Multiple Bonds

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Alkene to Carbyne: Tandem Lewis Acid Activation and Dehydrogenation of a Molybdenum Ethylene Complex**

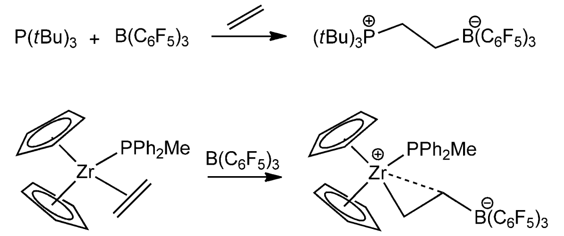
*Tom E. Stennett, Mairi F. Haddow, and Duncan F. Wass**

Since the discovery of the first transition-metal carbene complex in 1964,[1] the chemistry of metal–carbon multiple bonds has gone on to become one of the great success stories of organometallic chemistry. In particular, the discovery of alkene metathesis, and later alkyne metathesis, has had a significant impact on the formation of carbon–carbon multiple bonds in organic synthesis, to the extent of the pioneers being awarded a Nobel Prize.[2] Advances in this field have led to the isolation of elegant, highly active, and bench-stable homogeneous catalysts which facilitate a wide range of organic transformations.[3] However, for large-scale industrial alkene production processes, such as the cross-metathesis of ethylene and 2-butene to form propene, heterogeneous catalysts based on Re, Mo, and W are still favored because of their high stability and ease of product separation.[4] It is established that the active sites on such catalysts consist of metal carbene moieties, but the route of their formation from the free alkene is not fully understood.[2a,5] For many heterogeneous systems, less than 2 % of the metal content of the catalyst consists of active carbene species,[5,6] and insights into the activation mechanism are therefore highly desirable in terms of increasing catalyst efficiency. Acidity of the active site in heterogeneous alkene metathesis catalysts has been repeatedly positively correlated with catalytic activity.[7] In particular, both Lewis and Brønsted acidity have been shown to promote the catalyst initiation step, in which the active carbene species is formed.[7a,f]

A number of pathways have been proposed for the generation of active carbene sites in alkene metathesis, including a metal-mediated 1,2-hydrogen shift from an alkenyl ligand,[8] rearrangement of an η^3-allyl hydride intermediate into a metallacyclobutane,[9] and metathesis of an alkene with a metal-oxo precursor.[10] The most recent evidence, reported by Trunschke et al. for a Mo-based propene metathesis catalyst, points to a hydrogen shift mechanism in which the key steps involve oxidative addition of the alkene and transfer of an α-hydrogen atom to the β-carbon atom.[5] In this mechanism, the primary role of the acidic precatalyst seems to be protonation of the incoming alkene, thus generating free coordination sites by acetone dissociation. Here we show that attack of a Lewis acid at the β-carbon atom can facilitate M=C multiple bond formation, thus providing evidence for a link between Lewis acidity and α-hydrogen transfer in metal alkene complexes.

This chemistry was discovered through our ongoing interest in transition-metal-containing frustrated Lewis pairs (FLPs). The concept of FLP chemistry[11] has been a significant development regarding the activation of small molecules.[12] We have extended this concept to transition-metal systems, specifically zirconocene-phosphine pairs in which the electrophilic zirconium fragment plays the role of the Lewis acid.[13] As complexes in which the metal serves as a Lewis base are known for the majority of mid to late transition metals,[14] we envisaged a situation where we could utilize a transition metal as the Lewis base.

