ORGANOMETALLICS

Volume 21, Number 23, November 11, 2002

Communications

Novel Ruthenium-Mediated Conversion of Aldimines and Aminals to Aminocarbene Complexes

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Received August 14, 2002

Summary: *The reaction of* $[RuCp(L)(CH_3CN)_2]PF_6$ *(L =* CH_3CN*,* PMe_3*) with (E)-N-(phenylmethylene)-2-pyridinamine (py-N=CHPh) affords the cyclic aminocarbene complexes* $[RuCp(L)(=CPhNH\text{-}py)]PF_6$*, whereas with L =* PPh_3*, CO the reaction stops already at the stage of the imine complex* $[RuCp(L)(\kappa^2N,N\text{-}py\text{-}N=CHPh)]PF_6$*. This reaction arguably does not proceed via a direct 1,2-hydrogen shift but seems to involve hydrido iminoacyl intermediates as a result of C−H bond activation and deprotonation steps.*

Heteroatom-stabilized carbene complexes play a central role in organometallic chemistry.[1] They have found widespread application as reactive intermediates in organic synthesis, initiating a wide range of C−C and C−heteroatom bond-forming reactions.[2] Moreover, heteroatom-stabilized carbenes, in particular N-heterocyclic ones, have been recognized as extraordinarily useful spectator ligands instead of or in addition to phosphine ligands.[3] It is thus of great interest to find new synthetic routes to afford carbene complexes, especially if they are available from simple organic precursors in a one-pot procedure. This has been achieved recently by converting amines,[4] ethers,[5] and activated olefins (see Scheme 1)[6] into the respective carbene complexes.

All these reactions are thermodynamically favorable, primarily due to the presence of a strong π-donor group. In fact, for nonactivated olefins (X = H in Scheme 1), the reaction is strongly endothermic and carbenes are often converted to the respective olefins; i.e., the reverse process takes place.[7] The analogous conversion of aldimines to aminocarbenes (Scheme 2), which is to the best of our knowledge not known, would be related to this reaction. We now report for the first time a facile rearrangement of aldimines and also aminals to yield cyclic aminocarbenes.

Accordingly, treatment of $[RuCp(CH_3CN)_3]PF_6$ (**1**) or $[RuCp(PMe_3)(CH_3CN)_2]PF_6$ (**2a**) with 1 equiv of (*E*)-*N*-(phenylmethylene)-2-pyridinamine (py-N=CHPh)[8] af-

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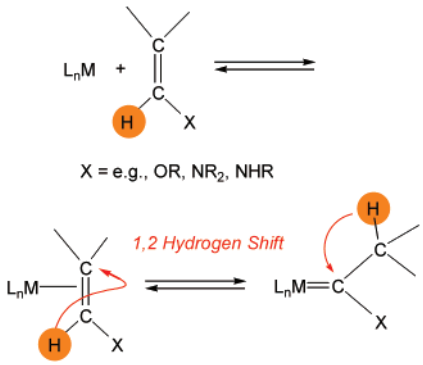
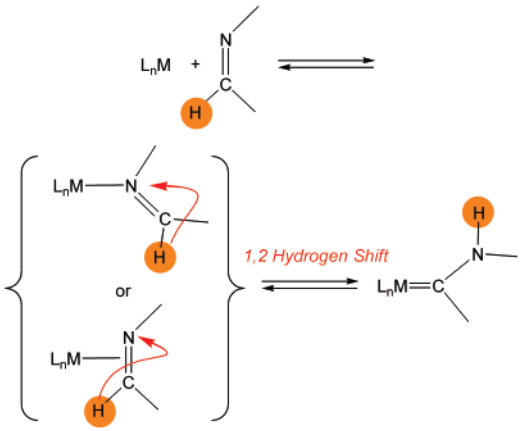
10.1021/om020664c CCC: $22.00
Publication on Web 10/15/2002

