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Reactions of Manganese and Rhenium Vinylidene Complexes with Hydrophosphoryl Compounds

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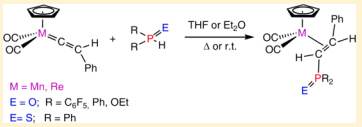
Supporting Information

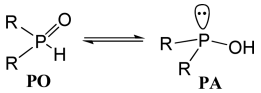
ABSTRACT: We studied the reactions of manganese and rhenium phenylvinylidenes $Cp(CO)_2M{=}C{=}C(H)Ph$ (**Mn1** M = Mn; **Re1** M = Re) with $HP(O)R_2$ (R = C_6F_5, Ph, and OEt) and $HP(S)Ph_2$, which resulted in the selective formation of η^2-*E*-phosphorylalkene complexes $Cp(CO)_2M\{\eta^2$-*E*-$H[R_2(O)P]C{=}C(H)Ph\}$ (**Mn2**, **Re2** R = C_6F_5; **Mn3**, **Re3** R = Ph; and **Mn6**, **Re6** R = OEt) and $Cp(CO)_2M\{\eta^2$-*E*-$H[Ph_2(S)P]C{=}C(H)Ph\}$ (**Mn5**, **Re5**). The DFT/B3LYP(6-31G*) analysis showed the model reactions of **Mn1** with $HP(O)Me_2$ and $HP(O)(OMe)_2$ to proceed via the initial transition state $Cp(CO)_2\{Ph(H)C{=}C{=}\}Mn{\cdots}HO{-}PR_2$ (**TS1**) where the minor **PA** form $HO{-}PR_2$ is hydrogen-bonded to the metal, followed by stereoselective (*trans*- to the phenyl group) addition of the **PA** phosphorus atom to the C_α-vinylidene atom, which defines both the rate of the process and the anti-Markovnikov structure of the reaction product. The reactions can proceed at a relatively low content of the reactive **PA** form.



INTRODUCTION

Although tautomeric hydrophosphoryl compounds (HPCs) exist predominantly as the P(V) forms $HP(O)R_2$ (hereinafter referred to as **PO** forms, R = alkyl, aryl, or alkoxyl), their reactivities are defined mainly by the minor nucleophilic P(III) forms $HO{-}PR_2$ (hereinafter, **PA** forms; Scheme 1).

Scheme 1



A considerable content of the **PA** form is typical of compounds with electron-withdrawing substituents at the phosphorus atom; the existence of single **PA** tautomer in dilute solutions was noted only for $(CF_3)_2P{-}OH$ and $(C_2F_5)_2P{-}OH$.[1a,b] The presence of both tautomers was observed for a series of HPCs based on the ^{31}P NMR data and DFT estimations of the relative energies of tautomers, for example, $HP(O)R_2$ with R = C_6F_5,[1a,c−e] C_5F_4N,[1f] *t*-Bu,[1d] Ph,[1f] *p*-Tol,[1f] *p*-C_6H_4F,[1f] and 3,5-$(CF_3)_2C_6H_3$.[1f] The tautomeric equilibrium was observed also for the HPCs of cyclic structure.[1h,i] Even if the content of **PA** is insufficient for a reliable identification by ^{31}P NMR spectroscopy, its "latent" presence in solution follows from indirect signs, for example, from the temperature dependence of $^1J_{PH}$.[1d] Although tautomerization via the intramolecular 1,2-P,O-hydrogen shift is forbidden by the energy barrier (50−60 kcal/mol),[2] the **PA** and **PO** forms can be interconverted reversibly even at room temperature due to synchronous hydrogen migration between the oxygen and phosphorus atoms within dimer associates.[3] Due to a "latent" presence of **PA** forms, HPCs both react with organic substrates (hydrophosphorylation of compounds with polar carbon−carbon and carbon-heteroatom multiple bonds, addition of sulfur, etc.)[4] and form complexes with transition metals.[5−8] In recent years, the interest in hydroxyphosphine and dialkyl phosphite complexes (**PA**)M increased significantly thanks to their efficient catalytic applications.[9,10] Coordination of a HPC to a transition metal shifts the tautomeric equilibrium in favor of the minor **PA** form. The analogous shift of the tautomeric equilibrium may be expected also upon nucleophilic addition of HPCs to the M=C bonds of transition metal cumulene complexes; however, such reactions have not been studied until now.[11] Since the electrophilic C_α atom in the manganese and rhenium vinylidenes $Cp(CO)_2M{=}C{=}C(H)$-Ph (hereinafter, **Mn1** M = Mn, **Re1** M = Re) is well-known to add phosphines and phosphites,[12] it was interesting to study whether these complexes can add HPCs. In the present work, we studied the reactions of manganese **Mn1** and rhenium **Re1** vinylidenes with secondary phosphine oxides $HP(O)Ph_2$ and $HP(O)(C_6F_5)_2$, diphenylphosphine sulfide $HP(S)Ph_2$, and diethyl phosphite $HP(O)(OEt)_2$, which are shown to afford selectively η^2-*E*-phosphorylalkenes $Cp(CO)_2M\{\eta^2$-$Ph(H)C{=}CHP(E)R_2\}$ (M = Mn and Re; E = O and S; R = C_6F_5, Ph, and OEt). The reactions of **Mn1** with $HP(O)Me_2$ and $HP(O)(OMe)_2$ were examined theoretically, which allowed revealing the reaction pathway where the initial nucleophilic **PA** addition

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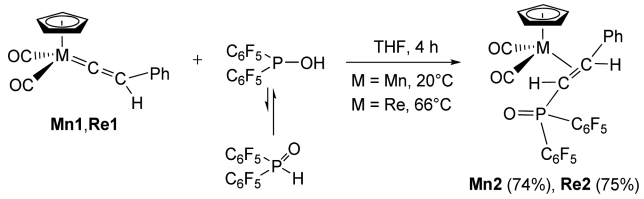
to the C_α atom is the rate-limiting step and defines the product geometry.

RESULTS AND DISCUSSION

Reactions of Mn1 and Re1 with Secondary Phosphine Oxides. *A priori* one can expect **Mn1** and **Re1** to react only with the **PA** form, and the rate of these reactions to be defined primarily by the content of this form. A relatively high content of the **PA** form is typical of $HP(O)(C_6F_5)_2$. According to the DFT calculations, the **PA** form is 1.7 kJ/mol[1a] more stable than the **PO** one, and its content in solution as for other **PA** forms is defined by associative interactions with a solvent. In oxygen-containing solvents, the **PA** content is quite high (18%[1a] in methanol, 43%[1a] in dimethoxyethane, 60[1a] and 71%[1e] in diethyl ether, 55%[1a] in THF, and 76%[1a] in DMSO). At the same time, the ^{31}P NMR spectra of $HP(O)(C_6F_5)_2$ in toluene, dichloromethane, acetonitrile, carbon tetrachloride, C_6D_6, and CD_3NO_2 show the **PO** form to be the only one in solution.[1a,d,e] For this reason, Et_2O and THF seemed to be optimum solvents for the reactions with $HP(O)R_2$, especially, in the cases when there are no reliable data on the content of tautomeric **PA** form (e.g., $HP(S)Ph_2$ and $HP(O)(OEt)_2$).

The reaction between **Mn1** and $HP(O)(C_6F_5)_2$ proceeds in THF at room temperature to afford η^2-*E*-phosphinylstyrene complex $Cp(CO)_2Mn\{\eta^2\text{-}Ph(H)C{=}C(H)P(O)(C_6F_5)_2\}$ (**Mn2**) in yield of 74% (Scheme 2 and Table 1). The same reaction of **Re1** does not proceed in THF at room temperature but proceeds smoothly in refluxing THF to yield the rhenium analog **Re2** (Scheme 2). Complexes **Mn2** and **Re2** were characterized by IR, ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy and the molecular geometry of **Re2** was established by X-ray diffraction (Figure 1 and Table S1).

Scheme 2



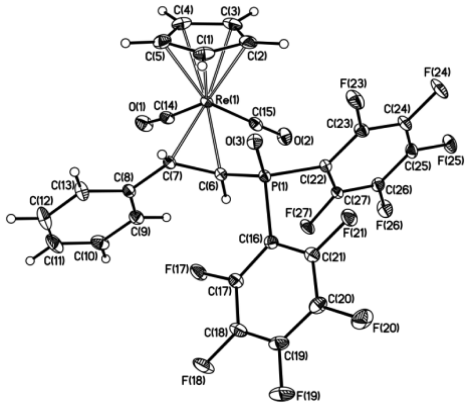


Figure 1. Molecular structure of $Cp(CO)_2Re\{\eta^2\text{-}Ph(H)C{=}C(H)P(O)(C_6F_5)_2\}$ (**Re2**). Selected bond lengths (Å): Re1–C6 2.2237(14), Re1–C7 2.2442(13), Re1–C14 1.9049(15), Re1–C15 1.9185(16), P1–O3 1.4772(11), P1–C6 1.7764(14), C6–C7 1.441(2), Re1–X1 1.961(2) (X1 is the centroid of the Cp ring); selected torsion angles (deg): P1–C6–C7–C8 133.35(12); X1–Re1–C6–P1 −31.8(2), X1–Re1–C7–C8 121.5(2).

