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Synthesis and Reactions of Group 4 Imido Complexes Supported by Cyclooctatetraene Ligands

Simon C. Dunn, Nilay Hazari, Andrew R. Cowley, Jennifer C. Green,* and Philip Mountford*

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

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The reactions of the pseudo-two-coordinate titanium imido complexes [Ti(N^{t}Bu)(COT)] (**1**) (COT = η^8-C_8H_8), [Ti(N^{t}Bu)(COT″)] (**2**) (COT″ = η^8-1,4-$C_8H_6(SiMe_3)_2$), and [Ti(NAr)(COT)] (**3**) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with a variety of organic substrates are reported. Reaction of **1** with CO$_2$, ^{t}BuNCO, or ArNCO and reaction of **3** with CO$_2$ or ^{t}BuNCO afforded the organic products ^{t}BuNCO, ^{t}BuNCN^{t}Bu, ^{t}BuNCNAr, ArNCO, and ArNCN^{t}Bu, respectively, and a titanium oxo species. These reactions proceeded via an initial [2 + 2] cycloaddition to form an N,O-bound intermediate of the type [Ti{N(R)C(O)R′}(COT)], which subsequently underwent a retrocycloaddition to give an organic product and the titanium oxo species. In contrast, reaction of **3** with ArNCO led to the formation of the N,N-bound [2 + 2] cycloaddition product [Ti{N(Ar)C(O)N(Ar)}(COT)] (**7**). In general, the reactions of **1** and **3** with CS$_2$ and isothiocyanates also resulted in an initial [2 + 2] cycloaddition to form an N,S-bound intermediate of the type [Ti{N(R)C(S)R′}(COT)], which also subsequently underwent a retrocycloaddition to give an organic product and a metal sulfide species. However, the N,S-bound compound [Ti{N(Ar)C(S)S}(COT)] (**10**) was stable to retrocycloaddition and was isolated. Proton transfer reactions occurred between pinacol and compounds **1**−**3** to form the bis(alkoxide) species [Ti{OC(Me)$_2$C(Me)$_2$O}(COT)] (**11**) (from **1** or **3**) or [Ti{OC(Me)$_2$C(Me)$_2$O}(COT″)] (**12**) (from **2**) and the corresponding free amine. The reactions between **1**−**3** and 2 equiv of the thiols ^{t}BuSH and HS-2,4,6-^{i}Pr$_3$C$_6$H$_2$ all resulted in the oxidation of the thiol to the disulfides ^{t}BuS−S^{t}Bu and (2,4,6-^{i}Pr$_3$C$_6$H$_2$)S−S(2,4,6-^{i}Pr$_3$C$_6$H$_2$). Treatment of **1** with ^{t}BuNC in the presence of 1,3,5,7-cyclooctatetraene led to formal nitrene group transfer and the formation of the Ti(II) species [Ti(COT)(η^4-C_8H_8)] (**13**) and ^{t}BuNCN^{t}Bu. The analogous reactions between **2** and **3** and ^{t}BuNC resulted in the formation of the adducts [Ti(N^{t}Bu)(COT″)(CN^{t}Bu)] (**15**) and [Ti(NAr)(COT)(CN^{t}Bu)] (**17**), and similarly the reaction between **1** and pyridine led to the isolation of the adduct [Ti(N^{t}Bu)(COT)(py)] (**19**) (py = pyridine). Complex **19** was crystallographically characterized. DFT studies indicated that the interaction between pyridine and the Ti center in **19** and ^{t}BuNC and the Ti center in **17** was electrostatic in nature. Complexes of the type [Ti(NR)(COT)(AlMe$_{3-x}$Cl$_x$)] (R = ^{t}Bu, $x = 0$ (**20**); R = Ar, $x = 0$ (**21**); R = ^{t}Bu, $x = 1$ (**22**); R = Ar, $x = 1$ (**23**)) were formed through the reactions of **1** and **3** with AlMe$_3$ and AlMe$_2$Cl, and DFT studies indicated that they contained four-membered metallacyclic rings. Attempts to prepare monomeric zirconium imido cyclooctatetraene complexes through the reactions of [Zr$_2$(μ-NR)$_2$Cl$_4$(THF)$_x$] (R = ^{t}Bu, $x = 3$; R = 2,6-Me$_2$C$_6$H$_3$(Ar′), $x = 4$) with K$_2$COT, Li$_2$COT″·1.8(THF), or Li$_2$[COT*] (COT* = 1,4-C$_8$H$_6$(SiMe$_2{}^t$Bu)$_2$) were unsuccessful. Only the crystallographically characterized dimeric species [Zr$_2$(μ-NAr′)$_2$(COT″)$_2$] (**24**) was isolated.

Introduction

Terminal titanium imido complexes of the type (L)$_n$Ti═NR (where (L)$_n$ represents a supporting ligand set and R is generally an alkyl or aryl group) were first structurally characterized in 1990.[1,2] Since then, a large number of such complexes with different ancillary ligands have been synthesized and considerable effort has been spent on investigating their reactivity.[3−8] These compounds have proven capabilities in materials chemistry (as a source of TiN),[9−12] as intermediates in hydroamination,[13−20] and as catalysts for olefin polymerization (Ti═NR acting as a "spectator ligand").[7,21,22] However, it is the

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* To whom correspondence should be addressed. E-mail: philip.mountford@chem.ox.ac.uk.

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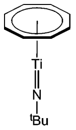
ability of the Ti═NR bond to act as a reactive site toward unsaturated substrates that has attracted the most attention. Titanium imides react with many organic substrates including alkenes, allenes, alkynes, heterocumulenes, nitriles, isonitriles, isocyanates, and phosphaalkynes, and in many cases these reactions result in the formation of both novel organic products and metal-containing species.[8]

We recently reported the syntheses of a series of highly unusual pseudo-two-coordinate titanium imido cyclooctatetraenyl complexes of the type [Ti(NR)(COT)] or [Ti(NR)(COT″)] (R = alkyl or aryl, COT = η^8-C_8H_8, COT″ = η^8-1,4-$C_8H_6(SiMe_3)_2$).[23] Density functional theory (DFT) analysis indicated that in these complexes binding of the titanium to the imido nitrogen atom is primarily through σ- and π-interactions, whereas binding to the COT or COT″ rings is almost exclusively through δ-symmetry orbitals. Both the geometry and the electronic structure of these complexes are unique in early transition metal chemistry, and therefore we hoped that these species would display unusual reactivity compared with other metal imido complexes. In this contribution we describe the reactivity of the titanium imido cyclooctatetraenyl species [Ti(N^{t}Bu)(COT)] (**1**), [Ti(N^{t}Bu)(COT″)] (**2**), and [Ti(NAr)(COT)] (**3**) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with CO_2, CS_2, isocyanates, PhNO, isothiocyanates, alcohols, thiols, isocyanides, and Lewis acids and bases, together with attempts to synthesize analogous monomeric zirconium imido cyclooctatetraene complexes.



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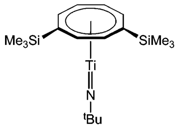

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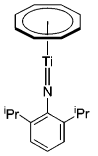

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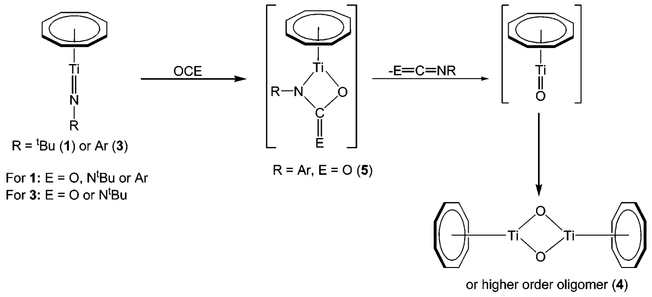
Results and Discussion

Reactions with CO_2, Isocyanates, and PhNO. Cycloaddition reactions of titanium imides with CO_2 have been reported for a number of systems.[24−30] In general these reactions result in [2 + 2] cycloaddition of CO_2 to the Ti═NR bond to generate a carbamate product of the type [(L)$_n$Ti{OC(O)N(R)}], although these are not always sufficiently stable to be observed. Thus, depending on the identity of (L)$_n$ and R, the carbamates can in turn extrude the corresponding isocyanate RNCO via a retro-cycloaddition process forming either terminal or dimeric titanium oxo products, or another molecule of CO_2 can insert into the Ti−N bond of the carbamate. The reactions of titanium imido compounds with isocyanates RNCO are also well established and can lead to either N,O- or N,N-bound ureate complexes.[25−28,30−34] These can often be isolated but may also extrude either a molecule of carbodiimide (RN═C═NR′) to form the corresponding titanium oxo compound or a molecule of a different isocyanate (RNCO), leading to a new titanium imido compound.

Scheme 1



The reactions of [Ti(N^{t}Bu)(COT)] (**1**) with CO_2, ^{t}BuNCO, and ArNCO (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) and of [Ti(NAr)(COT)] (**3**) with ^{t}BuNCO all generated an organic product and an insoluble brown powder (**4**) (Scheme 1). The organic products were identified by ^{1}H and ^{13}C NMR spectroscopy when the reaction was performed on an NMR tube scale. The organic products were ^{t}BuNCO in the reaction of **1** with CO_2, ^{t}BuNCN^{t}Bu in the reaction of **1** with ^{t}BuNCO, ^{t}BuNCNAr[35] in the reaction of **1** with ArNCO, and ^{t}BuNCNAr[35] in the reaction of **3** with ^{t}BuNCO. As a result of the insolubility of **4**, it was not possible to purify it or obtain any NMR data on its composition. However, the IR spectra of **4** revealed that a common species was being formed in all four reactions. These observations are consistent with the formulation of **4** as an oxo species.

Terminal titanium oxo compounds of the form [(L)$_n$Ti(O)] are rare and generally dimerize to generate bridging oxo species of the type [{(L)$_n$}$_2$Ti$_2$(μ-O)$_2$].[26,27,36−39] Given the minimal steric requirements of the COT ligand, a terminal oxo species of the type [Ti(O)(COT)] could potentially oligermize to form a higher order oxo species of the form [Ti(O)(COT)]$_n$ (**4**). The low solubility of **4** is consistent with a dimeric (or oligomeric) structure, and we have previously shown that monomeric titanium COT compounds such as **1**−**3** are significantly more soluble than related dimeric compounds such as [Ti$_2$(μ-NAr′)$_2$(COT)$_2$] (Ar′ = 2,6-Me$_2$C$_6$H$_3$) and [Ti$_2$(μ-NPh)$_2$(COT″)$_2$].[23] Unfortunately, satisfactory elemental analysis could not be achieved for **4**, as low %C analyses were consistently obtained

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compared with the expected composition. This is attributed to incomplete combustion, which has previously been observed for other titanium cyclooctatetraene compounds.[23] In addition, neither a parent ion peak nor an identifiable fragment was observed in the mass spectrum of **4**.

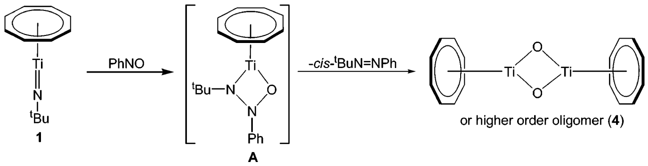
The proposed mechanism for the formation of **4** and the organic product involves an initial [2 + 2] cycloaddition between **1** or **3** and the unsaturated substrate to give an N,O-bound intermediate (Scheme 1). This intermediate undergoes a retrocycloaddition to give an oxo species and the organic product. The oxo species then dimerizes/oligmerizes as explained above. Although no evidence for either a [2 + 2] cycloaddition product or a transient terminal oxo species was observed in the reactions described above, the intermediate [Ti{N(Ar)C(O)O}(COT)] (**5**) was observed by ^{1}H and ^{13}C NMR spectroscopy in the reaction of [Ti(NAr)(COT)] (**3**) with CO_2. When the reaction was performed on an NMR tube scale, resonances corresponding to **5** were initially present along with resonances corresponding to the organic product ArNCO. Five minutes after the addition of CO_2 to the reaction mixture the ratio of **5** to ArNCO was approximately 95:5. Over time the resonances corresponding to ArNCO increased in intensity, while those associated with **5** decreased. A brown solid precipitated out of solution and was isolated and characterized as the oxo species **4** in a preparative scale reaction.

The presence of [Ti{N(Ar)C(O)O}(COT)] (**5**) in the reaction mixture is supported by several characteristic features in the ^{1}H and ^{13}C NMR spectra. First, two separate resonances are observed in both the ^{1}H and ^{13}C NMR spectra for the ring isopropyl methyl groups. This is consistent with the loss of symmetry that occurs when **3** is converted to **5** and is also indicative of restricted rotation around the $N-C_{aryl}$ bond. Second, a resonance is observed at δ 164.5 ppm in the ^{13}C NMR spectrum. This low-field chemical shift is typical for the carbon atom in four-membered metallacycles, which arise from the cycloaddition of CO_2 with titanium imides.[25−27,30]

Attempts to isolate [Ti{N(Ar)C(O)O}(COT)] (**5**) in preparative scale reactions were unsuccessful due to the tendency of **5** to undergo retrocycloaddition, and a pure sample could not be isolated. However, the detection of the intermediate **5** by ^{1}H and ^{13}C NMR spectroscopy clearly supports the mechanism proposed for the formation of an oxo species from an imide and CO_2 or isocyanate. In addition, there is significant precedent for this mechanism, as there are many examples of isolated N,O-bound [2 + 2] cycloaddition products from the reactions of CO_2 and isocyanates with titanium imido species.[25−27,30,34] There are also numerous examples of these cycloaddition products then undergoing retrocycloadditions to give an oxo species and an organic product.[25−27,30,33] Furthermore, it has previously been observed that aryl imido substituents confer slightly greater stability on the intermediate cycloaddition species than alkyl imido substituents.[26,34] This may explain why [Ti{N(Ar)C(O)O}(COT)] (**5**) is observed in the reaction between **3** and CO_2, whereas no intermediate is detected in the reaction of [Ti(N^{t}Bu)(COT)] (**1**) with CO_2.

To confirm the identity of **4**, it was synthesized using an alternative route. Recently, metathesis reactions of terminal imido compounds $(L)_nM = NR$ (M = Ti or Zr) with PhNO to form metal oxo species and diazo compounds RN═NPh have been reported.[34,40−42] The reaction of [Ti(N^{t}Bu)(COT)] (**1**) with nitrosobenzene afforded the *cis* azo compound ^{t}BuN═NPh and a brown powder (**4**) (Scheme 2). The IR spectrum of the brown powder (**4**) was identical to the sample obtained above from the reactions of **1** and **3** with CO_2 and ^{t}BuNCO (Scheme 2). The organic product *cis*-^{t}BuN═NPh was characterized by NMR spectroscopy from the NMR tube scale reaction and is the kinetic product of this reaction. Over a period of 24 h the organic product underwent a known thermal rearrangement to form *trans*-^{t}BuN═NPh.[43] The initial formation of *cis*-^{t}BuN═NPh implies that the first-formed intermediate in this reaction is probably the [2 + 2] cycloaddition product **A** shown in Scheme 2.

