

Formation and Characterization of η^2 -Imine and η^2 -Azobenzene Derivatives of Titanium Containing Ancillary Aryloxo Ligation

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Treatment of the mono(η^2 -iminoacyl) compound $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2(\eta^2\text{-Bu}^t\text{NCCH}_2\text{Ph})(\text{CH}_2\text{Ph})$ with 1 equiv of pyridine ligands $L =$ pyridine (py) 4-phenylpyridine (py-4-Ph) 4-ethylpyridine (py-4-Et) 4-pyrrolidinopyridine (py-4-pd) leads to the quantitative formation of the η^2 -imine compounds $\text{Ti}(\text{OAr}-2,6\text{Pr}^i)_2[\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2](L)$ (**1a**, $L =$ py; **1b**, $L =$ py-4-Ph; **1c**, $L =$ py-4-Et; **1d**, $L =$ py-4-pd). The η^2 -CN binding of the imine ligands in compounds **1** was confirmed both by spectroscopic data and by a single-crystal X-ray diffraction analysis of **1b** and **1c**. In both compounds, the presence of an azametallacyclopropane (metallaaziridine) ring was shown with distances $\text{Ti}-\text{N} = 1.846$ (4), 1.855 (2) Å, $\text{Ti}-\text{C} = 2.158$ (5), 2.150 (2) Å, and $\text{N}-\text{C} = 1.421$ (7), 1.410 (3) Å for **1b** and **1c**, respectively. These parameters are interpreted in terms of a $\text{Ti}(\text{IV})$ metal center bound to a dianionic $[\text{R}'\text{N}-\text{CR}_2]^{2-}$ fragment and not as a neutral imine ligand loosely π -bound to $\text{Ti}(\text{II})$. Consistent with this is the treatment of **1** with H_2O to generate the amine $\text{Bu}^t\text{NHCH}(\text{CH}_2\text{Ph})_2$ along with titanium oxo species. Treatment of **1** with the α -diimine $\text{PhN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NPh}$ leads to the formation of the enediamide compound $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2[\text{PhNC}(\text{Me})=\text{C}(\text{Me})\text{NPh}]$ (**2**). The η^2 -bound imine in **1** will also undergo reaction with azobenzene to generate free $\text{Bu}^t\text{N}=\text{C}(\text{CH}_2\text{Ph})_2$ and the η^2 -azobenzene complex $\text{Ti}(\text{OAr}-2,6\text{Pr}^i)_2(\eta^2\text{-PhNNPh})(\text{py})_2$ (**3**). A single-crystal X-ray diffraction analysis of **2** showed the azobenzene strongly bound with $\text{Ti}-\text{N} = 1.95$ Å (average) and with an $\text{N}-\text{N}$ single-bond distance of 1.42 Å (average). Crystal data for $\text{TiO}_2\text{N}_2\text{C}_{54}\text{H}_{66}$ (**1b**) at -155 °C: $a = 12.970$ (4), $b = 12.927$ (3), $c = 28.140$ (4) Å; $\beta = 97.38$ (2)°; $Z = 4$; $d_{\text{calcd}} = 1.168$ g cm^{-3} in space group $P2_1/c$. Crystal data for $\text{TiO}_2\text{N}_2\text{C}_{50}\text{H}_{67}$ (**1c**) at -100 °C: $a = 10.748$ (2), $b = 17.424$ (3), $c = 24.673$ (2) Å; $\beta = 98.442$ (9)°; $Z = 4$; $d_{\text{calcd}} = 1.128$ g cm^{-3} in space group $P2_1/c$. Crystal data for $\text{TiO}_2\text{N}_4\text{C}_{46}\text{H}_{54}$ (**3**) at -162 °C: $a = 38.770$ (6), $b = 17.858$ (30), $c = 9.892$ (3) Å; $\beta = 97.18$ (2)°; $Z = 6$; $d_{\text{calcd}} = 1.089$ g cm^{-3} in space group $C2$.

Introduction

The classical coordination chemistry of organic imine (Schiff base) ligation with later transition elements has been a well-explored area of research.¹ Furthermore, the incorporation of imine functionalities into polydentate organic molecules has been an important aspect in the development of macrocyclic coordination chemistry.² The coordination properties of imine ligands toward later d-block elements typically involve simple σ -donation to the metal via the nitrogen lone pair.¹⁻³ However, the last few years has seen a rapid development of early-transition-metal chemistry associated with imine functional groups.⁴⁻⁷ In this case the imine linkage is typically found to bind strongly to the metal in an η^2 -CN fashion. The interaction

(1) Calligaris, M.; Randaccio, L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Chapter 20.1.

(2) Curtis, N. F. Chapter 21.2 in ref 1.

(3) Other coordination modes can involve chelation achieved via cyclometalation pathways; see: (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 73. (b) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* 1976, 18, 327. (c) Constable, E. C. *Polyhedron* 1984, 3, 1037.

(4) The formation of η^2 -imine ligands at early-transition-metal centers can be achieved by cyclometalation of dialkylamido ligands,⁵ alkyl or hydride reduction of η^2 -imino acyl ligands,⁶ or in a few cases by addition of imines directly to low-valent metal centers.⁷

(5) (a) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* 1983, 105, 2651. (b) Nugent, W. A.; Overall, D. W.; Holmes, S. J. *Organometallics* 1983, 2, 161.

