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Chameleon Behavior of a Newly Synthesized Scandium Nitrilimine Derivative

Jiaxiang Chu,† Christos E. Kefalidis,‡ Laurent Maron,*,‡ Xuebing Leng,† and Yaofeng Chen*,†

†State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

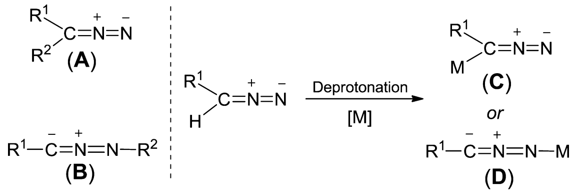
‡LPCNO, CNRS & INSA, Université Paul Sabatier, 135 Avenue de Rangueil, Toulouse 31077, France

Ⓢ *Supporting Information*

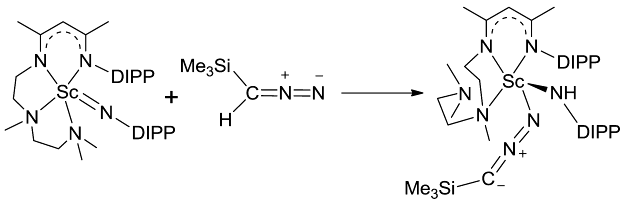
ABSTRACT: The synthesis, structural characterization, and reactivity of the first example of a scandium -substituted nitrilimine are presented. This unique complex exhibits high thermal stability but shows a rich reactivity toward a variety of unsaturated substrates, including aldehyde, ketone, nitrile, and allene derivatives. The versatility of the complex was further highlighted by density functional theory mechanistic studies.

Diazoalkanes $(R^1)(R^2)CN_2$ (**A** in Scheme 1) are important reagents in organic synthesis, and they are widely used as 1,3-dipoles for the synthesis of carbon−nitrogen heterocycles[1] and as facile source of carbenes.[2] The main reaction of hydrogen-substituted diazoalkanes $(R^1)(H)CN_2$ with metal complexes, apart from N_2 loss to give metal carbene complexes, is deprotonation leading to metal complexes containing $[(R^1)CN_2]^-$ anions, which can coordinate to the metal centers through the carbon atom (**C**) or the terminal nitrogen atom (**D**). Metal complexes with N-bonded $[(R^1)CN_2]^-$ ligands are of interest as a type of metal-substituted nitrilimines (**B**), which are important nitrogen-containing 1,3-dipoles in addition to diazoalkanes.[1,3] Nitrilimines substituted with main-group metals have been known for a long time, and a considerable number of these complexes have been synthesized, including Li,[4] Al,[5] Ga,[6] and Ge[7] derivatives. However, to the best of our knowledge, there are no examples of transition-metal-substituted nitrilimines. On the other hand, C-bonded $[(R^1)CN_2]^-$ anions have been reported in a variety of transition-metal complexes, such as Pd,[8] Rh/Os,[9] Ni,[10] Au,[11] and rare-earth-metal complexes.[12] Recently, we synthesized scandium terminal imido complexes and studied their reactivity.[13] During these studies, we obtained the first example of a scandium-substituted nitrilimine. This unique complex shows a rich reactivity to a variety of unsaturated substrates. Herein we report the synthesis, crystal structure, and reactivity of this scandium nitrilimine derivative as well as a mechanistic study with different substrates performed using dispersion-corrected density functional theory (DFT-D).

Scheme 1. Resonance Structures of Diazoalkane (A) and Nitrilimine (B) and the Corresponding Metal-Substituted Analogues C and D



Scheme 2. Synthesis of Scandium Nitrilimine 1



Reaction of the scandium terminal imido complex [LSc═N(DIPP)] (L = $[MeC(N(DIPP))CHC(Me)(NCH_2CH_2N(Me)CH_2CH_2NMe_2]^-$, DIPP = 2,6-$(^iPr)_2C_6H_3$)[13b] with (trimethylsilyl)diazomethane, $(Me_3Si)(H)CN_2$, in toluene at room temperature gave scandium nitrilimine complex **1** in 72% yield (Scheme 2). Complex **1** was characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (Figure 1). During the reaction of the imido complex with $(Me_3Si)(H)CN_2$ (Scheme 2), proton transfer from $(Me_3Si)(H)CN_2$ to the imido group yields a

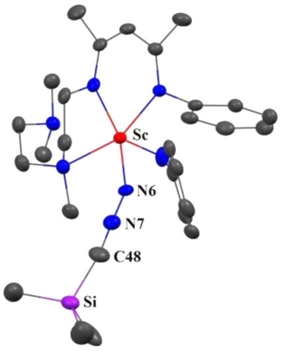


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Figure 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. The DIPP isopropyl groups and the H atoms have been removed for clarity.

