Directed Formation of Allene Complexes upon Reaction of Non-heteroatom-Substituted Manganese Alkynyl Carbene Complexes with Nucleophiles

Stéphane Sentets, Rémi Serres, Yannick Ortin,† Noël Lugan,* and Guy Lavigne

Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France

Received January 23, 2008

The non-heteroatom-substituted alkynyl carbene $Cp'(CO)_2Mn{=}C(Tol)C{\equiv}CPh$ (**1**, $Cp' \equiv (\eta^5\text{-}MeC_5H_4)$) is first shown to react at low temperature with lithium diorganophosphide $LiPR_2$ (R = Ph, Cy) to form an anionic species. Subsequent treatment with CF_3SO_3H affords the η^4-vinylketene complex $Cp'(CO)_2Mn[\eta^4\text{-}\{R_2P(Ph)C{=}CHC(Tol){=}C{=}O\}]$ (**2**; **2a**: R = Ph (70% yield), **2b**: R = Cy (55% yield)) as the major compound, along with trace amounts of the η^2-allene complex *syn*-$Cp'(CO)_2Mn[\eta^2\text{-}\{Ph_2P(Tol)C{=}C{=}C(Ph)H\}]$ (*syn*-**3a**) for R = Ph, or along with the η^2-allene complex $Cp'(CO)_2Mn[\eta^2\text{-}\{H(Tol)C{=}C{=}C(Ph)PCy_2\}]$ (**4b**, 26% yield, 1:2 mixture of *syn*/*anti* isomers) for R = Cy. On the other hand, subsequent treatment with NH_4Cl_{aq} affords only η^2-allene complexes, obtained either as a ca. 1:9 mixture of *syn*-**3a** and $Cp'(CO)_2Mn[\eta^2\text{-}\{H(Tol)C{=}C{=}C(Ph)PPh_2\}]$ (**4a**) (75% yield) for R = Ph or as a 1:2 mixture of *syn*- and *anti*-**4b** for R = Cy (74% yield). Combined NMR and single-crystal X-ray diffraction studies (for **2a**, *anti*-**4b**, and *syn*-**4b**) revealed that both type **2** and type **4** species result from a nucleophilic attack of the diorganophosphide onto the remote alkynyl carbon atom in **1** (C_γ), whereas type **3** species results from a nucleophilic attack of the carbene carbon atom (C_α). Complexes **3a** and **4a**,**b** are prone to undergo a thermal rearrangement to give the η^1-phosphinoallene complexes $Cp'(CO)_2Mn[\eta^1\text{-}\{Ph_2P(Tol)C{=}C{=}C(Ph)H\}]$ (**5a**) and $Cp'(CO)_2Mn[\eta^1\text{-}\{R_2P(Ph)C{=}C{=}C(Tol)H\}]$ (**6**; **6a**: R = Ph, **6b**: R = Cy), respectively. Reaction of **1** with *p*-toluenethiol in the presence of NEt_3 (20%) affords a 1.8:1 mixture of $Cp'(CO)_2Mn[\eta^2\text{-}\{TolS(Tol)C{=}C{=}C(Ph)H\}]$ (*syn*-**11**), resulting from a nucleophilic attack at C_α in **1**, and $Cp'(CO)_2Mn[\eta^2\text{-}\{H(Tol)C{=}C{=}C(Ph)STol\}]$ (**12**), resulting from a nucleophilic attack at C_γ, whereas treatment of **1** with lithium *p*-toluenethiolate at –80 °C followed by protonation with NH_4Cl_{aq} gave the same *syn*-**11** and **12** complexes now in a 1:2.3 ratio. Finally, **1** was found to react with cyclohexanone lithium enolate to afford, upon protonation, the η^2-allene complex $Cp'(CO)_2Mn[\eta^2\text{-}\{H(Tol)C{=}C{=}C(Ph)CH(CH_2)_4C(O)\}]$ (*syn*-**13**), resulting from a nucleophilic attack at C_γ in **1**. The solid-state structures of *syn*-**11** and *syn*-**13** are also reported.

Introduction

Since their discovery more than 40 years ago,[1] Fischer-type carbene complexes have been subject to intensive studies.[2] In recent years, heteroatom-substituted alkynyl complexes—of chromium and tungsten in particular—have emerged as a very useful and versatile subclass of carbene complexes having explicit applications in organic synthesis.[3] Their reactivity is dictated by the strong electron-withdrawing properties of the metal fragment, enabling these species to undergo 1,2-, or 1,4-nucleophilic addition reactions as well as cycloaddition reactions. By contrast, little is known about the reactivity of their non-heterotaom-substituted counterpart,[4] though recent findings by Iwasawa et al.,[5] Casey et al.,[6] or Barluenga et al.[7] provide

* Corresponding author. E-mail: lugan@lcc-toulouse.fr.
† Present address: NMR Centre, UCD School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.

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

(2) For reviews on applications of Fischer-type carbene complexes to organic synthesis see for instance: (a) Aumann, R.; Neinaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163. (b) Wulff, W. D. *Comprehensive Organometallic Chemisry II*; Abel, E. W., Stone, F. G. A., Wilkinson G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, Chapter 5.3. (c) Herndon, J. W. *Coord. Chem. Rev.* **1999**, *181*, 177. (d) Zaragoza Dörwald, F. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999. (e) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (f) Barluenga, J.; Frañanás, F. J. *Tetrahedron* **2000**, *56*, 4597. (g) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257. (h) Dötz, K. H.; Minatti, A. *Transition Metals for Organic Synthesis*, 2nd ed.; 2004; Vol. *1*, p 397. (i) *Metal Carbenes in Organic Synthesis: Topics in Organometallic Chemistry*; Dötz, K. H., Ed.; Wiley: New York, 2004; Vol. 13. (j) Gómez-Gallego, M.; Mancheo, M. J.; Sierra, M. A. *Acc. Chem. Res.* **2005**, *38*, 44. (k) Wu, Y.-T.; Kurahashi, T.; De Meijere, A. *J. Organomet. Chem.* **2005**, *690*, 5900. (l) Herndon, J. W. *Coord. Chem. Rev.* **2006**, *250*, 1889. (m) Sierra, M. A.; Gómez-Gallego, M.; Martínez-Alvarez, R. *Chem.—Eur. J.* **2007**, *13*, 736.

(3) For reviews being more specific to applications of heteroatom-substituted alkynyl carbene complexes to organic synthesis see: (a) De Meijere, A.; Schriemer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (b) Aumann, R. *Eur. J. Org. Chem.* **2000**, 17. (c) Barluenga, J. *Pure Appl. Chem.* **2002**, *74*, 1317. (d) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539.

(4) For the synthesis of non-heteroatom-substituted alkynyl carbene complexes, see for instance: (a) Terry, M. R.; Kelley, C.; Lugan, N.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3607. (b) Weng, W.; Arif, J. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824. (c) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 5766. (d) Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Modrego, J.; Onate, E. *Organometallics* **1997**, *16*, 5826. (e) Dovesi, S.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2388. (f) Casey, C. P.; Ktaft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3771. (g) Bassetti, M.; Marini, S.; Diaz, J.; Gamasa, M. P.; Gimeno, J.; Rodriguez-Alvarez, Y.; Garcia-Granda, S. *Organometallics* **2002**, *21*, 4815.

(5) Iwasawa, N.; Maeyama, K.; Saitou, M. *J. Am. Chem. Soc.* **1997**, *119*, 1486.

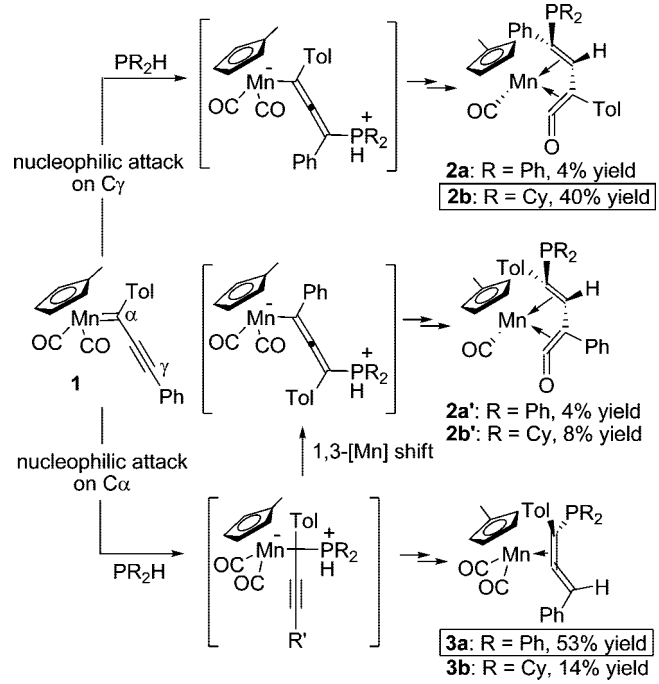
10.1021/om800060v CCC: $40.75
Publication on Web 04/09/2008

a hint that research in this area may be equally rewarding in terms of unique applications to organic synthesis.

We have recently shown that non-heteroatom-substituted *manganese* alkynyl carbene complexes of the type Cp′-$(CO)_2$Mn═C(Ar)C≡CAr′ (Cp′ ≡ (η^5-MeC_5H_4); Ar, Ar′ = Ph or Tol) are readily accessible upon reaction of simple alkynyllithium reagents, LiC≡CAr′, with the stable cationic carbyne complexes [Cp′$(CO)_2$Mn≡CAr][BPh_4] readily available on a large scale from low-cost methylcyclopentadienyl manganese tricarbonyl (MMT).[8,9] Interestingly, subtle reactivity patterns of these alkynyl carbene complexes were established in studies of their interaction with various phosphorus probes.[10] In the presence of PPh_3, just like their parent group 6 heteroatom-substituted alkynyl carbene complexes[11] or their rhenium analogues,[12] they act as a Michael acceptors and are subject to nucleophilic attack at the remote alkynyl carbon atom to afford σ-allenylphosphonium complexes Cp′$(CO)_2$MnC(Ar)═C═C-(PPh_3)Ar′. By contrast, in the presence of PMe_3, a more basic and more nucleophilic phosphine, they behave as typical Fischer carbene complexes and experience a nucleophilic attack at the carbenic carbon to afford σ-propargylphosphonium complexes Cp′$(CO)_2$MnC(Ar)(PMe_3)C≡CAr′. An even more specific behavior is observed in the presence of secondary phosphines HPR_2 (R = Ph, Cy). Indeed, as shown in Scheme 1, the alkynyl carbene complex Cp′$(CO)_2$Mn═C(Tol)C≡CPh (**1**)—complex taken as reference—reacts via two apparently competing pathways to afford mixtures of two regioisomeric η^4-vinylketene complexes, Cp′(CO)Mn[η^4-{R_2P(Ph)C═CHC(Tol)═C═O}] (**2**) and Cp′(CO)Mn[η^4-{R_2P(Tol)C═CHC(Ph)═C═O}] (**2′**), and an η^2-allene complex, *syn*-Cp′$(CO)_2$Mn[η^2-{R_2P(Ph)C═C═C(Tol)H}] (**3**).[10] The position of the PR_2 group with respect to the Tol/Ph substituents clearly indicates that the first complex, **2**, results from an initial nucleophilic attack of the secondary phosphine onto the remote alkynyl carbon atom C_γ, whereas the later two species, **2′** and **3**, result from a nucleophilic attack at the carbenic carbene center C_α. Parallel experiments carried out with $HPPh_2$ and $HPCy_2$ suggest that the regioselectivity of the attack is dictated by steric factors. Indeed, whereas the allene complex **3a** is obtained predominantly in the reaction of **1** with $HPPh_2$, the η^4-vinylketene complex **2b** becomes predominant when **1** is reacted with $HPCy_2$, thereby indicating that nucleophilic attack by the bulkier phosphine takes place preferentially at the less hindered remote alkynyl carbon atom.

To date, manganese carbene complexes derived from MMT have found much less applications to organic synthesis[13] than their group 6 analogues, certainly because of the reduced electrophilicity of their carbenic carbon atom inherent to the relatively poor electron-withdrawing ability of the Cp′$(CO)_2$Mn fragment.[14] As far as manganese carbene chemistry is concerned, the observations summarized in Scheme 1 are quite gratifying for two reasons. First, they reveal that manganese carbene complexes are prone to develop a pronounced Fischer-type carbene character provided they are not heteroatom-substituted.[15] Second, it appears that the fate of the intermediate species resulting from the initial nucleophilic attack differs significantly from what we know from group 6 congeners. Indeed, the literature shows that group 6 alkynyl[alkoxy] carbene complexes react with secondary phosphines to yield *2*-phosphino alkenyl carbenes resulting from typical conjugate addition of the P—H bond across the C≡C bond.[11,16] The observation of a different behavior of manganese complexes prompted us to investigate further the reactivity of complex **1** toward nucleophiles, including anionic nucleophiles, with the aim of establishing general reactivity patterns, eventually offering new possibilities of controlling the nature of the final products. In the present paper, we report our recent findings on the reactivity of the alkynylcarbene complex **1** toward a series of nucleophiles including

Scheme 1



(6) (a) Casey, C. P.; Dzwiniel, T. L.; Kraft, S.; Guzei, I. A. *Organometallics* **2003**, *22*, 3915. (b) Casey, C. P.; Dzwiniel, T. L. *Organometallics* **2003**, *22*, 5285.

(7) (a) Barluenga, J.; Bernardo de la Rúa, R.; de Sáa, D.; Ballesteros, A.; Tomás, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4981. (b) Barluenga, J.; García-García, P.; de Sáa, D.; Fernández-Rodríguez, M. A.; Bernardo de la Rúa, R.; Ballesteros, A.; Aguilar, E.; Tomás, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2610.

(8) Ortin, Y.; Coppel, Y.; Lugan, N.; Mathieu, R.; McGlinchey, M. J. *Chem. Commun.* **2001**, 1690.

(9) In a parallel work, Casey et al. have shown that the thermally stable, yet air sensitive, anionic acyl complexes [CpMn$(CO)_2$C(O)R]Li·Et_2O may constitute a viable alternative to cationic carbyne complexes as starting materials for the preparation of non-heteroatom-substituted manganese alkynyl carbene complexes; see ref 6b.

(10) Ortin, Y.; Lugan, N.; Mathieu, R. *Dalton Trans.* **2005**, 1620.

(11) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Chem. Ber.* **1994**, *127*, 2475.

(12) Casey, C. P.; Kraft, S.; Powell, D. R.; Kavana, M. *J. Organomet. Chem.* **2001**, *617–618*, 723.

