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Heterocumulene Metathesis by Iridium Guanidinate and Ureylene Complexes: Catalysis Involving Reversible Insertion To Form Six-Membered Metallacycles

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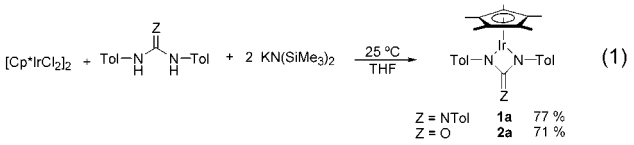
Since the development of modern catalysts for alkene and alkyne metathesis a decade ago,[1] these reactions have come into widespread use.[2] Such advances have spawned increasing interest in the metathesis of other types of double bonds, and several catalysts for imine[3] and carbodiimide[4] metathesis have now been reported. These metathesis processes have long been understood to proceed by reversible [2 + 2] cycloaddition of an olefin (or C═N bond) to a catalytically active metal alkylidene (or imido) complex.[3b,5] We report herein the development of a new, highly active catalyst for the metathesis of aryl carbodiimides that departs from this mechanistic scheme. The iridium guanidinate complex **1a** catalyzes the rapid metathesis of aryl-substituted carbodiimides at room temperature and that of carbodiimides with isocyanates at 45 °C. Strong evidence suggests that the mechanisms for these transformations involve ring expansion to six-membered metallacycles and not cycloreversion to metal-imido species.

The pentamethylcyclopentadienyl iridium guanidinate complex **1a** can be prepared most conveniently by treatment of $[Cp^*IrCl_2]_2$ with *N*,*N*′,*N*″-tri-*p*-tolyl guanidine and base in THF at room temperature followed by recrystallization of the green product from toluene and pentane (eq 1). A similar ureylene complex **2a** can be produced by the same general method, and the crystal structure of this complex was confirmed by X-ray diffraction. While late metal ureylenes have been reported previously,[6] the complexes reported here are unique in that they are sterically unencumbered, 16 e^- species.

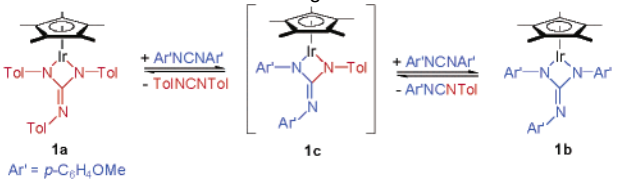


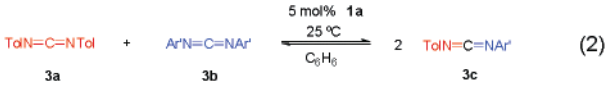
(1)

The guanidinate complex **1a** undergoes exchange reactions with a variety of heterocumulenes to form new heterocycles and liberate carbodiimides. For example, treatment of **1a** with a large excess of methoxyphenyl-substituted carbodiimide **3b** at room temperature produces upon mixing the newly substituted guanidinate complex **1b**, as well as 1 equiv each of di-*p*-tolylcarbodiimide (**3a**) and the mixed carbodiimide species **3c** bearing one tolyl group and one *p*-methoxylphenyl substituent (Scheme 1). We presume that this transformation occurs via two separate exchange processes through intermediate **1c**, and treatment of **1a** with 1 or 2 equiv of **3b** does yield an equilibrium mixture containing multiple guanidinate complexes bearing both *p*-tolyl and *p*-methoxylphenyl substituents.

The observation of mixed carbodiimide **3c** above led us to investigate the activity of complex **1a** as a catalyst for carbodiimide metathesis. Treatment of carbodiimides **3a** and **3b** (solutions 10 mM in each) with 5 mol % guanidinate complex **1a** at room temperature leads to complete equilibration (K_{eq} = 1.8 ± 0.1) between the starting carbodiimides and the mixed species **3c** within 3 min (eq 2). The rate of this metathesis stands in stark contrast to those of previously reported carbodiimide metathesis systems, most of which require temperatures above 100 °C. The catalyst remains active at the end of these runs, as equilibrium is rapidly re-established when additional substrate is added.

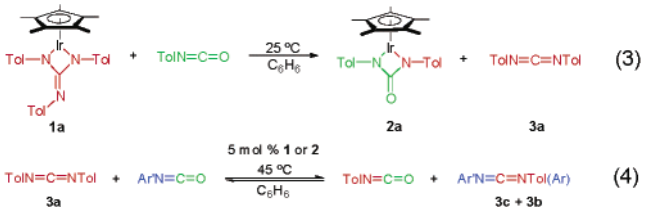
Scheme 1. Carbodiimide Exchange





(2)

Complex **1a** also reacts with just 1 equiv of *p*-tolylisocyanate, yielding the ureylene complex **2a** in 83% yield (eq 3). One equivalent of free carbodiimide **3a** is also observed in this transformation. This led us to explore the metathesis of **3a** and isocyanate *p*-$CH_3O(C_6H_4)NCO$ (yielding TolNCO and carbodiimides **3b** and **3c**), which cannot be achieved by known heterocumulene metathesis catalysts without concomitant disproportionation of isocyanate to CO_2 and carbodiimide. This transformation can indeed be achieved without disproportionation using 5 mol % of either **1a** or **2a** at 45 °C (eq 4).



