Metal-Assisted Regio- and Stereospecific Insertion of Alkynes into a C−H Bond, Leading to Functionalized Diphosphane Ligands

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*Summary: Reaction of the complex fac-[Mn(CNtBu)(CO)$_3${(PPh$_2$)$_2$C−H}] (**1**) with dimethyl acetylenedicarboxylate and methyl propiolate affords the compounds fac-[Mn(CNtBu)(CO)$_3${(PPh$_2$)$_2$CC(R)═C(R′)−H}] (**2a**, R = R′ = CO$_2$Me; **2b**, R = H, R′ = CO$_2$Me), as a result of regio- and stereospecific insertion of the alkynes into the C−H bond of the diphosphanylmethanide ligand, allowing highly selective metal-assisted synthesis of new functionalized diphosphane derivatives.*

Carbon−carbon bond formation through metal-mediated addition of C−H bonds to unsaturated molecules, affording new organic compounds, is a subject of major current interest.[1] Thus, addition of aromatic and olefinic C−H bonds to alkenes and acetylenes involving direct C−H bond cleavage by various metals is well documented, in either stoichiometric or catalytic organic synthesis.[2] More rarely, activation of a C−H bond leading to C−C coupling in complexes occurs without direct interaction of that bond with the metal, as in the insertion of tetracyanoethylene and 7,7,8,8-tetracyano-*p*-quinodimethane into a C−H bond of the substituted phenyl ring in the complexes [(η^5-C$_5$Me$_5$)MCl(MDMPP-*P*,*O*)] (M = Rh, Ir; MDMPP-*P*,*O* = PPh$_2$(2-O-6-MeO-C$_6$H$_5$)).[3] In this regard here we describe a rare example of regio- and stereospecific insertion of alkynes into the P$_2$C−H bond of the complex *fac*-[Mn(CN*t*Bu)(CO)$_3$-{(PPh$_2$)$_2$C−H}] (**1**),[4] which can be applied to the synthesis of new functionalized diphosphane ligands.

Complex **1** reacts with an excess of dimethyl acetylenedicarboxylate (DMAD) or methyl propiolate in refluxing toluene to give the new compounds *fac*-[Mn(CN*t*Bu)(CO)$_3${(PPh$_2$)$_2$CC(R)═C(R′)−H}] (**2a**, R = R′ = CO$_2$Me; **2b**, R = H, R′ = CO$_2$Me), as a result of insertion of the alkynes into the C−H bond of the central carbon atom of the diphosphanylmethanide ligand (Scheme 1).

Coordination of the P$_2$C−H ligand to the metal through the phosphorus atoms is essential for the reaction to be chemoselective on the central carbon atom; in fact, it is known that reaction of DMAD with free phosphanes[5] or diphosphanes[6] produces λ^5-phosphole or λ^5-diphosphole derivatives, owing to the involvement of the phosphorus atoms in the addition process.[7] The insertion proved to be stereospecific, affording the *E* isomers of the new olefinic compounds **2a**,**b**. In the case of the terminal alkyne the reaction is also regiospecific, with the central carbon atom of the ligand coupled exclusively to the unsubstituted carbon atom of the alkyne. The structures of **2a** and **2b** were determined by X-ray crystallography and are depicted in Figure 1 along with selected bond lengths and angles. Both structures clearly show the olefinic fragment on the chelating ligand essentially coplanar with the P1−P2−C9 skeleton, allowing delocalization of the negative charge of the methanide carbon atom over a π system through the carbon chain and making the two phosphorus atoms inequivalent. Consequently, the ^{31}P{^{1}H} NMR spectrum of **2a** at 293 K and that of **2b** below 273 K in CD$_2$Cl$_2$ show two signals. Nevertheless, when the temperature was raised to 313 K for **2a** and to 293 K for **2b**, a single resonance was observed in the spectrum, which indicates the existence of free rotation around the P$_2$C−C bond above those temperatures. The slight difference of free rotation temperature between **2a** and **2b** can be attributed to the different steric impedances of one of the substituents on carbon atom C10 (CO$_2$Me for **2a** and H for **2b**).

