Carbon-carbon double-bond formation in the intermolecular acetonitrile reductive coupling promoted by a mononuclear titanium(II) compound. Preparation and characterization of two titanium(IV) imido derivatives

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Download date: 17. Oct. 2020
Two Titanium(11) Imido Derivatives
Titanium(I1) Compound. Preparation and Characterization of

Sandro Gambarotta,* Sandro and Michael Y. Chiang'

Reflexed for 4 h. The resulting solution was analyzed by GLC and then
dicarba-nidc-undecaborate
rate. The latter was extracted with pentane [the yield of PhIClz
dicarborane. The latter was extracted with pentane [the yield of PhIClz
2.5 h. Internal standard (chlorobenzene) was added, and the organic
370-50-36-9; 9-m-C2BloH, ,I, 73050-37-0, 2-p-C2BloH,F; 22762-43-2;
iiodonium tetrafluoroborate (0.24 mmol), NaCl (0.04 g; 1.9 mmol), water
residual solid gave 0.26 g (99.5%) of analytically pure 2-fluoro-p-
m-iodo-m-carborane, mp 267-268 OC (hexane; sealed tube). The compound was

2-Fluoro-p-carborane. A mixture of 7 (0.7 g; 1.6 mmol), NaF (0.2 g; 4.8 mmol), water (4 mL), and dichlormethane (5 mL) was vigorously
mp 267-268 °C (hexane; sealed tube). The compound was
found to be identical with an authentic sample.5,6


Reactions of 2-6 with NaF: A mixture of aryl(m-carboran-9-yl)
iontium tetrafluoroborate (0.62 mmol), NaF (0.08 g; 1.9 mmol), water
1.34 g; 5.1 mmol), and dry chlororormine (10 mL). The exothermic reaction was complete within 5–6 min. The liquid phase was
analyzed by GLC and then evaporated, and the residue was chromatographed on alumina (benzene–hexane, 1:3) to give 0.52 g (93%) of 9-
fluoro-m-carborane, mp 287-288 °C (from benzene–hexane; sealed tube).
The compound was found to be identical with an authentic sample.5,6

Reactions of 3–6 with NaCl: A mixture of 9-fluoro-9-m-carborane (1.50 g; 3.5 mmol) was
vigorously stirred under reflux for 6 h. Internal standard (chlorobenzene)
was added, and the organic layer was analyzed by GLC and GC-MS.

Registry No. 1, 81353-28-8; 2, 81353-35-5; 3, 99506-45-3; 4,
99506-39-5, 5, 99506-41-9; 6, 99506-43-1; 7, 882/42-78-6; 9-o-C2BOHF;
73050-36-9; 9-m-C2BOHF; 7, 73050-37-0, 2-p-C2BOHF; 7, 22762-43-2;
9-m-C2BOHF; 7, 17157-06.

Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, and Department of Chemistry, Washington University.
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Carbon–Carbon Double-Bond Formation in the Intermolecular Acetonitrile Reductive Coupling Promoted by a Mononuclear Titanium(II) Compound. Preparation and Characterization of Two Titanium(IV) Imido Derivatives
Robert Duchateau,* Antony J. Williams,* and Michael Y. Chiang*†

Received May 15, 1991

Introduction

Reactions forming carbon–carbon bonds are among the most fundamental organic chemical transformations mediated by

early-transition-metal complexes. Today, reductive couplings and insertion reactions are successfully used with a considerable number of transition metals, to form C–C bonds through either catalytic or stoichiometric reactions.1 While the insertion reactions are the most versatile chemical pathway for polymerization processes,1,2 reductive couplings are target of continuous studies for polymer– and stereocontrol metal–ligand cotic syntheses.2 Group 4 transition metals seem to be especially versatile for this second class of reactions,1,4,5 reductive couplings being documented for the large majority of unsaturated organic compounds (dienes,3 olefins,4 acetylenes,5 isocyanides,6 nitriles, and carbon monoxide9). We were especially interested in defining the chemical reactivity of (TMEDA)2TiCl2 (TMEDA = N,N',N'-tetramethyl-
ethylene diamine),9 which is one of the rare examples of low-valent titanium complexes.12,13 In this paper we describe the reaction
with a few unsaturated nitrogen-containing organic substances (nitriles, azo compounds, and azides). The main interest in the reactivity with these substrates results from the rarity of the organic functionality which may be generated (diaminato, \textit{en}ediaminato, \textit{ened}iimido, \textit{im}idato, or \textit{az}ido) depending on (i) the number of electrons transferred by the transition metal to the organic substrate and (ii) the reducing power of the transition metal.

