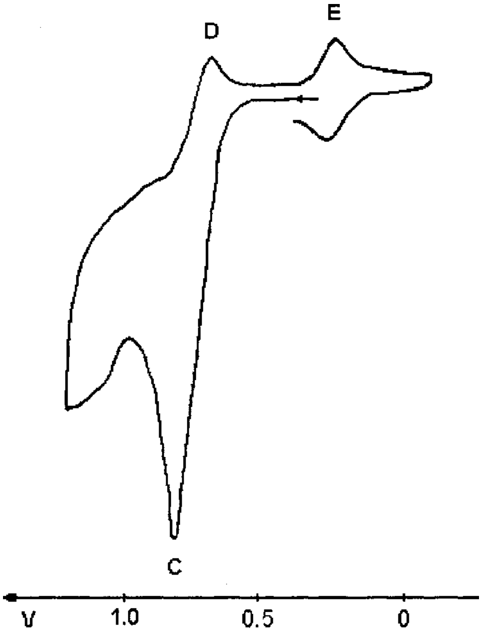
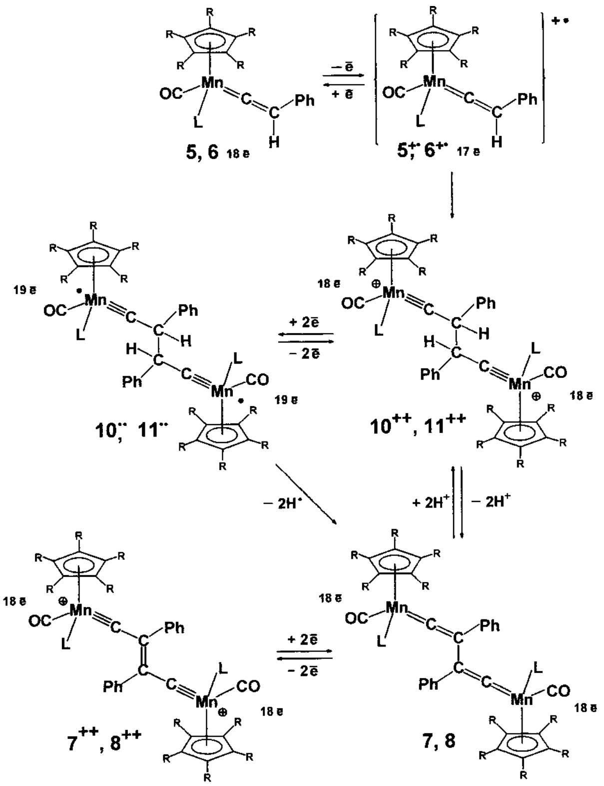


Figure 2. CV of vinylidene complex **5** at 20 °C.

that dehydrodimerization of **5** proceeds through the $C_{(\beta)}-C_{(\beta)}$ coupling of the radical cations $\mathbf{5}^{+\cdot}$ leading to the bis-carbyne dication $[(\eta^5\text{-}C_5Me_5)(CO)_2Mn{\equiv}C-CPhH-CPhH-C{\equiv}Mn(CO)_2(\eta^5\text{-}C_5Me_5)]^{2+}$ ($\mathbf{10}^{++}$) (Scheme 3). The latter is reduced by $(\eta\text{-}C_6H_6)_2Cr$ to the 19e-, 19e-diradical $\mathbf{10}^{\cdot\cdot}$, which further converts into the bis-vinylidene complex **7** via homolysis of the $C_{(\beta)}-H$ bonds of the bis-carbyne ligand. Complex $\mathbf{10}^{++}$ is long-lived in solution below −10 °C but is not readily isolable; it was characterized only by its IR spectrum in CH_2Cl_2 solution (ν_{CO} 2012, 1974 cm^{-1}).

In order to confirm the validity of the mechanism shown in Scheme 3, we studied the oxidative dehydrodimerization of the triphenylphosphine-substituted phenylvinylidene complex $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Mn{=}C{=}CHPh$ (**6**), since we expected the product of direct $C_{(\beta)}-C_{(\beta)}$ coupling $[(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Mn{\equiv}C-CPhH-CPhH-C{\equiv}Mn(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]^{2+}$ ($\mathbf{11}^{++}$) to be rather stable. Complex **6** was prepared by photolysis of **1** with triphenylphosphine in hexane.[10] These conditions were chosen to minimize the formation of by-products $(\eta^5\text{-}C_5H_5)(CO)_2Mn(PPh_3)$ and $(\eta^5\text{-}C_5H_5)(CO)_2Mn^{-}-C(PPh_3^{+}){=}CHPh$. The structure of **6** was unequivocally proved by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. According to the NMR data (the presence of two signals of the cyclopentadienyl protons and two cyclopentadienyl carbon resonances, as well as two phosphorus singlets), **6** exists as a mixture of two isomers in the approximate ratio 9:1. We believe that the vinylidene ligand in **6** is vertically oriented, as in the parent complex **1**,[11] and that the isomers differ in the orientation of the phenyl group relative to the cyclopentadienyl ring.

