Oxidative Activation of the Manganese Bis-vinylidene Complexes [(η^5-C$_5$R$_5$)(CO)$_2$Mn=C=CPh]$_2$ (R = H, Me) toward Addition of Nucleophiles

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A new approach to the activation of transition metal bis-vinylidene (μ-1,3-butadiene-1,4-diylidene) complexes toward nucleophilic addition is proposed, based on their two-electron oxidation to corresponding μ-2-butene-1,4-diylidyne compounds of a bis-carbyne type. The latter are more electrophilic and able to react with nucleophiles that are inert to the former. In line with this synthetic methodology the reaction of the manganese bis-vinylidene complexes [(η^5-C$_5$R$_5$)(CO)$_2$Mn=C=CPh]$_2$ (**1**, R = H; **2**, R = Me) with oxygen nucleophiles (H$_2$O and OH$^-$) to form binuclear cyclic bis-carbene compounds [(η^5-C$_5$R$_5$)(CO)$_2$Mn]$_2$(μ-C$_4$Ph$_2$O) (**5**, R = H; **6**, R = Me) is induced by oxidation, 2 equiv of oxidant (Cp$_2$FeBF$_4$) being required to complete the reaction of **1** with water, resulting in **5** with 76% yield. The oxidation of **1** with 1 equiv of AgBF$_4$ leads to the thermally unstable radical cation **7**, which reacts with water to give an equimolar mixture of **1** and **5**. Two-electron oxidation of **1** leads to the dicationic bis-carbyne complex (η^5-C$_5$H$_5$)(CO)$_2$Mn$^+$≡CC(Ph)=C(Ph)C≡Mn$^+$(CO)$_2$(η^5-C$_5$H$_5$) (**3**), which exists as the solvate **3·2THF** (**11**) in THF solution and reacts with water smoothly to give **5** in about 90% yield. Unlike **1**, the bis-vinylidene complex **2** does not react with water even in the presence of oxidant. Complex **6** can be obtained in 15% yield by the reaction of the bis-carbyne dicationic complex (η^5-C$_5$Me$_5$)(CO)$_2$Mn$^+$≡CC(Ph)=C(Ph)C≡Mn$^+$(CO)$_2$(η^5-C$_5$-Me$_5$) (**4**) with Bu$_4$NOH. The different reactivities of **1** and **2** are also confirmed by cyclic voltammetry. The crystal structures of **2**, **5**, and **6** are reported.

Introduction

Nucleophilic addition to ligands is one of the most important methods for the selective formation of C−C and C−X bonds (X = O, N, S, etc.)[1] and is of fundamental importance for modern organometallic chemistry, these processes typically proceeding better for positively charged compounds. Such reactions for late transition metal vinylidene complexes occur via the attack of nucleophiles at the electrophilic C$_\alpha$ atoms in the vinylidene ligands; many examples of such transformations have been reported for mononuclear vinylidene complexes with a wide variety of nucleophiles.[2] In particular, the ruthenium-catalyzed addition of oxygen nucleophiles to the intermediate transition metal vinylidenes is the key step in the synthesis of vinylcar-

bamates, enol ethers, *trans*-alkenyl esters, 2,3-dihydro-furans, and other important organic compounds from terminal alkynes.[3] However, until now, oxidatively induced nucleophilic additions to vinylidene complexes have not been reported. Further for binuclear complexes with bridging 1,3-butadiene-1,4-diylidene ligands (further denoted as bis-vinylidene complexes), no examples of nucleophilic addition reactions have been reported.

We began a systematic study of oxidatively induced nucleophilic additions to the C$_\alpha$ atoms in transition metal bis-vinylidene compounds as shown in the general Scheme 1. If these carbon atoms are insufficiently electrophilic to undergo addition of protonic nucleophiles (Scheme 1, (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 1, (b)). Both C$_\alpha$ carbons in such compounds are more electrophilic relative to those of the initial complexes **I**, facilitating the formation of nucleophilic addition products **III** and **IV**. We believe that oxidative activation of nucleophilic addition is more promising for bis-vinylidenes **I** in comparison with mononuclear vinylidene

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Scheme 1. Oxidative Activation of Nucleophilic Additions to Transitional Metal Bis-vinylidene Complexes
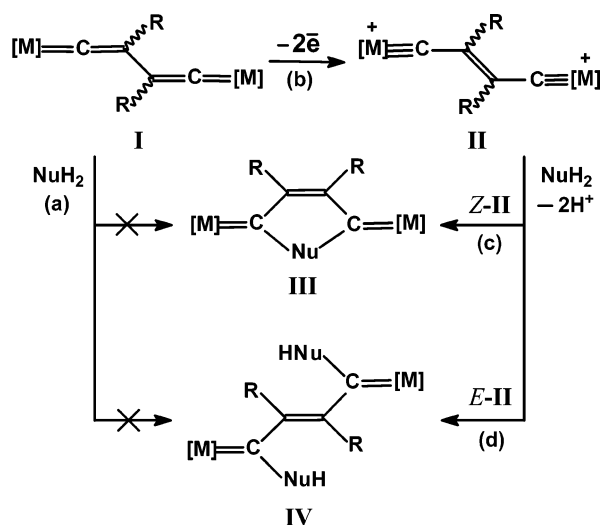
complexes since complexes **II** resulting from the oxidation of **I** have the same even electron configuration as the starting compounds **I** due to redistribution of the $M-C_\alpha$, $C_\alpha-C_\beta$, and $C_\beta-C_\beta$ bond orders. Therefore the probability for **II** to have sufficient lifetime to undergo subsequent addition (c) or (d) is essentially higher than for odd-electron radical cations formed by the oxidation of mononuclear vinylidene complexes. For diprotonic nucleophiles and isomers of **II** with a Z-$C_\beta-C_\beta$ central double bond, a nucleophilic addition (Scheme 1, (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 bridging 2-butene-1,4-diylidene ligands.

