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Evidence for Silica Surface Three- and Five-Membered Metallacycle Intermediates in the Catalytic Cycle of Hydroaminoalkylation of Olefins Using Single-Ti-Metal Catalysts

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ABSTRACT: The single-site silica-supported group IV metal amido complex $[Ti(NMe_2)_4]$ gives the tris(amido)-supported fragment $[(\equiv Si-O-)Ti(-NMe_2)_3]$, which transforms into a three-membered metallacycle (called a metallaaziridine) by an α -H transfer between two amido ligands. When the three-membered metallacycle reacts with 1-octene, it gives a five-membered metallacycle by insertion of the double bond into the M–C bond of the metallaziridine. These two metallacycles, key intermediates in the catalytic cycle of the hydroaminoalkylation of terminal olefins, were isolated and fully characterized following the surface



organometallic chemistry (SOMC) concept and procedures. This paper shows that surface organometallic chemistry can be used to identify and fully characterize three- and five-membered metallacycles of Ti in the hydroaminoalkylation of olefins.







Figure 2. Catalytic mechanism of homogeneous hydroaminoalkylation. $^{3,4,7-15}$

of an α -amino C–H moiety across an alkene double bond (Figure 1).²⁻⁴

This reaction is a new path for functionalizing simple amines, which are essential in the pharmaceutical, agrochemical, and fine chemical industries.⁵ In homogeneous



Figure 3. Expected surface three- and five-membered metallacycle key intermediates for hydroaminoalkylation.

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Figure 4. Titanium tris(amido) fragment immobilized on SiO₂₋₇₀₀.



Figure 5. Titanaaziridine (1) formation at room temperature and under dynamic vacuum (10^{-5} mbar) .

catalysis, the reaction mechanism was proposed and the fivemembered-ring formation was demonstrated under experimental conditions $(X-ray)^6$ to occur by insertion of terminal alkene into the M–C bond of a metallaaziridine (Figure 2).^{3,4,7–16}

As is well-known, the objectives of surface organometallic chemistry (SOMC) are predicting (by rational approach) new reactions, improving existing ones, and understanding the mechanism, using the single-site concept (Figure 3).¹⁷⁻²⁸

Therefore, in the present study, we have explored the possibility of grafting the homoleptic tetrakis(dimethylamido) complexes [Ti(NMe₂)₄] on highly dehydroxylated silica (SiO₂₋₇₀₀), with the intent of drawing a full image of what was done previously in our group with the homoleptic zirconuim complex.^{29–31} The objective was to isolate, using SOMC concepts and tools,^{32–35} all or some of the elementary steps of the catalytic cycle of heterogeneous hydroaminoalkylation previously proposed in homogeneous catalysis.^{36–39}

The reason to choose SOMC is as follows. By immobilization of surface organometallic fragments on surfaces, (1) it prevents bimolecular reactions and (2) it can isolate and fully characterize reaction intermediates.

We should notie here that the five-membered metallacycle was suggested in the case of hydroaminoallylation, but it was in the case of Zr and with propene as the olefin. Obviously as frequently occurs with group IV metals, there is a strong similarity of mechanisms among all of these metals.

Consequently, with this objective in mind, an isolation of the surface $[(\equiv Si-O-)Ti(-NMe_2)_3]$ has been tested by reacting the homoleptic $[Ti(NMe_2)_4]$ complex with SiO_{2-700} (highly dehydroxylated silica treated at 700 °C) (Figure 4).

Interestingly, the isolated species was a three-membered cycle (called a metallaziridine^{39–47}) obtained at room temperature under vacuum (dynamic vacuum, 10^{-5} mbar for 3 h) (Figure 5) and this three-membered metallacycle was very well characterized by FTIR, elemental analysis, SS NMR, and DNP SENS.^{45,48}

THREE-MEMBERED-RING FRAGMENT: PREPARATION AND CHARACTERIZATION

FTIR and elemental analysis have been carried out for the titanium tris(amido) complex. The obtained results were



Figure 6. FTIR spectra of $SiO_{2.700}$ (black), and the isolated metallacycles (1) $[(\equiv Si-O-)Ti(\eta^2-MeNCH_2)(\eta^1-NMe_2)(\eta^1-HNMe_2)]$ (red) and (1') $[(\equiv Si-O-)Ti(HNMe_2)(\eta^2-NMeCH_2CH-(C_6H_{13})CH_2)(-NMe_2)]$ (blue).