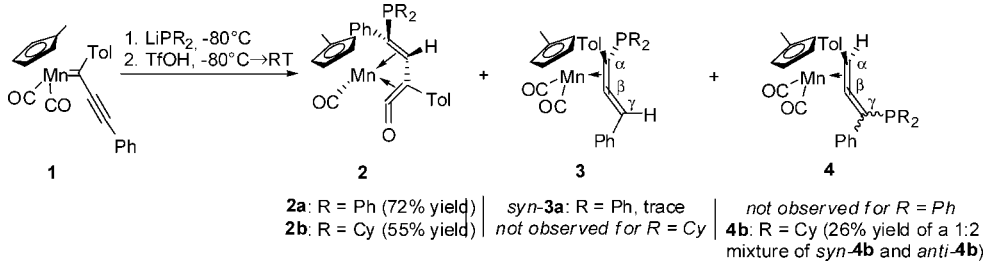
(13) For applications of group 7 carbene complexes to organic synthesis see for instance: (a) Aumann, R.; Heinen, H. *Chem. Ber* **1988**, *121*, 1085. (b) Aumann, R.; Heinen, H. *Chem. Ber.* **1989**, *122*, 77. (c) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1990**, *9*, 3014. (d) Balzer, B. L.; Cazanoue, M.; Sabat, M.; Finn, M. G. *Organometallics* **1992**, *11*, 1759. (e) Balzer, B. L.; Cazanoue, M.; Finn, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 8735. (f) Mongin, C.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 3873. (g) Mongin, C.; Ortin, Y.; Lugan, N.; Mathieu, R. *Eur. J. Inorg. Chem.* **1999**, 739. (h) Mongin, C.; Gruet, K.; Lugan, N.; Mathieu, R. *Tetrahedron Lett.* **2000**, *41*, 7341. (i) Casey, C. P.; Dzwiniel, T. L.; Kraft, S.; Kozee, M.; A.; Powell, D. R. *Inorg. Chim. Acta* **2003**, *345*, 320. (j) Ortin, Y.; Sournia-Saquet, A.; Lugan, N.; Mathieu, R. *Chem. Commun.* **2003**, 1060. See also ref 6.

(14) Dötz, K. H.; Böttcher, D.; Jendro, M. *Inorg. Chim. Acta* **1994**, *222*, 291.

(15) (a) Manganese ethoxy carbene complexes do *not* react spontaneously with phosphines. Only under photolytic conditions does the substitution of a carbonyl ligand for the phosphine occur.[15b,c] (b) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735. (c) Fischer, H.; Schleu, J. *Chem. Ber.* **1996**, *129*, 385.

(16) (a) Llebaria, A.; Moretó, J. M.; Ricart, S.; Ros, J.; Viñas, J. M.; Yáñez, R. *J. Organomet. Chem.* **1992**, *440*, 79. (b) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 231. (c) Aumann, R.; Fröhlich, R.; Prigge, J.; Meyer, O. *Organometallics* **1999**, *18*, 1369.

Scheme 2



(i) organophosphides, (ii) a thiol and its thiolate derivative, and (iii) an enolate.

Results and Discussion

PR_2^-/H^+ vs PR_2H: Sequential Treatment of the Alkynyl Carbene Complex Cp′(CO) $_2$Mn=C(Tol)C≡CPh (1) with a Diorganophosphide $LiPR_2$ (R = Ph, Cy) and an Acid. The alkynyl carbene complex $Cp'(CO)_2Mn{=}C(Tol)C{\equiv}CPh$ (**1**) reacts instantaneously at –80 °C with lithium dicyclohexyl or lithium diphenylphosphide. IR monitoring showed a strong bathochromic shift of the ν_{CO} bands of ca. –90 cm^{-1} (for the leftmost bands), consistent with the formation of an anionic complex. Intriguingly, the newly formed species exhibits *three* bands in the ν_{CO} region, at 1873(s), 1798(m), and 1755(m) cm^{-1}, whereas only two are expected for a dicarbonyl $Cp'(CO)_2ML$ unit. This feature, which was also observed for the so-called carbene anion $[Cp'(CO)_2Mn{=}C(OEt)CH_2][Li]$,[17] is tentatively ascribed to an interaction of lithium cations with the oxygen atoms of the CO ligands.[18,19] These intermediates evolve instantaneously upon protonation at low temperature. Significantly, subsequent workup revealed that the nature of the reaction products dramatically depends on the type of acid used.

Subsequent Protonation with a Strong Acid, the Case Where R = Ph. The stepwise treatment of **1** with diphenylphosphide and CF_3SO_3H resulted in the formation of a new species exhibiting a single ν_{CO} band at 1960 cm^{-1}. More precisely, chromatographic workup provided two compounds readily identified as the η^4-vinylketene complex $Cp'(CO)_2Mn[\eta^4$-$\{Ph_2P(Ph)C{=}CHC(Tol){=}C{=}O\}]$ (**2a**) and the η^2-allene complex *syn*-$Cp'(CO)_2Mn[\eta^2$-$\{Ph_2P(Tol)C{=}C{=}C(Ph)H\}]$ (*syn*-**3a**), the latter existing as trace amounts only (Scheme 2). Complex **2a**, which is accountable for the characteristic ν_{CO} band observed at 1960 cm^{-1} in the crude reaction mixture, was isolated in 72% yield. Both these complexes had already been obtained upon reaction of **1** with $HPPh_2$, but in the first instance, complex *syn*-**3a** was the major reaction product (see Scheme 1).[10] In addition, no trace of the previously identified regioisomer $Cp'(CO)_2Mn[\eta^4$-$\{Ph_2P(Tol)C{=}CHC(Ph){=}C{=}O\}]$ (**2a′**, Scheme 1) was detected in the present reaction.

Structure of $Cp'(CO)_2Mn[\eta^4$-$\{Ph_2P(Ph)C{=}CHC(Tol){=}C{=}O\}]$ (2a). The structure of **2a**, which was hitherto inferred only from NMR data,[10] has now been firmly established by a single-crystal X-ray diffraction analysis. An ORTEP drawing of complex **2a** is given in Figure 1. Relevant crystallographic data are set out in Tables 1 and 3. The vinyl ketene ligand backbone bound to the Cp $(CO)_2Mn$ unit is comprised of the O2, C2, and C3 atoms for the ketene part and C4 and C5 carbon atoms for the vinyl part. The diphenylphosphide and phenyl fragments are occupying adjacent positions on the carbon atom C5 of the allene ligand moiety, thus confirming that **2a** results from a nucleophilic attack of the diphenylphosphide at the remote alkynyl carbon atom. Metrical features within complex **2a** are naturally very similar to those of complex $Cp'(CO)_2Mn[\eta^4$-$\{Ph_2P(Ph)C{=}CHC(Tol){=}C{=}O\}]$ described earlier.[10]

Subsequent Protonation with a Strong Acid, the Case Where R = Cy. IR monitoring allowed the observation of three bands at 1975, 1960, and 1925 cm^{-1}, indicative that at least two complexes were formed in that case. Chromatographic workup effectively afforded two fractions, namely, a yellow one

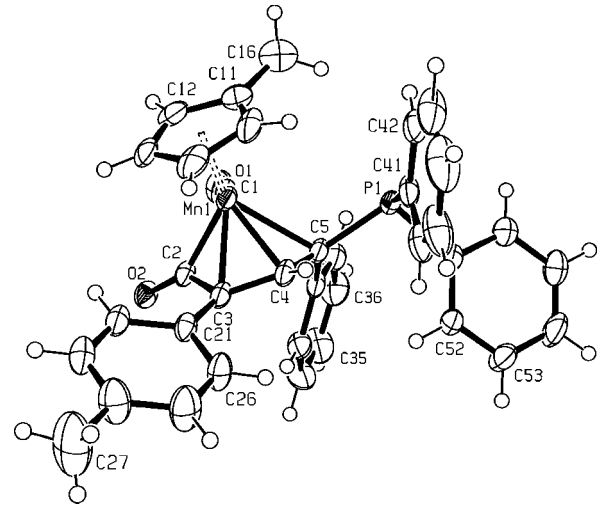


Figure 1. Perspective view of complex $Cp'(CO)_2Mn[\eta^4$-$\{Ph_2P(Ph)C{=}CHC(Tol){=}C{=}O\}]$ (**2a**). Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Bond Lengths (Å) and Angles (deg) for the Complex 2a

Mn1−C1	1.789(3)	O1−C1	1.145(4)
Mn1−C2	1.927(3)	O2−C2	1.199(3)
Mn1−C3	2.115(3)	C2−C3	1.453(4)
Mn1−C4	2.100(3)	C3−C4	1.429(4)
Mn1−C5	2.298(2)	C4−C5	1.394(4)
P1−C5	1.858(3)		
C1−Mn1−C2	77.30(13)	Mn1−C3−C21	130.17(18)
C1−Mn1−C3	111.67(12)	C4−C3−C21	122.2(2)
C1−Mn1−C4	114.25(12)	Mn1−C4−C3	70.75(14)
C2−Mn1−C3	41.82(10)	Mn1−C4−C5	79.44(16)
C2−Mn1−C4	75.42(10)	C3−C4−C5	123.3(2)
C5−P1−C41	104.89(14)	Mn1−C5−P1	114.68(13)
C5−P1−C51	103.47(12)	P1−C5−C4	123.17(19)
C41−P1−C51	98.60(13)	P1−C5−C31	111.19(19)
Mn1−C1−O1	173.5(3)	C4−C5−C31	121.2(2)
Mn1−C2−O2	145.8(2)		

(17) Mongin, C. Thèse de l'Université Paul Sabatier, 1997.

(18) (a) Ulmer, S. W.; Skarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4470. (b) York Darensbourg, M.; Burns, D. *Inorg. Chem.* **1974**, *13*, 2970. (c) York Darensbourg, M.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127.

(19) (a) We have observed that addition of 1 molar equiv of 12-crown-4 ether, a specific trap for the lithium cation, causes a very significant decrease of the lower frequency band with concomitant enhancement of the band at 1798 cm^{-1}. On the other hand, when potassium diphenylphosphide is used in place of lithium diphenylphosphide, the anionic species exhibits *two* bands in the ν_{CO} region at 1873(s) and 1798(ms) cm^{-1}, very close in position to those of the carbene anion $[Cp'(CO)_2Mn{=}C(OEt)CH_2][K]$.[19b](b) Rabier, A.; Lugan, N.; Mathieu, R.; Geoffroy, G. L. *Organometallics* **1994**, *13*, 4676.

followed by a brown one. The complex extracted from the second band was readily identified as the η^4-vinylketene complex $Cp'(CO)_2Mn[\eta^4\text{-}\{Cy_2P(Ph)C{=}CHC(Tol){=}C{=}O\}]$ (**2b**) already encountered as the major product of the reaction of **1** with $HPCy_2$ (Scheme 1).[10] It was isolated in 55% yield as a brown crystalline material. The regioisomeric complex **2b′** depicted in Scheme 1 was not observed under the present conditions. The IR spectrum of the first (yellow) fraction showed two relatively sharp ν_{CO} bands at 1978 and 1922 cm^{-1}, very similar in position to those of type **3** complexes. NMR spectra, however, clearly indicated that this fraction actually contains a 1:2 mixture of two stereoisomers of a new η^2-allene complex, namely, *syn*-$Cp'(CO)_2Mn[\eta^2\text{-}\{HC(Tol){=}C{=}C(Ph)PCy_2\}]$ (*syn*-**4b**) and *anti*-$Cp'(CO)_2Mn[\eta^2\text{-}\{HC(Tol){=}C{=}C(Ph)PCy_2\}]$ (*anti*-**4b**), which were obtained in 26% overall yield (Scheme 2). Both isomers could be ultimately isolated in a pure form upon fractional crystallization. They were fully characterized both by usual spectroscopic techniques and by single-crystal X-ray diffraction.

At 303 K, the $^{31}P\{^1H\}$ NMR spectrum of *syn*-**4b** shows one broad singlet at 10.5 ppm (121.5 MHz, toluene-d_8) clearly indicating that the phosphorus atom is not coordinated to manganese.[20] Upon cooling, the singlet splits into two singlets, revealing the occurrence of a dynamic process in solution. Examination of the coalescence behavior of the ^{31}P resonances in the 193–303 K range (121.5 MHz, toluene-d_8) leads to activation barriers of ca. 14.9 kcal mol^{-1} for the dynamic processes involved ($\Delta\delta_P = 37$ Hz; $T_c = 298$ K).[21] All isomers of *syn*-**4b**, which are in a fast exchange (NMR time scale), could be fully characterized at low temperature. The $^{13}C\{^1H\}$ NMR spectrum shows two sets of three doublets at δ 188.1 ($J_{CP} \approx$ 24 Hz), 131.8 ($J_{CP} = 38$ Hz), and 27.6 ($J_{CP} = 15$ Hz), and δ 186.4 ($J_{CP} = 24$ Hz), 130.9 ($J_{CP} = 38$ Hz), and 27.7 ($J_{CP} = 15$ Hz) ppm, attributable to the C_β, C_γ, and C_α carbon atoms (see Scheme 2 for labeling scheme) for the coordinated allene ligand in each isomer, respectively. The ^1H spectrum shows one singlet for each isomer at δ 3.84 and 3.44 ppm attributable to the proton attached to C_α. The chemical shift of that proton actually constitutes the spectroscopic signature of allene complexes **4** as compared with their isomer **3**, considering that in the later species the proton attached to the allene ligand possesses a vinylic character and thus appears at much lower field, in the 8.2–8.7 ppm range.[10] Accordingly, we interpret the dynamic process observed for *syn*-**4b** in terms of a fast (NMR time scale) propeller rotation of the coordinated allene around the axis joining the Mn atom and the centroid of the coordinated C=C bond. This excludes the occurrence of a fast 1,2-shift of the allene ligand, of the type previously observed, for instance, in cationic $[Fp(\eta^2\text{-allene})]^+$ complexes.[22] On the other hand, the activation barrier estimated here fits well with those previously reported by Lentz et al. for the propeller rotation of the allene in a series of parent $(\eta^5\text{-}R_5C_5)(CO)_2Mn[\eta^2\text{-}\{allene\}]$ complexes (9–15 kcal mol^{-1}).[23]

(20) Chemical shifts for the phosphorus nuclei in complexes of the type $Cp(CO)_{2-n}L_nMnPR_3$ are typically in the 80–120 ppm range: Ginzburg, A. G.; Fedorov, L. A.; Petrovskii, P. V.; Fedin, E. I.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1974**, *73*, 77., see also ref 15b.

(21) The activation energy barrier was estimated using the approximation of the Eyring equation: $\Delta G^{\ddagger} = RT_c(22.96 + \ln T_c/\delta\nu)\eta$, where T_c (K) is the coalescence temperature of two signals separated by $\delta\nu$ (Hz).

(22) (a) Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231. (b) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160.

(23) (a) Lentz, D.; Willemsen, S. *Organometallics* **1999**, *18*, 3962. (b) Lentz, D.; Nickelt, N.; Willemsen, S. *Chem.−Eur. J.* **2002**, *8*, 1205.

