

# Tandem couplings of imines and other unsaturated organic compounds with a half-open titanocene

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The half-open titanocene  $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})(\text{PEt}_3)$  ( $\text{C}_7\text{H}_{11}$  = dimethylpentadienyl) has been found to incorporate a second equivalent of  $\text{PhC}(\text{H})=\text{NMe}$  more slowly than the first, with coupling occurring between the imine's carbon atom and the diene's terminal  $\text{CH}_2$  groups. The structure of this complex has been confirmed through a diffraction study. The fact that a second imine could be incorporated has allowed mixed couplings involving initial incorporation of one equivalent of imine followed by another type of unsaturated compound. Thus, after addition and coupling of one equivalent of  $\text{PhC}(\text{H})\text{-NPr}^i$ , addition of an excess of acetone or  $\text{Bu}^i\text{NC}$  leads to the respective incorporation of one or two equivalents of these species. X-Ray diffraction studies have been carried out for each, and reveal that one equivalent of ketone or nitrile has undergone coupling. A reaction involving the same imine and  $p\text{-MeC}_6\text{H}_4\text{NC}$  in the presence of  $\text{Bu}^i\text{OH}$  was found to lead to the incorporation of three equivalents of the isocyanide along with one equivalent of the alcohol. The nature of the coupled product has been revealed through a diffraction study, and a reasonable mechanism proposed for the product's formation.

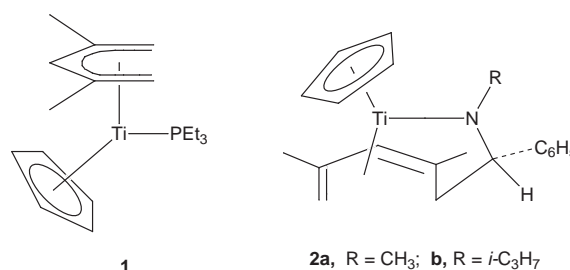
## Introduction

Half open titanocenes such as  $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})(\text{PEt}_3)$  contain two delocalized 5 electron donor ligands, one open and one closed, the former of which is both more strongly bound and more reactive than the latter.<sup>1,2</sup> To date, the most common reactions such species have been found to undergo are couplings with unsaturated organic molecules, such as alkynes, nitriles,<sup>1</sup> isocyanides,<sup>2</sup> alkynes,<sup>3</sup> imines,<sup>2</sup> and ketones.<sup>2</sup> In these reactions the pentadienyl ligand may commonly engage in as many as three couplings,<sup>†</sup> thereby serving in a formal sense as a pentadienyl trianion synthon [or a tris(Grignard) reagent]. In the cases in which polyfunctionalization has been observed, as with ketones and alkynes, one could generally not isolate intermediate products arising from fewer couplings, which appeared to be a significant limitation to this chemistry. However, it has now been observed that previously reported mono(imine) coupling products can incorporate a second imine, thus opening the door to a variety of mixed coupling products involving at least one imine. Here we report on the mixed species in which the second coupling partner can be a ketone, isocyanide, or another imine.

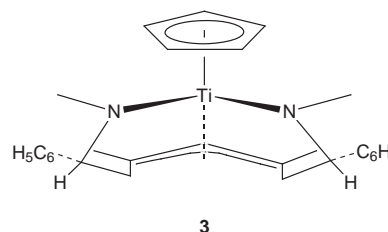
## Results and discussion

The reaction of  $\text{Ti}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})(\text{PEt}_3)$  **1** with one equivalent of  $\text{C}_6\text{H}_5\text{CH}=\text{NCH}_3$  had earlier been reported to yield an oil, whose spectroscopic characterization suggested structure **2a**,<sup>2</sup> which is consistent with a variety of other reaction products derived from organometallic compounds and imines.<sup>4</sup> It has now been found that the related imine  $\text{PhCH}=\text{NPr}^i$  undergoes a similar reaction, yielding a crystalline solid product, **2b**. The occurrence of a single coupling process at one end of the pentadienyl ligand is readily evidenced by the observation of a small  $J(^{13}\text{C}\text{-H})$  value for one of the terminal  $\text{CH}_2$  groups of the pentadienyl fragment (128 vs. 150 Hz), consistent with  $\text{sp}^3$  hybridization. A similarly small  $J(^{13}\text{C}\text{-H})$  value of 132 Hz is

<sup>†</sup> Once a third formal insertion between a Ti-C bond occurs the titanium center has formally reached the +4 oxidation state. Additional couplings may still occur,<sup>2</sup> but obviously do not lead to any further oxidation of the titanium center.



