Generation of α-Phosphinocarbene Complexes and Their Evolution: New Light on Relevant Isomerization Pathways

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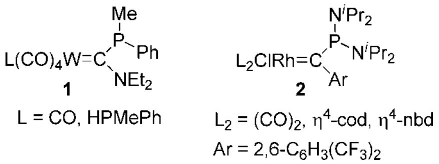
Summary: The η^1-α-phosphinocarbene complex Cp(CO)$_2$Mn=CR(PHMes) (R = Ph, Me) is generated by nucleophilic attack of MesPH$_2$ at the electrophilic center of the cationic Mn−carbyne complex [Cp(CO)$_2$Mn≡CR]$^+$, followed by deprotonation. One of its identified isomerization pathways to η^1-phosphaalkene derivatives is shown to be both base-catalyzed and stereoselective, and to involve a transient phosphidocarbene species engaged in an acid-catalyzed migratory CO-insertion step.

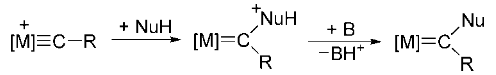
Since the seminal finding by Fischer and Maasböl some 40 years ago,[1] heteroatom-substituted transition-metal carbene complexes have received considerable attention in light of their broad application scope in organic synthesis.[2] Though the case of phosphino-substituted carbenes has been examined in detail,[3,4] η^1-α-phosphinocarbene complexes remain extremely scarce and their reactivity virtually unexplored.[5,6] Basically, there are only two known synthetic routes to such complexes. The first one, originally introduced by Fischer,[5] consists of a direct nucleophilic attack of a phosphide reagent at the electrophilic carbyne atom of a carbyne complex. The reaction of K[PMePh] with [(CO)$_5$W≡CNEt$_2$]$^+$ was indeed found to give the carbene complexes **1** (Scheme 1), albeit only in 3−4% yield. More recently, Bertrand et al. proposed a second approach,[6] consisting of the elaboration of a stable α-phosphinocarbene ligand to be subsequently reacted with a transition-metal complex. The method was only applied to one ligand, namely, (^{i}Pr$_2$N)$_2$P(Ar)C:, and was illustrated by the synthesis of **2**. Clearly, the search for a simple and general route to η^1-α-phosphinocarbene complexes remains an open area of investigation.

Scheme 1



A literature survey reveals that simple tertiary phosphines are prone to interact with the electrophilic carbon atom of transition-metal carbyne complexes to give isolable α-phosphoniocarbene compounds.[7] With these observations in mind, we became interested in exploring the method disclosed in Scheme 2, which is somewhat reminiscent of Fischer's method and proved to be efficient in the case of amines as nucleophiles for the preparation of aminocarbene complexes.[8] We envisioned that secondary and even primary phosphines might constitute ideal incoming nucleophiles NuH (Nu = PR′R″, PHR′), offering a convenient route to η^1-α-phosphinocarbene complexes.

Scheme 2



In a first set of experiments, the cationic carbyne manganese complex [**3a**]BPh$_4$[9] was treated with the secondary phosphines HPPh$_2$ and HP(N^{i}Pr$_2$)$_2$ at low temperature (Scheme 3). This led to the formation of the green α-phosphoniocarbene adducts [**4**]$^+$, whose IR characteristics[10] are very similar to those of the closely related complex [Cp(CO)$_2$Mn=C(Ph)PMe$_3$]BCl$_4$.[7b] Complex **4b**

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(1) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580–581.

(2) (a) Dörwald, F. Z. *Metal Carbenes in Organic Synthesis*, Wiley-VCH: Weinheim, Germany, 1999. (b) *Topics in Organometallic Chemistry*; Dötz, K. H., Ed.; Wiley: New York, 2004; Vol. 13.

(3) For η^2-α-phospinocarbene complexes see: (a) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Organometallics* **1982**, *1*, 1640–1644. (b) Fischer, E. O.; Reitmeier, R.; Ackermann, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 411–412. (c) Kreissl, F. R.; Wolfgruber, M.; Sieber, W. J. *J. Organomet. Chem.* **1984**, *270*, C4–C6. (d) Hovnanian, N.; Hubert-Pfalzgraf, L. G. *J. Organomet. Chem.* **1986**, *299*, C29–C31. (e) Kreissl, F. R.; Wolfgruber, M. *Z. Naturforsch.* **1988**, *43B*, 1307–1310. (f) Anstice, H. M.; Fielding, H. H.; Gibson, V. C.; Housecroft, C. E.; Kee, T. P. *Organometallics* **1991**, *10*, 2183–2191. (g) Kreissl, F. R.; Ostermeier, J.; Ogric, C. *Chem. Ber.* **1995**, *128*, 289–292. (h) Lehotkay, Th.; Wurst, K.; Jaitner, P.; Kreissl, F. R. *J. Organomet. Chem.* **1996**, *523*, 105–110. (i) Dovesi, S.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2388–2391. (j) Merceron-Saffon, N.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. *J. Organomet. Chem.* **2004**, *689*, 1431–1435.