As a starting point, we chose the complex *trans*-[Mo(C_2H_4)$_2$(dppe)$_2$] (**1**; dppe = 1,2-bis(diphenylphosphino)-ethane) as an easily accessible transition-metal alkene complex. The compound **1** can be prepared simply from *trans*-[Mo(N_2)$_2$(dppe)$_2$] by gentle heating under an ethylene atmosphere.[15] Lewis pairs containing a main-group Lewis base such as P(tBu)$_3$ with B(C_6F_5)$_3$ will activate ethylene to form a zwitterionic phosphonium borate species (Scheme 1).[16] The interaction of this borane with metal complexes is also of interest from both fundamental and applied perspectives because of its high Lewis acidity.[17] Particularly noteworthy is that Piers and co-workers have shown the reaction of a zirconocene complex, having a coordinated ethylene ligand, with B(C_6F_5)$_3$ results in an alkyl-type compound.[18] We anticipated a similar reaction with the molybdenum fragment, thus resulting in formation of a molybdenum alkyl borate species.



Scheme 1. Ditopic activation of ethylene using a frustrated Lewis pair (top; Stephan and co-workers) and a zirconocene borane (bottom; Piers and co-workers).

Treatment of **1** with B(C_6F_5)$_3$ in benzene led to the formation of a homogeneous green-brown solution within

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[*] T. E. Stennett, Dr. M. F. Haddow, Prof. Dr. D. F. Wass
School of Chemistry, University of Bristol
Cantock's Close BS8 1TS (UK)
E-mail: duncan.wass@bristol.ac.uk
Homepage: http://www.wassresearchgroup.com

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5 minutes. Analysis by ^{31}P NMR spectroscopy showed complete consumption of the starting material and formation of a new species represented by a singlet at $\delta = 75.2$ ppm as the major product (ca. 60%). An X-ray diffraction study on crystals grown from a benzene/hexanes solution revealed that rather than the anticipated molybdenum alkyl species, the unexpected square-pyramidal Mo^{IV} carbyne complex $[Mo(CCH_2B(C_6F_5)_3)(dppe)_2]$ (**2**; Figure 1 and Table 1) was formed.

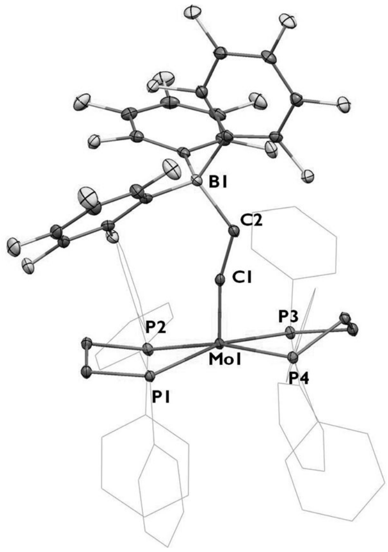


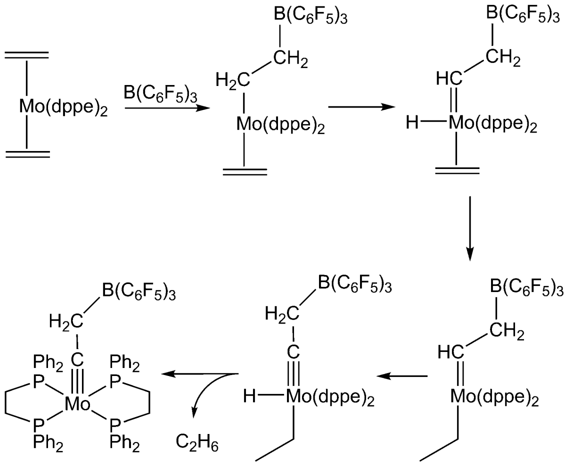
Figure 1. Molecular structure of **2**, with selected thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1: Selected bond lengths [Å] and angles [°] in **2** and **3**.