As for $HP(O)Ph_2$, DFT calculations show the **PO** form to be by 12.64 kJ/mol (enthalpy) more stable than the **PA** one whose portion should be only 0.73% in the absence of associative interactions.[1d] Nevertheless, the reactions of **Mn1** and **Re1** with diphenylphosphine oxide in Et_2O and THF also afford η^2-*E*-phosphinylstyrene complexes $Cp(CO)_2M\{\eta^2\text{-}Ph$-

Table 1. Experimental Details for the Reactions of Mn1 and Re1 with $HP(E)R_2$

run	$HP(E)R_2$	comp.	solv.	time, *t*	product	base
1	$HP(O)(C_6F_5)_2$	**Mn1**	THF	20 °C, $\tau_{1/2}$ = 17 min, 4 h for complete reaction	**Mn2** (74%)	
2		**Re1**	THF	20 °C, 2 h	no reaction	
3		**Re1**	THF	66 °C, 4 h	**Re2** (75%)	
4		**Mn9**	Et_2O	20 °C, 120 h	$(C_6F_5)_2P(O)CH(Ph)CH_2P(O)(C_6F_5)_2$	
5		**Mn1**	THF	20 °C, $\tau_{1/2}$ = 170 min, 20 h for complete reaction	**Mn3** (37.5%) + $Ph_2P(O)CH(Ph)CH_2P(O)Ph_2$	
6		**Mn1**	THF	20 °C, $\tau_{1/2}$ = 147 min, c_{max} after 6 h	**Mn3** + $Ph_2P(O)CH(Ph)CH_2P(O)Ph_2$ (17%)	Et_3N
7		**Mn1**	Et_2O	20 °C, 3 h	**Mn3** (79%) + $Ph_2P(O)CH(Ph)CH_2P(O)Ph_2$	
8	$HP(O)Ph_2$	**Re1**	THF	20 °C, 1 h	no reaction	
9		**Re1**	THF	66 °C, 6 h	**Re3** (59%) and $Ph_2P(O)CH(Ph)CH_2P(O)Ph_2$	
10		**Re1**	Et_2O	20 °C, 22 h	no reaction	
11		**Re1**	Et_2O	35 °C, 2 h	**Re3** (85%)	
12		**Mn1**	THF	20 °C, $\tau_{1/2}$ = 26 min, max. product conc. after 2 h	**Mn5**	Et_3N
13		**Re1**	C_6H_6	20 °C, 24 h	no reaction	
14	$HP(S)Ph_2$	**Re1**	C_6H_6	20 °C, $\tau_{1/2}$ = 6 h, 48 h for complete reaction	**Re5** (93%)	Et_3N
15		**Re1**	THF	66 °C, 1 h	no reaction	
16		**Re1**	THF	66 °C, 15 h	**Re5** (89%)	Et_3N
17	$LiSP(Ph)_2$	**Mn1**	THF	(1) r.t.; (2) $HBF_4{\cdot}OEt_2$; −60 °C → r.t.	**Mn5** (47%)	LiO*t*-Bu
18		**Mn1**	Et_2O	20 °C, 44 h	**Mn6** (51%)	
19		**Re1**	THF	66 °C, 3 h	no reaction	Et_3N
20	$HP(O)(OEt)_2$	**Re1**	THF	66 °C, 17 h	no reaction	$(CH_2)_6N_4$
21		**Re1**	THF	66 °C, 1 h	no reaction	K_2CO_3
22		**Re1**	Et_2O	35 °C, 48 h	no reaction	
23	$LiOP(OEt)_2$	**Mn1**	THF	20 °C, instantly	**Mn7** + NH_4Cl(aq) → **Mn6** (66%)	LiO*t*-Bu
24	$LiOP(OEt)_2$	**Re1**	THF	(1) 20 °C; (2) −60 °C → 20 °C	**Re7** + $HBF_4{\cdot}OEt_2$ → **Re6** (56%)	LiO*t*-Bu

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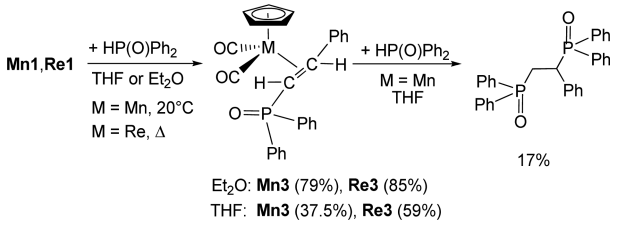
(H)C═C(H)P(O)Ph_2} (**Mn3** M = Mn and **Re3** M = Re) (Scheme 3), but they proceed slower than those with

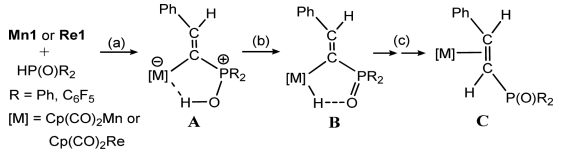
Scheme 3



$HP(O)(C_6F_5)_2$ (Table 1). The reaction between **Mn1** and $HP(O)Ph_2$ in THF at room temperature is not selective: Along with the target product **Mn3**, unidentified manganese complexes and $Ph_2P(O)CH(Ph)CH_2P(O)Ph_2$ (up to 20%) are produced. Presumably, the diphosphine dioxide results from the double addition of $HP(O)Ph_2$ which is in excess to **Mn3** due to a low rate of its formation in the initial step. An attempt to accelerate the formation of **Mn3** in the presence of triethylamine and thereby to decrease the amount of the diphosphine dioxide failed: In this case it was also the main isolated product (yield of 17%). We succeeded in diminishing the side reaction using diethyl ether as the reaction medium. In this solvent, **Mn3** was obtained in higher yield of 78%; this is likely due to a poor solubility of **Mn3** in Et_2O, which allows for withdrawal of it from the secondary reaction (in this case the diphosphine dioxide is produced in slight amounts). Complex **Re1** does not react with $HP(O)Ph_2$ either in diethyl ether or THF at room temperature, but reacts in these solvents upon reflux; the yield of **Re3** in Et_2O is higher than that in THF.

The reactions with phosphine oxides were assumed to proceed according to Scheme 4 via the following steps: (a) the

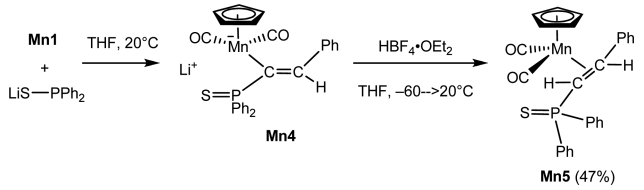
Scheme 4



"external" nucleophilic addition of HPC to form adduct **A** where the metal is hydrogen-bonded to the OH hydrogen; (b) hydrogen migration to the metal atom; and (c) C,H-reductive elimination in hydride **B** to rearrange into the reaction product **C**. We consider only the *trans*-addition of the **PA** form with regard to the Ph group, since earlier[12j] we have found exactly *trans*-addition of tertiary phosphines to **Mn1** and **Re1**. Intermediates **A** and **B**, which cannot be detected by IR and NMR spectroscopy, were identified on the potential energy surface upon theoretical study of the reactions of **Mn1** with HO−PMe_2 and HO−$P(OMe)_2$ (see below).

Reactions of Mn1 and Re1 with Diphenylphosphine Sulfide. In the absence of base, **Mn1** reacts with $HP(S)Ph_2$ in THF very slowly without forming the olefin complex $Cp(CO)_2Mn\{\eta^2$-*E*-PhHC═CHP(S)$(Ph)_2\}$ (**Mn5**). However, the addition of base (Et_3N) accelerates the reaction initially resulting in a rapid ($\tau_{1/2} \approx 26$ min) formation of **Mn5**, which upon long-term stirring in THF undergoes subsequent transformation into an unknown green product. We attempted to obtain a pure **Mn5** using a two-step procedure for the preparation of **Mn5** (Scheme 5) via the reaction with $LiSPPh_2$ obtained by deprotonation of $HP(S)Ph_2$ with *t*-BuOLi to form

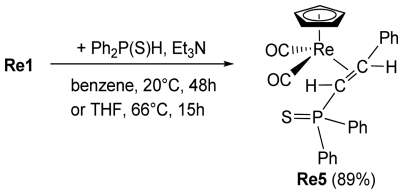
Scheme 5



a presumable anionic complex Li[$Cp(CO)_2Mn^-$−C(P(S)-Ph_2)═CHPh] (**Mn4**) and subsequent protonation of **Mn4** with $HBF_4 \cdot OEt_2$ to yield the target **Mn5**. The latter step is likely to proceed analogously to that of **Mn7** (see Scheme 8 below).

Neither does the rhenium vinylidene **Re1** react with diphenylphosphine sulfide in benzene in the absence of base. The addition of triethylamine to a benzene solution of the reaction mixture at room temperature induces a slow reaction ($\tau_{1/2} \approx 5$ h, the complete transformation requires ~48 h) to afford a η^2-*E*-thiophosphinylstyrene complex $Cp(CO)_2Re\{\eta^2$-*E*-PhHC═CHP(S)$(Ph)_2\}$ (**Re5**). Upon refluxing a mixture of **Re1** and $HP(S)Ph_2$ in THF in the presence of Et_3N, the reaction proceeds faster (Scheme 6). The structure of **Re5** was confirmed additionally by X-ray diffraction (see Figure 2 and Table S1).

Scheme 6



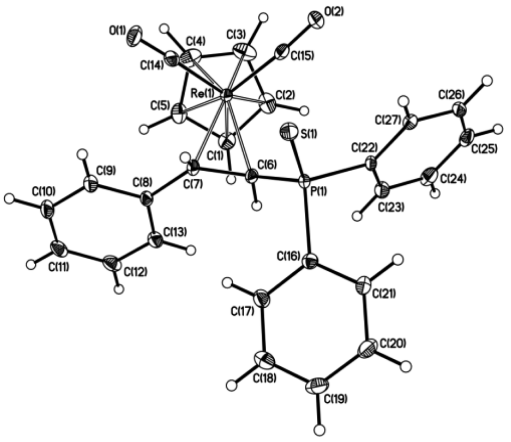


Figure 2. Molecular structure of $Cp(CO)_2Re(\eta^2$-PhCH═CHP(S)-Ph_2) (**Re5**). Selected bond lengths (Å): Re1−C6 2.210(3), Re1−C7 2.257(3), Re1−C14 1.907(3), Re1−C15 1.921(3), P1−S1 1.9678(10), P1−C6 1.793(3), C6−C7 1.438(3), Re1−X1 1.956(3) (X1 is the centroid of the Cp ring); selected torsion angles (deg): P1−C6−C7−C8−135.8(2); X1−Re1−C6−P1 136.2(3), X1−Re1−C7−C8−26.6(3).