Table 2. Bond Lengths (Å) and Angles (deg) for the Complexes *anti*-4b, *syn*-4b, *syn*-11, and *syn*-13

	anti-**4b**	*syn*-**4b**	*syn*-**11**	*syn*-**13**
Mn1−C1	1.783(2)	1.781(2)	1.768(2)	1.790(2)
Mn1−C2	1.784(2)	1.791(2)	1.770(2)	1.772(3)
Mn1−C3	2.180(2)	2.165(1)	2.122(2)	2.168(2)
Mn1−C4	2.011(2)	2.018(1)	1.995(2)	2.034(2)
C1−O1	1.154(3)	1.1490(2)	1.131(3)	1.149(3)
C2−O2	1.152(3)	1.148(2)	1.143(3)	1.153(3)
C3−S1			1.803(2)	
C3−C4	1.407(3)	1.403(2)	1.381(2)	1.391(3)
C3−C21	1.479(3)	1.486(2)	1.472(2)	1.477(3)
C4−C5	1.322(3)	1.329(2)	1.324(2)	1.341(3)
C5−P1	1.847(2)	1.839(1)		
C5−C31	1.493(3)	1.498(2)	1.451(3)	1.492(3)
C5−C41				1.517(3)
C41−P1	1.844(2)	1.868(5)		
C41−S1			1.751(2)	
C51−P1	1.846(2)	1.868(6)		
C1−Mn1−C2	88.84(9)	88.35(7)	87.15(10)	84.85(12)
C1−Mn1−C3	101.63(8)	102.85(6)	98.43(9)	84.22(11)
C1−Mn1−C4	83.14(8)	80.69(6)	82.57(9)	111.73(12)
C2−Mn1−C3	77.46(8)	80.69(6)	81.31(9)	107.42(12)
C2−Mn1−C4	111.13(9)	109.99(6)	115.87(10)	83.28(11)
C3−Mn1−C4	38.98(8)	38.98(5)	39.03(8)	38.50(9)
Mn1−C1−O1	179.23(19)	178.35(13)	177.94(19)	176.8(3)
Mn1−C2−O2	178.31(19)	179.32(14)	178.13(19)	177.8(2)
Mn1−C3−S1			113.18(9)	
Mn1−C3−C4	64.02(11)	64.85(7)	65.51(11)	65.53(14)
Mn1−C3−C21	119.00(13)	117.28(9)	115.98(13)	120.55(16)
S1−C3−C4			114.62(13)	
S1−C3−C21			113.94(14)	
C4−C3−C21	125.78(18)	123.70(12)	124.41(16)	123.9(2)
Mn1−C4−C3	77.00(12)	76.17(8)	75.46(11)	75.97(14)
Mn1−C4−C5	143.86(16)	142.08(10)	146.46(15)	140.02(19)
C3−C4−C5	139.11(19)	141.65(13)	138.05(18)	144.0(2)
C4−C5−C31	125.53(18)	118.34(11)	130.96(18)	121.5(2)
C4−C5−P1	114.69(15)	119.98(10)		
C4−C5−C41				121.0(2)
C31−C5−C41				117.50(19)
C31−C5−P1	119.66(14)	121.10(9)		
C5−P1−C41	102.43(9)	98.0(3)		
C5−P1−C51	101.55(9)	104.1(2)		
C41−P1−C51	105.30(9)	104.8(4)		
C3−S1−C41			101.35(10)	

Examination of the ^{31}P NMR spectra of *anti*-**4b** as a function of temperature also revealed that this complex also experiences a fluxional process in solution, with an estimated activation barrier of 12.8 kcal mol^{-1} (*anti*-**4b**: $\Delta\delta_P = 163$ Hz; $T_c = 273$ K (toluene-d_8)).[21] Considering the magnitude of the activation barrier, the fluxional process is attributed to the propeller rotation of the allene ligand, although for that complex a proper combination of solvent, temperature, and instrument allowing unambiguous characterization of each rotamer (only averaged ^1H and $^{13}C\{^1H\}$ spectra are given in the Experimental Part) could not be determined.

Structure of *anti*-$Cp'(CO)_2Mn[\eta^2\text{-}\{HC(Tol){=}C{=}C(Ph)PCy_2\}]$ (*anti*-4b). Relevant crystallographic data for *anti*-**4b** are shown in Tables 2 and 3. An ORTEP drawing of the molecule appears in Figure 2. The complex consists of an allene ligand, $HC(Tol){=}C{=}C(Ph)PCy_2$, bound to a $Cp'(CO)_2Mn$ fragment in an η^2-*C*,*C* mode through the carbon atoms C3 and C4, C3 bearing a tolyl group (which labels the carbene carbon atom in the antecedent species **1**), and a hydrogen atom. The noncoordinated carbon atom C5 bears a phenyl group and a dicyclohexylphosphido group. This clearly shows that the complex *anti*-**4b** results from a nucleophilic attack of the lithium dicyclohexylphosphide at the remote alkynyl carbene atom. Finally, the dicyclohexylphosphido group is found in a *transoid* position relative to the $MeCp(CO)_2Mn$ fragment on the C4−C5 double bond, thus conferring an *anti* configuration to the complex. The

Table 3. Crystal Data and Structure Refinements for Complexes 2a, *anti*-4b, *syn*-4b, *syn*-11, and *syn*-13

	2a	*anti*-**4b**	*syn*-**4b**	*syn*-**11**	*syn*-**13**
empirical formula	$C_{37}H_{32}Cl_2MnO_2P$	$C_{36}H_{42}MnO_2P$	$C_{36}H_{42}MnO_2P$	$C_{31}H_{27}MnO_2S$	$C_{30}H_{29}MnO_3$
M_r	665.44	592.61	592.61	518.56	492.47
T/K	180	100	120	160	180
λ/Å			0.71069		
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group (no.)	*C*2/*c* (#15)	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)
a/Å	24.054(4)	8.8673(4)	9.2247(9)	9.923(3)	13.88542(8)
b/Å	14.1761(14)	29.3918(12)	11.1454(10)	21.7612(17)	10.8128(6)
c/Å	19.2790(18)	12.0901(5)	30.466(3)	12.017(5)	17.1782(5)
β/deg	95.194(15)	107.574(4)	97.174(11)	104.77(5)	108.37(4)
V/Å^3	6547.0(13)	3003.9(2)	3107.8(5)	2509.1(14)	2442.2(6)
Z	8	4	4	4	4
D_c/g cm^{-3}	1.350	1.310	1.267	1.373	1.339
μ/mm^{-1}	0.647	0.524	0.507	0.636	0.572
F(000)	2752	1256	1256	1080	1032
θ_{max}/deg	25.98	32.09	33.38	32.5	30.3
completeness to θ_{max} (%)	0.98	0.94	0.90	0.94	0.99
index range, *hkl*	$-29 \le h \le 29$	$-13 \le h \le 12$	$-14 \le h \le 14$	$-14 \le h \le 1\,4$	$-20 \le h \le 19$
	$-17 \le k \le 17$	$-42 \le k \le 42$	$-17 \le k \le 17$	$-32 \le k \le 32$	$-12 \le k \le 15$
	$-23 \le l \le 23$	$-16 \le l \le 18$	$-42 \le l \le 44$	$-17 \le l \le 17$	$-24 \le l \le 24$
no. of reflns collected	31 480	31 224	10 897	27 553	11 2126
no. of indep reflns	6315	9853	5628	8530	7320
no. of data/restraints/params	6315/0/408	9853/0/363	5628/0/473	8530/0/319	7320/0/309
GOF	1.08	1.03	0.84	1.07	1.03
R [$I > 2\sigma(I)$]	0.0536	0.0560	0.0402	0.0424	0.0597
R_w [$I > 2\sigma(I)$]	0.1339	0.1088	0.0688	0.1048	0.1565
R (all data)	0.0669	0.0942,	0.0763	0.0781	0.1474
R_w (all data)	0.1417	0.1184	0.1072	0.1269	0.1789
$\Delta\rho_{max/min}$/e Å^{-3}	−0.44/0.63	−0.56/0.73	−0.26/0.43	−0.32/0.58	−0.75/1.18

phosphorus atom is clearly away from the manganese atom, as indicated by the nonbonding distance Mn1···P1 of 4.693(1) Å. Trends in the metrical features are similar to those found in other manganese allene complexes.[23,24] In particular, the manganese-to-central carbon atom distance (Mn−C4 = 2.011(2) Å) is significantly shorter than the manganese-to-terminal carbon atom (Mn−C3 = 2.180(2) Å). The noncoordinated C=C double bond (C4−C5 = 1.322(3) Å) compares reasonably well with those of the free allene molecules (1.307 Å),[25] in contrast to the coordinated one, which is significantly elongated (1.407(3) Å). As a consequence of its coordination to the metal, the allene is strongly bent (C3−C4−C5 = 143.86(16)°). As we can already see in Table 3, these features appear to be quite constant for all the Mn-[{η^2-allene}] complexes we shall encounter in the present report.

Structure of *syn*-Cp′(CO)$_2$Mn[η^4-{HC(Tol)=C=C(Ph)-PCy$_2$}] (*syn*-4b). As shown in Figure 3, complex *syn*-**4b** equally consists of a TolC(H)=C=C(Ph)PCy$_2$ allene ligand bound to the Cp′(CO)$_2$Mn fragment in an η^2-*C*,*C* fashion through the carbon atoms C3 and C4. As for *anti*-**4b**, C3 bears a hydrogen atom and a tolyl group, whereas the noncoordinated carbon atom C5 bears a dicyclohexylphosphine and a phenyl group, showing that the present complex also results from a nucleophilic attack of the phosphide at the remote alkynyl carbon atom. The later group now occupies a *cisoid* position relative to the metal fragment on the C5−C5 double bond, thus conferring a *syn* configuration to the complex. Even in that position, the phosphorus atom is clearly at a nonbonding distance of the manganese center (3.859(1) Å). As shown in Table 2, bonding distances and angles in both *syn*-**4b** and *anti*-**4b** complexes are otherwise similar within the experimental errors.

Subsequent Protonation with a Weak Acid. Treatment of **1** with the diorganophosphide LiPR$_2$ (R = Ph, Cy) followed by protonation with a saturated solution of NH$_4$Cl gave no traces of type- **2** complexes, whereas IR monitoring revealed the formation of allene complexes only. For R = Ph, the ^{31}P NMR analysis revealed the formation of an inseparable mixture of three different complexes (Scheme 3). The first one (14% spectroscopic yield based on the integration of ^{31}P signals) was readily characterized as the η^2-allene complex *syn*-Cp′(CO)$_2$Mn[η^2-{Ph$_2$P(Tol)C=C=C(Ph)H}] (*syn*-**3a**). The structure of the second complex, namely, Cp′(CO)$_2$Mn[η^2-{HC(Tol)=C=C-(Ph)Ph$_2$P}] (**4a**, 86% spectroscopic yield), was inferred from the spectroscopic data. Indeed, complex **4a** gives two singlets in the ^{31}P NMR spectra at 8.5 and 6.0 ppm (1:4 ratio, 121.5 MHz, 298 K), and, just like **4b**, it experiences a fluxional phenomenon. Examination of the coalescence behavior of the two ^{31}P signals led us to evaluate an energy barrier of 16.2

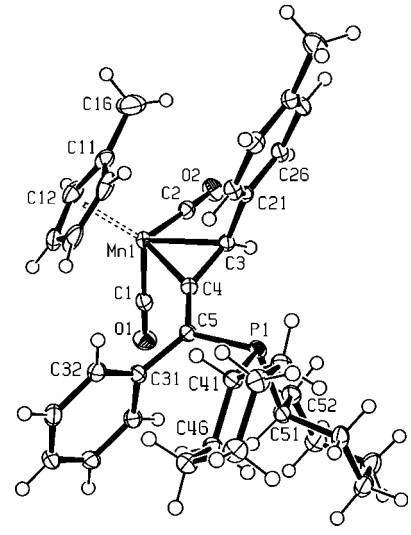


Figure 2. Perspective view of the complex *anti*-Cp′(CO)$_2$Mn[η^2-{HC(Tol)=C=C(Ph)PCy$_2$}] (*anti*-**4b**). Thermal ellipsoids are drawn at the 50% probability level.

(24) Franck-Neumann, M.; Neff, D.; Nouali, H.; Martina, D.; de Cian, A. *Synlett.* **1994**, 657.

(25) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, *S1*.

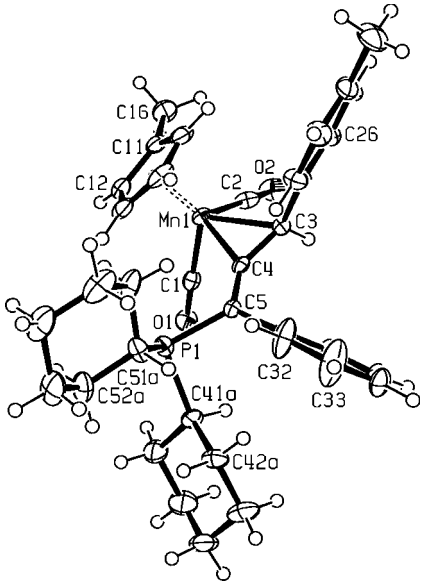


Figure 3. Perspective view of the complex *anti*-Cp′$(CO)_2$Mn[η^2-{HC(Tol)═C═C(Ph)PCy_2}] (*syn*-**4b**). Thermal ellipsoids are drawn at the 50% probability level.

kcal mol^{-1} ($\Delta\delta_P$ = 132 Hz; T_c = 338 K, toluene-d_8)[21] for the process attributed, as for **4b**, to the propeller rotation of the allene ligand.[23] In the ^{13}C NMR spectrum, each rotamer exhibits a characteristic set of three doublets at δ 191.10 ($J_{CP} \approx 53$ Hz), 132.6 ($J_{CP} \approx 20$ Hz), and 28.4 ($J_{CP} \approx 15$ Hz) ppm, and δ 189.74 ($J_{CP} \approx 53$ Hz), 132.3 ($J_{CP} \approx 20$ Hz), and 30.9 ($J_{CP} \approx 15$ Hz) ppm, respectively, for the C_β, C_γ, and C_α carbon atoms (see Scheme 3 for labeling scheme), whereas in the ^1H NMR spectrum, the protons attached to C_α provide two characteristic singlets at δ 4.05 and 3.96 ppm. ROESY experiments aimed at determining whether this complex was the *syn* or *anti* isomer remained, however, inconclusive. Finally, the ^{31}P spectrum also showed a set of singlets at 20.1 and 22.2 ppm (1:1 ratio, 121.5 MHz, 298 K) corresponding to a third complex present in trace amounts only (ca. 1% spectroscopic yield). These two signals were found to coalesce at 369 K due to a dynamic process, the barrier of which is about 17.2 kcal mol^{-1}.[21] Although the latter complex could not be more precisely characterized, we presume it may correspond to the second isomer: *syn* or *anti*-**4a**.

For R = Cy, ^{31}P NMR analysis of the crude reaction mixture (after filtration on an alumina plug) showed that the reaction affords *exclusively* complex **4b**. The latter was isolated in 74% yield as a 1:2 mixture of *syn* and *anti* isomers.

