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Notes

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Formation of a Terminal Aryl—Imido Compound of Titanium by Cleavage of the N=N Double Bond in Benzo[*c*]cinnoline

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Introduction

The formation, structure, and reactivity of group 4 metal compounds containing terminal imido ligands is an area of research that has attracted recent attention.[1-5] We have previously shown that thermolysis of an η^2-azobenzene (diazametallacyclopropane) complex of titanium can lead to the formation of terminal phenylimido derivatives of this metal.[4] Furthermore, studies have also shown that treatment of the titanacyclopentadiene complex $[(Ar''O)_2Ti(C_4Et_4)]$ (**1**) with azobenzene leads to an enediamido (2,5-diazametallacyclopentene) compound in which the N=N double bond has been cleaved.[6] We wish to report here upon the reaction of the titanacyclopentadiene compound (**1**) with benzo[*c*]cinnoline, a diazo substrate that is geometrically constrained to a cis configuration about the N=N double bond. The final product of this reaction contains a terminal aryl–imido ligand as well as an η^2-N,N-bonded benzo[*c*]cinnoline molecule.

Results

The titanacyclopentadiene complex $[(Ar''O)_2Ti(C_4Et_4)]$ (**1**) reacts only slowly with azobenzene at room temperature.[6] In contrast, treatment of **1** with benzo[*c*]cinnoline (1 equiv) results in the rapid formation of a new compound **2**. The reaction is complete in minutes in C_6D_6 solvent as monitored by ^1H NMR spectroscopy. Samples of pure **2** can be obtained as light yellow crystals from benzene/hexane mixtures. The formulation of **2** as containing a 2,3-diazametallacyclohepta-4,6-diene ring (Scheme I) is based upon NMR spectral data. In the ^1H NMR spectrum, four nonequivalent ethyl resonances are observed. All four of the methylene groups are diastereotopic, indicating a nonplanar configuration for the seven-membered metallacycle ring. A well-resolved doublet at δ 5.42 ppm can be assigned as being due to the aromatic proton ortho to the nitrogen atom in the 2-position of the ring. In the ^{13}C NMR spectrum of **2**, four nonequivalent Et groups are again evident. The presence of a Ti–C bond is confirmed by a resonance downfield at δ 210.7 ppm. This is a chemical shift region typical of Ti–*C*(sp^2 or aromatic) carbon nuclei.[6,7] Thermolysis of hydrocarbon solutions of **2** results in a mixture of products. However, in the presence of an extra 1 equiv of benzo[*c*]cinnoline, **2** is converted at 100 °C into a single product (**3**) in high yield (Scheme I). Compound **3** can also be obtained simply by heating the titanacyclopentadiene (**1**) in the presence of 2 equiv of benzo[*c*]cinnoline for 2 h at 100 °C. The ^1H and ^{13}C NMR spectra of **3** show two nonequivalent Et groups and the absence of any Ti–*C* bonds. The identity of **3** as an aryl-imido complex (Scheme I) was determined by a single-crystal X-ray diffraction study (Figure 1; Tables I and II). The molecule can be seen to consist of two aryloxide ligands, an η^2-N,N-bound benzo[*c*]cinnoline molecule, and a complicated aryl–imido group (Figure 1). If one considers the benzo[*c*]cinnoline molecule as occupying a single coordination site then the geometry about the metal can best be described as pseudotetrahedral.

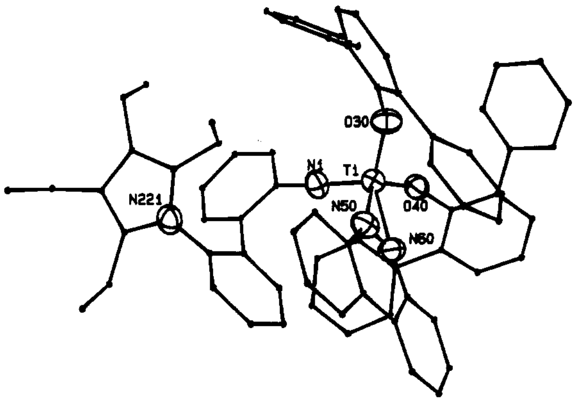

Figure 1. Partial ORTEP view of **3** emphasizing the central coordination sphere; thermal ellipsoids at 50%. A fully labeled ORTEP is given in the supplementary material.