	2	**3**
Mo1-P (average)	2.469	2.505
Mo1-C1	1.773(2)	1.823(3)
C1-C2	1.490(3)	1.480(4)
C2-B1	1.670(4)	1.674(4)
Mo1-N1	–	2.306(2)
Mo1-C1-C2	163.97(19)	163.7(2)
P1-Mo1-P2	77.70(2)	78.23(2)

The short Mo–C bond length of 1.773(2) Å confirms the triple-bond character being similar to the reported Mo^{IV} alkylidyne species,[19] although the Mo1-C1-C2 angle shows some deviation from linearity (163.97(19)°), presumably for steric reasons. The ^{11}B and ^{19}F NMR spectra of **2** both show quaternization at boron: the boron atom appears as a singlet at $\delta = -15.4$ ppm, while the ^{19}F NMR spectrum shows the expected signals at $\delta = -130.4$, -162.5, and -165.4 ppm for the C_6F_5 groups. The protons of the BCH_2 group appear as a broad singlet at $\delta = 3.49$ ppm in the ^1H NMR spectrum, comparable to the corresponding group in *cis*-$[Mo(CCH_2Ph)(CO)(dppe)_2][BF_4]$ (at $\delta = 3.19$ ppm).[19a] The other ^1H NMR data are consistent with the assignment of **2**. The alkylidyne carbon atom displays a broad signal in the expected region, for a Mo^{IV} alkylidyne, of the ^{13}C NMR spectrum at $\delta = 347.0$ ppm.

Key to understanding the formation of **2** was discovering the fate of the two H atoms lost from the ethylene ligand during the transformation. Performing the reaction in a sealed NMR tube in C_6D_6 revealed the evolution of ethane, as observed in the ^1H NMR spectrum, in 64% yield relative to **2**. We presume quantitative formation of ethane, but the 64% yield is lower because of incomplete solubility and/or gas escaping before the tube could be sealed. We propose a tentative mechanism for the reaction (Scheme 2) involving initial reduction of the ethylene double bond with subsequent α-hydride migration to the second ethylene ligand via the molybdenum center, thus giving a carbene and an ethyl ligand. A second α-hydride elimination then generates a species which can reductively eliminate ethane to generate **2**. It has been previously reported that, in similar fashion, W^{IV} alkyl complexes containing tetradentate triamidoamine ligands spontaneously and irreversibly lose dihydrogen by α,α-dehydrogenation to give the corresponding W^{VI} alkylidyne,[20] but the analogous molybdenum compounds are thermally stable with respect to loss of H_2.[21] It would seem that in the present case, the presence of a hydrogen acceptor facilitates the transformation, a concept which could be more widely applicable.



Scheme 2. Proposed mechanism for the formation of **2**.

Our results show that α-hydrogen transfer and concurrent M–C multiple bond formation can be assisted by reaction of the β-carbon atom of a bound ethylene molecule with a Lewis acid, and we suggest that such an interaction may explain the effect of support acidity on the activity of metathesis catalysts. This proposal is supported by a recent computational study[22] on active-site formation in a WO_3 catalyst. In the hydrogen transfer step, an interaction of the β-carbon atom with an adjacent W^{VI} centre is shown.

With the new species in hand, we were keen to explore its reactivity. Compound **2** is formally a 16-electron complex, and its free coordination site is presumably stabilized by the well-documented strong *trans* influence of carbyne ligands[23] and the steric protection of the dppe ligands. Addition of THF to a solution of **2** in C_6D_6 gave no reaction, but upon adding acetonitrile, the vivid green color changed to orange-yellow. The product precipitated from this solution as a crystalline solid, and X-ray diffraction confirmed the formation of *trans*-$[Mo(CCH_2B(C_6F_5)_3)(NCCH_3)(dppe)_2]$ (**3**). Coordination of an acetonitrile molecule causes an increase of approximately 5 pm in the Mo–C bond length to 1.823(3) Å, while the Mo-C1-C2 angle remains almost unchanged. Placing solid **3** under vacuum results in the slow regeneration of **2**, and after 2 hours under dynamic vacuum at 60 °C, complete removal of the acetonitrile was observed.

While this lability prevented the isolation of completely solvent-free **3**, the presence of acetonitrile made the compound easier to handle. Whereas **2** is extremely air-sensitive, **3** was found to decompose only slowly in an open flask. The superior crystallinity of **3** also led us to develop an improved synthetic procedure for **2**. By adding acetonitrile to the crude reaction mixture, **3** could be precipitated cleanly, before heating under vacuum to yield pure **2** in 40 % yield.

