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N-Acyliminoimidazolium Ylides as Precursors to Anionic *N*-Heterocyclic Carbene Ligands: Control of Topology and Reactivity

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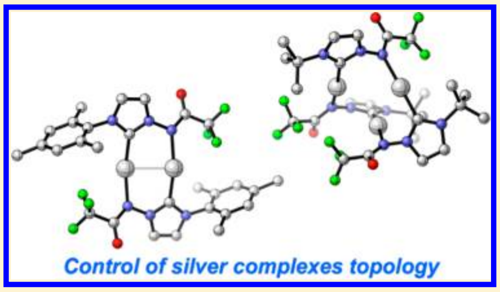
Supporting Information

ABSTRACT: A family of *N*-heterocyclic carbene ligands based on *N*-acyl iminoimidazolium ylides has been developed and investigated. The ylides are stable and are easily obtained in two steps. Following deprotonation, they form bidentate anionic NHC ligands. The synthesis of silver(I) complexes was explored. Different complex structures have been obtained, depending on the steric and electronic properties of the starting ylide proligands. Dimeric structures were usually obtained, but trimeric structures were observed under certain conditions. DFT calculations were used to explain these results. The electronic properties of the complexes can be modified by the choice of the electron-withdrawing group attached to the anionic tether. The silver complexes are proficient ligand transfer agents. The first example of a proligand/ligand exchange was demonstrated. The catalytic activity of the silver complexes was evaluated in a model (3 + 2) heterocycloaddition of an imino ester with an activated alkene.

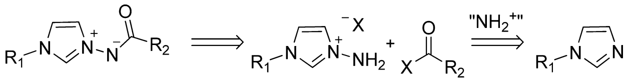

Control of silver complexes topology

INTRODUCTION

After two decades of intense research on *N*-heterocyclic carbenes (NHCs), it is now well-known that they are proficient ligands that have the feature of being strong σ-donors,[1] making them perfect substitutes for phosphine ligands.[2] The resulting NHC complexes have often been found to offer enhanced stability to oxygen, light, and water.[3] The classical structure of NHCs is formed by a 1,3-disubstituted imidazolylidene core that can present a broad range of reactivity and stability, depending on the electronic and steric properties of its substituents.[1c] While the classical formally neutral NHCs have been widely studied, there is new interest in a variant of NHC ligands, possessing an anionic tether.[4] Bidentate anionic ligands have already demonstrated their great potential in catalysis, some precisely implicating an important role of the tether in the catalytic reaction.[5] The anionic tether is used to rigidify the structure, leading to increased stability of the complex. As is shown in this article, it can also act as a base in a catalytic cycle.

Numerous kinds of anionic NHC ligands have been reported in the literature, depending on the nature of the anionic tether, such as alkoxide,[6] aryloxide,[7] amino and arylamino,[8] amido,[9] and aryl.[10] While most of these ligands and their corresponding complexes are quite stable, and of catalytic interest, they present a nondelocalized anion initially formed by a strong base. Modulation of the electronic properties of those hard anions is not readily possible. Charette et al. previously reported the proof of concept of a new type of anionic NHC ligand based on a *N*-benzoyliminoimidazolium ylide and the formation of silver(I) and copper(II) complexes.[11] While this type of ligand presents great potential, a more thorough exploration is necessary. In principle, the ylide proligands can be made in a simple and modular way. Following amination of the corresponding mono-*N*-substituted imidazole, coupling of the *N*-amino salt with electrophiles such as acyl chlorides will give access to a wide range of ylides (Scheme 1). Therefore, the steric and electronic properties could be easily modulated to afford ligands with a wide range of properties.

Scheme 1. Retrosynthetic Analysis of Ylide Formation



The use of ylides as ligand precursors has another practical advantage. They are formal neutral compounds and can be easily purified using standard flash chromatography. Herein we report the development of an optimized synthetic route to access a family of *N*-acyl iminoimidazolium ylides, with varied steric and electronic properties. We also present new procedures to obtain the corresponding silver(I) complexes from these ylides, as well as structural and reactivity analyses of five new silver complexes showing different structures depending on the nature of the ligand.

RESULTS AND DISCUSSION

Synthetic Aspects of the Ylides. The synthetic sequence is initiated by the *N*-amination of corresponding *N*-substituted imidazoles. *O*-(2,4-Dinitrophenyl)hydroxylamine was selected for this transformation, as it is an efficient and stable aminating reagent for heterocycles.[12] Under the conditions described in eq 1, excellent yields were obtained for both *N*-aryl- and *N*-alkylimidazoles.

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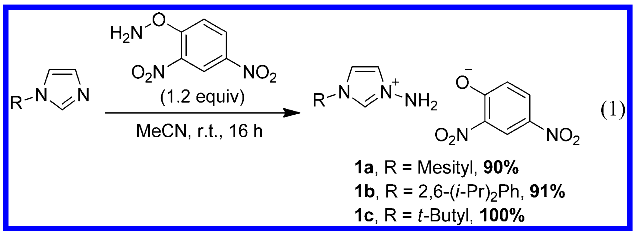
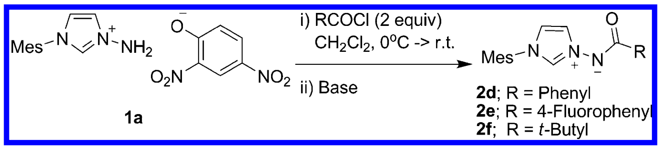


(1)

For the ylide formation step, we elected to develop conditions with broader scope, as the previously reported synthesis of ylide **2d** was difficult to expand to a wide range of acyl chlorides (i.e., benzoyl chloride as the solvent, 90 °C, 12 h).[11] A protocol relying on a near-stoichiometric quantity of the acyl chloride was developed, inspired by conditions optimized for the synthesis of *N*-acyliminopyridinium ylides.[12] The results are summarized in Table 1.

