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Synthesis of η^1-α-Phosphinocarbene Complexes of Manganese and Mechanistic Insight into Their Base-Induced Transformations

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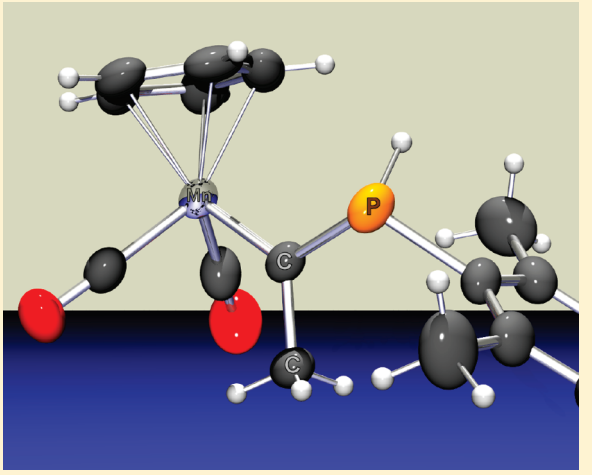
Supporting Information

ABSTRACT: A series of η^1-α-phosphinocarbene complexes of manganese, $Cp(CO)_2Mn{=}C(R)PR'R''$ (**3**; **3a**: R = Ph, R′ = H, R″ = Mes; **3b**: R = Me, R′ = H, R″ = Mes; **3c**: R = Ph, R′ = R″ = Ph; **3d**: R = Ph, R′ = R″ = $N(i\text{-}Pr)_2$; **3e**: R = Ph, R′ = Me, R″ = Mes), was generated at low temperature upon nucleophilic addition of the primary phosphine H_2PMes and secondary phosphines $HPPh_2$, $HP(N(i\text{-}Pr)_2)_2$, or (±)-HPMeMes to the cationic carbyne complexes $Cp(CO)_2Mn^+{\equiv}C{-}R$ ($[\mathbf{1}]^+$; $[\mathbf{1a}]^+$: R = Ph; $[\mathbf{1b}]^+$: R = Me), followed by deprotonation of the resulting α-phosphoniocarbene intermediates $Cp(CO)_2Mn{=}C(R)P^+(H)R'R''$ ($[\mathbf{2a{-}e}]^+$). The η^1-α-phosphinocarbene complexes **3c**−**e** derived from secondary phosphines were found to be highly thermolabile, giving upon intramolecular CO insertion the η^3-phosphinoketene complexes $Cp(CO)Mn(\eta^3\text{-}C(O)C(Ph)PR'R'')$ (**4c**: R′ = R″ = Ph, **4d**: *i*-Pr_2N; *RR*/*SS*-**4e**: R′ = Me, R″ = Mes) in 80−95% yield. The η^1-α-phosphinocarbene complexes **3a**,**b**, bearing a mesityl substituent, were isolated in 57−65% yield. The availability of the phosphorus lone pair in such compounds was assessed by their reaction with borane, giving the corresponding adducts $Cp(CO)_2Mn{=}C(R)P(BH_3)HMes$ (**5a**, R = Ph; **5b**, R = Me). Complexes **3a**,**b** slowly rearrange in a nonpolar solvent (benzene) to afford a mixture of the η^3-phosphinoketene complexes $Cp(CO)Mn(\eta^3\text{-}C(O)C(R)PHMes)$ (**4a**, R = Ph; **4b**, R = Me) and the η^1-phosphaalkene complexes $Cp(CO)_2Mn(\eta^1\text{-}P(Mes){=}C(H)R$ (**6a**, R = Ph; **6b**, R = Me), and ultimately pure **6a**,**b** as a mixture of *E*/*Z* stereoisomers (**6a**, *E*/*Z* 60:40; **6b**, *E*/*Z* 55:45). By contrast, a stereoselective rearrangement of **3a**,**b** into *E*-**6a**,**b** was observed in a polar solvent (THF), the process being considerably accelerated in the presence of catalytic amounts of base. Deprotonation of **3a** by *n*-BuLi at −80 °C affords the *dicarbonyl* phosphidocarbene anion $[Cp(CO)_2Mn{=}C(Ph)PMes]Li$ ($[\mathbf{7a}]Li$), which undergoes an instantaneous CO insertion process upon addition of traces of weak acids (H_2O, *t*-BuOH) to give the cyclic monocarbonylacyl anion $[Cp(CO)_2Mn(\eta^2\text{-}C(O)C(Ph){=}PMes]Li$ ($[\mathbf{8a}]Li$, R = Ph). Besides, deprotonation of **3a**,**b** by *t*-BuOLi affords directly the cyclic monocarbonylacyl anions $[\mathbf{8a,b}]Li$. The protonation of $[\mathbf{8a}]Li$ with various proton sources ($HBF_4{\cdot}Et_2O$, NH_4Cl_{aq}, $[Et_3NH]Cl$) leads to a stereoselective formation of *E*-**6a**, illustrating the key role of this anion in the stereoselective **3a** → *E*-**6a** rearrangement. Alkylation of $[\mathbf{8a}]Li$ by MeI resulted in formation of η^3-phosphinoketene complex *RR*/*SS*-**4e** as a single pair of diastereomers, whereas its treatment with iodine resulted in thermally unstable η^3-phosphinoketene complex $Cp(CO)Mn(\eta^3\text{-}C(O)C(Ph)PIMes)$ (**11**), evolving at room temperature into the η^1-phosphaalkene product $Cp(CO)_2Mn(\eta^1\text{-}P(Mes){=}C(I)Ph)$ (**12**) of *Z* conformation. The solid-state structures of **3b**, **4c**, **4d**, *RR*/*SS*-**4e**, and *Z*-**12** are reported.



INTRODUCTION

Since the seminal finding by Fischer and Maasböl some 40 years ago,[1] thousands of heteroatom-stabilized carbene complexes $L_nM{=}C(R)X$ (X = OR′, NR′$_2$, SR′, SnR′$_3$) have been synthesized in view of their anticipated application scope in organic synthesis.[2] Although the case of transition-metal α-P-substituted carbene complexes has been examined on several occasions,[3,4] the true phosphorus-containing homologues of Fischer carbenes, η^1-α-phosphinocarbenes of the type $L_nM{=}C(R)PR'_2$, have remained extremely scarce and their reactivity has been virtually unexplored.[5−7]

Historically, Fischer and Reitmeiter were the first to isolate an η^1-α-phosphinocarbene complex of tungsten, $(CO)_4(L)W{=}C(NEt_2)P(Me)Ph$ (L = CO, HP(Me)Ph), albeit in very low yield (3−4%), upon nucleophilic attack of a phosphide, [PMePh]K,

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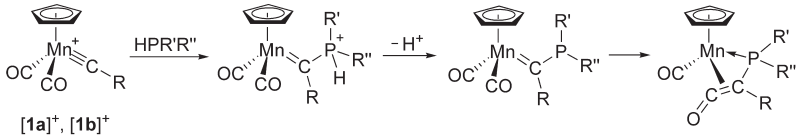
Scheme 1



a: R = Ph; R' = H, R" = Mes	[**2a**]$^+$	**3a** (65%)	**4a**
b: R = Me; R' = H, R" = Mes	[**2b**]$^+$	**3b** (57%)	**4b**
c: R = Ph; R' = R" = Ph	[**2c**]$^+$	{**3c**}	**4c** (80%)
d: R = Ph; R' = R" = *i*-Pr$_2$N	[**2d**]$^+$ (92%)	{**3d**}	**4d** (95%)
e: R = Ph; R' = Me, R" = Mes	[**2e**]$^+$	**3e**	RR/SS-**4e** (85%, 100% d.e.)

onto the electrophilic carbyne atom of the cationic carbyne complex $[(CO)_5W{\equiv}C{-}NEt_2]^+$.[5] The main reaction product in that case was a dimeric phosphorus-free species resulting from a reductive coupling of two carbyne units of the starting precursor.[5] Adopting a conceptually similar synthetic route, Yu et al.[6] recently reported that the cationic isonitrile complex $[Cp(CO)Fe^{-}C{\equiv}N(CH_2)_3PPh_2]BF_4$ undergoes nucleophilic attack by $[PPh_2]K$ to give, after protonation, the iron η^1-α-phosphinocarbene complex $[Cp(CO)Fe{=}C(PPh_2)NH(CH_2)_3PPh_2]BF_4$. This complex, however, was seen to undergo spontaneous elimination of diphenylphosphine to restore the initial isonitrile complex.[6] Besides, Bertrand and co-workers proposed a totally different approach consisting in the elaboration of a stable α-phosphinocarbene *ligand* to be subsequently reacted with a transition-metal precursor. The method was applied to (*i*-Pr$_2$N)$_2$P(Ar)C: and illustrated by the synthesis of the Rh(I) complexes $L_2ClRh{=}C(2,6\text{-}C_6H_3(CF_3)_2)P(N(i\text{-}Pr)_2)_2$ (L_2 = $(CO)_2$, η^4-cod, η^4-nbd).[7a,b] Such a synthetic method, which could be later extended to the case of a cyclic α,α′-bisphosphinocarbene,[7c,d] rests on the availability of stable α-phosphinocarbenes, which remains highly challenging.[8] Clearly, the search for a simple and general route to transition-metal η^1-α-phosphinocarbene complexes is still of current interest.

For our part, inspired by Fischer's seminal work and engaged for some time in a general program aimed at exploiting the availability, ease of use, and high reactivity of cationic manganese carbyne complexes derived from cymantrene,[9] we envisioned that the deprotonation α-*phosphonio*carbene complexes[10] resulting from nucleophilic attack of secondary and/or primary phosphine on such carbyne species would possibly afford η^1-α-phosphinocarbene complexes. In a preliminary communication of the present work,[11] such an approach was found to be viable, offering multiple advantages, such as (i) the simplicity of the procedure, (ii) the absence of constraints about the steric bulk of phosphorus substituents, and (ii) the simplicity and diversity of the phosphorus sources, often being commercially available. The present report gives a detailed description of the synthesis of these η^1-phosphinocarbene complexes of manganese and provides an account of their intrinsic reactivity.

RESULT AND DISCUSSION

Synthesis and Characterization of the η^1-α-Phosphinocarbene Complexes Cp(CO)$_2$Mn=C(R)PHMes (3; 3a: R = Ph, R″ = Mes; 3b: R = Me, R″ = Mes) and of the η^3-Phosphinoketene Complexes Cp(CO)Mn(η^3-C(O)C(Ph)PR′R″) (4; 4c: R′ = R″ = Ph; 4d: R′ = R″ = *i*-Pr$_2$N; 4e: R′ = Me, R″ = Ph). *Synthesis.* The interaction of tertiary phosphines with electrophilic transition-metal carbyne complexes $[L_nM{\equiv}CR]^+$ to afford stable[10a−c] or highly reactive[10d−f] α-phosphoniocarbene complexes of the type $[L_nM{=}C(R)PR_3]^+$ is well documented. Likewise, we have observed that the primary phosphine H_2PMes as well as secondary phosphines $HPPh_2$, $HP(N(i\text{-}Pr)_2)_2$, or (±)-HPMeMes readily reacts with the cationic manganese carbyne complexes $[Cp(CO)_2Mn{\equiv}CR]BX_4$ ([**1**]BX_4; [**1a**]BX_4: R = Ph, X = Cl or Ph; [**1b**]BCl_4: R = Me)[11] under very mild conditions (CH_2Cl_2, −40 to −80 °C) to give the corresponding thermolabile α-phosphoniocarbene adducts, $[Cp(CO)_2Mn{=}C(Ph)P(H)R'R'']BX_4$ ([**2**]BX_4; Scheme 1). Complexes [**2**]BCl_4 each display two bands in the ν_{CO} region; for a typical example [**2a**]BCl_4: IR (CH_2Cl_2) 2020, 1960 cm^{-1} (ν_{CO})), at a position very similar to that of their closely related analogue $[Cp(CO)_2Mn{=}C(Ph)PMe_3]BCl_4$.[10b] Although compounds [**2**]BCl_4 were found to be stable for several hours below −40 °C, they generally decompose at room temperature, which prevents their isolation in analytically pure form. Yet, complex [**2e**]BPh_4, generated upon reaction of [**1a**]BPh_4 with $HP(N(i\text{-}Pr)_2)_2$, could be isolated in 92% yield and fully characterized by NMR, highlighting its carbene character ($^{13}C\{^1H\}$ NMR δ 325.2 (d, $^1J_{PC}$ = 24.5 Hz, Mn=*C*)).

Deprotonation of the transient α-phosphoniocarbene [**2a**, **b**]BCl_4 at low temperature cleanly afforded the corresponding η^1-α-phosphinocarbene complexes $Cp(CO)_2Mn{=}C(Ph)PH$-Mes (**3a**,**b**, Scheme 1) in reasonable yields. Optimal results were obtained using either neutral alumina, for [**2a**]BCl_4, or NEt_3, for [**2b**]BCl_4, as bases. Noticeably, the deprotonation of [**2a**]BPh_4 generated upon reaction of [**1a**]BPh_4 with H_2PMes at low temperature was found to occur spontaneously when the solution was allowed to warm up to room temperature, leading to **3a** as the sole product.

Addition of NEt_3, or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), to cold CH_2Cl_2 solutions of α-phosphoniocarbene complexes [**2c**,**d**]BCl_4 did produce a color change, but the expected η^1-α-phosphinocarbene derivatives could never be isolated. These complexes were found to be barely stable enough to be identified by IR spectroscopy, and only during the course of the deprotonation of **2e** could an IR spectrum attributable to **3e** be recorded (IR (CH_2Cl_2): 1957, 1898 (ν_{CO})). Actually, workup led instead to the new η^3-phosphinoketene complexes $Cp(CO)Mn(\eta^3\text{-}C(O)C(Ph)PR'R'')$ (**4c**−**e**, Scheme 1), which were fully characterized, including by X-ray diffraction (see below and the Supporting Information). These complexes may be regarded as deriving from the expected η^1-α-phosphinocarbene complexes **3c**−**e** upon coordination of the phosphorus atom to manganese and concomitant CO insertion into the manganese−carbene bond.[12] They could be subsequently obtained in almost quantitative yield upon treatment of [**1a**]BPh_4 with the appropriate

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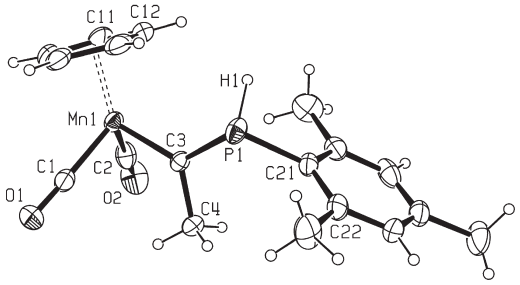


Figure 1. ORTEP drawing of **3b** (ellipsoids set at the 50% probability level). Selected bond lengths [Å] and angles [deg]: Mn1−C3 = 1.859(2), C3−P1 = 1.811(2), C3−C4 = 1.522(4); P1−C21 = 1.837(2); P1−H1 = 1.33(3); Mn1−C3−C4 = 124.96(17); Mn1−C3−P1 = 124.83(13); C4−C3−P1 = 109.84(16); C3−P1−C21 = 107.98(11); C3−P1−H1 = 101.0(12); C3−P1−H1 = 94.3(11).