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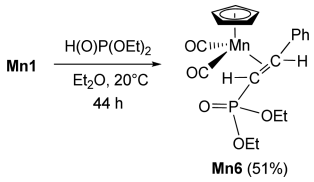
There are literature data on the structure of the closest analog of **Re2** and **Re5**, $Cp(CO)_2Mn[PhCH{=}CHP(O)(OEt)_2]$.[12e] In all structures, the substituents at the olefin ligand are in *trans*-disposition. The orientation of the $Cp(CO)_2Mn$ fragment relative to the olefin coincides with that of the $Cp(CO)_2Re$ fragment in the structure of **Re2**. In the structure of **Re5**, this fragment is rotated by about 180° relative to the axis passing through the Re atom and the center of the olefin bond. One can note that the η^2-coordinated double bond in the structures of **Re2** and **Re5** (1.441(2) and 1.438(3) Å, respectively) is elongated noticeably compared to that in the Mn analog (1.395(8) Å), which is explained by a higher back-donation from the rhenium atom. It is important to note that the significant difference in the electronic properties of substituents at the phosphorus atom in the structures of **Re2** and **Re5** has no effect on the olefin bond length and the characteristics of η^2-coordination to the rhenium atom (the distance Re(1)−centroid(C=C) is 2.115 Å in both complexes).

Reactions of Mn1 and Re1 with Diethyl Phosphite. Complex **Mn1** reacts slowly (44 h) with $HP(O)(OEt)_2$ in diethyl ether at room temperature to afford $Cp(CO)_2Mn\{\eta^2\text{-}E\text{-}PhHC{=}CHP(O)(OEt)_2\}$ (**Mn6**) in yield of 51% (Scheme 7). Along with ^1H and ^{31}P NMR characterization, the structure of **Mn6** was additionally confirmed by ^{13}C NMR and 2D NMR spectroscopy (see Figure S2).

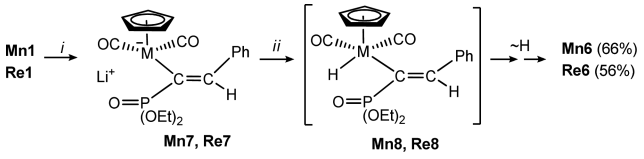
Scheme 7



Phosphorylstyrene complex **Mn6** was also obtained upon sequential treatment of **Mn1** with the lithium salt $Li[OP(OEt)_2]$[13] and an aqueous solution of NH_4Cl. The rhenium analog **Re1** does not react with neutral diethyl phosphite under any conditions (reflux in THF or diethyl ether in the presence of different-strength bases, Table 1, runs 19−22), but, analogously to **Mn1**, reacts with the deprotonated diethyl phosphite to produce the η^2-phosphorylstyrene complex **Re6** after protonation of the intermediate anion **Re7** with $HBF_4{\cdot}OEt_2$ (Scheme 8).

Protonation of the metalate anions **Mn7** and **Re7** proceeds analogously to that of the structurally close phosphoniostyryl zwitter-ions $[Cp(CO)_2M^-{-}C(^+PR_3){=}CHPh]$ (M = Mn and Re).[12j] Of crucial importance is that the reaction of **Mn1** with lithium diethyl phosphite $Li[O{-}P(OEt)_2]$ followed by

Scheme 8. Treatment of Mn6, Re6 from Mn1, Re1 and Li[OP(OEt)2][a]

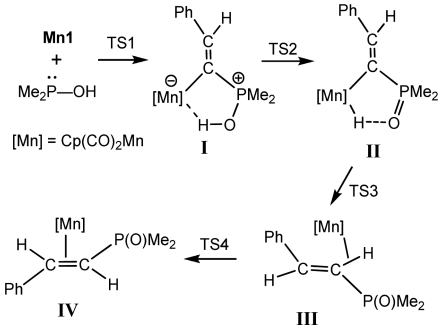


[a](i) $LiOP(OEt)_2$, THF, 20 °C; (ii) M = Mn, H_2O, and $NH_4Cl(aq)$, 12 h; M = Re and $HBF_4{\cdot}OEt_2$, −60 °C → 20 °C.

protonation (Scheme 8) and the reaction of **Mn1** with neutral diethyl phosphite (Scheme 7) afford the same stereochemical result (i.e., the formation of $E\text{-}\eta^2$-phosphorylstyrene complex **Mn6**). This suggests that the reaction of **Mn1** with the neutral diethyl phosphite also proceeds via an intermediate hydride **Mn8** corresponding to intermediate **B** in Scheme 4.

Theoretical Analysis of the Reactions between Mn1 and $HP(O)R_2$ (R = Me and OMe). During the reactions of **Mn1** and **Re1** with HPCs, the IR spectra of reaction mixtures display a gradual decrease in the ν_{CO} band intensities of the starting complexes **Mn1** and **Re1** and an increase in the ν_{CO} band intensities of the reaction products, *viz.*, η^2-phosphoryl- or phosphinylolefin complexes, with no ν_{CO} bands of intermediates being observed. For this reason, a deeper insight into the regularities of these reactions could be provided only by their theoretical study. Therefore, we studied the reactions of **Mn1** with dimethylphosphine oxide $HP(O)Me_2$ and dimethyl phosphite $HP(O)(OMe)_2$ by DFT (B3LYP/6-31G*). The study showed the reactions to proceed in agreement with Scheme 4 (with regard to some differences, see below); all stationary points corresponding to intermediates and transition states were identified on the potential energy surface. The course of the reaction between **Mn1** and $HP(O)Me_2$ was analyzed at 298.15 K for the gas phase and the diethyl ether medium, while the reaction between **Mn1** and $HP(O)(OMe)_2$ was studied only for the gas phase. Since the data obtained were found to be very similar in all cases under study, Scheme 9

Scheme 9



shows only the course of the reaction between **Mn1** and $HP(O)Me_2$ and Figure 4 reveals the energy profile of the same reaction in the gas phase (with regard to the reaction between **Mn1** and $HP(O)(OMe)$, see Scheme S1, Figure S1, and Tables S3 and S4).

The reaction **Mn1** + $HP(O)Me_2$ → **IV** is exothermic: ΔG = −49.07 kJ/mol and ΔH = −122.14 kJ/mol. A key step of the process is the initial nucleophilic addition of the **PA** form to the

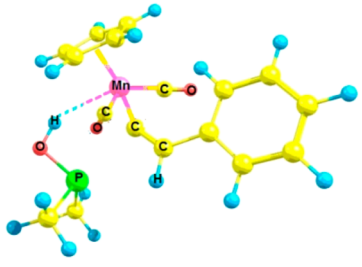


Figure 3. Transition state (**TS1** in Scheme 9) preceding the adduct $Cp(CO)_2Mn^-{-}C(^+P(OH)Me_2){=}CHPh$ (**I**).

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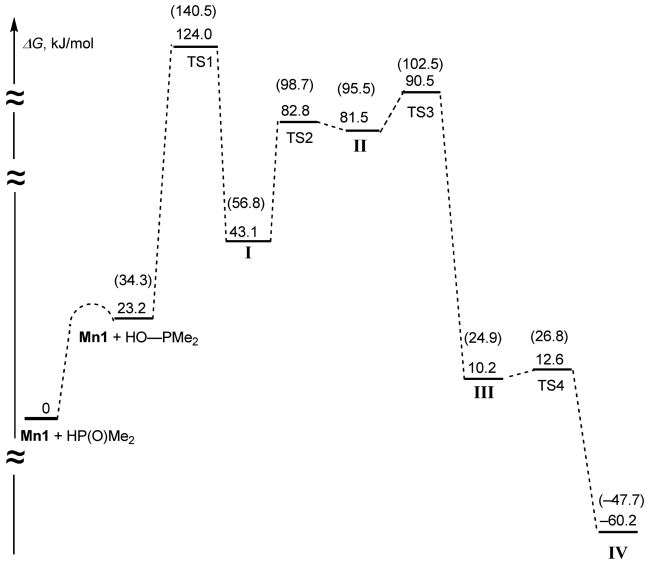

Figure 4. Gibbs energy change during the reaction between **Mn1** and $HP(O)Me_2$ in the gas phase (the values obtained in the diethyl ether medium are given in parentheses).

α-carbon vinylidene atom to form adduct **I**. First, it is characterized by the highest barrier ($\Delta G^{\#}$= 100.81 kJ/mol) and, therefore, defines the rate of the whole process. Second, the structure of **I** determines the stereochemistry of the phosphinylolefin **IV**, since the hydroxyphosphonium group in **I** is in the *trans*-position with regard to the phenyl ring and the subsequent reaction pathway, i.e. hydroxyl hydrogen transfer to the metal followed by C,H-reductive elimination in the intermediate hydride **II**, is already predetermined due to O–H···Mn hydrogen bonding in **I** (the Mn···H distance is 2.628 Å).