**Experimental Section**

All operations were performed under an inert atmosphere (N\(_2\) or Ar) by using standard Schlenk techniques, or in a nitrogen-filled drybox (Braun MB-200). TMEDA was chromatographed over Al\(_2\)O\(_3\) and distilled from melted potassium. (TMEDA)\(_2\)TiCl\(_4\) was prepared according to the published procedure.\(^{11}\) Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out at the Microanalytical Department of the State University of Groningen. NMR spectra were recorded on a Varian G 200-230 MHz solid-state magic-angle-spinning NMR spectrum (complex 1) was obtained under cross-polarization magic-angle-spinning and high-power proton-decoupling conditions at 45.267 MHz on a Bruker CXP-180 spectrometer. The sample was sealed under vacuum into a glass ampule, which fitted tightly into a 7-mm-o.d. ceramic rotor. The spectrum was obtained using a rotation speed of 1650 Hz. Chemical shifts are reported in ppm from TMS with elemental resonances being assigned a chemical shift of 16.9 ppm.

\[^{11}\text{The structure of tetramethylpyrazine has been reported in the literature.}^{20}\]
solved by direct methods. All the non-hydrogen atoms were refined of several reflections indicated no need for absorption corrections. Data was based on 1536 observed reflections. Neutral-atom scattering factors were taken from Cromer and Waber.\textsuperscript{18} Instrument stability (no decay correction was applied). Azimuthal scans remained constant throughout data collection, indicating crystal and insentative reflections, which were measured every 150 reflections, refined. The structure was solved by direct methods using the Siemens SHELXTL technique to a maximum 28 value of 47.0°. Of the 2628 reflections in the range 38.27°-160.48°, 1536 were used for the structure determination and 1092 were included in the structure refinement (R = 0.042). The data were corrected for Lorentz and polarization effects. The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table IV. Selected Bond Distances (Å) and Angles (deg)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distances (Å)</th>
<th>Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-N1-N2</td>
<td>2.302(4)</td>
<td></td>
</tr>
<tr>
<td>Ti-C1-C1</td>
<td>2.462(2)</td>
<td></td>
</tr>
<tr>
<td>N1-Ti-N1-C1</td>
<td>92.0(1)</td>
<td>93.4(1)</td>
</tr>
<tr>
<td>N1-Ti-N2-C1</td>
<td>97.8(2)</td>
<td>164.2(3)</td>
</tr>
<tr>
<td>C1-Ti-N1-C2</td>
<td>77.4(4)</td>
<td></td>
</tr>
<tr>
<td>Ti-N3-C7</td>
<td>1.699(4)</td>
<td>1.384(5)</td>
</tr>
<tr>
<td>Ti-C7-C7a</td>
<td>2.286(6)</td>
<td>1.337(10)</td>
</tr>
<tr>
<td>Ti-C7-C8</td>
<td>2.343(2)</td>
<td>1.518(8)</td>
</tr>
<tr>
<td>C1-Ti-C2-C2</td>
<td>93.7(1)</td>
<td>116.4(4)</td>
</tr>
<tr>
<td>C1-Ti-N1-C1</td>
<td>88.4(2)</td>
<td>121.6(5)</td>
</tr>
<tr>
<td>C1-Ti-N3-C3</td>
<td>107.3(4)</td>
<td>121.9(6)</td>
</tr>
<tr>
<td>Ti-N3-C7</td>
<td>175.2(4)</td>
<td></td>
</tr>
</tbody>
</table>

(TMEDA)Ti(NPh)Cl2. Neat azobenzene (0.6 g, 3.3 mmol) was added to a suspension of TiCl4(TMEDA)2 (2.3 g, 6.5 mmol) in THF (75 mL) at -90 °C. The mixture was stirred while warming it slowly to -30 °C, when a deep red color developed. Once all the purple crystals of starting material were dissolved, the resulting deep red solution was allowed to warm to room temperature. Deep orange crystals of 4 separated upon concentration and cooling to -30 °C (1.6 g, 85 mmol, 74%).

Table III. Relevant bond distances and angles are reported in Table IV. All calculations were performed using the TEXSAN\textsuperscript{19} crystallographic software package of the Molecular Structure Corp., using a Digital VAX computer.

Results and Discussion

The reaction of (TMEDA)2TiCl4 in neat acetonitrile proceeds at -30 °C to produce deep orange crystals of [trans-NC(Me)=CN][TiCl4(TMEDA)]; (1) (Scheme I).

The structure of 1, as demonstrated by X-ray diffraction analysis, consists of two square-pyramidal TiCl4(TMEDA) fragments linked together by a trans-[N-(C(Me)=C(Me)=N)] moiety (Figure 1). The Ti-N distance formed by the nitrogen atoms of the eneimidato group is very short [Ti-N = 1.699(4) Å], suggesting some triple bond character. The C-N distance [C7-N3 = 1.384(5) Å] and the C-C distance [C7-C7a = 1.337(10) Å] are in agreement with the proposed formulation and indicate a considerable electronic delocalization over the organic fragment. The geometry around the transition metal is best described as slightly distorted square-pyramidal with an axial eneimido group. Two chlorine and two nitrogen atoms from one molecule of TMEDA bound to the basal plane [C11-Ti-C12 = 93.7(1)°; C11-Ti-N1 = 88.4(2)°; N1-Ti-N2 = 77.8(2)°] reaching normal values of the Ti-Cl [Ti-C11 = 2.343(2) Å] and Ti-N [2.280(6) Å] distances.