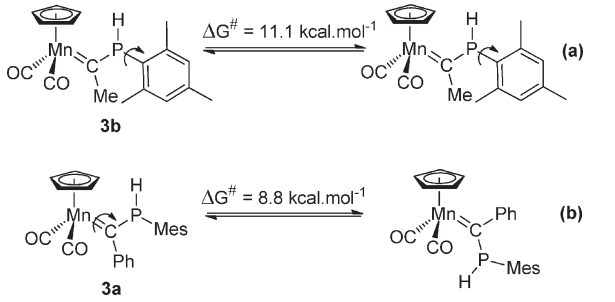
secondary phosphine, followed by addition of DBU at low temperature, and final warming to room temperature.

Analogous η^3-phosphinoketene complexes Cp(CO)Mn-(η^3-C(O)C(R)PHMes) (**4a**,**b**) were obtained from **3a**,**b** upon standing, along with the η^1-phosphaalkene derivatives Cp-$(CO)_2$Mn(η^1-P(Mes)=C(H)Ph) (**6a**,**b**). A specific paragraph will be devoted to the overall isomerization process (*vide infra*).

*Spectroscopic and Structural Characterization of the η^1-α-Phosphinocarbene Complexes **3a**,**b***. Complexes **3a**,**b** display characteristic low-field $^{13}C\{^1H\}$ NMR resonances at δ 358.2 and 366.5 ppm, respectively, with strong $^1J_{CP}$ direct coupling constants of 76 and 81 Hz, respectively, attributable to the carbene carbon atoms. $^{31}P\{^1H\}$ NMR spectra show singlets at δ 18.9 and 10.2 ppm, respectively. The IR spectra of **3a**,**b** in CH_2Cl_2 solution (**3a**: 1957, 1898 cm^{-1}; **3b**: 1970, 1906 cm^{-1}) display ν_{CO} stretching bands at frequencies much higher than those of homologous aminocarbene complexes such as $Cp(CO)_2Mn{=}C(Me)NHMe$,[13a] for instance ν_{CO} 1947, 1875 cm^{-1}, in a domain one would actually expect for non-heteroatom-substituted carbene complexes such as Cp-$(CO)_2Mn{=}CPh_2$[13b] (ν_{CO}: 1968, 1910 cm^{-1}). These data indicate that the present phosphinocarbene ligands are much less of electron donors than aminocarbene ligands and already suggest that the lone pair on phosphorus participates only very weakly in the carbene-to-metal bonding, contrary to the lone pair of the nitrogen atom in the parent aminocarbene complexes. The solid-state structure of **3b** corroborates such an analysis.

A perspective view of complex **3b** is shown in Figure 1. The carbene ligand displays the typical vertical coordination mode,[14] in which the carbene plane lies in the mirror plane of the $Cp(CO)_2Mn$ fragment ([cnt−Mn1−C3−P1]) = 7.1°; ideal, 0°), the PHMes substituent being on the Cp side. Noticeably, the manganese−carbene bond length (Mn1−C3 = 1.859(2) Å) appears to be among the shortest Mn=C bonds found in piano-stool Mn(I) carbene complexes,[15] including the non-heteroatom-substituted ones, and the phosphorus atom shows a significant pyramidalization (ΣP_α = 303°). This situation is in sharp contrast with the one found in homologous aminocarbene complexes, which invariably display (i) a long interatomic Mn=C bond distance,[16] actually being of the same magnitude as a Mn−C single bond, as found, for instance, in the Mn acyl complex $Cp(CO)_2Mn^-{-}C(O)Ph$ (1.951 Å),[17] and (ii) a trigonal-planar environment around N. This indicates that the phosphorus lone pair in the present phosphinocarbene complex

Scheme 2



is only partially delocalized over the P−$C_{carbene}$−Mn bonds. Yet, the corresponding bond length (P1−C3 = 1.811(2) Å) appears to be significantly shorter than the other one (P1−C21 = 1.837(2) Å), indicating that a certain degree of delocalization of the phosphorus lone pair occurs in the direction of the carbene carbon atom. Such a difference in the environment of the heteroatom in amino- and η^1-α-phosphinocarbene complexes was previously predicted on the basis of a DFT analysis of model tungsten carbene complexes of the type $(CO)_5W{=}C(R)XR'$ (X = N, P),[18] but we are observing here for the first time an effective pyramidalization around P. Indeed, in the only antecedent of structurally characterized η^1-α-phosphinocarbene complex, namely, (η^4-nbd)ClRh=C(Ar)P(N*i*-Pr_2)$_2$ (Ar = $C_6H_3(CF_3)_2$-2,6),[7a] the phosphorus atom was found to exhibit a trigonal-planar arrangement (ΣP_α = 358.3°) indicative of a significant contribution of the betaine σ-phosphavinyl form (η^4-nbd)$ClRh^-{-}C(Ar){=}P^+$(N*i*-Pr_2)$_2$ in that case,[19] certainly favored by the presence of the two amino substituents on phosphorus.

Finally, it is worth mentioning that examination of the NMR data in the temperature range 173−298 K reveals that complexes **3a**,**b** experience dynamic processes in solution. For complex **3b**, the observed motion translates into an exchange of *o*-Me groups of the mesityl substituent; examination of the coalescence behavior of the corresponding signals led to a $\Delta G^{\ddagger}$ value of 11.1 kcal mol^{-1}.[20] Such an exchange could be rationalized either in terms of a fast rotation [NMR time-scale] of the mesityl group around the P−C_{ipso} bond or in terms of an inversion of configuration at the phosphorus atom. However, we favor the first exchange pathway (Scheme 2a), considering that the value of the activation barrier of the present process, 11.1 kcal mol^{-1}, compares well with the value of the rotation barrier of the mesityl group in *t*-BuMesPH, 13.2 kcal mol^{-1},[21] and is considerably lower than the known unimolecular phosphorus inversion barrier for the free secondary phosphine (±)-Ph*i*-PrPH, which exceeds 23.3 kcal mol^{-1}.[22] Yet, it has to be taken into consideration that a possible contribution of the σ-phosphavinyl form Cp-$(CO)_2Mn^-{-}C(Me){=}P^+$HMes to the structure of **3b** may significantly lower the inversion barrier at phosphorus,[23] thus preventing totally excluding the latter hypothesis. Upon cooling, the ^1H NMR spectra of complex **3a** showed a more intricate evolution. In addition to changes in the 2.70−2.20 ppm region likely due, as above, to the hindered rotation of the Mes substituent, a second dynamic process that translates, in particular, into the splitting of the C_5H_5 resonance ($\Delta\delta$ = 0.38 ppm at 173 K) was clearly observed. Concomitantly, a splitting of the ^{31}P resonances was also detected. Examination of the coalescence

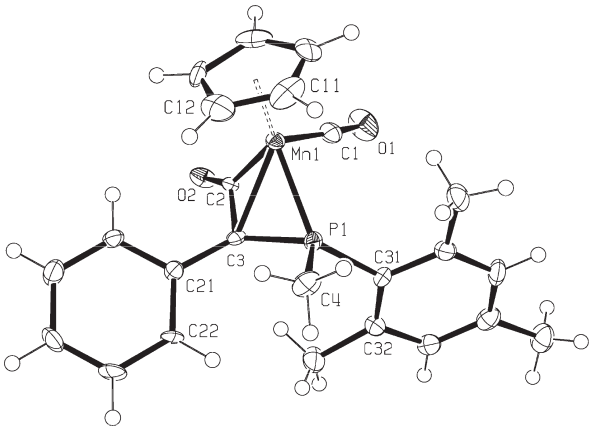


Figure 2. ORTEP drawing of $R_{Mn}R_P$-**4e** (ellipsoids are shown at the 30% probability level). Selected bond lengths [Å] and angles [deg]: Mn1−P1 = 2.1924(13), Mn1−C1 = 1.770(5), Mn1−C2 = 1.904(5), Mn1−C3 = 2.165(4), C1−O1 = 1.160(6), C2−O2 = 1.196(5), C2−C3 = 1.473(6), C3−P1 = 1.760(5), C4−P1 = 1.821(5); O2−C2−C3 = 135.0(4), C2−C3−P1 = 114.3(2).

behavior of the latter two signals in the 173−298 K range led to a $\Delta G^{\ddagger}$ value of 8.8 kcal mol^{-1} for the dynamic process involved. We tentatively attribute the second fluxional process to the fast rotation [NMR time-scale] of the carbene moiety around the Mn═C bond (Scheme 2b). It is noteworthy that the value of such a rotation barrier—8.8 kcal·mol^{-1}—is of the same magnitude as the one corresponding to the rotation barrier found in piano-stool Mn(I) vinylidene complexes (8.6−13.5 kcal mol^{-1}).[24]

*Spectroscopic and Structural Characterization of the η^3-Phosphinoketene Complexes **4a**−**e**.* The IR spectra of complexes **4a**−**e** in solution in CH_2Cl_2 display two bands, namely, a strong one in a 1918−1932 cm^{-1} range, attributed to the ν_{CO} of the unique carbonyl ligand, and a medium one in a 1697−1720 cm^{-1} range, attributed to the $\nu_{C=C=O}$ of the ketene ligand, which thus appears at a frequency close to that of η^2-ketene ligands in the parent $Cp(CO)_2Mn(\eta^2$-C(O)CRR) complexes.[25] The $^{13}C\{^1H\}$ NMR spectra of **4a**−**e** show distinct signals for the carbonyl ligands (Mn−*C*O: δ 230.4−234.1 ppm) and for the carbonyl of the ketene ligand (*C*═C═O: δ 237.5−239.9 ppm). The C_{sp2} carbon atom of the ketene moiety *C*═C═O appears at very high field (*C*═C═O: δ −36.2 to −24.7 ppm). The ^{31}P NMR spectra show a remarkable dispersion of signals due to the phosphorus atoms of the phosphinoketene ligand, which appear in a δ −41.4 (**4a**) to 110.4 (**4d**) ppm range (C_6D_6). Noticeably, the η^3-phosphinoketene complex **4e** (resulting from reaction of [**1a**]BPh_4 with (±)-HPMeMes), which possesses two stereogenic centers, namely, the manganese and the phosphorus atoms, is obtained as a single pair of diastereoisomers. The actual *RR*/*SS* stereochemistry of **4e** was determined by single-crystal X-ray diffraction analysis and was corroborated by 2D ROESY NMR experiments.

A perspective view of complex **4e**, isolated in the crystal in the $R_{Mn}R_P$ form, is shown in Figure 2.[26] The phosphinoketene ligand is indeed coordinated to the metal through P1 and through the carbon atoms C2 and C3 of the ketene moiety. The methyl substituent on P1 is located on the same side as the Cp ligand, conferring a $R_{Mn}R_P$ configuration to the complex. The Mn1−P1 bond is slightly shorter than typical Mn−P bonds in phosphorus-substituted Mn(I) piano-stool complexes (average value of 2.212 Å). Metrical features within the ketene moiety are similar to those found in other manganese η^2-ketene complexes[25] with, in particular, a manganese-to-central carbon atom distance (Mn1−C2 = 1.904(5) Å) longer than the manganese-to-terminal carbon atom distance (Mn1−C3 2.165(4) Å) and an elongated C2−C3 bond (C2−C3 = 1.473(6) Å) and a bent ketene moiety due to coordination (C3−C2−O2 = 135.0(4)°). The overall structure is similar to that of the related cationic tungsten complexes [Cp(CO)(L)W(η^3-C(O)C(R)PR_2)]X (L = PMe_3, R′ = Me, X = Cl; L = MeN≡C, R = Ph, R′ = Tol, X = BF_4), obtained upon reaction of chlorophosphine on cationic tungsten η^2-ketenyl complexes.[27]

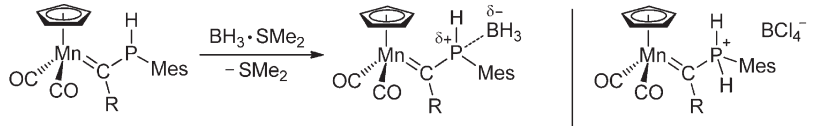
Reactions of η^1-α-Phosphinocarbene Complexes 3a,b with Lewis Acids and Relevant Modulation of the Electron Donicity of the Carbene Ligand. Keeping in mind the pyramidal arrangement of the phosphorus atom revealed by the X-ray diffraction study, we envisioned probing the availability of the phosphorus lone pair by coordination to a Lewis acid. The reaction of **3a,b** with the borane dimethylsulfide adduct at low temperature led to spectroscopically quantitative conversion of the starting compounds into the corresponding **5a,b** adducts (Scheme 3). Both complexes were fully characterized in solution by IR and NMR spectroscopy. A comparison of the IR spectra of **3a,b**, **5a,b**, and **2a,b** reveals a significant blue shift of the ν_{CO} stretching frequencies following the order $\langle\nu_{CO}\rangle$ **3a,b** < $\langle\nu_{CO}\rangle$ **5a,b** < $\langle\nu_{CO}\rangle$ **2a,b**, illustrating, as expected, that coordination of borane to the phosphorus atom in the η^1-α-phosphinocarbene complexes increases the electron acceptor ability of the overall carbene ligand, but not as much as a protonation at phosphorus. Although such an experiment brings further evidence for the availability of the phosphorus lone pair in the η^1-α-phosphinocarbene complexes **3a,b**, the thermal stability of the resulting α-phosphinocarbene complexes/borane adduct was found to be disappointingly low as compared with that of classical secondary phosphine/borane adducts,[28] and only **5a** could to be isolated in a pure form.