Scheme 2



The metathesis reaction between **1** and PhNO is similar to other reactions between imides and PhNO and confirms the identity of **4** as an oxo species.[34,40−42] As in the corresponding zirconium chemistry, the putative metallacyclic intermediate **A** was not observed.[40,42] The instability of **A** is consistent with the inherently weak nature of O−N and N−N single bonds, which is typically attributed to secondary electron−electron repulsion.[44]

We have previously shown that [Ti(N^{t}Bu)(COT)] (**1**) and [Ti(N^{t}Bu)(COT′′)] (**2**) have almost identical electronic structures, and hence we expected that they would display similar reactivity.[23] The reactions of **2** with CO_2 and ^{t}BuNCO resulted in the formation of an organic product and an insoluble black powder. The organic products ^{t}BuNCO (from the reaction with CO_2) and ^{t}BuNCN^{t}Bu (from the reaction with ^{t}BuNCO) were characterized by ^{1}H and ^{13}C NMR spectroscopy. The IR spectra of the black powders indicated the formation of a common product. These observations suggest that the reactions of **2** with CO_2 and ^{t}BuNCO are analogous to those of **1**. Thus, it is proposed that the black powder is a dimeric or oligomeric compound of the type $[Ti(O)(COT'')]_n$ (**6**).

In contrast to the reactions between compounds **1**−**3** and either CO_2 or the isocyanates shown in Scheme 1, the reaction of **3** with ArNCO led to the N,N-bound [2 + 2] cycloaddition product [Ti{N(Ar)C(O)N(Ar)}(COT)] (**7**) (eq 1). This reaction was facile, and complete conversion of **3** to **7** was observed in 5 min. Compound **7** was isolated in 75% yield and fully characterized. The high degree of symmetry in the ^{1}H and ^{13}C NMR spectra indicates that the N,N-bound rather than the N,O-bound product had been formed. The presence of a single set of resonances corresponding to the four isopropyl groups is indicative of the formation of a C_{2v}-symmetric N,N-bound complex rather than a C_s-symmetric N,O-bound product. Furthermore, the IR spectrum of **7** showed a strong ν(C═O) band at 1647 cm^{-1}, which is also consistent with the formation of an N,N-bound product (ν(C═O) range from 1628 to 1643 cm^{-1} for [Ti{N(R)C(O)N(R)}(Me$_n$taa)] (R = alkyl or aryl, n = 4 or 8)).[25]

In this reaction steric factors are presumably the driving force for the formation of the N,N-bound complex. This preference for N,N- over N,O-bound products in the reaction

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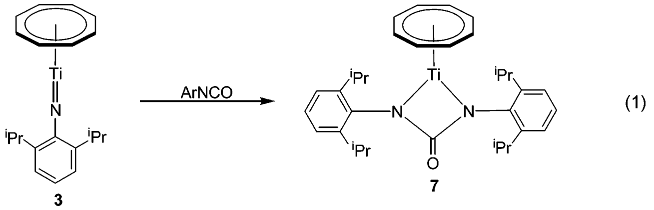
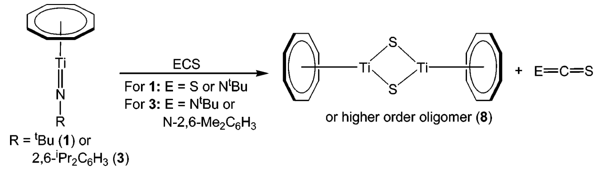


(1)

of titanium imides with isocyanates has been reported in one other system.[25]

Reactions with CS_2 and Isothiocyanates. Reactions between titanium imido species and CS_2 are less common than those between titanium imides and CO_2.[27,28,33,34] The reaction pathway typically involves cycloaddition followed by extrusion to form the corresponding isothiocyanate and a titanium sulfide. In contrast, there has only been one report describing reactions between titanium imido species and isothiocyanates.[34] These reactions also proceed via cycloaddition and subsequent extrusion of a carbodiimide to afford a titanium sulfide.

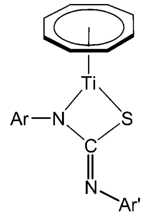
The reactions of $[Ti(N^tBu)(COT)]$ (**1**) with CS_2 and ^tBuNCS and $[Ti(NAr)(COT)]$ (**3**) with ^tBuNCS were analogous to those of **1** with CO_2 and ^tBuNCO and of **3** with ^tBuNCO (eq 2). In all three cases an organic product and an insoluble brown powder (**8**) were formed. The organic products (identified by ^1H and ^{13}C NMR spectroscopy when the reactions were performed on an NMR tube scale) were ^tBuNCS in the reaction of **1** with CS_2, $^tBuNCN^tBu$ in the reaction of **1** with ^tBuNCS, and $^tBuNCNAr$[35] in the reaction of **3** with ^tBuNCS. The IR spectra of the brown powders indicated the formation of a common species. The brown powder was characterized as $[Ti(S)(COT)]_n$ (**8**) by analogy with previous experiments between **1** and **3** and CO_2 and ^tBuNCO. The observation of the organic products also provides strong evidence for the formation of a sulfide species. It is proposed that the mechanism for the formation of **8** involves both cycloaddition and extrusion in a manner analogous to Scheme 1. However, the likely thiocarbamate intermediates $[Ti(COT)\{N(^tBu)C(R)S\}]$ (R = S or N^tBu) were not detected by NMR spectroscopy.



(2)

In contrast, the [2 + 2] cycloaddition intermediate $[Ti\{N(Ar)C(NAr')S\}(COT)]$(**9**) (Ar′ = $2,6\text{-}Me_2C_6H_3$) was observed by ^1H and ^{13}C NMR spectroscopy in the reaction between Ar′NCS and **3**. Compound **9** was unstable and ultimately decomposed into **8** and the carbodiimide Ar′N=C=NAr over a period of 10 h. The quantitative formation of **8** and Ar′N=C=NAr on decomposition of **9** supports the formation of an N,S-bound thiocarbamate isomer. Furthermore, the observation of a resonance at δ 198.3 ppm in the ^{13}C NMR spectrum, which is assigned to the central carbon of the metallacycle, is also consistent with the proposed structure.[34]

The reaction of CS_2 with **3** led to the isolation of the fully characterized metallacyclic complex $[Ti\{N(Ar)C(S)S\}(COT)]$ (**10**) in 39% yield (eq 3). Interestingly, **10** was stable even when heated at 50 °C and did not undergo retrocycloaddition to give **8** and the corresponding isothiocyanate. The presence of two distinct resonances for the methyl groups of the isopropyl substituents in the ^1H NMR spectrum of **10** indicates that there is restricted rotation about the $N-C_{aryl}$ bond. The ^{13}C NMR spectrum contained a resonance at δ 200.6 ppm, which was assigned to the carbon atom in the metallacyclic ring. This chemical shift is similar to that of the carbon in the metallacyclic ring of **9** and is also consistent with the chemical shifts observed for the carbon atom of other four-membered metallacycles, which have been formed through the reaction of titanium imides with CS_2.[34]



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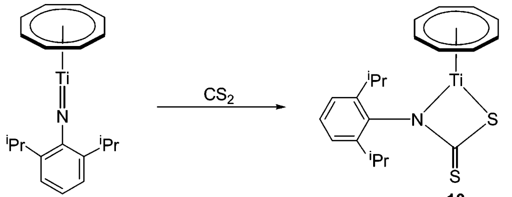

(3)

It has previously been found that the rate of reaction of imides with CS_2 is slower than with CO_2,[33,34] and the reactions of **3** with CS_2 and CO_2 followed this trend. However, the reactions of **1** with these substrates proceeded too rapidly for any difference in the reaction rates to be observed. In contrast, the reaction of **1** with ^tBuNCS was significantly slower than the corresponding reaction with ^tBuNCO. Five minutes after addition of ^tBuNCO to a solution of **1** in C_6D_6 no resonances corresponding to **1** were observed in the ^1H NMR spectrum, whereas it took 3 days for the resonances corresponding to **1** to disappear from the ^1H NMR spectrum in the reaction between **1** and ^tBuNCS. It is interesting to note that even though the reaction between **1** and ^tBuNCS was slow, no evidence was found for a thiocarbamate intermediate. This suggests that the thiocarbamate intermediate is unstable and rapidly undergoes retrocycloaddition.

The isolation of **10** is only the second example of the full characterization of a [2 + 2] cycloaddition product that is postulated to be an intermediate in the reactions of CS_2 with titanium imides.[34] At this stage the factors contributing to the stability of the metallacyclic product **10** are unclear. However, our previous results[34] and the findings of this work suggest that four-membered titanocycles that incorporate aryl substituents on the N atom are more stable to extrusion than the corresponding complexes that have alkyl substituents on the N atom.

Reactions with O−H and S−H Bonds. There have been several reports describing reactions between titanium imido complexes and alcohols or diols.[24,27,45] In general these reactions result in the transfer of a proton(s) from the alcohol to the imide, which results in the formation of a bis(alkoxy) or diolate complex and the free amine. The reactions of both $[Ti(N^tBu)(COT)]$ (**1**) and $[Ti(NAr)(COT)]$ (**3**) with 1 equiv of pinacol also resulted in proton transfer from pinacol to the imide and the formation of the diolate complex $[Ti\{OC(Me)_2C(Me)_2O\}(COT)]$ (**11**) (eq 4). The organic products of these reactions, $^tBuNH_2$ and $ArNH_2$, respectively, were identified through ^1H NMR spectroscopy when the reaction was performed on an NMR tube scale. Similarly, the analogous reaction between

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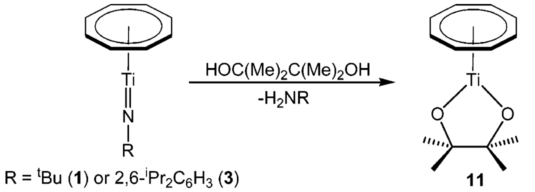
[45] Du, G.; Woo, K. L. *Organometallics* **2003**, *22*, 450.

$[Ti(N^tBu)(COT'')]$ (**2**) and pinacol resulted in the formation of $[Ti\{OC(Me)_2C(Me)_2O\}(COT'')]$ (**12**).



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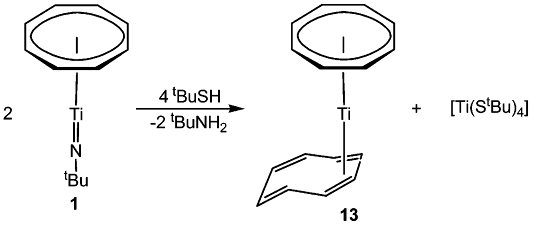
(4)

The driving force behind these reactions is presumably the formation of the strong Ti−O bond in the product. The reaction probably proceeds via two sequential proton transfer steps, although there is no direct evidence for an amido/alkoxide intermediate. In this case the early transition metal complexes **1**−**3** display analogous reactivity to other titanium imido systems[24,27,45] and the late transition metal complex $[Os(N^tBu)(\eta^6\text{-4-cymene})]$, which also reacts with pinacol to give a stable diolate complex.[46] Surprisingly, no tractable products were obtained from reactions between either 1 or 2 equiv of ^tBuOH and compounds **1**−**3**. Although $^tBuNH_2$ or $ArNH_2$ were generated in these reactions (detected by ^1H NMR spectroscopy), no metal-containing products could be identified. It is unclear why these reactions do not give the expected bis(alkoxide) species.

Both Bergman[46,47] and Mountford[24,27,48] have demonstrated that it is possible to activate S−H bonds with imido species. In these reactions the transfer of a proton from a thiol or hydrogen sulfide to the imide results in the formation of a complex containing either a metal−thiolate or metal−sulfide linkage. When a sample of $[Ti(N^tBu)(COT)]$ (**1**) was treated with 2 equiv of ^tBuSH in C_6D_6, an immediate color change from yellow to dark brown was observed. The ^1H NMR spectrum taken 5 min after the addition of ^tBuSH indicated that two major products were present along with free $^tBuNH_2$ (eq 5). The two major products were formed in quantitative yield and were identified as the titanium(II) complex $[Ti(COT)(\eta^4\text{-}C_8H_8)]$ (**13**) and the homoleptic species $[Ti(S^tBu)_4]$, by comparison of the observed ^1H NMR chemical shifts with the data reported in the literature.[49,50] Over a period of 48 h $[Ti(S^tBu)_4]$ decomposed to $^tBuS-S^tBu$ and an unknown metal product, while $[Ti(COT)(\eta^4\text{-}C_8H_8)]$ (**13**) decomposed to an unknown product. The thermal decomposition of $[Ti(S^tBu)_4]$ is known,[51] and the presence of $^tBuS-S^tBu$ in the NMR tube was confirmed by comparison with an authentic sample.



1 **13**

(5)

Interestingly, the outcome of the reaction was dependent on the number of equivalents of ^tBuSH added. Addition of less than 2 equiv of ^tBuSH gave a complex mixture of products (which included COT-containing species as well as $^tBuNH_2$), while addition of more than 2 equiv of ^tBuSH led only to resonances corresponding to $[Ti(S^tBu)_4]$, free ^tBuSH, and $^tBuNH_2$. No resonances associated with a COT-containing product were observed. When the reaction was monitored by NMR spectroscopy over a period of 5 h, the resonance associated with $[Ti(S^tBu)_4]$ disappeared while a resonance corresponding to $^tBuS-S^tBu$ appeared.

In contrast to the reactions between **1** and ^tBuSH, no characterizable metal products were obtained from the reactions between $[Ti(N^tBu)(COT'')]$ (**2**) or $[Ti(NAr)(COT)]$ (**3**) and 2 equiv of ^tBuSH. The only identifiable products were the free amines $^tBuNH_2$ and $ArNH_2$, respectively, and the disulfide $^tBuS-S^tBu$. In the reaction between **2** and 2 equiv of ^tBuSH, a number of new and unidentifiable resonances (including resonances consistent with COT''-containing products) were present in the ^1H NMR spectrum straight after the addition of ^tBuSH, along with resonances corresponding to $^tBuNH_2$ and $^tBuS-S^tBu$. The reaction between **3** and 2 equiv of ^tBuSH was significantly slower, as 4 days were required for **3** to be consumed. After this time a number of unidentified resonances were again present in the ^1H NMR spectrum, along with resonances corresponding to $ArNH_2$ and $^tBuS-S^tBu$.

In an attempt to gain a better understanding of this chemistry and isolate potential intermediates, several reactions were attempted between the bulky aryl thiol $HS\text{-}2,4,6\text{-}^iPr_3C_6H_2$ and compounds **1**−**3**.[52] These reactions all led to the formation of the disulfide $(2,4,6\text{-}^iPr_3C_6H_2)S-S(2,4,6\text{-}^iPr_3C_6H_2)$[52] and the corresponding primary amine ($^tBuNH_2$ in the reaction with **1** and **2** and $ArNH_2$ in the reaction with **3**). No metal-containing compounds could be isolated from any of the reactions. The reactions between $HS\text{-}2,4,6\text{-}^iPr_3C_6H_2$ and compounds **1** and **2** occurred almost immediately, while that between $HS\text{-}2,4,6\text{-}^iPr_3C_6H_2$ and **3** took 7 days to reach completion at room temperature.