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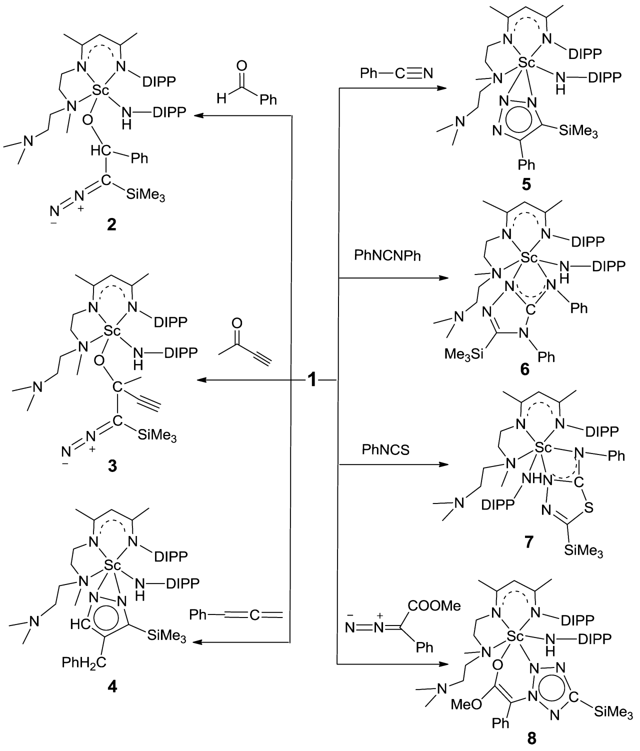
$[Me_3SiCN_2]^-$ anion, which coordinates to the Sc center through its terminal nitrogen atom. A DFT-D study showed that the activation barrier for the proton transfer reaction is low (13.6 kcal mol^{-1}) and that the reaction is thermodynamically favorable (32.6 kcal mol^{-1}) [see Figure S20 in the Supporting Information (SI)]. It is noteworthy that the $[(R^1)CN_2]^-$ anion has a strong tendency to bind two metal ions through the terminal nitrogen atom or through the terminal nitrogen atom and the carbon atom. Most of the reported main-group-metal-substituted nitrilimines exist as bimetallic or multimetallic species, and no example of crystallographically characterized mononuclear main-group-metal-substituted nitrilimine has been reported.[14] It is also noteworthy that reactions of $[(C_5Me_5)_2Sm][(\mu\text{-Ph})_2BPh_2]$ with $Li[Me_3SiCN_2]$ and $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$ with $(Me_3Si)(H)CN_2$ give the bimetallic isocyanotrimethylsilylamide complexes $\{(C_5Me_5)_2Sm[(\mu\text{-N-}(SiMe_3)NC]\}_2$ as a result of 1,3-silyl migration during the reactions.[15] The existence and thermal stability of monometallic complex **1** can be attributed to the presence of the bulky ligands L^- and $[NH(DIPP)]^-$. In **1**, the NNC unit of the $[Me_3SiCN_2]^-$ ligand is almost linear with an N6−N7−C48 angle of 176.5(5)°. The Sc−N6−N7 and N7−C48−Si angles are 149.5(3)° and 157.4(5)°, respectively. The C48−N7 bond [1.199(6) Å] is longer than a typical C−N triple bond (1.14 Å), and the N6−N7 bond [1.188(5) Å] is consistent with a double bond.[16] These structural data indicate that the NNC unit of the $[Me_3SiCN_2]^-$ ligand in **1** adopts an allenic structure rather than a propargylic one.[17] The $Sc-N^{nitrilimine}$ bond [2.075(3) Å] is similar in length to the $Sc-N^{amido}$ single bond [2.088(4) Å] and much longer than the $Sc-N^{imido}$ double bond in the scandium terminal imido complex [1.859(2) Å].[13b] In contrast to organic nitrilimines,[3] **1** is thermally stable and shows less than 5% decomposition over 12 h in C_6D_6 at 75 °C.