(4) For metallacyclic complexes containing M=C−PRR′ fragments, see: (a) Jamison, G. M.; Saunders, R. S.; Wheeler, D. R.; Alam, T. M.; McClain, M. D.; Loy, D. A. *Organometallics* **1996**, *15*, 3244–3246. (b) Scheer, M.; Kramkowski, P.; Schuster, K. *Organometallics* **1999**, *18*, 2874–2883. (c) Burrows, A. D.; Carr, N.; Green, M.; Lynam, J. M.; Mahon, M. F.; Murray, M.; Kiran, B.; Nguyen, M. T.; Jones, C. *Organometallics* **2002**, *21*, 3076–3078.

(5) Fischer, E. O.; Reitmeier, R. *Z. Naturforsch.* **1983**, *38b*, 582–586.

(6) (a) Despagnet, E.; Miqueu, K.; Gornitzka, H.; Dyer, P. W.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2002**, *124*, 11834–11835. (b) Despagnet, E. Ph.D. Thesis, Université Paul Sabatier, Toulouse, France, 2002 (national no. 2002TOU30073).

(7) (a) Kreissl, F. R.; Stückler, P. *J. Organomet. Chem.* **1976**, *110*, C9–C11. (b) Kreissl, F. R.; Stückler, P.; Meineke, E. W. *Chem. Ber.* **1977**, *110*, 3040–3045. (c) Filippou, A. C.; Wtissner, D.; Kociok-Köhn, G.; Hinz, I. *J. Organomet. Chem.* **1997**, *541*, 333–343. (d) Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6161–6165.

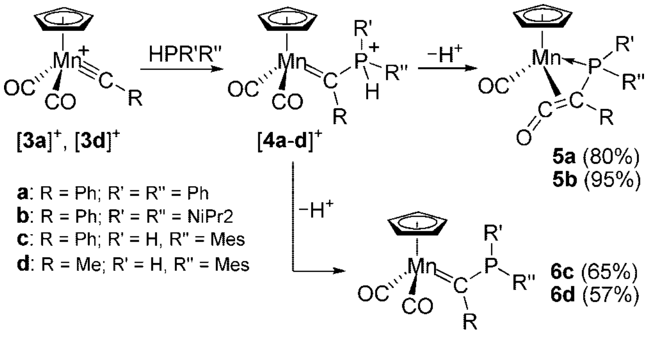
(8) (a) Kreissl, F. R. *Carbyne Complexes*; VCH: Weinheim, Germany, 1988; p 117. (b) McGeary, M. J.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 2102–2106.

(9) (a) Terry, M. R.; Mercado, L. A.; Kelley, C.; Geoffroy, G. L.; Lugan, N.; Nombel, P.; Mathieu, R.; Haggerty, B. S.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1994**, *13*, 843–865. (b) Ortin, Y.; Lugan, N.; Mathieu, R. *Dalton Trans.* **2005**, 1620–1636.

(10) IR (CH$_2$Cl$_2$): for **4a**, 2020 (s), 1960 (s) (ν_{CO}) cm^{-1}; for **4b**, 2018 (s), 1943 (s) (ν_{CO}) cm^{-1}; for [Cp(CO)$_2$Mn=C(Ph)PMe$_3$]BCl$_4$, 2010 (s), 1944 (s) (ν_{CO}) cm^{-1}.[7b]

10.1021/om800884v CCC: $40.75

Scheme 3



was found to be stable at room temperature and was fully characterized by NMR, highlighting its carbene nature.[11] Addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to [**4**]$^+$ at −80 °C induced the formation of an elusive species, which appeared to be extremely thermolabile, evolving rapidly into the η^3-phosphinoketene complexes **5**.