The reactions between compounds **1**−**3** and ^tBuSH and $HS\text{-}2,4,6\text{-}^iPr_3C_6H_2$ all resulted in the overall oxidation of the thiols to the corresponding disulfides. This formation of disulfides from the reaction of thiols with imido species has not previously been observed. Unfortunately, the metal products in these reactions are unknown and the mechanism by which these disulfides are formed is unclear. A number of attempts were made to synthesize bis(thiolate) species through the reactions of 1,2-benzenethiol with compounds **1**−**3**. It was hoped that the products of these reactions would be analogous to the diolate compounds **11** and **12**, which were formed through the reactions of compounds **1**−**3** with pinacol. However, these reactions also led to an intractable mixture of products.

Reactions with Isocyanides. There has only been one report of reactions between titanium imides and isocyanides. Mountford and Gade showed that the reaction of $[Ti(N^tBu)(N_2N^{py})(py)]$ ($N_2N^{py} = (2\text{-}C_5H_4N)C(Me)(CH_2NSiMe_3)_2$) with the sterically bulky Ar′NC led to the coupling of two molecules of the isocyanide with the Ti=N^{t}Bu bond and yielded the four-membered titanocycle $[Ti\{N(^tBu)C(=NAr')C(=NAr')\}(N_2N^{py})(py)]$.[53] The related reactions between $[Ti(N^tBu)(N_2N^{py})(py)]$ and alkyl isocyanides bearing H atoms α to the NC group resulted in sequential coupling of 3 molar equiv of the

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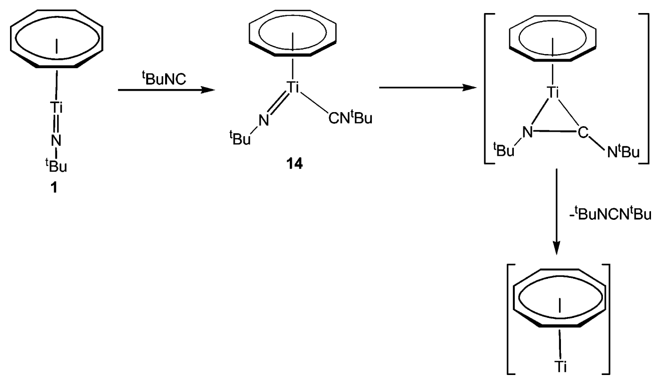
Scheme 3

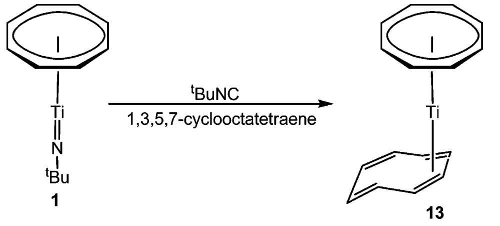


isocyanide with the imido complex and concomitant C−H bond migration to form dihydropyrimidine complexes.[53]

The reactions between MeNC or Ar′NC and [Ti(N^{t}Bu)(COT)] (**1**) resulted in the formation of a number of unidentified and intractable products. However, when ^{t}BuNC was added to a solution of **1** in C_6D_6 at room temperature, the adduct [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**) was immediately generated. The resonance corresponding to coordinated ^{t}BuNC in the ^{1}H NMR spectrum was broad, indicating that the ^{t}BuNC ligand is probably labile. Attempts to isolate **14** on a preparative scale were unsuccessful, as the coordinated isocyanide was lost under vacuum, regenerating **1** and ^{t}BuNC.

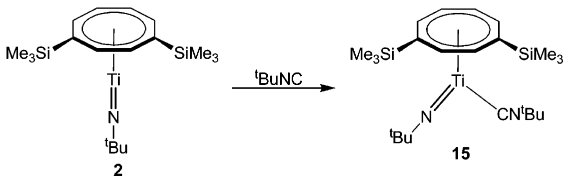
After 5 days at room temperature the resonances corresponding to [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**) had disappeared and a new resonance attributed to ^{t}BuNCN^{t}Bu was observed at δ 1.16 ppm. In addition, a brown solid had precipitated out of solution. The rate of conversion of **14** to ^{t}BuNCN^{t}Bu increased when the sample was heated at 100 °C and only took 48 h. The carbodiimide was formed in quantitative yield, as judged using 1,4-dimethoxybenzene as an internal standard. The generation of ^{t}BuNCN^{t}Bu suggests that a formal nitrene transfer reaction is occurring, in which the ^{t}BuN substituent migrates from the titanium center to the isocyanide. A possible mechanism for this transfer could involve the reductive elimination of ^{t}BuNCN^{t}Bu from the adduct [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**) (Scheme 3). This elimination step may be facilitated through the formation of an intermediate that incorporates a coordinated carbodiimide fragment. Although there was no evidence for such an intermediate in this work, complexes of this type have previously been observed.[54,55] A reductive elimination of this nature would also generate an extremely reactive Ti(COT) fragment.

Several attempts were made to trap a putative Ti(COT) fragment by performing the reaction in the presence of a suitable trapping agent. When the reaction between ^{t}BuNC and **1** was performed in the presence of 1,3,5,7-cyclooctatetraene, the Ti(II) complex [Ti(COT)(η^4-C_8H_8)] (**13**) was isolated in 70% yield (eq 6) (note that neither ^{t}BuNC or **1** reacted independently with 1,3,5,7-cyclooctatetraene). Reductive elimination of ^{t}BuNCN^{t}Bu from [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**) generates the coordinatively unsaturated Ti(COT) fragment. The addition of 1,3,5,7-cyclooctatetraene to this reactive fragment presumably accounts for the formation of **13**. Nitrene group transfer reactions of this type are rare. There is only one previous example of this type of reaction involving a titanium(IV) imide,[32] although similar reactions have been observed for well-defined tantalum(V),[56] cobalt(III),[57] iron(II),[58] and nickel(II)[55] imido complexes.



(6)

Surprisingly, the reaction between [Ti(N^{t}Bu)(COT″)] (**2**) and ^{t}BuNC led to the isolation of the terminal isocyanide adduct [Ti(N^{t}Bu)(COT″)(CN^{t}Bu)] (**15**) (eq 7). Compound **15** was fully characterized and is stable under vacuum for at least 12 h. The IR spectrum of **15** contains a ν(C≡N) stretch at 2167 cm^{-1}, which indicates that ^{t}BuNC is bound in a terminal fashion.[54,59] As expected, the ν(C≡N) in the coordinated ^{t}BuNC is shifted to a higher wavenumber than the ν(C≡N) in free ^{t}BuNC (2136 cm^{-1}).[60−62]



(7)

Prolonged heating of **15** (7 days in C_6D_6 at 80 °C) led to the formation of only trace quantities of the carbodiimide ^{t}BuNCN^{t}Bu even when free 1,3,5,7-cyclooctatetraene was present in the reaction mixture. Therefore, unlike [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**), **15** appears to be stable toward nitrene transfer. This different behavior of compounds **14** and **15** may cast doubt on the simple intramolecular mechanism proposed for the conversion of **14** into Ti(COT) and ^{t}BuNCN^{t}Bu because if the proposed mechanism is correct, the extra steric bulk of the COT″ would not be expected to inhibit the reaction. However, if the mechanism of nitrene transfer involved a bimetallic species, then the extra steric bulk could inhibit the reaction.

The reactions between [Ti(NAr)(COT)] (**3**) and the isocyanides MeNC, ^{t}BuNC, and Ar′NC all led to the adducts [Ti(NAr)(COT)(CNR)] (R = Me (**16**), ^{t}Bu (**17**), or Ar′ (**18**)) (eq 8). Compounds **16** and **18** were characterized only on the NMR tube scale, as they quickly decomposed into a mixture of uncharacterized products and could not be isolated in preparative scale reactions. Conversely, compound **17** was stable and was fully characterized. The ν(C≡N) stretch in the IR spectrum of **17** occurred at 2177 cm^{-1}, which indicates that the isocyanide is bound in a terminal η^1-fashion.[54,59] The isocyanide ligands are also proposed to bind to the titanium center in a terminal

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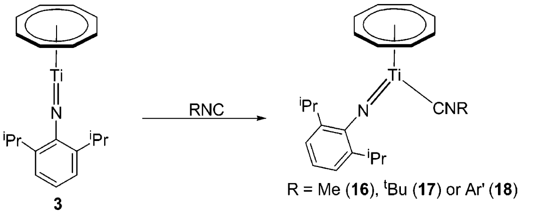
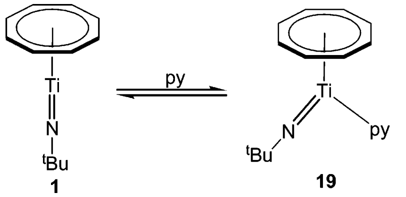
fashion in compounds **16** and **18** by analogy with compounds **15** and **17**. Prolonged heating of **17** (7 days in C_6D_6 at 80 °C) did not lead to the formation of any carbodiimide, and it appears that **17** is also completely stable toward reductive elimination. The stability of the Ti=NAr adduct **17** compared with the $Ti{=}N^tBu$ adduct **14** is similar to certain reactions between titanium imides and CO_2 and RNCO, which have also shown that adducts derived from $Ti{=}N^tBu$ are more likely to lose the NR-containing fragment than those from Ti=NAr.[8]



R = Me (**16**), ^{t}Bu (**17**) or Ar' (**18**)

(8)

Reaction between $[Ti(N^tBu)(COT)]$ (1) and Pyridine. The first step in the nitrene group transfer reaction between $[Ti(N^tBu)(COT)]$ (**1**) and ^{t}BuNC is proposed to be the formation of the adduct $[Ti(N^tBu)(COT)(CN^tBu)]$ (**14**). To investigate further the formation of adducts of this nature, **1** was reacted with several simple Lewis bases. The reaction of **1** with pyridine resulted in the formation of $[Ti(N^tBu)(COT)(py)]$ (**19**) (eq 9). Compound **19** was unstable under vacuum, and the pyridine ligand readily dissociated to generate **1** in quantitative yield. As a result, satisfactory elemental analysis was not obtained for **19**. The structure of **19** was elucidated by X-ray diffraction analysis (vide infra), and it was confirmed that the pyridine ligand binds to the Ti center. The ^{1}H NMR spectrum of **19** contains resonances consistent with coordinated pyridine, a *tert*-butylimido group, and an η^8-coordinated COT ring. The coordinated pyridine resonances are broad at room temperature but sharpen upon heating, consistent with this ligand being labile. When an excess of pyridine was added to a solution of **19** in C_6D_6, only one averaged resonance was observed.



(9)

Crystals of $[Ti(N^tBu)(COT)(py)]$ (**19**) suitable for X-ray diffraction analysis were obtained from a saturated ether solution at 0 °C. The solid-state structure is shown in Figure 1, and selected bond distances and angles are presented in Table 1 (together with those calculated by DFT, vide infra). The asymmetric unit contains four crystallographically distinct molecules, none of which have any crystallographically imposed symmetry. These occur as two pairs of similar molecules, each of which are related by an approximate translation. The pairs differ in the orientations of the *tert*-butyl group. The thermal ellipsoids of the COT C atoms are somewhat anisotropic, suggesting that vibrational motions of the ligands about the Ti⋯ring centroid axes have high amplitudes. In addition, the *tert*-butyl group C(18)−C(21) and the pyridine N(6)−C(43) also appear to have relatively high vibrational amplitudes.

The average values for the $Ti{=}N^tBu$ bond lengths and $Ti{=}N{-}CMe_3$ bond angles are 1.72 Å and 167.8°, respectively. This indicates that the imides are donating 4 electrons to the metal centers, giving them an overall valence electron count of 18 electrons. The slight bending of the $Ti{=}N{-}CMe_3$ bond angles in **19** compared to $[Ti(N^tBu)(COT)]$ (**1**) ($Ti{=}N{-}CMe_3$ in **1** is 177.5(1)°)[63] is probably due to steric factors. In compound **19** bending the $Ti{=}N{-}CMe_3$ bond angle minimizes interaction between the *tert*-butyl group of the imide and the coordinated pyridine. Previous studies have shown that the M−N−R bond angle in imido species is energetically "soft" and that small changes to this angle have only a relatively minor effect on the overall energy of the molecule.[64−66] The average $Ti{-}N_{pyr}$ distance is within the range normally observed for $Ti{-}N_{pyr}$ bonds.[67,68]

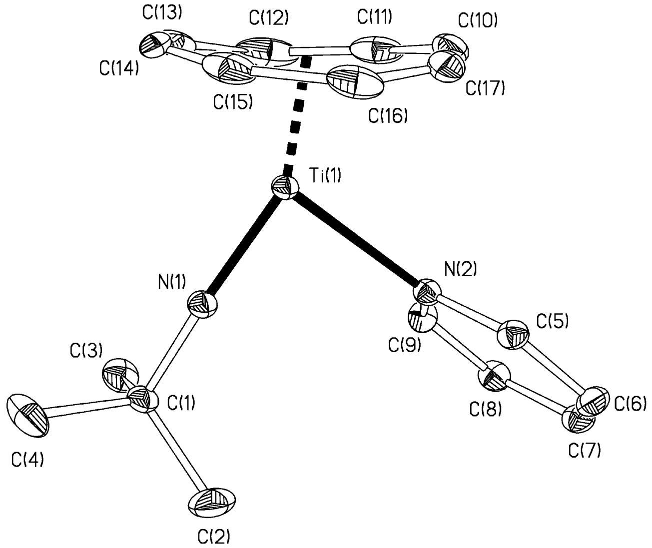


Figure 1. Displacement ellipsoid plot of one of the four crystallographically distinct molecules of $[Ti(N^tBu)(py)(COT)]$ (**19**) (25% probability). H atoms are omitted.

In all four molecules the geometry of the COT ligand is distorted from planarity. The ligands have shallow saddle shapes, and the Ti−C distances are variable, with the longest distances being those *trans* to the imido ligands. These distances reflect the strong *trans* influence of the imido ligand. The C−C distances in the COT ring vary from 1.364(4) to 1.454(4) Å, and the carbon atoms that are further away from the Ti center tend to form shorter C−C bonds. The average Ti⋯ring centroid distance is 1.56 Å, and the average ring centroid−$Ti{=}N^tBu$ bond angle is 119°. The elongated Ti⋯ring centroid distances observed in **19** compared to $[Ti(N^tBu)(COT)]$ (**1**) (Ti⋯ring centroid = 1.369 Å) can be explained by the loss in overlap that occurs between the ring and the titanium d orbitals on bending the ring centroid−Ti=N bond angle[23] and the higher coordination number around the Ti center. The average ring centroid−Ti=N bond angle in **19** is even more acute than in the dimeric compound $[Ti_2(\mu\text{-}NAr')_2(COT)_2]$[23] (ring centroid−Ti−N bond angle is 137°), and hence the Ti⋯ring centroid distance in **19** is also greater than in the dimeric species (Ti⋯ring centroid distances is 1.54 Å).

