

Reactivity of Group 4 Metal Alkyl and Metallacyclic Compounds Supported by Aryloxy Ligands Toward Organic Isocyanides

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The reactivity of the dimethyl compound $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2\text{Me}_2]$ (**1**) and titanabicyclic compounds $[(\text{ArO})_2\text{Ti}(\text{CH}_2\text{CH}(\text{C}_4\text{H}_8)\text{CHCH}_2)]$ (**6**, **7**) (formed by *trans*-coupling of 1,7-octadiene) toward organic isocyanides has been investigated. Dimethyl **1** reacts with 1 equiv of 2,6-dimethylphenylisocyanide (xyNC) to produce a cyclometalated product $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})(\text{OC}_6\text{H}_3\text{Ph}-\eta^1\text{-C}_6\text{H}_4)\{\text{N}(\text{xy})\text{CHMe}_2\}]$ (**2**), which was structurally characterized. Compound **2** is believed to arise via CH bond activation within an intermediate η^2 -imine (azatitanacyclopropane) formed by transfer of both methyl groups to the isocyanide. With an excess of xyNC , **1** produces an intermediate bis(η^2 -iminoacyl) **4**, which slowly converts to the enediamide $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2\{\text{N}(\text{xy})\text{CMeCMeN}(\text{xy})\}]$ (**5**). The solid-state structure of **5** shows the presence of a folded diazitanacyclopent-3-ene ring formed by intramolecular coupling of the two iminoacyl groups. Titanabicyclic compounds **6** and **7** react with Bu^tNC and xyNC respectively to generate products **8** and **9**, which both contain amide ligands derived by CH bond activation and an iminoacyl group formed by insertion into the new Ti–C bond. The solid-state structure of $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})\{\text{OC}_6\text{H}_3\text{Ph}-(\eta^2\text{-}(\text{C}_6\text{H}_4)\text{CNBu}^t)\}\{\text{Bu}^t\text{-NCH}(\text{C}_6\text{H}_{14})\}]$ (**8**) shows a *trans*-fusion between the five- and six-membered carbon rings as found in the initial titanabicyclic **6**. The treatment of **1** with xyNC in the presence of excess 3-hexyne or styrene produces azatitanacyclopent-2-ene **10** and azatitanacyclopentane **11** derivatives, respectively. These arise via coupling of the alkyne or olefin with an intermediate η^2 -imine. The solid-state structure of $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2\{\text{N}(\text{xy})\text{C}(\text{Me}_2)\text{C}(\text{Et})\text{C}(\text{Et})\}]$ (**10**) confirms its formulation.

Introduction

The migratory insertion of organic isocyanides (RNC) into early transition metal–alkyl, –hydride, –silyl, –amido, and –phosphido bonds is an important reaction in organometallic chemistry that has received considerable study over the last 25 years.^{1,2} The insertion chemistry of RNC with cationic group 4 transition metal systems has also recently received attention.³ Much of this interest has stemmed from the importance of relating this chemistry to the isoelectronic carbon monoxide (CO) molecule. The use of CO as a chemical feedstock through its activation by transition metal complexes and its subsequent conversion into useful organic molecules through migratory insertion–reductive elimination type reactions is an important area of study. Since organometallic compounds derived from reactions with RNC are generally more stable than their CO counterparts, in terms of the reversibility of insertion, their isolation and characterization is much easier. Therefore, RNC reactivity is often used as a model for CO reactivity.

An important characteristic feature of acyl, iminoacyl, and related transition metal complexes is the way in which the ligand binds to the metal center. Both η^1 - and

η^2 -type binding modes are possible. However, for high-valent, electron-deficient, early d-block, lanthanide, and

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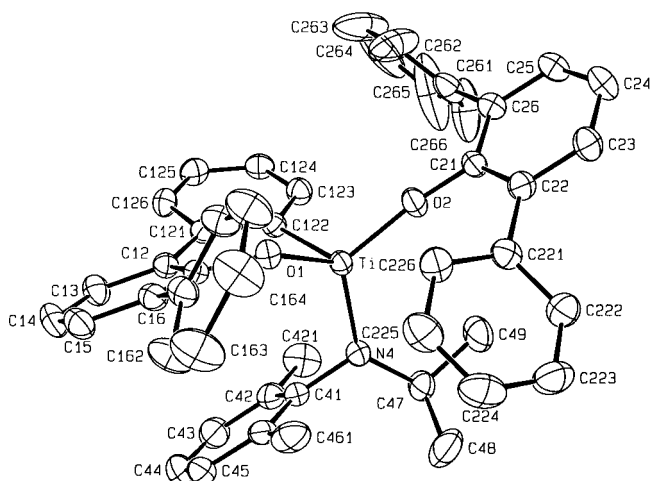