Oxidative dehydrodimerization of **6** was carried out under the same conditions as the analogous processes for **1** and **5**. The bis-vinylidene complex **8** proved to be rather unstable, and was obtained in 20% yield. Its structure was confirmed



R = Me, L = CO **5**, $\mathbf{5}^{+\cdot}$, $\mathbf{10}^{++}$, $\mathbf{10}^{\cdot\cdot}$, **7**, $\mathbf{7}^{++}$.
R = H, L = PPh_3 **6**, $\mathbf{6}^{+\cdot}$, $\mathbf{11}^{++}$, $\mathbf{11}^{\cdot\cdot}$, **8**, $\mathbf{8}^{++}$.

Scheme 3.

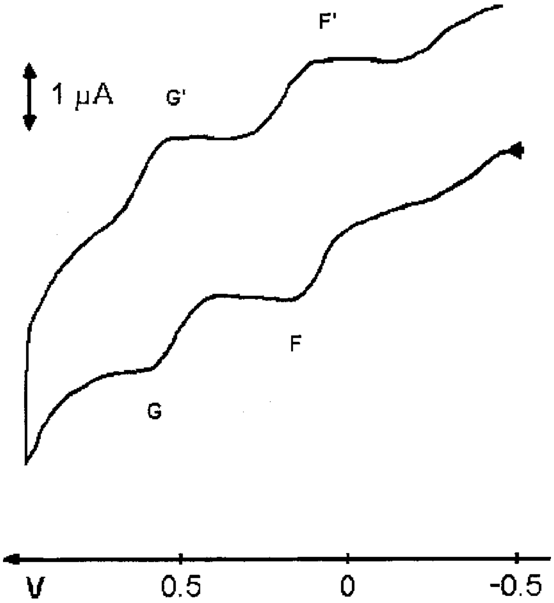


Figure 3. CV of bis-vinylidene complex **8** at 20 °C.

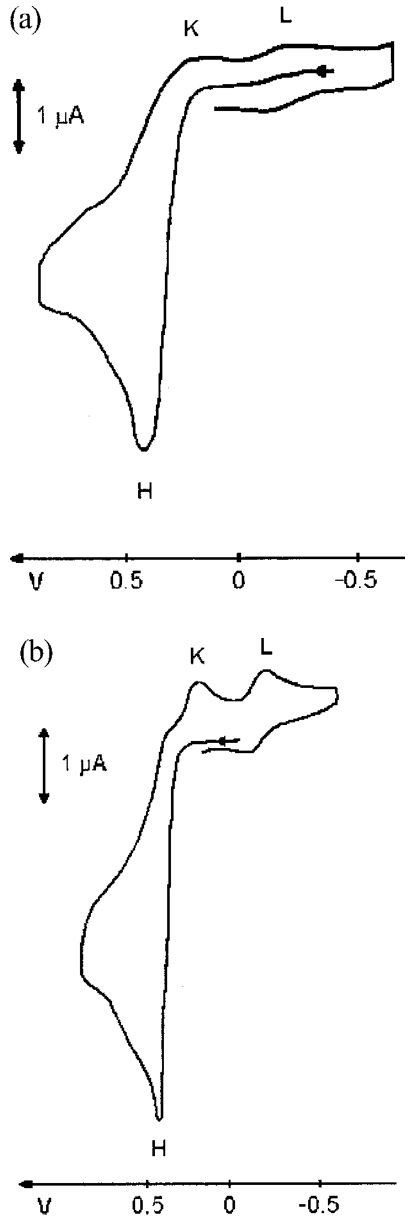


Figure 4. CV of vinylidene complex **6**: (a) at 20 °C; (b) at 35 °C.

by IR-, NMR ^{1}H, and ^{31}P spectroscopy and mass spectroscopy. According to the NMR spectra, complex **8** exists as a mixture of two diastereomers in 3:1 ratio.