The structure of **5** was inferred from spectroscopic data and confirmed by X-ray diffraction (see the Supporting Information). Here the presence of a π-bound η^3-phosphinoketene ligand could be understood as the result of an intramolecular CO insertion across the Mn=C bond[12] of the elusive targeted η^1-phosphinocarbene complexes, concomitant with a coordination of the pendant phosphine moiety.

In further attempts to intercept the η^1-phosphinocarbene complexes, the reaction was extended to a primary phosphine, namely, MesPH$_2$ (Mes = 2,4,6-trimethylphenyl). Gratifyingly, deprotonation of the transient phosphoniocarbene adduct [**4c**]$^+$ appeared to be spontaneous, leading to the desired η^1-phosphinocarbene **6c**. The parallel conversion of [**4d**]$^+$, starting from [**3a**]BCl$_4$, into **6d** was not spontaneous but could be completed upon addition of NEt$_3$.

Complexes **6c**,**d** were fully characterized by spectroscopic means,[13] complemented for **6d** by an X-ray diffraction study (see Figure 1).[14] The ^{31}P{^{1}H} NMR spectra for **6c**,**d** show signals at 18.9 and 10.1 ppm, respectively. Typical low-field ^{13}C{^{1}H} NMR resonances are observed for the carbene carbon atoms (**6c**, δ 358.2 (d, $^1J_{PC} = 75.5$ Hz); **6d**, δ 366.5 (d, $^1J_{PC} = 81$ Hz)). The IR ν_{CO} stretching bands in **6** appear at frequencies much higher than those of the corresponding bands in Mn alkoxy- and aminocarbene complexes,[15a] in a domain one would actually expect for non-heteroatom Mn complexes.[15b] This indicates that the present α-phosphinocarbene ligand prototype MesHP(R)C: is much less of an electron donor than common alkoxy- and aminocarbene ligands. Here, the absence of typical carbene stabilization is due to the lack of conjugation of the phosphorus lone pair with the carbene moiety, fully consistent with the occurrence of a pyramidal geometry around the phosphorus atom (sum of bond angles around P1 303°). It is noteworthy that *the exactly opposite situation* was encountered in the case of Bertrand's complexes **2**, where the NMR and X-ray data indicated a significant contribution of the betaine σ-phosphavinyl form L$_2$ClRh$^-$−(CAr)=P$^+$(N*i*Pr$_2$)$_2$.[16]

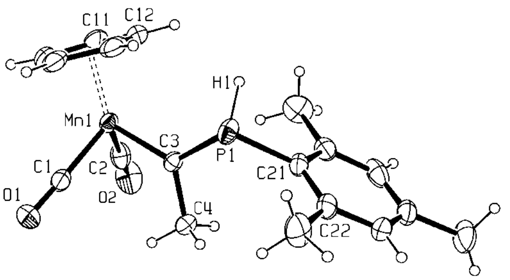


Figure 1. ORTEP drawing of **6d** (ellipsoids set at the 50% probability level). Selected bond lengths (Å) and angles (deg): Mn1−C3, 1.859(2); C3−P1, 1.811(2); C3−C4, 1.521(3); P1−C21, 1.837(2); P1−H1, 1.33(3); Mn1−C3−C4, 124.9(2); Mn1−C3−P1, 124.8(1); C4−C3−P1, 109.9(2); C3−P1−C21, 108.0(1); C3−P1−H1, 101(1); C3−P1−H1, 94(1).

Very characteristically, the carbene **6c**, which is relatively stable in nonpolar solvents, evolves rapidly in THF, affording the η^3-phosphinoketene **5c**[17] (Scheme 4) as the main transformation product after 15 min at 25 °C (>95% by NMR). The latter further transforms, albeit more slowly (ca. 36 h at 25 °C), into the η^1-(*E*)-phosphaalkene **7c**. The carbene **6d** undergoes similar isomerization in THF solution, but the ketene intermediate **5d** is by far less stable,[18] giving **7d** within ca. 1.5 h at 25 °C. The η^1-phosphaalkene structure of **7** was established by

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[11] Selected NMR data for **4b**: ^{31}P NMR (CD$_2$Cl$_2$) δ 25.5 (dt, $^1J_{PH}$ = 545.7 Hz, $^3J_{PH}$ = 14 Hz) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 325.2 (d, $^1J_{PC}$ = 24.5 Hz, Mn=*C*)) ppm.