Compound **2** reacts with CO (1 bar, in C_6D_6) immediately to give a yellow solution of a single species with four inequivalent phosphorus atoms. The IR spectrum displays a band at 1902 cm^{-1}, which is indicative of a bound CO molecule. We therefore assigned the new compound as *cis*-$[Mo(CCH_2B(C_6F_5)_3)(CO)(dppe)_2]$ (**4**). The characterizing data are in good agreement with the closely related species *cis*-$[Mo(CCH_2Ph)(CO)(dppe)_2][BF_4]$[19a] and *cis*-$[Mo(CC_6H_4Me)(CO)(dppe)_2][C_2B_{10}H_9Me_2]$.[24] We did not find any evidence of metathesis-type reactivity of the Mo–C bond with CO. Nor did **2** display any reactivity towards 1-phenyl-1-propyne, even after prolonged heating. The compound **2** is also stable with respect to H_2, and exposure at 1 bar to a C_6D_6 solution also produced no change.

To test the generality of this process, we prepared an analogue of the precursor ethylene complex based on a diphosphinoamine ligand. The complex $[Mo(N_2)_2(PNP)_2]$ (**5**; PNP = bis(diphenylphosphino)methylamine) was prepared in an identical process to that of $[Mo(N_2)_2(dppe)_2]$, and converted into the ethylene complex *trans*-$[Mo(C_2H_4)_2(PNP)_2]$ (**6**, Scheme 3). Compound **6** reacted with $B(C_6F_5)_3$ within 5 minutes to give an orange-brown solution containing multiple products. Subsequent purification resulted in the precipitation of pale-yellow crystals. Rather than the direct analogue of **2**, the compound was found to be *cis*-$[Mo(CCH_2(B(C_6F_5)_3)(C_2H_4)(PNP)_2]$ (**7**; Figure 2), and was isolated in 30 % yield. The Mo1-C1 and C1-C2 bond lengths are similar to those in **2**, at 1.794(4) and 1.474(6) Å, respectively, while the Mo1-C1-C2 bond angle is closer to linearity at 174.4(3)°. This probably reflects the reduced steric pressure on the borane fragment because of the small ethylene ligand. The phosphorus atom *trans* to the alkylidyne ligand displays a significantly elongated Mo–P bond, at 2.7759(11) Å, compared to the 2.42 to 2.55 Å range reported for the others.

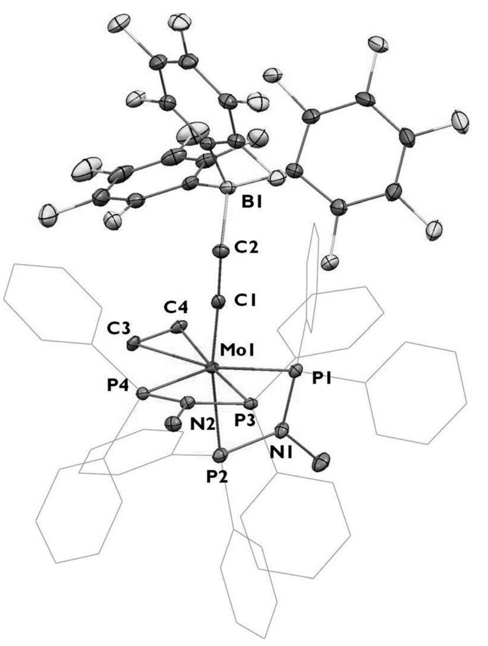
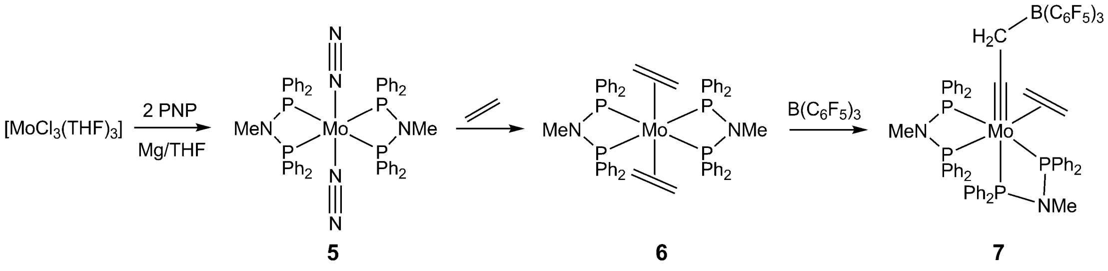