Further examination of the NMR spectra of **5a** in the 273−193 K range revealed, qualitatively, the same dynamic behavior as for **3a**, i.e., a decoalescence of the *o*-Me signals—magnetically equivalent at 273 K—at 243 K, followed by an additional decoalescence of the Cp resonance at δ 5.28 ppm into two distinct singlets at δ 5.76 (minor) and 5.51 (major) ppm, at 213 K. Concomitant splitting of the ^{31}P singlet at 28.8 ppm into two singlets at δ 30.8 (minor) and 28.0 (major) ppm was observed at 213 K. As for **3a**, the two dynamic processes are tentatively rationalized in terms of a fast rotation [NMR time-scale] of the mesityl group around the P−C_{ipso} bond and a fast rotation [NMR time-scale] of the carbene moiety around the Mn−C axis. Examination of the coalescence behavior of the appropriate signals led to estimated rotation barriers of 10.9 and 9.3 kcal mol^{-1} for the respective processes (Scheme 4).[20]

For complex **5b**, the magnetic inequivalence of the *o*-Me and *m*-H signals of the Mes substituent reveals a rigid [NMR time-scale] structure in solution at 273 K, but the relative instability of the complex in solution precluded a full analysis of its dynamic behavior.

Versatile Rearrangement of the η^1-α-Phosphinocarbene Complexes 3a,b Observed in a Nonpolar Solvent and under Basic Catalysis Conditions. Generation of the η^1-α-Phosphidocarbene Complex [7d]Li and Its Subsequent Isomerization into the Monocarbonyl Acyl Complex [8d]Li via Acid-Catalyzed Migratory CO Insertion. The η^1-α-phosphinocarbene complexes **3a,b** can be stored in the solid state at −20 °C for

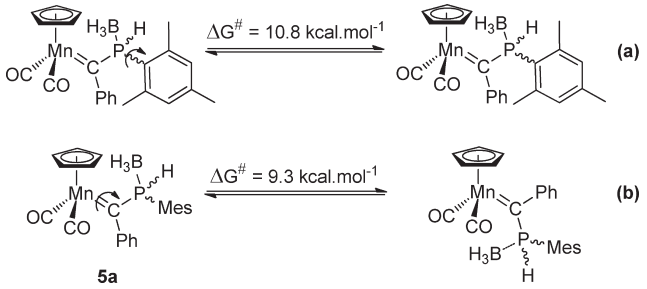
Scheme 3



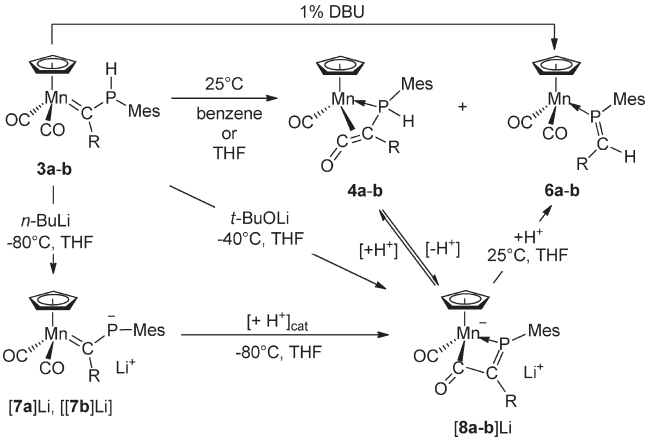
3a ν_{CO} 1973, 1910 cm^{-1} **5a** ν_{CO} 2003, 1941 cm^{-1} **2a** ν_{CO} 2021, 1960 cm^{-1}

3b ν_{CO} 1970, 1906 cm^{-1} **5b** ν_{CO} 1998, 1938 cm^{-1} **2b** ν_{CO} 2022, 1962 cm^{-1}

Scheme 4



Scheme 5



several months without significant decomposition. However, they cleanly rearrange in solution at room temperature to afford the corresponding η^3-phosphinoketene complexes Cp(CO)Mn(η^3-C(O)C(R)P(H)Mes), **4a**,**b**, along with the corresponding η^1-phosphaalkene complexes Cp(CO)$_2$Mn(η^1-P(Mes)=C(H)R) (**6a**,**b**, Scheme 5). Selected ^{31}P NMR monitoring data relative to this rearrangement are given in Table 1. Complex **4a**, which was fully characterized by IR and NMR spectroscopy, apparently forms as a single pair of diastereoisomers. Attempts to establish its stereochemistry by NMR remained inconclusive, due to the unavoidable presence of **3a** and **6a** in the samples. Complexes **6a**,**b** should be regarded as the thermodynamic products of the rearrangement process, since they are the sole remaining compounds observed after 3−4 days of reaction, then appearing as equilibrated mixtures of *E*/*Z* stereoisomers (**6a**: 60:40 *E*/*Z* ratio; **6b**: 55:45 *E*/*Z* ratio). No further interconversion of these *E*- and *Z*-isomers was observed for **6a**,**b** at room temperature, which is fully consistent with literature data.[29] The observed rearrangement of the η^1-α-phosphinocarbenes **3a**,**b** into the η^1-phosphaalkene complexes **6a**,**b** is reminiscent of the non-stereoselective migration of the *i*-Pr$_2$N group reported for the rhodium complex (CO)$_2$ClRh=C(Ar)P(N*i*Pr$_2$)$_2$, which was proposed to take place via a formal 1,2-amino group shift.[7a,b] With such a mechanistic proposal in mind, the present occurrence of η^3-phosphinoketene complexes **4a**,**b** as *apparent* intermediates on the way to the final products **6a**,**b** appeared rather puzzling, possibly indicating the occurrence of a competitive reaction pathway.

The structure of **6a**,**b** was established by the characteristic ^{1}H, ^{31}P, and ^{13}C NMR signals of the η^1-P(Mes)=C(H)R ligands, which are similar to those reported for η^1-P(Mes)=CPh$_2$ transition-metal complexes.[30] In the present case, the *E* or *Z* geometries around the P=C bond were inferred from additional NOE experiments.

Interestingly, the rearrangement was found to proceed faster in THF solution (ca. 36 h, and 1.5 h for **3a**, and **3b**, respectively) than in benzene or CH$_2$Cl$_2$, affording *in fine* the η^1-phosphaalkene complexes **6a**,**b**, in that case with ca. 95% *E*-selectivity. Again, the η^3-phosphinoketenes complexes **4a**,**b** were appearing in the course of the rearrangement. Keeping in mind that THF—unlike benzene and dichloromethane—can facilitate proton transfer processes and that related carbene-to-alkene rearrangements of group 6 Fischer-type alkoxycarbene complexes have been previously shown to be base-catalyzed,[31] we decided to examine the influence of an added base on the rearrangement processes encountered here. In a typical experiment, the addition of a catalytic amount (ca. 15%) of Et$_3$N to a solution of **3a** in CH$_2$Cl$_2$ at 25 °C resulted in its faster and spectroscopically quantitative conversion into **4a** within 2−3 min, whereas the subsequent rearrangement of **4a** into *E*-**6a** still required 3−4 h. It was found later that acceleration of this second step requires an excess of Et$_3$N (ca. 5 equiv), then leading to reaction completion within 5 min. By contrast, Et$_3$N did not affect the transformation of **3b** under the same reaction conditions, probably due to its lower P−H bond acidity. Effectively, the addition of a stronger base like DBU was found to promote the immediate and quantitative rearrangement of both **3a** and **3b** in CH$_2$Cl$_2$, affording the η^1-phosphaalkene species **6a** and **6b** with >99% *E*-selectivity. Let us recall that the base-catalyzed rearrangement of transition-metal alkoxycarbene complexes (CO)$_5$M=C(CH$_2$R)OR′ is typically *Z*-stereoselective.[31]

While looking for plausible explanations for the unexpected role of a CO insertion in the rearrangement process and eventually the origin of its stereoselectivity, we were led to investigate the deprotonation of the η^1-α-phosphinocarbene complexes **3a** and **3b**. Treatment of **3a** with *n*-BuLi in THF at −80 °C led smoothly to the formation of a deep red solution of the unprecedented anionic α-phosphidocarbene complex

Table 1. ^{1}H and ^{31}P NMR Monitoring of the Rearrangement of the η^1-α-Phosphinocarbene Complexes 3a,b at 298 K

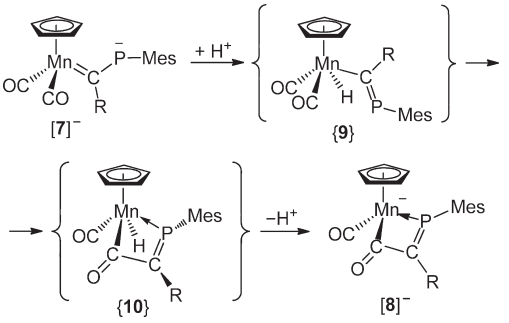
entry	complex	solvent, catalyst	reaction time	product(s), yield (*E*:*Z* ratio)
1	**3a**	C_6D_6	1 d	**4a**, 65% + **6a**, 34% (47:53)
2			3−4 d	**6a**, 100% (60:40)
3	**3b**	C_6D_6	3−4 d	**6b**, 100% (55:45)
4	**3a**	THF-d_8	4 h	**4a**, 67% + **6a**, 33% (95:5)
5		THF-d_8	36 h	**6a**, 100% (95:5)
6	**3b**	THF-d_8	30 min	**3b**, 15% + **4b**, 5% + **6b**, 80% (95:5)
7		THF-d_8	1.5 h	**6d**, 100% (95:5)
8	**3a**	CD_2Cl_2, NEt_3 (15%)	2−3 min	**4a**, 100%
9		CD_2Cl_2, NEt_3 (15%)	3−4 h	**6a**, 100%(99:1)
10		CD_2Cl_2, NEt_3 (500%)	5 min	**6a**, 100%(99:1)
11	**3b**	CD_2Cl_2, NEt_3 (500%)	30 min	**3b**, 90% + **6b**, 10% (55:45)
12	**3a**	CD_2Cl_2, DBU (1%)	1 min	**6a**, 100% (99:1)
13	**3b**	CD_2Cl_2, DBU (1%)	1 min	**6b**, 100% (99:1)

$[Cp(CO)_2Mn{=}C(Ph)PMes]Li$, [**7a**]Li, which appeared to be stable at room temperature for several hours (Scheme 5). Later on, it was found that complex [**7a**]Li can be also generated in one pot upon reaction of the carbyne precursor [**1a**]BPh_4 in THF with $MesPH_2$, followed by addition of *two* equivalents of *n*-BuLi at −80 °C. Although the formation of such anionic α-phosphidocarbene complexes is unprecedented, it is clearly reminiscent of the formation of anionic amidocarbene complexes upon deprotonation of Fischer-type aminocarbene complexes.[32]

Complex [**7a**]Li exhibits a three-band pattern in the ν_{CO} region (IR (THF): 1882 (vs), 1811 (s), 1772 (s) cm^{-1} (ν_{CO})), very similar to the one observed for the carbene anion $[Cp'(CO)_2Mn{=}C(OEt)CH_2]Li$ (IR (THF): 1870 (vs), 1795 (s), 1745 (s) cm^{-1} (ν_{CO}))[33] or for the η^1-allenyl anion $[Cp'(CO)_2Mn{-}C(Ph){=}C{=}C(Tol)Nu]Li$ (Nu = H, STol, PPh_2) (IR (THF): 1873 (vs), 1798 (s), 1755 (s) cm^{-1} (ν_{CO})).[34] The occurrence of a three-band pattern in these anionic dicarbonyl species was previously ascribed to an interaction of lithium cations with the oxygen atom of a CO group,[35] and it seems likely that the same phenomenon takes place here. Attempts to further characterize raw [**7a**]Li by NMR failed due to its extreme moisture sensitivity and unavoidable presence of paramagnetic impurities, whereas all attempts to purify it invariably led to the orange monocarbonyl acyl anion $[Cp(CO)_2Mn(\eta^2\text{-}C(O)C(Ph){=}PMes]Li$, [**8a**]Li (IR (THF): 1888 (s) cm^{-1} (ν_{CO}); 1620 (m) cm^{-1} ($\nu_{C=O}$)) (Scheme 5). It was soon found that the latter reaction is in fact acid-catalyzed. Indeed, addition of traces of water to a THF solution of [**7a**]Li was found to trigger its instantaneous and quantitative isomerization into [**8a**]Li, even at −80 °C. Parallel treatment of the η^1-α-phosphinocarbene complex **3b** by *n*-BuLi under the same reaction conditions led directly to the formation of the monocarbonyl species [**8b**]Li. The antecedent η^1-α-phosphidocarbene complex could not be intercepted in that case presumably due to the intrinsic existence of a proton source, namely, the methyl group in α-position relative to the carbenic carbon center.[36] Finally, the monocarbonylacyl anions [**8a**,**b**]Li could be conveniently generated through a deprotonation of carbene complexes with *t*-BuOLi, at −40 °C, in THF (Scheme 5).

The structure of [**8a**,**b**]Li was unambiguously established by $^{13}C\{^1H\}$ NMR spectroscopy, revealing in particular signals at δ 267.6−274.2 (s (br), *C*=O) and 233.6−235.6 (s (br), Mn−*C*O), along with the characteristic signal of the carbon of the four-membered ring (δ 143.2−146.4 (d, $^1J_{PC}$ = 57−60 Hz, P=*C*)). The latter data are in agreement with those reported for the related neutral iron complex $Cp(CO)Fe(\eta^2\text{-}C(O)C(R){=}PPR_2)$ (R = N*i*-Pr_2), exhibiting the same metallacyclic structure.[37]

Scheme 6



The present observation of an acid-catalyzed rearrangement of the dicarbonyl anion [**7a**,**b**]$^-$ into the monocarbonyl acyl derivatives [**8a**,**b**]$^-$ can be rationalized in terms of the proposed reaction sequence shown in Scheme 6 involving (i) a partial protonation of [**7**]$^-$ by a proton source, such as water, *t*-BuOH, or, in the case of **3b**, the η^1-α-phosphinocarbene carbene complex itself, giving the elusive hydridodicarbonyl species {**9**}; (ii) a fast migratory CO insertion of the σ-phosphaalkenyl fragment concomitant with coordination of the phosphorus atom to produce monocarbonylhydride {**10**}; and (iii) deprotonation of {**10**} by the remaining [**7**]$^-$ to give the final [**8**]$^-$.

The ease of the isomerization of {**9**} into {**10**} can be understood in terms of the enhanced electrophilicity of its carbonyl groups resulting from a reduction of the negative charge on the metal center upon protonation. This is reminiscent of earlier observations on the oxidative activation of the anionic acyl complex $[Cp'(CO)_2Mn{-}C(O)Tol\text{-}p]^-$[38] or neutral σ-alkyl[39] and σ-alkenyl[40] transition-metal complexes toward migratory CO insertion.