Mechanistic Considerations. As noted in the Introduction, the use of *neutral* phosphorus probes demonstrated that manganese alkynyl carbene complexes are prone to undergo nucleophilic attack at the remote carbon atom, a reaction pathway that, for bulky incoming substrates, is strongly favored over nucleophilic attack at the carbenic carbon center.[10] Here, the lithium diorganophosphides must be considered as bulky substrates due to their known ability to form aggregates in THF solution,[26] and they do appear even bulkier than their neutral secondary phosphine antecedents.[26c] Thus, nucleophilic attack of the organylphosphide at the remote alkynyl carbon atom to form the anionic η^1-allenyl metalate species **A** is likely to be strongly favored over the formation of anionic η^1-propargyl metalate species **B** (Scheme 4).[27] On one hand, protonation of **A** with a strong organic acid CF_3SO_3H takes place at the less hindered basic site, namely, the P atom, thus affording the zwitterionic η^1-allenyl species **C**. This intermediate species is identical to the one invoked by us in the course of the addition of secondary phosphines to **1** and, likewise, a fast rearrangement by 1,3-hydrogen migration followed by a CO insertion into the Mn═C bond en route to **2**. In the case where R = Cy, the P atom is more protected by steric hindrance. Thus, protonation may competively take place at the Mn center to produce the hydrido species **D**. Then, a reductive elimination from the incipient η^1-allenyl affords **4**, eventually as a mixture of *anti* and *syn* isomers. A similar mechanism was previously proposed by Casey et al. to account for the formation of the parent allene complex [(η^5-C_5H_5)$(CO)_2$Re[η^2-{TolC(H)═C═C(Ph)PPh_2Me}]-[OTf] upon protonation of the zwiterionic η^1-allyl complex [(η^5-C_5H_5)$(CO)_2$Re[η^1-{TolC═C═C(Ph)PPh_2Me}].[12] On the other hand, protonation with a weak acid, such as aqueous NH_4Cl, takes place only at the Mn center to afford **D**, as the unique (R = Cy) or largely major (R = Ph) intermediate species, ultimately producing **4** upon reductive elimination. Complex **3**, which was observed in trace amounts for R = Ph only and whatever the protonation source is, likely arises from protonation of the η^1-propargyl species **B** under such conditions. Such a protonation type has been shown in some instances to be highly *anti*-selective.[28]

Digression into the Thermal Rearrangement of the Phosphinoallene Complexes 3a and 4a,b. During the course of ^{31}P NMR experiments aimed at determining the rotation barrier of the allene ligands in **3** and **4**, we were led to observe that such complexes are easily transformed under thermal activation. A shift of the ^{31}P NMR signal from the 5–20 ppm range in **3** and **4** to the 96–98 ppm range, as well as a shift of IR ν_{CO} bands from 1977, 1922 cm^{-1} in **3** and **4** to 1934, 1872 cm^{-1}, were clearly indicative that coordination of the pendant phosphorus atom had taken place. The rearrangements of complexes **3a** and **4a** (always containing ca. 10% of **3a**, *vide supra*) and **4b** were found to be complete over 3 h in refluxing THF, thus giving Cp′$(CO)_2$Mn[η^1-{Ph_2P(Tol)C═C═C(Ph)H}] (**5a**), Cp′$(CO)_2$Mn[η^1-{Ph_2P(Ph)C═C═C(Tol)H}] (**6a**, contaminated by ca. 10% of **5a**), or (η^5-MeC_5H_5)$(CO)_2$Mn[η^1-{Cy_2P(Ph)C═C═C(Tol)H}] (**6b**), respectively, in good yields (Schemes 5 and 6). Complexes **5a** and **6a**,**b** were characterized by the usual spectroscopic techniques. In addition to the ^{31}P NMR and IR characteristics just mentioned, the spectroscopic signature of complexes **5a** and **6a**,**b** consists of a doublet at 209.4, 209.7, or 207.7 ppm, respectively, in the ^{13}C NMR spectra for the central carbon of the pendant allene moiety (J_{CP} = 3 Hz) and a doublet at 6.23, 6.23, or 6.45 ppm, respectively, in the ^1H NMR spectra for the allenic H atom (J_{HP} = 5 Hz).

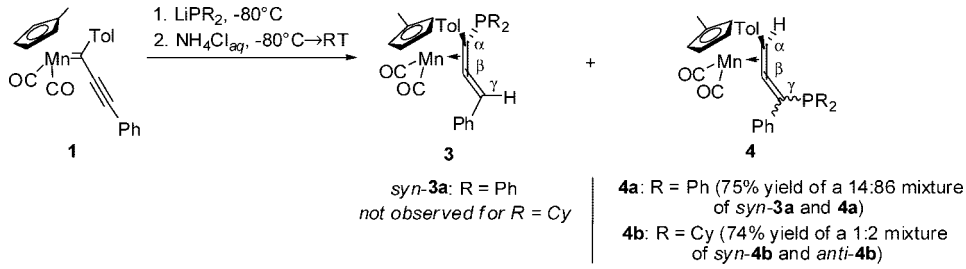
Although a detailed investigation of the mechanism of these transformations was beyond the present objective, we were intrigued by the fact that monitoring the transformation of **3a** by ^{31}P NMR spectroscopy revealed the presence of two transient

(26) (a) Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243. (b) Reich, H. J.; Dykstra, R. R. *Organometallics* **1994**, *13*, 4578. (c) Fernández, I.; Martínez-Viviente, E.; Pregosin, P. S. *Inorg. Chem.* **2004**, *15*, 4555.

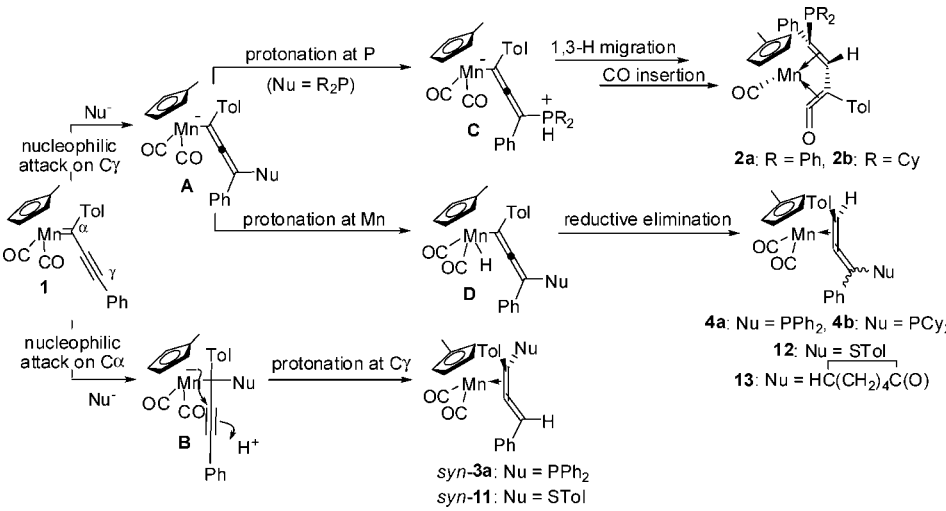
(27) The IR monitoring clearly reveals the anionic nature of the intermediate species, but neither supports nor contradicts the formation of an allenyl and/or a propargyl species. Indeed, one would expect a weak band at ca. 1840–1860 cm^{-1} ascribable to the $\nu_{C=C=C}$ vibration,[10] which is not clearly observed, possibly due to an overlap with the leftmost ν_{CO} band (1873 cm^{-1}). On the other hand, the propargylic species, which should display a weak IR band at ca. 2180 cm^{-1} for the $\nu_{C\equiv C}$ vibration,[10] may not be observable due to an extremely low concentration under these reaction conditions.

(28) (a) Lichtenberg, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 8271. (b) Lichtenberg, D. W.; Wojcicki, A. *J. Organomet. Chem.* **1975**, *94*, 311. (c) Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 3060.

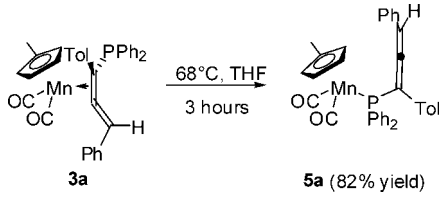
Scheme 3



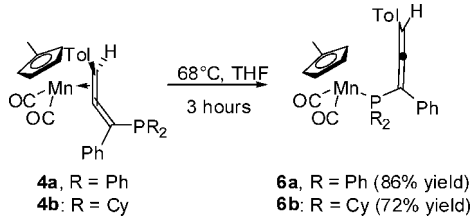
Scheme 4



Scheme 5



Scheme 6



species (Figure 4), which could eventually be intercepted by quenching the reaction at room temperature after 30 min.

The first species, **7a**, was identified as the free diphenyl(1-tolyl-3-phenyl-1,2-propadienyl) phosphine. Interestingly, **7a** could be alternatively obtained in a nearly quantitative yield upon photolysis of **3a** in dichloromethane solution (Scheme 7). The second transient species detected at intermediate stage appeared to be a *bimetallic* complex of the diphenyl(1-tolyl-3-phenyl-1,2-propadienyl) phosphino-allene ligand, namely, $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3\text{-}\{Ph_2P(Ph)C{=}C{=}C(Tol)H\}]$ (**8a**), in which the phosphino-allene ligand is bound to a first $Cp'(CO)_2Mn$ unit through the phosphorus atom and to a second $Cp'(CO)_2Mn$ unit via coordination of the C═C(H)Ph bond of the allene moiety. Noticeably, the same complex could also be prepared in good yields upon reaction of $Cp'(CO)_2Mn(THF)$ with either **5a** (66% yield) or **3a** (56% yield). The second route shows that, surprisingly enough, coordination of a $Cp'(CO)_2Mn$ unit to the pendant phosphorus atom of **3a** induces a slippage of the allene moiety, which otherwise does not occur spontaneously.

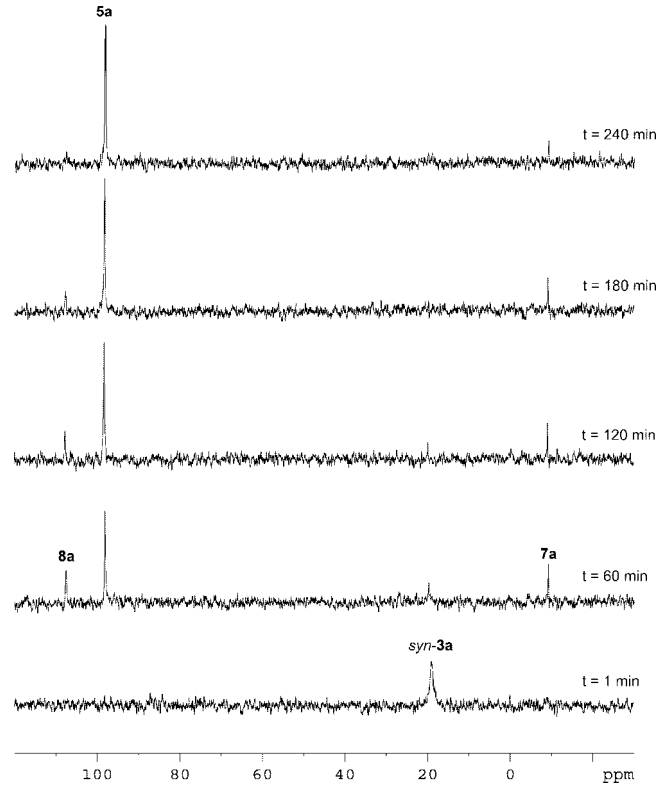
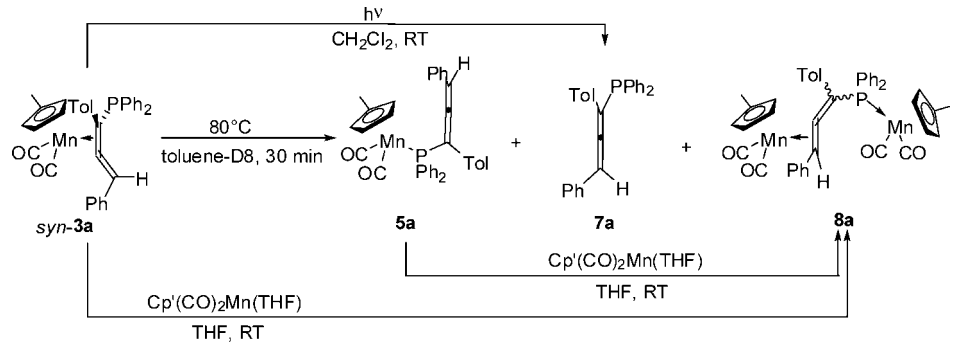
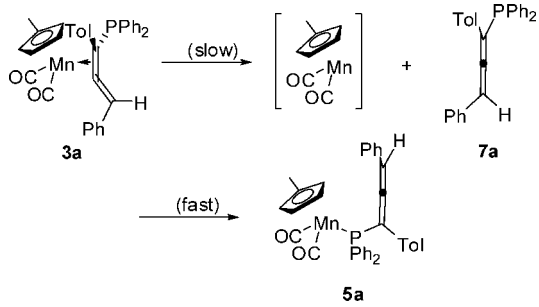


Figure 4. Monitoring by $^{31}P\{^1H\}$ NMR of the thermal rearrangement of **3a** to give **5a** (70 °C, toluene-d_8).

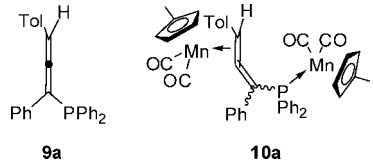
Scheme 7



Scheme 8



Scheme 9



Butler et al.[29] and Angelici et al.[30] have shown that the substitution of η^1-(thio)ethers or η^2-alkene attached to a $Cp(CO)_2Mn$ fragment for a phosphine proceeds through a dissociative S_N1 mechanism. On this basis, one could envisage that the rearrangement **3a** → **5a** proceeds through a similar dissociative pathway, where recapture of the liberated phosphinoallene ligand by an unsaturated $Cp'(CO)_2Mn$ fragment would take place irreversibly via the phosphorus atom—possibly within the solvent cage—ultimately leading to the final product **5a** (Scheme 8).

The accumulation of the bimetallic species **8a** at intermediate stage could arise from competitive capture of $Cp'(CO)_2Mn$ fragments either by the starting complex **3a** acting as an excellent σ-donor ligand or by the final complex, **5a**, acting as a potential π-donor ligand, or **7a** acting as a bidentate σ/π-donor ligand. On the other hand, no matter the source of **8a**, competitive dissociation of the allene-bound metal fragment "$Cp'(CO)_2Mn$" from **8a** would also lead to **5a**.

Monitoring the thermal rearrangement of **4a** led to a similar observation, namely, an accumulation of the diphenyl(1-phenyl-3-tolyl-1,2-propadienyl) phosphine (**9a**) and the bimetallic species $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3\text{-}\{Ph_2P(Ph)C{=}C{=}C(H)Tol\}]$ (**10a**) in the early stages of the reaction (Scheme 9), followed by total conversion into **6a**.

Finally, a monitoring of the thermal rearrangement of *syn*- and *anti*-**4b** shows very little accumulation of the transient species. Only traces of dicyclohexyl(1-phenyl-3-tolyl-1,2-propadienyl) phosphine (**9b**), which could otherwise be prepared by photolysis of *syn*/*anti*-**4b**, could be detected. Noticeably, when the rearrangement was performed starting from *pure syn*-**4b,** an accumulation of *anti*-**4b** was observed in the early stages of the reaction. This *syn* → *anti* isomerization may result from competitive recombination of transient $Cp'(CO)_2Mn$ fragments with **9b**, in the direction of the less hindered *anti* isomer.

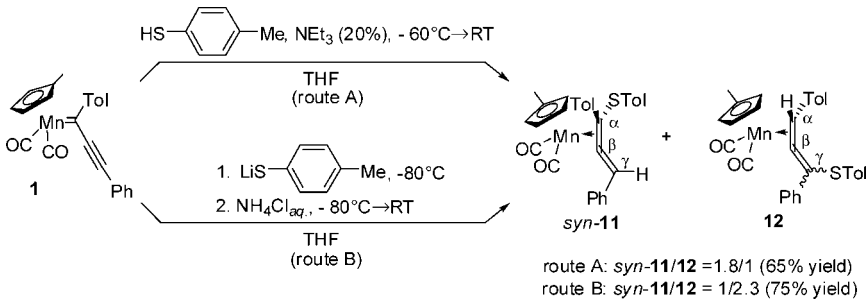
Extension to Representative S- and C-Nucleophiles. Reactivity of the Alkynyl Carbene $Cp'(CO)_2Mn{=}C(Tol)\text{-}C{\equiv}CPh$ (1) toward *p*-Toluenethiol and toward Lithium *p*-Toluenethiolate Followed by Protonation. Although preliminary experiments indicated that the alkynyl carbene complex $Cp'(CO)_2Mn{=}C(Tol)C{\equiv}CPh$ (**1**) does not spontaneously react with *p*-toluenethiol, we were led to observe that a reaction takes place in the presence of a substoichiometric amount of triethylamine (20%). IR monitoring showed the appearance of two ν_{CO} bands at 1920 and 1972 cm^{-1}, compatible with the formation of an allene species $Cp'(CO)_2Mn[\{\eta^2\text{-allene}\}]$. Although chromatographic workup afforded a single yellow band, subsequent NMR analyses revealed that the reaction product consists of a 1.8:1 mixture of two inseparatable isomeric allene complexes, formulated as $Cp'(CO)_2Mn[\eta^2\text{-}\{TolS(Tol)C{=}C{=}C\text{-}(Ph)H\}]$ (**11**) and $Cp'(CO)_2Mn[\eta^2\text{-}\{H(Tol)C{=}C{=}C(Ph)STol\}]$ (**12**) (Scheme 10, route A).