Lithium nitrilimines have been extensively used as reagents in organic synthesis.[18] However, they are multimetallic species and coexist with their lithium diazoalkane isomers in solution, and therefore, a deeper understanding of their reactivity is difficult to eluicidate.[4] Bertrand and co-workers synthesized a mononuclear aluminum nitrilimine and found that it reacts with a 1,3-dipolarophile (Lawesson's reagent) to give a [3+2] addition product, but its reactivity toward other substrates was not reported.[5] The high thermal stability of **1** allowed a detailed investigation of its reactivity. Complex **1** is very reactive with a variety of unsaturated substrates and displays interesting reaction patterns (Scheme 3). The reaction of **1** with 1 equiv of benzaldehyde in toluene at −35 °C for 2 h gave scandium alkoxide complex **2** in 68% yield. The molecular structure of **2** is shown in the SI. After coordination of the substrate, the carbon atom of the nitrilimine ligand in **1** undergoes nucleophilic attack at the carbon atom of benzaldehyde, yielding a 2-diazo-1-phenyl-2-(trimethylsilyl)ethoxide ligand, which leads to cleavage of the Sc−N σ bond with subsequent formation of a Sc−O bond. The C−N [1.289(4) Å] and N−N [1.145(4) Å] bonds in the 2-diazo-1-phenyl-2-(trimethylsilyl)-ethoxide ligand in **2** are consistent with double bonds, showing a typical structural feature of diazoalkanes.[19] It should be noted that (trimethylsilyl)diazomethane does not react with benzaldehyde in C_6D_6 at room temperature or even at 75 °C, as monitored by ^1H NMR spectroscopy.[20] The aforementioned reaction is also different from those of organic nitrilimines with benzaldehyde, which give 1,3,4-oxadiazolines.[1a] The reaction of **1** with the unsaturated ketone but-3-yn-2-one was subsequently investigated. In contrast with the reaction of (trimethylsilyl)diazomethane with but-3-yn-2-one, which yields a pyrazole compound via a 1,3-cycloaddition to the C≡C triple bond of but-3-yn-2-one, the reaction of **1** with this substrate gave scandium alkoxide complex **3** in 89% yield (similar to the reactivity with benzaldehyde). The structural features of **3** are similar to those of **2**, and the C−N and N−N bond lengths of the 1-diazo-2-methyl-1-(trimethylsilyl)but-3-yn-2-ol ligand in **3** are 1.311(4) and 1.138(3) Å, respectively (see the SI). Complexes **2** and **3** offer the possibility of further reactivity at the diazo moiety.

Scheme 3. Reactions of 1 with Unsaturated Substrates



Complex **1** can also react with several other unsaturated substrates such as allene derivatives and nitriles. ^1H NMR monitoring of the reaction of **1** with phenylallene in C_6D_6 at 75 °C showed that **1** was almost fully converted into the new complex **4** in 2 days. A subsequent scaled-up reaction in toluene provided **4** in 59% isolated yield. **4** is a scandium 1,2-diazolato complex, as shown in Scheme 3, and its molecular structure is shown in the SI. The formation of **4** implies a [3+2] cycloaddition followed by a 1,3-hydrogen shift. Complex **1** reacted rapidly with benzonitrile. The reaction was complete within 15 min at room temperature and afforded scandium 1,2,3-triazolato complex **5** in 87% yield. It is worth mentioning that reactions of organic nitrilimines with benzonitrile give 1,2,4-triazoles[4] while that of diazomethane with cyanic bromide gives 1,2,3-triazole.[21] Therefore, the reaction of **1** with benzonitrile is similar to those of diazoalkanes rather than those of organic nitrilimines. In **5**, the 1,2,3-triazolato ligand coordinates to the Sc center through two nitrogen atoms with two nonequivalent Sc−N bonds [the Sc−N6 and Sc−N7 bond lengths are 2.180(2) and 2.281(2) Å, respectively] (Figure 2), which is consistent with the different electronic donating abilities of these two nitrogen atoms.