Finally, the protonation of [**8a**]Li with various proton sources ($HBF_4\cdot Et_2O$, NH_4Cl_{aq}, $[Et_3NH]Cl$) leads to a stereoselective formation of *E*-**6a** (Scheme 5). The protonation of [**8b**]Li proceeds similarly with the same *E*-stereoselectivity and typically

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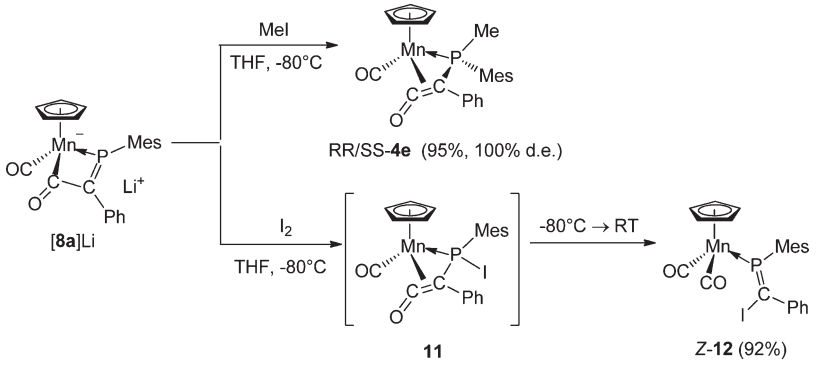
Scheme 7



faster than for [**8a**]Li when using weak acids (for [**8b**]Li reaction takes 15−20 min for completion, instead of 2 h required in the case of [**8a**]Li). Interestingly, the transient formation of the η^3-phosphinoketene complexes **4a** and **4b** was observed by IR spectroscopy only with the weakest proton donor, $[Et_3NH]^+$.

On the basis of the above observations, we propose that the base-catalyzed rearrangement of η^1-α-phosphinocarbene complexes **3a**,**b** into the η^1-phosphalkene complexes **6a**,**b** and—depending on the reaction conditions—the η^3-phosphaketene complexes **6a**,**b** proceeds *in THF or* CH_2Cl_2 through acidic−basic processes involving the anionic monocarbonyl acyl complexes [**8a**,**b**]$^-$ as *the key transient species*. The latter would arise from initial deprotonation of **3a**,**b** into the η^1-α-phosphidocarbene complex [**7a**,**b**]$^-$ followed by a CO insertion. Reversible protonation at the phosphorus atom would lead to the η^3-phosphinoketenes **4a**,**b**, which may or may not accumulate, depending on the strength of the base used as catalyst.[41] Competitive protonation at the central carbon atom and concomitant CO deinsertion would produce **6a**,**b** as the final product, under an exclusive *E* configuration.

In an effort to assess the above intermolecular acidic−basic process for the overall rearrangement **3a**,**b** → **6a**,**b** in THF—and to exclude an alternate direct intramolecular concerted 1,2-hydrogen shift,[42] which, we consider, could competitively operate in C_6D_6 to give the observed *E*/*Z* mixture of **6a**,**b** (Table 1)—we carried out crossover experiments with a mixture of the closely related $Cp(CO)_2Mn{=}C(p\text{-Tol})PHMes$, **3a**′, and deuterated *d*-**3a** complexes, in THF solution (see Experimental Section). Unfortunately, such an experiment did not shed light on the reaction mechanism since an unexpected quasi-instantaneous H/D exchange was found to occur between the two complexes, affording a statistical mixture of four possible carbene products, **3a**′, *d*-**3a**′, **3a**, and *d*-**3a**, generated before any other transformation.

Reactions of the Monocarbonyl Acyl Anion [8a]Li and the η^3-Phosphinoketene Derivatives with Electrophiles. Hoping to get additional clues about the η^1-α-phosphinocarbene/η^1-phospha-alkene rearrangement, we decided to examine the reactivity of the anion [**8a**]$^-$ toward electrophilic reagents in complement to the above protonation reactions.

The monocarbonyl acyl anion [**8a**]Li, generated upon treatment of the η^1-α-phosphinoketene complex **3a** with *t*-BuOLi at −80 °C, was found to react readily with MeI to afford the η^3-phosphinoketene complex *RR*/*SS*-**4e** (Scheme 7) in 95% yield and in a totally diastereoselective manner, in favor of the *RR*/*SS* diastereoisomer. On the other hand, reaction with iodine at −80 °C led to a thermally unstable species tentatively identified as the η^3-phosphinoketene complex $Cp(CO)_2Mn(\eta^3\text{-}C(O)C(Ph)PIMes)$, **11**, on the basis of its IR spectrum (IR (THF): 1945 (s) (ν_{CO}), 1736 (m) ($\nu_{C=C=O}$)). Upon warming to room temperature, the latter was found to rearrange into the η^1-phosphaalkene complex $Cp(CO)_2Mn(\eta^1\text{-}P(Mes){=}C(I)Ph)$, **12** (Scheme 7). Examination of the crude reaction mixture (after filtration through Celite) revealed two signals in the ^{31}P NMR, at δ 297 ppm (ca. 98%) and 302.3 ppm (ca. 2%), tentatively attributed to each the two isomers of **12**. After purification and recrystallization, the major compound was isolated in 92% yield and identified as the *Z* isomer on the basis of a single-crystal X-ray diffraction analysis. A perspective view of the complex is given in Figure 3. The transformation **11** → *Z*-**12** illustrates the possibility of a concerted 1,2-shift of the mobile group with concomitant CO deinsertion in manganese η^3-phosphinoketene complexes to give an η^1-phosphaalkene of *Z* conformation. This supports our view that the nonselective rearrangement of the η^1-α-phosphinocarbene **3a**,**b** into *E*- and *Z*-**6a**,**b** in a nonpolar solvent and in the absence of base may indeed be the result of competitive mechanisms, i.e., a concerted

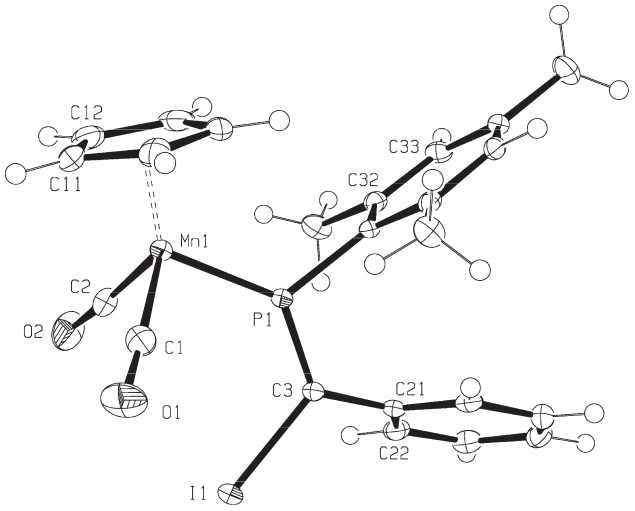


Figure 3. Perspective view of complex of *Z*-**12** (ellipsoids set at the 30% probability level). Selected bond lengths [Å]: Mn1−P1 2.1611(8), P1−C3 1.674(3), P1−C31 1.827(3), C3−C21 1.486(4), C3−I1 2.112(3).

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1,2-shift of the mobile proton responsible for the formation of the *Z* isomer and an acidic−basic process giving the *E* isomer, the latter pathway being largely favored in THF or in CH_2Cl_2 in the presence of base.

CONCLUSION

Whereas η^1-α-*phosphino*carbene complexes have long been regarded as elusive, except in rare specific examples, the present account has revealed a simple and rational synthetic pathway to such compounds, illustrated here by the case of manganese, and exploiting the ability of phosphines to form "*phosphonio*carbene" adducts with the electrophilic center of a cationic carbyne complex. Indeed, when such adducts are generated from a primary or a secondary phosphine, their simple deprotonation gives readily the desired η^1-α-phosphinocarbene complex. Here, the fully characterized η^1-α-phosphinocarbene complex **3**, derived from mesitylphosphine, was found to exhibit a fascinating reactivity characterized by a versatile behavior in the presence of different bases, in relevance to the mobility of the hydrogen atom remaining on its α-phosphorus center. Deprotonation of **3** by *n*-BuLi was found to yield the unprecedented α-*phosphido*carbene complex $[\mathbf{7}]^-$, which proved to be highly sensitive to traces of moisture and could be engaged in a proton-catalyzed isomerization to the acyl complex $[\mathbf{8}]^-$, a transformation understood as an unprecedented example of proton-induced migratory CO insertion. The key compound $[\mathbf{8}]^-$, also directly accessible from **3** upon treatment with *t*-BuOLi, is ultimately converted into the phosphaalkene complex **6** in a regioselective way upon stoichiometric addition of acids, affording the *E* derivative. By contrast, electrophilic addition of iodine to the same compound $[\mathbf{8}]^-$ gives the iodide-substituted phosphaalkene *Z*-**12** with opposite regioselectivity. The present work sheds new light on hitherto unknown and apparently complicated transformations of α-phosphinocarbene complexes, which are in fact perfectly rationalizable in terms of basic fundamental concepts.

EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Tetrahydrofuran and diethyl ether used for the synthesis were distilled under nitrogen from sodium benzophenone ketyl just prior to use. Other solvents (pentane, hexane, toluene, dichloromethane) were purified following standard procedure and stored under nitrogen. The following reagent grade chemicals BCl_3 (1.0 M solution in heptane), BH_3SMe_2 (2.0 M solution in toluene), *n*-BuLi (1.6 M solution in hexanes), $NaBPh_4$, MeI, I_2, D_2O, CF_3COOD, Et_3N, DBU, Ph_2PH, and *t*-BuOLi were obtained from commercial sources. Triethylamine and DBU were distilled over CaH_2 before use. Manganese complexes $Cp(CO)_2Mn{=}C(R)OEt$ (R = Me, Ph, *p*-Tol)[43] and $[Cp(CO)_2Mn{\equiv}C{-}Ph]BPh_4$ ($[\mathbf{1a}]BPh_4$)[9a] and phosphines $HP(Ni\text{-}Pr_2)_2$,[44] $MesPH_2$,[45] and Mes(Me)PH[46] were prepared according to known procedures.

A liquid nitrogen/ethanol slush bath was used to maintain samples at the desired low temperature. Chromatographic purification of the complexes was performed on silica (0.060−0.200 mm, 60 Å) or alumina (neutral, 0.050−0.200 mm, dried under vacuum at 150 °C during 4 h and stored under nitrogen) obtained from Acros Organics. Deuterium-enriched silica for purification of the deuterated phosphinocarbene complex *d*-**3a** was prepared by repetitive drying of SiO_2 at 150 °C and saturation with D_2O (three times). Solution IR spectra were recorded in 0.1 mm CaF_2 cells using a Perkin Elmer 983 G infrared spectrophotometer and are given in cm^{-1} with relative intensity in parentheses. ^1H, ^{31}P, ^{11}B, and ^{13}C NMR spectra were obtained on Bruker Avance 300, DPX 300, Avance 400, and Avance 500 spectrometers and referenced to the residual signals of deuterated solvent (^1H and ^{13}C) and to 85% H_3PO_4 and $BF_3{\cdot}OEt_2$ (^{31}P and ^{11}B, respectively, external standard). Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

Preparation of $MesPD_2$. Mesitylphosphine (0.76 g, 5 mmol) was dissolved in a mixture of THF (5 mL) and D_2O (3 mL, 150 mmol, >97% of deuterium), and a catalytic amount of CF_3COOD (12 μL, 0.1 mmol) was added. The solution was stirred at room temperature for 12 h; then THF was carefully evaporated under vacuum. The resulting emulsion was extracted with pentane (3 × 5 mL), the combined extracts were filtered through Celite and dried over CaH_2, and the pentane was evaporated under vacuum. The product thus obtained—containing ca. 15% of residual protons based on ^1H and ^{31}P NMR spectra—was treated again as described above to afford *in fine* $MesPD_2$ (0.68 g, 88% yield) with more than 96% isotopic purity, based on NMR analysis.

$MesPH_2$: ^1H NMR (400.1 MHz, C_6D_6, 298 K) δ 6.82 (s, 2H, *m*-H (Mes)), 3.72 (d, $^1J_{PH}$ = 203.8 Hz, 2H, PH_2), 2.32 (s, 6H, *o*-CH_3 (Mes)), 2.20 (s, 3H, *p*-CH_3 (Mes)); $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 25 °C) δ −155.9 (s).

MesPHD: ^1H NMR (400.1 MHz, C_6D_6, 298 K) δ 6.82 (s, 2H, *m*-H (Mes)), 3.70 (d (br), $^1J_{PH}$ = 203.8 Hz, 1H, PHD), 2.32 (s, 6H, *o*-CH_3 (Mes)), 2.20 (s, 3H, *p*-CH_3 (Mes)); $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 25 °C) δ −156.9 (t, $^1J_{PD}$ = 31.7 Hz).

$MesPD_2$: ^1H NMR (400.1 MHz, C_6D_6, 298 K) δ 6.82 (s, 2H, *m*-H (Mes)), 2.32 (s, 6H, *o*-CH_3 (Mes)), 2.20 (s, 3H, *p*-CH_3 (Mes)); $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 298 K) δ −157.9 (qv, $^1J_{PD}$ = 31.7 Hz).

Synthesis of $[Cp(CO)_2Mn{=}C(Ph)PH(Ni\text{-}Pr_2)_2]BPh_4$ ($[\mathbf{2d}]BPh_4$). The carbyne complex $[\mathbf{1a}]BPh_4$ (292 mg, 0.5 mmol) was suspended in CH_2Cl_2 (20 mL) at −50 °C, and $HP(Ni\text{-}Pr_2)_2$ (95 μL, 0.5 mmol) was added dropwise via syringe under vigorous stirring. The reaction mixture was allowed to slowly reach room temperature (ca. 1 h), giving a green solution of $[\mathbf{2d}]BPh_4$, which was filtered through Celite, concentrated to ca. 3 mL, and precipitated with diethyl ether (20 mL). The green solid obtained was washed with ether (3 × 10 mL) and dried under vacuum to afford 375 mg of $[\mathbf{2d}]BPh_4$ as a green powder (92% yield).