[12] For explicit intramolecular insertion of CO across the M=C bond see: (a) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368–378. (b) Grotjahn, D. B.; Bikzhanova, G. A.; Collins, L. S. B.; Concolino, T.; Lam, K.-C.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 5222–5223.

[13] Selected spectroscopic data for **6c**: ^{1}H NMR (300.1 MHz, C$_6$D$_5$CD$_3$, 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, $^1J_{PH}$ = 260.4 Hz, 1H, P*H*Mes), 6.69 (s, 2H, *m-H* (Mes)), 6.61 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *o-H* (Ph)), 4.49 (s, 5H, C$_5$*H*$_5$), 2.52 (s, 6H, *o*-C*H*$_3$ (Mes)), 2.04 (s, 3H, *p*-C*H*$_3$ (Mes)) ppm; ^{31}P NMR (121.5 MHz, C$_6$D$_5$CD$_3$, 298 K) δ 18.9 (d, $^1J_{PH}$ = 260.4 Hz) ppm; ^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_5$CD$_3$, 240 K) δ 358.2 (d, $^1J_{PC}$ = 75.5 Hz, Mn=*C*−P), 233.0 (br s, Mn−*C*O), 118.2−142.9 (Ph and Mes), 90.5 (s, *C*$_5$H$_5$), 24.1 (br s, *o*-*C*H$_3$), 20.9 (s, *p*-*C*H$_3$) ppm; IR (CH$_2$Cl$_2$) 1973, 1910 (s) (ν_{CO}), 1590 (w), 1570 (w) ($\nu_{C=C}$) cm^{-1}. Selected spectroscopic data for **6d**: ^{1}H NMR (300.1 MHz, C$_6$D$_6$, 298 K) δ 6.84 (s, 2H, *m-H* (Mes)), 6.39 (d, $^1J_{PH}$ = 261.5 Hz, 1H, P*H*Mes), 4.72 (s, 5H, C$_5$*H*$_5$), 3.16 (d, $^3J_{PH}$ = 14.5 Hz, 3H, Mn=C−C*H*$_3$), 2.43 (s, 6H, *o*-C*H*$_3$ (Mes)), 2.19 (s, 3H, *p*-C*H*$_3$ (Mes)) ppm; ^{31}P NMR (121.5 MHz, C$_6$D$_6$, 298 K) δ 10.15 (dq, $^1J_{PH}$ = 261.5 Hz, $^3J_{PH}$ = 14.5 Hz) ppm; ^{13}C{^{1}H} NMR (75.45 MHz, C$_6$D$_6$, 298 K) δ 366.5 (d, $^1J_{PC}$ = 81.1 Hz, Mn=*C*−P), 232.6 (br s, Mn−*C*O), 128.4−143.1 (Ph and Mes), 90.4 (s, C$_5$H$_5$), 47.7 (d, $^2J_{PC}$ = 11.6 Hz, Mn=C−*C*H$_3$), 23.5 (d, $^3J_{PC}$ = 11.6 Hz, *o*-CH$_3$), 20.9 (s, *p*-*C*H$_3$) ppm; IR (CH$_2$Cl$_2$) 1970 (s), 1906 (s) (ν_{CO}), 1610 (w), 1592 (w) ($\nu_{C=C}$) cm^{-1}.

[14] Crystal data for **6d**: C$_{18}$H$_{20}$MnO$_2$P, M_r = 354.25, monoclinic, space group $P2_1/n$, a = 13.045(4) Å, b = 10.2333(17) Å, c = 13.172(4) Å, β = 103.52(3)°, V = 1709.7(8), Z = 4, ρ_{calcd} = 1.376 g cm^{-3}, μ = 0.869 mm^{-1}, 2.8° > θ > 26.4°, 12 778 reflections (3488 independent, R_{int} = 0.049), 456 parameters, R1 ($I > 2\sigma(I)$) = 0.0467, wR2 (all data) = 0.1466, $\Delta\rho_{max/min}$ 1.07/−10.36 e Å^{-3}. CCDC-692689 contains full crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

