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Synthesis, Structure, and Characterization of the Hydrogen-Substituted Imido Complex $TiCl_2(NH)(OPPh_3)_2$

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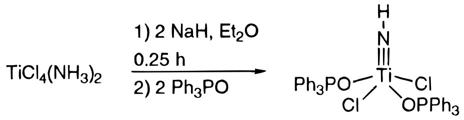
The reaction of high-valent early transition metal halides or alkylamides with ammonia represents one of the most common routes to metal(III) nitride films.[2,3] There has been considerable speculation that metal imido complexes of the formula L_nMNH (L = halide, NR_2) are important intermediates in such film deposition processes.[4−6] For example, imido complexes bearing TiNH groups have been suggested as intermediates along the reaction path leading to titanium nitride films from titanium tetrachloride and ammonia.[4] Imido complexes of the formula $Ti(NH)(NR_2)_2$ have been frequently proposed as intermediates in the formation of titanium nitride films by ammonolysis of $Ti(NR_2)_4$ (R = Me, Et).[5,6] We recently reported evidence that alkylimido complexes are important gas phase species in the deposition of titanium nitride,[7] niobium nitride,[8] and tantalum nitride[8] films from molecular precursors. In particular, mass spectrometry studies of the niobium and tantalum nitride deposition systems suggested that dealkylation of the alkylimido ligand occurs to afford the hydrogen-substituted imido complex.[8] Despite the relative abundance of group 4 and 5 alkylimido complexes with monomeric linkages,[9] there are only three reported complexes bearing terminal hydrogen-substituted imido groups in the group 5 metals[10] and none in the group 4 metals. As part of our program to explore coordination chemistry relevant to film depositions, we sought to develop routes to hydrogen-substituted imido complexes. Herein we report the synthesis, structure, and properties of $TiCl_2(NH)(OPPh_3)_2$, which constitutes the first group 4 complex containing a terminal hydrogen-substituted imido ligand.

Treatment of $TiCl_4(NH_3)_2$[11] with sodium hydride (2 equiv) in diethyl ether at ambient temperature led to rapid gas evolution (complete in <10 min) with concomitant formation of an orange-yellow suspension (eq 1). After 0.25 h, triphenylphosphine oxide (2 equiv) was added and the solution was refluxed for 18 h, during which the color changed to lemon yellow. Removal of the diethyl ether, extraction with dichloromethane, filtration, and crystallization from dichloromethane/hexane afforded $TiCl_2(NH)(OPPh_3)_2$ (**1**, 73%) as large, well-formed lemon yellow polygons.[12] The formulation for **1** was based upon spectral and analytical data, as well as on a crystal structure determination (vide infra). The ^1H NMR at 25 °C in chloroform-*d* or benzene-d_6 showed resonances attributable only to phenyl hydrogens; the imido proton was not detected. Low-temperature ^1H NMR spectra in chloroform-*d* (−55 to 0 °C) were similar to the spectrum at 25 °C and did not reveal the imido hydrogen. The imido hydrogen may be obscured by the phenyl protons, or the resonance could be broad due to coupling to ^{14}N (*I* = 1, 99.63%).[13,14]



1, 73%

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(12) Spectral and analytical data for **1**: mp >300 °C; IR (Nujol, cm^{-1}) 3161 (w), 1591 (m), 1378 (m), 1312 (m), 1279 (w), 1190 (vs), 1165 (s), 1146 (s), 1122 (vs), 1095 (s), 1072 (s), 1060 (s), 1027 (m), 997 (s), 971 (w), 939 (w), 862 (w), 847 (w), 763 (s), 751 (s), 722 (vs), 699 (vs); ^1H NMR ($CDCl_3$, δ, 23 °C) 7.70−7.45 (m, 2 $(C_6\boldsymbol{H}_5)_3PO$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm, 23 °C) 132.92 (s, ipso ***C*** of $P-C_6H_5$), 132.05 (d, J_{CP} = 9.0 Hz, ortho or meta ***C*** of $P-C_6H_5$), 131.88 (d, J_{CP} = 1.8 Hz, para ***C*** of $P-C_6H_5$), 128.44 (d, J_{CP} = 11.6 Hz, ortho or meta ***C*** of $P-C_6H_5$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm, 23 °C) 50.44 (s, minor), 48.04 (s, minor), 42.38 (s, major), 28.51 (s, minor). Anal. Calcd for $C_{36}H_{31}Cl_2NO_2P_2Ti$: C, 62.63; H, 4.53. Found: C, 61.98; H, 4.30.

(13) Further evidence for the imido hydrogen in **1** comes from the reaction with triethylamine (1.1 equiv) in dichloromethane (48 h, 23 °C), which afforded triethylammonium chloride (87% isolated yield, identified by melting point, ^1H NMR, and gravimetric analysis of chloride ion) and unidentified, insoluble titanium complexes.

(14) Because the imido hydrogen could not be detected by ^1H NMR, the deuterated complex $TiCl_2(ND)(OPPh_3)_2$ (**1**-*d*) was prepared as above from $TiCl_4(ND_3)_2$. Analysis of **1**-*d* by ^2H NMR did not show the imido deuterium resonance. The infrared spectrum of **1**-*d* was carefully compared with that of **1**. A very weak N−H stretch was tentatively assigned in **1** at 3161 cm^{-1}, while in **1**-*d* this stretch came at 2345 cm^{-1}. Examination of the fingerprint region showed six absorptions that shifted to lower energy by a factor of 1.012−1.023 upon going from **1** to **1**-*d*: 1279 (1262), 1165 (1139), 1060 (1047), 1101 (1088), 1060 (1047), 939 (925), and 763 (754) cm^{-1}. The bands that are sensitive to isotope substitution are probably associated with combination stretches involving the imido ligand and with N−H wagging modes: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; pp 191−205.