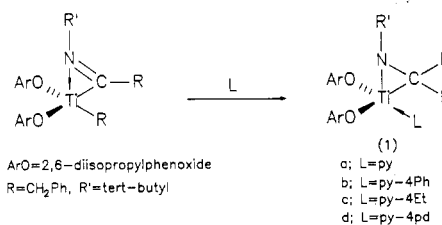
(6) (a) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* 1979, 101, 6450. (b) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Am. Chem. Soc.* 1980, 102, 7978. (c) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1981, 2088. (d) Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. D. *Polyhedron* 1989, 8, 341.

(7) (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* 1978, 109, 6551. (b) Brunner, H.; Wachter, J.; Schmidbauer, J. *Organometallics* 1986, 5, 2212. (c) Sielisch, T.; Behrens, U. *J. Organomet. Chem.* 1986, 310, 179.

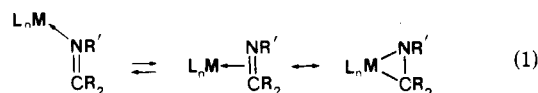
(8) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Foltling, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* 1987, 109, 390.

(9) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Foltling, K.; Huffman, J. C. *J. Am. Chem. Soc.* 1987, 109, 6068.

Scheme I



of the organic fragment with the metal can be described by using a Dewar-Chart-Duncanson model in which the CN double bond is π -bound to the metal (eq 1). If the



metal fragment formally contains a d^n ($n \geq 2$) electron configuration, the the back-donation from the metal can result in a bonding picture better described as an azametallacyclopropane (metallaaziridine). The result is that the imine has now been converted into an organometallic function, and it is possible for it to undergo various metal-mediated carbon-carbon bond-forming processes not found for simple σ -bound η^1 -imine ligands.⁵⁻¹⁰ In this paper we wish to report on the synthesis of a series of η^2 -imine derivatives of titanium. This work is significant in that it shows that although the azametallacyclopropane picture is structurally and in some cases chemically correct, it is still possible under certain circumstances to displace the unreduced imine group from the titanium metal center.

Results and Discussion

Previous work has shown that the dialkyl substrates of stoichiometry $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2(\text{R})_2$ ($\text{OAr}-2,6\text{-Pr}^i = 2,6$ -

(10) Durfee, L. D.; Kobriger, L. M.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* 1988, 110, 1463.

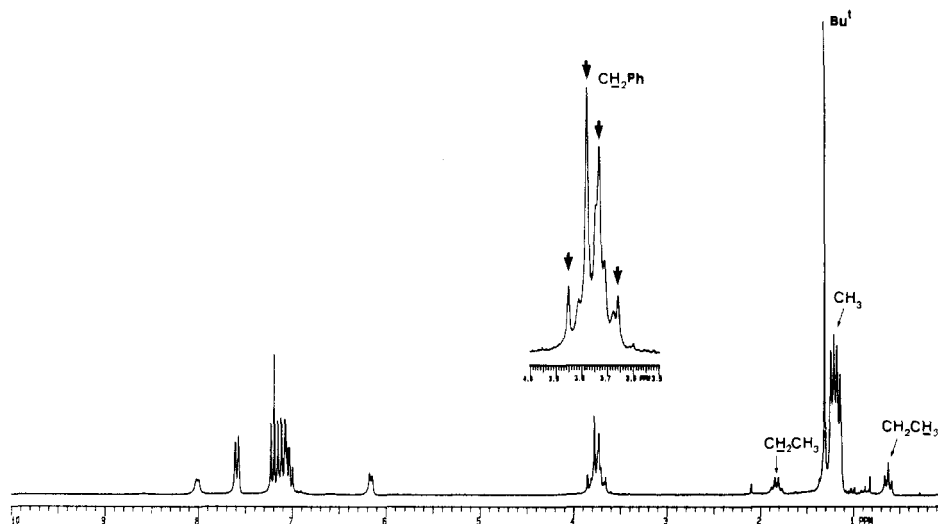
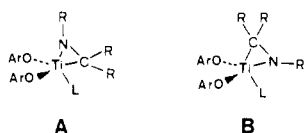


Figure 1. ^1H NMR spectrum (200 MHz) of **1c**.

Chart I



diisopropyl phenoxide; $\text{R} = \text{CH}_3, \text{CH}_2\text{Ph}, \text{CH}_2\text{SiMe}_3$) are useful starting materials for the formation of a series of bis(η^2 -iminoacyl) compounds by the migration insertion of organic isocyanides into the Ti-R bonds.⁸ The resulting compounds $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2(\eta^2\text{-RNCR})_2$ have been shown to subsequently undergo intramolecular coupling of the η^2 -iminoacyl groups to produce enediamide ligands, $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2[\text{RNC}(\text{R})=\text{C}(\text{R})\text{NR}]$.^{9,10} Treatment of the dibenzyl compound $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2(\text{CH}_2\text{Ph})_2$ with Bu^tNC (1 equiv) leads to the formation of the mono(η^2 -iminoacyl) compound $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2(\eta^2\text{-Bu}^t\text{NCCH}_2\text{Ph})(\text{CH}_2\text{Ph})$, which has been structurally characterized.⁸ The treatment of this bright yellow compound with pyridine ligands (L; 1 equiv) in hydrocarbon solvents is found to rapidly (typically minutes) produce orange solutions of the η^2 -imine compounds $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2[\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2](\text{L})$ (**1**) in high yield (Scheme I). Presumably the formation of **1** takes place by initial coordination of L to the metal, which induces the migration of the alkyl group to the η^2 -imino ligand. Consistent with this picture are a series of ^1H NMR experiments which clearly show that the rate of formation of **1** is enhanced by increasing the concentration of L present.¹¹