Table 1. Elemental Analysis for the Tris(amido) Complex 1

	ratio		
	N/C	N/M	C/M
complex 1 $(\pm 5\%)$	0.5	3.1	5.7
predicted for tris(amido)	0.5	3	6

consistent with the proposed structure of the surface complex $[(\equiv Si-O-)Ti(NMe_2)_3]$. The FTIR spectrum of the starting SiO_{2-700} shows an intense $\nu(O-H)$ peak located at 3745 cm⁻¹. This peak disappears after grafting of $[Ti(NMe_2)_4]$. A new range of signals appears for C-H (stretching and bending). Intense bands are observed at 2970–2776 cm⁻¹ ($\nu(CH)$) and weak bands at 1500–1400 cm⁻¹ ($\delta(CH)$). In addition, no band was observed which could be ascribed to a Si–NMe₂ moiety. This absence of Si–NMe₂ means that there is no formation of doubly or triply bridged Ti as would occur by opening of a Si–O–Si bond (Figure 6, spectrum 1).

In addition, an elemental analysis of the tentative structure of the surface complex $[(\equiv\!Si\!-\!O\!-)Ti(-NMe_2)_3]$ shows ratios $(\pm~5\%$ error) consistent with the predicted values for the tris(amido) complex $[(\equiv\!Si\!-\!O\!-)Ti(-NMe_2)_3]$ (Table 1).

Nonetheless, the ¹³C NMR and the ¹H NMR spectra are not consistent with the tentative structure $[(\equiv Si-O-)Ti-(-NMe_2)_3]$. Accordingly, the ¹H NMR spectrum of the compound obtained (Figure S4 in the Supporting Information) reveals a peak located at 2.5 ppm, assigned to the proton present in the dimethylamido ligands and a second peak at 1.6 ppm. The presence of these peaks is not consistent with the expected tris(amido) complex $[(\equiv Si-O-)Ti(--NMe_2)_3]$ that should show three equivalent dimethylamido ligands (one peak). Therefore, a different structure has to be well thought out: a metallaaziridine fragment, in which methylene



Figure 7. ¹⁵N MAS DNP SENS spectra (left) and 2D ¹H–¹³C HETCOR (heteronuclear correlation) NMR spectra (right) of $[(\equiv Si-O-)Ti(\eta^2-MeNCH_2)(\eta^1-NMe_2)](1)$.

was directly coordinated to the titanium atom. Additionally, the ¹³C NMR spectrum of the supported metal complex reveals three clearly identified signals: at 43 ppm (br), at 38 ppm (low intensity), and a signal of much lower intensity at 82 ppm. Therefore, further advanced SS NMR experiments were carried out to confirm this hypothesis.

The HETCOR spectrum reveals the ${}^{1}\text{H}{-}{}^{13}\text{C}$ correlations (Figure 7). Clear correlations are seen between the methyl protons at 2.5 ppm and the carbons at 38 and 43 ppm. Another more interesting correlation is observed between the signal at 82 ppm³⁹ and the proton at 4.6 ppm. Two-dimensional proton double- and triple-quantum (DQ, TQ) correlation experiments (Figure S4 in the Supporting Information) were performed to determine the number of protons attached to the same carbon and to differentiate between CH₂ and CH₃ groups. A strong autocorrelation peak observed for the proton at 2.5 ppm in both DQ and TQ spectra is compatible with the assignment of this resonance to methyl protons. The proton resonance at 4.6 ppm does not appear in DQ and TQ spectra because of the low intensity of this peak.

The natural-abundance ¹⁵N DNP spectrum obtained for 1 (Figure 7) displays three resonances at 6, 15, and 41 ppm. Considering their relative abundance, we assign the intense signal shifted downfield at 41 ppm to a σ -bonded $-NMe_2$ ligand. The second peak at 15 ppm is attributed to the N present in the aziridine fragment, and the weak upfield-shifted signal at 6 ppm is compatible with a π -bonded $NH(CH_3)_2$ (ligand type L coordinated group).

FIVE-MEMBERED-RING FRAGMENT: PREPARATION AND CHARACTERIZATION

To continue our investigation on the mechanism of hydroaminoalkylation, we isolated the five-membered-ring (key intermediate) complex $[(\equiv SiO-)Ti(\eta^1-HNMe_2)(\eta^2-NMeCH_2CH(C_6H_{13})CH_2)(-NMe_2)]$ (1') formed by insertion of 1-octene in the M–C bond of the metallaaziridine.

The titanaaziridine was treated with neat liquid 1-octene (1.5 equiv, 24 h, and 165 °C); the obtained product was washed with pentane and dried under vacuum (10^{-5} mbar) for 2–3 h (Figure 8). An FTIR spectrum of the obtained complex 1' shows an increase in the intensity of the ν (C–H) bands (2985–2776 cm⁻¹) that is expected by the insertion of the 1-



Figure 8. Five-membered metallacycle (1') formation by insertion of 1-octene into surface titanaaziridine (1).