In the context of the study of the reactions of Scheme 1 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 with torsion angles $C_\alpha-C_\beta-C_\beta-C_\alpha$ 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**.[4a-e] However, uniquely in the manganese complex $(\eta^5$-$C_5H_4Me)(dmpe)$-$Mn=C=C(Ph)-C(Ph)=C=Mn(dmpe)(\eta^5$-$C_5H_4Me)$ the value of the $C_\alpha-C_\beta-C_\beta-C_\alpha$ angle is 86.3°.[4f] If the conformation of **I** is known, straightforward prediction of the geometry of the $C_\alpha-C_\beta-C_\beta-C_\alpha$ moiety in **II** becomes possible, provided that the oxidation of **I** (i.e., *s-cis*-**I** → Z-**II** or *s-trans*-**I** → E-**II**) proceeds selectively. However, this assumption needs to be experimentally tested specifically for the reactions carried out in coordinating solvents.

To ensure successful realization of the reaction of the Scheme 1, 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 bis-vinylidenes **I**.

(3) The C_α atoms of bis-carbynes **II** should be sterically accessible for the attack by nucleophiles NuH_2.

Results and Discussion

Study of Oxidatively Induced Nucleophilic Addition of Water and Hydroxide Ion to Manganese Bis-vinylidene Complexes 1 and 2. Manganese bis-vinylidene complexes $[(\eta^5$-$C_5R_5)(CO)_2Mn=C=CPh]_2$ (**1**, R = H; **2**, R = Me) and oxygen nucleophiles (water, hydroxide ion) were chosen as precursors in the realization of the synthetic pathway shown in Scheme 1. Herein we have shown, that following Scheme 1, bis-vinylidenes **1** and **2** can be oxidatively activated toward the nucleophilic additions of water to **1** and hydroxide anion to **2**, these reactions resulting in cyclized products (Scheme 1, (b) + (c)). The results obtained are presented in Scheme 2. The preparations of **1** and **2** have been previously described.[5]

Both **1** and **2** are unreactive toward an excess of water at room and higher temperatures in different solvent media, but the addition of ferrocenium tetrafluoroborate to the solution of complex **1** in THF at room temperature immediately induces reaction with water to afford the cyclic bis-carbene complex **5** (Scheme 2). Two equivalents of oxidant are required to complete this reaction, and under these conditions the yield of the product is 76%. The structure of **5** was elucidated from spectroscopic and mass spectrometry data and confirmed by an X-ray diffraction study (see below).

This finding indicates that this reaction proceeds along the pathway (b) + (c), Scheme 1, so that the geometry of the central C_4 moiety in the intermediate **II** should be nearer *cis* rather than *trans*. It is noteworthy that such a *cis*-structure for 2-butene-1,4-diylidyne complexes is observed for the first time, since all known complexes of this type have previously displayed a *trans*-geometry.[4f,6] The formation of complex **5** can be explained by sequential nucleophilic attacks of the C_α carbons of the carbyne moiety by water oxygen followed by proton eliminations (Scheme 2, (c) + (d) + (e)). However, a study of the electrochemical behavior of **1** by cyclic voltammetry indicates some other reaction path.

Complex **1** in THF solution shows two reversible one-electron oxidation peaks A_1, A_2 (Figure 1a, Table 1), corresponding to the removal of the first and the second electron, respectively. Addition of water to the solution

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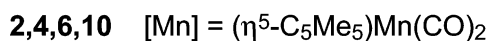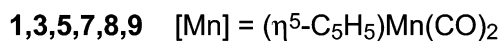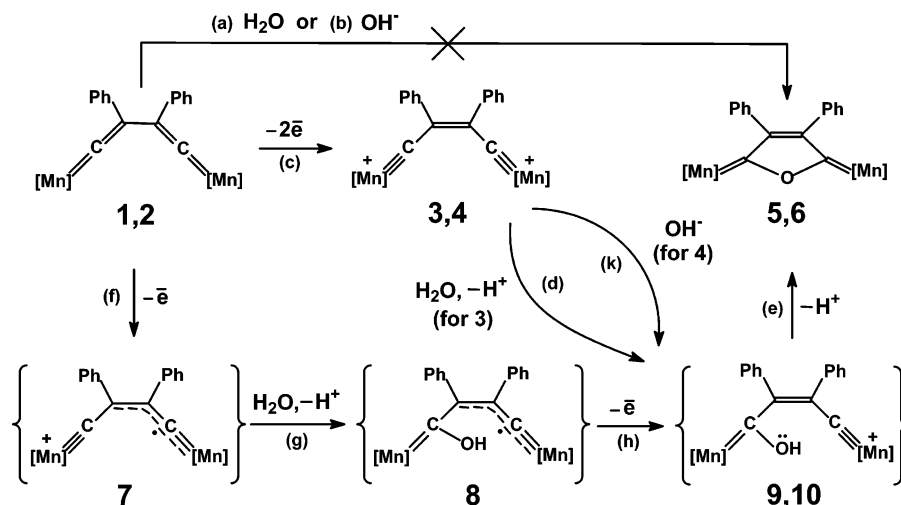
Scheme 2.   Oxidatively Induced Nucleophilic Addition Reactions of Bis-vinylidene Complexes 1 and 2 with Oxygen Nucleophiles (H$_2$O, OH$^-$)