Table 1. Protocol Optimization for the Synthesis of *N*-Acyliminoimidazolium Ylides



entry	R	base	time (min)[c]	yield (%)[d]
1	Ph	NaOH[a]	60	20
2	Ph	NaOH[a]	10	35
3	Ph	K_2CO_3[b]	10	75
4	Ph	$NaHCO_3$[b]	5	95
5	4-F-Ph	$NaHCO_3$[b]	5	90
6	*t*-Bu	$NaHCO_3$[b]	5	96

[a] A 1 M aqueous solution was used. [b] A saturated aqueous solution was used. [c] Time allowed for reaction with the aqueous base solution. [d] Isolated yield.

In contrast to the pyridinium-based ylides, the *N*-acyliminoimidazolium ylides were found to be very sensitive to basic conditions, leading to heavy decomposition in the presence of sodium hydroxide (commonly used for the synthesis of the former), regardless of reaction times (entries 1 and 2, Table 1). It was not possible to fully characterize specific degradation products, but this drastic difference in the stability of imidazolium-based ylides in comparison to their pyridinium analogues seems to originate from the more reactive 2-position on the imidazolium ring. As it was found that a base is required for the reaction to proceed, weaker bases were tested. Gratifyingly, the use of either K_2CO_3 (entry 3, Table 1) or $NaHCO_3$ (entry 4, Table 1) did lead to a noticeable increase in yield, the latter affording an excellent yield (95%) of ylide **2d**. The optimized reaction conditions were applied to other acyl chlorides, to afford ylides **2e**,**f** in similar yields. In all cases, 2 equiv of acyl chloride is required to obtain optimal yields. Under the reaction conditions, the 2,4-dinitrophenolate counterion of the *N*-amino salt reacts rapidly with the acyl chloride reagent to form the corresponding ester. The latter does not show sufficient electrophilicity to react with the *N*-amino salt to yield the final ylide, thus requiring the extra acyl chloride equivalent.

To investigate the modulation of the electronic properties of the anionic tether, the ylides **2a**−**c** were synthesized by the addition of trifluoroacetic anhydride (TFAA) to the corresponding salts **1a**−**c** (Scheme 2). Again, rapid treatment with an aqueous saturated solution of $NaHCO_3$ following the addition of the electrophile led to the formation of the desired ylides in very good to quantitative yields. In contrast to the acyl chlorides, the trifluoroacetyl ester resulting from the reaction of TFAA with the 2,4-dinitrophenolate counterion is electrophilic enough to react with the *N*-amino salt. As a result, only 1.5 equiv of TFAA was required to obtain optimal yields.

The structures of ylides **2a**,**d** were confirmed by X-ray diffraction analysis (Figures 1 and 2). In all cases, the N_3−N_4 bond lengths are indicative of a mostly single-bond character. Although charge delocalization can either be endocyclic or exocyclic, the structures illustrate that the negative charge of the ylide is mostly located on the exocyclic moiety (Scheme 3). The electronic effect of the acyl groups seems to be negligible by comparing the structural features of ylides **2a** and **2d**.

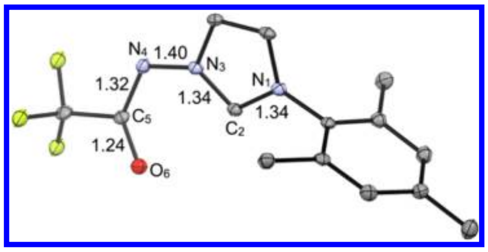


Figure 1. ORTEP plot of ylide **2a**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): N(3)−N(4) = 1.40, N(3)−C(2) = 1.34, C(2)−N(1) = 1.34, C(5)−N(4) = 1.32, C(5)−O(6) = 1.24; N(1)−C(2)−N(3) 107.5.

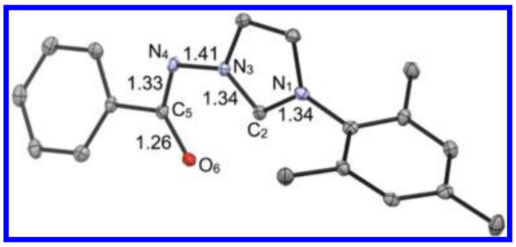
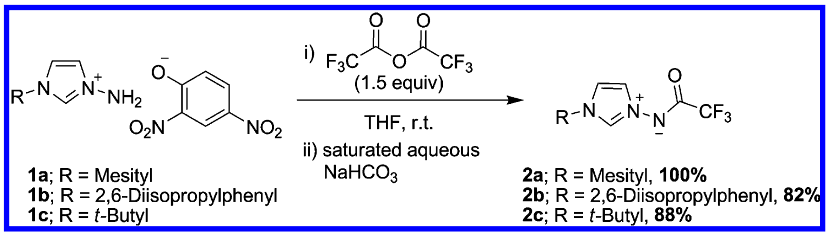
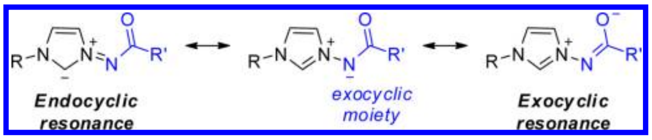


Figure 2. ORTEP plot of ylide **2d**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): N(3)−N(4) = 1.41, N(3)−C(2) = 1.34, C(2)−N(1) = 1.34, C(5)−N(4) = 1.33, C(5)−O(6) = 1.26; N(1)−C(2)−N(3) = 108.4.

