J|A|C|S COMMUNICATIONS

Published on Web 09/10/2010

C−H Activation of Acetonitrile at Nickel: Ligand Flip and Conversion of N-Bound Acetonitrile into a C-Bound Cyanomethyl Ligand

Anna Magdalena Oertel,[†] Vincent Ritleng,*[,†] Michael J. Chetcuti,*[,†] and Luis F. Veiros[‡]

Laboratoire de Chimie Organométallique Appliquée, UMR CNRS 7509, Ecole Européenne de Chimie, Polymères et Matériaux, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France, and Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

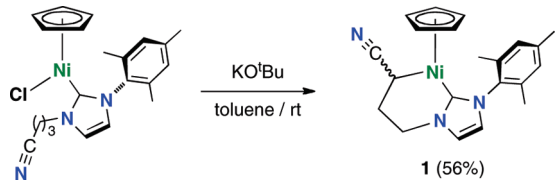
Received June 18, 2010; E-mail: vritleng@unistra.fr; michael.chetcuti@unistra.fr

Abstract: Nickel joins the fairly exclusive list of metals that can activate nitrile C−H bonds. We report the first example of the C−H activation of an acetonitrile ligand on a nickel center. The acetonitrile ligand formally loses a proton and undergoes a sharp flip to give a cyanomethyl ligand that is coordinated to the nickel atom. Structures of an initial N-bound acetonitrile−nickel complex and of a final cyanomethyl−nickel complex are both presented.

The activation of C−H bonds has emerged as a potent tool for the functionalization of organic molecules.[1] As sp^3-hybridized C−H bonds are much less reactive than most other bonds, their activation when they are proximal to other functional groups is nontrivial. Herein, we describe the first example of the C−H activation of a labile acetonitrile ligand on a nickel center. The ligand formally loses a proton and does a sharp flip to give a cyanomethyl−nickel complex. Structural data for an initial CpNi N-bound acetonitrile species, a final CpNi−CH_2CN complex,[2] and some DFT calculations are presented.

Our recent research has focused on nickel Cp and Cp* complexes with N-heterocyclic carbene (NHC) ligands. We have described the chemistry and some aspects of the catalytic behavior of [Ni(NHC)XCp†] (X = Cl, I) complexes.[3] In this context, we now report a [Ni(NHC)ClCp] complex in which the NHC ligand bears a $-(CH_2)_3CN$ side-chain group on one nitrogen atom and a mesityl group on the other. Upon treatment with KO*t*Bu, a C−H bond α to the nitrile group underwent an intramolecular activation to give the nickelacyclic species **1** (Scheme 1; see the Supporting Information).

Scheme 1. Formation of Nickelacycle **1** by Activation of a C−H Bond α to a Nitrile Group in a Side Chain Linked to the NHC Ligand



1 (56%)

The extension of this reaction to CH_3CN was of interest, as acetonitrile metalation to M−CH_2CN complexes is not only rare in general (it is a challenge to selectively cleave C−H bonds in the presence of other functional groups) but also completely unknown for nickel species.[4] Such activation has been observed virtually exclusively for group 8 and group 9 metal complexes.[5] X-ray data are also very limited for cyanomethyl complexes, and to our knowledge, no structural data for a CH_3CN complex and its corresponding cyanomethyl derivative have been reported.

We have shown that when CH_3CN solutions of the neutral complexes [Ni{(Mes_2)NHC}ClCp†] are treated with KPF_6, chloride abstraction affords the cationic complexes [Ni{(Mes_2)NHC}-$(NCCH_3)$Cp†]$^+$[PF_6^-] [Cp† = Cp (**2**), Cp* (**2***)] in high yield. The CH_3CN ligands in complexes **2** and **2*** are labile.[3c] An X-ray diffraction study of the cation of **2**, which is presented here (Figure 1), shows that the CH_3CN ligand is essentially linear but that the Ni−N bond is not perfectly collinear with this axis.

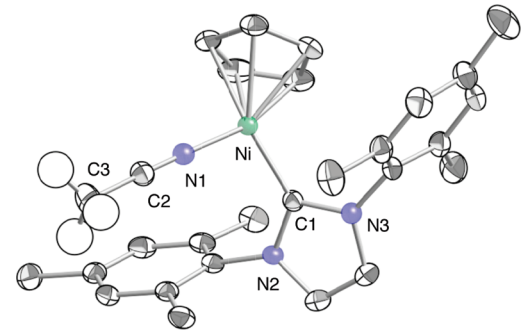
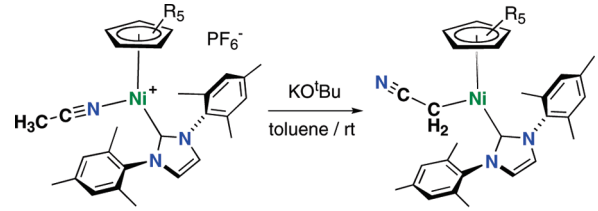