1,3,5,7,8,9   [Mn] = (η^5-C$_5$H$_5$)Mn(CO)$_2$

2,4,6,10   [Mn] = (η^5-C$_5$Me$_5$)Mn(CO)$_2$

Table 1.   Redox Properties of Compounds 1, 2, 5, and 6 (THF, glassy carbon electrode, 0.2 M Bu$_4$NPF$_6$, v = 200 mV, relative to the Cp$_2$Fe/Cp$_2$Fe$^{+\bullet}$ couple: +0.54 V, ΔE = 100 mV)

experiment	Figure no.	peak	E, V	n(ē)	ΔE, mV
1	1a	A$_1$	+0.04	1	100
		A$_2$	+0.20	1	100
1 + H$_2$O	1b	A$_1{}^a$	+0.04	1	
		B$_1{}^b$	−1.38		
		B$_2{}^b$	−1.87		
		B$_3{}^a$	+0.44		
		B$_4{}^a$	+0.80		
5	1c	B$_1{}^c$	−1.38	1	140
		B$_2{}^c$	−1.87	1	140
		B$_3{}^a$	+0.40	2	
		B$_4{}^a$	+0.90	2	
2	2a	C$_1$	−0.15	1	100
		C$_2$	+0.12	1	100
2 + H$_2$O	2b	C$_1$	−0.15	1	100
		C$_2{}^d$	+0.12	1	100
6	2c	D$_1$	−1.36	1	100
		D$_2$	−1.88	1	100
		D$_3$	−0.06	1	100

^{a} i_c/i_a = 0. ^{b} i_a/i_c = 0. ^{c} $i_a/i_c \approx$ 0.9. ^{d} $i_c/i_a \approx$ 1.3.

Figure 1. Cyclic voltammograms of complexes **1** (a), **1** + H$_2$O (b), and **5** (c) in THF solution.

of **1** in THF changes the cyclic voltammogram (CV) considerably (Figure 1b). 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 reference compound **5** but differ from the latter in their irreversibility (Figure 1c). We suppose that the irreversibility of peaks B$_1$ and B$_2$ under the conditions of reaction of **1** with water on the electrode is caused by the protonation of one- and two-electron reduction products of **5** with water. Since the reaction begins at the step of the monooxidized bis-vinylidene **7**, we believe it to proceed along the pathway (f) + (g) + (h) + (e), Scheme 2.

After removal of the first electron the starting complex **1** is converted into the radical cation **7**. The subsequent attack of the activated C$_\alpha$ atom by the water oxygen, followed by proton loss, results in a hydroxy-carbene radical intermediate **8**. The latter is easily
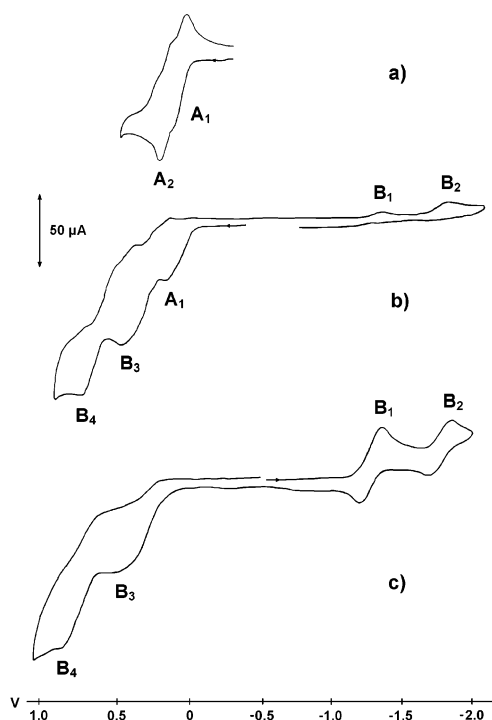
oxidized by the second equivalent of the oxidant to (hydroxycarbene)carbyne complex **9**, which is further converted into **5** through intramolecular nucleophilic attack and proton loss. Radical cation **7** can be smoothly generated at low temperature by the treatment of **1** with 1 equiv of strong oxidant AgBF$_4$ in THF or methylene chloride solution. We failed to isolate **7** due to its thermal instability, but on the basis of the results of IR monitoring (disappearance of bands of **1** (ν_{CO} 2008 (s), 1988 (s), 1936 (s), $\nu_{C=C}$ 1612, 1604, 1584 (m)) and

Scheme 3. Specific Solvation of Bis-carbyne Complex 3
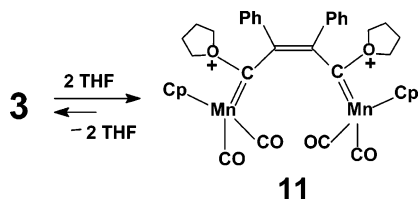
appearance of new bands of **7** (ν_{CO} 2008 (m), 1996 (s), 1952 (s)) the conversion **1 → 7** is nearly quantitative. Addition of water to the resulting solution of **7** led to the formation of a nearly equimolecular mixture of the initial bis-vinylidene compound **1** and bis-carbene complex **5**. We believe that in this case the radical **8** is oxidized by unreacted radical cation **7** (**7 + 8 → 9 + 1**) to make possible a further conversion of **9** into **5** as discussed above.