Figure 1. ORTEP (50% thermal ellipsoids) view of [Ti(OC₆H₃Ph₂-2,6)(OC₆H₃Ph- η^1 -C₆H₄){N(xy)CHMe₂}] (**2**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for [Ti(OC₆H₃Ph₂-2,6)(OC₆H₃Ph- η^1 -C₆H₄){N(xy)CHMe₂}], **2**

Ti–O(1)	1.829(1)	Ti–C(122)	2.075(2)
Ti–O(2)	1.804(1)	N(4)–C(41)	1.446(2)
Ti–N(4)	1.894(2)	N(4)–C(47)	1.487(2)
O(1)–Ti–O(2)	118.36(6)	Ti–O(1)–C(11)	130.2(1)
O(1)–Ti–N(4)	116.55(6)	Ti–O(2)–C(21)	163.5(1)
O(1)–Ti–C(122)	88.38(7)	Ti–N(4)–C(41)	113.9(1)
O(2)–Ti–N(4)	117.46(7)	Ti–N(4)–C(47)	131.7(1)
O(2)–Ti–C(122)	106.67(7)	C(41)–N(4)–C(47)	114.3(2)
N(4)–Ti–C(122)	102.41(7)		

Treatment of excess xyNC with **1** led to the bis(η^2 -iminoacyl) complex **4** (Scheme 1), which could not be isolated but was spectroscopically characterized. Hence it appears that the second insertion can compete with the second methyl migration within the intermediate mono(iminoacyl). The formation of **4** was most easily observed by noting the ¹³C NMR resonance of the iminoacyl carbon (δ 241.1). A solution of bis(η^2 -iminoacyl) **4** was also observed (¹H NMR, C₆D₆) to convert cleanly to a new product (**5**) over the course of several days. Layering of the final benzene solution with hexane afforded dark red crystals of the titanium enediamide **5**. The enediamide complex arises through intramolecular coupling of the η^2 -iminoacyl groups of **4**. Coupling of η^2 -iminoacyl ligands at group 4 metal centers has been extensively studied.⁴

Solid-state structural analysis of **5** (Figure 2, Table 2) shows a puckering of the five-membered diazametallacycle ring, resulting in the olefinic carbon atoms being brought closer to the metal center, possibly as an effort to relieve its electron deficiency. This type of structural distortion has been previously observed for related enediamide complexes.⁴ In the ¹H NMR spectrum of **5**, nonequivalent xylylmethyl signals show that both flipping of the nonplanar structure and aryl rotation are slow on the NMR time scale.

The reactivity described above for **1** contrasts with that found for the *trans*-titanabicyclic compounds [(ArO)₂Ti(CH₂CH(C₄H₈)CHCH₂)] **6** and **7**⁷ formed by intramolecular coupling of 1,7-octadiene (Scheme 2). Treatment of **6** and **7** with excess isocyanide led to orange products **8** and **9** (Scheme 2) that contain 2 equiv of isocyanide. Compounds **8** and **9** are related to the

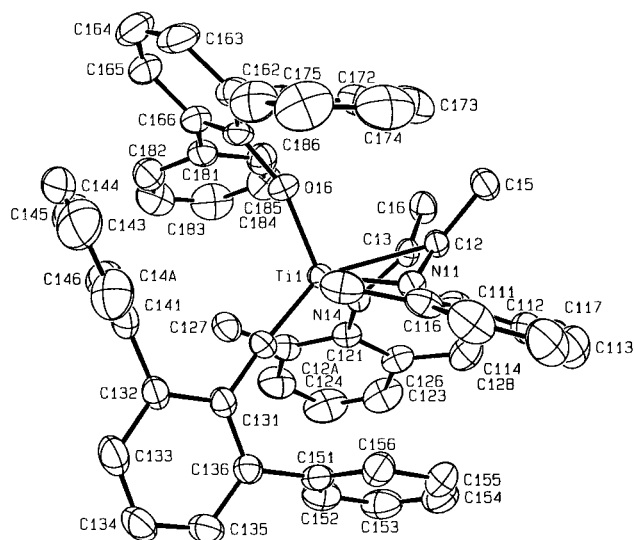


Figure 2. ORTEP (50% thermal ellipsoids) view of [Ti(OC₆H₃Ph₂-2,6)₂{N(xy)CMeCMeN(xy)}] (**5**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ti(OC₆H₃Ph₂-2,6)₂{N(xy)CMeCMeN(xy)}], **5**