O–H···Mn hydrogen bonding was unexpectedly found already in the transition state (**TS1**) (Figure 3). The Mn···H distance is 2.569 Å and the O–H–Mn angle is 148°, while the C_α–P bond (the distance between the phosphorus and carbon atoms is 2.554 Å) in **TS1** has not formed. Although this step is characterized by a negative enthalpy (−44.21 kJ/mol), the ΔG value is found to be positive (19.86 kJ/mol) due to the decrease in the entropy at this step.

At the next step, the hydroxyl hydrogen migrates to the manganese atom to form the hydridostyryl derivative **II** where the Mn–H bond length is 1.599 Å and the O···H distance increased to 1.89 Å, which corresponds to the presence of P=O···H hydrogen bonding. This step is slightly endothermic (ΔG = 38.47 kJ/mol and ΔH = 39.62 kJ/mol) and characterized by a low activation barrier of $\Delta G^{\#}$ = 39.73 kJ/mol.

The reductive elimination step **II** → **III** is very exothermic (ΔG = −71.32 kJ/mol and ΔH = −66.47 kJ/mol), and its activation barrier is low ($\Delta G^{\#}$ = 8.99 kJ/mol and $\Delta H^{\#}$ = 6.30 kJ/mol). The C–H bond in **III** (1.116 Å) is elongated due to the agostic interaction with the metal atom. The final exothermic transformation **III** → **IV** proceeds most rapidly due to an insignificant activation barrier ($\Delta G^{\#}$ = 2.59 kJ/mol).

General Regularities of the Reactions of Mn1 and Re1 with HPCs. Table 1 gives experimental details for the reactions of **Mn1** and **Re1** with secondary phosphine oxides, diphenylphosphine sulfide, and diethyl phosphite under different conditions. Complexes **Mn2**, **Mn3**, **Mn5**, and **Mn6** are light-yellow solids decomposing slowly in solution, and complexes **Re2**, **Re3**, **Re5**, and **Re6** are white solids with a prominently higher stability. All complexes were characterized by IR, ^1H and ^{31}P NMR spectroscopy, and in some cases by ^{19}F, ^{13}C NMR, and 2D NMR spectroscopy.

For the reactions under study, we can note general regularities as follows: (1) The reactions proceed via stereoselective (*trans* to the phenyl group) addition of the **PA** form, which is additionally favored by the presence of M···H–O–PR_2 hydrogen bonding as shown in Figure 3 (or M···H–S–PR_2 by analogy). Contrary to expectations, this hydrogen bonding precedes the C_α–P bond formation.[14] (2) Due to a higher electrophilicity of the C_α atom in **Mn1**, it always reacts faster than the rhenium analog **Re1**. A higher rate of the reaction between the hydrophosphoryl P(III) form and vinylidene complex **Mn1** compared to that of **Re1** was predicted by us *a priori*, since we have observed the same regularity for the reaction of **Mn1** and **Re1** with tertiary phosphines.[12j] This prediction[15] was confirmed during this experimental study. (3) The effect of base on the rate of reaction under study depends both on the acidity of $HP(E)R_2$ and on the base strength. Triethylamine considerably accelerates the reaction between **Mn1** or **Re1** and $Ph_2P(S)H$ and exhibits a slight effect in the reaction between **Mn1** and $Ph_2P(O)H$, since favoring proton transport between the phosphorus and oxygen atoms, it increases to a certain extent the portion of the **PA** form. In the cases when triethylamine or other medium-strength bases cannot induce the reaction (for example, between **Re1** and $HP(O)(OEt)_2$), one can use much stronger bases, such as *t*-BuOLi, capable of deprotonating an HPC to form $Li(O\text{-}PR_2)$ which reacts instantly with **Mn1** or **Re1** to form the anionic adduct **Mn7** or **Re7**. The anionic complexes are transformed into the target product by protonation (Scheme 8). (4) The ease of reactions with HPCs changes in the following order: $HP(O)(C_6F_5)_2$ > $HP(O)Ph_2$ > $HP(O)(OEt)_2$, and the hydrothiophosphinyl compound $HP(S)Ph_2$ is the least reactive in the absence of base but becomes more reactive than its oxygen analog in the presence of Et_3N. The order given above was suggested by the data from IR monitoring of the reaction mixtures and has only a qualitative meaning.

Reaction between Phenylacetylene Complex $Cp(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CH)$ (Mn9) and $HP(O)(C_6F_5)_2$. Although addition of phosphorus nucleophiles PR_3 to the alkyne ligand in 18$\bar{e}$ π-acetylene complexes $[M](\eta^2\text{-}RC{\equiv}CH)$ has been studied fragmentarily, the available data make it possible to assume with certainty that the process will result in the formation of corresponding *E*-β-phosphoniovinyl adducts $[M]^-–C(H){=}C(^+PR_3)R$ or $[M]^-–C(R){=}C(^+PR_3)H$ rather than α-phosphoniovinyl ones $[M]^-–C(^+PR_3){=}C(H)R$.[16a–c] We studied the reaction of the phenylacetylene complex $Cp(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CH)$ (**Mn9**) with bis-pentafluorophenylphosphine oxide which in diethyl ether is known[1e] to contain 71% of the **PA** form. Complex **Mn9** was obtained *in situ* from the photochemically generated ether complex $Cp(CO)_2Mn(OEt_2)$ by the reaction with phenylacetylene. While the vinylidene complex **Mn1** reacts rapidly with $HP(O)(C_6F_5)_2$ at room temperature ($\tau_{1/2}$ = 17 min in THF, Table 1, run 1), no signs of reaction are observed in first hours after addition of $HP(O)(C_6F_5)_2$ to a solution of **Mn9** in diethyl ether at room temperature. Only after stirring overnight did a few of yellow crystals presumably belonging to **Mn2** appear on flask walls. Upon subsequent stirring (for 5 days), the yellow crystals disappeared, and there appeared a bulky white precipitate of $(C_6F_5)_2P(O)CH_2CH$-

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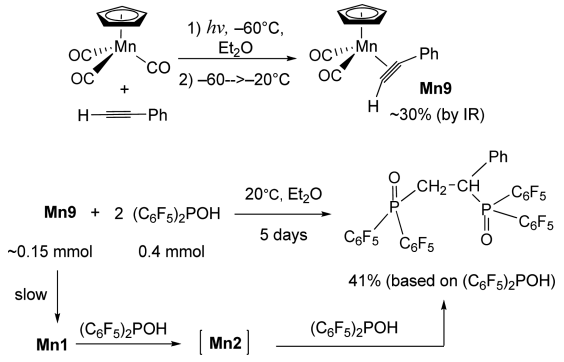
$(Ph)P(O)(C_6F_5)_2$ (41%) identified by ^1H, ^{31}P, and ^{19}F NMR spectroscopy. We assume the **PA** form $(C_6F_5)_2P{-}OH$ does not add to the π-acetylene complex **Mn9** due to an insufficient electrophilicity of the alkyne ligand but adds to the vinylidene complex **Mn1** as far as it forms from **Mn9** due to the acetylene-vinylidene rearrangement[17] (Scheme 10, the bottom part shows

Scheme 10



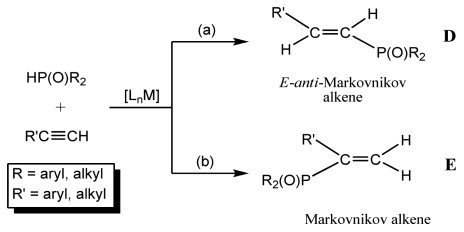
the proposed reaction pathway). In a special experiment, we demonstrated that in the absence of phosphine oxide **Mn9** slowly rearranges into **Mn1** in diethyl ether (20 h at room temperature). Due to a high excess of $(C_6F_5)_2P(OH)$ with regard to the intermediately formed **Mn2**, there occurs a double addition of the **PA** form to produce the diphosphine dioxide as observed in the reaction between **Mn1** and $HP(O)Ph_2$ (Scheme 3). Compared to the π-alkyne isomers, the increased ease of nucleophilic addition to vinylidene complexes forms the basis for transition metal complex-catalyzed reactions of terminal alkynes via vinylidene complexes as key intermediates.[18]

Catalysis of Terminal Alkyne Hydrophosphorylation/Hydrophosphinylation. From the data obtained in the present work, one can emphasize three features directly concerning the transition metal complex catalyzed hydrophosphorylation of terminal alkynes: (1) Hydrophosphorylation of vinylidenes **Mn1** and **Re1** proceeding via selective nucleophilic addition of the **PA** form to the C_α-vinylidene atom in the *trans*-position to the phenyl group (a rate-limiting step which defines the reaction stereochemistry). (2) Hydrogen bonding between the OH group of the **PA** form and the metal atom, $R_2P{-}OH\cdots[M]$ at the initial step. (3) Selective formation of the anti-Markovnikov-type phosphorylstyrene complexes $[M]\{\eta^2\text{-}E\text{-}H(R_2(O)P)C{=}C(H)Ph\}$.

Of doubtless interest is the question to which degree the above-mentioned steps upon hydrophosphorylation of transition metal vinylidene complexes can be involved in the catalytic cycles of transition-metal catalyzed hydrophosphorylation of terminal alkynes. These reactions are being studied intensively in the last 20 years in order to develop a selective approach to alkenyl-substituted organophosphorus compounds[19] and typically afford either linear anti-Markovnikov[20] (anti-M) *E*-1,2-adducts **D** (Scheme 11a) or branched Markovnikov (M) 1,1-adducts **E** (Scheme 11b). The result of the reaction depends on the type of HPC, catalyst, and additives.