Scheme 2. Synthesis of *N*-Trifluoroacetyliminoimidazolium Ylides



Scheme 3. Possible Resonance Forms of Anionic Charge Delocalization

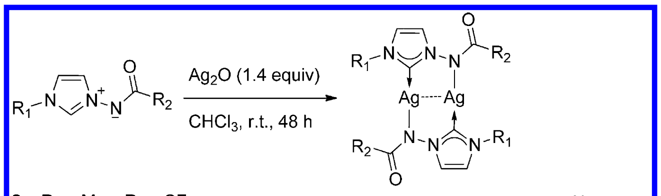


DFT calculations[13] were done on ylides **2a** and **2d** to determine the extent of charge separation (ESP charges). On ylide **2d**, 78% of the negative charge is found on the exocyclic moiety. In the case of ylide **2a**, 88% of the negative charge is on the exocyclic moiety. This small variation in charge separation is in accord with the structural properties mesured by X-ray crystallography.

The NMR chemical displacements of the C_2 proton on the imidazole ring of ylides **2a**,**d** are 9.89 and 9.68 ppm, respectively. Similar displacements are observed for ylides **2b**,**c**,**e**,**f**. These values are very similar to displacements observed for classical imidazolium salts. This is again indicative of the very small contribution of endocyclic resonance to these ylides.

Synthetic Aspects of the Complexes. It is well recognized that NHC−silver complexes are proficient ligand transfer agents.[1b] This is even more relevant in the case of anionic NHC−silver complexes, as the transfer reaction results in the direct exchange of a halogen group, leading to facile and irreversible silver halide salt precipitation (vide infra). For this reason, we elected to develop preparative methods to access silver complexes from this new family of ylide proligands. Previously optimized conditions[12] for the formation of silver complex **3d** from ylide **2d** proved to be unsuccessful for most of the new ylides synthesized, leading to low conversions to the corresponding silver complexes. Other conditions were attempted, and gratifyingly metalation involving reaction of the ylide with silver(I) oxide[14] at room temperature afforded the corresponding silver complexes in quantitative yields in most cases. The only drawback of the method is the long reaction time required (48 h) to obtain complete conversion. Purification is accomplished by simple filtration of the excess silver(I) oxide. Complexes **3a**,**b**,**d**,**e** were easily obtained by this method (Scheme 4).

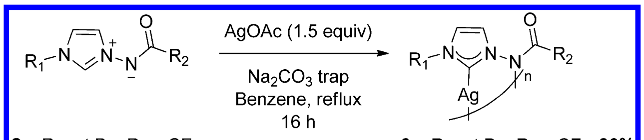
Scheme 4. Synthesis of Silver(I) Complexes



2a; R_1 = Mes, R_2 = CF_3 — **3a**; R_1 = Mes, R_2 = CF_3, **100%**
2b; R_1 = 2,6-(i-Pr)$_2$Ph, R_2 = CF_3 — **3b**; R_1 = 2,6-(i-Pr)$_2$Ph, R_2 = CF_3, **100%**
2d; R_1 = Mes, R_2 = Ph — **3d**; R_1 = Mes, R_2 = Ph, **100%**
2e; R_1 = Mes, R_2 = 4-F-Ph — **3e**; R_1 = Mes, R_2 = 4-F-Ph, **100%**

Unfortunately, this mild metalation method resulted in significant degradation for ylides **2c**,**f**, both bearing a *tert*-butyl group on either the imidazole or the acyl group. An alternative procedure was thus developed, involving silver acetate. Although the method solved the degradation problem, only low conversions were obtained. We hypothesized that the acetic acid formed in the reaction could result in protodemetalation, preventing complete conversion. Addition of various bases in the reaction mixture unfortunately resulted also in low conversions. To drive the reaction forward without the use of an in situ base, acetic acid was removed by azeotropic distillation in refluxing benzene through a solid Na_2CO_3 trap. Complexes **3c**,**f** were successfully obtained by this method in yields of 90% and 88%, respectively (Scheme 5).

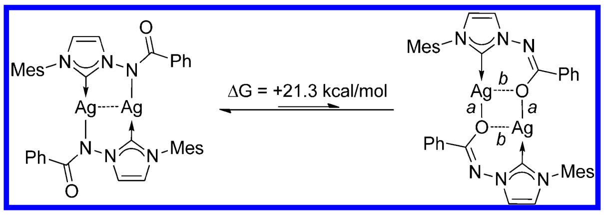
Scheme 5. Alternate Method for the Synthesis of Silver(I) Complexes



2c; R_1 = t-Bu, R_2 = CF_3 — **3c**; R_1 = t-Bu, R_2 = CF_3, **90%**
2f; R_1 = Mes, R_2 = t-Bu — **3f**; R_1 = Mes, R_2 = t-Bu, **88%**

As previously reported, **3d** is very stable to oxygen and light and is obtained as a dimeric complex.[11] In this dimeric structure, the anionic moiety of one ligand cooperatively binds the second silver atom through the nitrogen (*N*-bonded dimer). The *N*-bonded and *O*-bonded dimers of **3d** were optimized using DFT calculations,[15] and a large preference for the former is observed (Scheme 6). In the *O*-bonded dimer, chelation of the anionic moiety oxygen is absent, with Ag−O(*b*) distances of over 3.0 Å.

Scheme 6. Energetic Comparison of the *N*-Bonded and *O*-Bonded Dimers of 3d[a]



[a]Energies were obtained at the B3LYP/6-31G(d)+LANL2DZ(Ag) level. Thermodynamic corrections are unscaled.