molecule 1			
Ti(1)–O(13)	1.811(2)	Ti(1)–C(13)	2.394(3)
Ti(1)–O(16)	1.864(2)	N(11)–C(12)	1.396(4)
Ti(1)–N(11)	1.927(3)	N(14)–C(13)	1.379(4)
Ti(1)–N(14)	1.919(3)	C(12)–C(13)	1.391(5)
Ti(1)–C(12)	2.391(3)	O(16)–Ti(1)–C(13)	97.1(1)
O(13)–Ti(1)–O(16)	115.7(1)	N(11)–Ti(1)–N(14)	87.7(1)
O(13)–Ti(1)–N(11)	111.0(1)	Ti(1)–N(14)–C(13)	91.6(2)
O(13)–Ti(1)–N(14)	110.6(1)	N(14)–C(13)–C(12)	117.2(3)
O(13)–Ti(1)–C(12)	143.5(1)	C(13)–C(12)–N(11)	117.4(3)
O(13)–Ti(1)–C(13)	142.8(1)	N(11)–C(12)–Ti(1)	53.7(2)
O(16)–Ti(1)–N(11)	114.6(1)	N(14)–C(13)–Ti(1)	53.3(1)
O(16)–Ti(1)–N(14)	113.9(1)	Ti(1)–O(13)–C(131)	174.6(2)
O(16)–Ti(1)–C(12)	97.2(1)	Ti(1)–O(16)–C(161)	161.2(2)
molecule 2			
Ti(2)–O(23)	1.863(2)	Ti(2)–C(23)	2.392(3)
Ti(2)–O(26)	1.811(2)	N(21)–C(22)	1.398(4)
Ti(2)–N(21)	1.930(3)	N(24)–C(23)	1.395(4)
Ti(2)–N(24)	1.925(3)	C(22)–C(23)	1.381(5)
Ti(2)–C(22)	2.390(3)	O(26)–Ti(2)–C(23)	142.9(1)
O(23)–Ti(2)–O(26)	115.9(1)	N(21)–Ti(2)–N(24)	87.8(1)
O(23)–Ti(2)–N(21)	114.9(1)	Ti(2)–N(24)–C(23)	90.8(2)
O(23)–Ti(2)–N(24)	114.0(1)	N(24)–C(23)–C(22)	117.2(3)
O(23)–Ti(2)–C(22)	97.3(1)	C(23)–C(22)–N(21)	117.8(3)
O(23)–Ti(2)–C(23)	96.9(1)	N(21)–C(22)–Ti(2)	53.9(2)
O(26)–Ti(2)–N(21)	110.9(1)	N(24)–C(23)–Ti(2)	53.6(1)
O(26)–Ti(2)–N(24)	110.2(1)	Ti(2)–O(23)–C(231)	161.1(2)
O(26)–Ti(2)–C(22)	143.4(1)	Ti(2)–O(26)–C(261)	175.3(2)

cyclometalated species **3** except that a further equivalent of isocyanide has inserted into the cyclometalated Ti–C(aryl) bond. In this case it therefore appears that formation of the imine by ring closure within the monoiminoacyl intermediate is faster than the second insertion (Scheme 2). It has previously been shown that treatment of metallacyclopentadiene rings with isocyanide leads to η^2 -imine derivatives, which do not undergo cyclometalation.

Analysis of the solid-state structure of **8** (Figure 3, Table 3) shows the molecule to be pseudo-tetrahedral if one assumes that the η^2 -iminoacyl ligand occupies a single coordination site. Also indicated from the solid-state structure of **8** is that the bicyclic substituent of the amide ligand possess the *trans*-stereochemistry that is also present in the precursor **6**. There is evidence in