DFT Analysis of $[Ti(N^tBu)(COT)(py)]$ (19). To perform a comparison between the electronic structure of **1** and that of

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Table 1. Comparison between Selected Experimental (values for all four crystallographically distinct molecules given) and Calculated Bond Lengths and Angles for [Ti(N^{t}Bu)(COT)(py)] (19)

bond length or angle	Individual experimental values (Å or deg)	average values (Å or deg)	calc values (Å or deg)
Ti(1)−N(1)	1.717(2), 1.719(2), 1.716(2), 1.714(2)	1.72	1.70
Ti(1)−N(2)	2.251(2), 2.257(2), 2.258(2), 2.277(2)	2.26	2.21
Ti(1)−C(10)	2.589(3), 2.607(3), 2.532(3), 2.513(3)	2.56	2.54
Ti(1)−C(11)	2.459(3), 2.486(3), 2.398(3), 2.469(3)	2.45	2.41
Ti(1)−C(12)	2.301(3), 2.311(3), 2.316(3), 2.346(3)	2.32	2.29
Ti(1)−C(13)	2.300(3), 2.288(3), 2.354(3), 2.310(3)	2.31	2.31
Ti(1)−C(14)	2.331(3), 2.351(3), 2.355(3), 2.358(3)	2.35	2.35
Ti(1)−C(15)	2.312(3), 2.317(3), 2.297(3), 2.344(3)	2.32	2.30
Ti(1)−C(16)	2.363(3), 2.345(3), 2.358(3), 2.329(3)	2.35	2.33
Ti(1)−C(17)	2.511(3), 2.510(3), 2.519(3), 2.416(3)	2.49	2.48
N(1)−C(1)	1.452(3), 1.452(3), 1.455(3), 1.452(3)	1.45	1.42
N(1)−Ti(1)−N(2)	87.81(8), 87.60(9), 84.74(9), 85.59(8)	86.4	85
N(1)−Ti(1)−C(10)	162.61(10), 163.44(10), 157.85(10), 159.24(10)	160.8	160
N(1)−Ti(1)−C(11)	143.42(11), 145.53(11), 137.34(11), 150.42(11)	144.2	140
N(1)−Ti(1)−C(12)	120.09(13), 122.15(12), 116.85(11), 129.00(12)	122.0	118
N(1)−Ti(1)−C(13)	105.02(11), 106.12(11), 106.02(10), 111.89(11)	107.3	105
N(1)−Ti(1)−C(14)	102.88(10), 102.94(10), 104.73(10), 104.99(10)	103.9	103
N(1)−Ti(1)−C(15)	110.89(10), 109.78(10), 113.14(11), 107.51(11)	110.3	111
N(1)−Ti(1)−C(16)	129.07(11), 127.04(11), 132.38(11), 120.65(11)	127.3	128
N(1)−Ti(1)−C(17)	152.43(11), 150.39(11), 154.49(10), 141.92(12)	149.8	151
Ti(1)−N(1)−C(1)	167.76(18), 167.42(19), 168.46(18), 166.15(18)	167.4	172
Ti(1)−N(2)−C(5)	124.94(16), 123.20(17), 122.2(2), 122.73(18)	123.3	125
Ti(1)−N(2)−C(9)	117.27(16), 118.64(17), 120.3(2), 120.32(17)	119.9	118

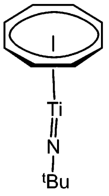
Table 2. Decomposition of the Bond Energy between the Pyridine and Ti(N^{t}Bu)(COT) Fragments in [Ti(N^{t}Bu)(COT)(py)] (19)

type of energy[a]	energy (kJ mol^{-1})
electrostatic energy (ΔV_{elst})	−278
orbital interaction (ΔE_{oi})	−121
Pauli repulsion ($\Delta E_{\mathrm{Pauli}}$)	282

[a] Bond decomposition energies taken from ADF fragment calculation in which a Ziegler−Rauk type energy decomposition method is followed.[69−71]

[Ti(N^{t}Bu)(COT)(py)] (**19**), DFT was used to model compound **19**. A geometry optimization with no symmetry restrictions was performed on **19**, together with a fragment analysis in which the molecule was split into Ti(N^{t}Bu)(COT) and pyridine fragments (in the computed geometry of the molecule). Important calculated bond lengths and angles are compared with the experimental values in Table 1, while Table 2 shows the energetic contribution of different types of bonding interactions[69−71] (orbital interaction, electrostatic, and Pauli repulsion) to the overall bonding energy between the Ti(N^{t}Bu)(COT) and the pyridine fragments.

Table 1 shows that there is good agreement between the calculated and experimental bond lengths in **19**, indicating that the model is valid. The SCF energies indicate that binding of the pyridine ligand to the metal center (relative to free relaxed fragments) is energetically favored by only 23 kJ mol^{-1}, which is consistent with the experimental observation that the pyridine ligand readily dissociates under vacuum. The Ti(N^{t}Bu)(COT) fragment of **19** can be considered as being similar to [Ti(N^{t}Bu)(COT)] (**1**), except that the ring centroid−Ti−N bond angle has been bent from approximately 180° in **1** to approximately 119° in the Ti(N^{t}Bu)(COT) fragment of **19**.



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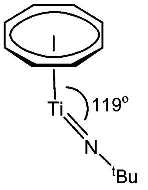

We have previously described the electronic effects of bending the ring centroid−Ti═N bond angle in the model compound [Ti(NH)(COT)],[23] and in this case, the changes in the electronic structure observed when moving from linear [Ti(N^{t}Bu)(COT)] (**1**) to the bent fragment are similar. There is a loss of overlap between the δ-symmetry orbitals of the COT ring and the metal d orbitals and a favorable bonding interaction develops between the Ti−N π-bonding orbitals and the COT ring in the bent Ti(N^{t}Bu)(COT) fragment compared with **1**. Interestingly, there is little change in the energy of the predominantly metal-based LUMO on bending, and the LUMO is of suitable shape to allow another ligand to bind to the metal center (Figure 2a). The HOMO of the pyridine fragment, which consists primarily of the nitrogen lone pair, is suitable for donating to a metal center in a σ-fashion (Figure 2b).

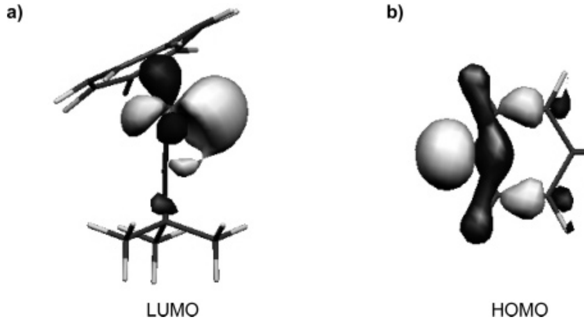

Figure 2. (a) LUMO of the Ti(N^{t}Bu)(COT) fragment of [Ti(N^{t}Bu)(COT)(py)] (**19**); and (b) HOMO of the pyridine fragment.

Surprisingly, MO analysis indicates the lack of a single MO depicting an interaction between pyridine and the titanium center. Figure 3 shows the two MOs of **19** (47A and 50A) which contain a greater than 5% contribution from the HOMO of the pyridine fragment, and in both cases there is no contribution from the metal. However, by analyzing the change in orbital occupancies of the Ti(N^{t}Bu)(COT) fragment and the pyridine

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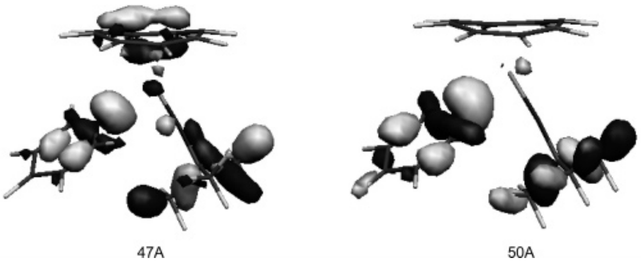


Figure 3. Orbitals 47A and 50A of [Ti(N^{t}Bu)(COT)(py)] (**19**).

fragment upon bonding it can be inferred that there is a covalent interaction between the pyridine and the metal center. In the pyridine fragment the HOMO is fully occupied and has occupancy 2, while in the Ti(N^{t}Bu)(COT) fragment the LUMO is unoccupied and has occupancy 0. Once the pyridine binds to the Ti(N^{t}Bu)(COT) fragment, the occupancies of both these orbitals change. The occupancy of the HOMO of the pyridine fragment drops to 1.84, while that of the LUMO of the Ti(N^{t}Bu)(COT) fragment rises to 0.14. The occupancies of the majority of the other orbitals of the pyridine fragment and the Ti(N^{t}Bu)(COT) fragment remain the same when [Ti(N^{t}Bu)(COT)(py)] (**19**) is formed. These occupancy changes indicate that there is a small but significant transfer of electron density from the lone pair on the nitrogen atom of the pyridine ring (represented by the HOMO of the pyridine fragment) to the titanium center (represented by the LUMO of the Ti(N^{t}Bu)(COT) fragment). The lack of a one to one interaction between a titanium d orbital and the orbital containing the pyridine lone pair is probably explained by the large difference in energy between the two sets of orbitals (the energy of the HOMO of the pyridine fragment is −5.877 eV, while the energy of the LUMO of the Ti(N^{t}Bu)(COT) fragment is −2.287 eV) and indicates that the interaction between the titanium and pyridine is probably more electrostatic in nature than covalent.

The electrostatic nature of the bonding between the pyridine and the Ti(N^{t}Bu)(COT) fragment is confirmed by decomposing the bond energy between the fragments into contributions associated with the various orbital and electrostatic interactions. The decomposition energies are shown in Table 2. The decomposition bond energies clearly indicate that the total stabilization to **19** from electrostatic interactions (ΔV_{elst} represents the classical electrostatic interaction between the prepared fragments) is almost double the stabilization from orbital interactions (ΔE_{oi} accounts for electron pair bonding and charge transfer interactions). The Pauli repulsion term represents the "steric" interaction or repulsion between the two fragments and is not significant in determining the covalency of the bond. Hence, it can be concluded that the main driving force for coordination of the pyridine fragment to the Ti(N^{t}Bu)(COT) fragment is a dipole−dipole attraction between the electron-rich nitrogen atom of the pyridine ring and the electron-deficient titanium center.

Density Functional Theory Analysis of the Reactions of ^{t}BuNC with [Ti(N^{t}Bu)(COT)] (1) and [Ti(NAr)(COT)] (3). The difference in reactivity between alkyl and aryl titanium imido complexes[8] is again highlighted by the reactions of ^{t}BuNC with **1** and **3**, respectively. Whereas the reaction between **3** and ^{t}BuNC results in the formation of the stable adduct [Ti(NAr)(COT)(CN^{t}Bu)] (**17**), the reaction between compound **1** and ^{t}BuNC leads to nitrene group transfer. A DFT-based study was performed to investigate further the difference in reactivity between compounds **1** and **3** and ^{t}BuNC in the presence of free 1,3,5,7-cyclooctatetraene. To study the reaction of **1** with ^{t}BuNC, geometry optimizations were performed on the starting materials, the reaction products, namely, ^{t}BuNCN^{t}Bu and [Ti(COT)(η^4-C$_8$H$_8$)] (**13**), and also the observed intermediate [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**). Similarly, to study the reaction of **3** with ^{t}BuNC, geometry optimizations were performed on the starting materials, the stable adduct [Ti(NAr)(COT)(CN^{t}Bu)] (**17**), and also the hypothetical products ^{t}BuNCNAr and [Ti(COT)(η^4-C$_8$H$_8$)] (**13**). For compounds **14** and **17** a fragment analysis was performed in which the molecule was split into either a Ti(N^{t}Bu)(COT) or a Ti(NAr)(COT) fragment and a ^{t}BuNC fragment. Figure 4a summarizes the relative energies of the reactants, intermediates, and products for the reaction of **1** with ^{t}BuNC in the presence of free 1,3,5,7-cyclooctatetraene, while Figure 4b provides the corresponding energies for the reaction between **3** and ^{t}BuNC in the presence of free 1,3,5,7-cyclooctatetraene.

The optimized geometries of compounds **14** and **17** are similar to that of the pyridine adduct [Ti(N^{t}Bu)(COT)(py)] (**19**). The SCF energies indicate that the binding of the isocyanide ligand to the metal center is energetically favored by 30 kJ mol^{-1} in the case of compound **14** and by 80 kJ mol^{-1} for **17**. This is consistent with the experimental results, which indicate that **14** readily dissociates to [Ti(N^{t}Bu)(COT)] (**1**) and ^{t}BuNC under vacuum, while compound **17** is stable. In an analogous manner to [Ti(N^{t}Bu)(COT)(py)] (**19**), the ring centroid−Ti−N angles are bent to accommodate the extra ligand, and the Ti−C (isocyanide) distances are 2.13 Å in **14** and 2.15 Å in **17**. There is a decrease in the overlap between the δ-symmetry orbitals of the COT ring and the Ti center in **14** and **17** compared with complexes **1** and **3**, and a favorable bonding interaction develops between the Ti−N π-bonding orbitals and the COT ring as a result of the bending of the ring centroid−Ti−N angle. Comparison of the SCF energies of the bent Ti(N^{t}Bu)(COT) fragment of **14** and the bent Ti(NAr)(COT) fragment in **17** with compounds **1** and **3** reveals that it is more favorable to bend the Ti−N−ring centroid angle in **3** than in **1** by approximately 20 kJ mol^{-1}. This is presumably related to the fact that the Ti═N bond in **3** is weaker than in **1**[23] and partially explains why it is energetically more favorable to form **17** than **14**. In both **14** and **17**, fragment analysis showed that the predominant interaction between the isocyanide ligand and the metal is electrostatic in nature rather than covalent.

Figure 4a shows that the conversion of **14** and 1,3,5,7-cyclooctatetraene into ^{t}BuNCN^{t}Bu and [Ti(COT)(η^4-C$_8$H$_8$)] (**13**) is energetically favored by 127 kJ mol^{-1} (SCF energies). The analogous reaction between [Ti(NAr)(COT)(CN^{t}Bu)] (**17**) and free 1,3,5,7-cyclooctatetraene to form ^{t}BuNCNAr and **13** is slightly less energetically favored by 108 kJ mol^{-1} (SCF energies) (Figure 4b). This suggests that the observed stability of **17** toward dissociation is related to the energy barrier that must be overcome to form **13** and ^{t}BuNCNAr, and this energy barrier must be lower for the decomposition of **14**. Unfortunately, the transition states for these reactions could not be modeled.

Overall, these calculations indicate that partially as a result of the weaker Ti═N bond in **3** than in **1**, the formation of the adduct [Ti(NAr)(COT)(CN^{t}Bu)] (**17**) from **3** and ^{t}BuNC is a more favorable process than the formation of [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**) from **1** and ^{t}BuNC. On the basis of SCF energies the extrusion of the carbodiimide is slightly more favored from **14** than from **17**.