Analogously to **3d**, most complexes were found to be solids particularly stable to oxygen and light. By slow diffusion of hexanes in concentrated dichlororomethane or benzene solutions of the complexes, crystals suitable for X-ray diffraction analysis were obtained for four of the new complexes. Structural analyses show most complexes to be dimers similar to **3d**: **3a** (Figure 3),

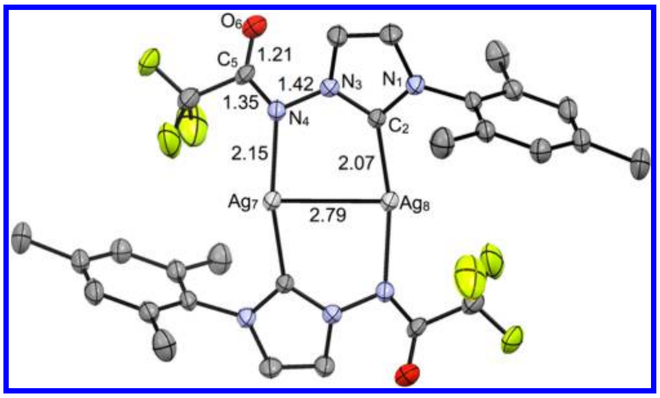


Figure 3. ORTEP plot of complex **3a**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): N(1)−C(2) = 1.36, C(2)−N(3) = 1.34, N(3)−N(4) = 1.42, N(4)−C(5) = 1.35, C(5)−O(6) = 1.21, C(6)−Ag(8) = 2.07, N(4)−Ag(7) = 2.15, Ag(7)−Ag(8) = 2.79; C(2)−Ag(8)−Ag(7) = 80.4, N(4)−Ag(7)−Ag(8) = 87.4, Ag(7)−N(4)−C(2)−Ag(8) = 16.6.

3b (Figure 4), and **3f** (Figure 5). One complex, however, was found to be a trimer: **3c** (Figure 6). This is particularly interesting, as reports of confirmed trimeric silver complexes are scarce.[16] In either the dimers or trimer, cooperative *N*-bonding of the anionic moiety is observed.

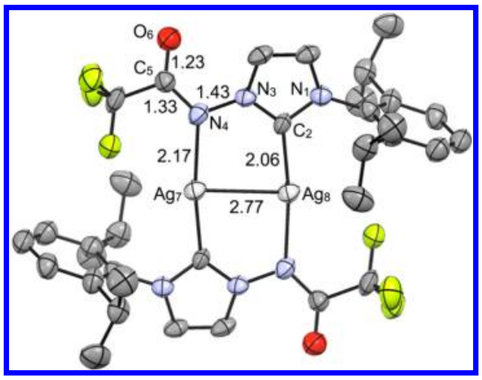


Figure 4. ORTEP plot of complex **3b**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): N(1)−C(2) = 1.39, C(2)−N(3) = 1.36, N(3)−N(4) = 1.43, N(4)−C(5) = 1.33, C(5)−O(6) = 1.23, C(2)−Ag(8) = 2.05, N(4)−Ag(7) = 2.17, Ag(7)−Ag(8) = 2.77; C(2)−Ag(8)−Ag(7) = 79.6, N(4)−Ag(7)−Ag(8) = 90.7, Ag(7)−N(4)−C(2)−Ag(8) = 10.8.

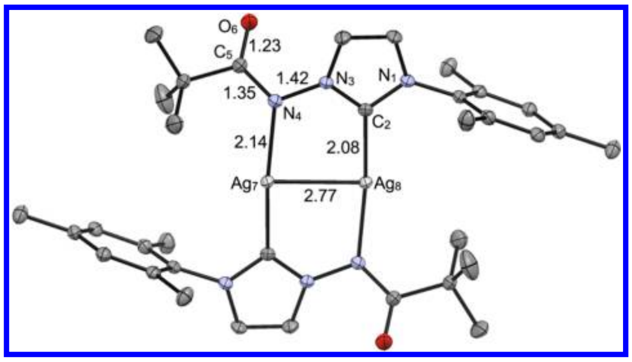


Figure 5. ORTEP plot of complex **3f**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): N(1)−C(2) = 1.36, C(2)−N(3) = 1.35, N(3)−N(4) = 1.42, N(4)−C(5) = 1.35, C(5)−O(6) = 1.23, C(2)−Ag(8) = 2.08, N(4)−Ag(7) = 2.14, Ag(7)−Ag(8) = 2.77; N(1)−C(2)−N(3) = 103.9, C(2)−Ag(8)−Ag(7) = 80.3, N(4)−Ag(7)−Ag(8) = 89.7, Ag(7)−N(4)−C(2)−Ag(8) = 12.3.

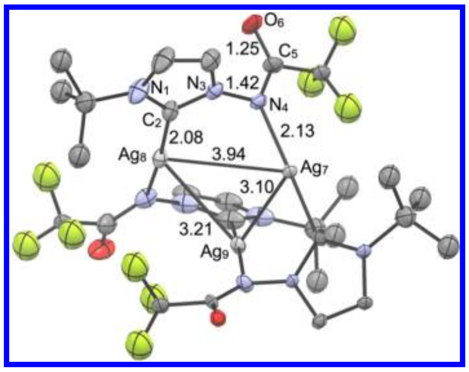
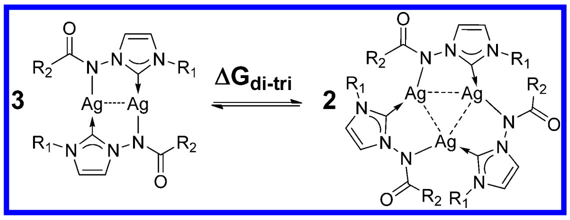


Figure 6. ORTEP plot of complex **3c**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): C(2)−N(1) = 1.36, C(2)−N(3) = 1.37, N(3)−N(4) = 1.42, N(4)−C(5) = 1.33, C(5)−O(6) = 1.25, C(2)−Ag(8) = 2.08, N(4)−Ag(7) = 2.13, Ag(7)−Ag(8) = 3.94, Ag(8)−Ag(9) = 3.21, Ag(7)−Ag(9) = 3.10; Ag(7)−N(4)−C(2)−Ag(8) = −67.1.