The reaction of **1** with diphenylcarbodiimide (heteroallene) was also rapid, and scandium 3-amino-1,2,4-triazolato complex **6** was obtained in 84% yield. Unlike the reactions of **1** with

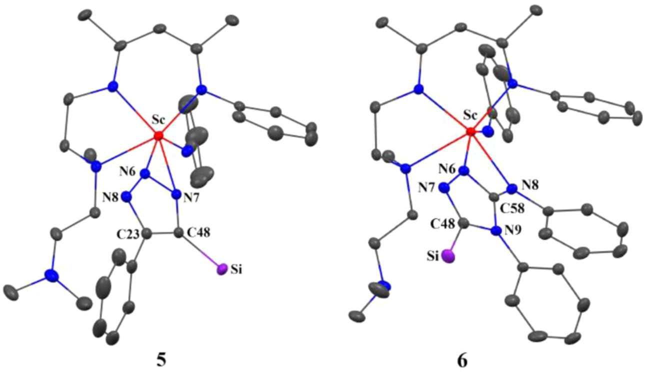


Figure 2. Molecular structures of **5** and **6** with thermal ellipsoids at the 30% probability level. Trimethylsilyl methyl groups, DIPP isopropyl groups, and H atoms have been removed for clarity.

benzaldehyde and benzonitrile, nucleophilic attack of the terminal nitrogen atom of the nitrilimine ligand at the carbon atom of diphenylcarbodiimide occurs. This is similar to the reactions of organic nitrilimines but different from those of diazoalkanes.[1a] In **6**, the 3-amino-1,2,4-triazolato ligand coordinates to the Sc center through one amino nitrogen atom and one nitrogen atom of triazolato ring, and the distance from the Sc center to the amino nitrogen atom [2.252(2) Å] is shorter than that to the nitrogen atom of triazolato ring [2.309(2) Å] (Figure 2). The reaction pattern of **1** with phenyl isothiocyanate was very similar to that with diphenylcarbodiimide, giving scandium 2-amino-1,3,4-thiadiazolato complex **7** in 85% yield. The reaction of **1** with methyl diazophenylacetate provided scandium tetrazolato derivative **8** in 93% yield. Apparently, the 1-methoxy-2-phenyl-2-(5-trimethylsilyl-2*H*-tetrazol-2-yl)ethenoxide ligand of **8** is formed through [3+2] cycloaddition of the nitrilimine ligand of **1** to the N═N double bond of methyl diazophenylacetate followed by an electronic rearrangement. The molecular structures of **7** and **8** were both determined by single-crystal X-ray diffraction (see the SI).

To gain further insight into the reactivity of **1**, DFT-D calculations were carried out at the B3PW91-D2 level of theory.[22] The reactions with diphenylcarbodiimide and benzonitrile were chosen as representative examples (see the SI). In the case of diphenylcarbodiimide, two plausible pathways were investigated (Figure 3). The first leads to the experimentally observed complex **6** and the second to the 1,2,3-triazolato complex **6′**. In the first case, the reaction proceeds through insertion of the C═N double bond of diphenylcarbodiimide into the Sc−$N_{\text{nitrilimine}}$ bond of **1** to form the metallacyclic intermediate **int2**. The activation barrier for this step is 11.3 kcal mol^{-1}, and the step is exoergic by 18.3 kcal mol^{-1}. The reaction continues via $\mathbf{TS_{int2-6}}$ corresponding to heterocyclic ring closure with an activation barrier of only 6.6 kcal mol^{-1}. Overall, the reaction is strongly exoergic by 58.2 kcal mol^{-1}, which is the driving force for this transformation. The computed low barrier, especially in view of the well-known problem of entropy overestimation by calculations, is in line with a rapid reaction. We also examined a second possibility in which, instead of the insertion, nucleophilic attack of the diphenylcarbodiimide at the nitrilimine carbon occurs. The activation barrier required for this step is higher than that for the insertion step (13.4 kcal mol^{-1} free energy difference). Also, the intermediate **int2′** is less stable by 33.1 kcal mol^{-1} relative to **int2**. In this pathway, the hypothetical 1,2,3-triazolato complex **6′** is formed after heterocyclic ring closure. Moreover, the formation of **6′** is exergonic by only 28.5 kcal mol^{-1}, making this pathway also less thermodynamically favored than the first one. The products arising from other regioisomeric insertions were found to be less favored than **int2** by 58 kcal mol^{-1}, ruling out the possibility that these complexes would be formed. For benzonitrile, the reaction is proposed to proceed through an inner-sphere 1,3-dipolar addition transition state to allow the formation of **5**. This reaction is predicted to be kinetically accessible ($\Delta G^{\ddagger}$ = 13.3 kcal mol^{-1}) and thermodynamically strongly exergonic (ΔG^{0} = −42.3 kcal mol^{-1}). This reaction is controlled by electrostatic repulsion between the incoming substrate and the nitrilimine ligand (see the SI for details of the mechanism).