The spectroscopic data on compounds **1** are highly informative concerning their structure in solution. In the ^1H NMR spectrum, the methylene protons of the benzyl groups, $\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2$, appear as a simple, sharp, resolved AB pattern (Figure 1). Hence, the structure of **1** is such that the two benzyl groups are equivalent but do not lie on a mirror plane. Similarly the 2,6-diisopropyl phenoxide ligands are equivalent, only one septet for the CHMe_2 proton being observed, but the diastereotopic isopropyl methyl groups appear as two doublets, consistent with a pseudotetrahedral environment about the titanium metal center.⁸⁻¹⁰ These data agree with the adoption of either of the two geometries shown (Chart I) for **1** in so-

Table I. Selected Bond Distances (Å) and Angles (deg) for $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2[\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2](\text{py}-4\text{-Ph})$ (**1b**)

Ti-O(100)	1.848 (3)	Ti-O(200)	1.829 (4)
Ti-N(300)	1.846 (4)	Ti-N(500)	2.216 (5)
Ti-C(400)	2.158 (5)	C(400)-N(300)	1.421 (7)
O(100)-Ti-O(200)	114.2 (2)	O(100)-Ti-N(300)	114.4 (2)
O(100)-Ti-N(500)	100.5 (2)	O(100)-Ti-C(400)	113.1 (2)
O(200)-Ti-N(300)	104.8 (2)	O(200)-Ti-N(500)	90.4 (2)
O(200)-Ti-C(400)	130.5 (2)	N(300)-Ti-N(500)	130.5 (2)
N(300)-Ti-C(400)	40.6 (2)	N(500)-Ti-C(400)	94.4 (2)
Ti-O(100)-C(101)	154.6 (3)	Ti-O(200)-C(201)	174.2 (3)

Table II. Selected Bond Distances (Å) and Angles (deg) for $\text{Ti}(\text{OAr}-2,6\text{-Pr}^i)_2[\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2](\text{py}-4\text{-Et})$ (**1c**)

Ti-O(10)	1.854 (2)	Ti-O(20)	1.840 (2)
Ti-N(4)	1.855 (2)	Ti-N(31)	2.224 (2)
Ti-C(4)	2.150 (2)	N(4)-C(4)	1.410 (3)
O(10)-Ti-O(20)	113.64 (7)	O(10)-Ti-N(4)	104.14 (8)
O(10)-Ti-N(31)	91.88 (7)	O(10)-Ti-C(4)	131.22 (8)
O(20)-Ti-N(4)	115.51 (8)	O(20)-Ti-N(31)	99.80 (7)
O(20)-Ti-C(4)	112.81 (8)	N(40)-Ti-N(31)	129.76 (7)
N(4)-Ti-C(4)	40.41 (8)	N(31)-Ti-C(4)	94.27 (8)
Ti-O(10)-C(11)	161.6 (1)	Ti-O(20)-C(21)	175.3 (2)

lution. The equivalent benzyl and $\text{OAr}-2,6\text{-Pr}^i$ groups require the TiNC ring to be coplanar with the Ti-N(py) bond. Furthermore, the Bu^t group bound to the imine nitrogen must be oriented so as to generate a plane of symmetry through the $\text{Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2$ group; i.e., the nitrogen has become an amido function. Both of these conclusions are born out by the solid-state structures (vide infra). The ^{13}C NMR spectra of **1** confirm this picture and also clearly indicate the η^2 -CN binding of the imine fragment. The $\text{Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2$ carbon atom is found to resonate in the $\delta \sim 95$ ppm region. This is considerably upfield of the δ 240–260 ppm region typical for the carbon nuclei of η^2 -imino groups bound to titanium⁸ and is upfield of the region typical for simple σ -bound $\eta^2\text{-RN}=\text{CR}_2$ groups.¹² However, the region at which this carbon resonates is entirely reasonable for the carbon atom within an azametallacycle ring and is consistent with values reported for other early-d-block η^2 -imine compounds.⁵⁻⁷

A single-crystal X-ray diffraction analysis of the 4-phenylpyridine and 4-ethylpyridine derivatives **1b** and **1c** was carried out in order to accurately define the bonding characteristics of the η^2 -imine group. Selected bond dis-

(11) Addition of excess pyridine eventually causes the formation of low-valent titanium compounds and $\text{Bu}^t\text{N}=\text{C}(\text{CH}_2\text{Ph})_2$; see: Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Foltz, K.; Huffman, J. C. *J. Am. Chem. Soc.* 1987, 109, 4720.

(12) Reference 1, p 719.

Scheme II

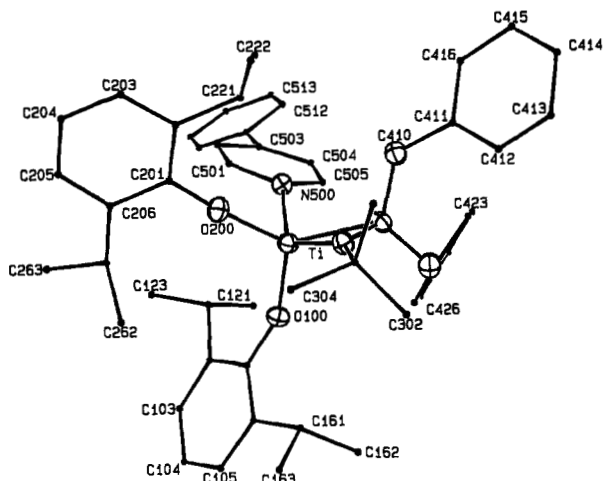
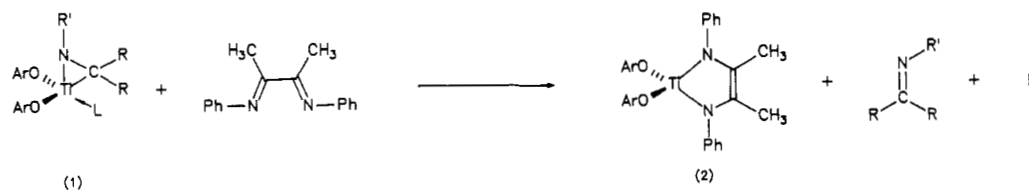