Structurally speaking, the dimers are symmetrical structures, with the two ligands in identical chemical environments. Although no formal Ag−Ag bond can exist in the dimers, they all show significant interactions between the two silver atoms, considering the sum of their van der Waals radii (3.4 Å). These interactions should diminish the reactivity of the coordinatively unsaturated (14e) silver centers and explain the surprisingly high stability of these complexes. Another particular feature is the almost negligible effect of the exocyclic moiety on the resulting coordination bond lengths. A comparison of C_2−Ag_8 and N_4−Ag_7 bond lengths in complexes **3a**,**b**,**f** shows almost no differences, despite large variation in terms of the steric bulk (**3a** vs **3b**) and electronic properties of the exocyclic moiety (**3a** vs **3f**). These similarities could explain why all these complexes present similar stabilities. One noticeable variation observed by comparing **3a** and **3b** is the orientation of the fluorine atoms on the trifluoroacetyl groups. This particular orientation is observed in **3b** to minimize steric interactions with the isopropyl groups.

In contrast to the other complexes, a trimer was observed for complex **3c** (Figure 6), where the three ligands and three silver atoms are disposed to form 12-membered metallacycles. The crystal structure shows the three ligands in different chemical environments, with specific bond angles and torsion angles, while keeping a linear geometry about the silver atom. In solution, a very simple ^{1}H NMR spectrum is obtained, however, indicative of rapid structural rearrangement. The trimeric structures also have an important consequence for the Ag−Ag interactions. For complex **3c**, the Ag−Ag distances measured are much longer than those observed for the dimers, with values of 3.10, 3.21, and 3.94 Å. These weaker Ag−Ag interactions could explain why the trimer is less stable and more prone to degradation in comparison to the dimers **3a**,**b**,**f**. The other important differences between the dimeric and trimeric complexes are the Ag_7−N_4-C_2−Ag_8 dihedral angles. While these angles in the dimers are less than 17°, they vary between 45 and 67° in trimer **3c**. In order to explain the preference of ylide **2c** to form the silver trimer **3c**, we turned to DFT calculations.[15] The free energies of reaction for the interconversion between the dimer and trimer forms of the silver complexes studied were computed for all ylides. The results are summarized in Table 2.

Table 2. Free Energies of Reaction of the Dimer−Trimer Interconversion Processes for Different Ligands



entry	R_1	R_2	$\Delta G_{\text{di-tri}}$ (kcal/mol)[a]
1	Mes	*t*-Bu	+6.5
2	Mes	Ph	+9.7
3	Mes	CF_3	+0.7
4	2,6-(*i*-Pr)$_2$Ph	CF_3	+2.9
5	***t*-Bu**	**CF_3**	**-6.1**

[a] Energies were calculated at the B3LYP/6-31+G(d,p)+LANL2DZ(Ag)//B3LYP/6-31G(d)+LANL2DZ(Ag) level. Thermodynamic corrections are unscaled.

With the exception of entry 5, the dimeric forms are favored in all cases. It is worth noting, however, that for entries 3 (ylide **2a**), and 4 (ylide **2b**), the free energy values computed are fairly small, and hence the trimeric form could be an accessible or observable state at room temperature. In the case of entry 5, related to ylide **2c**, a definite preference for the trimeric form is observed. The results presented in Table 2 thus reproduce well the preference observed by X-ray structural analysis. The preferred trimeric structure of complex **3c** could be explained by the steric properties of both the *N*-substituent of the imidazole and the exocyclic anionic moiety. While a mesityl group is considered to be sterically demanding, its steric hindrance is mostly perpendicular to the imidazole ring. In contrast, the *tert*-butyl group possesses a spherical steric hindrance (Figure 7). As such, the combination of both the *tert*-butyl and the trifluoroacetyl groups on ylide **2c** seems to be sufficient to push the equilibrium toward the trimer.

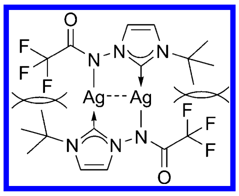
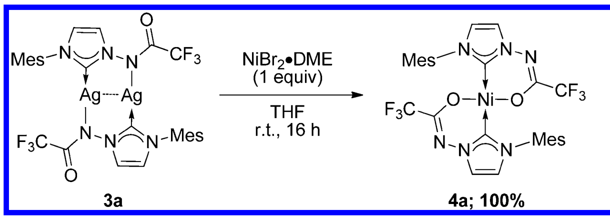


Figure 7. Rationale for the destabilization of the dimeric silver complex from ylide **2c**.

Analyses of silver complexes **3d**,**e** by ^{1}H NMR are indicative of a very symmetric system, showing only one set of signals for both ligands and displaying no restrained rotation of either the mesityl group or the exocyclic benzoyl group. No crystal structure was obtained for complex **3e**, but the strong preference for a dimeric structure can be assumed due to its high similarity with the spectroscopic data of complex **3d**. Additionally, mass spectroscopy did show the exclusive presence of the dimer. Interestingly, although only the dimers were present in the X-ray crystal structures of complexes **3a**,**b**,**f**, two distinct sets of signals by ^{1}H NMR in solution are observed. To determine if these signals are the result of restrained rotation or species interconversion, the effect of concentration was investigated on complex **3a**. A 0.015 M CDCl$_3$ solution of complex **3a** presented two distinct sets of signals, while a 0.25 M CDCl$_3$ solution resulted in the observation of only one set of signals, reminiscent of the highly symmetric system of **3d**. The effect of concentration is a clear indication of species interconversion in solution. A rationale can be found from the free energy of reaction calculated for the dimer−trimer interconversion of complex **3a** (Table 2, entry 3). A very small preference (0.7 kcal/mol) for the dimer is predicted. The dimeric and trimeric complexes would then be energetically accessible at room temperature, and dynamic equilibrium could be possible. The interconversion rate would be directly proportional to concentration, explaining coalescence of the two sets of signals at higher concentration. Considering that the free energy values in Table 2 are all fairly small, it is reasonable to assume that both multimeric forms could be accessible at room temperature. The highest preference found is for complex **3d** (entry 2, Table 2, +9.7 kcal/mol), in accord with the exclusive presence of one set of signals in ^{1}H NMR, regardless of concentration.

