J|A|C|S
COMMUNICATIONS

Cyclic *C*-Amino Phosphorus Ylides as a Source of Bidentate Heteroditopic Ligands (Phosphine/Aminocarbene) for Transition Metals

Joan Vignolle, Bruno Donnadieu, Didier Bourissou, Michèle Soleilhavoup, and Guy Bertrand*

UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957), Department of Chemistry, University of California - Riverside, Riverside, California 92521-0403, and Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069) Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex 09, France

Received August 29, 2006; E-mail: gbertran@ucr.edu

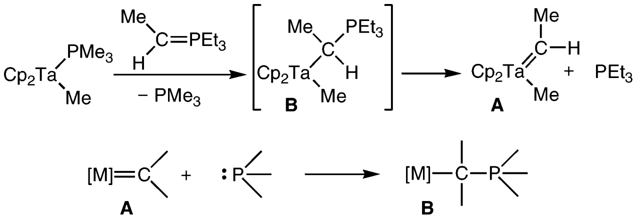
In 1979, Schrock et al. prepared the first ethylidene transition metal complex **A** by addition of a phosphorus ylide to TaCp$_2$(L)-Me complexes (Scheme 1).[1] Because a variety of main group ylides were readily available, this alkylidene transfer reaction appeared very promising for the preparation of metal complexes incorporating a number of different substituents at the carbene center. However, phosphorus ylides were subsequently proven to form exceedingly stable adducts with transition metals,[2] such as monodentate σ-complexes **B**. Furthermore, it has been shown that complexes of type **B** can also be prepared by addition of phosphines to carbene complexes,[3] which is the reverse reaction of that leading to **A**. Consequently, there are very few reports of main group ylides (including phosphorus[4] and sulfur ylides[5]) acting as genuine carbene transfer agents.

We have recently shown that C-amino-substituted phosphorus ylides are destabilized by the two-center, four-electron system and are keen to undergo fragmentation into phosphine and carbene.[6] This prompted us to investigate the possible use of such ylides as carbene transfer agents for transition metals. Here we report that the P═C bond of acyclic and cyclic *C*-amino phosphorus ylides can be activated by a variety of transition metal fragments, resulting in the formation of complexes featuring both the phosphine and the aminocarbene ligands.

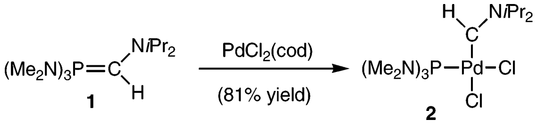
To test the feasibility of the carbene transfer reaction, versus the formation of stable ylide complexes, we reacted the acyclic *C*-amino phosphorus ylide **1**,[6] with PdCl$_2$(cod). A very clean reaction occurred, and after 12 h at room-temperature complex **2** was isolated as pale-yellow crystals in 81% yield (Scheme 2). The ^{13}C and ^{1}H NMR spectra showed a doublet at low field ($\delta_C = 213.9$ ppm, $J_{PC} = 14.3$ Hz; $\delta_H = 10.0$ ppm, $J_{PH} = 7.8$ Hz) suggesting the presence of both the carbene and phosphine ligands. This was confirmed by a single-crystal X-ray analysis, which shows a four-coordinate Pd atom in an essentially square-planar environment with the phosphine and carbene ligands mutually *cis*.[7]

In order to take full advantage of this process, the reactivity of cyclic *C*-amino phosphorus ylides toward metal centers was investigated. Assuming that the insertion takes place, complexes featuring bidentate heteroditopic ligands,[8] which contain two significantly different chemical donor functions, would be accessible. Such ligands are finding increasing use in transition metal catalysis, largely because of their potential aptitude to induce some electronic and steric asymmetry at the metal center and to display so-called "hemilabile" behavior in the coordination sphere of a metal. Addition of a stoichiometric amount of PdCl$_2$(cod) to the cyclic ylide prepared in situ[9] by deprotonation of the corresponding phosphonium salt **3**[6a] afforded, after 12 h at room temperature, complex **4**, which was isolated in 60% yield (Scheme 3). A single-crystal X-ray diffraction study demonstrated the insertion of the metal into the PC bond of **3**, which therefore acts as a mixed phosphine/carbene 1,5-bidentate ligand. It can be noted that the Pd−Cl bond *trans* to the P atom is shorter than that *trans* to the amino carbene by ca. 0.02 Å. This value is comparable to the discrepancy observed in analogous complexes featuring phosphine/NHC bidentate ligands, but in these cases the shorter Pd−Cl bonds are those *trans* to the NHC.[10]