Figure 2. ORTEP view of $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2[\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2](\text{py-4-Ph})$ (**1b**) emphasizing the central coordination sphere.

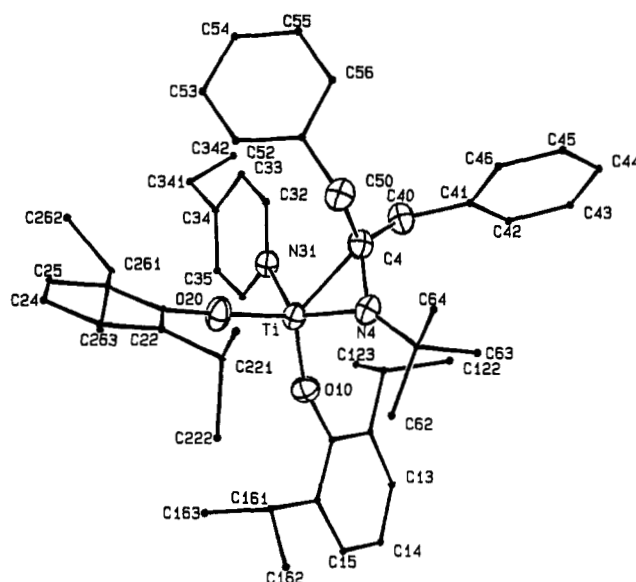


Figure 3. ORTEP view of $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2[\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2](\text{py-4-Et})$ (**1c**) emphasizing the central coordination sphere.

tances and angles are given in Tables I and II. It can be seen (Figures 2 and 3) that both molecules have very similar solid-state structures. If one considers the η^2 -imine group as occupying a single coordination site (cf. the olefin in Zeise's salt¹³), then the coordination environment about the metal is best described as pseudotetrahedral. In both molecules the CN vector of the η^2 -imine is approximately coplanar with the Ti-N(pyridine) bond. Also, consistent with the spectroscopic data, there is an effective (although not crystallographic) plane of symmetry through the molecules that make the aryloxy and benzyl groups equivalent. The O-Ti-O angle of 113–115° lies in the 110–125° range typical for many $(\text{ArO})_2\text{TiX}_2$ type molecules. Similarly the short Ti-O distances and large Ti-O-Ar angles are highly characteristic of aryloxy ligands bound to titanium(IV).^{8-10,14} It can be seen that the CN vector of the η^2 -imine ligand is oriented so that the nitrogen atom points away from the pyridine ligand. Hence, isomer A in Chart I is preferred. In this respect there is a great similarity between the solid-state structures of **1b** and **1c** and the η^2 -iminoacyl precursor $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2[\eta^2\text{-Bu}^t\text{NC}(\text{CH}_2\text{Ph})_2](\text{CH}_2\text{Ph})$.⁸ In the latter case the CN vector of the η^2 -imino group is coplanar with the Ti-C(benzyl) bond with the nitrogen atom pointing away.⁸

Of obvious specific interest to this study are the bonding parameters within the azametallacycle ring itself. It can be seen (Tables I and II) that these parameters differ only slightly between the two molecules in **1b** and **1c**. Furthermore, the C-N distances of 1.421 (7) Å and 1.410 (3) Å for **1b** and **1c** certainly are representative of single-bond distances: typical carbon-nitrogen single (amines), double (imines), and triple (alkyl isocyanides) bonds lie in the regions 1.47, 1.28, and 1.16 Å, respectively.^{8,9,15} This

distance is also elongated over the 1.257 (6)–1.286 (4)-Å range found for the CN bond of η^2 -imino ligands.⁸ The Ti-N(imine) distances of 1.846 (4) and 1.855 (2) Å are very short and comparable to distances found for dialkylamido ligands bound to titanium(IV) in which significant nitrogen p to metal d π -bonding is taking place.¹⁶ This distance is dramatically shorter than the distances of 2.216 (5) and 2.224 (8) Å to the pyridine ligands in **1b** and **1c**, respectively. The Ti-C(imine) distances 2.158 (5) and 2.150 (2) Å are comparable to the distances found to alkyl and aryl groups bound to titanium(IV).^{8,17} Hence, all of the structural parameters for **1b** and **1c** are totally indicative of the presence of an azametallacycle ring in which the imine fragment can be thought of as undergoing a two-electron reduction to produce an $(\text{RNCR}_2)^{2-}$ fragment. The CN bond has been reduced down to a bond order of 1, while the nitrogen and carbon atoms are bound to the metal in fashions typical of dialkylamido and alkyl groups, respectively.

Support for this bonding picture comes from the reaction of **1** with water, which results in the formation of titanium oxo products along with the organic amine $\text{Bu}^t\text{NHCH}(\text{CH}_2\text{Ph})_2$ in yields of 70–85%.¹⁸ Only trace (<5%) amounts of the imine $\text{Bu}^t\text{N}=\text{C}(\text{CH}_2\text{Ph})_2$ and its enamine tautomers¹⁹ could be observed from this reaction.