On the other hand, stepwise sequential treatment of the alkynyl carbene complex $Cp'(CO)_2Mn{=}C(Tol)C{\equiv}CPh$ (**1**) with lithium *p*-toluenethiolate and NH_4Cl_{aq} led eventually to a mixture of the same complexes, **11** and **12**, via the intermediacy of an anionic species (IR (ν_{CO}, THF): 1879(s), 1802(m), 1760(m) cm^{-1}). Significantly, under such conditions, complex **12** appears to be the major reaction product (Scheme 10, route B).

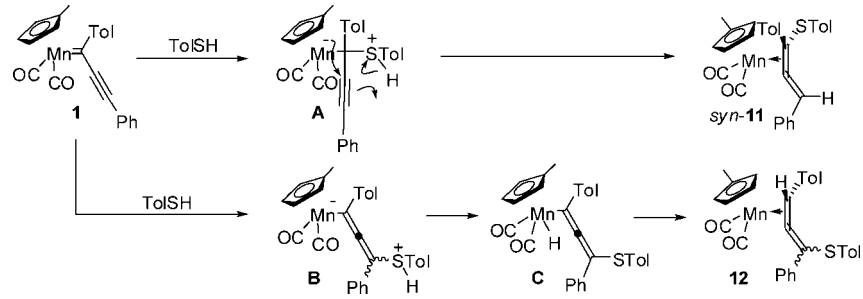
Complexes $Cp'(CO)_2Mn[\eta^2\text{-}\{TolS(Tol)C{=}C{=}C(Ph)H\}]$ (**11**) and $[Cp'(CO)_2Mn[\eta^2\text{-}\{H(Tol)C{=}C{=}C(Ph)STol\}]$ (**12**) were characterized by usual spectroscopic techniques complemented for **11** by an X-ray structure analysis revealing the *syn* configuration of the complex. The room-temperature $^{13}C\{^1H\}$ NMR spectrum of the *syn*-**11/12** mixture shows in particular two sets of three signals at δ 170.9 (br), 125.5 (br), and 38.5 (br) ppm and at δ 180.2 (br), 123.2 (br), and 33.3 (br) ppm, attributable to the C_β, C_γ, and C_α carbon atoms for the coordinated allenic chain within *syn*-**11** and **12**, respectively (see Scheme 10 for labeling). Each isomer gives very distinct and characteristic signals for the proton attached to the allenic chain at δ 8.20 (s br) ppm for *syn*-**11** and at δ 4.1 (s br) ppm for **12**. Upon cooling the samples in the NMR probe, all isolated signals are clearly seen to split, thereby revealing that both complexes actually experience a fluxional process in solution. Examination of the coalescence behavior of the two pairs of signals attributable to C_β within complexes *syn*-**11** and **12** led to the evaluation of activation barriers of ca. 13.0 and 14.0 kcal mol^{-1}, respectively (*syn*-**11**: $\Delta\delta_{C\beta} = 688$ Hz; $T_c = 293$ K; **12**: $\Delta\delta_{C\beta} = 545$ Hz; $T_c = 313$ K)[21] for the fluxional processes attributed,

(29) Angelici, R.; Loewen, W. *Inorg. Chem.* **1967**, *6*, 682.
(30) Butler, I. S.; Sawai, T. *Inorg. Chem.* **1975**, *14*, 2103.

Scheme 10



Scheme 11



as for **4**, to the propeller rotation of the allene ligands.[23] Apparently, each complex exists as a single stereoisomer (without taking rotamers into account). However, the structure of **12** has not been established in full since all attempts to determine by NMR the position of the *p*-toluenethiolate group relative to the Tol/Ph groups and the position of the *p*-toluenethiolate relative to the metal fragment remained inconclusive. The proposed structure for **12** appearing in Scheme 10 rests on the parallel that can be drawn from the reactivity of **1** toward diorganophosphide, the allene isomer bearing a hydrogen α to Mn resulting in a nucleophilic attack on the remote alkynyl carbon atom. On the other hand, single crystals of *syn*-**11** could be grown, allowing full structural characterization of the complex.

Prior to this work, Moretó et al.[16a] and de Meijere et al.[31] reported that group 6 alkynyl[alkoxy] carbene complexes react with simple thiols—including *p*-toluenethiol[16a]—to form 2-thio alkenyl complexes resulting formally from an addition of the S−H bond across the C≡C triple bond. In the present work, no complex of that sort was ever observed. A mechanism that may account for the formation of the isomeric allene complexes is shown in Scheme 11. Competitive nucleophilic attack of the thiol on either the carbenic carbon atom or the remote alkynyl carbon atom would result in the formation of both zwitterionic species **A** and **B**. Closely related species have been previously identified in the reaction of **1**[10] or rhenium analogues[12] with tertiary phosphines. Triethylamine, which appears to be necessary for a reaction to occur, is likely to assist the hydrogen transfer from sulfur to C_γ[28] or to C_α, respectively, possibly through the intermediacy of the hydrido species **C** in the second case, to afford complexes *syn*-**11** and **12**, respectively. The formation of *syn*-**11** and **12** could also result from direct nucleophilic attack of **1** by *p*-TolS$^-$—generated in equilibrium concentration upon reaction of NEt_3 and *p*-TolSH—following a route that would exactly match the reaction of Ph_2P^- with **1** (Scheme 4).

The later mechanism would be the only operating one in the formation of *syn*-**11** and **12** through route B shown in Scheme 10. Just like lithium diorganophosphides, lithium thiolates are known to form bulky aggregates in THF.[32] Accordingly, lithium *p*-toluenethiolate is expected to attack at the less hindered remote alkynyl carton atom, which may account for the predominance of complex **12** over complex *syn*-**11** in that case.

Structure of *syn*-Cp′(CO)$_2$Mn[η^2-{TolS(Tol)C═C═C-(Ph)H}] (*syn*-11). Relevant crystallographic data for *syn*-**11** are shown in Tables 2 and 3, along with those for complex **4b**. An ORTEP drawing of the molecule appears in Figure 5. As expected, complex *syn*-**11** consists of the allene complex Cp′(CO)$_2$Mn[{η^2-allene}]. The allene ligand is bound to the Cp′(CO)$_2$Mn fragment through both the central atom C4 and the neighboring atom C3 bearing a tolyl group and a *p*-toluenethiolate group. Clearly, the complex *syn*-**11** results from a nucleophilic attack of the thiol—or thiolate—at the carbenic carbon center of the antecedent species **1**. The noncoordinated carbon atom C5 bears both a phenyl group and a hydrogen atom, in such a way that the phenyl ring is in *cisoid* position relative to the Cp′(CO)$_2$Mn fragment, thus conferring a *syn* configuration to the complex. Metrical features within *syn*-**11** and *syn*- or *anti*-**4b** are otherwise very similar.

Reactivity of the Alkynyl Carbene Complex Cp′(CO)$_2$-Mn═C(Tol)C≡CPh (1) toward Cyclohexanone Lithium Enolate, Followed by Protonation. The alkynyl carbene complex Cp′(CO)$_2$Mn═C(Tol)C≡CPh (**1**) was found to react with cyclohexanone lithium enolate to form an anionic species (IR (ν_{CO}, THF): 1875(s), 1805(m), 1770(m) cm^{-1}). Subsequent protonation with NH_4Cl_{aq} gave a neutral species exhibiting two ν_{CO} bands at 1972 and 1920 cm^{-1} (THF). Chromatographic workup afforded a single new complex, which was subsequently identified as the η^2-allene complex *syn*-Cp′(CO)$_2$Mn[η^2-{H(Tol)C═C═C(Ph)CH(CH$_2$)$_4$C(O)}] (*syn*-**13**) (Scheme 12).

The $^{13}C\{^1H\}$ NMR spectrum of *syn*-**13** shows the now familiar set of three signals at δ 167.81, 126.72, and 30.28 ppm

(31) (a) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1993**, *12*, 2556. (b) de Meijere, A.; Schirmer, H.; Stein, F.; Funke, F.; Duetsch, M.; Wu, Y.-T.; Noltemeyer, M.; Belgardt, T.; Knieriem, B. *Chem.−Eur. J.* **2005**, *11*, 4132.

(32) (a) Sigel, G. A.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2819. (b) Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 4231. (c) Ruhlandt-Senge, K.; Power, P. P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 594.

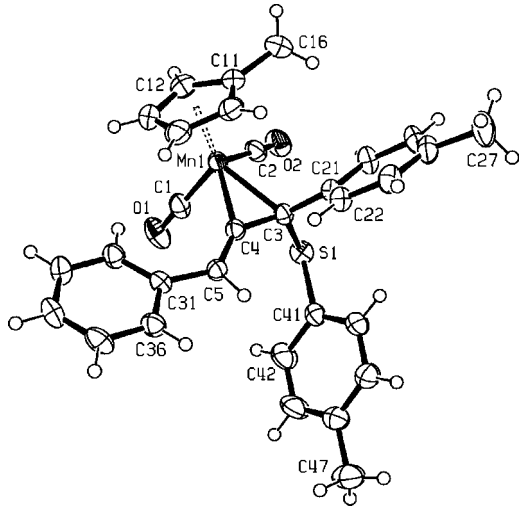
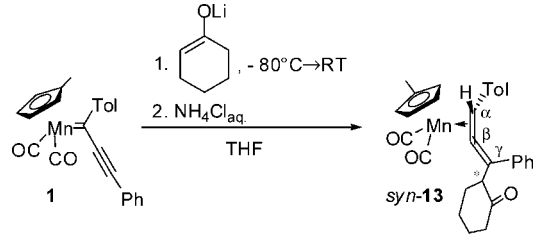


Figure 5. Perspective view of the complex *syn*-Cp′(CO)$_2$Mn[η^2-{TolS(Tol)C═C═C(H)Ph}] (*syn*-**11**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 12



attributable to the C_β, C_γ, and C_α carbon atoms of the allene chain (see Scheme 12 for labeling). The occurrence of a C-alkylation of the enolate is inferred from the spectroscopic data, clearly indicating the presence of a 2-oxocyclohexyl ring (IR ν_{CO} 1708(w) cm^{-1}; NMR ^{13}C{^{1}H} δ 211.52 (C═O), 61.06 (*C*H); NMR ^{1}H δ 4.62 (C*H*)). The ^{1}H NMR spectrum shows a characteristic signal at 3.85 ppm indicative that the allene moiety is bound to the Cp′(CO)$_2$Mn fragment via the carbon−carbon double bond H(Tol)C═C. No signal could ever be detected in the 8–9 ppm region, denoting the absence of any isomer in which the metal fragment would be bound to a carbon−carbon double bond like that of C═C(Ph)CH(CH$_2$)$_4$C(O). Although the C-alkylation of the enolate generates an additional stereogenic center within the coordinated allene ligand, all RT ^{13}C{^{1}H} NMR signals of *isolated syn*-**13** remain sharp, suggesting that not only one (*syn*) isomer is formed, but also that the C−C bond formation is diastereoselective. However, we cannot ascertain that the reaction is indeed *totally* diastereoselective since all attempts to obtain workable NMR data on the *crude* reaction material failed due to the presence of paramagnetic impurities.

Finally, single crystals of *syn*-**13** could be ultimately grown, allowing full structural characterization of the isolated complex.

Structure of *syn*-Cp′(CO)$_2$Mn[η^2-{H(Ph)C═C═C(Ph)-CHC(O)(CH$_2$)$_4$}] (*syn*-13). Relevant crystallographic data for *syn*-**13** are shown in Tables 2 and 3, along with those for complexes **4b** and *syn*-**11**. An ORTEP drawing of *syn*-**13** appears in Figure 6. As expected, the metal fragment Cp′(CO)$_2$Mn is coordinated to the H(Ph)C═C carbon−carbon double bond of the allene ligand, thus corroborating the information provided by ^{1}H NMR. The 2-oxocyclohexyl group attached to the noncoordinated carbon atom C5 of the allene ligand is adjacent to the phenyl ring that labels the remote

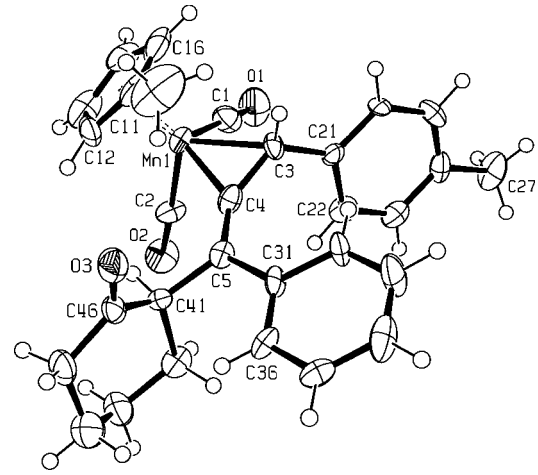


Figure 6. Perspective view of the complex *syn*-Cp′(CO)$_2$Mn[η^2-H(Ph)C═C═C(Ph)CH(CH$_2$)$_4$C(O)) (*syn*-**13**). Thermal ellipsoids are shown at the 50% probability level.

alkynyl carbon in the antecedent species **1**. Clearly, the X-ray structure revealed that complex *syn*-**13** effectively results from a nucleophilic attack of the enolate on this carbon atom, as shown in Scheme 12. Again, the bulkiness of lithium 2-cyclohexanone enolate[33] may account for a selective nucleophilic attack on that carbon atom. In addition, the phenyl ring attached to C5 is directed away from the Cp′(CO)$_2$Mn metal fragment, thus conferring a *syn* configuration to the complex. The carbon atom C41 shown in Figure 6 exhibits an *R* configuration, whereas the allene would have, if free, an *R* axial configuration (naturally, since complex *syn*-**13** crystallize in the $P2_1/n$ space group, the other enantiomer is present in the crystal). Metrical features within complex *syn*-**13**, *syn*-**11**, and **4b** are otherwise similar.

Conclusion

We have shown that the non-heteroatom-substituted alkynyl carbene complex Cp′(CO)$_2$Mn═C(Tol)C≡CPh (**1**) is prone to give η^2-allene complexes in good yields upon reaction of anionic P-, S-, or C-nucleophiles, followed by protonation. The fairly high regioselectivity observed here is understood in terms of a major mechanistic pathway involving conjugate addition of the nucleophile at the remote alkynyl carbon atom to give a transient η^1-allenylmetalate complex, which undergoes subsequent protonation at the metal followed by reductive elimination of the Mn−H bond to afford the final η^2-allene complex. Although group 6 allene complexes remain elusive, a similar mechanistic pathway may account for the observation of free allenes in certain reactions of [group 6 alkylalkoxy] alkynyl carbenes with nucleophiles.[11] The principal outgrowth of the present report is to provide the first explicit evidence for the formation of allene complexes through such a route, thereby adding a new facet to the reactivity of alkynyl carbene complexes. Although the stability of Cp$^{(\prime)}$(CO)$_2$Mn(η^2-allene) complexes might have been *a priori* regarded as a drawback for synthetic purposes, this is not the case, given that they are reactive enough to allow modifications of the coordinated allene ligand,[24,34] whereas the

(33) (a) Arnett, E. M.; Moe, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 7288. (b) Streitwieser, A.; Wang, D. Z.-R. *J. Am. Chem. Soc.* **1999**, *121*, 6213. (c) Streitwieser, A. *J. Mol. Model.* **2006**, *12*, 673.