The mechanism of terminal alkyne hydrophosphorylation is currently understudied. It is commonly assumed that the catalytic cycles involve only the **PO** forms initially undergoing oxidative addition at the P–H bond and alkyne insertion at the

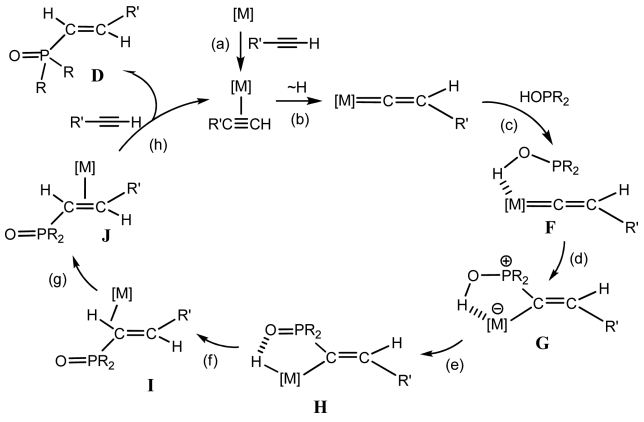
Scheme 11



M–H[21] or M–P[22] bonds followed by the C,P and C,H-reductive elimination at the final step to afford the alkene products **D** and **E**, respectively.[23]

In particular, this scheme does not consider in any way participation of the **PA** form of HPC in the catalytic cycle.[24] Moreover, possible proceeding of these processes via vinylidene intermediates has not been considered, although, as mentioned above, such "vinylidene path" is known for the catalytic addition of nucleophiles to terminal alkynes.[18] Based on the data for hydrophosphorylation of the vinylidene complexes **Mn1** and **Re1**, one can propose an alternative hypothetic Scheme 12 including alkyne coordination (step (a))

Scheme 12



and subsequent acetylene-vinylidene rearrangement (step (b)),[25] the formation of the hydrogen-bonded complex **F** (step (c)), nucleophilic addition of phosphorus to the vinylidene C_α atom to form adduct **G** (step (d)), hydrogen transfer to the metal atom to form the hydridophosphorylstyryl compound **H** (step (e)), C,H-reductive elimination affording the agostic complex **I** (step (f)), rearrangement of **I** to the olefin complex **J** (step (g)), and final substitution of alkyne for the phosphorylolefin ligand (step (h)).

It is noteworthy that the formation of hydrogen-bonded complex between the **PA** form and **Mn1**, *viz.*, $Me_2P{-}OH\cdots Mn{=}C{=}C(H)Ph(CO)_2Cp$, in the transition state of hydrophosphorylation of the vinylidene complex (**TS1** in Figure 3) has not been proposed earlier. This bonding predetermines the subsequent formation of Mn–H and C_α–P bonds (the presence of lone-pair electrons on phosphorus provides an easy nucleophilic addition of this atom to C_α, Scheme 12, step (d)). Another coordination of HPC to the metal in the 18-electron complex **Mn1** seems to be unfavorable, because it will afford complexes with more than 18-electron configuration.[26]

As applied to the manganese complexes under study ([M] = $Mn(CO)_2Cp$), this scheme is a model for the catalytic cycle involving the corresponding 18-electron compounds. In this

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case, the acetylene-vinylidene rearrangement proceeds by the concerted mechanism and its barrier (114 kJ/mol) has been determined for the close structural analog $Cp(CO)_2Mn{=}C{=}CH_2$.[27] One can assume that the rates of acetylene-vinylidene rearrangement and nucleophilic addition differ slightly. The catalysis of terminal alkyne hydrophosphorylation by Scheme 12 seems to be possible and requires further studies.[28]

CONCLUSIONS

New reactions of manganese and rhenium phenylvinylidene complexes $Cp(CO)_2M{=}C{=}C(H)Ph$ (**Mn1** M = Mn; **Re1** M = Re) with hydrophosphoryl compounds $HP(E)R_2$ (E = O, S) resulting in the stereoselective formation of η^2-*E*-phosphorylalkene complexes $Cp(CO)_2M\{\eta^2$-*E*-$H[R_2(E)P]C{=}C(H)Ph\}$ have been studied. The DFT analysis showed the reactions to proceed via initial formation of the complex $Cp(CO)_2\{Ph(H)C{=}C{=}\}Mn{\cdots}HO\text{-}PR_2$, where the minor PA form $HO\text{-}PR_2$ is hydrogen-bonded to the metal, followed by stereoselective addition of the **PA** form to the C_α vinylidene atom. It is a rate-limiting step and defines the anti-Markovnikov structure of the reaction product. The reactions can proceed also at a relatively low content of the reactive **PA** form which is in the tautomeric equilibrium with the PO form $HP(O)R_2$ not involved in the reaction. The reactions can be promoted by a base whose effect depends on the $HP(E)R_2$ acidity. The discovered transformations can be applied to other HPCs and vinylidene complexes of other transition metals, as well as to other proton-containing heteroatomic nucleophiles. Possible mechanisms of terminal alkyne hydrophosphorylation were discussed.

EXPERIMENTAL SECTION

All reactions were performed in argon atmosphere using the Schlenk technique. Low-temperature experiments were performed using an ethanol−dry ice mixture as the cooling liquid. The commercially available tetrahydrofuran, diethyl ether, benzene, and toluene were dried over sodium benzophenone ketyl and distilled in an argon atmosphere immediately prior to use. Saturated hydrocarbons (pentane, hexane, and petroleum ether), dichloromethane, and triethylamine were distilled over CaH_2. Acetone was purified from organic impurities by adding small portions of $KMnO_4$ at reflux until the violet color persists and dried with freshly annealed K_2CO_3. The commercially available silica gel (70−230 mesh, 60 Å, Aldrich) was evacuated and saturated with inert gas immediately prior to use. $HP(O)(C_6F_5)_2$,[1e] $HP(O)Ph_2$,[29] and $HP(S)Ph_2$[30] were prepared according to the literature procedures. The commercially available diethyl phosphite (Acros Organics) was distilled *in vacuo* over CaH_2 prior to use.

IR spectra were recorded on a Specord M80 IR spectrophotometer (Carl Zeiss, Germany). ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were measured on Bruker Avance 300 (^1H at 300.1 MHz and ^{31}P at 121.5 MHz), Bruker Avance 400 (^1H at 400.1 MHz, ^{31}P at 161.98 MHz, ^{19}F at 376.50 MHz, and ^{13}C at 100.58 MHz), and Bruker Avance 600 instruments (^{13}C at 150.93 MHz) using residual signals of deuterated solvents as the internal standard. Elemental analysis was performed on a Carlo Erba 1106 CHN analyzer.

Reaction between $Cp(CO)_2Re{=}C{=}CHPh$ (Re1) and $HP(O)(C_6F_5)_2$. A solution of **Re1** (100 mg, 0.244 mmol) and $HP(O)(C_6F_5)_2$ (93.2 mg, 0.244 mmol) in THF (5 mL) was refluxed for 4 h. The reaction mixture was concentrated and hexane was added (∼10 mL). The precipitate formed was separated by decantation and dried *in vacuo* to yield the olefin complex $Cp(CO)_2Re\{\eta^2$-$PhCH{=}CHP(O)(C_6F_5)_2\}$ (**Re2**) (145 mg, 75%) as a grayish-white crystalline powder. Calcd for $C_{27}H_{12}F_{10}O_3PRe \times 0.5THF$, %: C, 42.10; H, 1.95; F, 22.96. Found, %: C, 42.34; H, 2.31; F, 22.12. IR (THF, ν, cm^{-1}) 1988 (CO) s, 1920 (CO) s, 1644 (C=C) w. ^1H NMR (acetone-d_6, δ) 1.78 (q, 4H, CH_2 from 0.5 THF), 3.61 (t, 4H, O−CH_2 from 0.5 THF), 4.02 (br.m, 1H, $=CHP(O)(C_6F_5)_2$), 4.74 (br.m, 1H, $=CHPh$), 5.71 (s, 5H, Cp), 7.05 (m, 1H, *p*-C_6H_5), 7.25, 7.26 (2 br.s, 4H, *o*- and *m*-C_6H_5). $^{13}C\{^1H\}$ NMR (acetone-d_6, δ) 23.89 (s, $=CHP$), 26.78 (s, 2C, CH_2 from 0.5THF), 32.90 (s, $=CHPh$), 68.67 (s, 2C, O−CH_2 from 0.5THF), 89.84 (s, Cp), 127.15, 127.26, 129.65 (s, C_6F_5), 138.10, 140.48, 144.08 (s, Ph), 146.8, 147.2, 149.7 (d, Ph), 199.72, 204.56 (s, CO). $^{31}P\{^1H\}$ NMR (C_6D_6, δ) 16.57. $^{19}F\{^1H\}$ NMR (C_6D_6, δ) −161.6 (dm, 4F, $^4J_{FP}$ = 85.2 Hz, *m*-C_6F_5), −149.34 (dq, 2F, $^5J_{FP}$ = 134.7 Hz, *p*-C_6F_5), −133.0 (dm, 4F, $^3J_{FP}$ = 629.6 Hz, *o*-C_6F_5).

Reaction between $Cp(CO)_2Mn{=}C{=}CHPh$ (Mn1) and $HP(O)(C_6F_5)_2$. A solution of **Mn1** (100 mg, 0.359 mmol) and $HP(O)(C_6F_5)_2$ (144 mg, 0.377 mmol) in THF (5 mL) was stirred for 4 h at room temperature. IR monitoring shows the half-life of the starting compound to be 17 min. The reaction mixture was concentrated, and hexane (∼10 mL) was added. The precipitate formed was separated by decantation and dried *in vacuo* to yield the olefin complex $Cp(CO)_2Mn\{\eta^2$-$PhCH{=}CHP(O)(C_6F_5)_2\}$ (**Mn2**) (174.5 mg, 74%) as an amorphous yellow powder. IR (THF, ν, cm^{-1}) 1982 (CO) s, 1928 (CO), 1644 (FC=CF) w. ^1H NMR (acetone-d_6, δ) 4.5−5.3 (br.s, 7H, Cp signal overlaps with the signals for $HC{=}CH$), 7.15 (t, 1H, *p*-C_6H_5), 7.30 (t, 2H, *m*-C_6H_5), 7.42 (br.m, 2H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (acetone-d_6, δ) 17.36. $^{19}F\{^1H\}$ NMR (acetone-d_6, δ) −103.37 (dm, 4F, $^4J_{FP}$ = 124 Hz, *m*-C_6F_5), −90.84 (dq, 2F, $^5J_{FP}$ = 222.9 Hz, *p*-C_6F_5), −74.6 (dm, 4F, $^3J_{FP}$ = 388.6 Hz, *o*-C_6F_5).