Table I. Crystallographic Data

$TiO_2N_4C_{78}H_{68}$	space group *Pbca* (No. 61)
fw 1141.34	$T = -23$ °C
$a = 18.957$ (2) Å	$\lambda = 0.71073$ Å
$b = 19.542$ (4) Å	$\rho_{calc} = 1.194$ g cm^{-3}
$c = 34.270$ (3) Å	$\mu = 1.80$ cm^{-1}
$V = 12695$ (5) Å^3	$R(F_o) = 0.054$
$Z = 8$	$R_w(F_o) = 0.061$

Table II. Selected Bond Distances (Å) and Angles (deg) for **3**

Ti–O(30)	1.852 (4)	Ti–O(40)	1.878 (4)
Ti–N(1)	1.708 (5)	Ti–N(50)	2.125 (5)
Ti–N(60)	2.175 (5)	N(50)–N(60)	1.284 (6)
O(30)–Ti–O(40)	106.3 (2)	N(1)–Ti–O(30)	113.2 (2)
N(1)–Ti–O(40)	109.2 (2)	N(1)–Ti–N(50)	100.5 (2)
N(1)–Ti–N(60)	109.6 (2)	Ti–O(30)–C(31)	149.5 (4)
Ti–O(40)–C(41)	149.5 (4)	Ti–N(1)–C(1)	170.4 (4)

Discussion

The new aryl–imido group in **3** can be seen to be the result of cleavage of the N=N double bond in benzo[*c*]cinnoline. One of the nitrogen atoms is bound to titanium, while the other has become part of an azacyclopentadiene ring (Scheme I, Figure 1). The reaction of **1** with nitrosobenzene, PhNO, results in the formation of titanium–oxo compounds and the organic azacyclopentadiene $PhNC_4Et_4$.[8] It is unknown whether the aryl–imido ligand in **3** results from direct fragmentation of the metallacycle ring in **2** or whether the reaction proceeds through one or more intermediates.

The Ti–N(imido) distance of 1.708 (5) Å in (**3**) compares well with values of 1.719 (3) and 1.723 (4) Å found in the titanium aryl-imido compounds $[(Ar'O)_2Ti(NPh)(py')_2]$ (Ar'O = 2,6-diisopropylphenoxide, py' = 4-pyrrolidinopyridine) and

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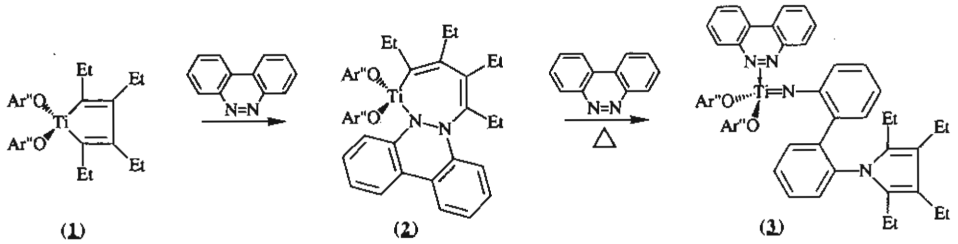
Scheme I



Ar"O=2,6-Diphenylphenoxide

[(Ar″O)$_2$Ti(NPh)(1,10-phenyl)]$_3$, respectively.[4,9] The bonding of the benzo[*c*]cinnoline ligand in **3** is also worthy of note. A number of group 4 metal η^2-azobenzene complexes are now known.[10–12] However, the azobenzene molecule is typically η^2-N,N bound to a formally d^2, M^{2+} metal center. Structural studies show the resulting molecules to be better described as containing diazametallacyclopropane rings, with short M–N and long N–N distances. In compound **3** the diazo unit is bound to a d^0 metal center with no prospects for any back-bonding from the metal into the π^* orbital of the N=N unit. The N–N distance of 1.284 (6) Å found in **3** is very close to the distance of 1.253 (3) Å found for uncoordinated azobenzene.[13] This distance is much shorter than the distances of 1.416 (8) and 1.42 (1) Å found for the two independent molecules in [(Ar′O)$_2$Ti(PhNNPh)(py)$_2$],[10] 1.339 Å in Cp$_2$Ti(η^2-PhNNPh)],[12] and 1.434 (4) Å for Cp$_2$Zr(η^2-PhNNPh)(py).[11] The Ti–N(diazo) distances in **3**, 2.175 (5) and 2.125 (5) Å, are much longer than the values of 1.949 (6) and 1.963 (6) Å in [(Ar′O)$_2$Ti(η^2-PhNNPh)(py)$_2$].[10] These latter distances are comparable to those expected for titanium–amido bonding, while the long distances in **3** are closer to simple dative bond distances.[14] Hence, the benzo[*c*]cinnoline molecule in aryl–imido **3** represents a diazo ligand that is purely σ-bound to titanium with no evidence for metal to ligand π-back-bonding.