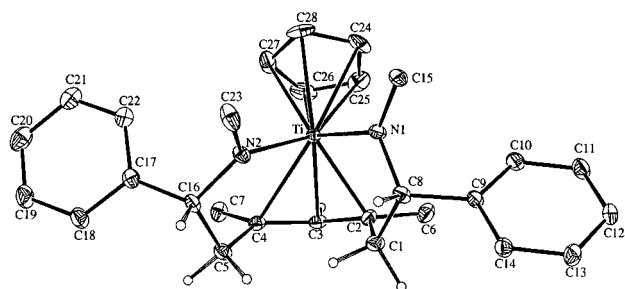
observed for the imine's coupled carbon atom, which has now selectively become a chiral center. While the spectroscopic data do not unambiguously establish the configuration at that atom, structural determinations of the mixed coupling products (see below) all reveal a configuration identical to that shown above, with the phenyl substituent directed away from the open edge of the pentadienyl fragment. No evidence for the opposite configuration was obtained for any of the isolated products, although it is possible that smaller amounts of the alternative products could have been produced in these reactions.



For complex **2a**, but not **2b**, prolonged exposure in solution to an excess of the imine led to slow conversion from deep red into bright green, reflecting the incorporation and coupling of a second equivalent of the imine. Compared to **2a** and **2b**, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the product **3** are much simplified, signifying the reestablishment of formal mirror plane symmetry in the molecule. Thus, a single resonance is observed for the equivalent  $\text{CH}_2$  groups in the 1 and 5 positions of the original pentadienyl fragment, with a  $J(^{13}\text{C}\text{-H})$  value of

**Table 1** Pertinent bonding parameters (distances in Å, angles in °) for compound **3**

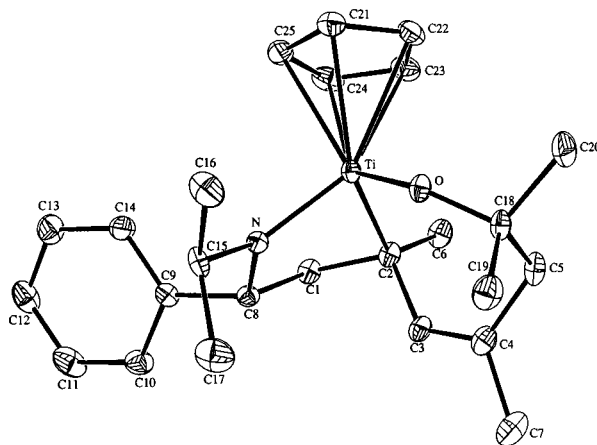
Ti–N1	1.959(3)	C1–C2	1.513(6)
Ti–N2	1.955(3)	C1–C8	1.521(6)
Ti–C2	2.252(4)	C2–C3	1.421(6)
Ti–C3	2.354(4)	C2–C6	1.505(6)
Ti–C4	2.575(4)	C3–C4	1.397(6)
Ti–C24	2.389(4)	C4–C5	1.507(6)
Ti–C25	2.443(5)	C4–C7	1.508(6)
Ti–C26	2.456(5)	C5–C16	1.519(6)
Ti–C27	2.372(5)	C8–C9	1.529(6)
Ti–C28	2.334(5)	C16–C17	1.534(6)
N1–C8	1.479(5)	N2–C16	1.468(5)
N1–C15	1.461(5)	N2–C23	1.442(5)
N1–Ti–N2	97.0(1)	C2–C3–C4	133.6(4)
Ti–N1–C8	116.3(2)	C3–C4–C5	126.8(4)
Ti–N1–C15	130.4(3)	C3–C4–C7	117.7(4)
C8–N1–C15	111.5(3)	C5–C4–C7	113.4(4)
N1–C8–C1	106.5(3)	C4–C5–C16	113.1(4)
N1–C8–C9	115.1(3)	C5–C16–C17	113.2(3)
C9–C8–C1	112.3(4)	C5–C16–N2	106.4(3)
C8–C1–C2	113.7(4)	C17–C16–N2	114.7(4)
C1–C2–C3	125.3(4)	C16–N2–Ti	129.7(3)
C1–C2–C6	114.9(4)	C16–N2–C23	111.3(3)
C3–C2–C6	114.9(4)	C23–N2–Ti	119.0(3)