Reactivity of the Complexes. As stated above, silver−NHC complexes are proficient ligand transfer agents. They are especially useful for anionic NHC ligands, as formal exchange of an anionic halogen ligand is possible through irreversible precipitation of a silver halide salt. Complex **3d** was previously used for the synthesis of a Cu(II) complex.[11] To evaluate the potential of the new complexes bearing a trifluoroacetyl group, transmetalation was performed with silver complex **3a** to form nickel complex **4a** (eq 2). The transmetalation process is mild, and only simple filtration of the insoluble silver halide salt is required to obtain pure complex **4a** in quantitative yield.



3a **4a; 100%** (2)

An X-ray structural analysis of complex **4a** confirmed its monomeric nature and the square-planar geometry at the Ni(II) center (Figure 8). In this case, the anionic NHC ligands chelate the nickel center through internal *O*-bonding. This illustrates another interesting feature of this family of ligands; the anionic moiety possesses multiple binding sites to accommodate different geometries.[17]

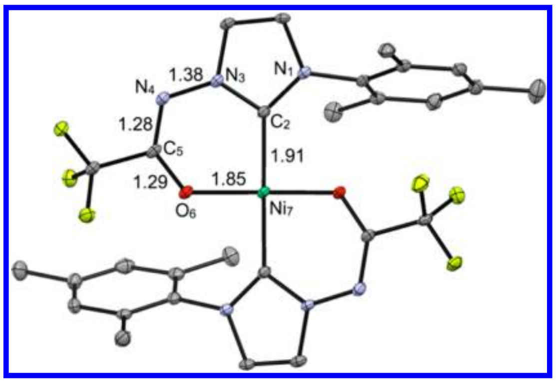
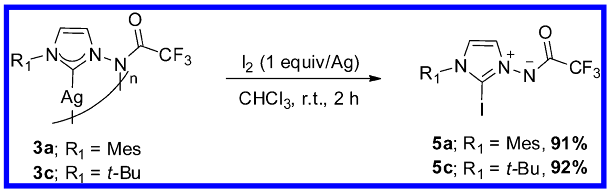


Figure 8. ORTEP plot of complex **4a**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): N(1)−C(2) = 1.35, C(2)−N(3) = 1.35, N(3)−N(4) = 1.38, N(4)−C(5) = 1.28, C(5)−O(6) = 1.29, O(6)−Ni(7) = 1.85, Ni(7)−C(2) = 1.91; C(2)−Ni(7)−O(6) = 90.9.

The reactivity of the silver complexes toward an oxidizing agent such as iodine was evaluated.[18] Treatment of complexes **3a**,**c** with 1 equiv of molecular iodine per silver atom led to rapid iododemetalation at room temperature, affording the iodo-substituted ylides **5a**,**c** in excellent yields (Scheme 7).

Scheme 7. Iododemetalation of Complexes 3a,c using Molecular Iodine



The structure of ylide **5c** was confirmed by X-ray diffraction analysis (Figure 9). These derivatives could potentially be exploited for metal complex synthesis through oxidative insertion into the C−I bond.

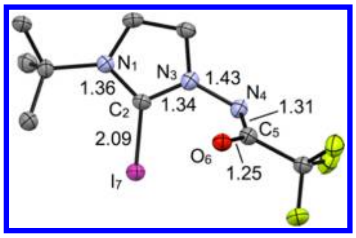
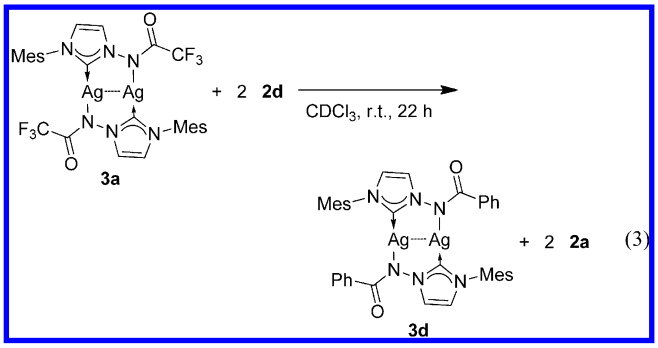


Figure 9. ORTEP plot of ylide **5c**. Ellipsoids are drawn at the 30% probability level. Selected distances (Å) and angles (deg): N(1)–C(2) = 1.36, C(2)–I(7) = 2.09, C(2)–N(3) = 1.34, N(3)–N(4) = 1.43, N(4)–C(5) = 1.31, C(5)–O(6) = 1.25; C(2)–N(3)–N(4)–C(5) = 83.9.