Figure 2. Molecular structure of **7**, with selected thermal ellipsoids at the 30 % probability level. Hydrogen atoms are omitted for clarity.

The origin of the ethylene ligand of **7** is not clear. No H_2 formation is observed by ^1H NMR spectroscopy if the reaction is performed in a sealed vessel, with ethane again produced instead. The possibility of the reaction of generated H_2 with unreacted **6** producing ethane was ruled out by pressurizing a benzene solution of **6** with hydrogen, as no reaction was observed after 16 hours. Given these observations and the sub-50 % conversion into **7**, we speculate that the product may form by the route, proposed above, for **2** before acquiring an ethylene ligand. Experiments to clarify the mechanism of the formation of **2** and **7** are ongoing.

In conclusion, we have reported the synthesis and characterization of Mo^{IV} alkylidyne complexes by a novel route from a bound ethylene ligand, and proposed a mechanism for the transformation. The coordination chemistry of one of the new species has been investigated, thus yielding



Scheme 3. Synthesis of N_2 and ethylene complexes of Mo^0 supported by PNP ligands, and alkylidyne formation.

acetonitrile and CO complexes. These results suggest the possibility of the concerted action of Lewis-acidic cocatalysts in the formation steps of multiply bonded organometallic species in heterogeneous metathesis catalysts. We are also hopeful that this may represent a more general route from alkenes to carbyne complexes, and this is the current focus of our studies.

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[1] E. O. Fischer, A. Maasböl, *Angew. Chem.* **1964**, *76*, 645 – 645; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 580 – 581.

[2] a) Y. Chauvin, *Angew. Chem.* **2006**, *118*, 3824 – 3831; *Angew. Chem. Int. Ed.* **2006**, *45*, 3740 – 3747; b) R. R. Schrock, *Angew. Chem.* **2006**, *118*, 3832 – 3844; *Angew. Chem. Int. Ed.* **2006**, *45*, 3748 – 3759; c) R. H. Grubbs, *Angew. Chem.* **2006**, *118*, 3845 – 3850; *Angew. Chem. Int. Ed.* **2006**, *45*, 3760 – 3765.

[3] a) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746 – 1787; b) A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140 – 3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012 – 3043; c) X. Wu, M. Tamm, *Beilstein J. Org. Chem.* **2011**, *7*, 82 – 93; d) R. R. Schrock, *J. Chem. Soc. Dalton Trans.* **2001**, 2541 – 2550; e) R. R. Schrock, *Chem. Rev.* **2002**, *102*, 145 – 180; f) A. Mayr, H. Hoffmeister in *Advances in Organometallic Chemistry*, *Vol. 32* (Eds.: F. G. A. Stone, W. Robert), Academic Press, New York, **1991**, pp. 227 – 324.

[4] a) J. C. Mol, *Catal. Today* **1999**, *51*, 289 – 299; b) J. C. Mol, *J. Mol. Catal. A* **2004**, *213*, 39 – 45.

[5] K. Amakawa, S. Wrabetz, J. Kröhnert, G. Tzolova-Müller, R. Schlögl, A. Trunschke, *J. Am. Chem. Soc.* **2012**, *134*, 11462 – 11473.

[6] Y. Chauvin, D. Commereuc, *J. Chem. Soc. Chem. Commun.* **1992**, 462 – 464.