Scheme 2

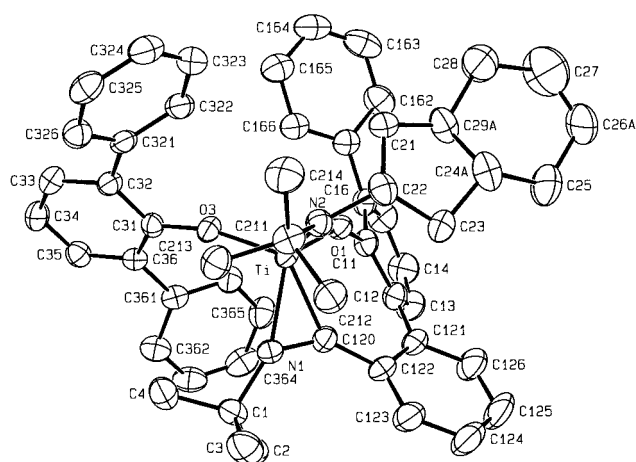
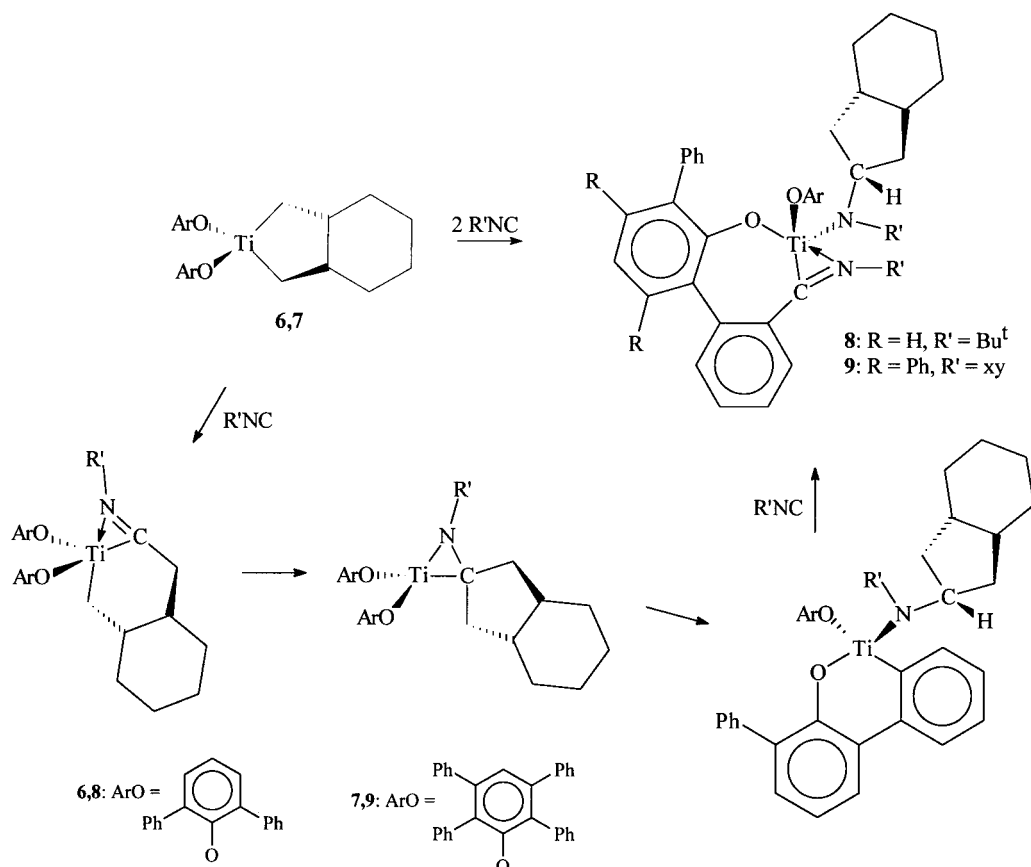


Figure 3. ORTEP (50% thermal ellipsoids) view of $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)\{\text{OC}_6\text{H}_3\text{Ph}-(\eta^2\text{-C}_6\text{H}_4\text{CNBu}^t)\}\{\text{Bu}^t\text{NCH}(\text{C}_8\text{H}_{14})\}]$ (**8**).

the solution ^1H and ^{13}C NMR spectra of **8** for two isomeric species being present in solution. For example, the ^{13}C NMR of **8** shows two iminoacyl resonances (δ 225.1 and 224.7), along with four Ti–O–C *ipso* carbon (δ 161.3, 160.9, 160.6, 160.6) and four N–CMe₃ (δ 29.7, 29.6, 28.91, 28.88) resonances, respectively. We interpret these data as being evidence for the presence of two diastereoisomers in the reaction product. These isomers are related by the stereochemistries of the three chiral carbon atoms within the amido substituent.

There has also been some investigation into the coupling of isocyanides with alkynes and olefins at group 4 metal centers.^{7,8} These coupling reactions are often

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)\{\text{OC}_6\text{H}_3\text{Ph}-(\eta^2\text{-C}_6\text{H}_4\text{CNBu}^t)\}\{\text{Bu}^t\text{NCH}(\text{C}_8\text{H}_{14})\}]$, **8**

Ti–O(1)	1.858(2)	Ti–C(120)	2.000(3)
Ti–O(3)	1.902(2)	N(1)–C(120)	1.258(4)
Ti–N(1)	2.085(2)	N(2)–C(22)	1.478(4)
Ti–N(2)	1.907(3)		
O(1)–Ti–O(3)	104.2(1)	N(1)–Ti–N(2)	110.3(1)
O(1)–Ti–N(1)	119.7(1)	N(1)–Ti–C(120)	35.8(1)
O(1)–Ti–N(2)	103.9(1)	N(2)–Ti–C(120)	105.6(1)
O(1)–Ti–C(120)	88.2(1)	Ti–C(120)–N(1)	75.8(2)
O(3)–Ti–N(1)	100.18(9)	C(120)–N(1)–Ti	68.4(2)
O(3)–Ti–N(2)	119.4(1)	Ti–O(1)–C(11)	142.6(2)
O(3)–Ti–C(120)	127.8(1)	Ti–O(3)–C(31)	166.0(2)