$[\mathbf{2d}]BPh_4$: ^1H NMR (300.1 MHz, CD_2Cl_2, 298 K) δ 8.12 (d, $^1J_{HP}$ = 546 Hz, 1H, PH), 7.60−6.70 (m, 25H, Ph), 5.09 (s, 5H, C_5H_5), 3.66 (m, 4H, $CH(CH_3)_2$), 1.44 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.13 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$); ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K) δ 25.5 (dt, $^1J_{HP}$ = 546 Hz, $^3J_{HP}$ = 14.0 Hz); $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2, 298 K) δ 325.2 (d, $^1J_{CP}$ = 24.7 Hz, Mn=*C*), 229.4 (d, $^3J_{CP}$ = 10.6 Hz, Mn−*C*O), 164.1−121.3 (Ph), 95.0 (s, C_5H_5), 48.8 (d, $^2J_{CP}$ = 4.7 Hz, $CH(CH_3)_2$), 23.5 (d, $^3J_{PC}$ = 1.7 Hz, $CH(CH_3)_2$), 22.8 (d, $^3J_{PC}$ = 3.8 Hz $CH(CH_3)_2$)); IR (CH_2Cl_2) 2018 (s), 1943 (s) (ν_{CO}). Anal. Calcd for $C_{50}H_{59}BMnN_2O_2P$: C, 73.53; H, 7.23; N, 3.43. Found: C, 72.90; H, 7.54; N, 3.25.

Synthesis of $Cp(CO)_2Mn{=}C(Ph)PHMes$ (3a) from $[\mathbf{1a}]BPh_4$. A sample of the carbyne complex $[\mathbf{1a}]BPh_4$ (292 mg, 0.5 mmol) was suspended in CH_2Cl_2 (20 mL) at −40 °C, and a solution of $MesPH_2$ (76 μL, 0.5 mmol) in CH_2Cl_2 (1 mL) was added dropwise via syringe under stirring. After stirring for 30 min, a homogeneous green solution was obtained. IR monitoring showed the phosphinocarbene complex **3a** to be the sole reaction product (IR (CH_2Cl_2): 1973 (s), 1910 (s) (ν_{CO})). The solvent was removed under vacuum, and the green residue was purified by a rapid column chromatography on silica (2 × 10 cm), under a nitrogen atmosphere. The green band of **3a** was eluted with pure hexane to afford 162 mg of crude product after solvent removal (78% yield). Subsequent recrystallization from pentane at −20 °C afforded 135 mg of analytically pure **3a** as black crystals (65% yield).

3a: ^1H NMR (300.1 MHz, toluene-d_8, 298 K) δ 6.99 (t, $^3J_{HH}$ = 6.6 Hz, 2H, *m*-H (Ph)), 6.81 (t, $^3J_{HH}$ = 6.6 Hz, 1H, *p*-H (Ph)), 6.80 (d, $^1J_{HP}$ = 260.4 Hz, 1H, PHMes), 6.69 (s, 2H, *m*-H (Mes)), 6.61

(d, $^3J_{HH}$ = 7.3 Hz, 2H, *o*-H (Ph)), 4.49 (s, 5H, C_5H_5), 2.52 (s, 6H, *o*-CH_3 (Mes)), 2.04 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, toluene-d_8, 298 K) δ 18.9 (d, $^1J_{HP}$ = 260.4 Hz); $^{13}C\{^1H\}$ NMR (125.8 MHz, toluene-d_8, 240 K) δ 358.2 (d, $^1J_{CP}$ = 75.5 Hz, Mn=*C*−P), 233.0 (s (br), Mn−*C*O), 142.9−118.2 (Ph and Mes), 90.5 (s, C_5H_5), 24.1 (s (br), *o*-CH_3 (Mes)), 20.9 (s, *p*-CH_3 (Mes)); IR (CH_2Cl_2) 1973 (s), 1910 (s) (ν_{CO}). Anal. Calcd (%) for $C_{23}H_{22}MnO_2P$: C, 66.35; H, 5.29. Found: C, 66.33; H, 5.54.

Synthesis of Cp(CO)$_2$Mn=C(Ph)PDMes (*d*-3a). A sample of the carbyne complex [**1a**]BPh_4 (175 mg, 0.3 mmol) was suspended in CH_2Cl_2 (10 mL) at −40 °C, and a solution of $MesPD_2$ (46 μL, 0.3 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise via syringe. After stirring for 30 min, a homogeneous green solution was obtained. The solvent was removed under vacuum, and the green residue was purified by column chromatography on a deuterium-enriched silica column (1 × 3 cm), under a nitrogen atmosphere. The green band of *d*-**3a** was eluted with pure hexane. The resulting green solution was filtered through Celite, concentrated, and crystallized at −20 °C, affording 77 mg of *d*-**3d** as black crystals (62% yield). The isotopic purity of the compound thus prepared was estimated by ^{1}H and ^{31}P NMR spectra to be higher than 93%.

d-***3a***: ^{31}P NMR (162.0 MHz, C_6D_6, 298 K) δ 17.7 (t, $^1J_{PD}$ = 40.1 Hz, PDMes).

Synthesis of Cp(CO)$_2$Mn=C(*p*-Tol)PHMes (3a′). Boron trichloride (4.4 mL of 1.0 M solution in heptane, 4.4 mmol) was added rapidly to a solution of Cp(CO)$_2$Mn=C(*p*-Tol)OEt (650 mg, 2 mmol) in hexane (40 mL) cooled to −60 °C, under vigorous stirring. After stirring for an additional 15 min, the supernatant was removed by means of a cannula tipped with filter paper. The pale yellow precipitate of [Cp(CO)$_2$Mn≡C(*p*-Tol)]BCl_4, [**1a′**]BCl_4 was washed with hexane (20 mL) and then suspended in CH_2Cl_2 (30 mL). A solution of $MesPH_2$ (0.3 mL, 2 mmol) in CH_2Cl_2 (2 mL) was added dropwise at −80 °C via syringe. This resulted in the formation of a deep green solution of [Cp(CO)$_2$Mn=C(*p*-Tol)PH_2Mes]BCl_4, [**2a′**]BCl_4 (IR (CH_2Cl_2): 2021 (s), 1958 (s) (ν_{CO})). The cold solution was rapidly filtered through a short column of alumina, which was subsequently washed with cold (−80 °C) ether (30 mL). [**NOTE:** the alumina used for the filtration should be thoroughly dried, otherwise the yield in **3a′** drastically decreases.] The resulting solution was evaporated under vacuum at ca. −20 °C, giving a green-brown residue, which was extracted with a 4:1 hexane−CH_2Cl_2 mixture (4 × 15 mL), whereas the extracts were filtered through Celite. The resulting green solution was concentrated under vacuum and left overnight at −20 °C to give **3a′** as a microcrystalline material. After removal of the supernatant by decantation, the residue was washed with pentane (2 × 10 mL) and finally dried under vacuum to afford 404 mg of **3a′** obtained as a brown microcrystalline solid (47% yield).

Complex **3a** (358 mg, 43% yield) could be prepared according to the same procedure from Cp(CO)$_2$Mn=C(Ph)OEt (620 mg, 2 mmol), BCl_3 (4.4 mL of 1.0 M solution in heptane, 4.4 mmol), and $MesPH_2$ (0.3 mL, 2 mmol).

3a′: ^{1}H NMR (400.1 MHz, C_6D_6, 298 K) δ 6.85 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-H (*p*-Tol)), 6.83 (d, $^1J_{PH}$ = 260.6 Hz, 1H, P*H*Mes), 6.71 (s, 2H, *m*-H (Mes)), 6.62 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *m*-H (*p*-Tol)), 4.53 (s, 5H, C_5H_5), 2.57 (s, 6H, *o*-CH_3 (Mes)), 2.03 (s, 3H, *p*-CH_3 (Mes)), 2.02 (s, 3H, *p*-CH_3 (*p*-Tol)). ^{31}P NMR (162.0 MHz, C_6D_6, 298 K) δ 18.5 (d, $^1J_{PH}$ = 260.6 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 253 K) δ 360.1 (d, $^1J_{PC}$ = 76.1 Hz, Mn=*C*−P), 233.0 (s (br), Mn−*C*O), 143.4−118.2 (*p*-Tol and Mes), 90.8 (s, C_5H_5), 24.1 (d, $^3J_{PC}$ = 11.1 Hz, *o*-CH_3 (Mes)), 21.0 (s, *p*-CH_3 (Mes)), 20.8 (s, *p*-CH_3 (*p*-Tol)); IR (CH_2Cl_2) 1971 (s), 1909 (s) (ν_{CO}). Anal. Calcd for $C_{24}H_{24}MnO_2P$: C, 66.98; H, 5.58. Found: C, 67.16; H, 5.72.

Synthesis of Cp(CO)$_2$Mn=C(Me)PHMes (3b). Boron trichloride (5.3 mL of 1.0 M solution in heptane, 5.3 mmol) was added rapidly to a solution of Cp(CO)$_2$Mn=C(Me)OEt (600 mg, 2.4 mmol) in hexane (40 mL) cooled to −60 °C, under vigorous stirring. After stirring for an additional 15 min, the supernatant was removed by means of a cannula tipped with filter paper. The pale yellow precipitate of [**1b**]BCl_4 was washed with hexane (20 mL) and then suspended in CH_2Cl_2 (30 mL). A solution of $MesPH_2$ (0.37 mL, 2.4 mmol) in CH_2Cl_2 (2 mL) was added dropwise at −80 °C via syringe. This resulted in the formation of a deep blue solution of [**2b**]BCl_4 (IR (CH_2Cl_2): 2022 (s), 1962 (s) (ν_{CO})). An excess of Et_3N (0.68 mL, 4.8 mmol) was then added, causing the reaction medium to turn deep green. IR monitoring showed the phosphinocarbene complex **3b** to be the sole reaction product (IR (CH_2Cl_2): 1970 (s), 1906 (s) (ν_{CO})). The cold solution was rapidly filtered through a short column of alumina, and the volatiles were removed under vacuum. The green-brown residue was purified by rapid column chromatography on silica (2 × 10 cm), under a nitrogen atmosphere. The deep green band of **3b** was eluted with pure hexane, affording 600 mg of crude product after solvent removal (70% yield). Subsequent recrystallization of the product from pentane at −20 °C afforded 490 mg of analytically pure **3b** as green-black crystals (58% yield), some of them being suitable for an X-ray diffraction analysis.

3b: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 6.84 (s, 2H, *m*-H (Mes)), 6.39 (d, $^1J_{HP}$ = 261.5 Hz, 1H, P*H*Mes), 4.72 (s, 5H, C_5H_5), 3.16 (d, $^3J_{HP}$ = 14.5 Hz, 3H, Mn=C−*CH*$_3$), 2.43 (s, 6H, *o*-CH_3 (Mes)), 2.19 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ 10.15 (dq, $^1J_{HP}$ = 261.5 Hz, $^3J_{HP}$ = 14.5 Hz); $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 298 K) δ 366.5 (d, $^1J_{CP}$ = 81.0 Hz, Mn=*C*−P), 232.6 (s (br), Mn−*C*O), 143.1−128.4 (Ph and Mes), 90.4 (s, C_5H_5), 47.7 (d, $^2J_{CP}$ = 11.5 Hz, Mn=C−*CH*$_3$), 23.5 (d, $^3J_{CP}$ = 11.5 Hz, *o*-*CH*$_3$ (Mes)), 20.9 (s, *p*-CH_3 (Mes)); IR (CH_2Cl_2) 1970 (s), 1906 (s) (ν_{CO}). Anal. Calcd for $C_{18}H_{20}MnO_2P$: C, 61.02; H, 5.65. Found: C, 60.73; H, 5.49.

Synthesis of Cp(CO)Mn(η^3-C(O)C(Ph)PPh$_2$) (4c). A sample of the carbyne complex [**1a**]BPh_4 (292 mg, 0.5 mmol) was suspended in CH_2Cl_2 (20 mL) at −50 °C, and Ph_2PH (87 μL, 0.5 mmol) was added dropwise via syringe under vigorous stirring. IR monitoring showed the reaction to be complete within 30 min, giving a green solution of [Cp(CO)$_2$Mn=C(Ph)PPh_2H]BPh_4 ([**2c**]BPh_4) (IR (CH_2Cl_2): 2020 (s), 1960 (s) (ν_{CO})). The reaction mixture was cooled to −80 °C and treated with one equivalent of DBU (76 μL, 0.5 mmol). This resulted in the formation of a brown solution of a thermally unstable intermediate. Upon subsequent warming up to −20 °C, the color of the solution turned red and the IR monitoring showed complex **4c** to be the only reaction product (IR (CH_2Cl_2) 1932 (s) (ν_{CO}), 1700 (m) ($\nu_{C=C=O}$)). After solvent removal under vacuum at −20 °C, the resulting red, waxy residue was extracted with a 2:1 toluene−pentane mixture (4 × 5 mL) at the same temperature and separated from [DBUH]BPh_4 by filtration through Celite. Pentane (40 mL) was added to the combined extracts, and the solution was left overnight at −20 °C, causing complex **4c** to crystallize out as a microcrystalline powder. The supernatant was removed, and the precipitate was washed with pentane (2 × 10 mL) and dried under vacuum to afford 180 mg of **4c** as a brown microcrystalline solid (80% yield). Crystals of **4c** suitable for an X-ray diffraction analysis were grown from a diethyl ether−hexane mixture, at room temperature.

4c: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 6.90−7.70 (m, 15H, Ph), 4.65 (s, 5H, C_5H_5); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ 25.85 (s); $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 298 K) δ 238.6 (d, $^2J_{CP}$ = 24.4 Hz, P-C=*C*=O), 231.6 (d, $^2J_{CP}$ = 34.8 Hz, Mn-*C*O), 138.4−124.5 (Ph), 85.7 (s, C_5H_5), −28.6 (d, $^1J_{CP}$ = 32.2 Hz, P-*C*=C=O); IR (CH_2Cl_2) 1932 (s) (ν_{CO}), 1700 (m) ($\nu_{C=C=O}$). Anal. Calcd for $C_{26}H_{20}MnO_2P$: C, 69.33; H, 4.44. Found: C, 68.83; H, 4.87.

Synthesis of Cp(CO)Mn(η^3-C(O)C(Ph)P(N*i*-Pr$_2$)$_2$) (4d). A solution of complex [**2d**]BPh_4 generated from [**1a**]BPh_4 (292 mg, 0.5 mmol) and HP(N*i*-Pr$_2$)$_2$ (95 μL, 0.5 mmol) as described above was cooled to −80 °C and treated with DBU (76 μL, 0.5 mmol) to give an intense red-violet solution containing a thermally unstable intermediate.