Figure 1. Molecular structure of the cation of **2**. Key atoms are labeled. Only H atoms of acetonitrile are shown (as isotropic spheres). Selected distances (Å) and angles (deg): Ni−C1, 1.902(2); Ni−N1, 1.8685(19); C2−N1, 1.138(3); Ni−N1−C2, 174.52(19); N1−C2−C3, 177.9(2); N1−Ni−C1, 96.93(8).

When **2** was reacted with KO*t*Bu, ^{1}H NMR data indicated the rapid, quantitative deprotonation of the CH_3CN ligand. The resulting cyanomethyl group coordinated to the nickel atom, leading to the isolation of the neutral species [Ni{$(Mes)_2$NHC}(CH_2CN)Cp] (**3**). The Cp* species **2*** similarly generated complex **3*** (Scheme 2).

Scheme 2. Base-Promoted C−H Activation of Coordinated CH_3CN



2, R = H
2*, R = Me

3, R = H (85%)
3*, R = Me (47%)

Spectroscopic data for **3** and **3*** (see the Supporting Information) are in accord with their proposed structures. The structure of **3** was confirmed by X-ray diffraction (Figure 2). The transformation of

[†] Université de Strasbourg.
[‡] Instituto Superior Técnico.

10.1021/ja105368p

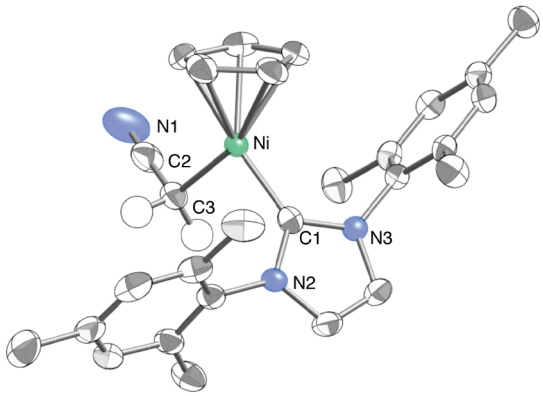


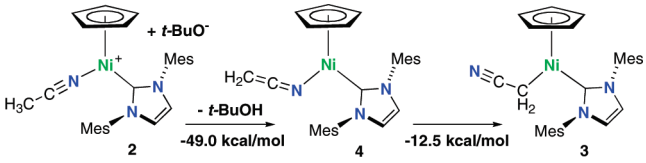
Figure 2. Molecular structure of **3**. Key atoms are labeled. Only H atoms of the cyanomethyl ligand are shown (as isotropic spheres). Selected distances (Å) and angles (deg): Ni−C1, 1.877(2); Ni−C3, 1.961(2); C2−C3, 1.429(3); C2−N1, 1.147(3); Ni−C3−C2, 112.5(2); C3−C2−N1, 178.5(6); C1−Ni−C3, 91.9(1).

the CH_3CN ligand into a CH_2CN group resulted in a nonlinear Ni−C3−C2 angle of 112.5(2)°.

Much effort has targeted the C−H functionalization of arenes and heteroarenes,[6] and this field is now recognized as an economically and environmentally attractive alternative to the traditional cross-coupling reactions with organometallic reagents. The activation of C(sp^3)−H bonds represents a significantly greater challenge because of the large HOMO−LUMO gap between the C−H σ and σ^* orbitals, and less success has been achieved here.[7] In particular, C(sp^3)−H bond functionalization in molecules with reactive functional groups is somewhat restricted, as these groups are often much more reactive toward the metal center.

The reaction mechanism has not yet been fully established. The N-coordination of CH_3CN seen in the solid state is probably strongly favored and retained in solution, but a weaker side-bound π-(κ^1-*C*, κ^1-*N*) coordination mode could a priori be envisaged as a minor, higher-energy state.[8] Nevertheless, preliminary density functional theory (DFT) calculations[9] to investigate mechanistic details of the reaction by screening possible intermediates indicated that a side-bound ligand was unlikely. Indeed, all attempts to optimize a side-bound π-coordinated CH_3CN species failed, resulting instead in the N-coordinated reagent **2**. The calculations instead suggested a two-step pathway: deprotonation of **2** to yield an intermediate with an N-coordinated $H_2C{=}C{=}N$ ligand (**4**, Scheme 3) followed by a

Scheme 3. DFT-Calculated Energy Balance for the Reaction



ligand flip from the N- to the final C-bound species. The calculated energies indicated that both steps are thermodynamically favorable.