The low-temperature-stable μ-2-butene-1,4-diylidyne complex **3** can be generated by the interaction of **1** with 2 equiv of AgBF$_4$. It exists in THF solution as an adduct with two THF molecules **11** (Scheme 3), as is apparent from the IR spectrum (**11**: ν_{CO} (THF) 1964 (s), 1920 (s), containing abnormally low band wavenumbers for cationic carbonylcarbyne complexes).

The nucleophilic attack at the highly electrophilic C$_\alpha$ carbyne atom by the THF molecule with the formation of solvent adducts $[(\eta^5\text{-}C_5H_5)(CO)_2Mn=C(THF)CH_2R]^+$ (R = H, Me) has been observed earlier for mononuclear cationic manganese complexes $(\eta^5\text{-}C_5H_5)(CO)_2Mn^+\equiv$ CCH$_2$R (R = H, Me).[2c] In feebly coordinating methylene chloride the carbonyl stretching frequencies of **3** (ν_{CO} (CH$_2$Cl$_2$) 2056 (s), 2004 (s)) resemble those reported for $(\eta^5\text{-}C_5H_5)(CO)_2Mn^+\equiv$ CCH$_3$ (ν_{CO} (CH$_2$Cl$_2$) 2093 (s), 2053 (s)).[2c] Thus the dicationic complex generated by two-electron oxidation of bis-vinylidene complex **1** can exist as bis-carbyne compound **3** only in weakly coordinating solvents such as CH$_2$Cl$_2$, whereas in THF solution a reversible solvation of **3** occurs to give the adduct **11**. The addition of water to an equilibrium mixture of **3** and **11** in THF at $-10°$ C leads to the bis-carbene complex **5** with 90% yield. Despite the prevalence of adduct **11** in the equilibrium mixture, we believe that it is **3**, not **11**, that is responsible for the reaction with water to give **5**. The formation of **5** from **3** in CH$_2$Cl$_2$ takes a few hours under the same conditions. This difference is probably caused by the low solubility of water in methylene chloride.

Somewhat different results were obtained for the reactions of the manganese bis-vinylidene complex **2** containing the Cp* ligand. The oxidation of **2** with 2 equiv of oxidant affords the thermally unstable bis-carbyne complex **4**. Due to the combined effect of electronic (lower electrophilicity of C$_\alpha$ atoms) and steric (greater shielding of the reactivity centers) factors, the reactivity of **4** toward nucleophiles is reduced relative to **3**, because first, **4** is not solvated by THF unlike **3** and therefore its ν_{CO} band wavenumbers in THF and CH$_2$Cl$_2$ are very similar, and second, **4** does not react with water. The addition of 2 equiv of oxidant to a solution of **2** and water in THF resulted in no reaction to yield any expected cyclic product **6**, the structural analogue of **5**. This inertness of **2** was also confirmed by the cyclic voltammetry data. Complex **2** in THF
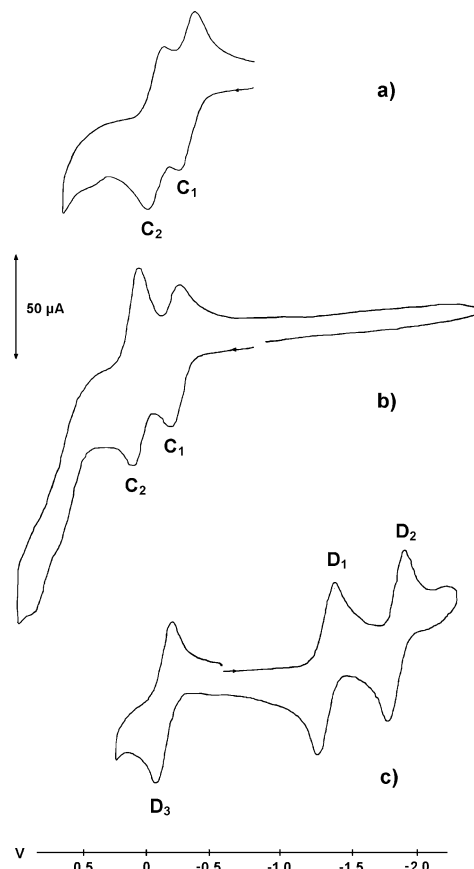

Figure 2. Cyclic voltammograms of complexes **2** (a), **2** + H$_2$O (b), and **11** (c) in THF solution.

solution displays two one-electron reversible oxidation peaks, C$_1$ and C$_2$ (Figure 2a), which retain their reversibility in the presence of water (Figure 2b). The absence of reduction peaks of the product on the cathodic branch of the CV in addition to retention of reversibility strongly indicates that the products of one- and two-electron oxidation of **2** do not react with water.