Reactions with AlMe$_3$ and AlMe$_2$Cl. The Ti═N bonds in compounds **1**−**3** are polarized, with the titanium centers bearing a small positive charge and the nitrogen atoms a small negative charge.[23] In this present contribution we have already shown

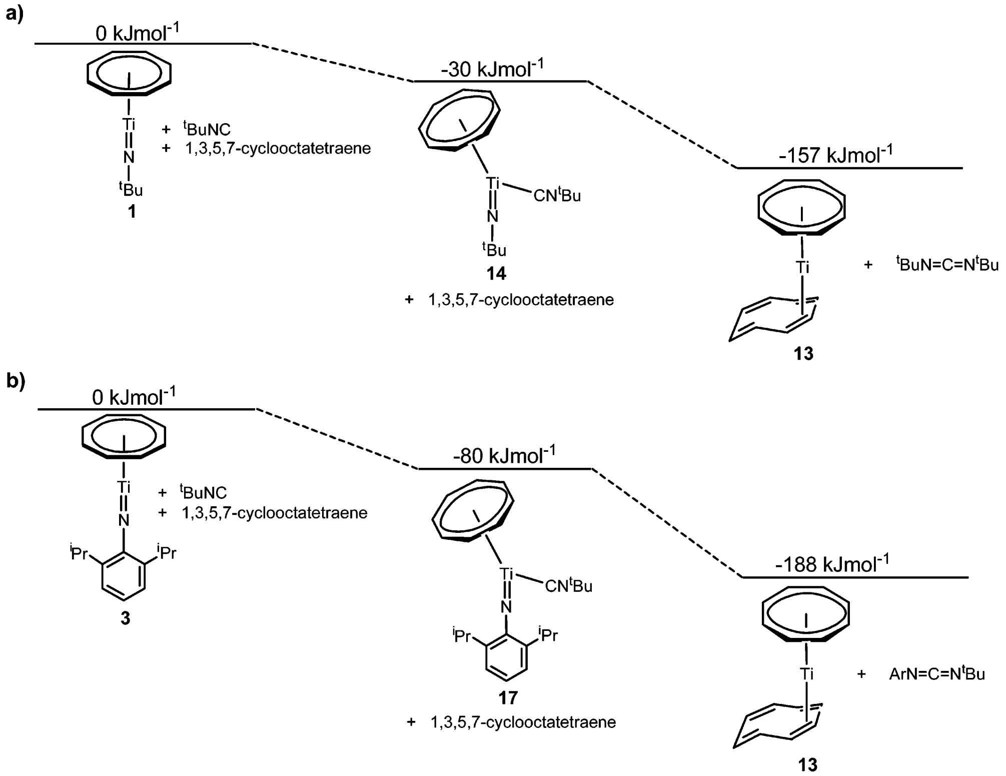
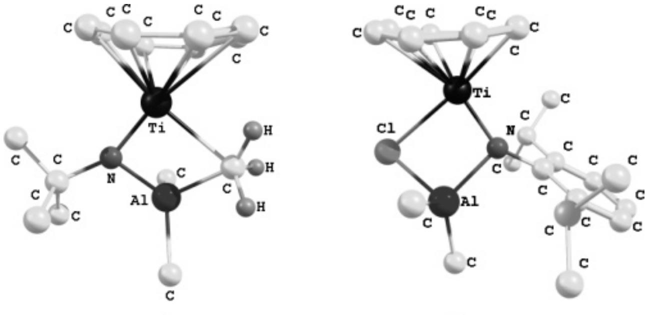


Figure 4. Relative energies (SCF) of starting materials, intermediates, and products in the reaction of (a) [Ti(N^{t}Bu)(COT)] (**1**) with ^{t}BuNC in the presence of free 1,3,5,7-cyclooctatetraene; and (b) [Ti(NAr)(COT)] (**3**) with ^{t}BuNC in the presence of free 1,3,5,7-cyclooctatetraene.

that certain Lewis bases react with compounds **1**−**3** at the titanium center. Given the negative charge of the nitrogen atom, we were also interested in exploring the reactivity of Lewis acids with these compounds.

The reactions of compounds **1** and **3** with half an equivalent of Al_2Me_6 afforded [Ti(N^{t}Bu)(COT)($AlMe_3$)] (**20**) and [Ti(NAr)(COT)($AlMe_3$)] (**21**), in isolated yields of 82 and 76%, respectively. Satisfactory elemental analysis could not be achieved for compounds **20** and **21**, as they readily decomposed under vacuum to give **1** and **3**, respectively. Similarly, treatment of **1** and **3** with $Al_2Me_4(\mu\text{-Cl})_2$ resulted in the formation of [Ti(N^{t}Bu)(COT)($AlMe_2Cl$)] (**22**) and [Ti(NAr)(COT)($AlMe_2Cl$)] (**23**). Compounds **22** and **23** were characterized only on the NMR tube scale, as they quickly decomposed to a mixture of products and could not be isolated in preparative scale reactions. Although the ^{1}H and ^{13}C NMR data for compounds **20**−**23** clearly indicate that the $AlMe_3$ or $AlMe_2Cl$ unit is coordinated to the starting complexes, the exact bonding mode of $AlMe_3$ or $AlMe_2Cl$ is unclear. Even at low temperature a single resonance was observed for the $AlMe_3$ or $AlMe_2Cl$ group in both the ^{1}H and ^{13}C NMR spectra of compounds **20**−**23**.

Repeated attempts to grow crystals of **20** and **21** were unsuccessful, and thus a DFT investigation was performed to gain further insight into possible structures and bonding of compounds **20**−**23**. The geometries of **20**−**23** were optimized and the energies of structures that contained a four-membered metallacylic ring compared with simple adducts that contained either a Ti−C (for Al_2Me_6) or Ti−Cl (for $AlMe_4(\mu\text{-Cl})_2$) bond or an N−Al bond. For all four compounds the lowest energy structure contains a four-membered metallacyclic ring, which includes a bond between the nitrogen atom of the imide and the aluminum atom (Figure 5). In compounds **20** and **21** there is also an interaction between one carbon atom of the $AlMe_3$ group and the Ti center, whereas in compounds **22** and **23** there is an interaction between the Cl atom of the $AlMe_2Cl$ group and the Ti center. The preference for bridging chlorides as opposed to bridging methyls in compounds **22** and **23** is presumably because the chloride ligand can form two two-electron two-center bonds, while the bridging methyl ligand forms one two-electron three-center bond.



21 23

Figure 5. Optimized structures of [Ti(N^{t}Bu)(COT)($AlMe_3$)] (**21**) and [Ti(NAr)(COT)($AlMe_2Cl$)] (**23**). H atoms are omitted except for those associated with the μ-Me unit in **21**.

The optimized Ti−N bond lengths are 1.78 and 1.80 Å in compounds **20** and **22**, respectively, and 1.80 and 1.81 Å in **21** and **23**, respectively. These distances are longer than those observed in compounds **1** and **3** (Ti−N = 1.699(6) Å in **1** and Ti−N = 1.7217(18) Å in **3**)[23] and indicate that on formation of the metallacyclic ring there is a decrease in the Ti−N bond order. The Ti−C(H_3)$AlMe_3$ bond distance in both **20** and **21** is 2.42 Å, which is consistent with the titanium-bound methyls participating in three-center, two-electron bonding to aluminum.[72] The terminal Al−Me bonds are shorter (1.96 and 1.97 Å in **20** and 1.95 and 1.97 Å in **21**) than the corresponding bridging bonds (2.05 Å in **20** and 2.06 Å in **21**), and the

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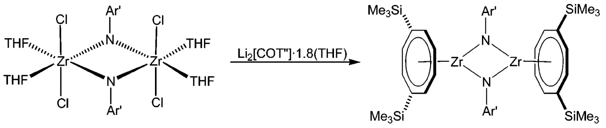
(72) Bolton, P. D.; Clot, E.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3313.

geometry of the central carbon atoms of the μ-Me units is distorted trigonal bipyramidal with one hydrogen atom and the aluminum atom occupying the axial sites. Interestingly, in the optimized structures of **20** and **21** there is only *one* short Ti···H contact for the μ-Me group (2.31 Å in **20** and 2.26 Å in **21**), whereas all the previously reported rare earth AlR_3 adducts have *two* close Ln···H contacts and feature the Al atoms lying in the equatorial plane of the local $\{LnCH_3Al\}$ trigonal bipyramids.[73−79] Similarly, the heterobimetallic cation $[Ti(N^tBu)(Me_3[9]aneN_3)(\mu\text{-}Me)_2AlMe_2]^+$ has only *one* short Ti···H contact per μ-Me group, but in this compound the central carbons of the μ-Me groups are approximately square-based pyramidal.[72]

The optimized structures of **21** and **23** are consistent with the ^{13}C NMR data, as we have previously observed that the *ipso* carbon of aryl imido substituents is shifted to high field when the imide is incorporated into a metallacycle. In compounds **21** and **23** the ^{13}C NMR chemical shifts of the *ipso* carbons are δ 135.9 and 140.7 ppm, respectively, whereas in **3** the resonance corresponding to the *ipso* carbon is observed at δ 159.9 ppm. The reactions of **1** and **3** contrast with the reaction of $[Ti(N^tBu)(Me_3[9]aneN_3)Me]^+$ with $AlMe_3$, which resulted in the formation of the heterobimetallic cation $[Ti(N^tBu)(Me_3[9]aneN_3)(\mu\text{-}Me)_2AlMe_2]^+$.[72]

Synthesis of Zirconium Imido Complexes Containing the COT Ligand. Given the unusual reactivity of the monomeric titanium imido COT complexes, several attempts were made to synthesize analogous zirconium species in this work. Previously, Wigley et al. synthesized the dinuclear μ-arylimido COT complex $[Zr_2(\mu\text{-}NAr)_2(COT)_2]$ through the reaction of $[Zr_2(\mu\text{-}NAr)_2Cl_4(THF)_4]$ with K_2COT.[80] However, they were unable to confirm crystallographically the nuclearity of this species, and this is the only report of a zirconium imido COT complex. The formation of monomeric titanium imido COT complexes is favored by increasing the steric bulk of the substituents both on the COT ring and on the nitrogen atom of the imide.[23] Therefore, several attempts were made to synthesize monomeric zirconium imido COT complexes using sterically bulky imido groups and substituted COT rings. The facile syntheses of zirconium imido dichloride compounds of the type $[Zr_2(\mu\text{-}NR)_2Cl_4(THF)_4]$ (R = Ar, Ar′, or Ph) and $[Zr_2(\mu\text{-}NR)_2Cl_4(THF)_3]$ (R = ^tBu, ^iPr, or CH_2Ph) have recently been described by Mountford et al.,[81] and these were utilized as the zirconium starting materials.

Reaction of $[Zr_2(\mu\text{-}N^tBu)_2Cl_4(THF)_3]$ with either K_2COT or $Li_2COT''\cdot1.8(THF)$ resulted in the formation of a mixture of products, which could not be characterized or isolated. Similarly, the reaction of $[Zr_2(\mu\text{-}NAr)_2Cl_4(THF)_4]$ with $Li_2COT''\cdot1.8(THF)$ resulted in a complex mixture of products. In contrast, the reaction of $[Zr_2(\mu\text{-}NAr')_2Cl_4(THF)_4]$ with $Li_2COT''\cdot1.8(THF)$ generated the dimeric crystallographically characterized complex (vide infra) $[Zr_2(\mu\text{-}NAr')_2(COT'')_2]$ (**24**) in 65% yield (eq 10). The ^1H and ^{13}C NMR spectra of **24** were similar to those observed for related titanium imido complexes. The protons of the COT″ ring of **24** form an AA′XX′YY′ spin system. In the ^1H NMR spectrum two multiplet resonances are observed at δ 6.60 (XX′) and 5.96 (YY′) ppm, and a singlet resonance was observed at δ 6.48 (AA′) ppm. A NOE experiment confirmed that **24** retained its dimeric structure in solution, as a strong NOE was observed between the methyl protons of the aryl substituent and the protons of the COT″ ring. Unlike dimeric titanium imido COT complexes, which are insoluble in hydrocarbon solvents and tend to be dark in color, **24** was soluble in hydrocarbon solvents and highly colored (orange).



24

(10)

In a further attempt to make a monomeric analogue of **24**, $[Zr_2(\mu\text{-}NAr')_2Cl_4(THF)_4]$ was treated with the sterically bulky $Li_2[COT^*]$ ($COT^* = 1,4\text{-}C_8H_6(SiMe_2{}^tBu)_2$) in THF.[82] However, this reaction resulted in the formation of a mixture of products, as did similar reactions between $[Zr_2(\mu\text{-}NAr)_2Cl_4(THF)_4]$ and $Li_2[COT^*]$ or $[Zr_2(\mu\text{-}N^tBu)_2Cl_4(THF)_3]$ and $Li_2[COT^*]$. At this stage, it is unclear why the reactions between K_2COT, $Li_2COT''\cdot1.8(THF)$, and $Li_2[COT^*]$ and sterically bulky zirconium precursors give a mixture of products. It is possible that monomeric zirconium complexes of the type $[Zr(NR)(COT^R)]$ (COT^R = COT, COT″, or COT*) are unstable and decompose extremely quickly. This could explain why only dimeric complexes of the form $[Zr_2(\mu\text{-}NR)_2(COT)_2]$ have been isolated.

X-ray diffraction quality crystals of $[Zr_2(\mu\text{-}NAr')_2(COT'')_2]$ (**24**) were grown from a saturated ether solution at room temperature. The solid-state structure is shown in Figure 6, and selected distances and angles are given in Table 3. The asymmetric unit of the crystal contains two crystallographically distinct dimeric complexes, each of which is located on a crystallographic center of inversion. There are no major differences between the geometries of the two molecules, which have approximate $2/m$ (D_{2h}) point symmetry if the trimethylsilyl substituents are ignored.