(34) (a) Franck-Neuman, M.; Brion, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 688. (b) Franck-Neuman, M.; Martina, D.; Neff, D. *Tetrahedron: Asymmetry* **1998**, *9*, 697.

free allene may be released either by oxidation[34] or, as shown in the present work, upon photolysis, thus giving new hopes for future development.

Experimental Part

General Procedures. Tetrahydrofuran and diethyl ether used for the syntheses were distilled under nitrogen from sodium benzophenone ketyl just before use. Other solvents were purified following standard procedure and stored under nitrogen. The reagent grade chemicals *n*BuLi (1.6 M solution in hexane), $HPPh_2$, $HPCy_2H$, TolSH, and trimethylsilyloxycyclohexene were obtained from Aldrich and used without further purification. $Cp'(CO)_2Mn{=}C(Tol)C{\equiv}CPh$ (**1**) was prepared following literature procedures.[10] All synthetic manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. A liquid N_2/2-propanol slush bath was used to maintain samples at the desired low temperature. Chromatographic separation of the complexes was performed on alumina (neutral, activity III (Aldrich)). Solution IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer with 0.1 mm cells equipped with CaF_2 windows. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on Bruker AC200, WM250, DPX300, AMX400, or AMX500 spectrometers and were referenced to the residual signals of the deuterated solvent. NMR spectra were recorded at room temperature unless otherwise specified. Mass spectra were recorded on AEI-MS9 or Nermag R10-10 mass spectrometers (EI). Microanalyses of C and H elements were performed on a Perkin-Elmer 2400 CHN analyzer.

Formation of $Cp'(CO)_2Mn[\eta^4$-{$Ph_2P(Ph)C{=}CHC(Tol){=}C{=}O$}] (2a) and $Cp'(CO)_2Mn[\eta^2$-{$Ph_2P(Tol)C{=}C{=}C(Ph)H$}] (*syn*-3a) upon Reaction of 1 with $LiPPh_2$ Followed by Protonation with CF_3SO_3H. A THF solution of lithium diphenylphosphide—generated *in situ* by addition of *n*BuLi (0.470 mL of a 1.6 M solution in hexane, 0.67 mmol) to a solution of $HPPh_2$ (0.100 mL, 0.57 mmol) in THF (3 mL) at 0 °C—was added dropwise to a solution of complex $Cp'(CO)_2Mn{=}C(Tol)CCPh$ (**1**, 0.197 g, 0.50 mmol) in THF (10 mL) at –80 °C. The solution turned orange. A slight excess of CF_3SO_3H (0.050 mL, 0.57 mmol) was added, inducing a darkening of the solution. After stirring the solution for 2 min, the cold bath was removed and the solvent was removed under high vacuum to give an oily brown residue, which was subject to treatment by column chromatography on alumina. An initial elution with a 1:4 diethyl ether/pentane mixture gave a yellow band containing trace amount of $Cp'(CO)_2Mn[\eta^2$-{$Ph_2P(Tol)C{=}C{=}C(Ph)H$}] (*syn*-**3a**, ca. 0.005 g, ca. 2%). A second elution with a 1:1 diethyl ether/pentane mixture afforded a brown band containing $Cp'(CO)_2Mn[\eta^4$-{$Ph_2P(Ph)C{=}CHC(Tol){=}C{=}O$}] (**2a**), which was subsequently isolated as a brown microcrystalline solid (0.203 g, 0.36 mmol, 72% yield). Crystals of **2a** suitable for an X-ray diffraction analysis were grown from a dichloromethane/hexane mixture in the cold.

2a: ^1H NMR (400.1 MHz, 233 K, CD_2Cl_2) δ 8.00–6.28 (m, C_6H_5 and MeC_6H_4), 6.24 (d, 1H, H_β, $^3J_{HP}$ = 9 Hz), 4.40–3.64 (m, 4H, MeC_6H_4), 2.41 (s, 3H, *Me*C_6H_4), 1.88 (s, 3H, *Me*C_5H_4); $^{13}C\{^1H\}$ NMR (100.6 MHz, 233 K, CD_2Cl_2) δ 237.4, 232.0 (*C*O), 142.9–124.8 (C_6H_5 and MeC_6H_4), 101.3, 89.7, 88.5 (d, $^3J_{CP}$ = 2 Hz), 86.4 (d, $^3J_{CP}$ = 2 Hz), 86.1 (d, $^3J_{CP}$ = 2 Hz) (MeC_5H_4), 83.3 (d, C_β, $^2J_{CP}$ = 33 Hz), 73.9 (d, C_η, $^1J_{CP}$ = 32 Hz), 29.1 (d, C_α, $^3J_{CP}$ = 8 Hz), 21.4 (*Me*C_6H_4), 13.6 (*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (121.5 MHz, 233 K, CD_2Cl_2) δ 18.4; MS (EI) *m*/*z* 580 $[M]^+$, 552 $[M - CO]^{+\cdot}$, 524 $[M - 2CO]^+$; IR (CH_2Cl_2): 1961, 1724 (η_{CO}). Anal. Calcd for $C_{36}H_{30}MnO_2P$: C, 74.47; H, 5.21. Found: C, 74.35; H, 5.23.

syn-**3a**: ^1H NMR (400.1 MHz, CD_2Cl_2) δ 8.72 (s, 1H, H_η), 8.8–6.9 (m, C_6H_5 and MeC_6H_4), 4.52, 4.46, 3.96, 3.17 (m, 4H, MeC_5H_4), 2.45 (s, 3H, *Me*C_6H_4), 1.96 (s, 3H, *Me*C_5H_4); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2) δ 236.5 (d, $^3J_{PC}$ = 16 Hz), 228.9 (*C*O), 165.1 (d, C_β, $^2J_{CP}$ = 7 Hz), 147.0–124.5 (C_6H_5 and MeC_6H_4), 126.2 (C_η), 103.0, 95.4, 92.3, 89.9, 82.1 (MeC_5H_4), 35.3 (d, C_α, $^1J_{CP}$ = 24 Hz), 21.6 (*Me*C_6H_4), 13.7 (*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ 21.5; MS (EI) *m*/*z* 580 $[M]^{+\bullet}$, 524 $[M - 2(CO)]^{+\bullet}$, 390 $[M - Cp'(CO)_2Mn]^+$; IR (CH_2Cl_2): 1977, 1922 (ν_{CO}).

Formation of $Cp'(CO)_2Mn[\eta^4$-{$Ph_2P(Ph)C{=}CHC(Tol){=}C{=}O$}] (2b) and $Cp'(CO)_2Mn[\eta^2$-{$H(Tol)C{=}C{=}C(Ph)PCy_2$}] (4b) upon Reaction of 1 with $LiPCy_2$ Followed by Protonation with CF_3SO_3H. In a typical experiment, a THF solution of lithium dicyclohexylphosphide—generated *in situ* by addition of *n*BuLi (0.70 mL of a 1.6 M solution in hexane, 1.1 mmol) to a solution of $HPCy_2$ (0.240 mL, 1.1 mmol) in THF (3 mL) at 0 °C—was added dropwise to a solution of complex $Cp'(CO)_2Mn{=}C(Tol)CCPh$ (**1**, 0.099 g, 0.25 mmol) in THF (20 mL) at –80 °C. The solution turned orange. A slight excess of CF_3SO_3H (0.030 mL, 0.34 mmol) was then added. After stirring the solution for 2 min, the cold bath was removed and the solvent was removed under high vacuum to give an oily residue, which was subject to treatment by column chromatography on alumina. An initial elution with a 1:10 diethyl ether/pentane mixture gave a yellow band containing complex $Cp'(CO)_2Mn[\eta^2$-{$Tol(H)C{=}C{=}C(Ph)PCy_2$}] (**4b**) as a ca. 1:2 mixture of *syn*/*anti* isomers, which were isolated as a yellow foam upon removal of the solvents (0.039 g, 0.065 mmol, 26% yield). A second elution with a 1:1 diethyl ether/pentane mixture afforded a brown band containing $Cp'(CO)_2Mn[\eta^4$-{$Cy_2P(Ph)C{=}CHC(Tol){=}C{=}O$}] (**2b**), which was subsequently isolated as a brown microcrystalline solid (0.083 g, 0.14 mmol, 55% yield). Analytically pure *syn*-**4b** and *anti*-**4b** were obtained by fractional crystallization from a solution in a 1:1 ether/hexane mixture. Some of the crystals obtained were suitable for X-ray diffraction analyses.

2b: ^1H NMR (400.1 MHz, 233 K, CD_2Cl_2) δ 7.8–6.2 (m, C_6H_5 and MeC_6H_4), 5.92 (d, 1H, H_β, $^3J_{HP}$ = 13 Hz), 5.0–4.2 (m, 4H, η^5-MeC_5H_4), 2.9–0.8 ($C_{11}H_{22}$), 2.40 (s, *Me*C_6H_4), 1.74 (s, *Me*C_5H_4); $^{13}C\{^1H\}$ NMR (100.6 MHz, 213 K, CD_2Cl_2) δ 237.2–232.8 (CO), 144.4–125.1 (C_6H_5 and MeC_6H_4), 102.5, 88.6, 88.4 ($^3J_{CP}$ = 5 Hz), 86.5 ($^3J_{CP}$ = 6 Hz), 86.1 (MeC_5H_4), 89.7 (C_β, $^2J_{CP}$ = 43 Hz), 71.9 (C_γ, $^1J_{CP}$ = 41 Hz,), 31.8 (C_α, $^3J_{CP}$ = 15 Hz), 38.0–26.9 ($C_{11}H_{22}$), 21.7 (*Me*C_6H_4), 13.3 (*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (202.6 MHz, 213 K, CD_2Cl_2) δ 36.2; MS (CI) *m*/*z* 593 $[MH]^+$, 564 $[MH - CO]^+$, 536 $[MH - 2CO]^+$; IR (THF) 1960, 1745 (η_{CO}). Anal. Calcd for $C_{36}H_{42}MnO_2P$: C, 72.94; H, 7.15. Found: C, 72.87; H, 7.08.

syn-**4b**: ^1H NMR (500.3 MHz, 213 K, CD_2Cl_2) δ 7.2–6.8 (m, MeC_6H_4 and C_6H_5), 4.95, 4.77, 4.75, 4.56 (m, MeC_5H_4, major rotamer), 4.93, 4.89, 3.90, 3.36 (m, MeC_5H_4, minor rotamer), 3.84 (s, H_α, major), 3.44 (s, H_α, minor), 2.17 (s, *Me*C_6H_4), 1.95 (s, *Me*C_5H_4, major), 1.84 (s, *Me*C_5H_4, minor), 2.3–0.9 (m, C_6H_{11}); $^{13}C\{^1H\}$ NMR (125.8 MHz, 213 K, CD_2Cl_2) δ 235.7, 230.5 (*C*O, minor), 233.1, 231.0 (*C*O, major), 188.1 (d, C_β, $^2J_{CP}$ = 24 Hz, major), 186.4 (d, C_β, $^2J_{CP}$ = 24 Hz, minor), 144.5–127.4 (MeC_6H_4 and C_6H_5), 131.8 (d, C_γ, $^1J_{CP}$ = 38 Hz, major), 130.9 (d, C_γ, $^1J_{CP}$ = 38 Hz, minor), 102.8, 89.9, 88.5, 85.3, 84.9 (MeC_5H_4, major), 102.6, 91.5, 91.4, 89.3, 83.5 (MeC_5H_4, minor), 36.2–26.4 (C_6H_{11}), 27.7 (d, C_α, $^3J_{CP}$ = 15 Hz, minor), 27.6 (d, C_α, $^3J_{CP}$ = 15 Hz, major), 21.1 (*Me*C_6H_4, major), 21.0 (*Me*C_6H_4, minor), 13.4 (*Me*C_5H_4, minor), 13.0 (*Me*C_5H_4, major); $^{31}P\{^1H\}$ NMR (121.5 MHz, 298 K, toluene-d_8) δ 10.5 (br s); $^{31}P\{^1H\}$ NMR (121.5 MHz, 263 K, toluene-d_8) δ 9.5, 9.3; IR (THF): 1978, 1922 (ν_{CO}); MS (EI) *m*/*z* 592 $[M]^+$, 536 $[M - 2CO]^+$, 402 $[M - Cp'(CO)_2Mn]^+$. Anal. Calcd for $C_{36}H_{42}MnO_2P$: C, 72.96; H, 7.14. Found: C, 73.01; H, 7.51.

anti-**4b**: ^1H NMR (500.3 MHz, 223 K, CD_2Cl_2) δ 7.8–6.5 (m, MeC_6H_4 and C_6H_5), 4.53, 4.43, 4.28, 3.89 (m, 4H, MeC_5H_4), 3.61 (s, 1H, H_α), 2.29 (s, 3H, *Me*C_6H_4), 1.61 (s, *Me*C_5H_4), 2.0–0.9 ($C_{11}H_{22}$); $^{13}C\{^1H\}$ NMR (125.8 MHz, 213 K, CD_2Cl_2) δ 233.4, 230.1 (*C*O), 182.5 (d, C_β, $^2J_{CP}$ = 28 Hz), 143.1–125.2 (MeC_6H_4 and C_6H_5), 131.4 (d, C_γ, $^1J_{CP}$ = 34 Hz), 101.5, 86.8, 86.7, 85.3, 84.7, (MeC_5H_4), 35.4–26.4 ($C_{11}H_{22}$), 27.4 (d, C_α, $^3J_{CP}$ = 13 Hz), 21.1 (s, *Me*C_6H_4), 12.8 (s, η^5-*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (121 MHz,

298 K, toluene-d_8) δ 33.2; $^{31}P\{^1H\}$ NMR (121.5 MHz, 213 K, toluene-d_8) δ 31.8, 30.4; IR (THF) 1978, 1922 (ν_{CO}); MS (EI) *m/z* 592 $[M]^+$, 536 $[M - 2CO]^+$, 402 $[M - Cp'(CO)_2Mn]^+$. Anal. Calcd for $C_{36}H_{42}MnO_2P$: C, 72.96; H, 7.14. Found: C, 72.98; H, 7.00.

Formation of $Cp'(CO)_2Mn[\eta^2$-{$Ph_2P(Tol)C{=}C{=}C(Ph)H$}] (*syn*-3a) and $Cp'(CO)_2Mn[\eta^2$-{$H(Tol)C{=}C{=}C(Ph)PPh_2$}] (4a) upon Reaction of 1 with $LiPPh_2$ Followed by Protonation with NH_4Cl_{aq}. A THF solution of lithium diphenylphosphide—generated *in situ* by addition of ^{n}BuLi (0.850 mL of a 1.6 M solution in hexane, 1.36 mmol) to a solution of $HPPh_2$ (0.190 mL, 1.1 mmol) in THF (3 mL) at 0 °C—was added dropwise to a solution of complex $Cp'(CO)_2Mn{=}C(Tol)C{\equiv}CPh$ (**1**, 0.394 g, 1 mmol) in THF (20 mL) at –80 °C. The solution turned orange. A saturated solution of NH_4Cl (ca. 0.2 mL) in water was then added. After stirring the solution for 2 min, the cold bath was removed, 10 mL of diethyl ether was added, and the organic phase was transferred into another Schlenk flask by mean of a canula. The solvents were removed under high vacuum, and the oily yellow residue was purified by chromatography on alumina. An initial elution with a 1:4 diethyl ether/pentane mixture gave a yellow band. Removal of the solvents under high vacuum left a yellow foam (0.435 g, 0.75 mmol, 75% yield). NMR analysis showed the foam to contain 86% of $Cp'(CO)_2Mn[\eta^2$-{$H(Tol)C{=}C{=}C(Ph)PPh_2$}] (**4a**), 12% of isomer $Cp'(CO)_2Mn[\eta^2$-{$Ph_2P(Tol)C{=}C{=}C(Ph)H$} (*syn*-**3a**), and ca. 2% of an impurity that may correspond to a second isomer of **4a**.