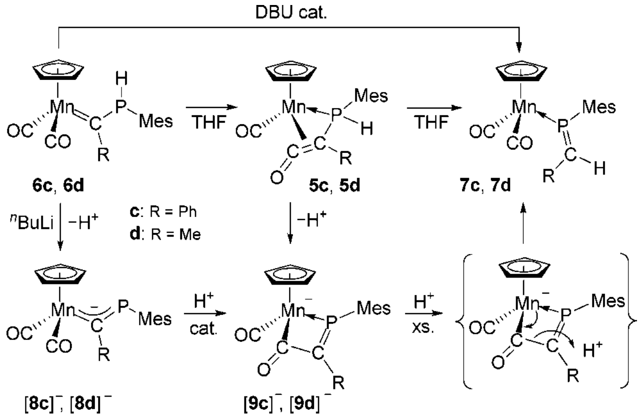
[15] (a) For example, IR (CH$_2$Cl$_2$): for Cp(CO)$_2$Mn=C(OEt)Me, 1947 (s), 1875 (s) (ν_{CO}) cm^{-1}; for Cp(CO)$_2$Mn=C(NHMe)Me, 1912 (s), 1841 (s) (ν_{CO}) cm^{-1}. (b) IR (CH$_2$Cl$_2$): for **6d**, 1970 (s), 1906 (s) (ν_{CO}) cm^{-1}; for Cp(CO)$_2$Mn=CPh$_2$, 1968 (s), 1910 (s) (ν_{CO}) cm^{-1}.

[16] (a) Chemical shifts of carbene C$_\alpha$ atoms in L$_2$ClRh=C(Ar)P(N^{i}Pr$_2$)$_2$ (δ 114.4 ppm, L$_2$ = (CO)$_2$; δ 120.6 ppm, L$_2$ = η^4-*nbd*)^{6a} are very upfield compared to shifts for the structurally similar (η^4-*cod*)ClRh=C(OEt)R (δ 291.1 ppm)^{16b} and [(η^4-*cod*)(CO)Rh=C(OEt)R]$^+$ (δ 281.2−297.4 ppm).^{16c} Also, the Rh−C$_\alpha$ bond distance in (η^4-*nbd*)ClRh=C(Ar)P(N^{i}Pr$_2$)$_2$ (2.097 Å^{6a}) is longer than the regular Rh=C bond (for example *d*(Rh−C$_\alpha$) = 1.994 Å in [(η^4-*cod*)(CO)Rh=C(OEt)CH=CHC$_6$H$_4$OMe]$^+$)^{16c}) and the P−C$_\alpha$ bond (1.637 Å) is significantly shorter than a single bond (*d*(P−C) = 1.80−1.82 Å). (b) Göttker-Schnetmann, I.; Aumann, R.; Bergander, K. *Organometallics* **2001**, *20*, 3574–3581. (c) Barluenga, J.; Vicente, R.; Lopez, L. A.; Rubio, E.; Tomas, M.; Alvarez-Rua, C. *J. Am. Chem. Soc.* **2004**, *126*, 470–471.

[17] Selected spectroscopic data for **5c**: ^{31}P NMR (THF-d_8, 298 K): δ−44.0 (d, $^1J_{PH}$ = 403.8 Hz) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_5$CD$_3$, 233 K) δ 239.9 (d, $^2J_{PC}$ = 19 Hz, P−C=*C*=O), 230.4 (d, $^2J_{PC}$ = 27.5 Hz, Mn−*C*O),−28.2 (d, $^1J_{PC}$ = 31.5 Hz, P−*C*=C=O) ppm; IR (THF) 1932 (s) (ν_{CO}), 1725 (m br) ($\nu_{C=C=O}$) cm^{-1}.

[18] Selected spectroscopic data for **5d**: ^{31}P NMR (THF-d_8, 298 K) δ−24.9 (d, $^1J_{PH}$ = 390 Hz); IR (THF) 1930 (s) (ν_{CO}), 1730 (m br) ($\nu_{C=C=O}$) cm^{-1}.

Scheme 4



NMR spectroscopy,[19] and the *E* geometry of the P═C bond was inferred from NOE experiments.

The observed rearrangement of the η^1-α-phospinocarbene ligand of **6** into an η^1-phosphaalkene by a formal 1,2-hydrogen shift is reminiscent of the N^{i}Pr$_2$ group migration reported by Bertrand in the case of complex **2** (L$_2$ = (CO)$_2$; vide supra), which was, however, nonstereoselective.[6b] In this respect, the occurrence of the phosphinoketenes **5c**,**d** *as intermediates* on the stereoselective way to the final η^1-phosphaalkene products **7** appeared to be rather puzzling to us. Keeping in mind that closely related carbene−alkene rearrangements of Fischer-type alkoxycarbene complexes of group 6 metals are base-catalyzed,[20] we examined the influence of a base on the isomerization encountered here.