**Fig. 1** Solid state structure of compound **3**.

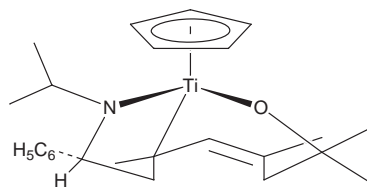
127 Hz, indicative of  $sp^3$  hybridization. Once again, a similar  $J(^{13}\text{C}-\text{H})$  value (135 Hz) is observed for the imine's coupled carbon atoms.

A single crystal diffraction study has confirmed the structural formulation for **3** (Fig. 1, Table 1). During the coupling process, the imine's phenyl substituents have been oriented away from the open edge of the pentadienyl fragment, thereby selectively generating chiral centers at each location. Based on the general structural result, one can consider the product formally to be a  $\text{Ti}(\text{C}_5\text{H}_5)(\text{allyl})(\text{amide})_2$  complex. The Ti–N bond distances are essentially equivalent at 1.957(2) Å, and when taken together with the nearly trigonal planar arrangements about N1 and N2 this suggests that the amides are functioning as 3 electron donors, through an additional  $\pi$  interaction each. These  $\pi$  interactions may be exerting a significant effect on the Ti– $\text{C}_5\text{H}_5$  bonding, as the two carbon atoms (C25, C26) most opposite to N1 and N2 are clearly furthest from Ti at *ca.* 2.450(4) Å, with C24 and C27 closer at *ca.* 2.381(4) Å, and C28 closest at 2.334(5) Å. Also notable is the asymmetry in the titanium–allyl bonding. With the Ti–C(2–4) distances progressively increasing [2.252(4), 2.354(4), 2.575(4) Å], and the C2–C3 bond appearing to be longer than C3–C4 [1.421(6) *vs.* 1.397(6) Å], one could consider the possibility of some contribution of a  $\sigma$ -allyl complex. However, in such a case a much shorter Ti–C2 distance should be observed (see below), as well as a greater difference between the C–C distances. It is likely best to consider the allyl co-ordination as  $\eta^3$ , although there may be some contribution from a localized bonding mode (*i.e.*, with a Ti–C2 single bond and C3=C4 also co-ordinated). The origin for this asymmetry could be a result of some asymmetry in the titanium–amide interactions. While the angles about the C(1 *vs.* 5) and C(8 *vs.* 16) atoms are similar, those about N1 and N2 are not (except



**Fig. 2** Perspective view of compound **4**.

for their C–N–C angles). Thus, the Ti–N1–C8 angle of 116.3(2)° is less than the Ti–N2–C16 angle of 129.7(3)°, while the opposite is true for the Ti–N(1 or 2)–C(15 or 23) angles, 130.4(3) *vs.* 119.0(3)°. Whether this is a result of an attempt to relieve eclipsing  $\text{CH}_3 \cdots \text{CH}_3$  interactions, to optimize the two  $\pi$  interactions with the titanium center, or simply is a response to packing forces is unclear. In any event, the upward drift of N1 relative to N2 then seems responsible for the asymmetry in the titanium–allyl bonding, as this leads to more of a *trans* relationship with C4.