The structure of $[Zr_2(\mu\text{-}NAr')_2(COT'')_2]$ (**24**) closely resembles that of $[Ti_2(\mu\text{-}NAr')_2(COT)_2]$.[23] As with the titanium complex, the $Zr_2(\mu\text{-}N)_2$ core of **24** is asymmetric, such that the Zr−N bond lengths are different (Zr(1)−N(1) = 2.123(2) and 2.144(2) Å, Zr(1)−N(1A) = 2.051(2) and 2.056(3) Å). These distances are longer than those observed in the titanium complex due to the larger atomic radius of zirconium. The Zr−N distances are also longer than those observed in the $[Zr_2(\mu\text{-}NAr')_2Cl_4(THF)_4]$ starting material (Zr−N = 2.018(5) and 2.115(5) Å in the starting material) due to a combination of steric factors and the higher valence electron count for the Zr centers in **24**.[81] The Zr···Zr distances within the two molecules are 3.2205(5) and 3.2212(5) Å, and these are similar to those observed in other related species.[3,81] Unlike the dinuclear zirconium imido species $[Zr_2(\mu\text{-}NAr)_2(\eta^5\text{-}C_5H_4Me)_2Cl_2]$, there is no interaction between either of the *ipso* carbons of the bridging μ-N-2,6-$Me_2C_6H_3$ ligands in **24** and the zirconium center, which is consistent with the higher valence electron count for the Zr centers in **24**.[80]

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Table 3. Selected Bond Lengths and Angles for $[Zr_2(\mu\text{-}NAr')_2(COT'')_2]$ (24)[a]

bond lengths	experimental values (Å)	bond angles (deg)	experimental values (deg)
Zr(1)−N(1)	2.123(2) and 2.144(2)	N(1)−Zr(1)−N(1A)	79.02(10) and 78.86(10)
Zr(1)−N(1A)	2.051(2) and 2.056(3)	Zr(1)−N(1)−Zr(1A)	100.98(10) and 101.14(10)
Zr(1)−C(9)	2.494(3) and 2.474(3)	N(1)−Zr(1)−C(9)	136.27(10) and 134.02(10)
Zr(1)−C(10)	2.503(3) and 2.501(3)	N(1)−Zr(1)−C(10)	168.25(10) and 165.82(10)
Zr(1)−C(11)	2.486(3) and 2.497(3)	N(1)−Zr(1)−C(11)	158.90(10) and 161.29(10)
Zr(1)−C(12)	2.465(3) and 2.477(3)	N(1)−Zr(1)−C(12)	127.29(9) and 104.55(10)
Zr(1)−C(13)	2.477(3) and 2.465(3)	N(1)−Zr(1)−C(13)	102.60(9) and 104.55(10)
Zr(1)−C(14)	2.531(3) and 2.530(3)	N(1)−Zr(1)−C(14)	89.67(9) and 90.55(10)
Zr(1)−C(15)	2.515(3) and 2.519(3)	N(1)−Zr(1)−C(15)	91.59(10) and 91.17(10)
Zr(1)−C(16)	2.440(3) and 2.444(3)	N(1)−Zr(1)−C(16)	108.37(9) and 107.00(10)
N(1)−C(1)	1.409(4) and 1.407(4)	Zr(1)−N(1)−C(1)	125.20(18) and 125.78(19)

[a] Values provided for both crystallographically different molecules in the Unit cell.

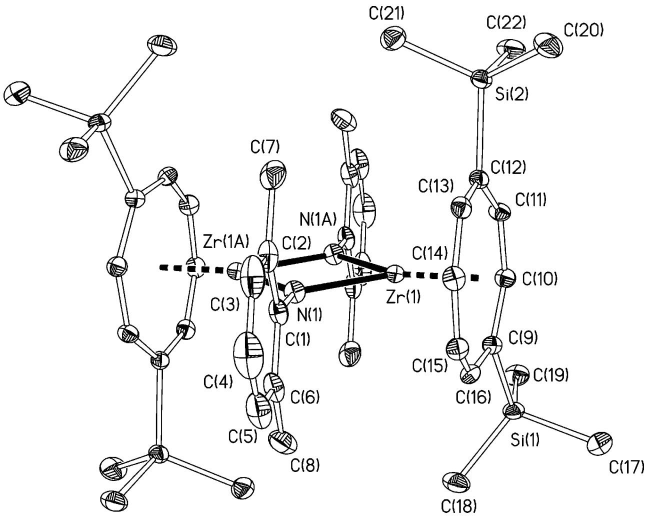

Figure 6. Displacement ellipsoid plot of one of the crystallographically distinct molecules of $[Zr_2(\mu\text{-}NAr')_2(COT'')_2]$ (**24**) (30% probability). H atoms are omitted. Atoms carrying the suffix "A" are related to their counterparts by the operator [1−*x*, −*y*, −*z*].

Conclusions

Overall, we have established that the Ti═NR linkage in compounds **1**−**3** is reasonably reactive. Despite their novel geometries, in some cases the reactivity pattern of compounds **1**−**3** mirrors the trends that have previously been established for titanium imido complexes. For example, the reactions of compounds **1**−**3** with CO_2, CS_2, isocyanates, and isothiocyanates generally result in cycloaddition−elmination reactions. However, in other cases the reactivity of compounds **1**−**3** is unusual. The reaction between **1** and ^tBuNC results in formal nitrene group transfer, and **1** is only the second example of a titanium imido species that will undergo reactions of this type. The reactions of **1**−**3** with thiols result in the unusual oxidation of the thiol to the disulfide. Important differences were observed between the reactivity of the *tert*-butyl imido species, **1**, and the aryl imido complex, **3**. In their reactions with CO_2 and CS_2 *tert*-butyl imido species are more prone to cycloaddition−elimination reactions, while aryl imido complexes are more likely to form stable cycloaddition products. Furthermore compound **3** forms stable adducts with ^tBuNC, while **1** undergoes nitrene group transfer reactions. Unfortunately, attempts to form mononuclear Zr analogues of compounds **1**−**3** were unsuccessful, and only dimeric products could be isolated.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^1H and ^{13}C spectra were recorded on Varian Unity Plus 300 and Varian Mercury 500 spectrometers. ^1H and ^{13}C assignments were confirmed when necessary with the use of NOE and two-dimensional $^1H-^1H$ and $^{13}C-^1H$ NMR experiments. All spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls between NaCl plates and were recorded on Perkin-Elmer 1600 and 1700 series spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of the University of Oxford's Inorganic Chemistry Laboratory. Combustion analyses were recorded by the elemental analysis service at the London Metropolitan University.

Density functional calculations were carried out using the Amsterdam Density Functional program suite ADF 2002.02.[83] Scalar relativistic corrections were included via the ZORA method.[84−88] The generalized gradient approximation was employed, using the local density approximation of Vosko, Wilk, and Nusair[89] together with nonlocal exchange correction by Becke[90,91] and nonlocal correlation corrections by Perdew.[92] TZP basis sets were used with triple-ζ accuracy sets of Slater type orbitals and two polarization functions added to the main group atoms. The cores of the atoms were frozen up to 1s for C, N and 2p for Ti. Fragment analyses use the MOs of the chosen fragments as the basis set for the molecular calculation. Initial spin-restricted calculations are

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carried out on the fragments with the geometry that they have in the molecule; thus the fragments are in a prepared singlet state.

Literature Preparations. [Ti(N^{t}Bu)(COT)] (**1**),[23] [Ti(N^{t}Bu)(COT″)] (**2**),[23] [Ti(NAr)(COT)] (**3**),[23] HS-2,4,6-^{i}Pr$_3$C$_6$H$_2$,[52] (2,4,6-^{i}Pr$_3$C$_6$H$_2$)S−S(2,4,6-^{i}Pr$_3$C$_6$H$_2$),[52] MeNC,[93] and [Ti(COT)(η^4-C$_8$H$_8$)] (**13**)[94] were prepared using literature methods.

Reaction between [Ti(N^{t}Bu)(COT)] (1) and CO$_2$. The following is a representative procedure for the reactions between compound **1** and CO$_2$, ^{t}BuNCO, ArNCO, and PhNO, and compound **3** and ^{t}BuNCO. For full details about each of these reactions see the Supporting Information.

A solution of [Ti(N^{t}Bu)(COT)] (**1**) (0.10 g, 0.45 mmol) in THF (15 mL) was exposed to ca. 1 atm CO$_2$ via a dual-manifold Schlenk line. The solution immediately changed color from yellow to dark brown and was left to stir for 14 h. The solvent was removed under reduced pressure to give a brown residue. The residue was washed with pentane (3 × 15 mL) and the solid dried in vacuo. The solid was characterized as [Ti(O)(COT)]$_n$ (**4**). The organic product of the reaction, ^{t}BuNCO, was identified through ^{1}H NMR spectroscopy when the reaction was performed on an NMR tube scale. The presence of ^{t}BuNCO in the NMR tube was confirmed by adding an authentic sample of ^{t}BuNCO to the reaction mixture.

IR data for **4** (NaCl plates, Nujol mull, cm^{-1}): 1260 (sh, s), 1093 (br, s), 1020 (br, s), 864 (w), 800 (s), 722 (w), 670 (w). Anal. Found (calcd for (C$_8$H$_8$OTi)$_n$: C 54.1 (57.2), H 4.5 (4.8). Low %C analysis is attributed to incomplete combustion.[23]

NMR Tube Scale Synthesis of [Ti{N(Ar)C(O)O}(COT)] (5). A solution of [Ti(NAr)(COT)](**3**) (10 mg, 31 μmol) in C$_6$D$_6$ (0.4 mL) was exposed to ca. 1 atm CO$_2$ via a dual-manifold Schlenk line. The solution immediately changed color from orange to light brown. The reaction mixture was monitored by ^{1}H NMR spectroscopy, and the quantitative conversion of **3** to [Ti{N(Ar)C(O)O}(COT)] (**5**) was observed.

^{1}H NMR (C$_6$D$_6$, 300.0 MHz, 298 K): δ 7.18 (2H, m, meta-NAr), 7.13 (1H, app d, para-NAr), 6.71 (8H, s, C$_8$H$_8$), 2.91 (2H, sept, C*H*Me$_2$, ^3J = 6.7 Hz), 1.38 (6H, d, CH*Me$_2$*, ^3J = 6.7 Hz), 1.14 (6H, d, CH*Me$_2$*, ^3J = 6.7 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): δ 164.5 (−NC(O)O−), 144.9 (*ipso*-NAr), 143.5 (*ortho*-NAr), 126.1 (*para*-NAr), 123.3 (*meta*-NAr), 103.2 (C$_8$H$_8$), 29.0 (*C*HMe$_2$), 25.7 (CH*Me$_2$*), 23.4 (CH*Me$_2$*).

Reaction between [Ti(N^{t}Bu)(COT″)] (2) and CO$_2$. The following is a representative procedure for the reactions between compound **2** and CO$_2$ and ^{t}BuNCO. For full details about each of these reactions see the Supporting Information.

A solution of [Ti(N^{t}Bu)(COT″)] (**2**) (0.10 g, 0.27 mmol) in THF (15 mL) was exposed to ca. 1 atm CO$_2$ via a dual-manifold Schlenk line. The solution immediately changed color from yellow to dark brown and was left to stir for 14 h. The solvent was removed under reduced pressure to give a brown residue. The residue was washed with pentane (3 × 15 mL) and the solid dried in vacuo. The solid was characterized as [Ti(O)(COT″)]$_n$ (**6**). The organic product of the reaction, ^{t}BuNCO, was identified through ^{1}H NMR spectroscopy when the reaction was performed on an NMR tube scale. The presence of ^{t}BuNCO in the NMR tube was confirmed by adding an authentic sample of ^{t}BuNCO to the reaction mixture.

IR data for **6** (NaCl plates, Nujol mull, cm^{-1}): 1260 (sh, s), 1092 (br, s), 1019 (br, s), 837 (s), 800 (s), 665 (w). Anal. Found (calcd for (C$_{14}$H$_{24}$OSi$_2$Ti)$_n$: C 50.2 (53.8), H 7.8 (7.7). Low %C analysis is attributed to incomplete combustion.[23]

Synthesis of [Ti{N(Ar)C(O)N(Ar)}(COT)] (7). A solution of ArNCO (124 mg, 0.61 mmol) in THF (10 mL) was added to a stirred solution of [Ti(NAr)(COT)] (**3**) (0.20 g, 0.61 mmol) in THF (10 mL). The reaction mixture was stirred for 3 h, during which time it darkened from orange to red. The volatiles were removed under reduced pressure and the residue washed with pentane (2 × 15 mL). The solid was dried in vacuo to afford **7** as a red powder. Yield: 0.16 g (50%).

^{1}H NMR (C$_6$D$_6$, 300.0 MHz, 298 K): δ 7.20 (2H, m, *para*-NAr), 7.13 (4H, partially obscured m, *meta*-NAr), 6.71 (8H, s, C$_8$H$_8$), 2.94 (4H, sept, C*H*Me$_2$, ^3J = 6.9 Hz), 1.42 (12H, d, CH*Me$_2$*, ^3J = 6.9 Hz), 1.19 (12H, d, CH*Me$_2$*, ^3J = 6.9 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): δ 164.6 (−NC(O)N−), 144.9 (*ipso*-NAr), 143.5 (*ortho*-NAr), 126.1 (*para*-NAr), 123.1 (*meta*-NAr), 103.2 (C$_8$H$_8$), 28.9 (*C*HMe$_2$), 25.7 (CH*Me$_2$*), 23.4 (CH*Me$_2$*). IR (NaCl plates, Nujol mull, cm^{-1}): 2726 (w), 2671 (w), 2361 (w), 2341 (w), 1647 (s), 1320 (m), 1277 (s), 1261 (s), 1096 (br, m), 1021 (br, m), 798 (s), 767 (s), 722 (s), 665 (m). EI-MS: *m/z* 531 (M)$^+$, 426 (M − COT)$^+$, 327 (Ti(NAr)(COT))$^+$, 203 (ArNCO)$^+$, 188 (ArNCO−Me)$^+$, 152 (Ti−COT)$^+$. Anal. Found (calcd for C$_{33}$H$_{42}$N$_2$OTi): C 74.6 (74.7), H 8.0 (8.0), N 5.1 (5.3).

Reaction between [Ti(N^{t}Bu)(COT)] (1) and CS$_2$. The following is a representative procedure for the reactions between compound **1** and CS$_2$ and ^{t}BuNCS and compound **3** and ^{t}BuNCS. For full details about each of these reactions see the Supporting Information.

A solution of CS$_2$ (31 mg, 0.45 mmol) in THF (10 mL) was added to a stirred solution of [Ti(N^{t}Bu)(COT)] (**1**) (0.10 g, 0.45 mmol) in THF (10 mL). Upon addition of the CS$_2$ solution, the color of the reaction mixture immediately changed from yellow to brown. The reaction mixture was stirred for 3 h, and the volatiles were removed under reduced pressure. The light brown residue was washed with pentane (2 × 15 mL), and the solid was dried in vacuo. The solid was characterized as [Ti(S)(COT)]$_n$ (**8**). The organic product of the reaction, ^{t}BuNCS, was characterized by ^{1}H NMR spectroscopy when the reaction was performed on an NMR tube scale. The presence of ^{t}BuNCS in the NMR tube was confirmed by adding an authentic sample of ^{t}BuNCS to the reaction mixture.

IR data for **8** (NaCl plates, Nujol mull, cm^{-1}): 1260 (sh, s), 1170 (w), 1092 (br, s), 1020 (br, s), 802 (w), 723 (s), 685 (w), 666(w). Anal. Found (calcd for (C$_8$H$_8$STi)$_n$: C 48.7 (52.2), H 4.1 (4.4). Low %C analysis is attributed to incomplete combustion.[23]

NMR Tube Scale Synthesis of [Ti{N(Ar)C(NAr′)S}(COT)] (9). A solution of Ar′NCS (5.0 mg, 31 μmol) in C$_6$D$_6$ (0.1 mL) was added to a solution of [Ti(NAr)(COT)] (**3**) (10 mg, 31 μmol) in C$_6$D$_6$ (0.3 mL). Upon addition of Ar′NCS, the reaction mixture immediately changed color from orange to brown. The reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy, and the conversion of **3** to [Ti{(NAr)C(NAr′)S}(COT)] (**9**) was observed.