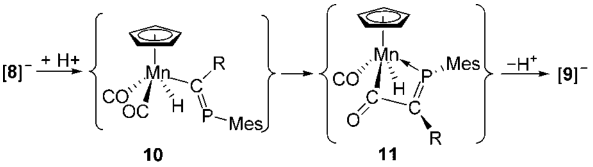
As shown below, such experiments led us to the tantalizing observation of apparently *adverse* effects of different bases on the course of the reaction and the nature of intermediates.

In our first experiments, addition of a catalytic amount of Et$_3$N (ca. 15%) to a solution of **6c** in CH$_2$Cl$_2$ at 25 °C resulted in its faster and spectroscopically quantitative conversion into **5c**, now within 2−3 min, whereas subsequent isomerization into **7c** required 3−4 h. This second step could be even more efficiently accelerated upon addition of an excess of Et$_3$N (ca. 5 equiv, 5 min reaction time). In contrast, Et$_3$N did not affect the transformation of **6d** under the same reaction conditions. A stronger base, namely DBU, effectively led to the immediate and quantitative isomerization of both **6c** and **6d** in CH$_2$Cl$_2$, affording the η^1-phosphaalkene species **7** *with >99% E selectivity*.

To establish the origin of the high stereoselectivity of the isomerization process and the unexpected role of CO insertion in its course, we studied in detail the deprotonation of carbenes **6c**,**d**. It was found that the reaction of **6c** with ^{n}BuLi in THF at −80 °C leads smoothly to the formation of a deep red anionic species, [**8c**]$^-$, which appeared to be stable at room temperature for several hours. Its IR spectrum displays the three-band pattern (IR (THF): 1882 (vs), 1811 (s), 1772 (s) cm^{-1} (ν_{CO})) typical for a *dicarbonyl* species of the type [Cp(CO)$_2$M(L)]Li.[21] Quite surprisingly, the deprotonation of **6c** with another base, ^{t}BuOLi, led to the quantitative formation of the orange *monocarbonyl acyl* anion (IR (THF): 1888 (s) cm^{-1} (ν_{CO}); 1620 (m) cm^{-1} ($\nu_{C=O}$)) [**9c**]$^-$, whose structure was unambiguously established by ^{13}C{^{1}H} NMR spectroscopy, showing signals at δ 233.6 (br s, Mn−*C*O) and 267.6 (br s, *C*═O), along with the characteristic signal of the carbon of the four-membered ring (δ 143.2 (d, $^1J_{PC}$ = 60 Hz, P═*C*). Such data are in agreement with those corresponding to the known neutral iron complex Cp(CO)Fe−C(O)C(R)═P−PR$_2$ (R = N^{i}Pr$_2$), exhibiting the same metallocyclic structure.[22] Further experiments indicated that the addition of traces of water to [**8c**]$^-$, even at −80 °C, triggers its instantaneous and quantitative conversion into [**9c**]$^-$. On another hand, parallel attempts to prepare the dicarbonyl anion [**8d**]$^-$ from **6d** and ^{n}BuLi under the same reaction conditions led only to the quantitative formation of the *monocarbonyl* species [**9d**]$^-$, probably due to intrinsic existence of a proton source, the relatively acidic methyl group of the carbene ligand.[23]

The observation of an acid-catalyzed rearrangement of the anionic *dicarbonyl* anions [**8**]$^-$ into the *monocarbonyl acyl* derivatives [**9**]$^-$ can be rationalized in terms of the proposed reaction sequence shown in Scheme 5, involving (i) a protonation of [**8**]$^-$ by a proton source—water, ^{t}BuOH, or complex **6d** itself—giving the elusive hydrido species **10**, (ii) a fast migratory CO-insertion of the σ-phosphaalkenyl fragment concomitant with coordination of the phosphorus atom to produce **11**, and (iii) deprotonation of **11** by the remaining [**8**]$^-$ to give [**9**]$^-$.

Scheme 5



The ease of the isomerization of **10** into **11** is 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)$_2$Mn−C(O)Tol]$^-$ [24] or neutral σ-alkyl[25] and σ-alkenyl[26] transition-metal complexes toward migratory CO insertion.

