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Protonation of Zwitterionic Manganese and Rhenium Phosphoniostyryl Complexes $(\eta^5\text{-}C_5H_5)(CO)_2M^{-}\text{–}C(^{+}PR_3)\text{=}C(H)Ph$: Experimental and DFT Study

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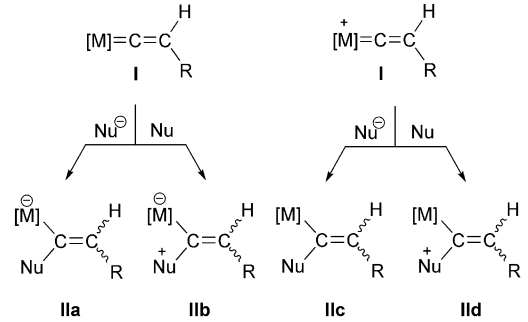
Stereoselective addition of tertiary phosphanes to manganese and rhenium phenylvinylidenes $(\eta^5\text{-}C_5H_5)(CO)_2M\text{=}C\text{=}C(H)Ph$ (**1** M = Mn; **2** M = Re) gave the corresponding zwitterionic *Z*-phosphoniostyryl adducts $(\eta^5\text{-}C_5H_5)(CO)_2M^{-}\text{–}C(^{+}PR_3)\text{=}C(H)Ph$ (**3** M = Mn, PR_3 = PPh_2Me; **4** Mn, $PPhMe_2$; **5** Mn, PMe_3; **6** Re, PPh_2Me; **7** Re, PMe_3). Protonation of **3**–**7** with $HBF_4\cdot OEt_2$ resulted in the formation of the η^2-phosponioalkene complexes $(\eta^5\text{-}C_5H_5)(CO)_2M(\eta^2\text{-}E\text{-}HC(^{+}PR_3)\text{=}C(H)Ph)$ (**8** Mn, PPh_2Me; **9** Mn, $PPhMe_2$; **10** Mn, PMe_3; **11** Re, PPh_2Me; **12** Re, PMe_3) rather than in the corresponding phosphoniocarbene complexes $(\eta^5\text{-}C_5H_5)(CO)_2M\text{=}C(^{+}PR_3)CH_2Ph$. It was shown by DFT calculations (B3LYP/6-31G*) that the protonation of **5** proceeds at the metal atom followed by C,H-reductive elimination in the intermediate hydride *cis*-$(\eta^5\text{-}C_5H_5)(CO)_2(H)Mn\text{–}C(^{+}PMe_3)\text{=}C(H)Ph$ (**14**) to form the agostic complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn\{\eta^2\text{-}H\text{–}C\text{-}(^{+}PMe_3)\text{=}C(H)Ph\}$ (**15**) and subsequent isomerization of the latter into the final η^2-phosphonioalkene **10**. In line with the theoretical data, the low-temperature protonation (–80°C) of **3** with triflic acid in an NMR tube directly gave the corresponding phosponioalkene complex **8**. Unlike **3**, the protonation of their rhenium analogues **6** and **7** under the same conditions revealed the quantitative formation of *cis*-hydride intermediates *cis*-$[(\eta^5\text{-}C_5H_5)(CO)_2(H)Re\text{–}C(^{+}PR_3)\text{=}C(H)Ph]$-OTf (**16**, **17**), which undergo conversion into the corresponding η^2-phosponioalkene complexes **11** and **12** at ca. –30°C

Introduction

Highly selective addition of nucleophiles to C_α atoms in neutral and cationic transition-metal vinylidene complexes have been shown to serve as the key step in catalytic anti-Markovnikov transformations of terminal alkynes.[1]

Depending on the nature of the starting vinylidene complex **I** and the nucleophile (Nu), a wide variety of α-heteroatom-substituted σ-vinyl complexes **II** can be obtained (Scheme 1). The transient formation of anionic **IIa** and neutral **IIc** species have been postulated in some catalytic reactions, e.g. cyclization of 1,ω-alkynols[2] and anti-Markovnikov addition of water[3] and carboxylic acids[4] to terminal alkynes. The formation of betaine-type complexes **IIb** presumably takes place in the ruthenium-catalyzed addition of Me_2NNH_2 to terminal alkynes,[5] and the occurrence of the cationic intermediates **IId** has been proposed in the catalytic anti-Markovnikov addition of PPh_2H and $PPh_3/MeSO_2OH$ to terminal alkynes displaying remarkably different stereoselectivity. Addition of PPh_2H to propargyl alcohols $HC\equiv CC(OH)RR'$ catalyzed by $(\eta^5\text{-}C_5Me_5)Ru(Cl)L_2$ [L_2 = $(PPh_3)_2$, η^4-cod] leads to the formation of *Z*-$Ph_2P(H)\text{-}C\text{=}C(H)C(OH)RR'$ (*Z*-selectivity 75–95%),[6] whereas the reaction of aliphatic and aromatic alkynes $HC\equiv CR$ with PPh_3 in the presence of acid using $(\eta^4\text{-cod})_2RhCl$ or $(PPh_3)_4RhH$ as catalyst precursors affords *E*-vinylphosphonium salts *E*-$Ph_3P^{+}(H)C\text{=}C(H)R$ (*E*-selectivity > 90%).[7]



Scheme 1. General scheme for the nucleophilic addition to transition-metal vinylidene complexes **I**.

Although the structure of intermediates **II** and the regularities of their protonation are indeed responsible for the

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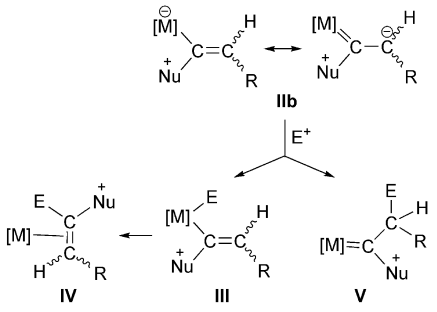
regio- and stereoselectivity of these catalytic processes, the chemistry of such species have been quite poorly investigated to date. This is probably caused by the fact that only few stable adducts **IIb** and **IId** are known, mostly prepared by the stoichiometric reactions of neutral[8] and cationic[9] vinylidene complexes with tertiary amines and phosphanes. Since the structure of α-phosphoniovinyl adducts **IIb** can be represented as a hybrid of two resonance forms, the electrophilic addition to them can proceed both at the metal and the β-carbon atoms, which leads to the η^2-alkene **IV** and carbene **V** complexes, respectively (Scheme 2).



Scheme 2. Possible reactivity of α-phosphoniovinyl complexes **IIb** towards electrophiles.

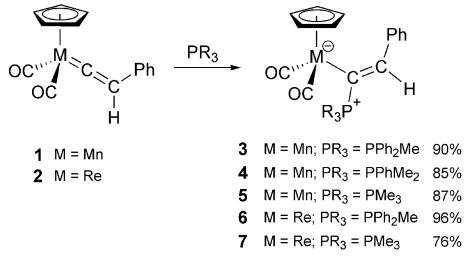
To the best of our knowledge, the only clear example of electrophilic addition to α-phosphoniovinyl adducts **IIb** was noted for $(\eta^5\text{-}C_5H_5)(CO)_2Mn^-\text{–}C(^+PPh_3)=C(H)Ph$, which was protonated to give the η^2-alkene product $[(\eta^5\text{-}C_5H_5)(CO)_2Mn[(\eta^2\text{-}E\text{-}H(^+PPh_3)C=C(H)Ph]Cl$.[8g] The protonation of the structurally close β-phosphoniovinyl complexes can proceed through both indicated reaction pathways: in the case of $(\eta^5\text{-}C_5H_4R)(CO)_2Mn^-\text{–}CH=CH(^+PEt_3)$ (R = H, Me), the formation of the corresponding η^2-alkene complexes **IV** was observed,[10] whereas protonation of the related chromium complex $(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(CO)_2Cr^-\text{–}CH=CH(^+P\textit{n}Bu_3)$ gave the phosphoniocarbene product **V**.[11] The latter process is also characteristic of the protonation of neutral transition-metal σ-vinyl complexes.[12]

Since regularities of protonation of transition-metal σ-phosphoniovinyl complexes **IIb** remain unclear, we have started a systematic study on the reactivity of these species towards electrophiles. We report here the experimental and theoretical studies of the protonation of the betaine-type σ-phosphoniostyryl complexes $(\eta^5\text{-}C_5H_5)(CO)_2M^-\text{–}C(^+PR_3)=C(H)Ph$ (M = Mn, Re).