Reaction between Re1 and $HP(O)Ph_2$. A solution of **Re1** (100 mg, 0.244 mmol) and $HP(O)Ph_2$ (49.4 mg, 0.244 mmol) in Et_2O (5 mL) was refluxed for 2 h (the color changed from orange to pale-yellow and a slight precipitate formed; on cooling the solution became thick). The mixture was evaporated to dryness, and the residue was dissolved in toluene (1 mL) and chromatographed at low temperature (below −20 °C) on a silica gel column (10 × 1 cm). The first yellow-orange fraction of the remaining starting **Re1** was eluted with pure toluene. The second yellow fraction was eluted with acetone−toluene (1:10). The third colorless fraction of the reaction product $Cp(CO)_2Re\{\eta^2$-$PhCH{=}CHP(O)Ph_2\}$ (**Re3**) was eluted with acetone−toluene (1:5) and evaporated to dryness. The residue was washed with pentane and dried *in vacuo* to yield **Re3** (126.3 mg, 84.5%) as a grayish-white crystalline powder. Calcd for $C_{27}H_{22}O_3PRe \times 0.25C_6H_5CH_3$, %: C, 54.41; H, 3.81; P, 4.88. Found, %: C, 54.67; H, 3.87; P, 5.08. IR (Et_2O, ν, cm^{-1}) 1984 (CO) s, 1916 (CO) s. ^1H NMR (acetone-d_6, δ) 4.02 (dd, 1H, $^3J_{HH}$ = 11.1 Hz, $^2J_{HP}$ = 13.04 Hz, $=CHP(O)Ph_2$), 4.60 (dd, 1H, $^3J_{HH}$ = 11.1 Hz, $^3J_{HP}$ = 15.6 Hz, $=CHPh$), 5.53 (s, 5H, Cp), 6.9−8.1 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR (acetone-d_6, δ) 31.75. Upon reaction in refluxing THF for 6 h, **Re3** was obtained in yield of 59%.

Reaction between Mn1 and $HP(O)Ph_2$. (a) A solution of **Mn1** (100 mg, 0.359 mmol) and $HP(O)Ph_2$ (72.6 mg, 0.359 mmol) in Et_2O (5 mL) was stirred at room temperature for 24 h (after 3 h stirring, the formation of an abundant yellow precipitate was already observed and the solution color changed from red to orange). The precipitate formed was separated by decantation and dried *in vacuo* to yield **Mn3** (135.5 mg, 78.5%) as a yellow powder. To obtain the analytically pure substance, the powder of **Mn3** was dissolved in dichloromethane (1 mL) and chromatographed on a silica gel column (1 cm × 10 cm) at low temperature (below −20 °C). The yellow fraction of the product was eluted with $Et_2O{-}CH_2Cl_2$ (1:2) and the eluate was evaporated to dryness. The residue was washed with pentane (3 × 5 mL) and dried *in vacuo* to yield 114 mg of **Mn3** (66%). Calcd for $C_{27}H_{22}MnO_3P$, %: C, 67.51; H, 4.62; Mn, 11.44. Found, %: C, 67.51; H, 4.86; Mn, 10.0. IR (THF, ν, cm^{-1}) 1976 (CO) s, 1920 (CO) s. ^1H NMR (acetone-d_6, δ) 3.99 (br.m, 1H, $=CHP(O)Ph_2$), 4.55 (br.m, 1H, $=CHPh$), 4.71 (s, 5H, Cp), 7.08−8.19 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR (acetone-d_6, δ) 30.64. (b) When the reaction between **Mn1** and $HP(O)Ph_2$ was performed in THF for 6 h, complex **Mn3** was obtained in yield of 37.5%. The same reaction in the presence of Et_3N afforded the diphosphine dioxide $Ph_2P(O)C(Ph)H{-}CH_2P(O)Ph_2$ as the main product isolated in yield of 17% as a white powder poorly soluble in the most of solvents. ^1H NMR (CD_2Cl_2, δ) 2.75 (br.s, 1H, CH_2), 3.20 (br.s, 1H, CH_2), 4.28 (br.s, 1H, $CHPh$), 6.9−8.0

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(m, 25H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ) 28.58 (br.s, 1P, $CH_2P(O)Ph_2$), 33.59 (br.s, 1P, $C(Ph)HP(O)Ph_2$).

Reaction between Re1 and HP(S)Ph$_2$. (a) To a solution of **Re1** (100 mg, 0.244 mmol) and $HP(S)Ph_2$ (53.3 mg, 0.244 mmol) in benzene (5.5 mL) was added Et_3N (34 μL, 0.244 mmol). The reaction mixture was stirred at room temperature for 48 h (as far as the reaction proceeded, the orange mixture became less colored) and evaporated to dryness. The residue was dissolved in toluene (1 mL) and hexane (10 mL) was added slowly to afford on cooling white crystals which were separated by decantation and dried *in vacuo*. The yield of $Cp(CO)_2Re\{\eta^2$-PhCH=CHP(S)$Ph_2\}$ (**Re5**) was 143 mg (93%). Calculated for $C_{27}H_{22}O_2PReS$, %: C, 51.66; H, 3.53; P, 4.93; Re, 29.66; S, 5.11. Found, %: C, 51.90; H, 4.01; P, 5.06; Re, 29.5; S, 4.93. IR (THF, ν_{CO}, cm^{-1}) 1984, 1912. ^1H NMR (C_6D_6, δ) 3.96 (dd, 1H, $^3J_{HH}$ = 10.4 Hz, $^2J_{HP}$ = 10.8 Hz, =C*H*P(S)Ph_2), 4.85 (s, 5H, Cp), 5.12 (dd, 1H, $^3J_{HH}$ = 10.4 Hz, $^3J_{HP}$ = 19 Hz, =C*H*Ph), 6.9–8.3 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, δ) 56.08.

Single crystals of **Re5** suitable for the X-ray diffraction study were obtained by a slow diffusion of hexane into a solution of this complex in $CDCl_3$ in a NMR tube.

(b) Upon reaction between **Re1** (50 mg, 0.122 mmol) and $HP(S)Ph_2$ (25.3 mg, 0.134 mmol) in refluxing THF (5 mL) in the presence of Et_3N (17 μL, 0.122 mmol), complex **Re5** was obtained in yield of 89% (67.8 mg) as a white powder. IR (THF, ν_{CO}, cm^{-1}) 1984 s, 1912 s. ^1H NMR (acetone-d_6, δ) 4.61 (m, 2H, C(P)*H*=C*H*Ph), 5.32 (s, 5H, Cp), 7.0–8.3 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR (acetone-d_6, δ) 54.55.

Reaction between Mn1 and LiSPPh$_2$. To a solution of diphenylphosphine sulfide (67.4 mg, 0.309 mmol) in THF (2 mL), a 1 M solution of LiO*t*-Bu in THF (325 μL, 0.325 mmol) was added using a microsyringe, and the mixture was stirred for 10 min. The resulting solution of $LiSPPh_2$ was added through a cannula to a solution of **Mn1** (86 mg, 0.309 mmol) in THF (2 mL), an instant change in the solution color from red to brown-red being observed. The mixture was stirred for 10 min and cooled to −60 °C and $HBF_4\cdot OEt_2$ (44 μL, 0.325 mmol) was added. After warming to room temperature, the IR spectrum of the reaction mixture displays only the bands corresponding to the π-olefin complex $Cp(CO)_2Mn\{\eta^2$-PhCH=CHP(S)$Ph_2\}$ (**Mn5**) (ν_{CO}, cm^{-1} 1980 s, 1920 s) appeared. The solution was evaporated to dryness. The residue was dissolved in toluene (1 mL) and chromatographed on a silica gel column (1 × 10 cm) below −20 °C. The first red-violet fraction of the binuclear μ-vinylidene complex $[Cp(CO)_2Mn]_2$=C=CHPh was eluted with pure toluene. The second yellow fraction of **Mn5** was eluted with THF–toluene (1:5), and the eluate was concentrated under reduced pressure until the total volume of about 5 mL. At the end of concentration, the solution color became green, and a yellow precipitate formed. The IR spectrum of the mother liquor displays additional low-intensity bands at ν_{CO} 1930, 1848, cm^{-1}. On keeping in a freezer, the mother liquor became brown. The precipitate was separated from the mother liquor by decantation, washed with hexane (2 × 2 mL), and dried *in vacuo* to yield a yellow powder of **Mn5** (72.7 mg, 47%). IR (toluene, ν_{CO}, cm^{-1}) 1980 s, 1924 s. ^1H NMR (CD_2Cl_2, δ) 3.86 (br.m, 1H, =C*H*P(O)Ph_2), 4.24 (s, 5H, Cp), 4.44 (br.m, 1H, =C*H*Ph), 7.03 (br.t, 1H, *p*-C_6H_5 from P(S)*Ph*), 7.10–7.3 (3 br.m, 6H, *o*- and *m*-C_6H_5), 7.41 (br.t, 2H, *m*-C_6H_5 from P(S)*Ph*), 7.53 (br.t, 4H, *o*-C_6H_5 from P(S)*Ph*), 8.1 (br.m, 2H, *o*-C_6H_5 from =CH*Ph*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ) 54.08.