(15) Table 4 of ref 1, p 720, and: Kennard, O., Ed. *Molecular Structures and Dimensions*; N. V. A. Oosthoek's Uitgevers Mij, Utrecht, The Netherlands, 1972.

(16) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980.

(17) Cf. Ti-C distances of 2.106 (5), 2.070 (5), and 2.051 (4) Å in ref 14b and 2.131 (6) Å in: Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981.

(18) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. Submitted for publication in *Inorg. Chem.*

(13) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

(14) (a) Durfee, L. D.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 4569. (b) Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2019.

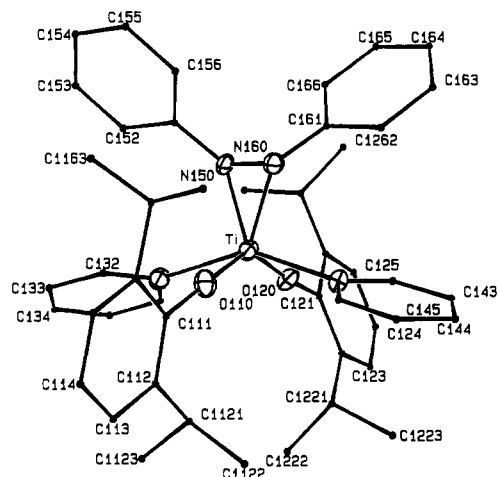
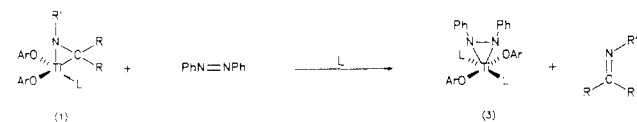


Figure 4. ORTEP view of $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2(\eta^2\text{-PhNNPh})(\text{py})_2$ (**3**) emphasizing the central coordination sphere.

Scheme III



Careful hydrolysis of **1d** in the presence of excess 4-pyrrolidinopyridine has in this case allowed isolation of a discrete titanium(IV) oxo compound, $\text{Ti}(\text{O})(\text{OAr-2,6-Pr}^i_2)_2(\text{py-4-pd})_2$.¹⁸ Structural studies have shown the presence of a terminal titanium-oxo group in this compound.¹⁸

Despite these results, it is also possible to carry out reactions with **1** that lead to the displacement of the imine compound $\text{Bu}^t\text{N}=\text{C}(\text{CH}_2\text{Ph})_2$ in high yield.¹¹ Hence, treatment of **1a** with the α -diimine molecule $\text{PhN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NPh}$ in hydrocarbon solvents leads to the displacement of pyridine and $\text{Bu}^t\text{N}=\text{C}(\text{CH}_2\text{Ph})_2$ and formation of an orange compound of stoichiometry $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2[\text{PhNC}(\text{Me})\text{C}(\text{Me})\text{Ph}]$ (**2**) (Scheme II). Spectroscopic data on **2** are consistent with it containing an enediamido ligand bound to titanium(IV).⁹ Similar compounds have been isolated from the intramolecular coupling of bis(η^2 -iminoacyl) precursors and structurally characterized.^{9,10} The overall reaction can be envisioned as involving the removal of the imine group in **1a** to leave behind a d^2 Ti(II) fragment, " $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2$ ", which then binds and reduces the α -diimine molecule. However, it is extremely doubtful that the reaction actually proceeds via a discrete Ti(II) intermediate.²⁰ Instead, the displacement of the initially bound imine group probably takes place by the incoming diimine. The transformation from strongly η^2 bound to simple η^1 (σ) bound is presumably a key step in the liberation of the imine from **1**.

Related reactivity is seen between **1a** and azobenzene. Heating a mixture of **1a** and $\text{PhN}=\text{NPh}$ in hexane at 80 °C in a sealed flask results, on cooling, in the formation of deep red needles of a compound of stoichiometry $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2(\text{PhNNPh})(\text{py})_2$ (**3**) (Scheme III). Carrying out the reaction in the presence of an extra 1 equiv of pyridine leads to a much higher yield of **3**, while analysis

Table III. Selected Bond Distances (Å) and Angles (deg) for $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2(\eta^2\text{-PhNNPh})(\text{py})_2$ (**3**)

Molecule 1			
Ti(1)-O(110)	1.836 (5)	Ti(1)-O(120)	1.845 (5)
Ti(1)-N(131)	2.271 (6)	Ti(1)-N(141)	2.267 (6)
Ti(1)-N(150)	1.949 (6)	Ti(1)-N(160)	1.963 (6)
N(150)-N(160)	1.416 (8)		
O(110)-Ti(1)-O(120)	138.4 (2)	O(110)-Ti(1)-N(131)	81.9 (2)
O(110)-Ti(1)-N(141)	384.3 (2)	O(110)-Ti(1)-N(150)	113.5 (3)
O(110)-Ti(1)-N(160)	104.4 (2)	O(120)-Ti(1)-N(131)	86.7 (2)
O(120)-Ti(1)-N(141)	84.6 (2)	O(120)-Ti(1)-N(150)	105.4 (2)
O(120)-Ti(1)-N(160)	114.2 (2)	N(131)-Ti(1)-N(141)	147.8 (2)
N(131)-Ti(1)-N(150)	86.3 (2)	N(131)-Ti(1)-N(160)	127.1 (2)
N(141)-Ti(1)-N(150)	126.0 (2)	N(141)-Ti(1)-N(160)	84.6 (2)
N(150)-Ti(1)-N(160)	42.4 (2)	Ti(1)-O(110)-C(111)	169.4 (4)
Ti(1)-O(120)-C(121)	175.7 (5)		
Molecule 2			
Ti(2)-O(210)	1.852 (6)	Ti(2)-N(231)	2.259 (6)
Ti(2)-N(250)	1.955 (8)	N(250)-N(250')	1.42 (1)
O(210)-Ti(2)-O(210')	136.5 (3)	O(210)-Ti(2)-N(231)	83.7 (2)
O(210)-Ti(2)-N(231)'	85.0 (2)	O(210)-Ti(2)-N(250)	116.0 (3)
O(210)-Ti(2)-N(250)'	104.7 (3)	N(231)-Ti(2)-N(231)'	149.2 (3)
N(250)-Ti(2)-N(250)'	42.7 (3)	Ti(2)-O(210)-C(211)	169.1 (5)