Results and Discussion

Synthesis of Manganese and Rhenium σ-Phosphoniostyryl Complexes $(\eta^5\text{-}C_5H_5)(CO)_2M^-\text{–}C(^+PR_3)=C(H)Ph$ (3–7): Investigation of Their Stability and Structure

The betaine-type σ-phosphoniostyryl complexes **3**–**7** were prepared in good yields by addition of the corresponding phosphane to solutions of vinylidene complexes **1** and **2** in hexane at room temperature (Scheme 3). Under these conditions, the target products **3**–**7** precipitated in an analytically pure state.



Scheme 3. Synthesis of σ-phosphoniostyryl complexes **3**–**7**.

It was shown by IR and NMR spectroscopy that the stability of adducts **3**–**7** towards dissociation into the starting materials in solution depends both on the metal and nucleophilicity of the phosphane. For example, the adduct of a moderately nucleophilic triphenylphosphane $(\eta^5\text{-}C_5H_5)(CO)_2Mn^-\text{–}C(^+PPh_3)=C(H)Ph$ strongly dissociates in dichloromethane solution at room temperature (ca. 90% based on the IR data), whereas only traces of vinylidene **1** and PPh_2Me were detected in a dichloromethane solution of manganese complex **3** under the same conditions. The analogous rhenium PPh_2Me adduct **6** shows no evidence of dissociation, as well as complexes **4**, **5**, and **7** derived from more nucleophilic phosphanes.

The molecular geometry of rhenium complex **6** was determined by X-ray diffraction (Figure 1). Compound **6** has a typical pseudo-octahedral piano-stool geometry. The Re–C(8) and C(8)–C(9) distances of 2.151(3) and 1.362(5) Å, respectively, in **6** are within the typical ranges for Re–C single bonds and C=C double bonds. The C(8)–C(9) bond length in betaine-type complex **6** is longer than the C=C double bonds in the structurally similar iron cationic complexes $(\eta^5\text{-}C_5H_5)(CO)(L)Fe\text{–}C(^+PPh_3)=C(H)R$ (L = CO, R

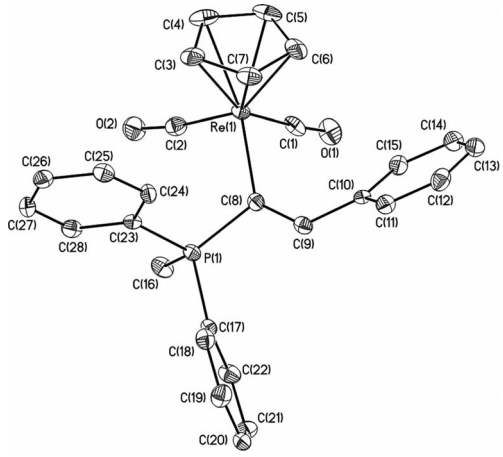


Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)(CO)_2Re^-\text{–}C(^+PPh_2Me)=C(H)Ph$ (**6**) (thermal ellipsoids are shown with 30% probability, hydrogen atoms are omitted for clarity.). Selected bond lengths [Å] and angles [°]: Re(1)–C(1) 1.883(4), Re(1)–C(2) 1.873(4), Re(1)–C(8) 2.151(3), P(1)–C(8) 1.796, C(8)–C(9) 1.362(5); C(1)–Re–C(2) 89.34(14), Re(1)–C(8)–P(1) 116.13(16), Re(1)–C(8)–C(9) 130.9(2).

= Ph, 1.35(1) Å;[9a] L = PPh_3, R = H, 1.327(11) Å[9b]), which is presumably a result of the contribution of the carbanionic resonance form (Scheme 2, right structure of **IIb**).

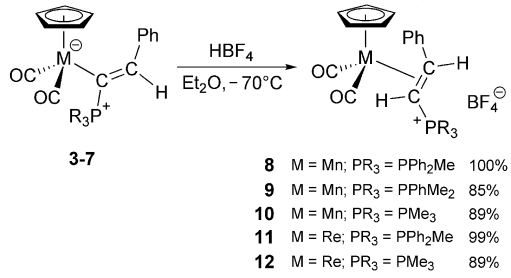
The *Z* geometry of all σ-phosphoniostyryl complexes **3**–**7** was confirmed by ^1H and ^{31}P NMR spectroscopy. The values of $^3J_{H,P}$ coupling constants observed (40–44 Hz) are very close to those ($^3J_{H,P(cis)}$ 40–43 Hz; $^3J_{H,P(trans)}$ 68–74 Hz) reported for the structurally similar manganese betaine-type α-phosphoniovinyl complexes (η^5-$C_5Me_nH_{5-n}$)$(CO)_2$-Mn^-–C($^+PR_3$)=CH_2 (R = Me, Et; *n* = 0, 1, 5).[10a] The same large difference between the coupling constants of the phosphorus atom with the vinylic *cis*- and *trans*-hydrogen atoms was observed for the related cationic rhenium [(η^5-C_5H_5)(NO)(PPh_3)Re–C($^+PMe_3$)=C(H)Me]OTf ($^3J_{H,P(cis)}$ 36 Hz; $^3J_{H,P(trans)}$ 61 Hz),[9c] iron [(η^5-C_5H_5)(CO)(PPh_3)Fe–C($^+PR_3$)=CH_2]BF_4 (PR_3 = PPh_3, $PPhMe_2$; $^3J_{P,H(cis)}$ 23 Hz, $^3J_{P,H(trans)}$ 46–53 Hz),[9b] and ruthenium [(η^5-C_5H_5)(Ph_2Me)$_2$-Ru–C($^+PPh_2Me$)=CH_2]PF_6 ($^3J_{P,H(cis)}$ 39 Hz, $^3J_{P,H(trans)}$ 73 Hz) complexes.[9e] Importantly, the *Z* isomer of **5** was calculated to be more stable by 13–14 kJ/mol than the corresponding *E* isomer (see below).

Stereoselective Protonation of σ-Phosphoniostyryl Complexes 3–7 to the Cationic η^2-Phosphonioalkene Products [(η^5-C_5H_5)$(CO)_2$M(η^2-*E*-H($^+PR_3$)C=C(H)Ph)]-BF_4 (8–12)

We found in our initial experiments that the addition of a strong protic acid (HBF_4·OEt_2) to the dichloromethane solution of manganese σ-phosphoniostyryl complex **3** at –70 °C afforded the η^2-phosphonioalkene complex [(η^5-C_5H_5)$(CO)_2$Mn(η^2-*E*-H($^+PPh_2Me$)C=C(H)Ph)]BF_4 (**8**) in a good yield. The purity of isolated **8** was confirmed by IR spectroscopy and elemental analysis; however, ^1H NMR characterization of this compound was complicated by traces of paramagnetic impurities. The appearance of these unidentified admixtures is presumably caused by acid-induced oxidation processes,[13] which results in persistent paramagnetic radicals such as those recently reported [(η^5-C_5H_5)$(CO)_2$Mn·–C($^+PR_3$)=CHPh]PF_6[14] or Mn^{II} and Mn^{III} salts as products of its further decomposition. The separation of **8** from paramagnetic by-products was only achieved by low-temperature chromatography (–20 to –40 °C) on silica by using a polar eluent (CH_2Cl_2/acetone, 10:1).

However, a more convenient synthetic procedure for these manganese η^2-phosphonioalkene complexes that avoids the use of chromatography was then discovered. It was found that the protonation of solutions of **3**–**5** in ether at –70 °C led to the precipitation of the target compounds **8**–**10** in an analytically pure state free of paramagnetic admixtures (Scheme 4). The related rhenium complexes **11** and **12** were prepared similarly in high yields.

Phosphonioalkene complexes **8**–**12** are bright to pale yellow crystalline substances stable in air for a long time when solids; this is especially relevant to the rhenium compounds. The values of the coupling constants ($^3J_{H,H}$ = 11–12 Hz, $^3J_{H,P}$ = 17–18 Hz, and $^2J_{H,P}$ = 7.5–7.7 Hz) clearly show that the alkene ligands in **8**–**12** have the *E* configuration (see ref.[10b]). NMR analysis of crude products shows no evidence of the presence of the corresponding *Z* isomers of **8**–**12**. Though our attempts to get reasonable NMR $^{13}C\{^1H\}$ data for the manganese complexes **3**–**5** and **8**–**10** failed, presumably because of the drastic loss of sensitivity caused by the formation of traces of paramagnetic impurities during the experiment, the related rhenium analogues **6**, **7**, **11** and **12** were fully characterized by NMR spectroscopy.