Compound **1** did not react with nonactivated alkynes such as phenylacetylene and diphenylacetylene, showing that enhancement of electrophilicity of the alkyne by electron-withdrawing substituents is essential for the

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(2) (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Kakiuchi, F.; Tomohiro, U.; Tanaka, Y.; Chatani, N.; Murai, S. *J. Mol. Catal. A: Chem.* **2002**, *182*−*183*, 511 and references therein.
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(7) We have also confirmed that reaction of Li{(PPh$_2$)$_2$CH} with DMAD affords an intractable mixture of products, as a consequence of the participation of both the methanide carbon atom and the phosphorus atoms in the addition process of the diphosphanylmethanide anion to the alkyne.

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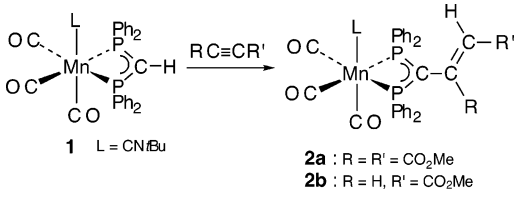
Scheme 1



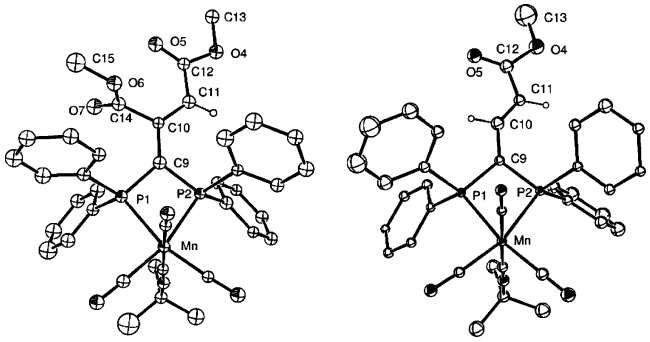
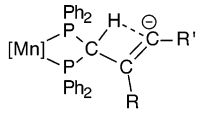


Figure 1. ORTEP drawings of **2a** (left) and **2b** (right). For **2b** only one of the two conformations adopted by the positionally disordered CC(H)=C(H)CO_2Me group is shown. Selected bond distances (Å) and angles (deg) are as follows. **2a**: P1−C9 = 1.7592(19), P2−C9 = 1.7588(18), C9−C10 = 1.429(2), C10−C11 = 1.358(3); P1−C9−P2 = 99.33(9), C9−C10−C11 = 125.71(17), C9−C10−C14 = 115.55(16), C11−C10−C14 = 118.74(16). **2b**: P1−C9 = 1.765(2), P2−C9 = 1.760(2), C9−C10 = 1.409(3), C10−C11 = 1.229(3); P1−C9−P2 = 98.34(10), C9−C10−C11 = 138.1(3).

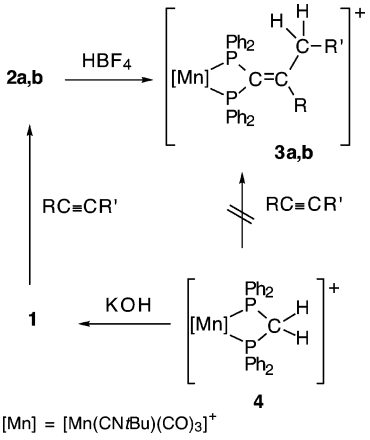
Chart 1



reaction to take place. These results suggest a mechanism for the insertion involving nucleophilic attack of the central carbon atom of the chelating ligand to the alkyne (HOMO−LUMO interaction)[8,9] and subsequent proton migration. This mechanism also accounts for the regiospecific formation of **2b**, as the LUMO orbital of methyl propiolate is centered on the unsubstituted carbon atom of the alkyne.[10] Furthermore, the stereospecific obtention of the *E* isomers of **2a**,**b** suggests that the intramolecular proton transfer proceeds through a four-centered transition state (Chart 1), which additionally allows the formation of the less impeded product.