Electrochemical oxidation of **6** and **8** was studied by cyclic voltammetry (CV) in dichloromethane solution. The cyclic voltammogram of the bis-vinylidene complex **8** showed two reversible one-electron oxidation peaks at +0.19 V and +0.61 V (Fig. 3, peaks F and G respectively). The cyclic voltammogram of the mononuclear vinylidene complex **6** displayed one irreversible oxidation peak at +0.43 V (Fig. 4, peak H). The reverse scanning of potential revealed new peaks at +0.24 V and −0.15 V (peaks K and L respectively), which did not coincide with reduction peaks of $\mathbf{8}^{++}$ (peaks F′, G′).

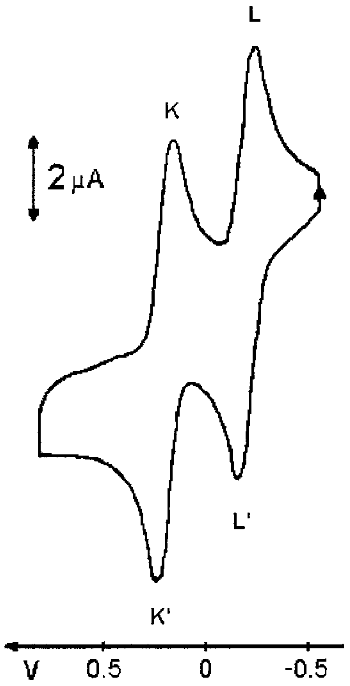


Figure 5. CV of bis-carbyne complex $\mathbf{11}^{++}$ at 20 °C.

We conclude, therefore, that the mechanism of oxidation of both **5** and **6** differs from that found for oxidation of **1** (Scheme 1). Preparative chemical oxidation of **6** without addition of reducing agent at the final step afforded the intermediate bis-carbyne complex $[\mathbf{11}^{++}](BF_4)_2$ in 70% yield, which was identified by IR, ^{1}H, and ^{31}P NMR spectra. This intermediate, having four stereocenters, exists as a mixture of a great number of stereoisomers and its NMR spectra are rather complex (eight cyclopentadienyl proton resonances in the ^{1}H spectrum and four broad singlets in the ^{31}P spectrum). The complex structure of $[\mathbf{11}^{++}](BF_4)_2$ caused no great difficulties for studying its CV, since all the stereoisomers had the same redox potentials. We have found that $\mathbf{11}^{++}$ is reduced in two reversible one-electron waves (Fig. 5) and its reduction peaks K and L coincide with those observed in the cyclic voltammogram of complex **6**.

Thus, we conclude that $\mathbf{11}^{++}$ is the initial oxidation product of $\mathbf{6}^{+\cdot}$ and that oxidation of **6** proceeds as shown in Scheme 3. We also showed that **8** is easily protonated by $HBF_4{\cdot}Et_2O$ to give $\mathbf{11}^{++}$, and the latter can be deprotonated to give **8**.

CONCLUDING REMARKS

Two findings from this work are noteworthy. The first is the fact that oxidation of the structurally similar vinylidene complexes $(\eta^5-C_5H_5)(CO)_2Mn{=}C{=}CHPh$ (**1**), on the one hand, and $(\eta^5-C_5R_5)(CO)(L)Mn{=}C{=}CHPh$ (**5, 6**), Q7 on the other hand, proceed with different reaction mechanisms. In the case of the complex **1**, the primary oxidation product **1**$^{+\cdot}$ undergoes homolysis of the $C_{(\beta)}-H$ bond and $C_{(\beta)}-C_{(\beta)}$ coupling takes place subsequently. Unlike **1**$^{+\cdot}$, the radical cations **5**$^{+\cdot}$ and **6**$^{+\cdot}$ undergo direct $C_{(\beta)}-C_{(\beta)}$ coupling, i.e. the dimerization step precedes homolysis of the $C_{(\beta)}-H$ bond. We believe that this distinction is caused by the different stabilities of the bis-carbyne dications **3**$^{++}$, **10**$^{++}$ and **11**$^{++}$. Owing to the instability of **3**$^{++}$, the dimerization equilibrium between **1**$^{+\cdot}$ and **3**$^{++}$ is shifted to the side of the monomer **1**$^{+\cdot}$ and the homolysis of the $C_{(\beta)}-H$ bond becomes the predominant process. For the more basic **5** and **6** the dimers **10**$^{++}$ and **11**$^{++}$ are more stable and the $C_{(\beta)}-C_{(\beta)}$ coupling takes place instead of homolysis of the $C_{(\beta)}-H$ bond.