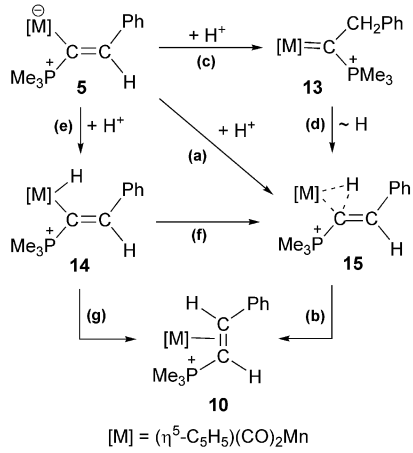


Scheme 4. Synthesis of η^2-phosphonioalkene complexes **8**–**12**.

In the family of transition-metal π-alkene complexes, phosphonioalkene ligands are quite rare.[8g,9e,10,15] Besides the protonation of σ-vinylphosphonium adducts,[8g,10] these compounds have been prepared by the innersphere phosphane/alkenyl coupling (for ruthenium[9e] and palladium[15] complexes) or by direct coordination of alkenylphosphonium salts (Pd complexes[15e]).

DFT Study of the Protonation of the Manganese Phosphoniostyryl Complex (η^5-C_5H_5)$(CO)_2Mn^-$–C-($^+PMe_3$)=C(H)Ph (5)

The transformation of α-phosphoniostyryl complexes **3**–**7** into η^2-phosphonioalkene derivatives **8**–**12** corresponds formally to the direct protonation of the Mn–C_α bond. Besides this straightforward route [Scheme 5, path (**a**) + (**b**)], other reaction pathways could be proposed that involve ini-



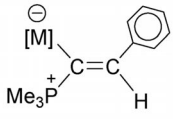
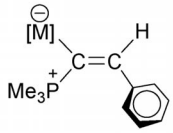
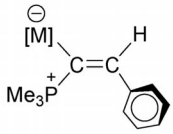
Scheme 5. Possible reaction pathways for the protonation of the σ-phosphoniostyryl complex (η^5-C_5H_5)$(CO)_2Mn^-$–C($^+PMe_3$)=C-(H)Ph (**5**).

tial protonation either at the C_β atom of the σ-phosphoniostyryl ligand or at the metal atom in complexes **3**–**7** [path (**c**) and (**e**), respectively]. To get a better insight into the mechanism of the protonation, the possible reaction pathways (Scheme 5) were calculated for manganese complex **5** by using Becke–Lee–Young–Parr density functional hybrid approach. The main part of calculations was performed by using the 6-31$^+$G* basis set, which was extended in some cases to 6-31^{++}G** one (see Experimental Section for details).

The Relative Stability of the Regioisomers and Conformers for Manganese σ-Phosphoniostyryl Complex 5

Phosphoniostyryl complexes **3**–**7** can exist as conformationally stable *E* and *Z* isomers at room temperature, as was experimentally found for the structurally related rhenium complexes $(\eta^5\text{-}C_5H_5)(NO)(PPh_3)Re\text{–}C(^+PMe_3)=C(H)\text{-}CH_3$.[9c] According to our calculations, the most stable is the experimentally observed *Z* isomer of **5**, which has the phosphane and the phenyl group in a *trans* disposition to each other (Table 1). Complex *Z*-**5** displays the degenerated rotation across the Mn–C_α bond with an activation barrier of 32.2 kJ/mol. The less stable *E* isomer has two conformers *E*-**5a** and *E*-**5b**, which differ in the values of the dihedral angle between the phenyl ring and the σ-phosphoniostyryl ligand planes.

Table 1. Formation energies and relative stabilities of the isomers of **5** (in kJ/mol).

№	Structure[a]	Δ^1E^0 [b]	Δ^1E^Z [c]	Δ^2E^0	Δ^2E^Z
Z-**5**		–11.6	0	–24.5	0
E-**5a**		–4.2	+7.4	–9.8	+14.7
E-**5b**		N/A[d]	N/A	–11.2	+13.3

[a] [M] = $(\eta^5\text{-}C_5H_5)(CO)_2Mn$. [b] Δ^1E^0 and Δ^2E^0 – formation energies of isomers **5** from vinylidene complex **1** and PMe_3 for 6-31G* and 6-31^{++}G** basis sets, respectively, in kJ/mol. [c] ΔE^Z – thermodynamic stability with respect to complex *Z*-**5**. [d] N/A – the corresponding stationary point was not found.

According to both calculation and experimental data, the *E* isomers of **5** are not present in the reaction mixture in noticeable amounts; therefore, their protonation was excluded from consideration.

The Properties of the HOMO Orbital of *Z*-5: Impossibility of Direct Protonation Across the Mn–C_α Bond in *Z*-5

The protonation site in betaine-type complex *Z*-**5** should be determined mainly by the charges of the potential reaction centers (the metal atom and the C_α, and C_β atoms of the σ-phosphonioalkenyl ligand) and by the contribution of the center orbitals to the HOMO of the molecule. The charge distribution in *Z*-**5** was calculated in terms of the NBO approach, which reveals the following charge density values for the Mn (–0.31), C_α (–0.50), and C_β (–0.26) atoms, and therefore show the C_α atom as the preferred protonation site in a charge-controlled reaction.

However, the analysis of the orbital population for *Z*-**5** reveals the most significant contribution of the metal atom orbitals in the HOMO (Figure 2), whereas the participation of the C_α atom orbitals is negligibly small. Thus, protonation of *Z*-**5** at this atom, which leads to the formation of the agostic complex **15**, cannot proceed, irrespective of its high negative charge [Scheme 5, path (**a**) + (**b**)].

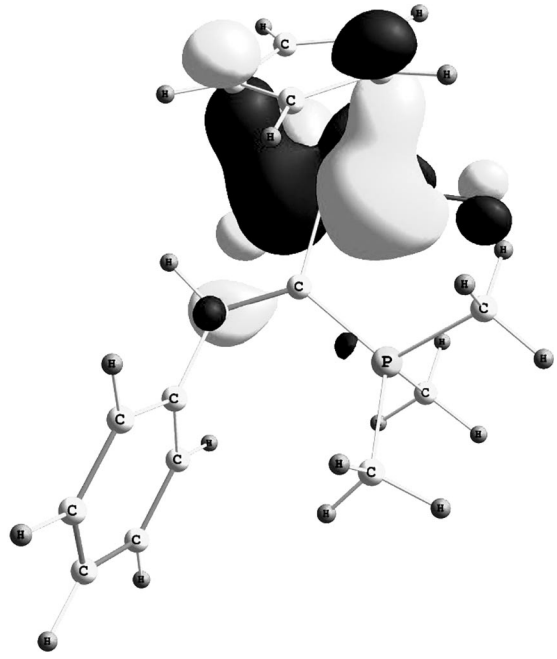


Figure 2. HOMO orbital geometry of *Z*-**5**.

The protonation of *Z*-**5** can thus proceed either at the C_β atom or at the manganese atom [Scheme 5, path (**c**) and (**e**), respectively]. The latter pathway seems more preferable when orbital control is taken into account.

General Calculation Details on the Protonation of *Z*-5

Since the protonation of σ-phosphoniostyryls (Scheme 4) was carried out by using $HBF_4{\cdot}OEt_2$ in dichloromethane or ether, the dimethyloxonium cation $[HOMe_2]^+$ was considered as a protic acid model in the gas phase for the calculation. At the B3LYP/6-31^{++}G** level of theory, a proton transfer from $[HOMe_2]^+$ either to the manganese atom or to the C_β atom was shown to be barrier free, which is quite

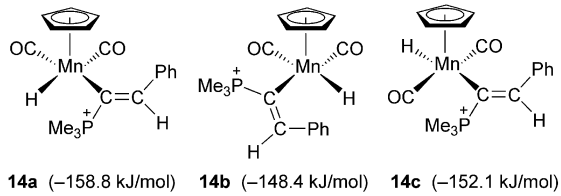
similar to the typical proton transfer processes to O, N, F and S centers.[16] On the other hand, the impossibility of determining the barrier for proton addition may be caused by the fact that $[HOMe_2]^+$ is not a fully appropriate proton model for the reaction conditions used in the synthesis of **8**–**12** (Scheme 4). It should also be noted that the small molecule $[HOMe_2]^+$, which has a localized positive charge, is highly destabilized in the gas phase relative to the protonation products **13** and **14** in which the positive charge is largely delocalized. Therefore, high protonation energies obtained for the transformations *Z*-**5** → **13** (ΔE = –208.9 kJ/mol) and *Z*-**5** → **14a**,**b** (ΔE = –158.8 and –148.4 kJ/mol, respectively) are not fully reliable for the real protonation process in solution. The utilization of other proton models including an increased number of solvent molecules such as $[H(OMe_2)_2]^+$ is very time consuming and was not performed in this work. Nevertheless, one can believe that the activation barriers to proton addition at both reaction sites (Mn and C_β) are small, and, therefore, the outcome of the protonation process should be determined by subsequent reaction steps.