Compounds **2a**,**b** readily react with HBF_4 to give the cationic complexes *fac*-[Mn(CN*t*Bu)$(CO)_3${$(PPh_2)_2$C=C(R)(CH_2R')}]$^+$ (**3a**,**b**) (Scheme 2). Protonation occurs on the *β*-carbon atom of the alkenyl substituent of the diphosphanylmethanide ligand, instead of on the P_2C carbon atom,[11] leading to the formation of new diphosphane ligands of the1,1-bis(diphenylphosphino)ethene type, bearing carboxylic ester functionalities.[12,13] The spectroscopic data of **3a**,**b** support this proposition (see the Supporting Information), especially the presence of the CH_2 resonance both in the ^{1}H NMR (3.25 ppm for **3a** and 3.02 ppm for **3b**) and in the ^{13}C NMR spectra (39.2 ppm for **3a** and 38.1 ppm for **3b**). Interestingly, compounds **3a**,**b** can be viewed as derived from the parent dppm complex *fac*-[Mn(CN*t*Bu)$(CO)_3${$(PPh_2)_2$-CH_2)}]$^+$ (**4**), in which the acetylene molecule has been inserted into the two methylenic C−H bonds of the dppm ligand. However, direct reaction of **4** with dimethyl acetylenedicarboxylate or methyl propiolate, which could afford **3a**,**b** as a result of insertion of the alkyne into a C−H bond followed by 1,3-proton migration, does not take place even under forcing conditions. Thus, deprotonation of **4** to give **1** is mandatory for obtaining **3a**,**b** as described above (Scheme 2).

Scheme 2



This result can definitively clarify the mechanism of the previously reported formal insertion of acetylide into a C−H bond of dppm occurring in the reaction of the trinuclear platinum clusters $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ with NaCCH, in which a process involving deprotonation of a *μ*-dppm ligand was considered likely but never proved.[14]

In conclusion, we present here the first example of insertion reactions of alkynes into the C−H bond of diphosphanylmethanide ligands. This reaction, which is chemo-, regio-, and stereospecific, has been shown to be a useful tool for the synthesis of functionalized diphosphanylmethanide and diphosphane derivatives. Further studies to extend this reactivity to alkenes and

(8) For nucleophilic degradation of molecules such as I_2, $(SCN)_2$, and S_8 by diphosphanylmethanide complexes see: (a) Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; Díaz, M. R. *Organometallics* **1998**, *17*, 4562. (b) Ruiz, J.; Ceroni, M.; Quinzani, O. V.; Riera, V.; Piro, O. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 220. (c) Ruiz, J.; Ceroni, M.; Quinzani, O. V.; Riera, V.; Vivanco, M.; García-Granda, S.; Van der Maelen, F.; Lanfranchi, M.; Tiripicchio, A. *Chem. Eur. J.* **2001**, *7*, 4422.

(9) For nucleophilic attack of diphosphanylmethanide complexes at XR substrates giving the corresponding alkylated derivatives see: (a) Al-Jibori, S.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 286. (b) Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *74*, 235. (c) Falvello, L. R.; Forniés, J.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 309.

(10) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: London, 1976.

(11) Protonation of diphosphanylmethanide ligands to afford diphosphane derivatives usually takes place on the P_2C carbon atom. See, for instance, ref 8a.

(12) For the scope of phosphinocarboxylic esters and other hemilabile O,P ligands see: (a) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27. (b) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 681.

(13) We are currently exploring experimental approaches to recover these new ligands from the complexes, as the usual methodology to liberate functionalized diphosphane ligands from manganese(I) (see: Ruiz, J.; Riera, V.; Vivanco, M.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1998**, *17*, 3835) does not apply to complexes **3a**,**b**.

(14) Jennings, M. C.; Manojlovic-Muir, J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 745.

heterocumulenes, as well as to metal complexes electronically richer than those of Mn(I) described herein that could eventually react with nonactivated unsaturated molecules, are currently in progress.

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Supporting Information Available: Crystallographic data of **2a**,**b** (as CIF files) and text giving experimental preparations and characterization data for **2a**,**b** and **3a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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