The reaction of **4** with hydroxide ion (30% aqueous solution of Bu$_4$NOH, a stronger nucleophile than water) proceeds in THF solution to afford the target cyclic compound **6** in low yield (15%) (Scheme 2, (k) + (e)). The neutral bis-vinylidene **2** failed to react with Bu$_4$-NOH. Complex **6** was fully characterized by spectral data and elemental analysis, and its structure was established by X-ray structural analysis (see the text below).

X-ray Diffraction Study of Bis-vinylidene Complex 2 and Bis-carbene Complexes 5 and 6. The molecular structure of **2** has been determined by an X-ray diffraction study. It is shown in Figure 3. The most important bond distances and valence angles are given in Table 2.

The conformation of the diene moiety is closer to the *s-cis* possibility (the torsion angle C$_1$−C$_2$−C$_3$−C$_4$ is $-76.4°$), whereas the Cp-metal fragments are disposed *trans* to each other (the pseudo-torsion angle Cp1−Mn1$\cdots$Mn2−Cp2 is 152.4°). Such a structure has not previously been observed for transition metal bis-vinylidene complexes. Thus the bis-carbyne dication **4** can also be expected to have a *cis*-configuration of the central C$_4$ moiety and, consequently, to form cyclic products in reactions with nucleophiles.
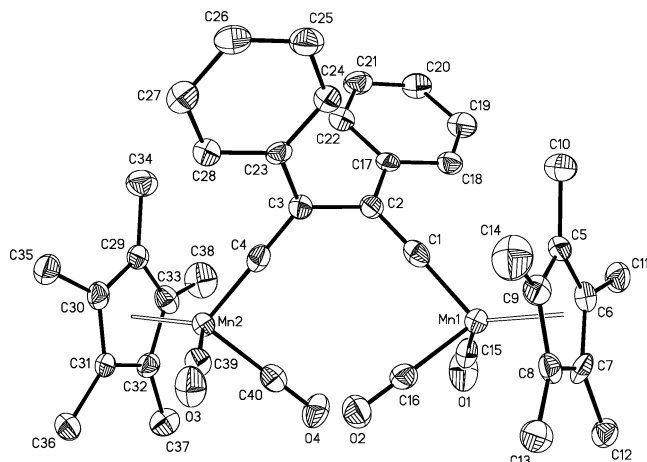
Figure 3. Molecular projection of [(η^5-C$_5$Me$_5$)(CO)$_2$-Mn=C=CPh]$_2$ (**2**). The solvate benzene molecule is not shown.

Figure 4. Molecular projection of [(η^5-C$_5$H$_5$)(CO)$_2$Mn]$_2$(μ-C$_4$Ph$_2$O) (**5**). Atoms A are symmetry related.

Figure 5. Molecular projection of [(η^5-C$_5$Me$_5$)(CO)$_2$Mn]$_2$-(μ-C$_4$Ph$_2$O) (**6**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Mn(1)−C(1)	1.762(5)	Mn(2)−C(40)	1.815(5)
Mn(1)−C(15)	1.775(6)	Mn(2)−Cp	1.784(5)
Mn(1)−C(16)	1.809(5)	C(1)−C(2)	1.332(6)
Mn(1)−Cp	1.782(5)	C(2)−C(3)	1.510(6)
Mn(2)−C(4)	1.760(5)	C(3)−C(4)	1.342(6)
Mn(2)−C(39)	1.789(5)		
C(1)−Mn(1)−C(15)	90.2(2)	C(4)−Mn(2)−Cp	127.9(2)
C(1)−Mn(1)−C(16)	90.5(2)	C(39)−Mn(2)−Cp	121.9(2)
C(15)−Mn(1)−C(16)	92.3(2)	C(40)−Mn(2)−Cp	122.0(2)
C(1)−Mn(1)−Cp	128.1(2)	Mn(1)−C(1)−C(2)	176.3(4)
C(15)−Mn(1)−Cp	122.6(2)	Mn(2)−C(4)−C(3)	176.7(4)
C(16)−Mn(1)−Cp	122.9(2)	C(1)−C(2)−C(3)	115.2(4)
C(4)−Mn(2)−C(39)	90.5(2)	C(2)−C(3)−C(4)	116.0(4)
C(4)−Mn(2)−C(40)	92.8(2)	C(1)−C(2)−C(3)−C(4)	−76.4(5)
C(39)−Mn(2)−C(40)	92.1(2)		

The molecular geometry of **5** was determined by an X-ray difraction study (Figure 4). Complex **5** has the usual pseudo-tetrahedral coordination geometry around the metal center, the values of all bond distances and valence angles lying in the usual intervals (selected values are given in Table 3). The phenyl rings are not conjugated with the dihydrofuran ring. The metal