Protonation of Complex *Z*-5 at the C_β Atom

The formation of η^2-phosphonioalkene complex **10** through the initial protonation of *Z*-**5** at the C_β atom includes the formation of the phosphoniocarbene complex **13** and the concerted intramolecular 1,2-hydrogen shift in the latter complex[17] [Scheme 5, (**c**) + (**d**) + (**b**)]. The first step (**c**), i.e. the formation of the phosphoniocarbene **13**, is highly exothermic (ΔE = –208.9 kJ/mol). The conversion of **13** into the agostic complexes **15** (path **c**) is also thermodynamically feasible (ΔE = –9.9 and + 1.8 kJ/mol for the formation of **15a** and **15b**, respectively; see Scheme 7), but, very importantly, it is forbidden because of the high activation barrier (173.1 kJ/mol for the transformation **13** → **15a**). Thus, the only possible pathway for the phosphoniocarbene → phosphonioalkene isomerization **13** → **10** is the base-catalyzed rearrangement of Fischer-type carbene complexes[18] including the protonation of σ-phosphoniostyryl complex **5** at the metal atom, which is considered below.

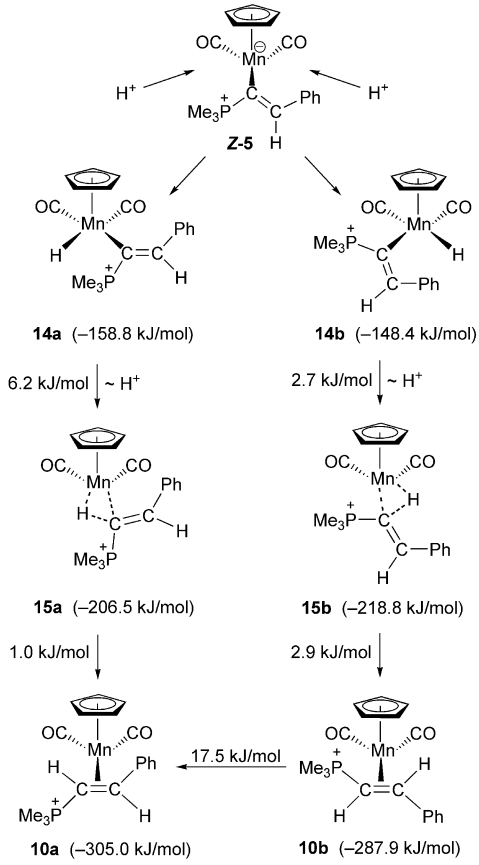
Protonation of Complex *Z*-5 at the Metal Atom

The protonation of *Z*-**5** at the metal atom can lead to the formation of hydride species having a *cis*- (**14a** and **14b**) and *trans*- (**14c**) four-leg piano-stool geometry (Scheme 6).



Scheme 6. Structure and relative energies of isomers of the manganese hydride complex **14**.

Hydride complexes **14a** and **14b** are conformers that differ in the disposition of the PMe_3 fragment to the hydride ligand (*syn*- and *anti*-, respectively). Importantly, they cannot interconvert easily because of a relatively high rotation barrier of the phosphoniostyryl group around the Mn–C_α bond (31.8 kJ/mol), which noticeably exceeds their barriers for further reductive elimination processes. Complexes **14a** and **14b** result from direct protonation of complex *Z*-**5** from the side of the PMe_3 and the styryl group, respectively (Scheme 7).



Scheme 7. Two possible reaction pathways for protonation of *Z*-**5** at the metal atom. The formation energies (ΔE_X) of complexes arising from the protonation process *Z*-**5** + $HOMe_2^+$ → Me_2O + X are given in parenthesis. The activation barriers are given near the reaction arrows.

On the basis of the shape of the HOMO of *Z*-**5** (Figure 2), *trans*-hydride **14c** cannot be formed by direct protonation because of the absence of the space between the two carbonyl ligands for proton-to-metal binding and can arise from the rearrangement of the initially formed *cis*-hydrides **14a** and **14b** only. Since **14c** is an unproductive compound, unable to undergo the reductive elimination (deprotonation or rearrangement to **14a** are only possible), it was excluded from consideration.

The conversion of hydrides **14a** and **14b** into the corresponding η^2-phosphonioalkene complex **10** was found to proceed in two steps [Scheme 5, (**f**) + (**b**)] rather than one

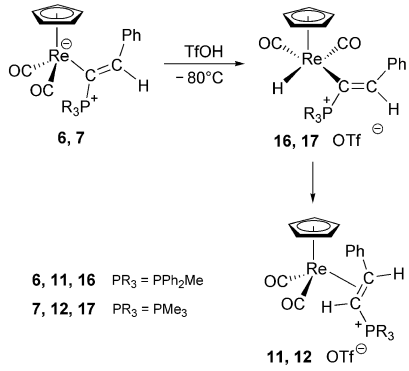
[Scheme 5, (**g**)]. The intermediate agostic structures **15a** and **15b** were identified on the potential energy surface (Scheme 7), and the activation barriers to their formation were calculated to be 6.2 and 2.7 kJ/mol, respectively. The further transformations of agostic compounds **15** are also fast and selectively afford two different rotamers of η^2-phosphonioalkene complex **10a** and **10b**. Importantly, the nature of the rotamer formed from *Z*-**5** is a function of the side on which the initial protonation takes place (from the PMe_3 side or the styryl side in *Z*-**5** for the formation of **10a** or **10b**, respectively). Finally, the less stable conformer **10b** should undergo rotation along the alkene ligand to afford **10a** as a single or predominant product.

The calculated rotational barrier for **10** (17.5 kJ/mol) is significantly lower than the experimental values found for manganese η^2-alkene complexes $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}H(R)C{=}C(R)H)$ (35–50 kJ/mol; R = H, Br, OMe, CO-OMe).[19] Variable-temperature NMR studies of η^2-phosphonioalkene rhenium complexes **11** and **12** reveal an increase in the rotational barrier for the alkene ligand bearing the more bulky phosphonio moiety. Complex **12**, having a small PMe_3 fragment, displays one set of NMR signals even at –100 °C in CD_2Cl_2 solution, whereas for **11**, which has a PPh_2Me moiety, decoalescence of both ^1H and ^{31}P signals is observed at –70 °C to afford clearly the slow-exchange NMR pattern at –100 °C. The estimated rotational barrier $\Delta G^{\#}$ = 35.5 kJ/mol is again lower than those observed for coordinated *E*- and *Z*-alkene ligands in $[(\eta^5\text{-}C_5H_5)(NO)(PPh_3)Re(\eta^2\text{-}H(R)C{=}C(R)H)]BF_4$ (R = alkyl, aryl; $\Delta G^{\#}$ = 46.2–78.1 kJ/mol).[20]

Low-Temperature Protonation of σ-Phosphoniostyryl Complexes 3, 6, and 7 with Triflic Acid

On the basis of the calculation data, the reductive elimination process in the manganese hydrides **14** proceeds very easily; thus the probability of NMR detection of the initial protonation products $[(\eta^5\text{-}C_5H_5)(CO)_2(H)Mn\text{–}C(^+PR_3){=}C(H)Ph]OTf$ is rather unlikely. In line with this expectation, the addition of CF_3SO_2OH (TfOH, 1.1 equiv.) to a CD_2Cl_2 solution of the manganese complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn^-\text{–}C(^+PPh_2Me){=}C(H)Ph$ (**3**) at –80 °C led to its gradual transformation into η^2-phosphonioalkene product **8** without any detectable hydride intermediates. Gratifyingly, the protonation of the related rhenium complexes **6** and **7** under the same conditions resulted in the hydride species **16** and **17**, respectively, as only products (Scheme 8). Complex **16** undergoes reductive elimination above –30 °C, whereas for its less bulky PMe_3 analogue **17**, this process proceeds slowly even at –40 °C (ca. 30% conversion after two hours).

The ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data show unambiguously that rhenium hydride complexes **16** and **17** exist in solution as single regioisomers. The presence of two different CO groups in the $^{13}C\{^1H\}$ NMR spectra [**16**: 195.8 (d, $^3J_{C,P}$ = 7.8 Hz), 192.5 (s); **17**: 198.5 (br. s), 191.1 (s)] allows us to clearly attribute the observed compounds to *cis*-hydrides. The upfield CO resonance in each case corresponds probably to the carbonyl group *trans*-disposed to the σ-phosphoniovinyl moiety because of the presence of $^3J_{C,P}$ coupling. The 2D NOESY spectrum of complex **16** reveals a strong cross-peak between the Me and Ph substituents of the PPh_2Me moiety, as well as weak cross-peaks of the hydride ligand with the PPh_2Me and Cp groups. This data together with the absence of the $^3J_{H,P}$ coupling in the signals of the hydride ligands lead us to propose that hydride complexes **16** and **17** have a *syn*-conformation as in the calculated manganese complex **14a**.



Scheme 8. Low-temperature protonation of rhenium complexes **6** and **7**.

To the best of our knowledge, complexes **16** and **17** represent the first examples of half-sandwich rhenium *cis*-organylhydrides of the type $(\eta^5\text{-}C_5H_5)(CO)_2(X)ReH$ that are stable at low temperature and fully characterized. The formation of *cis*-phosphonioallenylhydride intermediate by protonation of the related γ-phosphonioallenyl complex $(\eta^5\text{-}C_5H_5)(CO)_2Re^-\text{–}C(Tol){=}C^{13}{=}C^{13}(Ph)^+PPh_2Me$ was proposed by Casey et al.[21] on the basis of ^1H, ^{31}P, ^{13}C (labeled atoms) NMR spectroscopy. This complex proved to be highly thermolabile ($\tau_{1/2}$ 30 min at –80 °C) and readily undergoes conversion into the corresponding η^2-phosphonioallene complex $[(\eta^5\text{-}C_5H_5)(CO)_2Re(\eta^2\text{-}HC(Tol){=}C^{13}{=}C^{13}(Ph)PPh_2Me)]OTf$. The transient formation of the *cis*-hydridoacyl *cis*-$(CO)_2(H)Re\text{–}C(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ from the corresponding *trans* precursor was also proposed to explain the results of its thermal reaction with PPh_3 to form $(\eta^5\text{-}C_5H_4CH_2CH_2CHO)(CO)_2Re(PPh_3)$.[22]

It is noteworthy that dicarbonyl *trans*-organylhydride rhenium complexes are generally more stable than their *cis* isomers, as was evidenced both experimentally[23] and by DFT calculations (*cis* isomers are 18–20 kJ/mol less stable)[24] for a series of σ-arylhydride complexes $(\eta^5\text{-}C_5R_5)(CO)_2(H)Re\text{–}Ar$ (R = H, Me; Ar = C_6F_5, 2,3,5,6-C_6F_4H, 2,4-$C_6H_3F_2$). The NMR spectra of the *cis*-σ-phosphoniovinylhydrides **16** and **17** in a temperature region of –100 to –40 °C show no traces of an isomeric hydride species. We suppose that for complexes **16** and **17** *selectively formed at low temperature*, as well as for the related *cis*-σ-phosphonioallenylhydride complex reported by Casey,[21] the reductive elimination process is much easier than the isomerization into the potentially more stable *trans*-hydride compounds.

An additional DFT study on the relative stability of the *cis*- and *trans* isomers and on the reductive elimination process for such rhenium hydride complexes may shed light on this phenomenon.

Conclusions

The protonation of manganese and rhenium σ-phosphoniostyryl complexes *Z*-(η^5-C_5H_5)$(CO)_2$M$^-$–C($^+$$PR_3$)=C(H)Ph (**3**–**7**) results in stereoselective formation of the η^2-phosphonioalkene complexes [(η^5-C_5H_5)$(CO)_2$M(η^2-*E*-H($^+$$PR_3$)C=C(H)Ph)]$BF_4$ (**8**–**12**), and no phosphoniocarbene by-products (η^5-C_5H_5)$(CO)_2$M=C($^+$$PR_3$)$CH_2$Ph resulting from the protonation at the C_β atom were detected. DFT calculations of the reaction pathways for manganese complex (η^5-C_5H_5)$(CO)_2$Mn$^-$–C($^+$$PMe_3$)=C(H)Ph (**5**) reveals the initial proton addition at the metal atom to afford the *cis*-hydride intermediate *cis*-(η^5-C_5H_5)$(CO)_2$(H)Mn–C($^+$$PPh_2$Me)=C(H)Ph (**14**), followed by its subsequent low-barrier transformations into the agostic complex [(η^5-C_5H_5)$(CO)_2$Mn(η^2-(C,H)-*E*-**H**–**C**($^+$$PPh_2$Me)=C(H)Ph)] (**15**), and finally to the η^2-phosphonioalkene product **10**. In line with these calculation data, all attempts to detect the manganese hydride intermediate in the low-temperature protonation of **3** with triflic acid failed, but the protonation of their rhenium analogues **6** and **7** resulted in quantitative formation of the corresponding *cis*-hydrides, *cis*-(η^5-C_5H_5)$(CO)_2$(H)Re–C($^+$$PR_3$)=C(H)Ph (**16**, **17**), which are stable below –50 °C and readily undergo reductive elimination above –40 °C. Complexes **16** and **17** represent the first examples of fully spectroscopically characterized half-sandwich rhenium *cis*-hydrides of the type (η^5-C_5H_5)-$(CO)_2$(X)ReH.

As was briefly mentioned in the introduction the protonation of transition-metal σ-phosphonioalkenyl complexes is a likely final step of the catalytic addition of tertiary and secondary phosphanes to terminal alkynes.[6,7] Our results show clearly that the protonation of σ-phosphoniovinyl complexes of the type **IIb** and **IId** (see Scheme 1) only fixes the geometry of the alkenyl moiety, which is determined for half-sandwich vinylidene complexes by the phosphane addition step. Having these data in mind, one can assume that the opposite stereoselectivity (*E* and *Z* products, respectively) in the catalytic addition of PPh_3/$MeSO_2OH$[7] and PPh_2H[6] to terminal alkynes is caused by the different structure of the reaction intermediates **IId**. The *Z*-stereoselective addition of PPh_3 to rhodium cationic vinylidene complexes followed by rapid protonation of *Z*-**IId** with acid to give *E*-alkene products[7] corresponds ideally to the same processes studied here for manganese and rhenium phenylvinylidenes. The *E*-stereoselective PPh_2H addition to the ruthenium vinylidene intermediates (η^5-C_5Me_5)L_2Ru^+=C=C(H)C(OH)RR′ to form *E*-**IId** is probably caused by the bulkiness of both the metal fragment and substituents at the C_β atom of the vinylidene ligand, which destabilizes the usual addition product *Z*-**IId**. This assumption is well confirmed by the results obtained for less bulky (η^5-C_5H_5)-L_2Ru^+=C=C(H)C(OH)RR′ (*E*-alkene selectivity 55–65%), in which the formation of *Z*-**IId** becomes even more preferable than *E*-**IId**. The regularities of phosphane addition to vinylidene complexes are not completely understood yet, and additional studies are required to gain a better insight into such type of processes.

Experimental Section

All operations were carried out under an argon atmosphere by using standard Schlenk techniques. Solvents were purified by using standard procedures and distilled under argon prior to use. IR spectra were recorded on a Specord 75 IR spectrophotometer (Carl Zeiss, Jena) and are given in cm^{-1} with relative intensity in parenthesis. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance 300, Bruker Avance 400, and Bruker Avance 600 instruments at 25 °C and referenced to the residual deuterated solvent signals (^1H and ^{13}C NMR) and external 85% H_3PO_4, respectively. Vinylidene complexes **1**[25] and **2**[26] and phosphanes PPh_2Me,[27] $PPhMe_2$,[28] and PMe_3[29] were prepared according to literature procedures.