useful for the construction of cyclic and noncyclic compounds containing nitrogen heteroatoms. The formation of an η^2 -imine complex upon the treatment of **1** with 1 equiv of RNC was not observed but rather inferred on the basis of the formation of the final *ortho*-metallated product **2** (Scheme 1). However, trapping of the η^2 -imine complex with alkynes or olefins was achieved by prior addition of a large excess of 3-hexyne or styrene to **1** to RNC addition (Scheme 3). The resulting azatitanacyclopent-4-ene **10** and azatitanacyclopentane **11** species are formed from the reductive coupling of the η^2 -imine (formed from RNC) and 3-hexyne or styrene, respectively. If a large amount of

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Scheme 3

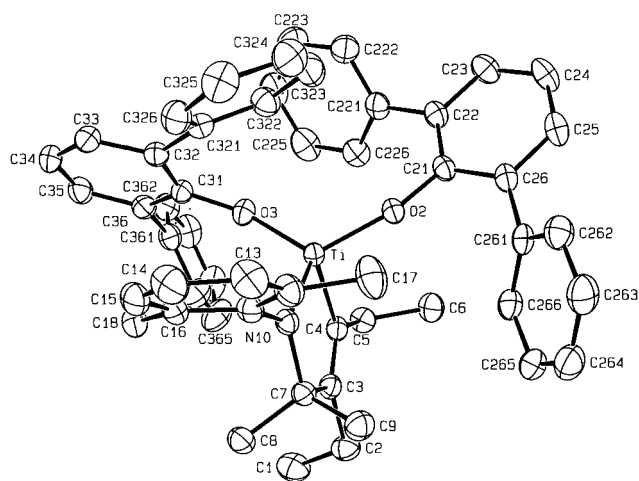
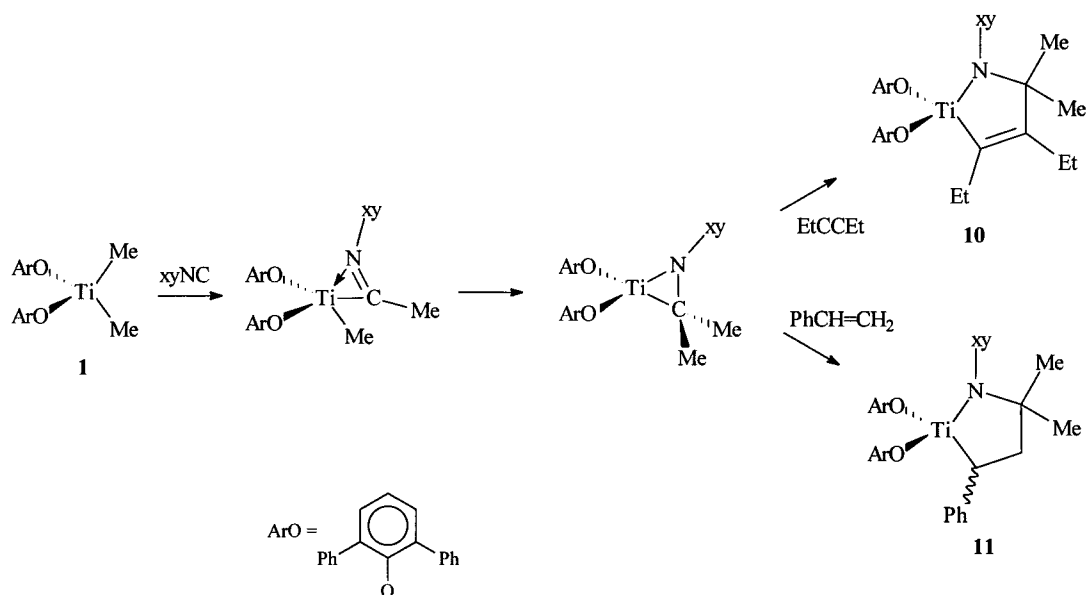


Figure 4. ORTEP (50% thermal ellipsoids) view of $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2\{\text{N}(\text{xy})\text{C}(\text{Me})_2\text{C}(\text{Et})\text{C}(\text{Et})\}]$ (**10**).