The second finding deserving attention is the fact that homolysis of the $C_{(\beta)}-H$ bond proceeds easily in the 19e$^-$ bis-carbyne diradicals **10**$^{\cdot\cdot}$ and **11**$^{\cdot\cdot}$ to give bis-vinylidene complexes **6** and **7** respectively. There are few examples of such C−H activation reported in the literature.[12] This reductive C−H activation is only possible if dibenzenechromium is used as a reducing agent in the final step of dehydrodimerization of **5** and **6**. However, interaction of **10**$^{++}$ and **11**$^{++}$ with triethylamine and potassium t-butylate can also proceed via deprotonation. An additional investigation is needed to reveal the true course of the reactions in the latter cases.

EXPERIMENTAL

All operations were carried out under a purified argon atmosphere using Schlenk techniques. All photochemical procedures were performed with an immersed ultraviolet mercury lamp (125 W). Reagent-grade saturated hydrocarbons, benzene, and diethyl ether were dried and distilled under benzophenone-ketyl prior to use. Dichloromethane was distilled first from P_4O_{10} and, just prior to use, from $LiAlH_4$. Pentamethylcymantrene was obtained with ~20% admixture of $(\eta^5\text{-}C_5Me_4H)Mn(CO)_3$.[13]

Cyclic voltammograms were measured on 'PN-50-1' apparatus (Gomel', Belarus) with glassy carbon as a working electrode ($S = 2\ mm^2$), a platinum plate as an auxiliary electrode, and a saturated calomel electrode (SCE) as a reference. The number of electrons consumed was estimated by comparison of the currents of the peaks observed with those of the one-electron decamethylferrocene/decamethylferrocenium couple at the same concentrations. The redox properties of compounds **5–8** and **11**$^{++}$ under the CV conditions used are given in Table 1.

Melting points were determined in sealed capillaries under argon atmosphere. IR spectra were measured on Specord 75 IR instrument. NMR spectra were obtained on Bruker DPX-300 and Bruker AMX 400 spectrometers. Elemental analyses were performed on a Carlo Erba 1106 CHN analyzer. Electron impact mass-spectra (70 eV, 150 °C) were obtained on a Finnegan MAT SSQ 710 spectrometer.

Preparation of complex 5

The photochemical reactor was charged with a magnetic stir bar and 150 ml of benzene solution containing 2.2 g (8 mmol) of $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$ [containing 20% of $(\eta^5-C_5Me_4H)Mn(CO)_3$ as admixture] and 2 ml (24 mmol) of phenylacetylene. The reaction mixture was cooled to 0–5 °C and irradiated with vigorous magnetic stirring for 2 h. During this time, new IR bands ν_{CO} 1954, 1890, $\nu_{C\equiv C}$ 1820 cm^{-1} corresponding to the π-acetylene complex $(\eta^5\text{-}C_5Me_5)Mn(CO)_2(\eta^2\text{-}PhC{\equiv}CH)$ (**9**) appeared. To induce the acetylene–vinylidene rearrangement of **9**, a catalytic amount of hexamethylenetetramine (0.22 g, 1.6 mmol) in 3 ml of H_2O was added and the solution was kept at 65 °C for 4 h. Evaporation of the solvent *in vacuo* gave a red oil. This was chromatographed on silica (Aldrich, 70–230 mesh, 60 Å; eluent: petroleum ether) to afford a mixture of $(\eta^5C_5Me_5)(CO)_2Mn{=}C{=}CHPh$, $(\eta^5\text{-}C_5Me_4H)(CO)_2Mn{=}C{=}CHPh$, and some unreacted $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$. Crude product was recrystallized from hexane to remove the tetramethylcyclopentadienyl complex. Red crystals (0.8 g, 29%) of analytically pure complex **5** were obtained. M.p. 124–125 °C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1982, 1922, $\nu_{C=C}$ 1630–1570. Anal. Found: C, 69.28; H, 5.92; Mn, 16.91. Calc. for $C_{20}H_{21}MnO_2$ ($M = 348$) C, 68.97; H, 6.03; Mn, 15.80. ^1H NMR (C_6D_6, δ): 1.62 (s, 15H, C_5Me_5); 6.59 (s, 1H, $=C-H$); 7.01, 7.23, 7.29 (m, 5H, Ph). ^{13}C NMR (C_6D_6, δ) 11.0 (Me); 100.4 (CMe); 120.9, 125.2 (C_{ortho}, C_{meta}); 124.4 (C_{para}); 129.0 (C_{ipso}); 134.5 ($C_{(\beta)}$); 229.0 (CO); 377.9 (C_α).