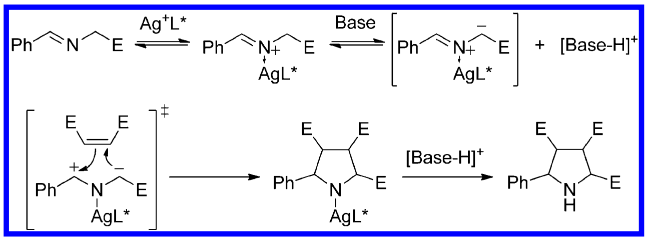
Ligand Exchange of the Complexes. Ligand exchange is an alternative strategy to synthesize new complexes. Various ligands have been reported to displace NHC ligands. For example, being strong σ-donors, phosphines[19] and other NHCs[19,20b] can serve to displace NHC ligands. However, the displacing ligand is fully formed (i.e., free NHC), in all reported cases. This involves, in the case of NHCs, the use of a strong base to deprotonate the imidazolium salt proligand. Due to the apparent dynamic nature of the silver complexes obtained from the ylides, and the anionic nature of the resulting NHC ligands, we envisioned that ligand–proligand exchange could be possible. This would result in a simplified ligand exchange strategy. To test this hypothesis, complex **3a** was mixed with 2 equiv of ylide **2d** in $CDCl_3$ at room temperature. Gratifyingly, complete exchange on the silver centers was observed, leading to complete conversion in 22 h to complex **3d** and 2 equiv of ylide **2a** (eq 3). To the best of our knowledge, this is the first example of a direct NHC ligand–proligand exchange, without the need for formation of a formal carbene prior to exchange. The conversion toward complex **3d** is explained by the stronger donating ability of the benzoyl-substituted exocyclic anionic moiety, in comparison to the trifluoroacetyl-substituted group. This effectively leads to a better stabilization of coordinatively unsaturated silver(I) centers. It is another demonstration of the easy modulation of the electronic properties of the ligands.



(3)

Complexes in Catalysis. While silver–NHC complexes are commonly used as ligand transfer agents, their use in catalytic applications is scarce.[1b] Nonetheless, homogeneous silver-mediated catalysis is broad and offers great potential, owing to the Lewis acidity and oxophilicity of silver.[20] Due to the particularly high stability and well-defined structures of the silver complexes synthesized, we investigated their potential as catalysts in a model reaction in order to compare their activity. Silver is an excellent transition metal for the catalysis of certain cycloaddition reactions.[21] For example, the (3 + 2) heterocycloaddition of in situ generated azomethine ylides with electrophilic alkenes generates polysubstituted pyrrolidines, known to be important pharmaceutical compounds.[22] The mechanism is described in Scheme 8.

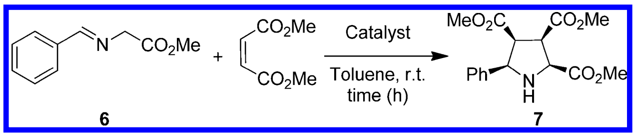
Scheme 8. Mechanism of the Silver-Mediated (3 + 2) Heterocycloaddition of Azomethine Ylides



Numerous groups have developed enantioselective variants of this reaction, traditionally using chelating ligands based on amine and phosphine combined with commercially available silver salts. Because of the instability of the formed complexes, they are generated in situ prior to reaction. Additionally, an external base is usually required to facilitate the azomethine ylide formation (Scheme 8). To the best of our knowledge, silver–NHC complexes have never been employed for this reaction.

Silver complexes **3a–f** were evaluated as catalysts for the (3 + 2) cycloaddition of imino ester **6** with dimethyl maleate, to produce pyrrolidine **7**. Silver(I) oxide and silver acetate were evaluated for the sake of catalytic reference. They are known to be highly active, due to the absence of donating ligands reducing their Lewis acidity. The results are summarized in Table 3. Due to the anionic nature of the NHC ligands, no additional base was required. In all cases, reactions are very clean and only the *endo* adduct **7** is observed. Lewis acidity has a drastic effect on activity. Catalysts with more donating anionic moieties (**3d–f**) require long reaction times to achieve complete conversions. For similar *N*-substituents on the imidazole, replacement of the benzoyl group for a trifluoroacetyl group on the anionic tether has a noticeable effect on activity, as can be seen by comparing catalysts **3a,d** (entry 3 vs entry 6, Table 3). Complex **3c**, possessing weakly coordinating anionic groups and no Ag–Ag interactions due to its trimeric nature in the solid state, was found to be the most active catalyst (entry 5, Table 3). The topology of the complexes

Table 3. Evaluation of Catalytic Activity of the Silver Complexes in the Azomethine Ylide Cycloaddition



entry	catalyst	loading (Ag mol %)	time (h)[a]	yield (%)[b]
1	Ag_2O	4	0.75	91
2	AgOAc	4	1	89
3	**3a**	4	3	93
4	**3b**	4	3.5	90
5	**3c**	4	0.5	92
6	**3d**	4	12	96
7	**3e**	4	9	93
8	**3f**	4	12	92

[a] Reaction time required to observe >95% conversion by GC/MS. [b] Isolated yield.

could thus also have an important effect on activity. With their stability to light and moisture and well-defined structures, these new silver complexes demonstrate the potential to access well-defined, bench-stable, chiral catalysts for this type of transformation.

CONCLUSIONS

In summary, optimized synthetic methods were developed in order to access a broader family of *N*-acyl iminoimidazolium ylide proligands. Six new anionic NHC−Ag(I) complexes were synthesized and characterized. These surprisingly stable and well-defined silver complexes have led to a better understanding of the structure−property relationship of this class of ligand. The complexes can serve as ligand transfer agents, as exemplified by the rapid synthesis of a nickel(II) complex, to study their properties on a variety of transition metals. The unprecedented ligand−proligand exchange opens the door to alternative metal complex synthesis methods and interesting self-assembly systems. These new directions are currently under investigation. While stable and isolable, the complexes have demonstrated good catalytic activity for the silver-mediated (3 + 2) heterocycloaddition of azomethine ylides with electrophilic alkenes. The development of chiral variants of these ylides, as well as the investigation of possible catalytic applications, is currently underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving details of the syntheses and characterization data and NMR spectra for all new compounds, selected crystallographic data for compounds **2a**,**d**, **3a**−**c**,**f**, **4a**, and **5c**, the full Gaussian reference, Cartesian coordinates, and electronic and zero-point vibrational energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Mathew, J.; Cherumuttathu, H. S. *Inorg. Chem.* **2010**, *49*, 4665−4669. (b) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978−4008. (c) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687−703.

(2) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172.

(3) (a) Praetorius, J. M.; Crudden, C. M. *RSC Catal. Ser.* **2011**, *6*, 77−118. (b) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev.* **2007**, *251*, 841−859.