The cooling bath was removed, and the reaction mixture was allowed to slowly reach room temperature (ca. 1 h), giving a red solution of complex **4d** (IR (CH_2Cl_2): 1918 (s) (ν_{CO}), 1697 (m) ($\nu_{C=C=O}$)). The solvent was removed under vacuum, and then the product was thoroughly extracted with ether (6 × 10 mL). The combined extracts were filtered through Celite, and the solvents were removed under vacuum. The remaining microcrystalline orange powder was washed with pentane (2 × 10 mL) and dried under vacuum to afford 235 mg of pure **4d** (95% yield). Crystals of **4d** suitable for an X-ray diffraction analysis were grown from a diethyl ether−hexane mixture, at room temperature.

4d: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 7.53 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *o*-H (Ph)), 7.25 (t, $^3J_{HH}$ = 7.4 Hz, 2H, *m*-H (Ph)), 7.15 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-H (Ph)), 4.63 (s, 5H, C_5H_5), 4.24 (d sept, $^3J_{HP}$ = 11.0 Hz, $^3J_{HH}$ = 7 Hz, 2H, $CH(CH_3)_2$), 3.87 (sept (br), $^3J_{HP}$ = 7.4 Hz, $^3J_{HH}$ = 6.6 Hz, 2H, $CH(CH_3)_2$), 1.35 (d (br) $^3J_{HH}$ = 5.4 Hz, 6H, $CH(CH_3)_2$), 1.13 (d, $^3J_{HH}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.07 (d, $^3J_{HH}$ = 7.0 Hz, 3H, $CH(CH_3)_2$); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ 110.4 (dd, $^3J_{HP}$ = 11.0 Hz, $^3J_{HP}$ = 7.4 Hz); $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 298 K) δ 237.5 (d, $^2J_{CP}$ = 28.5 Hz, P−C=C=O), 234.1 (d, $^2J_{CP}$ = 47.0 Hz, Mn-*C*O), 137.8−125.4 (Ph), 85.5 (s, C_5H_5), 51.0 (s (br), 49.4 (d, $^2J_{CP}$ = 12.0 Hz, $CH(CH_3)_2$), 25.0 (s, $CH(CH_3)_2$), 23.4 (d, $^3J_{CP}$ = 6.0 Hz, $CH(CH_3)_2$), 23.1 (s (br), $CH(CH_3)_2$), −36.2 (d, $^1J_{CP}$ = 43.0 Hz, P-*C*=C=O); $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 193 K) δ 245.2 (d, $^2J_{CP}$ = 26.5 Hz, P-C=*C*=O), 233.3 (d, $^2J_{CP}$ = 43.0 Hz, Mn-*C*O), 135.7−122.2 (Ph), 86.1 (s, C_5H_5), 52.9, 48.1 (s, $CH(CH_3)_2$), 41.5, 34.9, (s (br), $CH(CH_3)_2$), 21.3, 25.5, 27.9, 29.6 (s, $CH(CH_3)_2$), −34.6 (d, $^1J_{CP}$ = 42.5 Hz, P-C=*C*=O); IR (CH_2Cl_2) 1918 (s) (ν_{CO}), 1697 (m) ($\nu_{C=C=O}$). Anal. Calcd for $C_{26}H_{38}O_2MnN_2P$: C, 62.90; H, 7.66; N, 5.65. Found: C, 63.25; H, 7.42; N, 5.58.

Synthesis of *RR/SS*-Cp(CO)Mn(η^3-C(O)C(Ph)P(Me)Mes) (*RR/SS*-4e). A sample of the carbyne complex [**1a**]BPh_4 (292 mg, 0.5 mmol) was suspended in CH_2Cl_2 (20 mL) at −50 °C, and Mes(Me)PH (83 μL, 0.5 mmol) was added dropwise via syringe under vigorous stirring. IR monitoring showed the reaction to be complete within 30 min, giving a green-brown solution of [$Cp(CO)_2Mn$=C-(Ph)P(Me)(Mes)H]BPh_4 ([**2e**]BPh_4) (IR (CH_2Cl_2): 2018 (s), 1958 (s) (ν_{CO})). The reaction mixture was cooled to −80 °C and treated with one equivalent of DBU (76 μL, 0.5 mmol). This resulted in the formation of a brown solution containing an elusive thermally unstable intermediate (IR (CH_2Cl_2): 1957 (s), 1898 (s) (ν_{CO})). Upon subsequent warming to room temperature, the color of the solution turned red. At that stage, IR monitoring revealed complex **4e** as the sole reaction product (IR (CH_2Cl_2) 1930 (s) (ν_{CO}), 1720 (m, br) ($\nu_{C=C=O}$)). After the solvent was removed under vacuum, the red, waxy residue was extracted with ether (4 × 5 mL) and separated from [DBUH]BPh_4 by filtration through Celite. The combined extracts were evaporated under vacuum, giving the crude complex **4e**, an analytically pure sample of which was prepared by recrystallization from an ether−hexane mixture to afford 183 mg of **4e** as a red microcrystalline solid (85% yield), containing some crystals suitable for an X-ray diffraction analysis.

RR/SS-***4e***: ^{1}H NMR (400.1 MHz, C_6D_6, 298 K) δ 7.56 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *o*-H (Ph)), 7.26 (t overlapped with residual solvent protons, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-H (Ph)), 7.12 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-H (Ph)), 6.80 (d, $^4J_{PH}$ = 4.8 Hz, 1H, *m*-H (Mes)), 6.56 (s, 1H, *m*-H (Mes)), 4.39 (d, J_{PH} = 1.2 Hz, 5H, C_5H_5), 2.81 (s, 3H, *o*-CH_3 (Mes)), 2.59 (s, 3H, *o*-CH_3 (Mes)), 2.07 (s, 3H, *p*-CH_3 (Mes)), 1.58 (d, $^2J_{PH}$ = 11.7 Hz, 3H, PCH_3); ^{31}P NMR (162.0 MHz, C_6D_6, 298 K) δ −7.8 (s); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K) δ 238.7 (d, $^2J_{CP}$ = 20.8 Hz, P-C=*C*=O), 230.9 (d, $^2J_{CP}$ = 29.0 Hz, Mn-*C*O), 142.3−124.4 (Ph and Mes), 85.2 (s, C_5H_5), 23.0 (d, $^3J_{PC}$ = 4.2 Hz, *o*-CH_3 (Mes)), 21.3 (d, $^3J_{PC}$ = 16.6 Hz, *o*-CH_3 (Mes)), 20.8 (s, *p*-CH_3 (Mes)), 13.4 (d, $^1J_{PC}$ = 26.3 Hz, PCH_3), −24.7 (d, $^1J_{CP}$ = 33.2 Hz, P-*C*=C=O); IR (CH_2Cl_2) 1930 (s) (ν_{CO}), 1720 (m, br) ($\nu_{C=C=O}$). Anal. Calcd for $C_{24}H_{24}MnO_2P$: C, 66.98; H, 5.58. Found: C, 66.69; H, 5.73.

Synthesis of $Cp(CO)_2Mn$=C(Ph)P(BH_3)(H)Mes (5a). A solution of $BH_3 \times SMe_2$ (0.18 mL of 2.0 M solution in toluene, 0.36 mmol) was added dropwise to a solution of complex **3a** (125 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) cooled to −30 °C under stirring. After 30 min, IR monitoring revealed the presence of complex **5a** as the sole reaction product (IR (CH_2Cl_2): 2003 (s), 1941 (s) (ν_{CO})). The volatiles were removed under vacuum at ca. −10 °C, and the residue was extracted with a 4:1 hexane−CH_2Cl_2 mixture (3 × 5 mL). The combined extracts kept at −10 °C were rapidly filtered through Celite into the flask cooled at −10 °C, concentrated at ca. 0 °C until the beginning of the crystallization, and finally left at −20 °C overnight. The precipitate thus obtained was separated by decantation, washed with pentane (2 × 5 mL), and dried under vacuum to afford 97 mg of complex **5a** as a green microcrystalline powder (75% yield).

Although quite stable in the solid state, complex **5a** was seen to gradually decompose in solution at room temperature, with concomitant formation of paramagnetic impurities. Accordingly, samples suitable for NMR analysis were prepared upon dissolution of **5a** in CD_2Cl_2 at −40 °C followed by a rapid filtration through Celite directly into the NMR tube, which was then inserted into a precooled (−40 °C) NMR probe.

5a: ^{1}H NMR (400.1 MHz, CD_2Cl_2, 298 K) δ 7.11 (m, 3H, *m*-H + *p*-H (Ph)), 7.06 (d (br), $^1J_{HP}$ = 395 Hz, 1H, P*H*(BH_3)Mes), 6.79 (m, 2H, *o*-H (Ph)), 6.44 (s, 2H, *m*-H (Mes)), 5.28 (s, 5H, C_5H_5), 2.26 (s, 3H, *p*-CH_3 (Mes)), 2.18 (s, 6H, *o*-CH_3 (Mes)), 1.70−0.60 (two singlets at 1.32 and 0.93 on the broad multiplet background, 3H, PH(BH_3)Mes)); ^{1}H NMR (400.1 MHz, CD_2Cl_2, 193 K) δ 7.29 (s (br), 1H, *m*-H (Mes)), 7.01 (d (br), $^1J_{HP}$ = 400 Hz, 1H, P*H*(BH_3)Mes), 7.20−6.70 (m, 5H, Ph), 6.60 (s, 1H, *m*-H (Mes)), 5.76 (s, C_5H_5 minor isomer), 5.51 (s, C_5H_5 major isomer), 2.43 (s, 3H, *o*-CH_3 (Mes)), 2.20 (s, 3H, *p*-CH_3 (Mes)), 1.60 (s, 3H, *o*-CH_3 (Mes)), 1.30−0.70 (m, 3H, PH-(BH_3)Mes)); ^{31}P NMR (162.0 MHz, CD_2Cl_2, 233 K) δ 28.8 (d (br), $^1J_{HP}$ = 400.5 Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 193 K) δ 30.8 (s, minor isomer), 28.0 (s, major isomer); $^{11}B\{^1H\}$ NMR (128.4 MHz, CD_2Cl_2, 233 K) δ −33.6 (s); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 213 K) δ 230.6 (s (br), Mn-*C*O), 145.7−125.6 (Ph and Mes), 93.0 (s, C_5H_5), 24.2, 21.7 (s, *o*-CH_3 (Mes)), 21.3 (s, *p*-CH_3 (Mes)); IR (CH_2Cl_2) 2003 (s), 1941 (s) (ν_{CO}). Anal. Calcd (%) for $C_{23}H_{25}BMnO_2P$: C, 64.19; H, 5.81. Found: C, 64.00; H, 6.09.

Formation of $Cp(CO)_2Mn$=C(Me)P(BH_3)(H)Mes (5b). A solution of $BH_3 \times SMe_2$ (0.12 mL of 2.0 M solution in toluene, 0.24 mmol) was added dropwise to a solution of complex **3b** (70 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) cooled to −40 °C under stirring. After 30 min, IR monitoring revealed the presence of complex **5b** as the sole reaction product (IR (CH_2Cl_2): 1998 (s), 1932 (s) (ν_{CO})). The volatiles were removed under vacuum at ca. −20 °C, giving **5b** as a brown solid. All attempts to prepare an analytically pure sample of the latter by crystallization failed due to the thermal instability of the compound. A sample suitable for NMR analysis was prepared upon dissolution of crude **5b** in CD_2Cl_2 at −40 °C followed by a rapid filtration through Celite directly into the NMR tube, which was then rapidly inserted into a precooled (−40 °C) NMR probe. A gradual increase in the temperature of the sample allowed us to obtain good quality ^{1}H spectra in a −40 to 0 °C temperature range (rapid decomposition was observed at room temperature over 1−2 min).

5b: ^{1}H NMR (400.1 MHz, CD_2Cl_2, 273 K) δ 6.98 (s, 2H, *m*-H (Mes)), 6.81 (d (br), $^1J_{HP}$ = 398 Hz, 1H, P*H*(BH_3)Mes), 5.35 (s, 5H, C_5H_5), 3.08 (d, $^3J_{HP}$ = 18.0 Hz, 3H, Mn=C-CH_3), 2.51 (s, 3H, *o*-CH_3 (Mes)), 2.32 (s, 3H, *p*-CH_3 (Mes)), 2.28 (s, 3H, *o*-CH_3 (Mes)), 1.90−0.60 (m (br), 3H, PH(BH_3)Mes)); ^{31}P NMR (162.0 MHz, CD_2Cl_2, 233 K) δ 26.8 (d (br), $^1J_{HP}$ = 404 Hz); $^{11}B\{^1H\}$ NMR (128.4 MHz, CD_2Cl_2, 233 K) δ −21.0 (s); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 233 K) δ 341.6 (d (br), $^1J_{CP}$ = 27.0 Hz, Mn=*C*-P), 231.3 (s (br), Mn-*C*O), 143.2−130.2 (Mes), 92.1 (s, C_5H_5), 48.6 (d, $^2J_{CP}$ = 13.0

Hz, Mn=C-CH_3), 26.2, 23.9 (s, *o*-CH_3 (Mes)), 21.2 (s, *p*-CH_3 (Mes)); IR (CH_2Cl_2) 1998 (s), 1932 (s) (ν_{CO}).

Evolution of Cp(CO)$_2$Mn=C(Ph)PHMes (3a) in Benzene Solution. Complex **3a** (42 mg, 0.1 mmol) was dissolved in 0.5 mL of C_6D_6, and the solution was filtered through a plug of Celite directly into an NMR tube for monitoring. The composition of the solution was analyzed by integration of the ^{1}H and ^{31}P NMR signals. After 30 min at room temperature, NMR monitoring revealed the presence of **3a** (87%), **4a** (~10%), and **6a** (~3%). After 24 h, **3a** was present in only trace amounts (~1%), with **4a** being the major compound (65%), along with **6a** (34%; 53:47 *E*/*Z* ratio). After 3 days, NMR monitoring showed **4a** in only trace amounts (~3%), **6a** being then the main product (97% yield; 60:40 *E*/*Z* ratio).