4

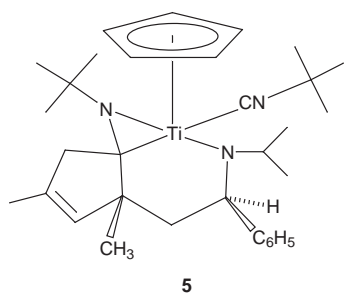
As one would expect from the fact that two equivalents of a ketone can couple to a half-open titanocene, addition of acetone to compound **2b** leads to the anticipated coupling between the carbonyl group and the previously uncoupled diene terminus. This is quite evident from the  $J(^{13}\text{C}-\text{H})$  values of 125 and 118 Hz for the two  $\text{CH}_2$  groups, reflecting formal  $sp^3$  hybridization. Thus, although **2b** will not incorporate a second imine, a smaller and more reactive ketone may be added. However, a large difference in chemical shift is observed for the C2 and C4 positions of the original diene fragment,  $\delta$  83.7 *vs.* 126.7, which should reflect a major bonding difference relative to **3**. This is in fact observed from the structural result (Fig. 2, Table 2). As can be seen, in this case the product may be considered to be a  $\text{Ti}(\text{C}_5\text{H}_5)(\sigma\text{-allyl})(\text{alkoxide})(\text{amide})$  species **4**. The  $\sigma$ -allyl interaction is clearly indicated by the short Ti–C2 distance of 2.153(3) Å, and the sizeable asymmetry in the C2–C3 and C3–C4 distances [1.512(4) *vs.* 1.338(5) Å]. There are no apparent overriding steric or geometric reasons for the change in allyl co-ordination mode, but since a  $\sigma$  interaction has also been found in bis(ketone) coupling products the formal presence of potentially 5 electron donor alkoxide group(s) would seem to be implicated. The Ti–O–C18 angle of 146.1(2)°, while not the ideal 180° value one might expect, is nonetheless significantly greater than the value of *ca.* 133° expected for 3 electron donation,<sup>5</sup> and the Ti–O distance of 1.803(2) Å is clearly shorter than related examples which are considered as 3 electron donors,<sup>2,5</sup> so there is good reason to implicate at least some contribution of the alkoxide ligand as a 5 electron donor. The Ti–N distance of 1.914(3) Å is actually slightly shorter than the values for **3**, and with the nearly planar arrangement about N clearly reflects its formal donation of 3 electrons. It can

**Table 2** Pertinent bonding parameters (distances in Å, angles in °) for compound **4**

Ti–O	1.803(2)	O–C18	1.410(4)
Ti–N	1.914(3)	C1–C2	1.547(5)
Ti–C2	2.153(3)	C1–C8	1.535(5)
Ti–C21	2.383(3)	C2–C3	1.512(4)
Ti–C22	2.457(3)	C2–C6	1.531(5)
Ti–C23	2.461(4)	C3–C4	1.338(5)
Ti–C24	2.438(3)	C4–C5	1.510(5)
Ti–C25	2.407(3)	C4–C7	1.498(5)
N–C8	1.470(4)	C5–C18	1.550(5)
N–C15	1.467(4)	C8–C9	1.521(4)
O–Ti–N	107.9(1)	C5–C4–C7	116.0(3)
O–Ti–C2	104.9(1)	C4–C5–C18	114.5(3)
N–Ti–C2	85.7(1)	N–C8–C1	107.7(2)
Ti–O–C18	146.1(2)	N–C8–C9	114.4(3)
Ti–N–C8	115.0(2)	C1–C8–C9	111.0(3)
Ti–N–C15	129.3(2)	C8–C9–C10	119.5(3)
C8–N–C15	114.6(2)	C8–C9–C14	122.4(3)
C2–C1–C8	112.7(3)	C10–C9–C14	118.1(3)
Ti–C2–C1	95.4(2)	C9–C10–C11	120.9(3)
Ti–C2–C3	106.0(2)	C10–C11–C12	120.1(3)
Ti–C2–C6	125.1(2)	C11–C12–C13	120.0(3)
C1–C2–C3	108.9(3)	C12–C13–C14	119.3(4)
C1–C2–C6	109.6(3)	C9–C14–C13	121.6(3)
C3–C2–C6	110.3(3)	N–C15–C16	109.5(3)
C2–C3–C4	130.5(3)	N–C15–C17	112.4(3)
C3–C4–C5	123.4(3)	C16–C15–C17	109.9(3)
C3–C4–C7	120.5(3)	O–C18–C5	107.7(2)

be further noted that the decrease in bond distance going from Ti–C2 to Ti–N to Ti–O [2.153(3), 1.914(3), 1.803(2) Å] is in each case significantly greater than the decrease in covalent radii for these non-metals,<sup>6</sup> and also can not be fully accounted for by electronegativity differences.<sup>7</sup>