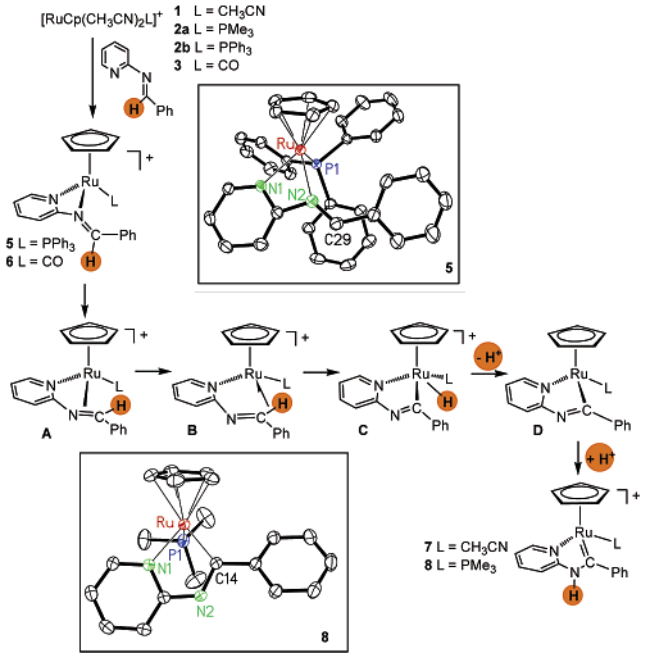
Scheme 1



Scheme 2



Scheme 3



forded the aminocarbene complexes [RuCp(CH$_3$CN)(=CPhNH-py)]PF$_6$ (**7**) and [RuCp(PMe$_3$)(=CPhNH-py)]PF$_6$ (**8**) in high yields (Scheme 3). This process is not restricted to RuCp complexes; RuTp(COD)Cl (**4**) also readily reacts with py-N=CHPh at elevated temperatures to give the aminocarbene complex RuTp(=CPhNH-py)Cl (**9**). In addition to full spectroscopic and analytical characterizations of all the products, the solid-state structure of **8** (in the form of **8**·(CH$_3$)$_2$CO) has been determined by single-crystal X-ray diffraction (Scheme 3).

Characteristic $^{13}C\{^1H\}$ NMR spectroscopic features of **7** and **8** comprise marked low-field resonances at 266.5 and 264.9 ppm, respectively, assignable to the carbene carbon atom of the =CPhNH-py moiety. Complex **8** adopts a typical three-legged piano-stool conformation. The Ru−C(14) bond distance is 1.959(1) Å, comparable to that in other heteroatom-stabilized ruthenium carbene complexes.

Interestingly, if [RuCp(PPh$_3$)(CH$_3$CN)$_2$]PF$_6$ (**2b**) and [RuCp(CO)(CH$_3$CN)$_2$]PF$_6$ (**3**) are reacted with py-N=CHPh, the reaction does not proceed to give an aminocarbene but affords the complexes [RuCp(PPh$_3$)(κ^2N,N-py-N=CHPh)]PF$_6$ (**5**) and [RuCp(CO)(κ^2N,N-py-N=CHPh)]PF$_6$ (**6**), featuring a κ^2N,N-coordinated py-N=CHPh ligand (Scheme 3), even if kept at elevated temperature for 24 h. Complexes **5** and **6** have been fully characterized by NMR spectroscopy and elemental analyses. The structure of **5** has been confirmed also by X-ray crystallography.

The reaction mechanism shown in Scheme 3 represents our initial working hypothesis for providing the amino carbene complexes, and the four key intermediates **A**−**D** are proposed. The formulations of these intermediates are also supported by preliminary DFT (B3LYP) calculations using py-N=CH$_2$ and HCN as model ligands (Figure 1).[9] The overall reaction is exothermic by 8.0 kcal/mol. For the first step, the initially formed κ^2N,N-py-N=CHPh complex converts into **A**, where the imine moiety is side-on coordinated. Subsequently, C−H bond activation occurs via the intermediacy of **B** to give eventually the hydrido iminoacyl intermediate **C**.[10] Such intermediates have been also suggested recently in the reaction of [RuHCl(P-i-Pr$_3$)$_2$]$_2$ with imines, eventually yielding, however, isonitriles rather than aminocarbenes.[11] Moreover, the observation that neither **2b** nor **3** undergoes a C−H activation/oxidative addition reaction may also support our proposal. While in the first case steric restrictions may account for the lack of reactivity, in the latter case the strongly π-accepting CO ligand may prevent an oxidative addition step. Although we have as yet no conclusive evidence for this pathway, we believe that **C** undergoes a facile deprotonation (e.g., assisted by adventitious water, counterion, or solvent) to give the strongly basic neutral iminoacyl complex **D**, which readily uptakes a proton to afford the final products. A

(9) All calculations were performed using the Gaussian98 software package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