Preparation of complex 6

A solution of 0.56 g (2 mmol) of complex **1** and 1.05 g (4 mmol) of PPh_3 in 50 ml of hexane was irradiated at 5–7 °C for 1.5 h. The reaction mixture was then concentrated to 5 ml and chromatographed on alumina (Reanal, activity II, neutral). Some unreacted complex **1** and PPh_3 were eluted with pentane; an orange zone containing $CpMn(CO)_2(PPh_3)$ was eluted with pentane–Et_2O (100:1). The main product was obtained from a broad orange–red zone eluted with pentane–Et_2O (50:1). The yield of **6** was 0.25 g (24%). M.p. 175 °C (dec., ether). IR (CH_2Cl_2) ν_{CO} 1895, $\nu_{C=C}$ 1600–1550 cm^{-1}; (KBr) ν_{CO} 1912, $\nu_{C=C}$ 1604, 1580, 1556 cm^{-1}. Anal. Found: C, 73.83; H, 5.11. Calc. for $C_{32}H_{26}MnOP$ ($M = 512$): C, 75.00; H, 5.08. ^1H NMR ($CDCl_3$, δ, J(PH)): 4.65 (d, $J = 1.15$ Hz, 5H, C_5H_5), 5.03 (br. s, C_5H_5), the ratio of integral intensities 9:1; 6.17 (d, $J_4 = 5.5$ Hz, 1H, $=C-H$); 6.90–6.99, 7.10–7.18, 7.26–7.28, 7.53–7.58 (m, 20H, Ph). ^{31}P NMR ($CDCl_3$, δ): 29.5, 89.8 (s, ratio of integral intensities 1:9). ^{13}C NMR ($CDCl_3$, δ, J(PC)): 87.8, 88.3 (C_5H_5, ratio 1:10); 123.6, 123.8, 124.3 (C_{ortho}, C_{meta}, C_{para} $=CHPh$); 128.3 (d, $J_2 = 9.7$ Hz, C_{ortho} PPh); 128.6 (C_{para} PPh); 128.7 (C_{ipso} $=CHPh$); 129.9 (d, $J_3 = 1.9$ Hz, C_{meta} PPh); 133.3 (d, $J_1 = 10.5$ Hz, C_{ipso} PPh); 137.5 (d, $J_3 = 4.2$ Hz, C_β).

Dehydrodimerization of 5 using (η-C_6H_6)$_2$Cr as reducing agent

A solution of 0.1 g (0.29 mmol) of complex **5** in 10 ml of CH_2Cl_2 was oxidized with 0.135 g (0.29 mmol) of $AgBF_4$·3dioxane at −40 °C. The color of the reaction mixture changed immediately to bright green and a silver mirror appeared. After stirring for 2 h at this temperature the solution became cherry red and its IR spectrum contained new ν_{CO} bands at 2012, 1974 cm^{-1} corresponding to the bis-carbyne complex **10**$^{++}$. A large excess (0.3 g) of (η-C_6H_6)$_2$Cr was added as a reductant. The reaction mixture was slowly warmed up to room temperature. The color of the solution changed to red–brown and the IR bands of **10**$^{++}$ were transformed into new bands of **7**: ν_{CO} 1992, 1972, 1918; $\nu_{C=C}$ 1650–1540 cm^{-1}. The solution was filtered through Celite, evaporated *in vacuo* and the residue extracted with hexane (10 × 5 ml). The red solution obtained was filtered, evaporated to one-fifth of its volume, and cooled to −20 °C. After repetitive recrystallization, 0.04 g (41%) of compound **7** was obtained as a brown powder. M.p. 204–205 °C. IR (CH_2Cl_2): ν_{CO} 1992, 1972, 1918; $\nu_{C=C}$ 1650–1540 cm^{-1}. Anal. Found: C, 68.81; H, 6.02. Calc. for $C_{40}H_{40}Mn_2O_4$ (*M* = 694): C, 69.16; H, 5.76. ^{1}H NMR (C_6D_6, δ, *J*(HH)): 1.65 (s, 30H, Me); 7.13 (t, J_3 = 6.5 Hz, 2H, Ph); 7.39 (t, J_3 = 6.5 Hz, 4H, Ph); 7.45 (d, J_3 = 6.5 Hz, 4H, Ph). ^{13}C NMR (C_6D_6, δ): 10.2 (Me); 100.3 (CMe); 125.0, 128.6 (C_{ortho}, C_{meta}); 126.1 (C_{para}); 126.4 (C_{ipso}); 137.8 (C_β); 229.1 (CO). MS (EI) *m/z*: 694 (M^+), 638 ($M^+ - 2CO$), 582 ($M^+ - 4CO$).