In summary, the synthesis, structural characterization, and reactivity of the first example of a scandium-substituted nitrilimine have been presented. The high thermal stability of this scandium derivative allowed a detailed analysis of its reactivity toward several unsaturated substrates, including aldehyde, ketone, nitrile, and allene derivatives.[23] In the two

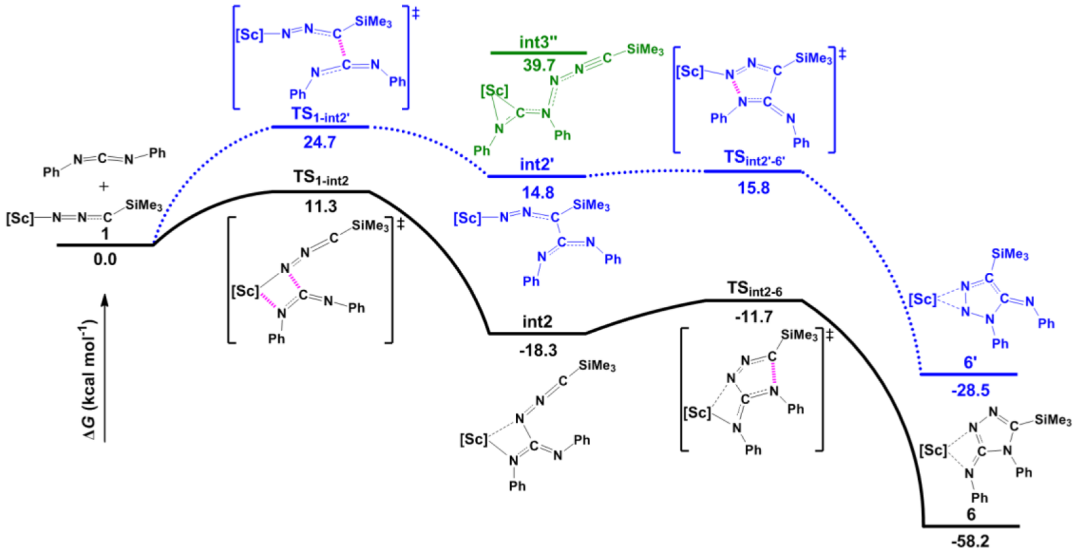


Figure 3. Gibbs free energy profile for the formation of **6**. In the structures shown, the ligands of Sc have been removed for clarity.

latter cases, the versatility of the nitrilimine ligand coordinated to the scandium center was demonstrated by analogy with organic nitrilimines. Indeed, with the nitrile substrate, the nitrilimine ligand reacted more like a diazoalkane, whereas with the heteroallene, the reactivity was closer to that of an organic nitrilimine. This versatility was investigated by computing the reaction pathways for the diphenylcarbodiimine and benzonitrile substrates using DFT. It has been shown that the formation of the 1,2,4-triazolato ring is both thermodynamically and kinetically driven. In the case of benzonitrile, the difference in the barrier is associated with repulsion between the negatively charged carbon and nitrogen atoms in the 1,3-dipolar addition transition state. To date, the present work is the only joint experimental/theoretical study that deals with a transition-metal nitrilimine complex, and it exhibits the unique and rich chemistry of such a complex.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details and a zip file containing CIFs for **1−8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

laurent.maron@irsamc.ups-tlse.fr; yaofchen@mail.sioc.ac.cn

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. (b) Kobayashi, S.; Jørgensen, K. A. In *Cycloaddition Reactions in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2001. (c) Sharp, J. T. *Chem. Heterocycl. Compd.* **2002**, *59*, 473.

(2) (a) Doyle, M. P. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Eds.; Wiley-Interscience: New York, 2004. (b) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704.

(3) Bertrand, G.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 527.

