Synthesis and Reactivity of Vinylimido Complexes of Titanocene

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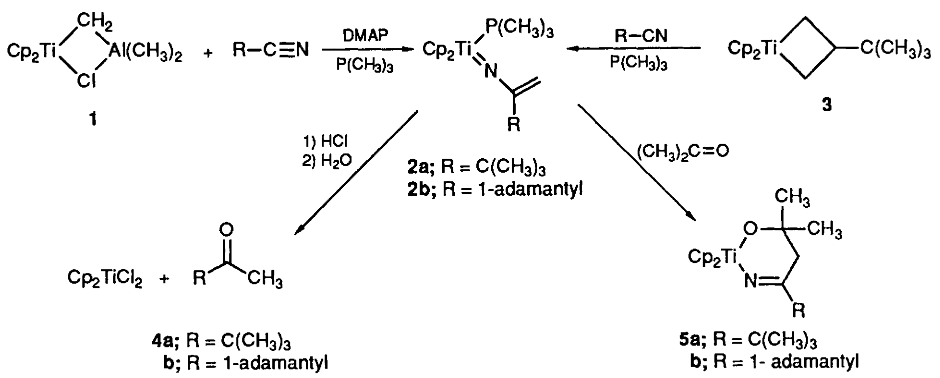
Tebbe's reagent ($Cp_2TiCH_2 \cdot AlMe_2Cl$) or titanocene metallacyclobutanes react with nitriles in the presence of a Lewis base such as trimethylphosphine to afford vinylimido complexes of titanocene; these undergo follow-up reactions with unsaturated organic molecules to yield new heterocyclic compounds of titanocene.

As part of a continuing investigation of the reactivity of the methylidene complex of titanocene with nitriles, we have developed an efficient synthetic route for the preparation of vinylimido complexes of titanocene. These are apparently the first imido complexes of titanocene to be reported[1] and represent rare members of the virtually unstudied class of vinylimido complexes.[2,3] The vinylimido complexes react with unsaturated organic species to afford new metallacyclic products; this allows the cross-coupling of nitriles with other unsaturated organic compounds, including ketones and



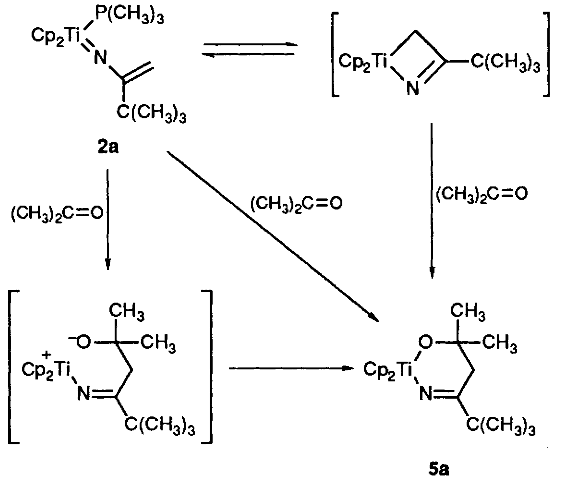
Scheme 1

nitriles, affording products containing two new carbon–carbon bonds.

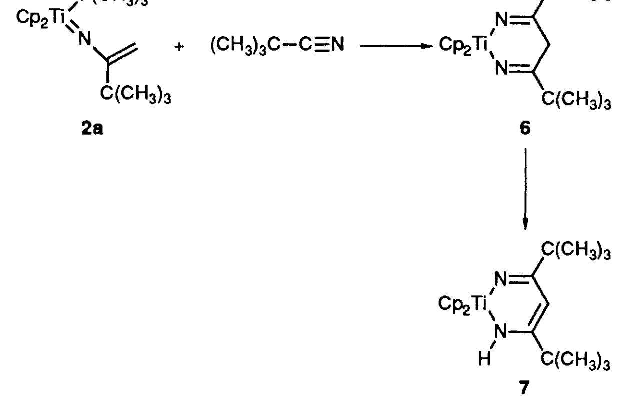
Treatment of Tebbe's reagent[4] **1** with one equivalent of pivalonitrile or 1-cyanoadamantane and excess PMe_3 at room temperature, with an equivalent of 4-dimethylaminopyridine present to scavenge the dimethylaluminium chloride by-product, affords the vinylimido complexes, **2a** and **2b** (Scheme 1). The same products are obtained from the reaction of titanacyclobutane[5] **3** with one equivalent of nitrile and excess PMe_3 at 40 °C (Scheme 1).[6]