3-hexyne or styrene was not used, then a substantial amount of orthometalated product **2** was observed (^1H NMR) to form. Even in the presence of excess alkyne or olefin, small amounts of **2** were generated, which hampered purification. However, both **10** and **11** were characterized spectroscopically, and the regiochemistry of these organometallic products was readily confirmed by NMR methods.⁹ Specifically in the case of **11** the Ti-CHPh resonance at $\delta 101.6$ ppm compares with a value of 107.5 ppm found for the Ti-CHPh signal in azatitanacyclopentane $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2\{\text{CH}(\text{Ph})\text{CH}_2\text{CH}(\text{Ph})\text{N}(\text{Ph})\}]$.⁷

The solid-state structure of azatitanacyclopent-4-ene **10** was also obtained (Figure 4, Table 4). The molecular structure of **10** is best described as pseudo-tetrahedral, with bond distances and angles similar to other compounds of this type. The C(3)-C(4) bond distance is noticeably shorter [1.345(2) Å] than the C-C single bond distances in **10**, as expected.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2\{\text{N}(\text{xy})\text{C}(\text{Me})_2\text{C}(\text{Et})\text{C}(\text{Et})\}]$, **10**

Ti-O(2)	1.841(1)	C(3)-C(4)	1.345(2)
Ti-O(3)	1.829(1)	N(10)-C(11)	1.443(2)
Ti-N(10)	1.881(1)	C(7)-C(8)	1.535(3)
Ti-C(4)	2.053(2)	C(7)-C(9)	1.535(3)
N(10)-C(7)	1.506(2)	C(3)-C(2)	1.521(2)
C(7)-C(3)	1.540(2)	C(4)-C(5)	1.514(2)
O(2)-Ti-O(3)	119.98(6)	Ti-N(10)-C(7)	117.6(1)
O(2)-Ti-C(4)	102.15(6)	N(10)-C(7)-C(3)	106.3(1)
O(2)-Ti-N(10)	121.81(6)	C(7)-C(3)-C(4)	120.2(2)
O(3)-Ti-C(4)	109.91(6)	Ti-C(4)-C(3)	110.6(2)
O(3)-Ti-N(10)	110.70(6)	Ti-O(2)-C(21)	166.5(1)
N(10)-Ti-C(4)	84.73(7)	Ti-O(3)-C(31)	150.8(1)

Experimental Section

All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The hydrocarbon solvents were distilled from sodium benzophenone and stored over sodium ribbons under nitrogen until use. All other reagents were purchased from Aldrich Chemical Co., Inc., or Strem and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini-200, Inova-300, or General Electric QE-300 spectrometer and referenced to protio impurities of commercial benzene- d_6 or deuterated chloroform as internal standards. Mass spectra, elemental analyses, and molecular structures were obtained through Purdue in-house facilities.

Synthesis of $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})(\text{OC}_6\text{H}_3\text{Ph-}\eta^1\text{-C}_6\text{H}_4)\{\text{N}(\text{xy})\text{-CHMe}_2\}]$ (2**).** A sample of $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2\text{Me}_2]$ (**1**) (500 mg, 0.88 mmol) was dissolved in benzene. One equivalent of xyNC (115 mg, 0.88 mmol) dissolved in benzene was added, and the mixture was stirred for 30 min and evacuated to dryness. A minimal amount of hexane was added and upon standing yellow crystals of **2** formed (490 mg, 80%). Anal. Calcd for $\text{C}_{47}\text{H}_{41}\text{NO}_2\text{Ti}$: C, 80.68; H, 5.91; N, 2.00. Found: C, 80.49; H, 6.11; N, 1.89. ^1H NMR (C_6D_6 , 30 °C): δ 6.56–7.60 (aromatics); 3.01 [sp, $^3J(\text{H}-^1\text{H}) = 6.3$ Hz, CH], 1.40 (s), 1.34 (s, xyMe); 1.18 (d), 0.50 [d, $^3J(\text{H}-^1\text{H}) = 6.3$ Hz, CHMe₂]. ^{13}C NMR (C_6D_6 , 30 °C): δ 159.5 (Ti-O-C); 142.4, 140.4, 140.2, 138.5, 135.4, 135.2, 133.7, 133.4, 130.8, 130.6, 129.7, 129.3, 129.2, 128.5, 127.3, 126.8, 126.7, 126.5, 126.4, 124.6, 121.9 (aromatic); 61.6 (NCH); 23.6, 23.5, 20.5, 18.3 (Me).

Synthesis of $[\text{Ti}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})(\text{OC}_6\text{H}_3\text{Ph-}\eta^1\text{-C}_6\text{H}_4)\{\text{N}(\text{xy})\text{-CHMe}_2\}]$ (2**).** A sample of **2** was dissolved in benzene- d_6 in a

(9) (a) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (b) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *J. Am. Chem. Soc.* **1989**, *111*, 776.