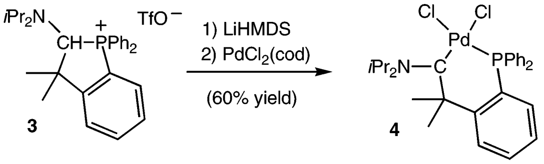
Scheme 1



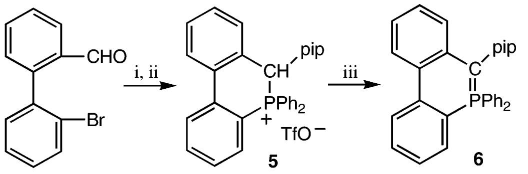
Scheme 2



Scheme 3



Scheme 4 [a]

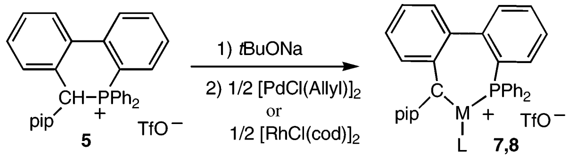


[a] Reagents and conditions: i: Ph$_2$PH, Et$_3$N, Pd(PPh$_3$)$_4$; ii: pipSiMe$_3$, Me$_3$SiOTf; iii: *t*-BuONa; pip: piperidine.

To demonstrate the broad applicability of this synthetic route, we decided to vary the structure of the *C*-amino phosphorus ylide, and also to test different transition metal fragments. Among chelating bidentate ligands, those supported by biaryl skeletons,[11] which include optically active species such as BINAP,[12] are by far the most popular. For a proof of principle, we investigated the possibility of preparing complexes based on the simplest of the biaryl backbones, namely biphenyl. The phosphonium precursor **5** was prepared in two steps from the readily available 2-bromo-2′-formylbiphenyl[13] as shown in Scheme 4. Deprotonation with sodium

10.1021/ja0662725 CCC: $33.50 © 2006 American Chemical Society

Scheme 5 [a]



7: M = Pd, L = Allyl (78% yield); **8**: M = Rh, L = cod (86% yield)

[a] Reagents and conditions: **7**: M = Pd, *L* = Allyl (78% yield); **8**: M = Rh, *L* = cod (86% yield).

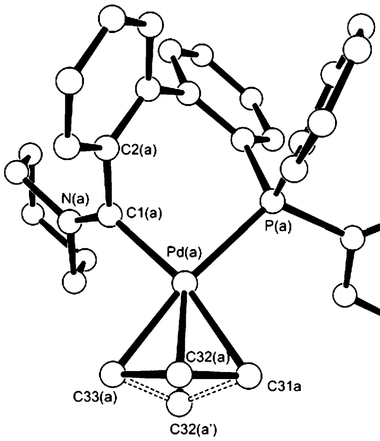


Figure 1. Molecular view of the crystal structure of **7** (H atoms and the triflate anion are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Pd(a)−C1(a) 2.002(2), Pd(a)−P(a) 2.2908(6), Pd(a)−C31(a) 2.200(3), Pd(a)−C32(a) 2.173(4), Pd(a)−C32(a′) 2.213(9), Pd(a)−C33(a) 2.166(3), C1(a)−N(a) 1.294(3); C1(a)−Pd(a)−P(a) 90.75(7), Pd(a)−C1(a)−C2(a) 110.40(17), Pd(a)−C1(a)−N1(a) 129.22(19), N(a)−C1(a)−C2(a) 120.4(2).

tert-butoxide led after workup to the salt-free ylide **6**, which was isolated in 95% yield.

Addition of 0.5 equiv of allylpalladium chloride dimer to the solution of **6** prepared in situ[9] afforded, after 2 h at room temperature, complex **7**, which was isolated in 78% yield as a 1/1.3 mixture of diastereomers (according to ^{1}H NMR spectroscopy), due to the two positions of the allyl ligand with respect to the facing dissymmetric P,C-chelate. The X-ray crystallographic study confirmed the presence of the two diastereomers (1/1.5 mixture), the meso carbon atoms of all the allyl groups being disordered over two positions.[14] Of course, due to the presence of the biphenyl unit, each diastereomer exists as a racemate (space group $P\bar{1}$), and Figure 1 shows one of the enantiomers. Similarly, using 0.5 equiv of bis(*μ*-chlorocyclooctadienerhodium), the cationic Rh(I) complex **8**, as a racemate (space group $P\bar{1}$), was obtained in 86% yield and fully characterized, including a single-crystal X-ray diffraction study.

This work demonstrates that in contrast to the so-called stabilized, semi-stabilized, and even nonstabilized phosphorus ylides (featuring an electron-withdrawing, aryl, and alkyl group, respectively, at the ylidic carbon), the destabilized *C*-amino phosphorus ylides readily act as aminocarbene/phosphine transfer agents toward various transition metal centers. This methodology allows for the straightforward preparation of bidentate heteroditopic ligands that are hardly available by other routes. It is important to note that the topology of the 1,6-bidentate phosphine/carbene ligands based on biaryl backbones is similar to that found in BINAP and related compounds, and it is not feasible using NHCs as the carbene fragment; with the latter, only 1,7-bidentate ligands can be obtained. The synthesis of phosphorus ylides based on more sophisticated biaryl scaffolds, including enantiomerically pure binaphthyl, is under current investigation, as well as the catalytic properties of the ensuing complexes.