Synthesis of *Z*-(η^5-C_5H_5)$(CO)_2$Mn$^-$–C($^+$$PPh_2$Me)=C(H)Ph (3): PPh_2Me (160 mg, 0.8 mmol) was added to a solution of **1** (112 mg, 0.4 mmol) in hexane (10 mL) at room temperature, and the mixture was stirred for 2 h. The yellow precipitate formed was filtered off, washed with hexane, and dried in vacuo to yield **3** as a yellow solid. Yield: 172 mg (90%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1890 (s, CO), 1814 (s, CO) cm^{-1}. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 8.04–7.00 (m, 15 H, C_6H_5), 7.73 [d, $^3J_{H,P}$ = 43.9 Hz, 1 H, =C(*H*)Ph], 4.27 (s, 5 H, C_5H_5), 2.23 (d, $^2J_{H,P}$ = 12.9 Hz, 3 H, PCH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): δ = 11.7 (s) ppm. $C_{28}H_{24}MnO_2P$ (478): calcd. C 70.30, H 5.06; found C 70.51, H 5.02.

Synthesis of *Z*-(η^5-C_5H_5)$(CO)_2$Mn$^-$–C($^+$$PMe_2$Ph)=C(H)Ph (4): Similarly, from a solution of **1** (56 mg, 0.2 mmol) in hexane (5 mL) and $PPhMe_2$ (55 mg, 0.4 mmol), complex **4** was obtained as a yellow solid. Yield: 71 mg (85%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1888 (s, CO), 1814 (s, CO) cm^{-1}. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 7.98–7.00 (m, 10 H, C_6H_5), 7.69 [d, $^3J_{P,H}$ = 41.4 Hz, 1 H, =C(*H*)Ph], 4.13 (br. s, 5 H, C_5H_5), 1.37 [br. s, 6 H, P(CH_3)$_2$] ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): δ = 8.0 (s) ppm. $C_{23}H_{22}MnO_2P$ (416): calcd. C 66.35, H 5.33, Mn 13.2; found C 66.17, H 5.21, Mn 13.4.

Synthesis of *Z*-(η^5-C_5H_5)$(CO)_2$Mn$^-$–C($^+$$PMe_3$)=C(H)Ph (5): Similarly, from a solution of **1** (55 mg, 0.2 mmol) in hexane (5 mL) and a solution of PMe_3 (18 mg, 0.24 mmol) in diethyl ether (2 mL), complex **5** was obtained as a yellow solid. Yield: 61 mg (87%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1896 (s, CO), 1811 (s, CO) cm^{-1}. ^1H NMR (300.1 MHz, [D_6]acetone, 25 °C): δ = 7.94 [d, $^3J_{H,P}$ = 42.5 Hz, 1 H, =C(*H*)Ph], 7.75 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{ortho} Ph), 7.36 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{meta} Ph), 7.21 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, H_{para} Ph), 4.07 (s, 5 H, C_5H_5), 1.93 [d, $^2J_{H,P}$ = 12.4 Hz, 9 H, P(CH_3)$_3$] ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_6]acetone, 25 °C): δ = 13.1 (s) ppm.

Synthesis of *Z*-(η^5-C_5H_5)$(CO)_2$Re$^-$–C($^+$$PMePh_2$)=C(H)Ph (6): Similarly, from a solution of **2** (64 mg, 0.16 mmol) in hexane (15 mL) and PPh_2Me (0.043 mL, 0.24 mmol), complex **6** was obtained as a pale yellow solid. Yield: 89 mg (96%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1880 (s, CO), 1806 (s, CO) cm^{-1}. ^1H NMR (300.1 MHz, CD_2Cl_2, 25 °C): δ = 7.64–7.51 (m, 12 H, PPh_2, H_{ortho} Ph), 7.41 [d, $^3J_{H,P}$ = 41.1 Hz, 1 H, =C(*H*)Ph], 7.29 (m, 2 H, H_{meta} Ph), 7.20 (m, 1 H, H_{para} Ph), 4.66 (s, 5 H, C_5H_5), 2.58 (d, $^2J_{H,P}$ = 12.6 Hz, 3 H, PCH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ = 20.1 (s) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2, 25 °C): δ = 208.9 (d,

$^3J_{C,P}$ = 19.8 Hz, Re–*C*O), 159.2 (d, $^3J_{C,P}$ = 12.5 Hz, C_{ipso} =CPh), 146.5 (d, $^1J_{P,C}$ = 36.7 Hz, C_{ipso} PPh_2), 136.2–132.1 (CPh, PPh_2), 130.4 (d, $^1J_{C,P}$ = 74.8 Hz, P*C*=CPh), 129.5 (s, PC=*C*Ph), 87.7 (s, C_5H_5), 15.8 (d, $^1J_{C,P}$ = 71.9 Hz, P*C*H$_3$) ppm. $C_{28}H_{24}O_2PRe$ (609.2): calcd. C 55.28, H 4.09, P 5.01; found C 55.16, H 3.97, P 5.08.

Synthesis of *Z*-(η^5-C_5H_5)(CO)$_2$Re$^-$–C($^+$PMe$_3$)=C(H)Ph (7): Similarly, from a solution of **2** (30 mg, 0.07 mmol) in hexane (7 mL) and a solution of PMe_3 (7.6 mg, 0.1 mmol) in diethyl ether (1 mL), complex **7** was obtained as a pale yellow solid. Yield: 27 mg (76%). IR (C_6H_6): ṽ = 1890 (s, CO), 1808 (s, CO) cm^{-1}. ^{1}H NMR (400.1 MHz, [D$_6$]acetone, 25 °C): δ = 7.82 [d, $^3J_{H,P}$ = 40.2 Hz, 1 H, =C(*H*)Ph], 7.72 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{ortho} Ph), 7.31 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{meta} Ph), 7.21 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, H_{para} Ph), 4.67 (s, 5 H, C_5H_5), 2.00 [d, $^2J_{H,P}$ = 12.5 Hz, 9 H, P(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (162.0 MHz, [D$_6$]acetone, 25 °C): δ = 20.1 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 209.7 (s, Re–*C*O), 149.1 (d, $^2J_{C,P}$ = 10.6 Hz, PC=*C*Ph), 143.6 (d, $^1J_{C,P}$ = 35.1 Hz, P*C*=CPh), 129.2–126.2 (Ph), 84.6 (s, C_5H_5), 12.7 [d, $^1J_{C,P}$ = 57.3 Hz, P(*C*H$_3$)$_3$] ppm.

Preparation of [(η^5-C_5H_5)(CO)$_2$Mn(η^2-*E*-HC(P$^+$Ph$_2$Me)=C(H)Ph)]BF$_4$ (8) in a Dichloromethane Solution: An ethereal solution of HBF_4 (54%, 0.04 mL, 0.3 mmol) was added to a solution of **8a** (113 mg, 0.24 mmol) in CH_2Cl_2 (4 mL) cooled to –70 °C, with stirring. The reaction mixture was stirred for 30 min at this temperature, and ether (20 mL) was added. The yellow precipitate formed was filtered off, washed with diethyl ether, and dried to afford crude **8**, which was further purified by column chromatography on silica at low temperature (–20 to –40 °C). The light yellow fraction was eluted with a CH_2Cl_2/acetone (10:1) mixture. The eluate was evaporated in vacuo to afford **8** as a yellow powder. Yield: 96 mg (74%). IR (CH_2Cl_2): ṽ = 1982 (s, CO), 1924 (s, CO) cm^{-1}. ^{1}H NMR (300.1 MHz, [D$_6$]acetone, 25 °C): δ = 8.35–7.23 (m, 10 H, C_6H_5), 4.82 [dd, $^3J_{H,H(trans)}$ = 11.65, $^2J_{H,P}$ = 7.7 Hz, 1 H, =C(*H*)P], 4.74 (s, 5 H, C_5H_5), 4.58 [dd, $^3J_{H,H(trans)}$ = 12.5, $^3J_{H,P(cis)}$ = 17.8 Hz, 1 H, =C(*H*)Ph], 2.47 (d, $^2J_{H,P}$ = 12.9 Hz, 3 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]acetone, 25 °C): δ = 32.1 (s) ppm. $C_{28}H_{25}BF_4MnO_2P$ (566): calcd. C 59.40, H 4.45; found C 59.50, H 4.61.