(3)
(4)

Attempts to observe stoichiometric exchange reactions involving isocyanates and ureylenes revealed the formation of a new type of complex in mixtures of these reagents. Treatment of the ureylene complex with 1 equiv of *p*-tolylisocyanate causes a color change from green to brown-red and the appearance of new ^1H NMR resonances at δ 2.39 (3H), 2.28 (6H), and 0.95 (15H) ppm in addition to those of the remaining starting material and free isocyanate. We attribute these resonances to complex **4a**, a six-membered metallacycle (featuring a dianionic biureto ligand) resulting from isocyanate insertion into the chelate ring (Scheme

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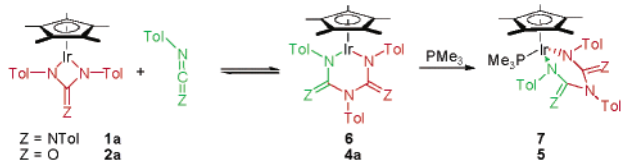
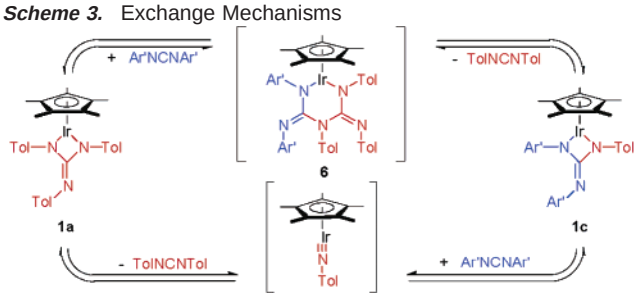
Scheme 2. Heterocumulene Insertion

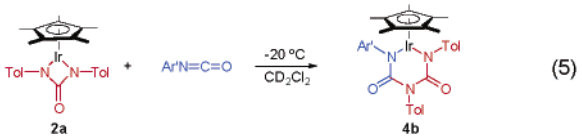


Scheme 3. Exchange Mechanisms



2). Such late metal birueto complexes,[7] and even insertion reactions to form them,[6d] have been reported.

Although complexes **2a** and **4a** equilibrate rapidly at room temperature, and their relative solubilities have prevented us from isolating **4a** cleanly, experiments at low temperature have allowed us to study **4a** where equilibration with **2a** is very slow. In particular, we sought to confirm that **4a** is an insertion product rather than a dative isocyanate adduct of the ureylene. Addition of *p*-methoxyphenyl-substituted isocyanate to the *p*-tolyl ureylene complex **2a** at −20 °C yields complex **4b**, the ^{1}H NMR spectrum of which exhibits two distinct tolyl resonances (δ 2.40 (3H), 2.29 (3H) ppm), as well as one signal for the methoxy group of the newly bound isocyanate moiety (δ 3.81 (3H) ppm) (eq 5). Also,

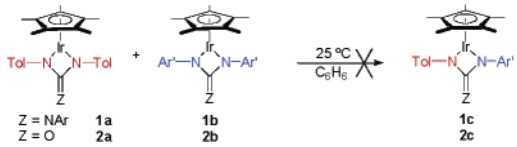


(5)

treatment of **4a** with PMe_3 at −20 °C yields a new phosphine adduct **5** still exhibiting two tolyl resonances integrating in a 6:3 ratio (Scheme 2). These two results support the formulation of **4a** as an insertion product, because a dative ligand adduct would have higher symmetry than that observed for complex **4b** (the two tolyl groups would be equivalent) and would presumably fail to react with PMe_3 before losing the isocyanate ligand.

On closer examination, complex **1a** exhibits similar reversible insertion chemistry with carbodiimides. Although treatment of the guanidinate complex **1a** with additional carbodiimide **3a** at room temperature yields no evidence of reaction, cooling this mixture to −78 °C causes its color to change from green to brown. Examination of the brown solution by ^{1}H NMR spectroscopy revealed a new complex **6**, with five incorporated tolyl group resonances at δ 2.38 (6H), 2.30 (3H), and 2.07 (6H) ppm (Scheme 2). This complex, like **4a** above, appears to be an insertion product and forms PMe_3 adduct **7**.

The observation of these insertion products demonstrates that the exchange reactions described above likely proceed via reversible insertion reactions to form six-membered metallacycles **4** and **6** (Scheme 3, upper path).[8] To rule out the possibility of exchange via reversible extrusion of heterocumulene to form imido complexes[9] (Scheme 3, lower path), which one would expect by analogy to other metathesis systems, crossover experiments were conducted in both the guanidinate and the ureylene systems (eq 6). Treatment of the tolyl-substituted ureylene complex **2a** with the *p*-$CF_3C_6H_4$-substituted analogue **2b** at room temperature yields no trace of the mixed ureylene **2c** below 75 °C, and the analogous experiment with the guanidinate complexes **1a** and **1b** produces similar results. In both reactions, crossover occurs rapidly at 25 °C when a trace of the appropriate heterocumulene is added. These results clearly rule out the dissociative exchange mechanism (by which crossover would be as facile as catalysis) and suggest a catalytic cycle involving six-membered metallacycles rather than imido complexes.



(6)

In conclusion, we have found that guanidinate and ureylene complexes **1** and **2** serve as highly active catalysts for the metathesis of aryl carbodiimides with each other and for the more difficult metathesis of aryl carbodiimides with aryl isocyanates. These transformations appear to proceed via interconversion of four- and six-membered metallacycles, and the intermediates in such processes have been observed. While both the structural motifs and the basic reaction steps of the associative exchange have precedent, this is the first catalytic metathesis system in which such a mechanism has been implicated.

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Supporting Information Available: Complete synthesis and characterization of **1a**, **1b**, **2a**, **2b**, **3c**, and details of catalytic, low-temperature, and crossover experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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