The recent disclosure of Ni(II)-catalyzed C−H arylations of arenes and heteroarenes in the presence of tBuO$^-$ as a base[10] hints at the growing potential for use of nickel species (as opposed to more expensive palladium or ruthenium species) in transition-metal-catalyzed C−H bond functionalization.

C−H bonds α to other functional groups can also be activated at Cp†Ni(NHC) centers. Our recent results show that α-C−H bonds of ketones are activated to give [Ni(NHC){$CH_2C(O)R$}Cp] species.[11] We continue to investigate the scope and breadth of these activation reactions.

Acknowledgment. We thank the CNRS and the Université de Strasbourg for support. A.M.O. thanks the Ministère de l'Enseignement Supérieur et de la Recherche for a Ph.D. research scholarship.

Supporting Information Available: Full details of the synthesis and characterization of all new compounds; X-ray data (CIF) for **1**, **2**, and **3**; and full DFT computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (c) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047. (d) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (e) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (f) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (g) Bergman, R. G. *Nature* **2007**, *446*, 391. (h) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013. (i) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (j) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624.

(2) Abbreviations: Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5; Cp† = Cp or Cp*; Mes = 2,4,6-$C_6H_2Me_3$.

(3) (a) Ritleng, V.; Barth, C.; Brenner, E.; Milosevic, S.; Chetcuti, M. J. *Organometallics* **2008**, *27*, 4223. (b) Milosevic, S.; Brenner, E.; Ritleng, V.; Chetcuti, M. J. *Dalton Trans.* **2008**, 1973. (c) Ritleng, V.; Oertel, A. M.; Chetcuti, M. J. *Dalton Trans.* **2010**, *39*, 8153.

(4) Ni−CH_2CN complexes were synthesized by transmetalation from $LiCH_2CN$. See: (a) Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Organometallics* **1985**, *4*, 1178. (b) Alburquerque, P. R.; Pinhas, A. R.; Krause Bauer, J. A. *Inorg. Chim. Acta* **2000**, *298*, 239.

(5) Examples are known in group 8 and group 9 chemistry as well as in lanthanide chemistry. Group 8: (a) Itell, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **2002**, *649*, 64. (c) Foley, N. A.; Gunnoe, T. B.; Cundari, T. R.; Boyle, P. D.; Petersen, J. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 726. (d) Derrah, E. J.; Giesbrecht, K. E.; McDonald, R.; Rosenberg, L. *Organometallics* **2008**, *27*, 5025. Group 9: (e) English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 1648. (f) Vetter, A. J.; Rieth, R. D.; Jones, W. D. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6957. (g) Crestani, M. G.; Steffen, A.; Kenwright, A. M.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Organometallics* **2009**, *28*, 2904. (h) Evans, M. E.; Li, T.; Vetter, A. J.; Rieth, R. D.; Jones, W. D. *J. Org. Chem.* **2009**, *74*, 6907. Lanthanides: (i) Heeres, H. J.; Meetsma, A.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 420.

(6) (a) Campeau, L.-C.; Fagnou, K. *Chem. Commun.* **2006**, 1253. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (c) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (d) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269. (e) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792.

(7) (a) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083. (b) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem.—Eur. J.* **2010**, *16*, 2654.

(8) (a) Crestani, M. G.; Arevalo, A.; García, J. J.; Juventino, J. *Adv. Synth. Catal.* **2006**, *348*, 732. (b) Atesin, T. A.; Li, T.; Lachaize, S.; Brennessel, W. W.; García, J. J.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 7562. (c) Cristóstomo, C.; Crestani, M. G.; García, J. J. *J. Mol. Catal. A: Chem.* **2007**, *266*, 139. (d) Schaub, T.; Döring, C.; Radius, U. *Dalton Trans.* **2007**, 1993.

(9) DFT calculations were performed with the PBE1PBE functional using the Gaussian 03 package. The reported energy values include solvent effects obtained using the PCM model. See the Supporting Information for full details.

(10) (a) Canivet, J.; Yamaguchi, J.; Ban, I.; Itami, K. *Org. Lett.* **2009**, *11*, 1733. (b) Hachiya, H.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 1737. (c) Kobayashi, O.; Uraguchi, D.; Yamakawa, T. *Org. Lett.* **2009**, *11*, 2679.

(11) Oertel, A. M.; Ritleng, V.; Chetcuti, M. J. Unpublished results.

JA105368P