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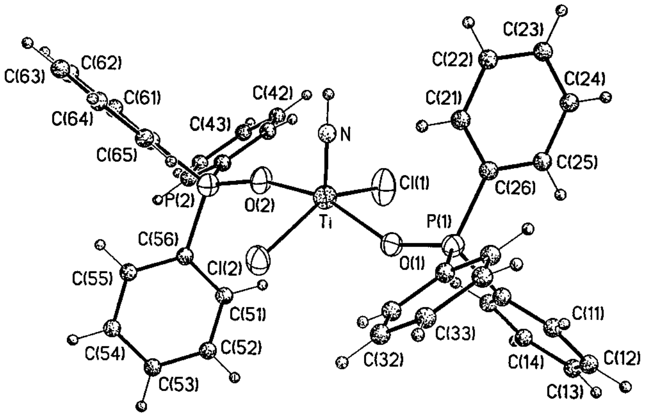

Figure 1. Perspective view of $C_{36}H_{31}Cl_2NO_2P_2Ti$ (**1**) with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (deg): Ti−N 1.627(8), Ti−Cl(1) 2.374(4), Ti−Cl(2) 2.355(4), Ti−O(1) 2.009(7), Ti−O(2) 2.023(8); N−Ti−Cl(1) 107.9(3), N−Ti−Cl(2) 105.4(3), N−Ti−O(1) 102.3(4), N−Ti−O(2) 100.7(4), Cl(1)−Ti−O(1) 86.9(2), Cl(1)−Ti−O(2) 84.7(2), Cl(2)−Ti−O(1) 87.2(2), Cl(2)−Ti−O(2) 88.1(2), Cl(1)−Ti−Cl(2) 146.7(2), O(1)−Ti−O(2) 156.9(3).

Figure 1 shows a perspective view of **1** along with selected bond lengths and angles.[15] The complex adopts approximately square pyramidal geometry, with nitrogen at the apex and trans-triphenylphosphine oxide ligands and trans-chloride ligands at the base. The titanium−nitrogen bond length (1.627(8) Å) is very short, while the titanium−chlorine bond lengths are typical at 2.355(4) and 2.374(4) Å. The titanium−oxygen bond lengths are 2.023(8) and 2.009(7) Å. These values are close to those expected for titanium−oxygen single bonds[16] and do not indicate significant multiple-bond character. The angles associated with the apical nitrogen range between 100.7 and 107.9°, which indicate that a "flat" square pyramid is formed. The angles associated with the base of the pyramid range between 84.7 and 88.1° for the cis ligands and between 146.7 and 156.9° for the trans ligands. The titanium−oxygen−phosphorus angles are suprisingly obtuse at 148.7(5)° (Ti−O(1)−P(1)) and 162.2(5)° (Ti−O(2)−P(2)). These large angles are probably the result of steric interactions involving the phenyl groups, rather than multiple bonding between titanium and oxygen.

In summary, deprotonation of $TiCl_4(NH_3)_2$ with sodium hydride, followed by addition of triphenylphosphine oxide, provides the hydrogen-substituted imido complex **1** in good yield. The formation of **1** presumably proceeds by elimination of ammonia from $TiCl_2(NH_2)_2$ to afford the imido species $[TiCl_2(NH)]_n$, which is then trapped by triphenylphosphine oxide to give **1**. The diethyl ether solvent probably coordinates weakly to $[TiCl_2(NH)]_n$, thereby stabilizing it and facilitating its formation. Complex **1** represents a base-stabilized structural model for a species that may play an important role in the formation of titanium nitride films. Moreover, the vibrational spectroscopy analysis presented herein[14] serves as a valuable benchmark for *in situ* infrared studies of film deposition processes[6] and may allow for definitive characterization of hydrogen-substituted imido species in such systems. Finally, the successful synthesis of **1** suggests that deprotonation of ammonia adducts of other high-valent early transition metal chlorides[17] should also provide hydrogen-substituted imido complexes. The synthesis of such species, as well as the study of their role in the deposition of metal nitride films, is being pursued in our laboratory.

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Supporting Information Available: Tables S1−S7, listing full experimental details for data collection and refinement, atomic coordinates, bond lengths, bond angles, and thermal parameters, for **1**, text giving preparative details for new compounds, and figures showing IR spectra for **1** and **1**-*d* (11 pages). An X-ray crystallographic file, in CIF format, is available. Access and ordering information is given on any current masthead page.

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(15) For $C_{36}H_{31}Cl_2NO_2P_2Ti$: monoclinic, $P2_1/c$, $a = 17.341(6)$ Å, $b = 18.390(6)$ Å, $c = 11.308(5)$ Å, $\beta = 98.37(3)°$, $V = 3568(2)$ Å^3, $Z = 4$, $T = 298$ K, $D_{calc} = 1.285$ g cm^{-3}, $R(F) = 8.50\%$ for 2178 observed independent reflections ($4° \leq 2\theta \leq 45°$). Carbon and nitrogen atoms were refined isotropically. Hydrogen atoms were refined as idealized contributions. All other atoms were refined anisotropically. Phenyl rings were refined as rigid bodies.

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