Preparation of complex 7 by deprotonation of 10^{++} with t-BuOK or triethylamine

To the solution of complex **10**$^{++}$ prepared as described above, 0.04 g (0.3 mmol) of t-BuOK or 0.2 ml (1.5 mmol) of triethylamine was added. After stirring for 10 min, the reaction mixture was filtered through Celite and evaporated *in vacuo*. The brown powder was thoroughly dried, washed with 5 ml of cold hexane, and dried. This procedure gave 0.085 g (85%) and 0.09 g (90%) of complex **7** using t-BuOK and triethylamine respectively.

Dehydrodimerization of 6 using (η-C_6H_6)$_2$Cr as reducing agent

A solution of 0.1 g (0.2 mmol) in 10 ml of compound **6** was oxidized with 0.09 g (0.2 mmol) $AgBF_4$·3dioxane at −30 °C. After 2 min, the reaction mixture became dark green, and after ~40 min the color of the solution changed to red and the IR spectrum of the mixture contained the band (ν_{CO} 2020 cm^{-1}) of the dicationic bis-carbyne complex **11**$^{++}$. Then, 0.05 g (0.2 mmol) (η-C_6H_6)$_2$Cr was added and the solution was allowed to reach room temperature. A new ν_{CO} band at 1900 cm^{-1} due to **8** was observed in the IR spectrum of the reaction mixture. The mixture was filtered to remove the silver powder, the solvent was evaporated in *vacuo*, the residue was reprecipitated four times from benzene with heptane to give 0.02 g (20%) of complex **6** as an orange powder. IR (CH_2Cl_2) ν_{CO} 1900 cm^{-1}. Good elemental analysis data for this compound were not obtained. ^{1}H NMR (C_6D_6, δ): 4.61, 4.66 (br. s, ratio 1:3, C_5H_5); 6.98–7.13, 7.68–7.86 (m, Ph). The ratio of the total integral intensity of the Cp protons to the total integral intensity of the Ph protons is 1:4. ^{31}P NMR (C_6D_6, δ): 91.04, 91.89 (s, ratio 1:3, PPh_3). MS (EI) *m/z*: 1022 (M^+), 966 ($M^+ - 2CO$).

Preparation of complex 11^{++}

The oxidation of **6** was carried out as described above. The red solution of **11**$^{++}$ was filtered through Celite, concentrated *in vacuo*, and the product was precipitated with ether. The yield of red microcrystalline **11**$^{++}$ was 0.075 g (75%). M.p. 175 °C. IR (CH_2Cl_2) ν_{CO} 2020 cm^{-1}. Anal. Found: C, 63.02; H, 4.50. Calc. for $C_{64}H_{52}B_2F_8Mn_2O_2P_2$ (*M* = 1198): C, 64.11; H, 4.34. ^{1}H NMR (CD_3NO_2, δ): 4.93, 4.97, 5.07, 5.09, 5.22, 5.28, 5.30, 5.43 (s, ratio 4.6:5.2:6.5:1.5:1.2:3.0:1.5:1, C_5H_5); 6.93–7.20, 7.42–7.55, 7.59–7.75 (m, Ph, $=C-H$). The ratio of the total integral intensity of the Cp protons to the total integral intensity of the Ph protons is 1:4. ^{31}P NMR (CD_3NO_2, δ): 65.1, 65.3, 66.1, 67.3 (br. s, ratio 2.5:1:6.3:2.6).

Protonation of complex 8 to 11^{++}

A solution of 0.03 g (0.03 mmol) of complex **8** in 10 ml of CH_2Cl_2 was treated with 0.09 ml (0.06 mmol) of 54% HBF_4·Et_2O. The reaction mixture became deep red immediately and a red solid precipitated. Then, 5 ml of ether was added and the mother liquor was removed. The residue was dissolved in 3 ml of CH_2Cl_2, and pure compound **11**$^{++}$ was obtained by adding 1 ml of ether. The yield of **11**$^{++}$ was 0.03 g (85%).

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