of the supernatant shows the presence of $\text{Bu}^t\text{N}=\text{C}(\text{CH}_2\text{Ph})_2$. A single-crystal X-ray analysis of **3** was undertaken in order to fully characterize the bonding mode of the azobenzene moiety (Figure 4). Some selected bond distances and angles for **3** are collected in Table III. There are two very similar, independent molecules within the unit cell of **3**. One of the molecules lies on a crystallographic mirror plane, while the other molecule occupies a general position, hence yielding $Z = 6$. The molecular structure of **3** is best described as square pyramidal about titanium with the η^2 -azobenzene group occupying the axial site. The mutually trans oxygen atoms and nitrogen atoms of the aryloxy and pyridine ligands form the basal sites with $\text{O-Ti-O} = 138.4(2)^\circ$ and $\text{N-Ti-N} = 147.8(2)^\circ$. The N-N vector of the η^2 -azobenzene is oriented approximately coplanar with the $\text{N}(\text{py})\text{-Ti-N}(\text{py})$ plane. The bonding of the aryloxy and pyridine ligands is as expected. The N-N bond lengths for the azobenzene ligands are 1.416 (8) and 1.42 (1) Å for the two independent molecules, very close to a single-bond distance (cf. the much shorter distance of 1.253 (3) Å in free $\text{PhN}=\text{NPh}$). This parameter, combined with the short Ti-N distances of 1.949 (6)–1.993 (6) Å, is consistent with a bonding picture involving $(\text{PhNNPh})^{2-}$ bound to titanium(IV).^{21,22} This picture is closely related to, in fact isoelectronic with, that observed for **1b** and **1c**. It is interesting that the N-N distances found in **3** are significantly longer than the distance of 1.339 Å reported for $\text{Cp}_2\text{Ti}(\eta^2\text{-PhNNPh})$. It therefore would appear, on the basis of this parameter, that the fragment " $\text{Ti}(\text{OAr})_2\text{L}_2$ " is more reducing than the bent titanocene unit, " Cp_2Ti ".

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either in a Vacuum Atmospheres Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone. The compound $\text{Ti}(\text{OAr-2,6-Pr}^i_2)_2(\eta^2\text{-Bu}^t\text{NCCH}_2\text{Ph})(\text{CH}_2\text{Ph})$ was obtained by previously reported procedures.⁸ The ^1H and ^{13}C NMR spectra were recorded on Varian Associates XL-200 and Varian Associates

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Table IV. Crystal Data and Data Collection Parameters

	1b	1c	3
formula	TiO ₂ N ₂ C ₅₄ H ₆₆	TiO ₂ N ₂ C ₅₀ H ₆₇	TiO ₂ N ₄ C ₄₆ H ₅₄
fw	823.04	776.00	742.87
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2
<i>a</i> , Å	12.970 (4)	10.748 (2)	38.770 (6)
<i>b</i> , Å	12.927 (3)	17.424 (3)	17.858 (3)
<i>c</i> , Å	28.140 (4)	24.673 (2)	9.892 (3)
β , deg	97.38 (2)	98.442	97.18 (2)
<i>V</i> , Å ³	4679 (3)	4570 (2)	6795 (5)
<i>Z</i>	4	4	6
density (calcd), g/cm ³	1.168	1.128	1.089
cryst size, mm	0.56 × 0.54 × 0.52	0.60 × 0.38 × 0.38	0.38 × 0.25 × 0.13
temp, °C	-155.0	-100	-162
radiation (λ , Å)	Cu K α (1.341 84)	Mo K α (0.710 73)	Mo K α (0.710 73)
linear abs coeff, cm ⁻¹	18.47	2.21	2.21
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	ω -2 θ	ω -2 θ	ω -2 θ
<i>h</i> , <i>k</i> , <i>l</i> limits	0 to 13, 0 to 13, -30 to 30	-11 to 11, 0 to 18, 0 to 26	0 to 41, 0 to 19, -10 to 10
2 θ range, deg	3.00-112.00	4.00-45.00	4.00-45.00
scan width, deg	0.80 + 0.35(tan θ)	0.50 + 0.35(tan θ)	0.52 + 0.35(tan θ)
takeoff angle, deg	4.60	1.90	1.80
program used	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius SDP
<i>F</i> ₀₀₀	1768.0	1676.0	2376.0
ρ factor used in weighting	0.070	0.060	0.040
no. of unique data	6427	6192	4603
no. of data with <i>I</i> > 3 σ (<i>I</i>)	3514	4812	4099
no. of variables	532	496	514
largest Δ/σ	0.05	0.08	0.00
<i>R</i> (<i>F</i>)	0.051	0.039	0.053
<i>R</i> _w (<i>F</i>)	0.068	0.056	0.081
goodness of fit	0.981	1.171	2.065

Gemini 200 spectrometers and are referenced to Me₄Si with use of protio impurities of commercial benzene-*d*₆ or toluene-*d*₈ as internal standards. Microanalytical data were obtained from the Purdue Microanalytical Laboratory.