4a (from a **4a**:*syn*-**3a** mixture): ^1H NMR (300.1 MHz, CD_2Cl_2, 303 K) δ 7.6–7.1 (m, MeC_6H_4 and C_6H_5), 5.0–4.7 (m, MeC_5H_4), 4.00 (s, H_α), 2.35 (s, *Me*C_6H_4), 2.05 (s, *Me*C_5H_4); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ 232.1, 230.2 (*C*O), 189.2 (d, $^2J_{CP} = 53$ Hz, C_β), 143.3–129.4 (MeC_6H_4 and C_6H_4), 132.6 (d, $^1J_{CP} = 45$ Hz, C_η), 103.3, 90.4, 89.3, 87.2, 86.1 (MeC_5H_4), 29.1 (d, $^3J_{CP} = 15$ Hz, C_α), 21.0 (*Me*C_6H_4), 13.3 (*Me*C_5H_4); ^1H NMR (500.3 MHz, CD_2Cl_2, 253 K) δ 7.9–6.9 (m, C_6H_5 and MeC_6H_4), 5.02, 4.97, 4.88, 4.78 (m, MeC_5H_4, major rotamer), 4.95, 4.67, 4.03, 3.61 (m, MeC_5H_4, minor rotamer), 4.05 (s, H_α, major), 3.96 (s, H_α, minor), 2.31 (s, *Me*C_6H_4, minor), 2.29 (s, *Me*C_6H_4, major), 2.00 (s, *Me*C_5H_4); $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 253 K) δ 232.1, 230.2 (*C*O, minor), 235.3, 229.9 (*C*O, major), 191.1 (d, C_β, $^2J_{CP} =$ 53 Hz, major), 189.7 (d, C_β, $^2J_{CP} = 53$ Hz, minor), 143.5–125.5 (C_6H_5 and MeC_6H_4), 132.6 (d, C_γ, $^1J_{CP} = 20$ Hz, major), 132.3 (d, C_γ, $^1J_{CP} = 20$ Hz, minor), 103.3, 90.4–87.2 (MeC_5H_4), 30.9 (d, C_α, $^3J_{CP} = 15$ Hz, minor). 28.4 (d, C_α, $^3J_{CP} = 15$ Hz, major), 21.0 (*Me*C_6H_4), 13.3 (*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8, 303 K) δ 8.5 (minor), 6.0 (major); IR (THF) 1975, 1925 (ν_{CO}); MS (CI) *m/z* 581 $[MH]^+$, 525 $[MH - 2CO]^+$, 391 $[MH - Cp'(CO)_2Mn]^+$. Anal. Calcd for $C_{36}H_{30}MnO_2P$: C, 74.47; H, 5.21. Found: C, 74.62; H, 5.03.

Synthesis of $Cp'(CO)_2Mn[\eta^2$-{$H(Tol)C{=}C{=}C(Ph)PCy_2$}] (4b) upon Reaction of 1 with $LiPPh_2$ Followed by Protonation with NH_4Cl_{aq}. A THF solution of lithium dicyclohexylphosphide—generated *in situ* by addition of ^{n}BuLi (0.690 mL of a 1.6 M solution in hexane, 1.1 mmol) to a solution of $HPCy_2$ (0.220 mL, 1.1 mmol) in THF (3 mL) at 0 °C—was added dropwise to a solution of complex $Cp'(CO)_2Mn{=}C(Tol)C{\equiv}CPh$ (**1**, 0.394 g, 1 mmol) in THF (20 mL) at –80 °C. The solution turned orange. A saturated solution of NH_4Cl (ca. 0.2 mL) in water was then added. After stirring the solution for 2 min, the cold bath was removed, 10 mL of diethyl ether was added, and the organic phase was transferred into another Schlenk flask by mean of a canula. The solvents were removed under high vacuum, and the oily yellow residue was purified by chromatography on alumina. Elution with a 1:10 diethyl ether/pentane mixture gave a yellow band. Removal of the solvents under high vacuum left **4b** as a yellow foam (0.480 g, 0.81 mmol, 81% yield). NMR analysis showed the foam to contain pure $Cp'(CO)_2Mn[\eta^2$-{$H(Tol)C{=}C{=}C(Ph)$-PCy_2}] (**4b**) as a 1:2 mixture of *syn* and *anti* isomers.

Synthesis of Complexes $Cp'(CO)_2Mn[\eta^1$-{$Ph_2P(Tol)C{=}C{=}C(Ph)H$}] (5a), $Cp'(CO)_2Mn[\eta^1$-{$Ph_2P(Ph)C{=}C{=}C(Tol)H$}] (6a), and $(\eta^5$-$MeC_5H_5)(CO)_2Mn[\eta^2$-$Cy_2P(Ph)C{=}C{=}C(Tol)H$}] (6b). In a typical experiment, a solution of *syn*-$Cp'(CO)_2Mn[\eta^2$-{$Ph_2P(Tol)C{=}C{=}C(Ph)H$}] (*syn*-**3a**, 0.580 g, 1 mmol) in THF (10 mL) was heated under reflux for 2 h, the time after which an IR monitoring showed total disappearance of *syn*-**3a** and the formation of a new complex. Heating was stopped, the solvent was removed under vacuum, and the yellow residue was treated by column chromatography on alumina. Elution with a 5:100 ether/pentane mixture afforded a pale yellow band containing $Cp'(CO)_2Mn[\eta^1$-{$Ph_2P(Tol)C{=}C{=}C(Ph)H$}] (**5a**), which was subsequently isolated as a pale yellow powder after removal of the solvents under high vacuum (0.480 g, 0.82 mmol, 82%).

A similar experiment carried out from 0.580 g (1 mmol) of a ca. 9:1 mixture of **4a** and *syn*-**3a** (*vide supra*) afforded a ca. 9:1 mixture of complexes $Cp'(CO)_2Mn[\eta^1$-{$H(Tol)C{=}C{=}C(Ph)PPh_2$}] (**6a**) and $Cp'(CO)_2Mn[\eta^1$-{$H(Tol)C{=}C{=}C(Ph)PPh_2$}] (**5a**) (0.419 mg, 0.72 mmol, 72% yield).

Similar treatment of complex **4b** (as a 1:2 mixture of *syn*/*anti* isomer) afforded complex $Cp'(CO)_2Mn[\eta^1$-{$H(Tol)C{=}C{=}C$-$(Ph)PCy_2$}] (**6b**) in 86% yield.

5a: ^1H NMR (500.3 MHz, 298 K, CD_2Cl_2) δ 7.7–7.2 (MeC_6H_4 and C_6H_5), 6.23 (d, 1H, =C(Ph)*H*, $J_{PH} = 5$ Hz), 4.11, 4.06 (m, 4H, MeC_5H_4), 2.33 (s, 3H, *Me*C_6H_4), 1.89 (s, 3H, *Me*C_5H_4); $^{13}C\{^1H\}$ NMR (125.8 MHz, 298 K, CD_2Cl_2) δ 232.8, 232.7 (*C*O), 209.4 (d, C_β, $^2J_{CP} = 3$ Hz), 138.5–127.1 (C_6H_5 and MeC_6H_4), 108.1 (d, C_α, $^1J_{CP} = 29$ Hz), 99.3, 83.6, 83.4, 81.5, 81.4 (MeC_5H_4), 96.5 (d, C_γ, $^3J_{CP} = 9$ Hz), 20.9 (*Me*C_6H_4), 13.5 (*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (202.6 MHz, 298 K, CD_2Cl_2) δ 96.7; IR (THF) 1934, 1872 (ν_{CO}); MS (CI) *m/z* 581 $[MH]^+$, 391 $[MH - Cp'(CO)_2Mn]^+$. Anal. Calcd for $C_{36}H_{30}MnO_2P$: C, 74.48; H, 5.21. Found: C, 74.45; H, 5.06.

6a (from a ca. 9:1 mixture of **6a** and **5a**): ^1H NMR (500.3 MHz, 298 K, CD_2Cl_2) δ 7.7–7.2 (MeC_6H_4 and C_6H_5), 6.23 (d, 1H, =C(Ph)*H*, $J_{PH} = 5$ Hz), 4.07 (m, MeC_5H_4), 2.39 (s, 3H, *Me*C_6H_4), 1.90 (s, *Me*C_5H_4); $^{13}C\{^1H\}$ NMR (125.8 MHz, 298 K, CD_2Cl_2) δ 232.8, 232.6 (*C*O), 209.7 (d, C_β, $^2J_{CP} = 3$ Hz), 137.1–126.4 (C_6H_5 and MeC_6H_4), 108.2 (d, C_γ, $^1J_{CP} = 30$ Hz), 99.3, 83.5, 83.3, 81.56, 81.3 (MeC_5H_4), 96.5 (d, C_α, $^3J_{CP} = 9$ Hz), 20.9 (*Me*C_6H_4), 13.5 (*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (202.6 MHz, 298 K, CD_2Cl_2) δ 97.0; IR (THF) 1934, 1871 (ν_{CO}); HRMS calcd for $[C_{36}H_{31}MnO_2P]^+$ *m/z* 581.1442, found *m/z* 581.1444.

6b: ^1H NMR (300.1 MHz, 298 K, CD_2Cl_2) δ 7.6–7.2 (MeC_6H_4 and C_6H_5), 6.45 (d, 1H, =C(Ph)*H*, $J_{PH} = 6$ Hz), 4.2–4.0 (m, 4H, MeC_5H_4), 2.37 (s, 3H, *Me*C_6H_4), 1.89 (s, *Me*C_5H_4), 2.1–0.9 (m, C_6H_{11}); $^{13}C\{^1H\}$ NMR (75.5 MHz, 298 K, CD_2Cl_2) δ 234.4, 234.1 (CO), 207.7 (d, C_β, $^2J_{CP} = 3$ Hz), 137.5–126.9 (C_6H_5 and MeC_6H_4), 105.9 (d, C_γ, $^1J_{CP} = 25$ Hz), 98.1, 82.3, 82.2, 80.7, 80.7 (MeC_5H_4), 94.6 (d, C_α, $^3J_{CP} = 7$ Hz), 20.9 (*Me*C_6H_4), 13.5 (*Me*C_5H_4); $^{31}P\{^1H\}$ NMR (121.5 MHz, 298 K, CD_2Cl_2) δ 99.6; IR (THF) 1918, 1856 (ν_{CO}); MS (CI) *m/z* 593 $[MH]^+$, 403 $[MH^+ - Cp'Mn(CO)_2]^+$. Anal. Calcd for $C_{36}H_{42}MnO_2P$: C, 72.96; H, 7.15. Found: C, 73.16; H, 7.24.

Synthesis of $Ph_2P(Tol)C{=}C{=}C(Ph)H$ (7a), $Ph_2P(Ph)C{=}C{=}C$-$(Tol)H$ (9a), and $Cy_2P(Ph)C{=}C{=}C(Tol)H$ (9b). In a typical experiment, complex *syn*-$Cp'(CO)_2Mn[\eta^2$-{$Ph_2P(Ph)C{=}C{=}C$-$(H)Tol$}] (*syn*-**3a**) (0.348 g, 0.6 mmol) was dissolved in dichloromethane (90 mL) and introduced into a Pyrex photolysis reactor equipped with a medium-pressure Hereaus TQ150 Hg lamp. The solution was irradiated for 45 min. From golden yellow, the solution turned colorless and showed a white suspension. After removal of the dichloromethane under vacuum, the residue was extracted with diethyl ether (10 mL) and filtered through a short column of alumina (10 × 2.5 cm) eluting with pure diethyl ether. After removal of the solvent, the phosphine $Ph_2P(Ph)C{=}C{=}C(H)Tol$ (**7a**) was obtained as a pale yellow oil (0.170 g, 91% yield).

A similar experiment carried out with 0.435 mg (0.75 mmol) of a ca. 9:1 mixture of **4a** and *syn*-**3a** (*vide supra*) afforded a ca. 9:1 mixture of $Ph_2P(Ph)C{=}C{=}C(Tol)H$ (**9a**) and $Ph_2P(Tol)C{=}C{=}C(Ph)H$ (**7a**) (268 mg, 91% yield).

Similar treatment of complex **4b** (as 1:2 mixture of *syn*/*anti* isomer) afforded $Cy_2P(Ph)C{=}C{=}C(Tol)H$ (**9b**) in 83% yield.

7a: ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 7.6–7.1 (MeC_6H_4 and C_6H_5), 6.50 (s, 1H, H_γ), 2.35 (s, 3H, MeC_5H_4); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 209.1 (C_β), 137.5–126.5 (MeC_6H_4 and C_6H_5), 106.30 (d, C_α, $^1J_{CP}$ = 20 Hz), 96.37 (d, C_γ, $^3J_{CP}$ = 2 Hz), 20.83 (MeC_6H_4); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ –10.8; HRMS calcd for $[C_{28}H_{24}P]^+$ *m*/*z* 391.1616, found *m*/*z* 391.1697.

9a: ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 7.7–7.0 (MeC_6H_4 and C_6H_5), 6.18 (s, 1H, H_α), 2.42 (s, 3H, MeC_5H_4); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ 209.9 (C_β), 137.0–126.4 (MeC_6H_4 and C_6H_5), 106.3 (d, C_γ, $^1J_{CP}$ = 20 Hz), 94.7 (d, C_α, $^3J_{CP}$ = 3 Hz), 20.9 (MeC_6H_4); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ –10.6; HRMS Calcd for $[C_{28}H_{24}P]^+$ *m*/*z* 391.1616, found *m*/*z* 391.1632.

9b: ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 7.4–7.2 (MeC_6H_4 and C_6H_5), 6.51 (s, 1H, H_α), 2.42 (s, 3H, MeC_5H_4), 2.2–1.2 (m, C_6H_{11}); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ 209.5 (C_β), 139.0–125.3 (MeC_6H_4 and C_6H_5), 102.7 (d, C_γ, $^1J_{CP}$ = 29 Hz), 94.7 (C_γ), 34.0–26.5 (C_6H_{11}), 21.0 (MeC_6H_4); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ –5.1; HRMS calcd for $[C_{28}H_{36}P]^+$ *m*/*z* 403.2555, found 403.2549.

Synthesis of $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3\text{-}\{Ph_2P(Tol)C{=}C{=}C(Ph)H\}]$ (8a) from 5a. A solution of **5a** (0.290 mg, 0.5 mmol) in solution in THF (10 mL) was added dropwise to a solution of (η^5-MeC_5H_5)$Mn(CO)_2$(THF)—generated extemporaneously by UV irradiation of (η^5-MeC_5H_5)$Mn(CO)_2$ (0.436 g, 2 mmol) in THF (100 mL)—in THF. After stirring for 1 h, the solvent was removed under vacuum, and the solid residue was treated by column chromatography on alumina. Elution with pure pentane afforded (η^5-MeC_5H_5)$Mn(CO)_3$, which was discarded. A second elution with a 1:10 diethyl ether/pentane mixture afforded a pale yellow band containing complex $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3$-$\{Ph_2P(Tol)C{=}C{=}C(Ph)H\}]$ (**8a**), which was subsequently isolated as a pale yellow powder (0.250 g, 66% yield).