4a: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 7.56 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-H (Ph)), 7.20 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-H (Ph)), 7.09 (t, $^3J_{HH}$ = 7.0 Hz, 1H, *p*-H (Ph)), 6.65 (d, $^4J_{PH}$ = 3.9 Hz, 2H, *m*-H, (Mes)), 5.94 (d, $^1J_{PH}$ = 392 Hz, 1H, P*H*Mes), 4.36 (s, 5H, C_5H_5), 2.58 (s, 6H, *o*-CH_3 (Mes)), 2.05 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ −41.4 (d, $^1J_{PH}$ = 392 Hz); ^{13}C{^{1}H} NMR (125.8 MHz, toluene-d_8, 233 K) δ 239.9 (d, $^2J_{PC}$ = 18.9 Hz, P-C=*C*=O), 230.4 (d, $^2J_{PC}$ = 27.7 Hz, Mn-*C*O), 85.6 (s, C_5H_5), 22.5 (s, *p*-CH_3 (Mes)), 22.1 (d, $^3J_{PC}$ = 6.3 Hz, *o*-CH_3 (Mes)), −28.2 (d, $^1J_{PC}$ = 31.5 Hz, P-*C*=C=O).

E-***6a***: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 8.51 (d, $^2J_{PH}$ = 18.1 Hz, 1H, P=C(*H*)Ph), 7.68 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *o*-H (Ph)), 7.28 (t overlapped with residual benzene protons, $^3J_{HH}$ = 7.9 Hz, 2H, *m*-H (Ph)), 7.11 (t, $^3J_{HH}$ = 7.0 Hz, 1H, *p*-H (Ph)), 6.83 (s, 2H, *m*-H (Mes)), 4.19 (d, J_{PH} = 2 Hz, 5H, C_5H_5), 2.55 (s, 6H, *o*-CH_3 (Mes)), 2.19 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ 281.6 (s (br)); ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6, 298 K) δ 229.6 (d, $^2J_{PC}$ = 25.8 Hz, Mn-*C*O), 166.9 (d, $^1J_{PC}$ = 46.8 Hz, P=*C*(H)Ph), 141.0−125.8 (Ph + Mes), 82.8 (s, C_5H_5), 22.4 (d, $^3J_{PC}$ = 6.5 Hz, *o*-CH_3 (Mes)), 20.9 (s, *p*-CH_3 (Mes)).

Z-***6a***: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 7.81 (d, $^2J_{PH}$ = 12.9 Hz, 1H, P=C(*H*)Ph), 6.98 (t, $^3J_{HH}$ = 7.0 Hz, 1H, *m*-H (Ph)), 6.90 (d, $^3J_{HH}$ = 7.0 Hz, 2H, *o*-H (Ph)), 6.69 (t, $^3J_{HH}$ = 7.0 Hz, 1H, *p*-H (Ph)), 6.78 (s, 2H, *m*-H (Mes)), 4.19 (s, 5H, C_5H_5), 2.53 (s, 6H, *o*-CH_3 (Mes)), 2.13 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ 273.0 (s (br)); ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6, 298 K) δ 229.8 (d, $^2J_{PC}$ = 25.6 Hz, Mn-*C*O), 153.2 (d, $^1J_{PC}$ = 46.8 Hz, P=*C*(H)Ph), 141.0−125.8 (Ph + Mes), 82.6 (s, C_5H_5), 21.5 (d, $^3J_{PC}$ = 6.5 Hz, *o*-CH_3 (Mes)), 20.95 (s, *p*-CH_3 (Mes)).

Evolution of Cp(CO)$_2$Mn=C(Me)PHMes (3b) in Benzene Solution. Complex **3b** (35 mg, 0.1 mmol) was dissolved in 0.5 mL of C_6D_6, and the solution was filtered through a plug of Celite directly into an NMR tube for monitoring. The composition of the solution was analyzed by integration of the ^{1}H and ^{31}P NMR signals. Traces (>1%) of the η^3-phosphinoketene complex **4b** could be detected by ^{31}P NMR after 2−3 h of reaction. A clean and quantitative isomerization of **3b** into **6b** (55:45 *E*/*Z* ratio) was observed when the solution was kept for 4 days at room temperature.

4b: ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ −22.2 (d, $^1J_{PH}$ = 393 Hz).

E-***6b***: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 7.29 ppm (dq overlapped with residual solvent protons, $^2J_{PH}$ = 15 Hz, $^3J_{HH}$ = 8 Hz, 1H, P=C(*H*)CH_3), 6.80 (s, 2H, *m*-H (Mes)), 4.19 (s, 5H, C_5H_5), 2.50 (s, 6H, *o*-CH_3 (Mes)), 2.25 (dd, $^3J_{PH}$ = 30.1 Hz, $^3J_{HH}$ = 7.9 Hz, 3H, P=C(H)C*H*$_3$), 2.17 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ 278.8 (s (br)); ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6, 298 K) δ 229.7 (d, $^2J_{PC}$ = 30 Hz, Mn-*C*O), 161.2 (d, $^1J_{PC}$ = 54.5 Hz, P=*C*(H)CH_3), 139.7−128.4 (Mes), 81.9 (s, C_5H_5), 22.3 (d, $^3J_{PC}$ = 7.4 Hz, *o*-CH_3 (Mes)), 20.9 (s, *p*-CH_3 (Mes)), 19.2 (d, $^2J_{PC}$ = 14.7 Hz, P=C(H)CH_3).

Z-***6b***: ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) δ 6.97 (dq, $^2J_{PH}$ = 18 Hz, $^3J_{PH}$ = 8 Hz, 1H, P=C(*H*)CH_3), 6.78 (s, 2H, *m*-H (Mes)), 4.15 (s, 5H, C_5H_5), 2.48 (s, 6H, *o*-CH_3 (Mes)), 2.16 (s, 3H, *p*-CH_3 (Mes)), 1.71 (dd, $^3J_{PH}$ = 26.9 Hz, $^3J_{HH}$ = 7.7 Hz, 3H, P=C(H)C*H*$_3$); ^{31}P NMR (121.5 MHz, C_6D_6, 298 K) δ 274.3 (s (br)); ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6, 298 K) δ 230.1 (d, $^2J_{PC}$ = 26.7 Hz, Mn-*C*O), 154.9 (d, $^1J_{PC}$ = 50.9 Hz, P=*C*(H)CH_3), 139.7−128.4 (Mes), 82.1 (s, C_5H_5), 21.5 (d, $^3J_{PC}$ = 6.6 Hz, *o*-CH_3 (Mes)), 20.9 (s, *p*-CH_3 (Mes)), 16.8 (d, $^2J_{PC}$ = 5.9 Hz, P=C(H)CH_3).

NMR Monitoring of the Isomerization of Cp(CO)$_2$Mn=C-(Ph)PHMes (3a) in THF-d_8 Solution. A sample of the carbene complex **3a** (42 mg, 0.1 mmol) was dissolved in THF-d_8 (0.5 mL) at room temperature, and the solution was filtered through a plug of Celite directly into an NMR tube for monitoring. The composition of the solution was analyzed by integration of the ^{1}H and ^{31}P NMR signals. The resulting data are given in Table S1 (see Supporting Information). The transformation was complete after ca. 36 h, giving **6a** as the only product (94:6 *E*/*Z* ratio).

3a: ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ 14.8 (d, $^1J_{HP}$ = 260.5 Hz).

4a: ^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 7.50 (m, 2H, *o*-H (Ph)), 7.20 (m, 2H, *m*-H (Ph)), 7.00 (m, 1H, *p*-H (Ph)), 6.94 (s, 2H, *m*-H (Mes)), 6.45 (d, $^1J_{HP}$ = 390.5 Hz, 1H, P*H*Mes), 4.66 (s, 5H, C_5H_5), 2.60 (s, 6H, *o*-CH_3 (Mes)), 2.26 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ −44.0 (d, $^1J_{HP}$ = 390.8 Hz).

E-***6a***: ^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 8.41 (d, $^2J_{HP}$ = 18.0 Hz, 1H, P=C(*H*)Ph), 7.53 (m, 2H, *o*-H (Ph)), 7.29 (m, 2H, *m*-H (Ph)), 7.16 (m, 1H, *p*-H (Ph)), 6.97 (s, 2H, *m*-H (Mes)), 4.55 (s, 5H, C_5H_5), 2.53 (s, 6H, *o*-CH_3 (Mes)), 2.31 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ 279.7 (s (br)).

NMR Monitoring of the Isomerization of Cp(CO)$_2$Mn=C-(Me)PHMes (3b) in THF-d_8 Solution. The carbene complex **3b** (36 mg, 0.1 mmol) was dissolved in THF-d_8 (0.5 mL) at room temperature, and the solution was filtered through a plug of Celite directly into an NMR tube for monitoring. The composition of the solution was analyzed by integration of the ^{1}H and ^{31}P NMR signals. The resulting data are given in Table S2 (see Supporting Information). The transformation was complete after ca. 1.5 h, giving **6b** as the main product (98:2 *E*/*Z* ratio).

3b: ^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 6.94 (s, 2H, *m*-H (Mes)), 6.47 (d, $^1J_{HP}$ = 261.5 Hz, 1H, P*H*), 5.20 (s, 5H, C_5H_5), 2.97 (d, $^3J_{HP}$ = 13.9 Hz, 3H, Mn=C-C*H*$_3$), 2.40 (s, 6H, *o*-CH_3 (Mes)), 2.28 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ 6.6 (dq, $^1J_{HP}$ = 260.8 Hz, $^3J_{HP}$ = 13.5 Hz).

4b: ^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 6.94 (s, 2H, *m*-H (Mes)), 5.64 (d, $^1J_{HP}$ = 390.0 Hz, 1H, P*H*), 4.76 (s, 5H, C_5H_5), 2.40 (s, 6H, *o*-CH_3 (Mes)), 2.28 (s, 3H, *p*-CH_3 (Mes)), 1.39 (d, $^3J_{HP}$ = 7.6 Hz, 3H, Mn=C−C*H*$_3$); ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ −24.85 (d, $^1J_{HP}$ = 390.0 Hz).

E-***6b***: ^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 7.29 (dq, $^2J_{HP}$ = 15.2 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, P=C(*H*)CH_3), 6.95 (s, 2H, *m*-H (Mes)), 4.46 (s, 5H, C_5H_5), 2.47 (s, 6H, *o*-CH_3 (Mes)), 2.30 (s, 3H, *p*-CH_3 (Mes)), 2.14 (dd, $^3J_{HP}$ = 29.8 Hz, $^3J_{HH}$ = 8 Hz, 3H, P=C(H)C*H*$_3$); ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ 278.0 (s (br)).

Crossover Experiment of the Isomerization of *d*-3a and 3a′ in THF-d_8 Solution. Samples of *d*-**3a** (25 mg, 0.06 mmol) and **3a′** (26 mg, 0.06 mmol) were dissolved in THF-d_8, and the resulting solution was filtered through a plug of Celite directly into an NMR tube. The composition of the solution was analyzed by integration of the ^{1}H and ^{31}P NMR signals. After 10−15 min at room temperature, an H/D exchange process between the η^1-phosphinocarbene complexes was observed, resulting in a mixture of the four different complexes **3a**, *d*-**3a**, **3a′**, and *d*-**3a′**. Further evolution led to a mixture of the corresponding deuterated and nondeuterated η^3-phosphinoketene complexes and finally to the formation of all possible varieties of η^1-phosphaalkene complexes with an *E*-selectivity of ca. 90%. Mass spectrometry analysis (EI) of the resulting mixture revealed the deuteration of *p*-tolyl

derivatives (ca. 35% of *d*-**6a**′) as well as the presence of a significant amount of **6a** (ca. 45% of *d*-**6a**).

3a: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 14.9 (d, $^1J_{PH}$ = 260 Hz); *d*-**3a**: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 13.6 (d, $^1J_{PD}$ = 40.2 Hz); **3a**′: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 14.8 (d, $^1J_{PH}$ = 259.5 Hz); *d*-**3a**′: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 13.5 (d, $^1J_{PD}$ = 40.2 Hz).

4a: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ −43.7 (d, $^1J_{PH}$ = 400.5 Hz); **4a**′: (162.0 MHz, THF-d_8, 298 K) δ −43.9 (d, $^1J_{PH}$ = 401 Hz); *d*-**4a** + *d*-**4a**′: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ −44.0 to −45.3 (t overlapped with each other).

E-***6a***: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 281.4 (s (br)); *d*-*E*-**6a**: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 280.7 (s (br)); *Z*-**6a**: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 273.7 (s (br)); *d*-*Z*-**6a**: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 273.1 (s (br)); *E*-**6a**′: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 275.4 (s (br)); *d*-*E*-**6a**: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 274.5 (s (br)); *Z*-**6a**′: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 267.0 (s (br)); *d*-*Z*-**6a**′: ^{31}P NMR (162.0 MHz, THF-d_8, 298 K) δ 266.4 (s (br)).

Synthesis of Cp(CO)$_2$Mn(η^1-*E*-P(R)=C(H)Ph (*E*-6a: R = Ph; *E*-6b: R = Me). A catalytic amount of DBU (3 μL, 0.02 mmol) was added at room temperature to a solution of **3a** (85 mg, 0.2 mmol) in CH_2Cl_2 (2 mL), causing an immediate color change of the reaction mixture from green to orange and the quantitative transformation of **3a** (IR (CH_2Cl_2) 1973 (s), 1910 (s) (ν_{CO})) into the η^1-phosphaalkene complex *E*-**6a** (IR (CH_2Cl_2) 1958 (s), 1900 (s) (ν_{CO})), observed upon IR monitoring. The solvent was removed under vacuum, and the residue was dissolved in ether (10 mL), cooled to −80 °C, and filtered quickly through a short column of alumina. The solvents were thoroughly removed under vacuum, leading to 82 mg of *E*-**6a**, recovered as an orange oil (95% yield, *ca.* 99% purity based on ^{1}H and ^{31}P NMR data).

Similar treatment of **3b** (70 mg, 0.2 mmol) gave *E*-**6b** as an orange oil (65 mg, 93% yield, ca. 99% purity based on ^{1}H and ^{31}P NMR data).

Reaction of Cp(CO)$_2$Mn=C(Ph)PHMes (3a) with Et$_3$N. A solution of **3a** (85 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) was treated with a catalytic amount of Et_3N (5 μL, 0.035 mmol) at room temperature. After 2−3 min of stirring, the color of the reaction mixture changed from green to red-orange, and IR monitoring revealed the quantitative transformation of **3a** (IR (CH_2Cl_2): 1973 (s), 1910 (s) (ν_{CO})) into **4a** (IR (CH_2Cl_2): 1930 (s) (ν_{CO}), 1700 (m) ($\nu_{C=C=O}$)). Subsequent transformation of **4a** into the final reaction product *E*-**6a** (IR (CH_2Cl_2): 1958 (s), 1900 (s) (ν_{CO})) was finally observed upon stirring for an additional 4 h at room temperature.