^{1}H NMR (C$_6$D$_6$, 300.0 MHz, 298 K): δ 7.19 (1H, m, *para*-NAr), 7.13 (2H, partially obscured m, *meta*-NAr), 7.07 (2H, d, *meta*-CNAr′, ^3J = 7.5 Hz), 7.02 (1H, m, *para*-CNAr′), 6.65 (8H, s, C$_8$H$_8$), 2.83 (2H, sept, C*H*Me$_2$, ^3J = 7.0 Hz), 2.16 (6H, s, N-2,6-*Me$_2$*C$_6$H$_3$), 1.41 (6H, d, CH*Me$_2$*, ^3J = 7.0 Hz), 1.37 (6H, d, CH*Me$_2$*, ^3J = 7.0 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): δ 198.3 (−NC(NAr′)S−), 147.9 (*ipso*-NAr′), 144.8 (*ipso*-NAr), 143.5 (*ortho*-NAr), 143.0 (*ortho*-NAr′), 132.8 (*para*-NAr′), 126.5 (*para*-NAr), 125.6 (*meta*-NAr′), 123.3 (*meta*-NAr), 104.2 (C$_8$H$_8$), 29.0 (*C*HMe$_2$), 26.2 (CH*Me$_2$*), 24.2 (CH*Me$_2$*), 18.3 (N-2,6-*Me$_2$*C$_6$H$_3$).

Synthesis of [Ti{N(Ar)C(S)S}(COT)] (10). A solution of CS$_2$ (47 mg, 0.61 mmol) in THF (10 mL) was added to a stirred solution of [Ti(NAr)(COT)] (**3**) (0.20 g, 0.61 mmol) in THF (10 mL). Upon addition of the CS$_2$ solution, the color of the reaction mixture changed immediately from orange to brown. The reaction mixture was stirred for 30 min, and the volatiles were removed under reduced pressure. The brown residue was extracted into ether (3 × 15 mL) and isolated by filtration. The volatiles were again removed under reduced pressure, and the light brown residue was washed with pentane (2 × 15 mL). The solid was dried in vacuo to afford **10** as a dark red powder. Yield: 0.095 g (39%).

^{1}H NMR (C$_6$D$_6$, 300.0 MHz, 298 K): δ 7.18 (2H, m, *meta*-NAr), 7.10 (1H, d, *para*-NAr), 6.77 (8H, s, C$_8$H$_8$), 2.82 (2H, sept, C*H*Me$_2$, ^3J = 6.8 Hz), 1.38 (6H, d, CH*Me$_2$*, ^3J = 6.8 Hz), 1.31

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(6H, d, $CH\mathit{Me}_2$, $^3J = 6.8$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 200.6 (−NC(S)S−), 144.9 (*ipso*-NAr), 143.5 (*ortho*-NAr), 126.6 (*para*-NAr), 123.3 (*meta*-NAr), 104.1 (C_8H_8), 29.1 ($\mathit{C}HMe_2$), 26.3 ($CH\mathit{Me}_2$), 24.1 ($CH\mathit{Me}_2$). IR (NaCl plates, Nujol mull, cm^{-1}): 2725 (w), 2361 (w), 2341 (w), 1526 (w), 1319 (m), 1281 (w), 1261 (s), 1237 (w), 1203 (s), 1096 (br, m), 1021 (br, m), 972 (m), 802 (s), 757 (m), 722 (m). EI-MS: *m/z* 327 (M − CS_2)$^+$, 162 (2,6-$^iPr_2C_6H_3$)$^+$, 152 (Ti−COT)$^+$, 104 (COT)$^+$. Anal. Found (calcd for $C_{21}H_{25}NS_2Ti$): C 62.6 (62.5), H 6.3 (6.3), N 3.6 (3.5).

Synthesis of [Ti{OC(Me)$_2$C(Me)$_2$O}(COT)] (11). A solution of pinacol (70 mg, 0.60 mmol) in THF (10 mL) was added to a stirred solution of [Ti(N^{t}Bu)(COT)] (**1**) (0.22 g, 0.60 mmol) in THF (10 mL). The reaction mixture was stirred for 16 h, during which time it turned dark brown. The volatiles were removed under reduced pressure, and the yellow residue was washed with Et_2O (2 × 15 mL). The solid was isolated by filtration and dried in vacuo to afford **11** as a yellow powder. Yield: 0.14 g (57%)

^1H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.79 (8H, s, C_8H_8), 0.90 (12H, s, OC(Me)$_2$C(Me)$_2$O). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 100.7 (C_8H_8), 96.8 ($O\mathit{C}(Me)_2\mathit{C}(Me)_2O$), 26.3 ($OC(\mathit{Me})_2C(\mathit{Me})_2O$). IR (NaCl plates, Nujol mull, cm^{-1}): 1260 (s), 1148 (m), 1090 (br, s), 1018 (m), 799 (s). EI-MS: *m/z* 268 (M)$^+$, 210 (M − OC(Me$_2$))$^+$, 152 (Ti−COT)$^+$. HR EI-MS for [Ti{OC(Me)$_2$C(Me)$_2$O}(COT)]: found (calcd for $C_{14}H_{20}O_2Ti$) *m/z* = 268.0942 (268.0943). Anal. Found (calcd for $C_{14}H_{20}O_2Ti$): C 62.7 (62.7), H 7.5 (7.5).

Alternative NMR Tube Scale Synthesis of [Ti{OC(Me)$_2$C(Me)$_2$O}(COT)] (11) from [Ti(NAr)(COT)] (3). A solution of pinacol (3.6 mg, 0.031 mmol) in C_6D_6 (0.1 mL) was added to a solution of [Ti(NAr)(COT)] (**3**) (10 mg, 0.031 mmol) in C_6D_6 (0.4 mL). The reaction mixture was monitored by ^1H NMR for 12 h. During this time the quantitative conversion of **3** to [Ti{OC(Me)$_2$C(Me)$_2$O}(COT)] (**11**) was observed.

Synthesis of [Ti{OC(Me)$_2$C(Me)$_2$O}(COT″)] (12). A solution of pinacol (70 mg, 0.60 mmol) in THF (10 mL) was added to a stirred solution of [Ti(N^{t}Bu)(COT″)] (**2**) (0.22 g, 0.60 mmol) in THF (10 mL). The reaction mixture was stirred for 16 h, during which time it turned dark brown. The volatiles were removed under reduced pressure, and the green residue was extracted into pentane (2 × 15 mL) and filtered. The solution was cooled for 1 day at −30 °C, during which time a yellow solid precipitated out of solution. The solid was isolated by filtration, washed with pentane, and dried in vacuo to afford **12** as a yellow powder. Analysis by ^1H NMR spectroscopy indicated that the sample was sufficiently pure for further studies. Yield: 0.14 g (57%).

^1H NMR (C_6D_6, 300.0 MHz, 298 K): δ 7.36 (2H, s, 2- and 3-$C_8H_6(SiMe_3)_2$), 7.25 (2H, m, 5- and 8-$C_8H_6(SiMe_3)_2$), 7.02 (2H, m, 6- and 7-$C_8H_6(SiMe_3)_2$), 0.85 (12H, s, OC(Me)$_2$C(Me)$_2$O), 0.51 (18H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 111.2 (1- and 4-$C_8H_6(SiMe_3)_2$), 106.7 (2- and 3-$C_8H_6(SiMe_3)_2$), 104.2 (5- and 8-$C_8H_6(SiMe_3)_2$), 103.4.8 (6- and 7-$C_8H_6(SiMe_3)_2$), 96.5 ($O\mathit{C}(Me)_2\mathit{C}(Me)_2O$), 26.5 ($OC(\mathit{Me})_2C(\mathit{Me})_2O$), −0.1 ($SiMe_3$). IR (Nujol mull, NaCl plates, cm^{-1}): 1260 (s), 1094 (br, s), 1020 (br, s), 836 (m), 800 (s). EI-MS: *m/z* 412 (M)$^+$, 354 (M − OC(Me$_2$))$^+$, 296 (M − OC(Me$_2$)C(Me$_2$)O)$^+$, 73 ($SiMe_3$)$^+$. HR EI-MS for [Ti{OC(Me)$_2$C(Me)$_2$O}(COT″)]: found (calcd for $C_{22}H_{36}O_2Si_2Ti$) *m/z* = 412.1734 (412.1733). Anal. Found (calcd for $C_{22}H_{36}O_2Si_2Ti$): C 58.0 (58.2), H 8.7 (8.8).

NMR Tube Scale Reaction between [Ti(N^{t}Bu)(COT)] (1) and ^{t}BuSH. The following is a representative procedure for the reactions of compounds **1**−**3** with ^{t}BuSH, HS-2,4,6-$^iPr_3C_6H_2$, and 1,2-benzenethiol. For full details about each of these reactions see the Supporting Information.

A solution of [Ti(N^{t}Bu)(COT)] (**1**) (10 mg, 0.045 mmol) in C_6D_6 (0.4 mL) was treated with 2 equiv of ^{t}BuSH (8.1 mg, 0.090 mmol). Upon addition of ^{t}BuSH, the reaction mixture changed color from yellow to brown. The reaction mixture was monitored by ^1H NMR spectroscopy for 2 days, and a brown solid precipitated out of solution. The presence of ^{t}BuS−S^{t}Bu in the NMR tube was confirmed by adding an authentic sample of ^{t}BuS−S^{t}Bu to the reaction mixture. The intermediates [Ti(COT)(η^4-C_8H_8)][49] (**13**) and [Ti(S^{t}Bu)$_4$][50] were detected by ^1H NMR spectroscopy.

NMR Tube Scale Synthesis of [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (14). ^{t}BuNC (5.7 mg, 67 μmol) was added to a solution of [Ti(N^{t}Bu)(COT)] (**1**) (15 mg, 67 μmol) in C_6D_6 (0.4 mL). The reaction mixture was monitored by ^1H and ^{13}C NMR spectroscopy, and the quantitative conversion of [Ti(N^{t}Bu)(COT)] (**1**) to [Ti(N^{t}Bu)(COT)(CN^{t}Bu)] (**14**) was immediately observed. After 5 days at room temperature the resonances corresponding to **14** had disappeared and a new resonance corresponding to ^{t}BuNCN^{t}Bu was present in the ^1H NMR spectrum.

^1H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.59 (8H, s, C_8H_8), 0.91 (9H, s, br, N^{t}Bu), 0.84 (9H, s, CN^{t}Bu). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 95.1 (C_8H_8), 68.1 ($N\mathit{C}Me_3$), 54.8 (br, $CN\mathit{C}Me_3$), 32.8 ($NC\mathit{Me}_3$), 30.3 (br, $CNC\mathit{Me}_3$), $\mathit{C}NCMe_3$ not observed.

Reaction between [Ti(N^{t}Bu)(COT)] (1), ^{t}BuNC, and 1,3,5,7-Cyclooctatetraene. ^{t}BuNC (56 mg, 0.67 mmol) and 1,3,5,7-cyclooctatetraene (70 mg, 0.67 mmol) were added to a stirred solution of [Ti(N^{t}Bu)(COT)] (**1**) (0.15 g, 0.67 mmol) in benzene (15 mL). The reaction mixture was heated for 48 h at 100 °C and changed color from orange to brown. The solvent was removed under reduced pressure and the brown solid washed with pentane (2 × 15 mL). The solid was dried in vacuo to afford [Ti(COT)(η^4-C_8H_8)][49] (**13**) as a light brown powder. Yield: 120 mg (70%).

The organic product of the reaction, ^{t}BuNCN^{t}Bu, was characterized by ^1H NMR spectroscopy when the reaction was performed on an NMR tube scale.

Synthesis of [Ti(N^{t}Bu)(COT″)(CN^{t}Bu)] (15). A solution of ^{t}BuNC (33 mg, 0.41 mmol) in THF (10 mL) was added to a stirred solution of [Ti(N^{t}Bu)(COT″)] (**2**) (0.15 g, 0.41 mmol) in THF (10 mL). The reaction mixture darkened upon addition of ^{t}BuNC and was left to stir for 14 h. The volatiles were removed under reduced pressure to give an orange powder. The solid was washed with pentane (2 × 15 mL) and dried in vacuo to give **15** as an orange powder. Yield: 0.13 g (69%).

^1H NMR (C_6D_6, 300.0 MHz, 298 K): δ 7.05 (2H, s, 2- and 3-$C_8H_6(SiMe_3)_2$), 6.93 (2H, m, 5- and 8-$C_8H_6(SiMe_3)_2$), 6.75 (2H, m, 6- and 7-$C_8H_6(SiMe_3)_2$), 0.87 (9H, s, CN^{t}Bu), 0.79 (9H, s, N^{t}Bu), 0.60 (18H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 167.4 ($\mathit{C}N^tBu$), 103.1 (2- and 3-$C_8H_6(SiMe_3)_2$), 100.6 (1- and 4-$C_8H_6(SiMe_3)_2$), 99.6 (6- and 7-$C_8H_6(SiMe_3)_2$), 97.8 (5- and 8-$C_8H_6(SiMe_3)_2$), 67.8 ($N\mathit{C}Me_3$), 55.2 ($CN\mathit{C}Me_3$), 33.0 ($NC\mathit{Me}_3$), 29.6 ($CNC\mathit{Me}_3$), 0.9 ($SiMe_3$). IR (Nujol mull, NaCl plates, cm^{-1}): 2167 (s), 1245 (s), 1208 (s), 1091 (br, m), 1045 (s), 1020 (m), 942 (w), 913 (w), 837 (s), 802 (m). EI-MS: *m/z* 450 (M)$^+$, 367 (M − CN^{t}Bu)$^+$, 352 (Ti(N^{t}Bu)(COT″)−Me)$^+$, 296 (Ti−COT″), 248 (COT″), 83 (CN^{t}Bu), 73 ($SiMe_3$)$^+$. Anal. Found (calcd for $C_{23}H_{42}N_2Si_2Ti$): C 61.2 (61.3), H 9.4 (9.3), N 6.1 (6.2).

NMR Tube Scale Synthesis of [Ti(NAr)(COT)(CNMe)] (16). MeNC (1.9 mg, 46 μmol) was added to a solution of [Ti(NAr)(COT)] (**3**) (15 mg, 46 μmol) in C_6D_6 (0.4 mL). The reaction mixture was monitored by ^1H and ^{13}C NMR spectroscopy, and the quantitative conversion of **3** to [Ti(NAr)(COT)(CNMe)] (**16**) was immediately observed.

^1H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.79 (2H, d, *meta*-NAr, $^3J = 7.6$ Hz), 6.69 (1H, partially obscured t, *para*-NAr), 6.59 (8H, s, C_8H_8), 3.48 (2H, sept, $C\mathit{H}Me_2$, $^3J = 6.8$ Hz), 1.79 (3H, s, CNMe), 1.20 (12H, d, $CH\mathit{Me}_2$, $^3J = 6.8$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ 165.1 ($\mathit{C}NMe$), 152.8 (*ipso*-NAr), 140.6 (*ortho*-NAr), 123.3 (*meta*-NAr), 121.7 (*para*-NAr), 96.4 (C_8H_8), 44.1 ($CN\mathit{Me}$), 28.8 ($\mathit{C}HMe_2$), 23.9 ($CH\mathit{Me}_2$).