8a: ^{1}H NMR (500.3 MHz, CD_2Cl_2, 273 K) δ 7.7–6.5 (MeC_6H_4 and C_6H_5), 4.7–3.4 (m, 4H, MeC_5H_4), 2.87 (s(br), 1H, C_γ), 2.48 (s, 3H, MeC_5H_4), 1.81 (s, 3H, MeC_5H_4), 1.77 (s, 3H, MeC_5H_4); $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 273 K) δ 234.9, 233.8, 232.0, 230.6 (*C*O), 179.4 (C_β), 144.5–124.7 (C_6H_5 and MeC_6H_4), 134.0 (C_γ), 101.2–80.9 (MeC_5H_4), 30.2 (C_α), 21.1 (MeC_6H_4), 13.6 (MeC_5H_4), 13.1 (MeC_5H_4); $^{31}P\{^1H\}$ NMR (202.6 MHz, CD_2Cl_2, 273 K) δ 105.5; IR (THF) 1975(m), 1922(s), 1857(m) (ν_{CO}); MS (CI) *m*/*z* 771 $[MH]^+$, 581 $[MH^+ - Cp'Mn(CO)_2]^+$. Anal. Calcd for $C_{44}H_{37}Mn_2O_4P$: C, 68.56; H, 4.84. Found: C, 68.91; H, 4.65.

Synthesis of $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3\text{-}\{Ph_2P(Tol)C{=}C{=}C(Ph)H\}]$ (8a) from *syn*-3a. A solution of *syn*-**3a** (357 mg, 0.62 mmol) in solution in THF (10 mL) was added dropwise to a solution of $Cp'Mn(CO)_2$(THF)—generated extemporaneously by UV irradiation of $Cp'Mn(CO)_2$ (0.436 g, 2 mmol) in THF (100 mL)—in THF. After stirring for 1 h, the solvent was removed under vacuum, and the solid residue was treated by column chromatography on alumina, as above. Complex $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3$-$\{Ph_2P(Tol)C{=}C{=}C(Ph)H\}]$ (**8a**) was subsequently isolated as a pale yellow powder (0.265 g, 56% yield).

Synthesis of $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3\text{-}\{Ph_2P(Ph)C{=}C{=}C(Tol)H\}]$ (10a) from 6a. A solution of a ca. 9:1 mixture of mixture **6a** and **5a** (0.406 g, 0.70 mmol) in solution in THF (10 mL) was added dropwise to a solution of $Cp'Mn(CO)_2$(THF)—generated extemporaneously by UV irradiation of $Cp'Mn(CO)_2$ (0.436 g, 2 mmol) in THF (100 mL)—in THF. After stirring for 1 h, the solvent was removed under vacuum, and the solid residue was treated by column chromatography on alumina. Elution with pure pentane afforded $Cp'Mn(CO)_3$, which was discarded. A second elution with a 1:10 diethyl ether/pentane mixture afforded a pale yellow band containing complex $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3$-$\{Ph_2P(Ph)C{=}C{=}C(Tol)H\}]$ (**10a**), which was subsequently isolated as a pale yellow powder (275 mg ; 48% yield). Considering the sample we have used contained traces of **5a**, **10a** should logically be contaminated by traces of **8a**, which, however, could not be clearly identified.

10a: ^{1}H NMR (500.3 MHz, CD_2Cl_2, 263 K) δ 7.6–6.2 (MeC_6H_4 and C_6H_5), 4.6–3.4 (m, 4H, MeC_5H_4), 2.93 (s(br), 1H, C_γ), 2.21 (s, 3H, MeC_5H_4), 1.81 (s, 3H, MeC_5H_4), 1.77 (s, 3H, MeC_5H_4); $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 273 K) δ 234.8, 233.9, 231.9, 231.0 (*C*O), 180.1 (C_β), 143.1–126.1 (C_6H_5 and MeC_6H_4), 98.7–80.9 (MeC_5H_4), 30.4 (C_α), 20.8 (MeC_6H_4), 13.6 (MeC_5H_4), 13.1 (MeC_5H_4); $^{31}P\{^1H\}$ NMR (202.6 MHz, CD_2Cl_2, 273 K) δ 105.1; IR (THF) 1975(m), 1922(s), 1857(m) (ν_{CO}); MS (CI) *m*/*z* 771 $[MH]^+$, 581 $[MH - Cp'Mn(CO)_2]^+$. Anal. Calcd for $C_{44}H_{37}Mn_2O_4P$: C, 68.56; H, 4.84. Found: C, 68.50; H, 4.75.

Synthesis of $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3\text{-}\{Ph_2P(Ph)C{=}C{=}C(Tol)H\}]$ (10a) from 4a. A solution of a ca. 9:1 mixture of **4a** and *syn*-**3a** (0.290 g, 0.5 mmol) in solution in THF (10 mL) was added dropwise to a solution of $Cp'Mn(CO)_2$(THF)—generated extemporaneously by UV irradiation of $Cp'Mn(CO)_2$ (0.436 g, 2 mmol) in THF (100 mL)—in THF. After stirring for 1 h, the solvent was removed under vacuum, and the solid residue was treated by column chromatography on alumina as above. Complex $[Cp'(CO)_2Mn]_2[\mu\text{-}\eta^3$-$\{Ph_2P(Ph)C{=}C{=}C(Tol)H\}]$ (**10a**) was subsequently isolated as a pale yellow powder (0.220 g, 57% yield). Considering the sample we have used contained traces of *syn*-**2a**, **10a** should logically be contaminated by trace amounts of **8a**, which, however, could not be clearly identified.

Formation of *syn*-$Cp'(CO)_2Mn[\eta^2$-{TolS(Tol)C=C=C(Ph)H}] (*syn*-11) and $Cp'(CO)_2Mn[\eta^2$-{H(Tol)C=C=C(Ph)STol}] (12) upon Reaction of 1 with *p*-Toluenethiol. Triethylamine (0.030 mL, 0.20 mmol) was added to a solution containing complex $Cp'(CO)_2Mn{=}C(Tol)CCPh$ (**1**, 0.394 mg, 1 mmol) and *p*-toluenethiol (0.136 mg, 1.1 mmol) cooled at –80 °C. After 45 min of reaction, the solution turned light brown. The cooling bath was removed and stirred an additional 30 min. The solvent was removed under high vacuum, and the solid residue was treated by column chromatography. Elution with a 4:96 mixture of diethyl ether/hexane mixture afforded a yellow band. Removal of the solvents under high vacuum left a yellow foam. NMR analysis showed the foam to consist of a 1.8:1 mixture of $Cp'(CO)_2Mn[\eta^2$-{TolS(Tol)C=C=C(Ph)H}] (*syn*-**11**) and $Cp'(CO)_2Mn[\eta^2$-{H(Tol)C=C=C(Ph)-STol}] (**12**) (0.336 g, 0.65 mmol, 65% yield). Complex *syn*-**11** was eventually obtained in a pure form upon crystallization from a diethyl ether/hexane mixture in the cold; some crystals were suitable for an X-ray structure determination.

syn-**11**: ^{1}H NMR (500.3 MHz, 253 K, CD_2Cl_2) δ 8.21, 7.74 (s, =C(Ph)*H*), 7.9–7.0 (m, MeC_6H_4 and C_6H_5), 4.9–4.0 (m, MeC_5H_4), 2.27, 2.15, 2.09, 1.86 (MeC_6H_4 and MeC_5H_4); $^{13}C\{^1H\}$ NMR (125.8 MHz, 253 K, CD_2Cl_2) δ 234.2, 233.1, 228.1 (CO), 172.4, 167.4 (C_β), 143.4–126.6 (C_6H_5,and MeC_6H_4), 125.5, 125.0 (C_γ), 104.3, 103.2, 95.5–81.3 (MeC_5H_4), 39.4, 39.1 (C_α), 30.9, 20.9 (MeC_6H_4), 13.5, 13.0 (MeC_5H_4); IR (CH_2Cl_2) 1920, 1972 (ν_{CO}); MS (CI) *m*/*z* 536.3 $[MNH_4]^+$, 519.3 $[MH]^+$, 463.3 $[MH - 2CO]^+$, 329.3 $[MH - 2CO - Cp'(CO)_2Mn]^+$. Anal. Calcd for $MnC_{31}H_{27}O_2S$: C, 71.80; H, 5.24. Found: C, 72.03; H, 5.08.

12 (from a **12**:*syn*-**11** mixture): ^{1}H NMR (500.3 MHz, 293 K, CD_2Cl_2) δ 8.36, 7.84 (s, =C(Ph)*H*), 7.8–6.7 (m, MeC_6H_4 and C_6H_5), 4.7–4.6 (m, MeC_5H_4), 2.29, 1.97 (MeC_6H_4 and MeC_5H_4); $^{13}C\{^1H\}$ NMR (125.8 MHz, 213 K, CD_2Cl_2) δ 234.3–228.3 (*C*O), 172.5, 167.4 (C_β), 139.1–125.4 (MeC_6H_4 and C_6H_5), 123.9, 123.3 (C_γ), 97.2–80.8 (MeC_5H_4), 33.4, 32.1 (C_α), 21.3, 21.0 (MeC_6H_4 and MeC_6H_4), 13.8, 13.2 (MeC_5H_4); IR (CH_2Cl_2) 1920, 1972 (ν_{CO}).

Formation of *syn*-Cp′(CO)$_2$Mn[η^2-{TolS(Tol)C═C═C(Ph)H}] (*syn*-11) and Cp′(CO)$_2$Mn[η^2-{H(Tol)C═C═C(Ph)STol}] (12) upon Reaction of 1 with *p*-Toluenethiolate followed by Protonation. A THF solution of lithium *p*-toluenethiolate—generated *in situ* by addition of ^{n}BuLi (0.690 mL of a 1.6 M solution in hexane, 1.1 mmol) to a solution of TolSH (0.136 g, 1.1 mmol) in THF (3 mL) at 0 °C—was added dropwise to a solution of complex Cp′(CO)$_2$Mn═C(Tol)C≡CPh (**1**, 0.394 mg, 1 mmol) in THF (20 mL) at –80 °C. The solution turned orange (IR (ν_{CO}): 1883(s), 1806(m); 1765(m) cm^{-1}). A saturated solution of NH_4Cl (ca. 0.2 mL) in water was then added. After stirring the solution for 2 min, the cold bath was removed, 10 mL of diethyl ether was added, and the organic phase was transferred into another Schlenk flask by means of a canula. The solvent was removed under high vacuum and the solid residue was treated by column chromatography. Elution with a 4:96 of diethyl ether/hexane mixture afforded a yellow band. Removal of the solvents under high vacuum left a yellow foam. NMR analysis showed the foam to consist of a 1:2.3 mixture of Cp′(CO)$_2$Mn[η^2-{TolS(Tol)C═C═C(Ph)H}] (*syn*-**11**) and Cp′(CO)$_2$Mn[η^2-{H(Tol)C═C═C(Ph)STol}] (**12**) (0.386 g, 0.72 mmol, 72% yield).

Synthesis of *syn*-Cp′(CO)$_2$Mn[η^2-{H(Tol)C═C═C(Ph)CH(CH$_2$)$_4$C(O)}] (*syn*-13). A THF solution of lithium 2-cyclohexanone enolate—generated extemporaneously by addition of ^{n}BuLi (0.690 mL of a 1.6 M solution in hexane, 1.1 mmol) to a solution of trimethylsilyloxycyclohexene (0.220 mL, 1.1 mmol) in THF (5 mL) at 0 °C—was added dropwise to a solution of complex Cp′(CO)$_2$Mn═C(Tol)C≡CPh (**1**, 0.394 mg, 1 mmol) in THF (20 mL) at –80 °C. The cooling bath was removed and the solution left for 2 h under stirring. The solution turned yellow-greenish (IR (ν_{CO}) 1875(s), 1805(m), 1770(m) cm^{-1}). A saturated solution of NH_4Cl (ca. 0.2 mL) in water was then added. After the solution stirred for 2 min, 10 mL of diethyl ether was added, and the organic phase was transferred into another Schlenk flask by means of a canula. The solvent was removed under high vacuum and the solid residue was treated by column chromatography. A first elution with a 5:100 mixture of diethyl ether/hexane afforded a pale yellow band containing traces of Cp′(CO)$_2$Mn, which was discarded. A second elution with a 10:100 mixture of diethyl ether/hexane afforded an orange band. Removal of the solvents under high vacuum left complex *syn*-Cp′(CO)$_2$Mn[η^2-{Tol(H)C═C═C(Ph)CH(CH$_2$)$_4$C(O)}] (*syn*-**13**) as an orange foam (0.304 g, 0.61 mmol, 61% yield).

syn-**13**: ^{1}H NMR (300.1 MHz, 293 K, CD_2Cl_2) δ 7.3–6.8 (m, C_6H_5 and MeC_6H_4), 4.8–4.5 (MeC_5H_4 and C*H*(CH$_2$)$_4$C(O)), 3.85 (s(br), 1H H$_\alpha$), 2.6–1.8 (CH$_2$), 2.26 (*Me*C$_6$H$_4$), 1.94 (*Me*C$_5$H$_4$); ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, CD_2Cl_2) δ 232.09, 231.02 (*C*O), 211.5 (C═O), 167.8 (C$_\beta$), 143.5–125.4 (*C*$_6$H$_5$ and Me*C*$_6$H$_4$), 126.7 (C$_\gamma$), 102.7, 87.9–84.0 (Me*C*$_5$H$_4$), 61.1 (*C*H(CH$_2$)$_4$C(O)), 42.2, 32.7, 26.0, 25.4 (CH$_2$), 30.3 (C$_\alpha$), 20.8 (*Me*C$_6$H$_4$), 12.6 (*Me*C$_5$H$_4$); IR (THF) 1975(s), 1913(s), 1708(w) (ν_{CO}); MS (CI) *m*/*z* 510 [MNH$_4$]$^+$, 468 [MH]$^+$, 320, [MNH$_4$ − Cp′(CO)$_2$Mn]$^+$. Anal. Calcd for $C_{30}H_{29}MnO_3$: C, 73.16; H, 5.93. Found: C, 72.98; H, 6.20.

X-ray Diffraction Studies. Crystals of **2a**, *syn*-**4b**, *anti*-**4b**, *syn*-**11**, and *syn*-**13** suitable for X-ray diffraction were obtained through recrystallization from dichloromethane/hexane (**3a**) or diethyl ether/hexane (*syn*-**4b**, *anti*-**4b**, *syn*-**11**, and *syn*-**13**) solutions in the cold. Data were collected on a Stoe IPDS (**2a**), Oxford Diffraction Xcalibur (*syn*-**4b**, *anti*-**4b**, *syn*-**11**), or Bruker Kappa (*syn*-**13**) diffractometer. All calculations were performed on a PC-compatible computer using the WinGX system.[35] Full crystallographic data are given in Table 1. The structures were solved by using the SIR92 program,[36] 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.[37] 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 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 cyclohexyl rings in the structure of complex *syn*-**4b** were found to be disordered; each set of rings were refined with structure factor occupancy of 0.5.

Acknowledgment. We thank the Ministère de l'Education Nationale for a fellowship to S.S. and Ethyl Corporation (USA) for a generous gift of Cp′Mn(CO)$_3$.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM800060V

(35) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(36) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(37) Sheldrick, G. M. *SHELX97* [Includes *SHELXS97*, *SHELXL97*, *CIFTAB*], Programs for Crystal Structure Analysis (Release 97-2); Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.