(4) (a) Boche, G.; Harms, K.; Marsch, M.; Schubert, F. *Chem. Ber.* **1994**, *127*, 2193. (b) Armstrong, D. R.; Davies, R. P.; Haigh, R.; Hendy, M. A.; Raithby, P. R.; Snaith, R.; Wheatley, A. E. H. *Eur. J. Inorg. Chem.* **2003**, 3363.

(5) Emig, N.; Gabbaï, F. P.; Krautscheid, H.; Réau, R.; Bertrand, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 989.

(6) Uhl, W.; Hannemann, F.; Saak, W.; Wartchow, R. *Eur. J. Inorg. Chem.* **1999**, 771.

(7) Leue, C.; Réau, R.; Neumann, B.; Stammler, H. G.; Jutzi, P.; Bertrand, G. *Organometallics* **1994**, *13*, 436.

(8) (a) Murahashi, S. I.; Kitani, Y.; Hosokawa, T.; Miki, K.; Kasai, N. *J. Chem. Soc., Chem. Commun.* **1979**, 450. (b) Murahashi, S. I.; Kitani, Y.; Uno, T.; Hosokawa, T.; Miki, K.; Yonezawa, T.; Kasai, N. *Organometallics* **1986**, *5*, 356.

(9) (a) Deydier, E.; Menu, M. J.; Dartiguenave, M.; Dartiguenave, Y.; Simard, M.; Beauchamp, A. L.; Brewer, J. C.; Gray, H. B. *Organometallics* **1996**, *15*, 1166. (b) Gallop, M. A.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1002.

(10) König, H.; Menu, M. J.; Dartiguenave, M.; Dartiguenave, Y.; Klein, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 5351.

(11) Tsui, E. Y.; Müller, P.; Sadighi, J. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8937.

(12) Siebald, H.; Dartiguenave, M.; Dartiguenave, Y. *J. Organomet. Chem.* **1992**, *438*, 83.

(13) (a) Lu, E. L.; Li, Y. X.; Chen, Y. F. *Chem. Commun.* **2010**, *46*, 4469. (b) Lu, E. L.; Chu, J. X.; Chen, Y. F.; Borzov, M. V.; Li, G. Y. *Chem. Commun.* **2011**, *47*, 743. (c) Chu, J. X.; Lu, E. L.; Liu, Z. X.; Chen, Y. F.; Leng, X. B.; Song, H. B. *Angew. Chem., Int. Ed.* **2011**, *50*, 7677. (d) Lu, E. L.; Zhou, Q. H.; Li, Y. X.; Chu, J. X.; Chen, Y. F.; Leng, X. B.; Sun, J. *Chem. Commun.* **2012**, *48*, 3403.

(14) Bertrand and co-workers synthesized a mononuclear aluminum nitrilimine that is an oil (see ref 5).

(15) Evans, W. J.; Montalvo, E.; Champagne, T. M.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 16.

(16) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(17) Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1993**, *115*, 7743.

(18) Shioiri, T.; Aoyama, T. In *Advances in The Use of Synthons in Organic Chemistry*; Dondoni, A., Ed.; JAI Press: London, 1993; Vol. *1*, pp 51−101.

(19) Zollinger, H. In *Diazo Chemistry II*; VCH: Weinheim, Germany, 1995.

(20) (Trimethylsilyl)diazomethane reacts with benzaldehyde in the presence of triethylamine to give a complicated mixture of two ketones and two epoxides. See: Hashimoto, N.; Aoyama, T.; Shioiri, T. *Heterocycles* **1981**, *15*, 975.

(21) (a) Pedersen, C. *Acta Chem. Scand.* **1959**, *13*, 888. (b) Diazomethane does not react with benzonitrile. See: Lappert, M. F.; Poland, J. S. *J. Chem. Soc. C* **1971**, 3910.

(22) See the SI for computational details.

(23) ^1H NMR monitoring of the reactions in C_6D_6 showed that (trimethylsilyl)diazomethane does not react with phenylallene and benzonitrile at room temperature (RT) or at 75 °C. (Trimethylsilyl)diazomethane also does not react with methyl diazophenylacetate at RT, but it gives a complicated mixture of products at 75 °C. Finally, it can react very slowly with diphenylcarbodiimide or phenyl isothiocyanate at room temperature to give complicated product mixtures.