(4) (a) Liddle, S. T.; Edworthy, I. S.; Arnold, P. L. *Chem. Soc. Rev.* **2007**, *36*, 1732−1744. (b) Liddle, S. T.; Arnold, P. L. *Chem. Commun.* **2006**, 3959−3971.

(5) (a) Grubbs, R. H.; Endo, K. *J. Am. Chem. Soc.* **2011**, *133*, 8525−8527. (b) Patel, D.; Liddle, S. T.; Mungur, S. A.; Rodden, M.; Blake, A. J.; Arnold, P. L. *Chem. Commun.* **2006**, 1124−1126. (c) Specht, Z. G.; Cortes-Llamas, S. A.; Tran, H. N.; van Niekerk, C. J.; Rancudo, K. T.; Golen, J. A.; Moore, C. E.; Rheingold, A. L.; Dwyer, T. J.; Grotjahn, D. B. *Chem. Eur. J.* **2011**, *17*, 6606−6609.

(6) (a) Arnold, P. L.; Scarisbrick, A. C. *Organometallics* **2004**, *23*, 2519−2521. (b) Waymouth, R. M.; Ketz, B. E.; Cole, A. P. *Organometallics* **2004**, *23*, 2835−2837. (c) Clavier, H.; Coutable, L.; Toupet, L.; Guillemin, J.-C.; Mauduit, M. *J. Organomet. Chem.* **2005**, *690*, 5237−5254.

(7) (a) Shen, Q.; Yao, H.; Zhang, Y.; Sun, H. *Eur. J. Inorg. Chem.* **2009**, 1920−1925. (b) Li, W.; Sun, H.; Chen, M.; Wang, Z.; Hu, D.; Shen, Q.; Zhang, Y. *Organometallics* **2005**, *24*, 5925−5928. (c) Dyson, G.; Frison, J.-C.; Simonovic, S.; Whitwood, A. C.; Douthwaite, R. E. *Organometallics* **2008**, *27*, 281−288.

(8) (a) Arnold, P. L.; Edworthy, I. S.; Blake, A. J.; Wilson, C. *Organometallics* **2007**, *26*, 3684−3689. (b) Arnold, P. L.; Liddle, S. T.; McMaster, J.; Jones, C.; Mills, D. P. *J. Am. Chem. Soc.* **2007**, *129*, 5360−5361. (c) Douthwaite, R. E.; Houghton, J.; Kariuki, B. M. *Chem. Commun.* **2004**, 698−699. (d) Fryzuk, M. D.; Spencer, L. P.; Winston, S. *Organometallics* **2004**, *23*, 3372−3374.

(9) Sakaguchi, S.; Kawakami, M.; O'Neill, J.; Yoo, K. S.; Jung, K. W. *J. Organomet. Chem.* **2010**, *695*, 195−200.

(10) (a) Hamilton, P. J. C.; Danopoulos, A. A.; Downing, S. P.; Pogorzelec, P. J. *Eur. J. Inorg. Chem.* **2009**, 1816−1824. (b) Sun, H. M.; Hu, D. M.; Wang, Y. S.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2007**, *692*, 903−907.

(11) Charette, A. B.; Legault, C. Y.; Kendall, C. *Chem. Commun.* **2005**, 3826−3828.

(12) Charette, A. B.; Legault, C. *J. Org. Chem.* **2003**, *68*, 7119−7122.

(13) Structures were optimized at the B3LYP level, using the 6-31+G(d,p) basis set. See the Supporting Information for details.

(14) (a) Eastham, G.; Kleinhenz, S.; Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S. *Dalton Trans.* **2000**, 4499−4506.

(15) See the Supporting Information for details.

(16) (a) Flores, J. A.; Komine, N.; Pal, K.; Pinter, B.; Pink, M.; Chen, C.-H.; Caulton, K. G.; Mindiola, D. J. *ACS Catal.* **2012**, *2*, 2066−2078. (b) Dominique, F. J.-B.; Gormitzka, H.; Hemmert, C. *J. Organomet. Chem.* **2008**, *693*, 579−583. (c) Slaughter, L. M.; Khan, M. A.; Wanniarachchi, Y. A. *Organometallics* **2004**, *23*, 5881−5884.

(17) Samantaray, M. K.; Pang, K.; Shalkh, M. M.; Ghosh, P. *Inorg. Chem.* **2008**, *47*, 4153−4165.

(18) Fu, C.-F.; Lee, C.-C.; Liu, Y.-H.; Peng, S.-M.; Warsink, S.; Elsevier, C. J.; Chen, J.-T.; Liu, S.-T. *Inorg. Chem.* **2010**, *49*, 3011−3018.

(19) (a) Zeller, A.; Bielert, F.; Haerter, P.; Herrmann, W. A.; Strassner, T. *J. Organomet. Chem.* **2005**, *690*, 3292−3299. (b) Titcomb, L. R.; Caddick, S.; Cloke, F. G. N.; Wilson, D. J.; McKerrecher, D. *Chem. Commun.* **2001**, 1388−1389. (c) Vieille-Petit, L.; Clavier, H.; Linden, A.; Blumentritt, S.; Nolan, S. P.; Dorta, R. *Organometallics* **2010**, *29*, 775−788.

(20) Naodovic, M.; Yamamoto, H. *Chem. Rev.* **2008**, *108*, 3132−3148.

(21) (a) Pale, P.; Blanc, A.; Weibel, J.-M. *Chem. Rev.* **2008**, *108*, 3149−3173. (b) Rodríguez-García, I.; Munoz-Dorado, M.; Álvarez-Corral, M. *Chem. Rev.* **2008**, *108*, 3174−3198.

(22) Sansano, J. M.; Nàjera, C. *Heterocycl. Chem.* **2008**, *12*, 117−145.