Ti(OAr-2,6-Prⁱ)₂[η^2 -Bu^tNC(CH₂Ph)₂](py) (1a). To a solution of Ti(OAr-2,6-Prⁱ)₂(η^2 -Bu^tNCCH₂Ph)(CH₂Ph) (1.90 g, 1.84 mmol) in benzene (30 mL) was added pyridine (1.1 equiv). The initially golden yellow solution rapidly darkened to red and was stirred for 2 h. Removal of solvent and excess pyridine in vacuo yielded the crude product in essentially quantitative yield. Anal. Calcd for TiC₄₈H₆₂N₂O₂: C, 77.18; H, 8.37; N, 3.75. Found: C, 76.95; H, 8.49; N, 3.88. ¹H NMR (δ , C₆D₆, 30 °C): 3.63 (d, 3.77 (d, CH₂Ph); 1.30 (s, Bu^t); 3.73 (septet, CHMe₂); 1.16 (d), 1.19 (d, CHMe₂); 8.01 (broad, ortho py). ¹³C NMR (δ , C₆D₆, 30 °C): 95.0 (Bu^tNC); 47.0 (CH₂Ph); 64.1 (CMe₃); 32.5 (CMe₃); 26.7 (CHMe₂); 24.2 (CHMe₂).

Ti(OAr-2,6-Prⁱ)₂[η^2 -Bu^tNC(CH₂Ph)₂](py-4-Ph) (1b). An experimental procedure essentially identical with that described for the synthesis of 1a, only with 4-phenylpyridine instead of pyridine, yielded 1b. Recrystallization from benzene/hexane mixtures gave X-ray quality crystals. Anal. Calcd for TiC₅₄H₆₆N₂O₂: C, 78.80; H, 8.08; N, 3.40. Found: C, 78.59; H, 8.01; N, 3.65. ¹H NMR (δ , C₆D₆, 30 °C): 3.83 (d), 3.95 (d, CH₂Ph); 1.44 (s, Bu^t); 3.88 (septet, CHMe₂); 1.28 (d), 1.35 (d, CHMe₂). ¹³C NMR (δ , C₆D₆, 30 °C): 96.8 (Bu^tNC); 47.2 (CH₂Ph); 64.2 (CMe₃); 32.6 (CMe₃); 26.7 (CHMe₂); 24.3 (CHMe₂).

Ti(OAr-2,6-Prⁱ)₂[η^2 -Bu^tNC(CH₂Ph)₂](py-4-Et) (1c). Anal. Calcd for TiC₅₀H₆₇N₂O₂: C, 77.49; H, 8.58; N, 3.62. Found: C, 77.93; H, 9.26; N, 3.57. ¹H NMR (δ , C₆D₆, 30 °C): 3.72 (d), 3.67 (d, CH₂Ph); 1.28 (s, Bu^t); 3.69 (septet, CHMe₂); 1.19 (d), 1.13 (d, CHMe₂); 7.98 (broad, ortho py-4-Et); 1.88 (q, py-4-CH₂CH₃); 0.69 (t, py-4-CH₂CH₃). ¹³C NMR (δ , C₆D₆, 30 °C): 96.3 (Bu^tNC); 47.1 (CH₂Ph); 64.1 (CMe₃); 32.6 (CMe₃); 26.7 (CHMe₂); 24.3 (CHMe₂); 28.0 (py-4-CH₂CH₃); 13.6 (py-4-CH₂CH₃).

Ti(OAr-2,6-Prⁱ)₂[η^2 -Bu^tNC(CH₂Ph)₂](py-4-pd) (1d). ¹H NMR (δ , C₆D₆, 30 °C): 3.87 (s, overlapping CH₂Ph); 1.36 (s, Bu^t); 3.89 (septet, CHMe₂); 1.31 (d), 1.28 (d, CHMe₂); 7.81 (broad, ortho py-4-pd); 5.46 (broad, meta py-4-pd); 2.26 (broad, ortho py-4-pd); 1.07 (broad, meta py-4-pd). ¹³C NMR (δ , C₆D₆, 30 °C): 93.7 (Bu^tNC); 46.4 (CH₂Ph); 63.7 (CMe₃); 32.3 (CMe₃); 26.4 (CHMe₂); 24.0 (CHMe₂); 47.2 (ortho py-4-pd); 24.4 (meta py-4-pd).

Ti(OAr-2,6-Prⁱ)₂[PhNC(CH₃)=C(CH₃)NPh] (2). To a red hexane (15 mL) solution of 1a (0.5 g, 0.67 mmol) was added PhN=C(CH₃)C(CH₃)=NPh (0.16 g, 0.67 mmol) in benzene/

hexane (1:1, 10 mL). The mixture was stirred for 2 days before the solvent was removed under vacuum. Addition of hexane gave the product as a red solid, yield 74%. Anal. Calcd for TiC₄₀H₅₀N₂O₂: C, 75.21; H, 7.89; N, 4.39. Found: C, 74.88; H, 8.11; N, 4.38. ¹H NMR (δ , C₆D₆, 30 °C): 2.09 (s, PhNCMe₂); 3.66 (septet, CHMe₂); 1.27 (d, CHMe₂); 7.0-7.5 (m, aromatics). ¹³C NMR (δ , C₆D₆, 30 °C): 14.9 (PhNCMe₂); 27.5 (CHMe₂); 23.2 (CHMe₂).