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 5

Mn−C(1)	1.884(6)	Mn−C(12)	1.779(5)
Mn−C(11)	1.764(7)	Mn−Cp	1.791(6)
C(1)−C(2)	1.434(7)	O(0)−C(1)	1.394(6)
C(2)−C(2a)	1.365(8)		
C(1)−Mn−C(11)	98.6(3)	Mn−C(1)−O(0)	118.1(3)
C(1)−Mn−C(12)	90.9(3)	Mn−C(1)−C(2)	137.2(4)
C(11)−Mn−C(12)	86.7(3)	C(1)−O(0)−C(1a)	112.3(4)
C(1)−Mn−Cp	123.3(3)	O(0)−C(1)−C(2)	104.5(5)
C(11)−Mn−Cp	122.6(3)	C(1)−C(2)−C(2a)	109.3(4)
C(12)−Mn−Cp	125.1(3)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 6

Mn(1)−C(1)	1.886(3)	Mn(2)−Cp	1.797(3)
Mn(1)−C(15)	1.801(3)	C(1)−C(2)	1.460(4)
Mn(1)−C(16)	1.805(3)	C(2)−C(3)	1.371(4)
Mn(1)−Cp	1.793(3)	C(3)−C(4)	1.461(4)
Mn(2)−C(4)	1.897(3)	O(1)−C(1)	1.406(3)
Mn(2)−C(39)	1.799(3)	O(1)−C(4)	1.393(3)
Mn(2)−C(40)	1.777(3)		
C(1)−Mn(1)−C(15)	99.04(13)	C(40)−Mn(2)−Cp	118.8(15)
C(1)−Mn(1)−C(16)	90.55(13)	Mn(1)−C(1)−O(1)	121.0(2)
C(15)−Mn(1)−C(16)	87.67(15)	Mn(2)−C(4)−O(1)	120.6(2)
C(1)−Mn(1)−Cp	126.8(14)	Mn(1)−C(1)−C(2)	134.8(2)
C(15)−Mn(1)−Cp	120.3(15)	Mn(2)−C(4)−C(3)	135.1(2)
C(16)−Mn(1)−Cp	122.7(14)	C(1)−O(1)−C(4)	113.0(2)
C(4)−Mn(2)−C(39)	91.72(12)	O(1)−C(1)−C(2)	104.2(2)
C(4)−Mn(2)−C(40)	93.48(13)	O(1)−C(4)−C(3)	104.3(2)
C(39)−Mn(2)−C(40)	95.61(14)	C(1)−C(2)−C(3)	109.1(2)
C(4)−Mn(2)−Cp	127.4(14)	C(2)−C(3)−C(4)	109.4(2)
C(39)−Mn(2)−Cp	121.9(14)		

environments are in an approximate *cisoid* conformation (pseudo-torsion angle Cp-Mn···MnA−CpA is 17.9°).

The structure of **6** is different from that of its cyclopentadienyl analogue **5** (Figure 5, Table 4). The metal atoms are in a *gauche* disposition (the pseudo-torsion angle Cp1−Mn1···Mn2−Cp2 is 79.7°), evidently a result of the larger steric requirements of the Cp* compared with the Cp ligand. The metal−metal distance changes insignificantly on passing from **2** to **6** (**2**, *d*(Mn−Mn) = 5.382(5) Å; **6**, *d*(Mn−Mn) = 5.742(5) Å), but the conformation of molecule changes from *trans* in **2** to *gauche* in **6**, the result of rotation around the metal−carbon double bond at one of steps of the nucleophilic addition process shown in Scheme 2.

According to literature data the rotation barriers around the M=C double bond in manganese vinylidene and bis-vinylidene complexes should lie within 10−15 kcal/mol.[4e,f] This barrier may be rather difficult to overcome under the experimental conditions used (the temperature is −10 °C) and may be the reason for the low yield of **6**.

Conclusion

It has been shown that manganese bis-vinylidene complexes **1** and **2** are adequate models to study nucleophilic addition reactions to the C_α atoms of the bis-vinylidene ligands. Two-electron oxidation of **1** and **2** proceeds stepwise and results in dications of the bis-carbyne type **3** and **4**, respectively. Complexes **3** and **4** in comparison with **1** and **2** are stronger electrophiles able to react with nucleophiles inert to **1** and **2**. The expected conversion **1** → **5** along the pathway (c) + (d) + (e), Scheme 2, can be accomplished only by the preliminary generation of **3** and subsequent addition of water. If the mixture of **1** and water is treated with oxidant, the reaction begins immediately after removal of the first electron and is thought to proceed via nucleophilic attack of the radical cation **7** by water. The less electrophilic **4** is inert to water but reacts with stronger nucleophile OH⁻. At the present time we are studying an opportunity of extending the methodology of Scheme 1 to bis-vinylidene complexes of other transition metals as well as to other nucleophiles.

Experimental Section

General Considerations. All operations were carried out under a purified argon atmosphere using Schlenk techniques. Reagent grade benzene, THF, and diethyl ether were dried and distilled from sodium benzophenone-ketyl prior to use. Saturated hydrocarbons and dichloromethane were freshly distilled from LiAlH₄. Silica gel (70−230 mesh, 60 Å) was obtained from Aldrich Chemical Co. Starting materials **1** and **2** were prepared by described methods.[5]

Cyclic voltammograms were measured on a "PI-50-1" instrument (Gomel', Belarus) in a THF solution with a glassy carbon working electrode ($S = 2$ mm²), a platinum plate as an auxiliary electrode, and a SCE as a reference. Bu₄NPF₆ (0.2 M) was used as the supporting electrolyte. All peak potentials are given relative to the ferrocene/ferrocenium couple ($E = +0.54$ V vs SCE, $\Delta E = 100$ mV). 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.