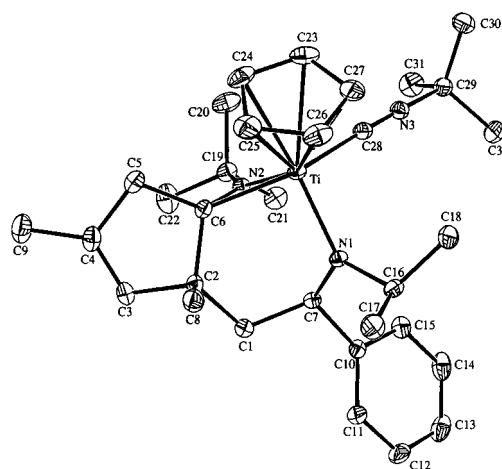
An obvious structural difference relative to compound **3** is the twist around the C2–C3 bond, which leads to a more sickle-shaped diene fragment. Such a twist was not observed for the bis(ketone) coupling product,<sup>2</sup> suggesting that it may be brought about by the imine's isopropyl group. The alteration of the oxygen atom location leads to significantly larger O–Ti–(C2, N) angles relative to the C2–Ti–N angle [104.9(1) and 107.9(1) vs. 85.7(1)°]. A final apparent result of the altered heteroatom locations is the slight asymmetry in Ti–C<sub>5</sub>H<sub>5</sub> bonding. As for **3**, the atoms furthest from a *trans* location (C21, C25) are those which are closest to the titanium center.



Reactions of compound **2b** with isocyanides were also investigated. With Bu<sup>t</sup>NC, two equivalents were incorporated. In this case spectroscopic data did not reveal much about the product **5**, other than the fact that both terminal CH<sub>2</sub> groups had coupled [ $J(^{13}\text{C}-\text{H}) = 125, 126 \text{ Hz}$ ], and that one isocyanide apparently had not undergone any coupling ( $\nu_{\text{C}-\text{N}} 2172 \text{ cm}^{-1}$ ). A structural determination was therefore carried out to elucidate the mode of coupling, and pertinent bonding parameters are presented in Table 3. As can be seen in Fig. 3, one of the isocyanides has simply co-ordinated to the metal center, while the second has had its terminal carbon atom couple to both ends of the former diene fragment, leading to structure **5**. This rather simple mode of coupling contrasts significantly with the much

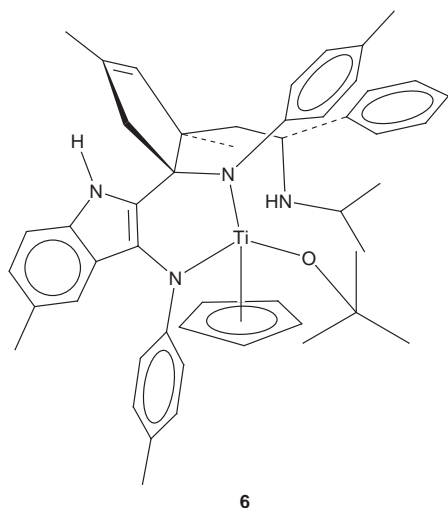
**Table 3** Pertinent bonding parameters (distances in Å, angles in °) for compound **5**