The structures proposed for the vinylimido complexes are based on ^1H, ^{13}C, ^{31}P NMR spectroscopy and mass spectrometry.† Most characteristic is the pair of signals for the two inequivalent vinylic protons, which appear as mutually coupled doublets in the ^1H NMR spectra of **2a** and **2b**. Both complexes display long-range ^{31}P coupling (as confirmed by analysis of the ^{31}P-decoupled ^1H NMR spectrum) to only one of these hydrogens ($^5J_{PH}$ 1.0 Hz). Single resonances are observed for the cyclopentadienyl rings of each complex in both their ^1H and their ^{13}C NMR spectra. (Long-range coupling to the phosphorus, J_{PH} 3.4 Hz, is apparent in the ^1H NMR spectra.)[7] We have not yet determined if the equivalence of the cyclopentadienyl rings is due to rapid rotation about the Ti=N bond at room temperature or to linearity of the Ti=N–C bond, though in a related zirconium imido complex, Bergman has reported that the Zr=N–R arrangement is approximately linear (174.4°).[8] Additional structural proof for imido complexes **2a** and **2b** is afforded by their acidolysis, affording the anticipated methyl ketones, **4a** and **4b**, respectively (Scheme 1).‡

The imido complexes react with acetone (one equiv.) in C_6D_6 at 50 °C to afford new metallacyclic complexes (**5a**,**b**, Scheme 1).[9] The structures of these complexes are suggested by their ^1H and ^{13}C NMR spectra and by high resolution mass spectrometry,§ and the structure of **5b** has been confirmed by X-ray diffraction analysis.[10] These reactions contrast sharply with reported reactions of other imido complexes of the early transition metals, in which a [2 + 2]-type metathesis reaction occurs with ketones, affording metal–oxo complexes and organic imines.[2c,11] Though one might reasonably propose a formal [4 + 2]-cycloaddition pathway[12] (either concerted or step-wise) for the formation of **5a** and **5b**, electrocyclic ring closure of the vinylimido complex to an azatitanacyclobutene,[6] followed by insertion of acetone into the Ti–C bond of such a titanacycle cannot be ruled out.[13]



Scheme 2



Scheme 3

Hydrolysis of complex **5a** affords the anticipated β-hydroxyketone,[14] suggesting possible future applications of this reaction sequence as an adjunct to traditional aldol chemistry.

Preliminary results show that in addition to acetone, the vinylimido complexes react similarly with nitriles and imines

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† Structure assigned to **2a** and **b** was fully supported by NMR and MS studies.

‡ Ketones **4a**,**b** were identified by spectral comparison with commercially obtained authentic samples and by characterization of their 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives.

§ NMR and MS studies fully support structure assignments for **5a** and **b**.

to give the expected diazatitanacyclic complexes. For example, the reaction of vinylimido complex **2a** with pivalonitrile gives a diazatitanacyclohexa-2,5-diene complex **6**, which tautomerizes to **7**.[15] Complex **7** was previously reported to be formed from the direct reaction of the titanacyclobutane **3** with two equivalents of pivalonitrile.[6,16] Complex **7** is also formed in the reaction of Tebbe's reagent **1** with two equivalents of pivalonitrile in presence of one equivalent of 4-*N*,*N*-dimethylaminopyridine (DMAP). Hydrolysis of these complexes affords synthetically useful β-ketoenamines.

We are continuing to study the reactivity of the vinylimido complexes with unsaturated organic substrates and the subsequent removal of titanium from the products of these reactions to afford acyclic and heterocyclic organic and main group inorganic compounds, and will report on these studies in due course.

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