Reaction between Re1 and LiOP(OEt)$_2$. To a solution of diethyl phosphite (35 μL, 0.268 mmol) in THF (2 mL), a 1 M solution of LiO*t*-Bu in THF (268 μL, 0.268 mmol) was added using a microsyringe, and the mixture was stirred for 10 min. The resulting solution of $LiOP(OEt)_2$ was added through a cannula to a solution of **Re1** (100 mg, 0.244 mmol) in THF (2 mL), an instant change in the solution color from orange to light-brown being observed. The IR spectrum displayed bands of an anionic complex $Li^+[Cp(CO)_2Re^-$—C(P(O)$(OEt)_2)$=CHPh$]^-$ (ν_{CO}, cm^{-1} 1876 s, 1804 w, and 1764 s). The mixture was stirred for 10 min and cooled to −60 °C, and $HBF_4\cdot OEt_2$ (40 μL, 0.293 mmol) was added. In the IR spectrum, the absorption bands of the anionic complex disappeared, and new bands corresponding to the π-olefin complex $Cp(CO)_2Re\{\eta^2$-PhCH=CHP(O)$(OEt)_2\}$ (**Re6**) (ν_{CO}, cm^{-1} 1984 s, 1912 s) appeared. The solution was evaporated to dryness. The residue was dissolved in toluene (1 mL) and chromatographed on a silica gel column (1 × 10 cm) below −20 °C. The first yellow-orange fraction of **Re1** was eluted with pure toluene. The second colorless fraction of the main product was eluted with acetone–toluene (1:5), and the eluate was evaporated to dryness. The residue was recrystallized from toluene, and the resulting crystals were washed with triturating in pentane (5 mL) to afford **Re6** (75.3 mg, 56%) as a white powder. Calculated for $C_{19}H_{22}ReO_5P$, %: C, 41.68; H, 4.51. Found, %: C, 41.86; H, 4.58. IR (toluene, ν_{CO}, cm^{-1}) 1984 s, 1912 s. ^1H NMR (acetone-d_6, δ) 1.19 (t, 3H, CH_3, $^3J_{HH}$ = 6.7 Hz), 1.34 (t, 3H, CH_3, $^3J_{HH}$ = 6.8 Hz), 3.05 (br.d, 1H, =C*H* P(O)(OEt) $_2$, $^2J_{HP} \approx$ 8.2 Hz), 3.98 (q, 2H, CH_2, $^3J_{HH}$ = 6.7 Hz), 4.13 (q, 2H, CH_2, $^3J_{HH}$ = 6.8 Hz), 4.37 (dd, 1H, =C*H*Ph, $^3J_{HP(cis)}$ = 16.6 Hz, $^3J_{HH(trans)}$ = 11.04 Hz), 5.60 (s, 5H, Cp), 6.99 (tm, 1H, *p*-C_6H_5), 7.11–7.24 (m, 4H, *o*- and *m*-C_6H_5). $^{31}P\{^1H\}$ NMR (acetone-d_6, δ) 33.42.

Reaction between Mn1 and HP(O)(OEt)$_2$. A solution of **Mn1** (200 mg, 0.719 mmol) and diethyl phosphite (102 μL, 0.791 mmol) in Et_2O (2 mL) was stirred for 44 h at room temperature (the formation of yellow precipitate was observed and the solution color changed from red to yellow-brown). Hexane (10 mL) was added, and the precipitate was separated by decantation and dried *in vacuo*. The residue was dissolved in toluene (1 mL) and chromatographed on a silica gel column (10 × 1 cm) below −20 °C. The light-pink fraction of **Mn1** was eluted by pure toluene, and the second yellow fraction of $Cp(CO)_2Mn\{\eta^2$-PhCH=CHP(O)$(OEt)_2\}$ (**Mn6**) was eluted with acetone–toluene (1:5). The eluate was evaporated to dryness, the oily residue solidified when left to stand, and the resulting yellow solid washed with triturating in pentane (5 mL) to yield **Mn6** (153.3 mg, 51.2%) as a yellow powder. Calculated for $C_{19}H_{22}MnO_5P$, %: C, 54.82; H, 5.33; Mn, 13.20. Found, %: C, 54.74; H, 5.31; Mn, 13.20. IR (Et_2O, ν_{CO}, cm^{-1}) 1984 s, 1928 s. IR (THF, ν_{CO}, cm^{-1}) 1980 s, 1924 s. ^1H NMR (acetone-d_6, δ) 1.19 (t, 3H, CH_3), 1.40 (t, 3H, CH_3), 2.81 (dd, 1H, =C*H* P(O)(OEt) $_2$), 3.96 (m, 2H, CH_2), 4.20 (dq, 2H, CH_2), 4.52 (dd, 1H, =C*H*Ph), 4.86 (s, 5H, Cp), 7.07 (t, 1H, *p*-C_6H_5), 7.21–7.28 (m, 4H, *o*- and *m*-C_6H_5). $^{31}P\{^1H\}$ NMR (acetone-d_6, δ) 33.13. $^{31}P\{^1H\}$ NMR (C_6D_6, δ) 33.13. $^{13}C\{^1H\}$ NMR (C_6D_6, 150.93 MHz, δ) 16.28 (d, 2C, $^3J_{CP}$ = 5.4 Hz, CH_3), 16.45 (d, 2C, $^3J_{CP}$ = 6.0 Hz, CH_3), 37.59 (d, 1C, $^1J_{CP}$ = 183.4 Hz, =CHP(O)), 58.66 (d, 1C, $^2J_{CP}$ = 4.7 Hz, =CHPh), 61.17 (d, 2C, $^2J_{CP}$ = 6.7 Hz, CH_2), 61.34 (d, 2C, $^2J_{CP}$ = 5.4 Hz, CH_2), 86.03 (s, 5C, Cp), 125.94 (br. s, 2C, *o*-C_6H_5), 126.27 (s, 1C, *p*-C_6H_5), 128.66 (s, 1C, *m*-C_6H_5), 144.74 (d, 1C, $^3J_{CP}$ = 10.7 Hz, *ipso*-C_6H_5), 229.65 and 234.82 (s, 1C each, CO).

Reaction between Mn1 and LiOP(OEt)$_2$. To a solution of diethyl phosphite (46.3 μL, 0.359 mmol) in THF (2 mL), a 1 M solution of LiO*t*-Bu in THF (359 μL, 0.359 mmol) was added using a microsyringe and stirred for 10 min. The resulting solution of $LiOP(OEt)_2$ was added through a cannula to a solution of **Mn1** (100 mg, 0.359 mmol) in THF (2 mL) (the solution darkened). The IR spectrum displayed the absorption bands of the anionic complex $Li^+[Cp(CO)_2Mn^-$—C(P(O)$(OEt)_2)$=CHPh$]^-$ (**Mn7**) (ν_{CO}, cm^{-1} 1884 s, 1816 m, 1776 s). The solution was stirred for 20 min, multiple excesses of a saturated aqueous solution of NH_4Cl added, and the mixture stirred overnight. As far as protonation proceeded, the IR bands of protonation product (**Mn6**) (ν_{CO}, cm^{-1} 1980 s, 1924 s) increased in intensity. The resulting dark-green solution was evaporated to dryness. The residue was dissolved in toluene (2 mL) and chromatographed on a silica gel column (1 cm × 10 cm) below −20 °C. The first blue-green band of unknown product was eluted with pure toluene, the second yellow-brown fraction eluted with acetone–toluene (1:10), and the yellow fraction of pure **Mn6** eluted with acetone–toluene (1:5). The yellow eluate was evaporated, and the resulting oily residue crystallizes when left to stand. The obtained yellow crystals were washed with hexane upon triturating with spatula and dried *in vacuo* to yield 98.2 mg of **Mn6** (66%). The spectral data of the product correspond to those given above.

Reaction between Cp(CO)$_2$Mn{η^2-HC≡CPh} (Mn9) and HP(O)(C$_6$F$_5$)$_2$ in Et$_2$O. A solution of cymantrene (102 mg, 0.5 mmol)

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and phenylacetylene (66 μL, 0.6 mmol) in Et_2O (20 mL) was irradiated externally by a DRL-400 UV lamp (400 W) with vigorous stirring for 1 h maintaining the temperature below −60 °C by dry ice−ethanol bath. The solution gained a crimson color corresponding to $Cp(CO)_2Mn(Et_2O)$. Upon slow warming, the mixture became brown, and the IR spectrum displayed bands of $Cp(CO)_2Mn(\eta^2\text{-PhC}{\equiv}\text{CH})$ (**Mn9**) (ν_{CO}, cm^{-1} 1976 s, 1912 s). $HP(O)(C_6F_5)_2$ (152.8 mg, 0.4 mmol) was added to the resulting solution of **Mn9**, and the mixture was stirred for 5 days at room temperature. After stirring overnight, a few yellow crystals appeared on the flask walls, which was followed by abundant precipitation of a flocculent white solid over the next days. The precipitate was separated by decantation, washed with diethyl ether, and dried *in vacuo* to afford 71.1 mg of $(C_6F_5)_2P(O)-CH_2CHPh-P(O)(C_6F_5)_2$ (41% based on $HP(O)(C_6F_5)_2$) as a white powder. Calculated $C_{32}H_8F_{20}O_2P_2$, %: C, 44.37; H, 0.93. Found, %: C, 44.20; H, 1.05. ^1H NMR (CD_2Cl_2, δ) 3.41 (br.s, 1H, C*H*H), 3.60 (br.s, 1H, CH*H*), 4.75 (br.s, 1H, C*H*Ph), 7.08 (br.s, 3H, *m* and *p*-C_6H_5), 7.40 (br.s, 2H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ) 15.27 (d, 1P, $^3J_{PP}$ = 67 Hz), 22.31 (d, 1P, $^3J_{PP}$ = 67 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, δ) −159.99, −159.39, 158.83, −158.07 (t, 8F, *m*-C_6F_5), −145.67, −144.41, −144.35, −143.88 (t, 4F, *p*-C_6F_5), −132.68, −132.24 (dm, 4F, $^3J_{FP}$ = 167.7 Hz, *o*-C_6F_5), −130.53, −130.07 (dm, 4F, $^3J_{FP}$ = 173.2 Hz, *o*-C_6F_5).