Melting points were determined in sealed capillaries under an argon atmosphere. Solution IR (cm⁻¹) and electron (nm) spectra were measured on Specord M80 and Specord M40 (Carl Zeiss Jena) instruments, respectively. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained using a Bruker AMX 400 spectrometer and referenced to residual solvent protons. Elemental analyses were performed on a Carlo Erba 1106 CHN analyzer. EI mass spectra (70 eV, 150 °C) were obtained using Finnegan MAT SSQ 710 and Kratos MS 890 spectrometers.

Preparation of (μ-3,4-Diphenyl-2,5-dihydrofuran-2,5-diylidene)bis[(η⁵-cyclopentadienyl)(dicarbonyl)manganese(I)] (5). Solid Cp₂FeBF₄ (100 mg, 0.36 mmol) was added in one portion to the red solution of complex **1** (100 mg, 0.18 mmol) together with several drops of water in 40 mL of THF at room temperature. The color of the reaction mixture

turned deep blue immediately. After stirring for 1 h the excess of water in the solution was removed with 4 Å molecular sieves, and the dry solution was filtered through Celite and evaporated to dryness under reduced pressure. The residue was extracted with cold hexane (5 × 3 mL) to remove ferrocene. The crude product was chromatographed on silica under an argon atmosphere. The deep blue band was eluted with benzene; evaporation of the solvent and reprecipitation from ether with heptane gave complex **5** (78 mg, 76%) as bright brown-violet crystals. **5**: Decomposed above 250 °C. Anal. Calcd for C₃₀H₂₀Mn₂O₅: C, 63.16; H, 3.51. Found: C, 62.93; H, 3.62. IR (THF): ν_{CO} 1980 (m), 1948 (s), 1912 (s). UV−vis (CH₂Cl₂): 348.7 ($\epsilon = 9600$), 596.9 ($\epsilon = 22\,900$). ¹H NMR (C₆D₆): δ 4.77 (s, 10H, Cp), 7.01 (t, $J_{HH} = 7.5$ Hz, 2H, p-Ph), 7.12 (t, $J_{HH} = 7.5$ Hz, 4H, m-Ph), 7.36 (d, $J_{HH} = 7.5$ Hz, 4H, o-Ph). ¹³C{¹H} NMR (C₆D₆): δ 85.6 (Cp), 122.4, 124.0 (C₍ortho₎-Ph, C₍meta₎Ph), 125.6 (C₍para₎Ph), 130.4 (C₍ipso₎Ph), 143.7 (C₍β₎), 229.7 (Mn−CO), 278.9 (Mn=C). MS (EI): m/z 570 (M⁺), 514 (M⁺ − 2CO), 458 (M⁺ − 4CO).

Reaction of Complex 7 with H₂O. To a solution of complex **1** (100 mg, 0.18 mmol) in 30 mL of THF was added 83 mg (0.18 mmol) of AgBF₄×3(dioxane) at −30 °C. The color of the solution turned from red to brown, and new bands (ν_{CO} 2008 (m), 1996 (s), 1952 (s)) of the radical cation **7** appeared in the IR spectrum of the mixture. Three drops of water were then added, and the reaction mixture was allowed to warm to −10 °C and stirred for 10 min. The resulting blue solution was warmed to room temperature, filtered through Celite, and concentrated to half of its volume. Crystallization at −20 °C followed by reprecipitation from benzene with heptane gave the initial complex **1** (45 mg, 45%). The mother liquor contained only the complex **5**, which was isolated by chromatography as described above (43 mg, 42%).

Preparation of Bis-carbene Complex 5 Using AgBF₄×3-(dioxane) as Oxidant. Complex **1** (100 mg, 0.18 mmol) was dissolved in 30 mL of THF and the solution cooled to −30 °C. AgBF₄×3(dioxane) (165 mg, 0.36 mmol) was added and the solution stirred for 30 min at this temperature. The color of the reaction mixture turned from red to violet, the IR bands of the initial complex (ν_{CO} 2008 (s), 1988 (s), 1936 (s), $\nu_{C=C}$ 1612, 1604, 1584 (m)) transforming to the IR bands of intermediate **11** (ν_{CO} 1964 (s), 1920 (s)). The solution was warmed to −20 °C, and three drops of water were added. After stirring at this temperature for 10 min the IR spectrum of the reaction mixture showed only the bands of the product **5** (ν_{CO} 1980 (m), 1948 (s), 1912 (s)). The solution was allowed to reach room temperature and filtered through Celite. The volatiles were removed in vacuo, and the product was isolated as described above to give the complex **5** (93 mg, 88%).

This synthesis may be performed in CH₂Cl₂ in the same manner, but in this case the reaction of complex **3** with H₂O proceeds more slowly (2−3 h) because of the low solubility of water in methylene chloride medium. The yield of **5** was 89 mg (85%).