Addition of an excess of Et_3N (140 μL, 1 mmol) to the solution of **4a** was found to induce a significant acceleration of the reaction, giving **6a** within 5 min. The latter was isolated in ∼95% yield as described above. Examination of the crude reaction mixture by NMR showed **6a** to form in a 97:3 *E*/*Z* ratio under these reaction conditions.

***In Situ* Formation of [Cp(CO)$_2$Mn=C(Ph)PMes]Li ([7a]Li) from 3a and Subsequent Isomerization into [Cp(CO)$_2$Mn(η^2-C(O)C(Ph)=PMes]Li ([8a]Li).** A Schlenk tube was charged with complex **3a** (42 mg, 0.1 mmol) and cooled to −80 °C, and freshly distilled THF (4 mL) was added. Further addition of *n*-BuLi (65 μL of 1.6 M solution in hexane, 0.1 mmol) via syringe under stirring was found to afford a deep red solution of [**7a**]Li (IR (THF): 1882 (vs), 1811 (s), 1772 (s) (ν_{CO})). The reaction medium was allowed to reach room temperature and was stirred at 25 °C for one more hour, during which IR monitoring did not show any significant change. Addition of traces of water to the solution (for example, simply by contact with a slightly wet glass pipet or a small piece of paper) resulted in an instantaneous reaction involving the formation of an orange solution of [**8a**]Li (IR (THF) 1888 (vs) (ν_{CO}), 1620 (m) ($\nu_{C=O}$), 1605 (w), 1561 (w) ($\nu_{C=C}$)). [**NOTE:** Given that the reaction is extremely sensitive to the presence of mobile protons, all glassware and solvents should be thoroughly dried. If not, [**8a**]Li will be quantitatively formed instead of [**7a**]Li.]

***In Situ* Formation of [Cp(CO)$_2$Mn=C(Ph)PMes]Li ([7a]Li) from the Carbyne Complex [1a]BPh$_4$.** A sample of the carbyne complex [**1a**]BPh_4 (292 mg, 0.5 mmol) was suspended in THF (7 mL) at −80 °C, and $MesPH_2$ (76 μL, 0.5 mmol) was added dropwise via syringe under stirring. The reaction mixture was allowed to warm to room temperature over a period of 30 min, affording a green solution of **3a**. The solution was cooled again to −80 °C, and *n*-BuLi (0.65 mL of 1.6 M solution in hexane, 1.0 mmol) was added dropwise, affording a red solution containing complex [**7a**]Li as the sole reaction product, identified by IR (IR (THF): 1882 (vs), 1811 (s), 1772 (s) (ν_{CO})).

Attempted *in Situ* Formation of [Cp(CO)$_2$Mn=C(Me)-PMes]Li. Addition of *n*-BuLi to a solution of complex **3b** in THF led exclusively and repeatedly to an orange solution of the anionic monocarbonyl species [Cp(CO)$_2$Mn(η^2-C(O)C(Me)=PMes]Li ([**8b**]Li). The anionic dicarbonyl species analogous to [**7a**]Li, namely, [Cp(CO)$_2$Mn=C(Me)PMes]Li, could never be intercepted.

***In Situ* Formation of [Cp(CO)$_2$Mn(η^2-C(O)C(R)=PMes]Li ([8a]Li, R = Ph; [8b]Li, R = Me) for NMR Analysis.** The appropriate carbene complex, **3a** or **3b** (0.15 mmol), was dissolved in 0.5 mL of THF-d_8 at −20 °C, and 20 mg (0.25 mmol) of *t*-BuOLi was added. After warming to room temperature, the solution was filtered through a plug of Celite directly into an NMR tube. The signals of *t*-BuO^- and *t*-BuOH (^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 3.30 (s (br), O*H*), 1.19 (s (br), CH_3); ^{13}C{^{1}H} NMR (300.1 MHz, THF-d_8, 298 K) δ 31.0 (s (br), CH_3)) could be easily separated from those of [**8a**]Li or [**8b**]Li.

[***8a***]*Li:* ^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 7.76 (d, $^4J_{HP}$ = 4.6 Hz, 2H, *m*-H (Mes)), 7.04 (m, 2H, *m*-H (Ph)), 6.86 (m, 1H, *p*-H (Ph)), 6.53 (m, 1H, *o*-H (Ph), 6.38 (m, 1H, *o*-H (Ph)), 4.20 (s, 5H, C_5H_5), 2.66 (s, 3H, *o*-CH_3 (Mes)), 2.36 (s, 3H, *o*-CH_3 (Mes)), 2.07 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ −75.4 (s); ^{13}C{^{1}H} NMR (75.45 MHz, THF-d_8, 298 K) δ 267.6 (s (br), P=C-C=O), 233.6 (s (br), Mn-CO), 150.0 (d, $^2J_{CP}$ = 21.0 Hz, *i*-C (Ph)), 143.2 (d, $^1J_{CP}$ = 60.0 Hz, P=*C*), 140.7 (d, $^1J_{CP}$ = 21.0 Hz, *i*-C (Mes)), 136.9, 129.8, (s, *o*, *p*-C (Mes)), 125.3−125.9 (*o*,*m*,*p*-C (Ph)), 120.2 (s, *m*-C (Mes)), 81.8 (d, J_{CP} = 6.0 Hz, C_5H_5), 20.0, 20.3 (s, *o*-CH_3 (Mes)), 18.4 (s (br), *p*-CH_3 (Mes)).

[***8b***]*Li:* ^{1}H NMR (300.1 MHz, THF-d_8, 298 K) δ 6.96 (s, 2H, *m*-H (Mes)), 4.33 (s, 5H, C_5H_5), 2.66 (s, 3H, *o*-CH_3 (Mes)), 2.37 (s, 3H, *o*-CH_3 (Mes)), 2.05 (s, 3H, *p*-CH_3 (Mes)), 1.57 (d, $^3J_{HP}$ = 8.1 Hz, P=C-CH_3); ^{31}P NMR (121.5 MHz, THF-d_8, 298 K) δ −50.3 (s); ^{13}C{^{1}H} NMR (75.45 MHz, THF-d_8, 298 K) δ 274.2 (s (br), P=C-C=O), 235.6 (s (br), Mn-CO), 146.4 (d, $^1J_{CP}$ = 57.0 Hz, P=*C*), 141.9 (d, $^1J_{CP}$ = 18.5 Hz, *i*-C (Mes)), 131.1, 138.3 (s, *o*,*p*-C (Mes)), 127.2 (s, *m*-C (Mes)), 81.7 (s, C_5H_5), 21.8 (d, $^2J_{CP}$ = 29.0 Hz, P=C-CH_3), 20.2 (s, *o*-CH_3 (Mes)), 19.9 (s (br), *p*-CH_3 (Mes)).

***In Situ* Formation of [Cp(CO)$_2$Mn(η^2-C(O)C(R)=PMes]Li ([8a]Li: R = Ph; [8b]Li: R = Me) and Subsequent Protonation with [Et$_3$NH]Cl or [NH$_4$]Cl$_{aq}$.** Complex **3a** (42 mg, 0.1 mmol) was dissolved in THF (3 mL) at −40 °C and treated with *t*-BuOLi (15 mg, 0.2 mmol). After stirring for 5 min at −40 °C, IR monitoring showed total conversion of **3a** into [**8a**]Li (IR (THF) 1888 (vs) (ν_{CO}), 1620 (m) ($\nu_{C=C=O}$)). The reaction mixture was allowed to reach room temperature and was acidified with [Et_3NH]Cl (50 mg, 0.35 mmol). An IR spectra recorded right after acidification showed partial conversion of [**8a**]Li into a mixture of **4a** (IR (THF) 1932 (s) (ν_{CO}), 1725 (m, br) ($\nu_{C=C=O}$)) and **6a** (IR (THF) 1959 (s), 1903 (s) (ν_{CO})). A total conversion into **6a** was observed after stirring at room temperature for an additional 2 h. The solution was then filtered through Celite, and the solvent was removed under vacuum to afford **6a** as an orange oil. Examination of the residue by NMR showed **6a** to form in a 98:2 *E*/*Z* ratio. Similar treatment of [**8a**]Li with an excess of [NH_4]Cl_{aq} also led to its quantitative conversion into **6a** (98:2 *E*/*Z* ratio) upon stirring for ca.

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2 h at room temperature. Again, complex **4a** was not observed by IR monitoring during the course of this reaction.

A similar experiment carried out from complex **3b** (35 mg, 0.1 mmol) led to the quantitative formation of **6b** (97:3 *E*/*Z* ratio), via [**8b**]Li (IR (THF) 1879 (vs) (ν_{CO}), 1625 (s) ($\nu_{C=O}$)) during 15−20 min at room temperature. Here too, the transient formation of **4b** could be observed only upon quenching with $[Et_3NH]Cl$.

Reaction of [Cp(CO)$_2$Mn(η^2-C(O)C(Ph)═PMes]Li ([8a]Li) with MeI. A solution of complex [**8a**]Li, generated *in situ* upon addition of solid *t*-BuOLi (24 mg, 0.3 mmol) to a solution of **3a** (125 mg, 0.3 mmol) in THF (5 mL) at −40 °C, was cooled to −80 °C, and MeI (28 μL, 0.45 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature, diluted with THF (10 mL), and cooled again to −80 °C. The cold solution was filtered rapidly through a short column of alumina and then evaporated to dryness under vacuum. NMR analysis of the crude product revealed the presence of the *RR*/*SS* diastereomer of **4e** as the only product (^{31}P NMR δ −7.8). The residue was extracted with a 1:1 ether−hexane mixture (3 × 10 mL), and the combined extracts were filtered through Celite, concentrated under vacuum, and cooled to −20 °C overnight. The precipitate was separated by decantation, washed with pentane (2 × 5 mL), and thoroughly dried to afford 122 mg of pure *RR*/*SS*-**4e** as a red microcrystalline solid (95% yield). Analytical and spectroscopy data for the product obtained were identical to those described above in the synthesis of **4e** from [**1a**]BPh_4 and HP(Me)Mes. Crystals of *RR*/*SS*-**4e** suitable for X-ray diffraction analysis were grown from a diethyl ether−hexane mixture, at room temperature.

Reaction of [Cp(CO)$_2$Mn(η^2-C(O)C(Ph)═PMes]Li ([8a]Li) with Iodine. A solution of complex [**8a**]Li, generated *in situ* upon addition of solid *t*-BuOLi (16 mg, 0.2 mmol) to a solution of **3a** (83 mg, 0.2 mmol) in THF (10 mL) at −40 °C, was cooled to −80 °C, and solid iodine (51 mg, 0.2 mmol) was added under a slow nitrogen flow. This caused an immediate color change of the solution from orange to deep red. IR monitoring showed the presence of a mixture of the η^3-phosphinoketene complex **11** (IR (THF): 1945 (s) (ν_{CO}), 1736 (m) ($\nu_{C=C=O}$)), along with the η^1-phosphaalkene complex **12** (IR (THF): 1963 (s), 1912 (ν_{CO})). The reaction mixture was allowed to warm slowly to room temperature and then stirred for an additional hour to afford an orange solution containing **12** as the only product (IR monitoring). The reaction mixture was diluted with THF (10 mL), cooled to −80 °C, and filtered through a short column of alumina. The volatiles were removed under vacuum. At that stage, ^{31}P NMR monitoring of the crude reaction mixture showed a main signal subsequently attributed to *Z*-**12** (δ 297.1 ppm, 98%), along with a minor signal tentatively attributed to *E*-**12** (δ 302.3, ∼2%). The crude reaction mixture was dissolved in a 1:1 ether−hexane mixture (30 mL), filtered through Celite, concentrated under vacuum, and cooled to −20 °C overnight. The solid was separated by decantation, washed with pentane (2 × 5 mL), and thoroughly dried to afford 100 mg of pure *Z*-**12** as an orange microcrystalline material (92% yield). Crystals of *Z*-**12** suitable for X-ray diffraction analysis were grown from a diethyl ether−hexane mixture, at room temperature.

Z-**12**: ^{1}H NMR (400.1 MHz, C_6D_6, 298 K) δ 7.16 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *o*-H (Ph)), 6.87 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-H (Ph)), 6.76 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-H (Ph)), 6.52 (s, 2H, *m*-H (Mes)), 4.29 (d, J_{PH} = 1.2 Hz, 5H, C_5H_5), 2.39 (s, 6H, *o*-CH_3 (Mes)), 1.93 (s, 3H, *p*-CH_3 (Mes)); ^{31}P NMR (162.0 MHz, C_6D_6, 298 K) δ 297.0 (s); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K) δ 228.9 (d, $^2J_{PC}$ = 27.6 Hz, Mn-CO), 146.6 (d, $^1J_{PC}$ = 10.2 Hz, P═C(I)Ph), 140.3−127.0 (Ph + Mes), 82.9 (s, C_5H_5), 21.9 (d, $^3J_{PC}$ = 6.6 Hz, *o*-CH_3 (Mes)), 20.8 (s, *p*-CH_3 (Mes)); IR (THF) 1963 (s), 1912 (s) (ν_{CO}). Anal. Calcd for $C_{23}H_{21}IMnO_2P$: C, 50.92; H, 3.87. Found: C, 50.74; H, 4.06.

X-ray Diffraction Studies. X-ray diffraction data were collected either on an Oxford Diffraction Xcalibur diffractometer (**3b**, **4c**, and **4d**), on an Oxford Diffraction Gemini diffractometer (**4e**), or on a Bruker D8 APEX II diffractometer (**12**), at 180 K. All calculations were performed on a PC-compatible computer using the WinGX system.[47] Full crystallographic data are given in Table S3 (see Supporting Information). The structures were solved using the SIR92 program,[48] which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXL97 program.[49] Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Mn and P atoms were included in F_c. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms—except H1 in the structure of **3b**—were set in idealized position (R_3CH, C−H = 0.96 Å; R_2CH_2, C−H = 0.97 Å; RCH_3, C−H = 0.98 Å; C(sp^2)−H = 0.93 Å; U_{iso} 1.2 or 1.5 time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached), and their positions were refined as "riding" atoms. The hydrogen H1 atom attached to P1 in the structure of **3b** was located from a difference electron density synthesis; its position and isotropic thermal parameters were refined. Selected bond distances and angles for complexes **3b**, **4c**, **4d**, **4e**, and **12** are given in Tables S4 to S6 (see Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. NMR monitoring data of the isomerization of **3a** and **3b** in THF-d_8 solution; perspective views of complexes **4c** and **4d**, including selected bond distances and angles, full crystallographic data for all complexes studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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