Table 2. Elemental Analysis for the Five-Membered Ring 1'

	ratio		
	N/C	N/M	C/M
complex 1' $(\pm 5\%)$	0.2	2.8	13.2
predicted for the five-membered metallacycle	0.21	3	14

octene in the titanaaziridine fragment (see Figure 6, spectrum 1'). The elemental analysis (Table 2) of complex 1' strongly confirms that one molecule of 1-octene has been incorporated in the metallaaziridine complex 1 very likely by simple 1,2-insertion in which the long alkyl fragment is away from the metal for obvious steric reasons.

The ¹H SSNMR spectrum of the complex 1' exhibits a peak at 2.9 ppm assigned to the CH_2 of the five-membered ring next to the metal center. This CH_2 peak overlaps with another CH_2 signal at 2.4 ppm in the five-membered ring. Two major signals, the first at 1.15 ppm for CH_2 and the second at 0.7 ppm for CH_3 , are present in the 1-octene tail. The CH_2 and CH_3 assignments were validated by the DQ and TQ correlations (Figure 9).

The 1.9 ppm peak assigned to the CH group in the fivemembered ring represents the more complex hydrocarbon motif around the titanium center; it appears as a very low intensity peak in the ¹H spectra logically without any autocorrelation in DQ or TQ frequencies. The ¹³C SSNMR



Figure 9. ${}^{1}H^{-1}H$ DQ spectra (top) and ${}^{1}H^{-1}H$ TQ spectra (bottom) for $[(\equiv Si-O-)Ti-(\eta^{1}-HNMe_{2})[\eta^{2}-NMeCH_{2}(C_{6}H_{13})-CH_{2}](-NMe_{2})]$ (1').



Figure 10. 2D ${}^{1}H$ - ${}^{13}C$ HETCOR NMR spectrum of the fivemembered-ring intermediate 1'.

spectrum of this complex shows six major peaks at 12, 22, 29, 31, 36, and 43 ppm. The resonance at 36 ppm is significantly intense in comparison to the others; this peak is assigned to the CH_2 of the five-membered ring next to the titanium center. This interpretation is compatible with the multiple-quanta experimental spectra that reveal autocorrelations in double-quantum (DQ) and triple-quantum (TQ) frequencies for the signals at 2.4 ppm.

In addition, the 2D $^{1}H-^{13}C$ HETCOR NMR spectrum (Figure 10) shows a correlation between the carbon peak at 36



Figure 11. ¹⁵N MAS DNP SENS spectrum of $[(\equiv Si-O-)Ti(\eta^1-HNMe_2)(\eta^2-NMeCH_2CH(C_6H_{13})CH_2)(-NMe_2)]$ (1').



Figure 12. Stack plot of the spectra for the three-membered (1) and five-membered complexes (1').

ppm and the proton peak at 2.4 ppm. The signal at 22 ppm for 13 C correlating with the 1.15 ppm signal for 1 H is consistent with the CH₂ fragments of the 1-octene queue.

A strong correlation is observed between the proton peak at 1.9 ppm and the carbon peak at 31 ppm; this signal is attributed to the CH group. The natural-abundance ¹⁵N SSNMR spectroscopy experi-

The natural-abundance ¹⁵N SSNMR spectroscopy experiments were performed for 1' using the DNP-SENS technique (Figure 11). The obtained spectrum exhibits three peaks, centered at 7, 40, and 66 ppm (Figure 12). The signals at 7 and 40 ppm are tentatively related to π -bonded NH(CH₃)₂ and σ -bonded –NMe₂, respectively. The new peak at 66 ppm in the spectrum of 1' Figure 12 is assigned to the N atom involved in the five-membered ring.

CATALYTIC TESTS

Hydroaminoalkylation reaction studies were conducted with a mixture of 1-octene and a selected dialkylamine in 1 mL of

Table 3. Hydroaminoalkylation Catalytic Tests with Titanaazizidine (1) as a Catalyst^a

entry	amine	combined conversion (%)
1	N-methylaniline	9.5
2	diethylamine	23
3	dibutylamine	15
4	N-ethylaniline	0
5	diphenylamine	0
6	dimethylamine	0
7	ethylmethylamine	0

"Conditions: 6 mol % of catalyst complex 1, 165 °C, 1.5 equiv of 1octene, 1 mL of toluene, 48 h.



Figure 13. 3D representation of the aziridine complex 3 and the ratedetermining transition state 4-5 intermediate complex 2'.

toluene and the titanaaziridine complex catalyst 1 that was heated at 165 $^{\circ}$ C for 48 h in a vacuum-sealed ampule.