X-ray Diffraction Study. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated MoKα radiation, λ = 0.71073 Å, ω-scan technique). The APEX II software[31] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction, while SHELXTL[32] was applied for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation. Crystallographic data for complexes **Re2** and **Re5** are presented in Table S2 and are deposited at the Cambridge Crystallographic Data Centre under the CCDC Nos. 1494809 and 1494810, respectively.

Computational Procedure. All DFT calculations were performed in the Gaussian 09 program[33] at the B3LYP/6-31G* level of theory. We chose the B3LYP functional,[34] since it is highly trusted and thus the default functional of choice for many researchers. The 6-31G* basis set was chosen as a golden mean between the computational accuracy and the computational time cost. The thermodynamic parameters of reactions were calculated at 298.15 K with optimization in the gas phase and in a diethyl ether solution using the PCM model.[35] Transition states were located by the Synchronous Transit-Guided Quasi-Newton (STQN) method[36] and verified analyzing vibrations corresponding to imaginary frequencies. The correspondence between transition states and reaction coordinates was confirmed by intrinsic reaction coordinate (IRC) calculations.[37]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00626.

Selected bond lengths, angles, crystal data, data collection, and structure refinement parameters for complexes **Re2** and **Re5**; 2D NMR spectrum for **Mn6**; calculation data for the reaction between **Mn1** and $HP(O)(OMe)_2$ (PDF)

Crystallographic data for **Re2** and **Re5** (CIF)

Computed Cartesian coordinates and energies for **Mn1** + $HP(O)Me_2$ in the gas phase and Et_2O and **Mn1** + $HP(O)(OMe)_2$ in the gas phase (XYZ)

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Notes

The authors declare no competing financial interest.

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(13) $Li[OP(OEt)_2]$ has to be preliminarily prepared by addition of LiO*t*-Bu to a solution of $HP(O)(OEt)_2$; upon generation of $Li[OP(OEt)_2]$ in a mixture of vinylidene **Re1** and diethyl phosphite by addition of lithium *tert*-butoxide, the vinylidene complex rather than phoshite is deprotonated first to form the phenylacetylide complex $Li^+[Cp(CO)_2Re^-{-}C\equiv CPh]$.

(14) Intramolecular hydrogen bonding $[M]\cdots HO-PR_2$ in the primary vinylidene−**PA** adduct (see structure **I** in Scheme 9) exists regardless of the side of **PA** attack. Conversely, such hydrogen bonding in the analogous **PA** adducts of η^2-alkyne complexes may be realized only if the **PA** form attacks the alkyne ligand from the "metal" side.

(15) Probably, this regularity should be observed also for other transition metal C1 (carbene, carbyne, and cumulenylidene) complexes where strong π-bonding between the Mn atom and the C1 ligand is realized (see refs 15a,b. On going from the period 1 transition metal (manganese) to the period 3 one (rhenium), the difference in their reactivities should become stronger due to the higher electron-donating ability of the heavier metal or due to the relativistic effect, which decreases the electrophilicity of the C_α atom (e.g., see the comparison between Cr and W carbene complexes given in ref 15c). (a) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974−982. (b) Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717−774. (c) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775−783.

(16) (a) According to Cowley et al., the vinylidene complexes $[Cp(Ph_3P)_2Ru=C=C(H)R]OTf$ add PPh_3 at the β-position to form the phosphoniovinyl adduct $[Cp(Ph_3P)_2Ru-C(H)=C(^+PPh_3)R]^-OTf$: Cowley, M. J.; Lynam, J. M.; Moneypenny, R. S.; Whitwood, A. C.; Wilson, A. J. *Dalton Trans.* **2009**, *43*, 9529−9542. (b) The reaction between $(\eta^5\text{-}C_5R_5)(CO)_2Mn(\eta^2\text{-}HC\equiv CH)$ and PEt_3 affords the zwitter-ionic β-adduct $(\eta^5\text{-}C_5R_5)(CO)_2Mn^-{-}C(H)=C(H)-{}^+PEt_3$ (C_5R_5 = C_5H_5, C_5H_4Me, C_5Me_5). This adduct is assumed to be a precursor for the corresponding α-adduct $(\eta^5\text{-}C_5R_5)(CO)_2Mn^-{-}C(^+PEt_3)=CH_2$; see Alt, H. G.; Engelhardt, H. E.; Steinlein, E. *J. Organomet. Chem.* **1988**, *344*, 227−234. (c) We performed an additional experiment which showed the formation of the β-phosphoniovinyl derivative *E*-$Cp(CO)_2Mn^-{-}CH=C(H)^+PMe_3$ as the only product in the reaction between $Cp(CO)_2Mn\{\eta^2\text{-}HC\equiv CH\}$ and PMe_3. To a solution of $Cp(CO)_2Mn\{\eta^2\text{-}HC\equiv CH\}$ (670 mg, 3.3 mmol) in petroleum ether (40 mL), a solution (50 mL) of PMe_3 (459 mg, 6 mmol) in diethyl ether was added. The mixture was stirred for 3 h at room temperature and left to stand overnight. The yellow precipitate formed (660 mg, 72%) was filtered off, washed with petroleum ether (3 × 5 mL), and dried *in vacuo*. IR (CH_2Cl_2, ν_{CO}, cm^{-1}) 1900 s, 1822 s. ^1H NMR (CD_2Cl_2, δ) 1.60 (d, 9H, CH_3, $^2J_{HP}$ = 13.0 Hz), 4.52 (s, 5H, Cp), 5.96 (1H, a part of the AX spectrum, H_α, $^3J_{H\alpha}H_\beta$ = 18.3 Hz, $^3J_{H\alpha,P}$ = 43.3 Hz), 11.39 (1H, X part of the AX spectrum, H_β, $^2J_{H\beta,P}$ = 33.2 Hz). ^{31}P NMR (CD_2Cl_2, δ) 8.04. The ^1H NMR spectrum suggests the product obtained to have the formula $Cp(CO)_2Mn^-{-}CH=CH(^+PMe_3)$. For the α-phosphonium structure $Cp(CO)_2Mn^-{-}C(^+PMe_3)=CH_2$, the signals for the olefin protons should be upfield shifted by about 5−7 ppm), and the difference between the positions of these signals should be smaller. Even more important is that the $^3J_{HP}$ coupling constants (*cis*- and *trans*-) should be about 40 and 70 Hz, respectively.

(17) The acetylene-vinylidene rearrangements of the manganese phenylacetylene complexes $Cp(CO)_2Mn(\eta^2\text{-}PhC\equiv CH)$ and $Cp^*(CO)_2Mn(\eta^2\text{-}PhC\equiv CH)$ are accelerated in the presence of catalytic amounts of hexamethylenetetramine, see ref 12b and Novikova, L. N.; Peterleitner, M. G.; Sevumyan, K. A.; Semeikin, O. V.; Valyaev, D. A.; Ustynyuk, N. A. *Appl. Organomet. Chem.* **2002**, *16*, 530−536. One can assume that the rearrangement **Mn9** → **Mn1** is promoted by $(C_6F_5)_2P-OH$ as a base or diethyl ether as a basic solvent. In a special experiment, we have shown that in the absence of phosphine oxide **Mn9** almost completely rearranges into **Mn1** in diethyl ether within 20 h.

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(24) (a) The formation of β-amino vinylphosphonates rather than the corresponding α-isomers in the Ni-catalyzed addition of dialkyl phosphites to ynamides was interpreted by intermediate coordination of the **PA** form to the nickel atom: Fadel, A.; Legrand, F.; Evano, G.; Rabasso, N. *Adv. Synth. Catal.* **2011**, *353*, 263−267. and (b) Ananikov et al.[22g] discarded the idea of that Ni-catalyzed hydrophosphorylation of tolan with diisopropyl phosphite can proceed through external addition of the **PA** form HO-P(O*i*-Pr)$_2$ to the coordinated tolan, since the *cis* phosphorylalkene *Z*-HC(Ph)═C(Ph)-P(O)(O*i*-Pr)$_2$ rather than the *trans* isomer was produced in this reaction..

(25) Acetylene-vinylidene rearrangements $L_nM(\eta^2\text{-RC}{\equiv}\text{CH}) \rightarrow L_nM[{=}\text{C}{=}\text{C(H)R}]$ are induced thermally or under the action of bases; see Wakatsuki, Y. *J. Organomet. Chem.* **2004**, *689*, 4092−4109. Thus, the real conditions for catalytic hydrophosphorylation of terminal alkynes (temperature above 80 °C and the presence of the **PA** form as a base) reasonably permits the formation of vinylidene complexes.

(26) In particular, hydrophosphorylation of **Mn1** and **Re1** via σ-bond metathesis involving the P−H bond of **PO** forms and the M═C bond is unlikely, since the formation of 20-electron intermediate $Cp(CO)_2(Ph(H)C{=}C{=})Mn(\eta^2\text{-}H,P\text{-HP(O)}R_2)$ is unfavorable.

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