Ti–N1	1.973(2)	C1–C2	1.538(3)
Ti–N2	1.919(2)	C1–C7	1.553(3)
Ti–C6	2.113(2)	C2–C3	1.528(3)
Ti–C23	2.433(3)	C2–C6	1.566(3)
Ti–C24	2.422(3)	C2–C8	1.542(3)
Ti–C25	2.400(3)	C3–C4	1.321(3)
Ti–C26	2.416(3)	C4–C5	1.513(3)
Ti–C27	2.427(3)	C4–C9	1.498(3)
Ti–C28	2.217(2)	C5–C6	1.540(3)
N1–C7	1.504(3)	N2–C19	1.488(3)
N1–C16	1.482(3)	N3–C28	1.154(3)
N2–C6	1.393(3)	N3–C29	1.456(3)
N1–Ti–N2	97.92(7)	C3–C2–C6	100.3(2)
N1–Ti–C6	94.44(8)	C2–C3–C4	112.4(2)
N1–Ti–C28	94.63(8)	C2–C3–C5	110.4(2)
N2–Ti–C6	40.07(8)	C3–C4–C9	128.9(2)
N2–Ti–C28	86.80(8)	C5–C4–C9	120.7(2)
C6–Ti–C28	126.85(8)	C4–C5–C6	103.3(2)
Ti–N1–C7	112.49(12)	Ti–C6–N2	62.43(11)
Ti–N1–C16	132.39(14)	Ti–C6–C2	114.37(13)
C7–N1–C16	115.0(2)	Ti–C6–C5	132.2(2)
Ti–N2–C6	77.50(12)	N2–C6–C2	122.2(2)
Ti–N2–C19	148.2(2)	N2–C6–C5	119.9(2)
C6–N2–C19	132.1(2)	C2–C6–C5	103.1(2)
C28–N3–C29	177.3(2)	N1–C7–C1	115.4(2)
C2–C1–C7	116.7(2)	N1–C7–C10	114.6(2)
C1–C2–C3	114.7(2)	C1–C7–C10	113.2(2)
C1–C2–C6	116.5(2)	Ti–C28–N3	173.1(2)

**Fig. 3** Solid state structure of compound **5**.

more complex processes observed with aromatic isocyanides (see below), likely the result of the additional steric bulk of the Bu<sup>t</sup> group.<sup>8</sup> For a pentadienyl ligand, a simple coupling of an isocyanide to the two diene ends would lead to an allyl fragment, as opposed to the present alkene, and the metal would need to remain attached to the allyl group. It is likely that the requirement that the metal remain attached to both the putative allyl and initial one end-coupled isocyanide prevented the other end from coupling, at least until a second isocyanide arrived and coupled between the first isocyanide and the other terminal group, yielding a seven membered ring. Even after that the allyl group may have problems interacting with the metal center, as further incorporation and couplings of isocyanides took place. In examining the bonding parameters for **5**, one finds nothing unusual about either the uncoupled isocyanide ligand or the Ti–N1 interaction. In the latter case the amide seems to function as a 3 electron donor, given a nearly planar disposition about N1. However, the Ti–N1 distance of 1.973(2) Å is slightly to somewhat longer than the values observed for **3** and **4**. The main point of interest is then the bonding involving the coupled isocyanide fragment. As shown above for **5**, one could consider

the Ti–C6 interaction to be a single bond, and the N2–Ti interaction to be that of a  $\pi$  amide (3 electron donation), and this would be consistent with the short Ti–C6 distance [2.113(2) Å], the Ti–N2 distance of 1.919(2) Å, and the nearly trigonal disposition about N2. However, the C6–N2 distance of 1.393(3) Å is clearly much shorter than it should be for a single bond (*cf. ca.* 1.47 Å for **3** and **4**). Furthermore, the angles about C6 (excluding those with Ti) average 115.1°, getting close to that expected for  $sp^2$  hybridization. It may therefore be that a partial  $\pi$  bond is being generated between C6 and N2, although the orientations of their available p (or hybrid) orbitals for such an interaction would be significantly twisted relative to the ideal situation.<sup>9</sup> In any case, should a net of 4 electrons be donated from C6 and N2, the titanium center could achieve an 18 electron configuration.