Experimental Section

Preparation of Ti(OAr″)$_2$(C$_4$Et$_4$–C$_6$H$_4$N–NC$_6$H$_4$) (2). To a benzene solution of Ti(OAr″)$_2$(C$_4$Et)$_4$ (**1**) (0.25 g, 0.36 mmol) was added 1 equiv of benzo[*c*]cinnoline (0.07 g, 0.36 mmol). The mixture was stirred for 1 h at room temperature; then the solvent was removed under vacuum. The resulting residue was redissolved in a minimum of fresh benzene and layered with hexane to induce formation of light yellow crystals of product. The crystals were washed with hexane and dried under vacuum. Anal. Calcd for TiC$_{60}$H$_{54}$N$_2$O$_2$ (**2**): C, 81.61; H, 6.16; N, 3.17. Found: C, 81.25; H, 6.56; N, 3.15. ^{1}H NMR (C$_6$D$_6$, 30 °C), δ: 6.50–7.87 (m, aromatics); 5.42 (dd, ortho proton on C$_6$H$_7$N–NC$_6$H$_7$); 2.71 (sextet), 1.73–2.10 (m, C*H*$_2$CH$_3$); 1.03 (t), 0.86 (t), 0.73 (t), 0.35 (t, CH$_2$C*H*$_3$). Selected ^{13}C NMR data (C$_6$D$_6$, 30 °C), δ: 210.7 (Ti–*C*); 160.7, 159.7 (Ti–O–*C*); 28.0, 23.3, 22.9, 20.7 (*C*H$_2$CH$_3$); 15.4, 15.1, 14.8, 13.8 (CH$_2$*C*H$_3$).

Preparation of Ti(OAr″)$_2$(=NC$_6$H$_4$—C$_6$H$_4$NC$_4$Et$_4$) (3). A benzene solution of Ti(OAr″)$_2$(C$_4$Et$_4$) (**1**) (0.25 g, 0.36 mmol) and 2 equiv of benzo[*c*]cinnoline (0.14 g, 0.72 mmol) was heated at 100 °C for 2 h. The solvent was then removed under vacuum, and the resulting residue was redissolved in a minimum of fresh benzene. The benzene solution was layered with hexane to induce formation of very dark yellow crystals of products that were suitable for X-ray diffraction. The crystals were washed with hexane and dried under vacuum. Anal. Calcd for TiC$_{72}$H$_{64}$N$_4$O$_2$ (**3**): C, 81.18; H, 6.06; N, 5.26. Found: C, 81.40; H, 6.36; N, 4.82. ^{1}H NMR (C$_6$D$_6$, 30 °C), δ: 5.08–7.80 (m, aromatics); 2.14 (q), 2.16 (m, C*H*$_2$CH$_3$); 1.13 (t), 0.77 (t, CH$_2$C*H*$_3$). Selected ^{13}C NMR data (C$_6$D$_6$, 30 °C), δ: 18.5, 18.2 (*C*H$_2$CH$_3$); 17.4, 16.3 (CH$_2$*C*H$_3$).

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Supplementary Material Available: A fully labeled ORTEP drawing of **3**, a textual presentation of the details of the crystallographic study, and tables of crystal data, fractional coordinates, temperature factors, and bond distances and angles (24 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Water-Soluble Organometallic Compounds. 1. Synthesis, Characterization, and X-ray Structure of [Na-kryptofix-221]$_3$[W(CO)$_5$P{C$_6$H$_4$-*m*-SO$_3$}$_3$]

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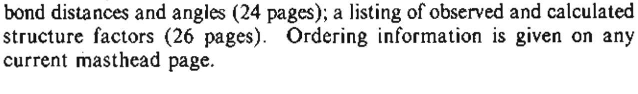
The interest in water-soluble organometallic complexes has increased dramatically since the development of the Rhone-Poulenc/Ruhrchemie biphasic catalysis process.[1,2] This procedure, which utilizes a water-soluble rhodium catalyst containing the TPPTS (trisodium tris(*m*-sulfonatophenyl)phosphine) ligand, is capable of performing the hydroformylation process outlined in eq 1. Other similar water-based organometallic catalysts have been employed for a variety of important chemical processes.[3] On spectroscopic evidence, it is generally felt with regard to the M–P bond that electronically the sulfonated phosphine is quite similar to that of its non-sulfonated analogue PPh$_3$. Nevertheless, the two ligands should differ significantly in their steric influence. In addition, when the metal center is multiply substituted with



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