Compound 1 is diamagnetic, and consistent 1H NMR data could be obtained only in CD3CN solution due to its extremely poor solubility in the common inert organic solvents. Fast decomposition was observed in chlorinated and coordinating solvents (THF, pyridine, DMF). 13C NMR spectra were recorded in the solid state, due to the very poor solubility of the sample and its limited thermal stability at room temperature. Formation of the dimetallic 1 proceeds probably via transfer of two electrons from the metal center to a coordinated molecule of CH2CN (Scheme I). The resulting carbene-like species forms


the formation in low yield of the thermally unstable (TME-
very short Ti-N distance, is probably high and is likely the
absorption at DA)TiCl2N3 as a light blue crystalline solid. The characteristic
of two "reactive" chlorine atoms in
There is no prohibitive steric hindrance in complex
alkylation reactions. The structure of
the inorganic residue failed.
the inorganic residue failed.
-30°C in THF to form the corresponding (TMEDA)C12Ti=NPh
contrast to the hard pyrolitic conditions employed for the prep-
formation of (ArO)2Ti(NPh)py2,16 underlying the versatility of
rangement of the [N-C(Me)=C(Me)-NI4- moiety from the
trans to the cis configuration. Attempts to isolate and identify
atmosphere with the use of

colorless crystalline material (Scheme

gave moderate yield (47%) of tetramethylpyrazine (TMP) as a


coulombic driving force for the preliminary reduction of
in this hypothesis, the Ti-imido function
This complex provides the first case where
the cyclic structure imply rearrangement of the [N—C(Me)==C(Me)—N]4+ moiety from the
trans to the cis configuration. Attempts to isolate and identify
the inorganic residue failed.

The stability of the Ti—N multiple bond, as suggested by the
very short Ti—N distance, is probably high and is likely the
thermodynamic driving force for the preliminary reduction of
CH3CN. In agreement with this hypothesis, the Ti-imido function
can be easily formed with other organic precursors. The reaction
of (TMEDA)2TiCl4 with azobenzene for example, proceeds at
-30°C in THF to form the corresponding (TMEDA)Cl2Ti=NPh
(2) in good yield (Scheme III). The ease of this reaction is in
contrast to the hard pyrolitic conditions employed for the
preparation of (ArO)2Ti(NPh)py2,16 underlying the versatility of
TiCl4(TMEDA)2 as a synthetic tool. Furthermore, the presence
of two "reactive" chlorine atoms in 1 and 2 is especially desirable for
further reactivity studies, including toward reduction and
alkylation reactions. The structure of 2, as demonstrated by X-ray
analysis, shows the monomeric complex basically isostructural with
the monomeric fragment of 1 forming comparable bond distances and
angles (Figure 2). The Ti—N distance [Ti—N = 1.702 (6)
Å] is slightly shorter than in the previously reported (ArO)2Ti-
(NPh)(py)2,16 probably as a result of decreased steric hindrance.

Finally the reaction of (TMEDA)2TiCl4 with Me3SiN3 led to
the formation in low yield of the thermally unstable (TMEDA)
TiCl2N3 as a light blue crystalline solid. The characteristic
absorption at ν = 1980 cm⁻¹ of the IR spectrum suggested the

Figure 2. ORTEP drawing of 2 showing the labeling scheme. Thermal
ellipsoids are drawn at the 50% probability level.

presence of a bent terminally bonded azido group.

Acknowledgment. This work was supported by the Natural
Sciences and Engineering Research Council of Canada (operating
grant) and the donors of the Petroleum Research Fund, admin-
istered by the American Chemical Society. We thank Dr. John
Repmester of the National Research Council (Ottawa) for al-
lowing us access to the solid-state NMR facilities.

Supplementary Material Available: Tables listing atomic positional
parameters, anisotropic thermal parameters, and complete bond distances
and angles for 1 and 2 (21 pages); tables listing observed and calculated
structure factors for 1 and 2 (24 pages). Ordering information is given
on any current masthead page.

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Simple Syntheses and Alkylation Reactions of
3-Iodo-o-carborane and 9,12-Diodo-o-carborane

Ji Li,* Cameron F. Logan, and Maitland Jones, Jr.

Received May 15, 1991

Although 3-chloro,2ab 3-bromo,2c and 3-fluoro-o-carborane2b
are all known, 3-iodo-o-carborane (1) is not. In this note, we first
describe a modification of our recent recipe for 3-bromo-o-
carborane2b that produces 1 in good yield and purity. Next, we
report an extension of our route to 9-iodo-o-carborane2c to give

(1) Support for this work from the National Science Foundation through
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University, 1991.

(2) (a) Zakharikin, L. I.; Kalinin, V. N.; Gedymin, V. V. J. Organomet.

3712. (b) See also: Zakharikin, L. I.; O'i sheviovaya, V. A.; Poroshina,
57, 1800.