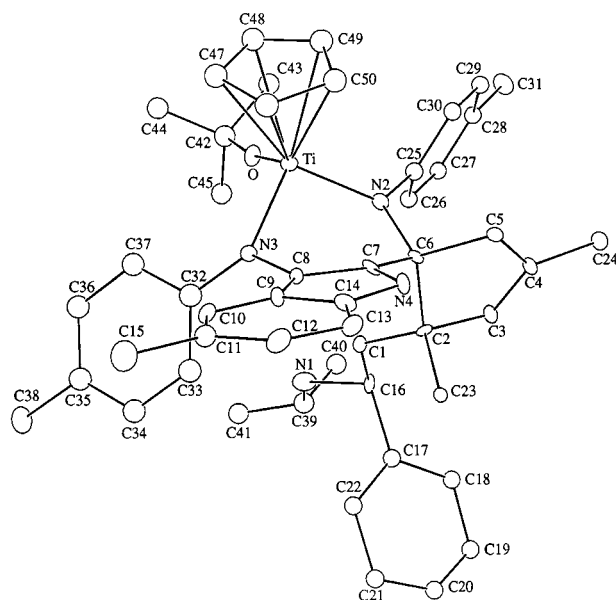


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As is often the case,<sup>10</sup> a more complex process is followed with aryl isocyanides. Unfortunately, some of the products from compound **2b** were not readily amenable to crystallization and isolation. However, a very small amount of crystalline solid was isolated in one case, as the result of a small Bu<sup>t</sup>OH impurity in the *p*-tolyl isocyanide, and it was subsequently observed that this species could be isolated in good yields by using a stoichiometric (1 : 3) ratio of the alcohol and isocyanide in the coupling reaction. Infrared and NMR data indicated that all isocyanides had coupled, as well as the original diene's two terminal CH<sub>2</sub> groups, but not the diene's central CH group. A diffraction study revealed the structure to be that of **6** (R = *p*-MeC<sub>6</sub>H<sub>4</sub>) (Fig. 4, Table 4), in which some rather complex couplings have occurred, along with conversion of the alcohol into alkoxide, with transfer of the proton to a nitrogen center. A possible mechanism for the formation of this complex is provided in Scheme 1. The key issue of contention in the mechanism would be the point at which the alcohol is incorporated. It has been observed that **2b** will react with Bu<sup>t</sup>OH, although relatively slowly compared to its reactions with isocyanides, resulting in the addition of a proton to the diene ligand, yielding an allyl ligand.<sup>11</sup> Thus, it is fairly clear that **2b** preferentially incorporates an isocyanide molecule instead of an alcohol. Given that conclusion, it seems most likely that the subsequent isocyanide incorporations occur prior to alcohol incorporation, although this point is not absolutely established. However, the alcohol incorporation must occur prior to the construction of the indole skeleton, as it is known that in the absence of the alcohol the formation of an indole is not competitive with the incorporation of a fourth equivalent of isocyanide.<sup>11</sup> Hence, the sequence presented in Scheme 1 affords a plausible explanation for the formation of the observed product, **6**. One interesting step is that in which the coupling of an azaallyl fragment (depicted as a  $\pi$  ligand, although  $\sigma$  co-ordination is also pos-