Preparation of (μ-3,4-Diphenyl-2,5-dihydrofuran-2,5-diylidene)bis[(η⁵-1,2,3,4,5-pentamethylcyclopentadienyl)(dicarbonyl)manganese(I)] (6). Complex **2** (70 mg, 0.1 mmol) in 40 mL of THF was oxidized with AgBF₄×3(dioxane) (92 mg, 0.2 mmol) at −40 °C. After stirring at this temperature for 30 min the lilac solution of the bis-carbyne complex **4** was formed (ν_{CO} 2036 (s), 1984 (s)). The reaction mixture was warmed to −15 °C, and the solid 30% solution of n-Bu₄NOH in water (95 mg, 0.11 mmol) was added. After stirring at this temperature for 1 h the solution became deep blue, with no bands of the cationic complexes remaining in the IR spectrum of the solution. After warming to room temperature the solution was filtered through Celite and evaporated to dryness in vacuo. The oily residue was extracted with a mixture of benzene/petroleum ether (1:1) and chromatographed on silica under an argon atmosphere. The dark blue band was eluted with benzene/petroleum ether (1:1). After evaporation and

Table 5. Crystallographic Data for 2, 5, and 6

	2·C_6H_6	**5**	**6**
empirical formula	$C_{46}H_{46}O_4Mn_2$	$C_{30}H_{20}O_5Mn_2$	$C_{40}H_{40}O_5Mn_2$
fw	772.7	570.3	710.6
temperature (K)	110(2)	293(2)	110(2)
cryst size (mm)	$0.30 \times 0.10 \times 0.10$	$0.38 \times 0.21 \times 0.15$	$0.30 \times 0.25 \times 0.05$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$C2/c$
a, Å	20.975(4)	20.202(16)	24.563(5)
b, Å	8.3693(19)	11.284(6)	12.723(2)
c, (Å)	22.039(5)	12.141(18)	24.554(5)
α (deg)	90	90	90
β (deg)	101.923(7)	113.44(9)	116.111(4)
γ (deg)	90	90	90
V (Å^3)	3785.5(15)	2539(5)	6891(2)
Z	4	4	8
d_c (Mg m^{-3})	1.356	1.492	1.370
$F(000)$	1616	1160	2960
μ (mm^{-1})	0.71	1.04	0.78
θ range (deg)	1.9 to 25	2.1 to 25	1.85 to 28
index range	$-24 \le h \le 22$	$0 \le h \le 23$	$-32 \le h \le 32$
	$-9 \le k \le 9$	$0 \le k \le 13$	$-16 \le k \le 16$
	$-26 \le l \le 26$	$-14 \le l \le 13$	$-32 \le l \le 31$
no. of reflns collected	21 705	2356	35 012
no. of unique reflns	6632	2233	8345
no. of reflns with $I > 2\sigma(I)$	3842	1409	5164
$R1$; $wR2$ ($I > 2\sigma(I)$)	0.068; 0.164	0.048; 0.047	0.059; 0.133
$R1$; $wR2$ (all data)	0.105; 0.184	0.078; 0.054	0.093; 0.145
no. of data/restraints/params	6632/0/469	1409/0/168	8345/0/584
GOF on F^2	0.91	1.13	0.93
max. shift/error	0.001	0.004	0.001
largest diff peak/hole (e Å^{-3})	2.15/−0.43	0.40/−0.29	1.87/−0.41
abs corr T_{max}; T_{min}	0.93; 0.82	0.89; 0.79	0.96; 0.79

recrystallization from hexane at −20 °C, 10.5 mg (15%) of black crystals of complex **6** were obtained. **6**: mp 175−176 °C (from hexane). Anal. Calcd for $C_{40}H_{40}Mn_2O_5$: C, 67.61; H, 5.63. Found: C, 67.46; H, 5.60. IR (THF): ν_{CO} 1960 (m), 1920 (s), 1896 (s). UV−vis (CH$_2$Cl$_2$): 374.9 (ϵ = 4800), 630.8 (ϵ = 21 400). ^{1}H NMR (C$_6$D$_6$): δ 1.71 (s, 30H, Me), 6.89−7.04 (m, 2H, p-Ph), 7.06−7.17 (m, 4H, m-Ph), 7.39−7.56 (m, 4H, o-Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 9.7 (Me), 100.4 (CMe), 126.6, 127.1 (C$_{ortho}$, C$_{meta}$Ph), 130.6 (C$_{para}$Ph), 135.6 (C$_{ipso}$Ph), 144.0 (C$_\beta$), 235.0 (Mn−CO), 287.2 (Mn=C). MS (EI): m/z 710 (M$^+$), 654 (M$^+$ − 2CO), 598 (M$^+$ − 4CO).

X-ray Structure Determinations. Data were measured using a Bruker SMART 1000 CCD diffractometer (compounds **2** and **6**) and an Enraf Nonius CAD4 diffractometer (compound **5**) and corrected for Lorentz and polarization effects[7a] and for absorption[7b] (for details see Table 5). The structures were solved by direct methods, followed by full-matrix least-squares refinement with anisotropic displacement parameter forms for the non-hydrogen atoms. The asymmetric unit of **2** contains 1

mol of solvate benzene. The hydrogen atoms in **2** and **5** were placed in calculated positions in the refinement using a riding model with fixed displacement parameters. The hydrogen atoms in **6** were located from a difference Fourier map and refined isotropically. All calculations were carried out by use of the SHELXTL (PC Version 5.10) (compounds **2** and **6**)[8a] and Xtal 3.5 (compound **5**)[8b] programs. Crystallographic data for **2**, **5**, and **6** have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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