Preparation of [(η^5-C_5H_5)Mn(CO)$_2$(η^2-*E*-HC(P$^+$Ph$_2$Me)=C(H)Ph)]BF$_4$ (8) in an Ethereal Solution: Complex **3** (48 mg, 0.1 mmol) was added as a solid to a solution of HBF_4·OEt_2 (0.014 mL, 0.1 mmol) in diethyl ether (5 mL) cooled to –70 °C, and the reaction mixture was slowly warmed to room temperature. Within the temperature interval 12–15 °C, the bright orange color of the starting solution changed to light yellow of the η^2-phosphonioalkene product. The mixture was then stirred for additional hour at room temperature. The precipitate **8** was filtered off, washed twice with ether, and dried first in an argon stream and then in vacuo. Yield: 57 mg (100%). IR (CH_2Cl_2): ṽ = 1982 (s, CO), 1924 (s, CO) cm^{-1}.

Synthesis of [(η^5-C_5H_5)Mn(CO)$_2$(η^2-*E*-HC(P$^+$PhMe$_2$)=C(H)Ph)]BF$_4$ (9): Similarly, from **4** (42 mg, 0.1 mmol) and HBF_4·Et_2O (0.014 mL, 0.1 mmol) in the ether (5 mL), complex **9** was obtained as a yellow solid. Yield: 43 mg (85%). IR (CH_2Cl_2): ṽ = 1984 (s, CO), 1924 (s, CO) cm^{-1}. ^{1}H NMR (300.1 MHz, [D$_6$]acetone, 25 °C): δ = 8.13–7.23 (m, 10 H, C_6H_5), 4.82 (s, 5 H, C_5H_5), 4.45 [dd, $^3J_{H,H(trans)}$ = 10.8, $^2J_{H,P}$ = 7.6 Hz, 1 H, =C(*H*)P], 4.36 [dd, $^3J_{H,H(trans)}$ = 10.8, $^3J_{H,P(cis)}$ = 17.0 Hz, 1 H, =C(*H*)Ph], 2.56 (d, $^2J_{H,P}$ = 13.4 Hz, 3 H, PCH_3), 2.21 (d, $^2J_{H,P}$ = 13.3 Hz, 3 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]acetone, 25 °C): δ = 33.1 (s) ppm. $C_{23}H_{23}BF_4MnO_2P$ (504): calcd. C 54.80, H 4.60, Mn 10.9; found C 54.45, H 4.61, Mn 10.4.

Synthesis of [(η^5-C_5H_5)Mn(CO)$_2$(η^2-*E*-HC(P$^+$Me$_3$)=C(H)Ph)]BF$_4$ (10): Similarly, from **5** (70 mg, 0.2 mmol) and HBF_4·Et_2O (0.028 mL, 0.2 mmol) in the ether (5 mL), complex **10** was obtained as a yellow solid. Yield: 78 mg (89%). IR (CH_2Cl_2): ṽ = 1983 (s, CO), 1916 (s, CO) cm^{-1}. ^{1}H NMR (300.1 MHz, [D$_6$]acetone, 25 °C): δ = 7.52 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{ortho} Ph), 7.32 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{meta} Ph), 7.22 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, H_{para} Ph), 4.83 (s, 5 H, C_5H_5), 4.26 [m, 1 H, =C(*H*)P], 4.15 [m, 1 H, =C(*H*)Ph], 2.08 (d, $^2J_{H,P}$ = 12.5 Hz, 9 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]acetone, 25 °C): δ = 35.1 (s) ppm. $C_{18}H_{21}BF_4MnO_2P$ (442): calcd. C 48.90, H 4.79, Mn 12.43; found C 48.72, H 4.68, Mn 12.48.

Synthesis of [(η^5-C_5H_5)Re(CO)$_2$(η^2-*E*-HC(P$^+$Ph$_2$Me)=C(H)Ph)]BF$_4$ (11): Similarly, from **6** (61 mg, 0.1 mmol) and HBF_4·Et_2O (0.014 mL, 0.1 mmol) in the ether (5 mL), complex **11** was obtained as a white powder. Yield: 69 mg (99%). IR (CH_2Cl_2): ṽ = 1982 (s, CO), 1906 (s, CO) cm^{-1}. ^{1}H NMR (600.2 MHz, CD_2Cl_2, 25 °C): δ = 7.80–7.34 (m, 10 H, PPh_2), 7.24 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, H_{ortho} CPh), 7.15 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, H_{meta} CPh), 6.99 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, H_{para} CPh), 5.08 (s, 5 H, C_5H_5), 4.33 [dd, $^3J_{H,H(trans)}$ = 10.4, $^3J_{H,P(cis)}$ = 15.9 Hz, 1 H, =C(*H*)Ph], 4.03 [dd, $^3J_{H,H(trans)}$ = 10.3, $^2J_{H,P}$ = 6.9 Hz, 1 H, =C(*H*)P], 2.14 (d, $^2J_{H,P}$ = 12.7 Hz, 3 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (243.0 MHz, CD_2Cl_2, 25 °C): δ = 32.6 (s) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 25 °C): δ = 201.4 (d, $^3J_{C,P}$ = 9.3 Hz, Re–*C*O$_{trans}$), 201.2 (s, Re–*C*O$_{cis}$), 143.4–122.3 (Ph, PPh_2), 91.2 (s, C_5H_5), 38.0 [s, =*C*(H)Ph], 7.9 [d, $^1J_{C,P}$ = 80.6 Hz, =*C*(H)P], 7.2 (d, $^1J_{C,P}$ = 61.3 Hz, P*C*H$_3$) ppm. $C_{28}H_{25}BF_4O_2PRe$ (697.2): calcd. C 48.22, H 3.61, P 4.44; found C 48.36, H 3.70, P 4.40.

Synthesis of [(η^5-C_5H_5)Re(CO)$_2$(η^2-*E*-HC(P$^+$Me$_3$)=C(H)Ph)]BF$_4$ (12): Similarly, from **6** (27 mg, 0.05 mmol) and HBF_4·Et_2O (0.007 mL, 0.05 mmol) in the ether (5 mL), complex **12** was obtained as a white solid. Yield: 39 mg (89%). IR (CH_2Cl_2): ṽ = 1987 (s, CO), 1903 (s, CO) cm^{-1}. ^{1}H NMR (600.2 MHz, [D$_6$]acetone, 25 °C): δ = 7.36 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{ortho} Ph), 7.30 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, H_{meta} Ph), 7.16 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, H_{para} Ph), 5.52 (s, 5 H, C_5H_5), 4.38 [dd, $^3J_{H,H(trans)}$ = 10.9, $^3J_{H,P(cis)}$ = 16.8 Hz, 1 H, =C(*H*)Ph], 4.27 [dd, $^3J_{H,H(trans)}$ = 10.6, $^2J_{H,P}$ = 6.8 Hz, 1 H, =C(*H*)P], 2.07 (d, $^2J_{H,P}$ = 12.5 Hz, 9 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (243.0 MHz, [D$_6$]acetone, 25 °C): δ = 35.1 (s) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 25 °C): δ = 202.0 (br. s, Re–*C*O), 201.2 (s, Re–*C*O), 143.4–129.0 (Ph), 90.9 (s, C_5H_5), 38.4 [s, =*C*(H)Ph], 10.2 [d, $^1J_{C,P}$ = 76.3 Hz, =*C*(H)P], 10.1 (d, $^1J_{C,P}$ = 56.4 Hz, P*C*H$_3$) ppm.

Variable-Temperature ^{1}H and ^{31}P{^{1}H} NMR Spectroscopy Data for [(η^5-C_5H_5)Re(CO)$_2$(η^2-*E*-HC(P$^+$Ph$_2$Me)=C(H)Ph)]OTf ([11]OTf): The activation energy barrier was calculated by using the approximation of the Eyring equation: $\Delta G^{\#} = RT_c(22.96 + \ln T_c/\delta\nu)$, where T_c [K] is the estimated coalescence temperature of two signals separated by δν [Hz].