NMR tube and titrated with 4-phenylpyridine, causing a change in the color of the solution from yellow to yellow/green. The solution was layered with hexane, inducing the formation of yellow/green crystals of **3**. Anal. Calcd for $C_{58}H_{50}N_2O_2Ti$: C, 81.49; H, 5.89; N, 3.28. Found: C, 80.36; H, 5.92; N, 2.88. 1H NMR (C_6D_6 , 30 °C): δ 8.54 [d, $^3J(H-H) = 7.0$ Hz, *ortho*-py]; 6.56–7.60 (aromatics); 5.46 [sp, $^3J(H-H) = 5.9$ Hz, *CH*]; 1.76 (s), 1.23 (s, *xyMe*); 0.77 (d), 0.74 (d, *CHMe*). ^{13}C NMR (C_6D_6 , 30 °C): δ 159.8, 158.1 (Ti–O–C); 150.4, 142.0, 137.0, 135.2, 134.1, 131.0, 130.8, 129.7, 129.6, 129.3, 128.8, 128.3, 127.8 (aromatic); 60.4 (NCH); 23.6, 22.0, 20.1, 19.7 (*Me*).

Synthesis of [Ti(OC₆H₃Ph₂-2,6)₂(η^2 -*xyNCMe*)₂] (4). To an excess of *xyNC* dissolved in deuterated benzene was added [Ti(OC₆H₃Ph₂-2,6)₂Me₂] (**1**), initially forming a red solution of the bis(η^2 -iminoacyl) product **4**, which could be spectroscopically characterized. 1H NMR (C_6D_6 , 30 °C): δ 6.70–7.59 (aromatics); 1.54 (s, *xyMe*); 1.10 (s, *NCMe*). ^{13}C NMR (C_6D_6 , 30 °C): δ 241.1 (*NCMe*); 161.3 (Ti–O–C); 144.9, 141.2, 132.1, 130.8, 130.2, 130.1, 128.8, 128.3, 128.2 (aromatic); 21.0 (*NCMe*); 18.2 (*xyMe*).

Synthesis of [Ti(OC₆H₃Ph₂-2,6)₂{N(*xy*)CMeCMeN(*xy*)}] (5). Over the course of several days compound **4** slowly converted to **5** as monitored by NMR. Layering of the resulting benzene solution with hexane afforded dark red crystals of **5**. Anal. Calcd for $C_{56}H_{50}N_2O_2Ti$: C, 80.95; H, 6.07; N, 3.37. Found: C, 80.88; H, 6.00; N, 3.44. 1H NMR (C_6D_6 , 30 °C): δ 6.71–7.28 (aromatic); 1.70 (s), 1.38 (s, *xyMe*); 1.44 (s, *CMe*). ^{13}C NMR (C_6D_6 , 30 °C): δ 158.8 (Ti–O–C); 146.6, 141.0, 139.6, 134.1, 133.2, 132.9, 131.0, 130.3, 130.1, 129.9, 129.8, 129.7, 129.3, 129.3, 128.7, 128.5, 127.5, 127.1, 127.0, 126.6, 126.0, 123.9, 121.6, 120.4, 110.7 (aromatic); 31.9 (*CMe*); 19.2, 15.3 (*xyMe*).

Synthesis of [Ti(OC₆H₃Ph₂-2,6){OC₆H₃Ph(η^2 -C₆H₄-CNBu^t)}] (6). A sample of [Ti(OC₆H₃Ph₂-2,6)₂{CH₂CH(C₄H₉)CHCH₂}] (**6**) (200 mg, 0.31 mmol) was dissolved in benzene. Six equivalents of *tert*-butylisocyanide (209 μ L, 1.85 mmol) was added, and the mixture was stirred for 1 h and then evacuated to dryness, affording a crude solid, which was recrystallized as orange crystals of **8** from benzene/pentane (150 mg, 60%). Anal. Calcd for $C_{54}H_{58}N_2O_2Ti$: C, 79.59; H, 7.17; N, 3.44. Found: C, 79.73; H, 7.05; N, 3.18. 1H NMR (C_6D_6 , 30 °C): δ 6.67–7.66 (aromatics); 0.26–2.90 (aliphatics); 0.84 (s), 0.83 (s), 0.76 (s), 0.75 [s, NC(CH₃)₃]. ^{13}C NMR (C_6D_6 , 30 °C): δ 225.1, 224.7 (η^2 -NC); 161.3, 160.9, 160.6, 160.6 (Ti–O–C); 143.8, 143.6, 142.3, 141.7, 141.5, 141.4, 134.5, 134.3, 133.9, 133.6, 133.4, 133.1, 132.0, 131.8, 131.0, 130.3, 130.2, 130.1, 128.9, 128.5, 127.8, 126.8, 126.6, 126.1, 122.5, 122.4, 120.9, 119.3 (aromatic); 62.0, 61.8, 61.4, 60.5, 59.1, 58.9, (NC); 46.7, 46.6, 46.4, 46.3, 46.1, 44.6, 43.8, 43.7, 32.9, 32.5, 31.9, 31.6, 27.1, 26.9 (aliphatics); 29.7, 29.6, 28.91, 28.88 [NC(CH₃)₃].