The screening was conducted using selected substrates such as dialkylamines (diethylamine and dibutylamine) and arylalkylamines (*N*-methylaniline and *N*-ethylaniline) (Figures S5-S7 in the Supporting Information). All the runs and blanks were carried out under similar conditions. Branched and linear alkylation products detected as expected.

Catalysis with *N*-methylaniline as the substrate (Table 3, entry 1) reached a combined conversion of 9.5%. For entries 2 and 3 with dialkylamine substrates there were higher combined conversions of 23% and 15%, respectively. However, in entries 4–7 there was no conversion observed, because the substrates are sterically hindered (Table 3).

DENSITY FUNCTIONAL THEORY (DFT) CALCULATIONS

All calculations were carried out with the Gaussian 09 suite of programs. Density functional theory (DFT) via the PBE1PBE functional (PBE0) was used for geometry optimizations. The SVP basis set was employed for the Si, C, N, O, and H atoms, and the SDD basis set was employed for Ti metal. Grimme D3 corrections were included in the energy evaluation. To obtain more accurate values, the reported energies have been obtained via single-point calculations using again the PBE0-D3 functional, by improving the main-group-atom basis set to the triple- ζ TZVP basis set.

Calculations have been performed using Ti as the metal and propene as the olefin. For the sake of simplicity, in the presence of HNMe2 we consider the tris(amido) amino complex 1 as the reference structure at 0 kcal/mol in energy. With 1 as the starting point, a fourth HNMe₂ molecule coordinates to 1, leading to 2. The first reactive step is a β -H transfer between two amido ligands, leading to the metallaaziridine species 3, via transition state 2-3 and an energy barrier of 32.9 kcal/mol. According to the calculations, 3 is located 14.1 kcal/mol above 1; therefore, the aziridine fragment is formed after the tris(amido) fragment is exposed to a high vacuum (10^{-5} mbar) for 24 h. The next step is the endergonic displacement of a dimethylamino ligand by propene, leading to 4, 21.8 kcal/mol above 1, followed by the rapid reaction of propene with the metallaaziridine moiety. Propene addition occurs via transition state 4-5, at 34.1 kcal/ mol, and leads to intermediate 4, only 4.4 kcal/mol above 1. We calculated that 1,2-insertion of propene into the Ti-N bond, leading to 5, is the favored regiochemistry, as it is favored by 4.4 kcal/mol over the transition state for 2,1insertion.



Figure 14. Energy profile for hydroaminoalkylation promoted by the Ti amido complex 1.

The reaction evolves via H transfer from an amido ligand to the metallacycle moiety via transition state 5-6, at 21.3 kcal/ mol, opening the metallacycle and leading to intermediate 5, -12.1 kcal/mol below 1. Coordination of an HNMe₂ molecule, followed by H transfer from the coordinated dimethylamino to the N atom of the alkylated amido ligand, via transition state 7-8 at 3.3 kcal/mol, leads to intermediate 8. The catalytic cycle is closed by displacement of the hydroaminoalkylated product by a dimethylamino ligand. The overall thermochemistry of the reaction is calculated to be -8.3 kcal/mol with the adopted computational protocol. The overall energy span from 1 to 4-5, 34.4 kcal/mol, is consistent with the experimentally required long reaction times and high temperatures. The structures of the metallaaziridine complex 3 and the rate-determining transition state 4-5 are shown in Figure 13. In complex 3 the Ti assumes a distortedtrigonal-bipyramidal geometry, with the Ti-O, the Ti-amido, and the Ti-aziridine bonds in the equatorial plane and the two amino ligands along the axis. This disposition is preserved in the rate-determining transition state 4-5, with propene replacing one of the amino ligands. The energy profile diagram is illustrated in Figure 14.

CONCLUSION

To summarize, we succeeded in isolating two metallacycles involved in the hydroaminoalkylation of olefins: a titanaaziridine obtained by α -H transfer between two adjacent σ -bonded $-N(CH_3)_2$ groups and the five-membered metallacycle obtained after insertion of 1-octene or any terminal alkene in the metal–carbon (M–C) bond of our well-characterized metallaaziridine fragment. It should be emphasized here that SOMC is unique in stabilizing such a metallacycle, especially the five-membered rings. Therefore, the reason for such a difference is very likely that there are no bimolecular reactions with surfaces, whereas in solution such bimolecular reactions easily occur.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00246.

FTIR, elemental analysis, NMR characterization, substrate analysis, and blank tests (PDF) $\ensuremath{\mathsf{PDF}}\xspace$

Cartesian coordinates for the calculate structures (XYZ)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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