Acknowledgment. We are grateful to the NIH (R01 GM 68825) for financial support of this work.

Supporting Information Available: Full experimental and spectroscopic data for all new compounds, and X-ray crystallographic data for **2**, **4**, **7**, and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.
(2) See, for example: (a) Kolodiazhnyi, O. I. *Tetrahedron* **1996**, *52*, 1855. (b) Kaska, W. C.; Ostoja Starzewski, K. A. In *Ylides and Imines of Phosphorus*; Johnson, A. W., Eds.; John Wiley & Sons: New York, 1993; Chapter 14. (c) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. (d) Vicente, J.; Chicote, M. T. *Coord. Chem. Rev.* **1999**, *193−195*, 1143. (e) Berno, P.; Gambarotta, S.; Kotila, S.; Erker, G. *Chem. Commun.* **1996**, 779. (f) Chauvin, R. *Eur. J. Inorg. Chem.* **2000**, 577. (g) Vicente, J.; Singhal, A. R.; Jones, P. G. *Organometallics* **2002**, *21*, 5887. (h) Carbo, M.; Falvello, L. R.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. *Eur. J. Inorg. Chem.* **2004**, 2338.
(3) See, for example: (a) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (b) Kreissl, F. R.; Held, W. *J. Organomet. Chem.* **1975**, *86*, C10. (c) Wong, W. K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (d) Lebel, H.; Paquet, V.; Proulx, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2887. (e) Zhang, X.; Chen, P. *Chem. Eur. J.* **2003**, *9*, 1852.
(4) (a) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347. (b) Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1. (c) Johnson, L. K.; Frey, M.; Ulibarri, T. A.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8167. (d) Falvello, L. R.; Llusar, R.; Margalejo, M. E.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2003**, *22*, 1132. (e) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952.
(5) (a) Gandelman, M.; Rybtchinski, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 5372. (b) Gandelman, M.; Naing, K. M.; Rybtchinski, B.; Poveranov, E.; Ben-David, Y.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 15265.
(6) (a) Canac, Y.; Conejero, S.; Soleilhavoup, M.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2006**, *128*, 459. (b) Conejero, S.; Song, M.; Martin, D.; Canac, Y.; Soleilhavoup, M.; Bertrand, G. *Chem. Asian J.* **2006**, *1*, 155.
(7) (a) Teuma, E.; Malbosc, F.; Etienne, M.; Daran, J. C.; Kalck, P. *J. Organomet. Chem.* **2004**, *689*, 1763. (b) Cucciolito, M. E.; Panunzi, A.; Ruffo, F.; Albano, V. G.; Monari, M. *Organometallics* **1999**, *18*, 3483. (c) Hartshorn, A.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348. (d) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; van Derveer, D. G. *Organometallics* **1982**, *1*, 103.
(8) For reviews, see: (a) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680. (b) Slone, C. S.; Weimberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233. (c) Constable, E. C.; Haverson, P.; Housecroft, C. E.; Nordlander, E.; Olsson, J. *Polyhedron* **2006**, *25*, 437.
(9) The presence of sodium triflate increased the rate and yield of reactions of cyclic ylides with metal fragments, and therefore they were prepared in situ from the corresponding phosphonium salts **3** and **5**.
(10) Lee, H. M.; Chiu, P. L.; Zeng, J. Y. *Inorg. Chim. Acta* **2004**, *357*, 4313.
(11) For reviews, see: (a) Bringman, G.; Tasler, S.; Pfeifer, R. M.; Breuning, M. *J. Organomet. Chem.* **2002**, *661*, 49. (b) Shimizu, H.; Nagasaki, I.; Saito, T. *Tetrahedron* **2005**, *61*, 5405. (c) Shibata, T.; Tsuruta, H.; Danjo, H.; Imamoto, T. *J. Mol. Catal. A: Chem.* **2003**, *196*, 117. (d) Genet, J. P. *Acc. Chem. Res.* **2003**, *36*, 908.
(12) (a) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (b) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801.
(13) Oba, M.; Iida, M.; Nishiyama, K. *Organometallics* **2001**, *20*, 4287.
(14) (a) Ding, Y.; Goddard, R.; Pörschke, K.-R. *Organometallics* **2005**, *24*, 439. (b) Gladiali, S.; Taras, R.; Ceder, R. M.; Rocamora, M.; Muller, G.; Solans, X.; Font-Bardia, M. *Tetrahedron Asymmetry* **2004**, *15*, 1477.

JA0662725