Synthesis of [Ti(OC₆HPh₄-2,3,5,6){OC₆HPh₃(η^2 -C₆H₄-CN^{xy})}] (9). A sample of [Ti(OC₆HPh₄-2,3,5,6)₂(CH₂CH(C₄H₉)CHCH₂)] (**7**) (200 mg, 0.20 mmol) was dissolved in benzene. Two equivalents of *xyNC* was added, and the mixture was stirred for 1 h and then evacuated to dryness, affording a crude solid, which was recrystallized as orange crystals from benzene/pentane (90 mg, 37%). Anal. Calcd for $C_{86}H_{74}N_2O_2Ti$: C, 84.99; H, 6.14; N, 2.30. Found: C, 85.59; H, 6.48; N, 2.10.

Synthesis of [Ti(OC₆H₃Ph₂-2,6)₂{N(*xy*)C(Me)₂C(Et)C(Et)}] (10). A sample of [Ti(OC₆H₃Ph₂-2,6)₂Me₂] (**1**) (500 mg, 0.88 mmol) was dissolved in benzene along with a large excess of 3-hexyne (approximately 2 mL). One equivalent of *xyNC* (115 mg, 0.88 mmol) dissolved in benzene was slowly added, and the mixture was stirred overnight and then evacuated to dryness. A minimal amount of hexane was added, and upon standing both yellow (minor) and orange crystals formed. The minor contaminant was observed to be **4**. The major component was the title complex. 1H NMR (C_6D_6 , 30 °C): δ 6.58–7.42 (aromatics); 1.84 [q, $^3J(H-H) = 7.6$ Hz, CH₂CH₃]; 1.77 (s,

xyMe); 1.71 [q, $^3J(H-H) = 7.6$ Hz, CH₂CH₃]; 0.98 (m, CH₂CH₃); 0.72 (s, *NCMe*). ^{13}C NMR (C_6D_6 , 30 °C): δ 217.7 (Ti–O); 159.7 (Ti–O–C); 140.2, 136.0, 133.2, 130.6, 129.6, 128.6, 128.5, 128.4, 126.8, 125.6, 121.4 (aromatic); 67.6 (*NCMe*); 27.4 (*xyMe*); 20.7, (*NCMe*); 21.2, 20.7 (CH₂CH₃); 15.0, 14.5 (CH₂CH₃).

Synthesis of [Ti(OC₆H₃Ph₂-2,6)₂{N(*xy*)C(Me)₂-CH₂CHPh}] (11). A sample of [Ti(OC₆H₃Ph₂-2,6)₂Me₂] (**1**) (300 mg, 0.53 mmol) was dissolved in benzene along with a large excess of styrene (approximately 2 mL). One equivalent of *xyNC* (70 mg, 0.53 mmol) dissolved in benzene was slowly added, and the mixture was stirred overnight and evacuated to dryness, affording a red oil. 1H NMR (C_6D_6 , 30 °C): δ 6.56–7.16 (aromatics); 4.08 (m, *CHPh*); 3.54 (dd), 2.56 (dd, *CH*); 2.10 (s), 1.07 (s, *xyMe*); 0.77 (s), 0.55 (s, *CMe*). ^{13}C NMR (C_6D_6 , 30 °C): δ 159.6 (Ti–O–C); 148.3, 135.6, 135.0, 131.1, 130.2, 129.8, 129.3, 129.1, 128.9, 128.8, 128.7, 128.4, 128.3, 127.3, 127.1, 126.9, 125.4, 125.2, 124.2, 121.8 (aromatic); 101.6 (Ti–CHPh), 63.6 (*xyNC*); 39.8, 31.9, 25.7, 28.2, 21.9, 20.4. A minimal amount of hexane was added, and upon extended standing dark red crystals formed, which were determined to be the enediamide compound **9**. Presumably formation of **9** occurred due to the presence of excess isocyanide being present in the initial reaction mixture, which lead to the formation of **8**.

X-ray Data Collection and Reduction. Full details are contained in the Supporting Information. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data.¹⁰ An empirical absorption correction using SCALEPACK was applied.¹¹ Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.¹² The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares, where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Scattering factors were taken from the "International Tables for Crystallography".¹³ Refinement was performed on a AlphaServer 2100 using SHELX-97.¹⁴ Crystallographic drawings were done using the programs ORTEP.¹⁵

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Supporting Information Available: Description of the experimental procedures for X-ray diffraction studies. Tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and multiplicities for **2**, **5**, **8**, and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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