[7] a) F. Schekler-Nahama, O. Clause, D. Commereuc, J. Saussey, *Appl. Catal. A* **1998**, *167*, 237 – 245; b) A. K. Rappe, W. A. Goddard, *J. Am. Chem. Soc.* **1982**, *104*, 448 – 456; c) X. Xiaoding, J. C. Mol, C. Boelhouwer, *J. Chem. Soc. Faraday Trans. 1* **1986**, *82*, 2707 – 2718; d) D. P. Debecker, K. Bouchmella, M. Stoyanova, U. Rodemerck, E. M. Gaigneaux, P. Hubert Mutin, *Catal. Sci. Technol.* **2012**, *2*, 1157 – 1164; e) W. A. Herrmann, W. Wagner, U. N. Flessner, U. Volkhardt, H. Komber, *Angew. Chem.* **1991**, *103*, 1704 – 1706; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1636 – 1638; f) X. Li, A. Zheng, J. Guan, X. Han, W. Zhang, X. Bao, *Catal. Lett.* **2010**, *138*, 116 – 123.

[8] Y. Iwasawa, H. Hamamura, *J. Chem. Soc. Chem. Commun.* **1983**, 130 – 132.

[9] J. R. McCoy, M. F. Farona, *J. Mol. Catal.* **1991**, *66*, 51 – 58.

[10] A. Salameh, C. Copéret, J.-M. Basset, V. P. W. Böhm, M. Röper, *Adv. Synth. Catal.* **2007**, *349*, 238 – 242.

[11] a) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535 – 1539; b) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50 – 81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46 – 76; c) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740 – 5746; d) G. Erker, *C. R. Chim.* **2011**, *14*, 831 – 841.

[12] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124 – 1126.

[13] A. M. Chapman, M. F. Haddow, D. F. Wass, *J. Am. Chem. Soc.* **2011**, *133*, 18463 – 18478.

[14] a) J. Bauer, H. Braunschweig, R. D. Dewhurst, *Chem. Rev.* **2012**, *112*, 4329 – 4346; b) H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924 – 3957; c) A. Amgoune, D. Bourissou, *Chem. Commun.* **2011**, *47*, 859 – 871.

[15] J. W. Byrne, H. U. Blaser, J. A. Osborn, *J. Am. Chem. Soc.* **1975**, *97*, 3871 – 3873.

[16] J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 5056 – 5059; *Angew. Chem. Int. Ed.* **2007**, *46*, 4968 – 4971.

[17] W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345 – 354.

[18] W. Piers, Y. Sun, L. M. Lee, *Top. Catal.* **1999**, *7*, 133 – 143.

[19] a) G. Nakamura, Y. Harada, Y. Mizobe, M. Hidai, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3305 – 3315; b) A. Mayr, A. M. Dorries, G. A. McDermott, D. Van Engen, *Organometallics* **1986**, *5*, 1504 – 1506.

[20] a) K.-Y. Shih, K. Totland, S. W. Seidel, R. R. Schrock, *J. Am. Chem. Soc.* **1994**, *116*, 12103 – 12104; b) R. R. Schrock, K.-Y. Shih, D. A. Dobbs, W. M. Davis, *J. Am. Chem. Soc.* **1995**, *117*, 6609 – 6610.

[21] a) K.-Y. Shih, R. R. Schrock, R. Kempe, *J. Am. Chem. Soc.* **1994**, *116*, 8804 – 8805; b) G. E. Greco, A. I. Popa, R. R. Schrock, *Organometallics* **1998**, *17*, 5591 – 5593.

[22] Z. Cheng, C. S. Lo, *ACS Catal.* **2012**, *2*, 341 – 349.

[23] W. M. Vaughan, K. A. Abboud, J. M. Boncella, *Organometallics* **1995**, *14*, 1567 – 1577.

[24] P. Dahlke, J. C. Jeffery, M. D. Mortimer, F. G. A. Stone, *Polyhedron* **1992**, *11*, 1587 – 1596.