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(19) Selected data for **7c**: ^{31}P NMR (C$_6$D$_6$, 298 K) δ 281.6 (br s) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K) δ 166.9 (d, $^1J_{PC}$ = 47 Hz, P═*C*) ppm. Selected data for **7d**: ^{31}P NMR (C$_6$D$_6$, 298 K) δ 278.8 (br s) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K) δ 161.2 (d, $^1J_{PC}$ = 54.5 Hz, P═*C*). These data are very similar to those of (η^1-P(Mes)═CPh$_2$) transition-metal complexes: Eshtiagh-Hosseini, H.; Kroto, H. W.; Nixon, J. F.; Maah, M. J.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1981**, 199–200.

(20) (a) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326–3331. (b) Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391–396.

(21) The occurrence of three-band patterns in such anionic complexes is ascribed to an interaction of lithium cations with the oxygen atom of a CO group: (a) Ulmer, S. W.; Scarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4469–4471. (b) Darensbourg, M. J.; Burns, D. *Inorg. Chem.* **1974**, *13*, 2970–2973. (c) Darensbourg, M. J.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127–3136. (d) Sentets, S.; Serres, R.; Ortin, Y.; Lugan, N.; Lavigne, G. *Organometallics* **2008**, *27*, 2078–2091.

(22) Kato, T.; Polishchuk, O.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. *J. Organomet. Chem.* **2000**, *613*, 33–36.

(23) (a) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230–1231. (b) Bernasconi, C. F.; Sun, W. *Organometallics* **1995**, *14*, 5615–5621. (c) Bernasconi, C. F.; Ruddat, V. *J. Am. Chem. Soc.* **2002**, *124*, 14968–14976.

(24) (a) Sheridan, J. B.; Johnson, J. R.; Handwerker, B. M.; Geoffroy, G. L. *Organometallics* **1988**, *7*, 2404–2411. (b) Bassner, S. L.; Sheridan, J. B.; Kelley, C.; Geoffroy, G. L. *Organometallics* **1989**, *8*, 2121–2126.

(25) (a) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790–5791. (b) Skagestad, V.; Tilset, M. *Organometallics* **1992**, *11*, 3293–3301.

(26) (a) Reger, D. L.; Mintz, E. *Organometallics* **1984**, *3*, 1759–1761. (b) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940–1949. (c) Reger, D. L.; Klaeren, S. A.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 181–189.

The protonation of [**9**]$^-$ by [Et$_3$NH]Cl[27] or NH$_4$Cl$_{aq}$ leads to the *E*-selective formation of **7**, bearing evidence for the key role of the *monocarbonyl acyl* anion [**9**]$^-$ in the base-catalyzed isomerization. The observed *E* stereoselectivity may be attributed to an external electrophilic attack of the outcoming proton at the carbon of the phosphaalkene moiety with concomitant deinsertion of the acyl. Let us remind the reader that the base-catalyzed rearrangement of Fischer-type alkoxycarbene complexes, for which the postulated mechanism naturally does not involve CO insertion, shows a preferred *Z* selectivity for the alkene.[20] The results obtained for **6** indicate that the CO insertion in the hydride **10** is kinetically preferred over reductive elimination, which would induce the opposite selectivity.

In summary, we have developed a simple and efficient method for the synthesis of transition-metal η^1-α-phosphinocarbene complexes by nucleophilic attack of primary or secondary phosphines at an electrophilic carbyne center, followed by deprotonation of the intermediate η^1-α-phosphoniocarbene. This led us to isolate the new species Cp(CO)$_2$Mn=C(R)PHMes (R = Me, Ph), representing the archetype of a η^1-α-phosphinocarbene complex, and to trace precisely the elementary steps of its subsequent stereoselective isomerization into η^1-phosphaalkene derivatives. Though such a transformation might have been regarded as predictable, evidence was provided that its intimate mechanism is not trivial and includes an acid-catalyzed migratory CO insertion as the key C−C bond forming step. Beyond the scope of the present work, we are convinced that such a mechanistic pathway is of fundamental relevance and will be possibly applicable to other types of anionic transition-metal σ-complexes.

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Supporting Information Available: Text and tables giving details of the synthesis and spectroscopic characterization of **[3a]**BPh$_4$, **5a**,**b**, **4b**, **6c**,**d**, **7c**,**d**, **8c[Li]**, and **9c**,**d**, details on the NMR monitoring of the isomerization of **6c**,**d**, and details on the X-ray diffraction studies of complexes **5a**,**b** and **6d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] The mixture of ketene (**5c** or **5d**) and phosphaalkene (**7c** or **7d**) complexes was observed during the reaction course, giving finally **7c** or **7d** in more than 97% *E* selectivity.