Synthesis of [Ti(NAr)(COT)(CN^{t}Bu)] (17). A solution of ^{t}BuNC (38 mg, 0.46 mmol) in THF (10 mL) was added to a stirred solution of [Ti(NAr)(COT)] (**3**) (0.15 g, 0.46 mmol) in THF (10 mL). The reaction mixture darkened upon addition of ^{t}BuNC and was left to stir for 14 h. The volatiles were removed under reduced pressure to give a light yellow powder. The solid was washed with pentane (2 × 15 mL) and dried in vacuo to give **17** as a yellow powder. Yield: 0.11 g (58%).

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.85 (2H, d, *meta*-NAr, $^3J = 7.6$ Hz), 6.66 (1H, partially obscured t, *para*-NAr), 6.66 (8H, s, C_8H_8), 3.45 (2H, sept, C*H*Me$_2$, $^3J = 7.1$ Hz), 1.22 (12H, d, CH*Me$_2$*, $^3J = 6.8$ Hz), 0.60 (9H, s, CN^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 160.0 (*C*NMe), 155.7 (*ipso*-NAr), 139.9 (*ortho*-NAr), 121.6 (*meta*-NAr), 120.2 (*para*-NAr), 96.4 (C_8H_8), 55.4 (CN*C*Me$_3$), 29.4 (CNC*Me$_3$*), 28.2 (*C*HMe$_2$), 23.7 (CH*Me$_2$*). IR (NaCl plates, Nujol mull, cm^{-1}): 2177 (s), 1320 (m), 1283 (m), 1260 (m), 1197 (m), 1153 (s), 1093 (br, s), 1020 (br, s), 964 (s), 801 (s), 754 (br, m), 737 (s), 721 (m), 665 (s). EI-MS: *m/z* 410 (M)$^+$, 327 (M − ^{t}BuNC)$^+$, 152 (Ti−COT)$^+$, 104 (COT)$^+$. Anal. Found (calcd for $C_{25}H_{34}N_2Ti$): C 73.0 (73.2), H 8.5 (8.4), N 6.8 (6.8).

NMR Tube Scale Synthesis of [Ti(NAr)(COT)(CNAr′)] (18). Ar′NC (4.0 mg, 31 μmol) was added to a solution of [Ti(NAr)(COT)] (**3**) (10 mg, 31 μmol) in C_6D_6 (0.4 mL). The reaction mixture was monitored by ^{1}H and ^{13}C NMR spectroscopy, and the quantitative conversion of **3** to [Ti(NAr)(COT)(Ar′NC)] (**18**) was immediately observed.

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.83 (2H, d, *meta*-NAr, $^3J = 7.5$ Hz), 6.69 (1H, partially obscured t, *para*-NAr), 6.68 (8H, s, C_8H_8), 6.66 (1H, partially obscured t, *para*-CNAr′), 6.45 (1H, d, *meta*-CNAr′, $^3J = 7.6$ Hz), 3.52 (2H, sept, C*H*Me$_2$, $^3J = 6.8$ Hz), 1.74 (6H, s, CN-2,6-*Me$_2$*C_6H_3), 1.21 (12H, d, CH*Me$_2$*, $^3J = 6.8$ Hz). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 163.1 (*C*NAr′), 157.6 (*ipso*-NAr), 152.8 (*ipso*-CNAr′), 139.9 (*ortho*-NAr), 135.5 (*ortho*-CNAr′), 129.3 (*para*-CNAr′), 127.1 (*para*-NAr), 121.7 (*meta*-NAr), 121.6 (*meta*-CNAr′), 96.9 (C_8H_8), 28.8 (*C*HMe$_2$), 23.5 (CH*Me$_2$*), 17.8 (CN-2,6-*Me$_2$*C_6H_3).

Synthesis of [Ti(N^{t}Bu)(COT)(py)] (19). Pyridine (73 mg, 0.67 mmol) was added to a stirred solution of [Ti(N^{t}Bu)(COT)] (**1**) (0.15 g, 0.67 mmol) in THF (10 mL). The reaction mixture was stirred for 1 h, during which time it turned dark yellow. The volatiles were removed under reduced pressure, and the brown residue was dried in vacuo. This gave **19** as a light brown powder. Analysis by ^{1}H NMR spectroscopy indicated that the sample was sufficiently pure for further studies. Yield: 0.16 g (79%). Light yellow crystals suitable for X-ray diffraction were obtained from a saturated solution of **19** in ether at room temperature.

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 8.47 (2H, br, *ortho*-py), 6.91 (1H, br, *para*-py), 6.58 (2H, br, *meta*-py), 6.63 (8H, s, C_8H_8), 0.63 (9H, s, N^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 150.1 (*ortho*-py), 135.4 (*para*-py), 123.2 (*meta*-py), 95.4 (C_8H_8), 69.1 (N*C*Me$_3$), 32.3 (NC*Me$_3$*). IR (NaCl plates, Nujol mull, cm^{-1}): 3070 (br, w), 2725 (br, w), 1306 (m), 1260 (sh, s), 1233 (sh, s), 1206 (m), 1170 (w), 1126 (s), 1094 (br, s), 1021 (br, s), 903 (m), 867 (s), 807 (m), 765 (s), 730 (w), 701 (sh, s). EI-MS: *m/z* 257 (M − 3Me)$^+$, 223 (M − py)$^+$, 208 (Ti(N^{t}Bu)(COT)−Me)$^+$, 167 (Ti(N^{t}Bu)(COT)−^{t}Bu)$^+$, 152 (Ti−COT)$^+$, 104 (COT)$^+$, 79 (py)$^+$.

Synthesis of [Ti(N^{t}Bu)(COT)(AlMe$_3$)] (20). To a stirred solution of [Ti(N^{t}Bu)(COT)] (**1**) (0.15 g, 0.67 mmol) in benzene (10 mL) was added Al_2Me_6 (48 mg, 0.34 mmol). The reaction mixture was stirred for 2 h, and the volatiles were removed under reduced pressure to give a brown powder. The powder was washed with pentane (2 × 15 mL) and carefully dried in vacuo to afford **20** as a light brown powder. Yield: 0.16 g (82%).

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.50 (8H, s, C_8H_8), 1.00 (9H, s, N^{t}Bu), −0.34 (9H, s, AlMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 101.4 (C_8H_8), 71.3 (N*C*Me$_3$), 33.3 (NC*Me$_3$*), −2.8 (AlMe$_3$). ^{27}Al{^{1}H} NMR (C_6D_6, 78.2 MHz, 298 K): δ 153.6 (AlMe$_3$). IR (Nujol mull, NaCl plates, cm^{-1}): 1260 (w), 1232 (m), 1210 (m), 1178 (w), 1165 (sh, s), 1125 (w), 1096 (br, w), 1025 (m), 955 (s), 921 (w), 907 (w), 806 (s), 767 (w), 744 (s), 730 (s), 687 (s). EI-MS: *m/z* 295 (M)$^+$, 223 (M − AlMe$_3$)$^+$, 209 (Ti(N^{t}Bu)(COT)−Me)$^+$, 209 (Ti(N^{t}Bu)(COT)−^{t}Bu)$^+$, 152 (Ti−COT)$^+$, 104 (COT)$^+$.

Synthesis of [Ti(NAr)(COT)(AlMe$_3$)] (21). To a stirred solution of [Ti(NAr)(COT)] (**3**) (0.20 g, 0.61 mmol) in benzene (10 mL) was added Al_2Me_6 (44 mg, 0.31 mmol). The reaction mixture was stirred for 2 h, and the volatiles were removed under reduced pressure to give a dark brown powder. The powder was washed with pentane (2 × 15 mL) and carefully dried in vacuo to afford **21** as a light brown powder. Yield: 0.19 g (76%).

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.97 (1H, t, *para*-NAr, $^3J = 7.0$ Hz), 6.85 (2H, d, *meta*-NAr, $^3J = 7.0$ Hz), 6.65 (8H, s, C_8H_8), 2.53 (2H, sept, C*H*Me$_2$, $^3J = 6.8$ Hz), 1.09 (12H, br, CH*Me$_2$*), −0.42 (9H, s, AlMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 142.0 (*ortho*-NAr), 135.9 (*ipso*-NAr), 129.2 (*meta*-NAr), 122.5 (*para*-NAr), 102.2 (C_8H_8), 28.4 (*C*HMe$_2$), 23.9 (CH*Me$_2$*), −6.0 (AlMe$_3$). ^{27}Al{^{1}H} NMR (C_6D_6, 78.2 MHz, 298 K): δ 164.7 (AlMe$_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 1582 (w), 1293 (m), 1261 (m), 1188 (br, w), 1163 (br, w), 1094 (br, m), 1021 (br, m), 983 (m), 908 (w), 820 (m), 794 (s), 767 (w), 741 (s), 722 (s). EI-MS: *m/z* 384 (M − Me)$^+$, 327 (M − AlMe$_3$)$^+$, 152 (Ti−COT)$^+$.

NMR Tube Scale Synthesis of [Ti(N^{t}Bu)(COT)(AlMe$_2$Cl)] (22). A 1.0 M solution of $Al_2Me_4(\mu\text{-}Cl)_2$ in hexane (4.5 mg, 45 μmol) was added to a solution of [Ti(N^{t}Bu)(COT)] (**1**) (10 mg, 45 μmol) in C_6D_6 (0.4 mL). Upon addition of $Al_2Me_4(\mu\text{-}Cl)_2$, the reaction mixture immediately darkened in color. The reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy, and the conversion of **1** to [Ti(N^{t}Bu)(COT)(AlMe$_2$Cl)] (**22**) was observed.

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.69 (8H, s, C_8H_8), 1.00 (6H, s, N^{t}Bu), −0.35 (9H, s, AlMe$_2$Cl). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 102.7 (C_8H_8), 70.0 (N*C*Me$_3$), 34.1 (NC*Me$_3$*), −1.8 (AlMe$_2$Cl).

NMR Tube Scale Synthesis of [Ti(NAr)(COT)(AlMe$_2$Cl)] (23). A 1.0 M solution of $Al_2Me_4(\mu\text{-}Cl)_2$ in hexane (3.1 mg, 31 μmol) was added to a solution of [Ti(NAr)(COT)] (**3**) (10 mg, 31 μmol) in C_6D_6 (0.4 mL). Upon addition of $Al_2Me_4(\mu\text{-}Cl)_2$, the reaction mixture darkened in color. The reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy, and the conversion of **3** to [Ti(NAr)(COT)(AlMe$_2$Cl)] (**23**) was observed.

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 6.98 (1H, t, *para*-NAr, $^3J = 7.6$ Hz), 6.85 (2H, d, *meta*-NAr, $^3J = 7.6$ Hz), 6.68 (8H, s, C_8H_8), 2.49 (2H, sept, C*H*Me$_2$, $^3J = 6.7$ Hz), 1.22 (6H, d, CH*Me$_2$*, $^3J = 6.7$ Hz), 0.81 (6H, d, CH*Me$_2$*, $^3J = 6.7$ Hz), −0.47 (6H, s, AlMe$_2$Cl). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 145.0 (*ortho*-NAr), 140.7 (*ipso*-NAr), 122.8 (*meta*-NAr), 122.6 (*para*-NAr), 103.4 (C_8H_8), 28.7 (*C*HMe$_2$), 25.7 (CH*Me$_2$*), 22.8 (CH*Me$_2$*), −3.8 (AlMe$_2$Cl).

Synthesis of [Zr$_2$(μ-NAr′)$_2$(COT″)$_2$] (24). A solution of Li$_2$[COT″]·1.8THF (0.18 g, 0.47 mmol) in benzene (10 mL) was added to a stirred solution of [Zr$_2$(μ-NAr′)$_2$Cl$_4$(THF)$_4$] (0.20 g, 0.24 mmol) in benzene (20 mL) over 15 min. The reaction mixture was stirred for 1 day, during which time it became orange. The volatiles were removed under reduced pressure, and the residue was washed with pentane (3 × 15 mL). The solid was dried in vacuo to afford **24** as an orange powder. Yield: 0.14 g (65%).

^{1}H NMR (C_6D_6, 300.0 MHz, 298 K): δ 7.13 (4H, d, *meta*-NAr′, $^3J = 7.2$ Hz), 6.81 (2H, t, *para*-NAr′, $^3J = 7.2$ Hz), 6.60 (4H, m, 5- and 8-C_8H_6(SiMe$_3$)$_2$), 6.48 (4H, s, 2- and 3-C_8H_6(SiMe$_3$)$_2$), 5.96 (4H, m, 6- and 7-C_8H_6(SiMe$_3$)$_2$), 2.11 (12H, s, N-2,6-*Me$_2$*C_6H_3), 0.28 (36H, s, SiMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 161.5 (*ipso*-NAr′), 128.9 (*ortho*-NAr′), 126.9 (*meta*-NAr′), 119.6 (*para*-NAr′), 107.2 (1- and 4-C_8H_6(SiMe$_3$)$_2$), 103.1 (2- and 3-C_8H_6(SiMe$_3$)$_2$), 101.2 (5- and 8-C_8H_6(SiMe$_3$)$_2$), 99.3 (6- and 7-C_8H_6(SiMe$_3$)$_2$), 33.1 (N-2,6-*Me$_2$*C_6H_3), 0.7 (SiMe$_3$). IR (NaCl

Table 4. Crystal Data Collection and Processing Parameters for [Ti(N^{t}Bu)(COT)(py)] (19) and [Zr$_2$(μ-NAr′)$_2$(COT″)$_2$] (24)

	19	**24**
empirical formula	$C_{17}H_{22}N_2Ti$	$C_{44}H_{66}N_2Si_4Zr_2$
fw	223.17	917.81
temp/K	150	150
wavelength/Å	0.710713	0.71073
space group	$P2_1/c$	$P\bar{1}$
a/Å	22.3354(2)	12.2894(3)
b/Å	8.8414(2)	14.0932(3)
c/Å	32.2753(3)	14.4434(3)
α/deg	90	89.7579(9)
β/deg	95.1230(4)	72.2524(9)
γ/deg	90	73.6913(9)
V/Å^3	6348.14(17)	2277.56(9)
Z	16	2
d(calcd)/Mg·m^{-3}	1.265	1.338
abs coeff/mm^{-1}	0.531	0.594
R indices R_1, R_w [$I > 3\sigma(I)$]	$R_1 = 0.043$ $R_w = 0.051$	$R_1 = 0.033$ $R_w = 0.038$

plates, Nujol mull, cm^{-1}): 1260 (s), 1090 (br, s), 1020 (br, s), 838 (s), 804 (m). EI-MS: m/z 918 (M)$^+$, 811 (M − Ar′)$^+$, 457 ($^1/_2$M)$^+$, 248 (COT″)$^+$. Anal. Found (calcd for $C_{44}H_{66}N_2Si_4Zr_2$): C 57.7 (57.6), H 7.2 (7.3), N 2.8 (3.1).

Crystal Structure Determination of [Ti(N^{t}Bu)(COT)(py)] (19) and [Zr$_2$(μ-NAr′)$_2$(COT″)$_2$] (24). Crystal data collection and processing parameters are given in Table 4. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer, and intensity data were processed using the DENZO-SMN package.[95] The structures were solved using SIR92,[96] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[97] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically, and weighting schemes were applied as appropriate. Full listings of atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **19** and **24** and further details of the DFT calculations and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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