[11]OTf: ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 7.86–7.38 (m, 10 H, PPh_2), 7.32 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H_{ortho} CPh), 7.18 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, H_{meta} CPh), 7.02 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, H_{para} CPh), 5.13 (s, 5 H, C_5H_5), 4.61 [dd, $^3J_{H,H(trans)}$ = 10.4, $^3J_{H,P(cis)}$ = 15.9 Hz, 1 H, =C(*H*)Ph], 4.06 [dd, $^3J_{H,H(trans)}$ = 10.3, $^2J_{H,P}$ = 6.9 Hz, 1 H, =C(*H*)P], 2.17 (d, $^2J_{H,P}$ = 12.7 Hz, 3 H, PCH_3) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, –100 °C): δ = 8.15–7.10 (m, 15 H, PPh_2, Ph), 5.22 (s, 5 H, C_5H_5), 4.82 [br. s, =C(*H*)Ph major isomer], 4.37 [br. s, =C(*H*)P major isomer], 4.01 [br. s, =C(*H*)Ph minor isomer], 3.57 [br. s, =C(*H*)P minor isomer], 2.70 (br. s, PCH_3 minor isomer), 2.01 (br. s, PCH_3 major isomer) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 31.65 (s) ppm. ^{31}P{^{1}H} NMR

(162.0 MHz, CD_2Cl_2, –100 °C): δ = 34.05 (s, minor isomer), 31.6 (s, major isomer) ppm.

Low-Temperature Protonation of Complex *Z*-(η^5-C_5H_5)$(CO)_2$Re$^-$–C($^+$PMePh_2)=C(H)Ph (6) in the NMR Tube: Complex **6** (30 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (ca. 0.5 mL), and the solution was filtered through Celite directly into an NMR tube. The NMR tube was capped with a rubber septum, and the sample was cooled to –80 °C. At this temperature, the solution of TfOH (5 μL, 0.055 mmol) in CD_2Cl_2 (0.1 mL) was added by a syringe, which led, after gentle shaking, to a change in the color of the solution from yellow to light rose. The NMR tube was rapidly inserted into the precooled NMR spectrometer probe (–80 °C), and the rhenium hydride complex *cis*-[(η^5-C_5H_5)$(CO)_2$(H)Re–C($^+$PMePh_2)=C(H)-Ph]OTf (**16**) was observed as the only product. Complex **16** was shown to be absolutely stable for hours below –50 °C. The reductive elimination process in **16** started at ca. –30 °C and was completed at about –10 to 0 °C to form quantitatively the η^2-phosphonioalkene complex **11**.

16: ^{1}H NMR (400.1 MHz, CD_2Cl_2, –80 °C): δ = 7.87–7.50 [m, 11 H, PPh_2, =C(*H*)Ph], 7.42 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, H_{meta} CPh), 7.35 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, H_{para} CPh), 7.29 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, H_{ortho} CPh), 5.07 (s, 5 H, C_5H_5), 2.72 (d, $^2J_{H,P}$ = 12.7 Hz, 3 H, PCH_3), –8.87 (s, 1 H, Re–H) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, –80 °C): δ = 36.35 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, –80 °C): δ = 195.8 (d, $^3J_{C,P}$ = 7.8 Hz, Re–CO_{trans}), 192.5 (s, Re–CO_{cis}), 169.3 (d, $^2J_{C,P}$ = 9.1 Hz, PC=*C*Ph), 141.2 (d, $^1J_{C,P}$ = 29.8 Hz, P*C*=CPh), 134.2–127.6 (Ph, PPh_2), 88.0 (s, C_5H_5), 9.9 (d, $^1J_{C,P}$ = 64.8 Hz, P*C*H_3) ppm.

Low-Temperature Protonation of Complex *Z*-(η^5-C_5H_5)$(CO)_2$Re$^-$–C($^+$$PMe_3$)=C(H)Ph (7) in the NMR Tube: Complex **7** (25 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (ca. 0.5 mL), and the solution was filtered through Celite directly into an NMR tube. The NMR tube was capped with rubber septum, and the sample was cooled to –80 °C. At this temperature, a solution of TfOH (5 μL, 0.055 mmol) in CD_2Cl_2 (0.1 mL) was added by a syringe, which led, after gentle shaking, to a change in the color of the solution from yellow to light rose. The NMR tube was rapidly inserted into the precooled NMR spectrometer probe (–80 °C), and the rhenium hydride complex *cis*-[(η^5-C_5H_5)$(CO)_2$(H)Re–C($^+$$PMe_3$)=C(H)Ph]-OTf (**17**) was observed as the only product. The reductive elimination process in **17** proceeded slowly at –40 °C (30% conversion into **12** after 2 h) and was completed at –20 °C to form quantitatively the η^2-phosphonioalkene complex **12**.

17: ^{1}H NMR (400.1 MHz, CD_2Cl_2, –60 °C): δ = 8.11 [d, $^3J_{P,H}$ = 35.2 Hz, 1 H, =C(*H*)Ph], 7.49–7.36 (m, 5 H, C_6H_5), 5.03 (s, 5 H, C_5H_5), 2.72 (br. d, $^2J_{H,P}$ = 11.0 Hz, 9 H, PCH_3), –8.61 (s, 1 H, Re–H) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2, –100 °C): δ = 8.05 [br. d, $^3J_{P,H}$ = 34 Hz, 1 H, =C(*H*)Ph], 7.48–7.25 (m, 5 H, C_6H_5), 4.96 (s, 5 H, C_5H_5), 1.96 (br. s, 9 H, PCH_3), –8.59 (s, 1 H, Re–H) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, –100 °C): δ = 34.6 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, –80 °C): δ = 198.5 (br. s, Re–CO_{trans}), 191.1 (s, Re–CO_{cis}), 162.6 (d, $^2J_{C,P}$ = 6.6 Hz, PC=*C*Ph), 140.9 (d, $^1J_{C,P}$ = 28.0 Hz, P*C*=CPh), 128.8–128.1 (s, Ph), 88.2 (s, C_5H_5), 11.5 (d, $^1J_{C,P}$ = 56.8 Hz, P*C*H_3) ppm.

Single-Crystal X-ray Diffraction Analysis: Single-crystal X-ray diffraction experiments for **6** were carried out with a Bruker SMART APEX II area detector diffractometer, by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å, ω-scans) at 100 K. The low temperature of the crystal was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated by using the SAINT software,[30,31] and absorption correction was applied semiempirically by using the SADABS program.[32] The structure was solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. All H(C) atoms were placed in geometrically calculated positions and refined in isotropic approximation with a riding model. All calculations were performed on an IBM PC/AT by using the SHELXTL software.[33] Crystallographic data and refinement parameters for **6** are given in Table 2. CCDC-742639 contains the supplementary crystallographic data for the structure of **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic details of **6**.

Compound	**6**
Molecular formula	$C_{28}H_{24}O_2PRe$
Crystal color, habit	Yellow, prism
Crystal size [mm]	0.18 × 0.12 × 0.11
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	15.8201(16)
b [Å]	12.1554(17)
c [Å]	11.9825(16)
α [°]	90
β [°]	97.034(3)
γ [°]	90
V [Å^3]	2286.9(5)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.771
$2\theta_{max}$ [°]	54
Absorption coefficient, μ(Mo-K_α) [mm^{-1}]	5.407
No. reflections collected	16879
Completeness	1.000
No. independent reflections	4994 (R_{int} = 0.0366)
No. observed reflections [I > 2σ (I)]	3494
Absolute structure parameters	
No. of parameters	290
R_1 (on F for observed reflections)	0.0326
wR_2 (on F^2 for all reflections)	0.0424
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ $P = 1/3(F_o^2 + 2F_c^2)$
a	0.01
b	1.00
F(000)	1192
GOF	1.043
Largest diff. peak and hole [e Å^{-3}]	0.923 and –0.543

Computational Details: Calculations were carried out for the gas phase by the Becke–Lee–Young–Parr density functional approach (B3LYP) by using the GAUSSIAN 03 program. Full geometry optimizations were performed with the 6-31G* basis set[34,35] for all the structures studied. The structures corresponding to local minima on the PES were also studied with the 6-31^{++}G** basis set.[36,37] The procedure for location and calculation of transition-state structures was made with QST2[38] and/or Opt(CalcAll,TS) methods. All stationary points were characterized by frequency calculations in the 6-31G* basis set to give positive definite Hessian matrices (minima on the PES) and a sole negative eigenvalue in their diagonalized force constant matrices (transition states). ZPE correction of the internal energy was performed for all minima and transition states in the 6-31G* basis set. The natural bonding orbital method[39] was used to analyze the electronic structures of the stable compounds.

Supporting Information (see footnote on the first page of this article): Energies and Cartesian coordinates of all calculated intermediates and transition states.

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