Ti(OAr-2,6-Prⁱ)₂(η^2 -PhNNPh)(py)₂ (3). To a hexane (20 mL) solution of 1a (0.5 g, 0.67 mmol) was added azobenzene (0.12 g, 0.67 mmol) and pyridine (1 equiv). The mixture was heated at 80 °C in a sealed flask for 12 h. Slow cooling of the final mixture yielded 3 as dark red needles. Anal. Calcd for TiC₄₆H₅₄O₂: C, 74.37; H, 7.27; N, 7.53. Found: C, 74.43; H, 7.01; N, 7.56. ¹H NMR (δ , 30 °C): 1.1 (broad, CHMe₂); 3.5 (broad, CHMe₂); 8.7 (m, ortho py); 6.5-7.2 (aromatics). ¹³C NMR (δ , C₆D₆, 30 °C): 26.4 (CHMe₂); 23.5 (CHMe₂).

Crystallographic Studies

Selected crystal data and data collection parameters are collected together in Table IV.

A suitable crystal for each of the three compounds was mounted in a glass capillary in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement with the scattering angles of 25 reflections in the range 22.8° < θ < 33.5° for 1b, 21.5° < θ < 22.4° for 1c, and 19.7° < θ < 20.2° for 3 as measured by the computer-controlled diagonal-slit method of centering. Systematic absences and subsequent least-squares refinement indicated the space group *P*2₁/*c* for 1b and 1c and *C*2 for 3. The data were collected at room temperature by using the ω - θ scan technique. Cu K α radiation was used for 1b, while Mo K α was used for 1c and 3. The scan rate varied from 2 to 20 deg/min in ω , and data were collected to a maximum 2 θ of 112° for 1b and 45° for 1c and 3. Moving-crystal, moving-counter background counts were made by scanning an additional 25% above and below the scan width. The counter aperture was adjusted as a function of θ . For intense reflections an attenuator (factor 12.9) was automatically inserted in front of the detector. As a check on crystal and electronic stability three standard reflections were remeasured every 5000 s of beam time. No decay in standards was observed for all three samples.

The structures were solved by using the Patterson heavy-atom method to reveal the position of titanium atoms. The remaining

heavy atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structures, but their positions were not refined. All calculations, including the full-matrix least-squares refinement, were performed with use of the Enraf-Nonius SDP program package on a VAX computer.

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Supplementary Material Available: Listings of fractional coordinates, anisotropic thermal parameters, and all bond distances and angles (48 pages); listings of observed and calculated structure factors (78 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, Reactivity, and Diastereoisomer Separation of (tropone)Fe(CO)₂L Complexes (L = PPh₃, (+)-Neomenthylidiphenylphosphine)

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The title complexes have been prepared by amine oxide substitution of (tropone)Fe(CO)₃. The solid-state molecular structure of (tropone)Fe(CO)₂PPh₃ reveals a distorted-square-pyramidal geometry with a basal PPh₃ trans to the keto-substituted C=C bond; in solution, both basal isomers are populated. Rates of normal and inverse electron demand cycloaddition, and of sigma-haptotropic rearrangement, are much enhanced relative to those for the tricarbonyl. The (tropone)Fe(CO)₂(+)-neomenthylidiphenylphosphine diastereoisomer of 6*S* planar chirality may be isolated by crystallization. Though the rate of the 1,3-shift is enhanced relative to that for the tricarbonyl, normal and inverse electron demand cycloadditions and electrophilic attack proceed under mild conditions without racemization of the planar chirality.

Introduction

Cyclic and acyclic (η^4 -polyene)Fe(CO)₃ complexes continue to attract attention as intermediates, particularly for asymmetric synthesis.¹ For η^4 -triene complexes such as (tropone)- or (cycloheptatriene)Fe(CO)₃, interest has centered particularly on the regio- and stereoselectivity of reactions at the uncoordinated double bond. Thus, (tropone)Fe(CO)₃ (**1a**) may be protonated² or acylated³ at C-1 and undergoes 1,2-cycloadduct formation with a variety of reagents, including 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine,⁴ cyclopentadiene,⁵ nitrile oxides⁶ or imines,⁷ and diazoalkanes.⁸ The last has received application in the synthesis of cyclohexenone⁹ and β -thujaplicin,³ while 1,2-addition of CpFe(CO)₂(η^1 -allyl) complexes to oxygen-alkylated (tropone)Fe(CO)₃ provides access to 4-keto-hydroazulenes.¹⁰ Concerted cycloaddition of tetracyanoethylene (TCNE)¹¹ or 4-phenyltriazoline-3,5-dione (NPT-D)¹² results in kinetically controlled, predominant 1,3-addition; isomerization yields the thermodynamically favored 1,5-cycloadducts, which on oxidative decomplexation yield the product of formal 1,4-addition to the free ligand.¹³

Improved preparations of the related Fe(CO)₂(PR₃) derivatives also make these complexes attractive candidates due to their enhanced reactivity toward electro-

philes,¹⁴ the greater regioselectivity of the reactions of the derived dienyl salts with nucleophiles,¹⁵ and the possibility

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