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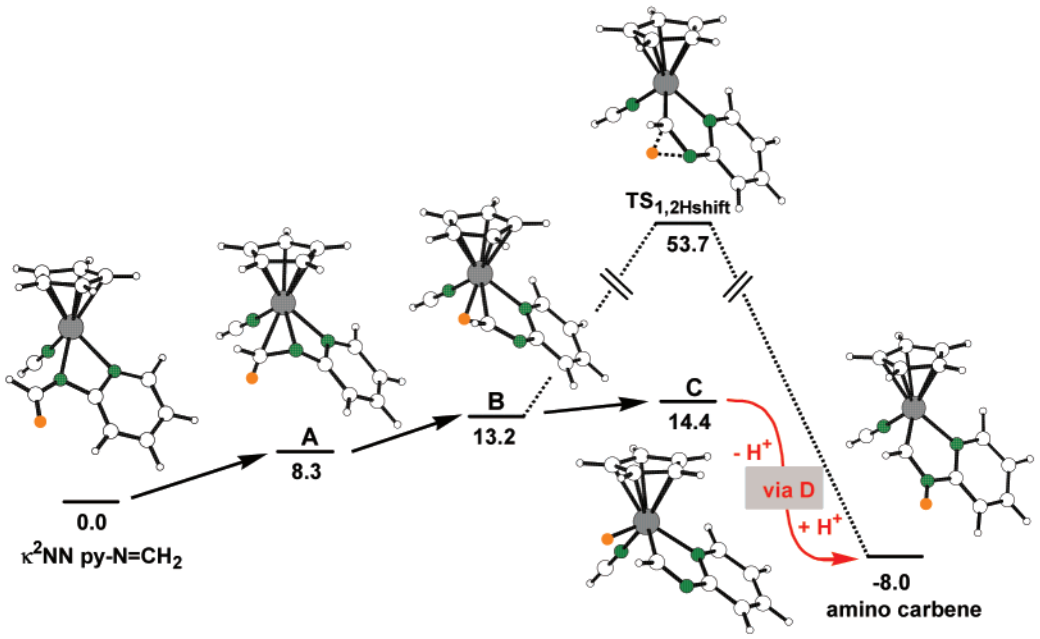
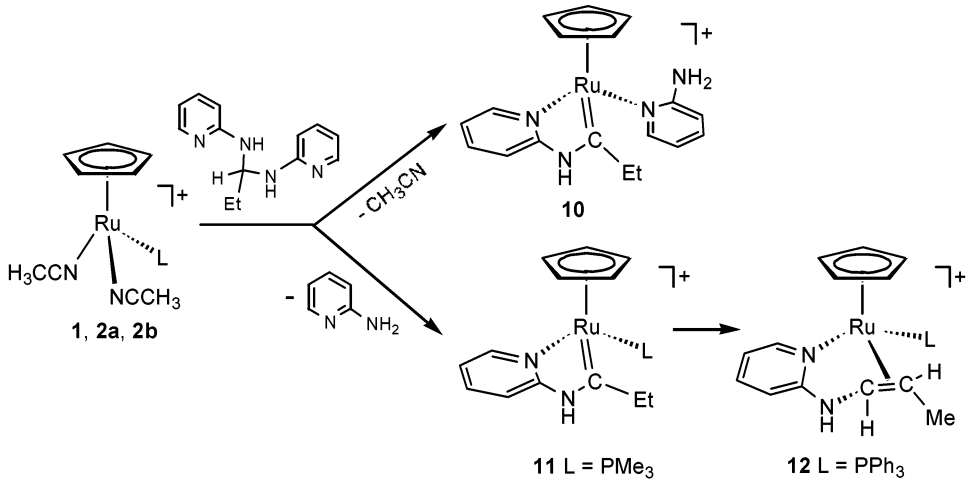


Figure 1. Optimized B3LYP geometries and relative energies (kcal/mol) for the conversion of [RuCp(κ^2N,N-py-N=CH_2)-(HCN)]$^+$ to the aminocarbene [RuCp(HCN)(=CHNH-py)]$^+$ (Ru sdd; C, H, N (6-31g**).

Scheme 4



direct 1,2-hydrogen shift process converting **B** directly into aminocarbene complexes seems to be unlikely. In fact, DFT calculations suggest such a process to be as high as 53.7 kcal (Figure 1).

Finally, we have investigated whether aminals which are readily derived from aldimines and amines can be converted into aminocarbenes. Indeed, the reaction of **1** and **2a** with the aminal *N*,*N*′-di-2-pyridinyl-1-propyldiamine (py-NHCH(Et)CHNH-py) affords the respective cyclic aminocarbene complexes [RuCp(py-NH_2)(=C(NH-py)Et)]PF_6 (**10**) and [RuCp(PMe_3)(=C(NH-py)Et]PF_6 (**11**) in high yields (Scheme 4). With **2b** the reaction does not stop at the aminocarbene stage but proceeds further to give the olefin complex **12**. All these reactions involve both C−H and C−N activation steps. It is interesting to note, however, that **2b** does not react with py-N=CHPh to give an aminocarbene complex or a rearrangement product thereof, suggesting that in the case of aminals a different mechanism may be operative.

In summary, we have shown for the first time that the reaction of aldimines and aminals with both RuCp and RuTp complexes furnishes a simple preparation for a class of carbene complexes that does not rely on the conventional routes to carbenes utilizing, for example, diazoalkanes. Our efforts are currently directed toward extending the scope of these reactions to other transition-metal complexes as well as other aldimines and aminals.

Acknowledgment. Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" (Project No. P14681-CHE) is gratefully acknowledged. Support from the EC through the COST D17 Action is also acknowledged.

Supporting Information Available: X-ray crystallographic data for **5** and **8**·$(CH_3)_2CO$ and spectroscopic data for **4**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020664C