**Table 4** Pertinent bonding parameters (distances in Å, angles in °) for compound **6**·OEt<sub>2</sub>

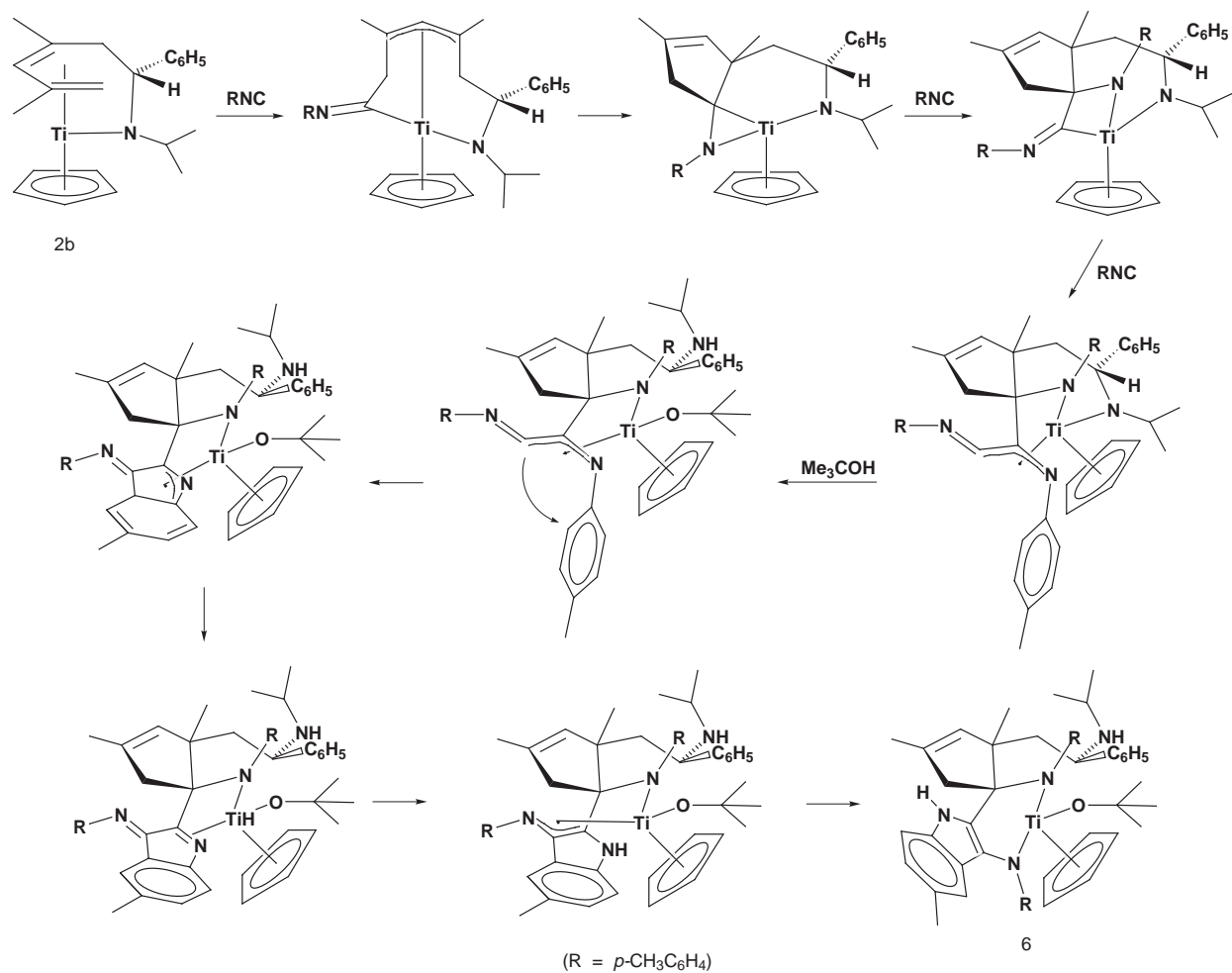
Ti–O	1.760(10)	N3–C32	1.39(2)
Ti–N2	1.946(12)	N4–C7	1.39(2)
Ti–N3	1.939(11)	N4–C14	1.39(2)
Ti–C46	2.42(2)	C1–C2	1.53(2)
Ti–C47	2.45(2)	C1–C16	1.51(2)
Ti–C48	2.43(2)	C2–C3	1.55(2)
Ti–C49	2.42(2)	C2–C6	1.61(2)
Ti–C50	2.40(2)	C3–C4	1.34(2)
O–C42	1.45(2)	C4–C5	1.51(2)
N1–C16	1.49(2)	C5–C6	1.56(2)
N1–C39	1.51(2)	C6–C7	1.51(2)
N2–C6	1.46(2)	C7–C8	1.37(2)
N2–C25	1.43(2)	C8–C9	1.45(2)
N3–C8	1.40(2)	C13–C14	1.39(2)
O–Ti–N2	101.1(5)	C2–C3–C4	110.6(15)
O–Ti–N3	102.7(5)	C3–C4–C5	112.5(14)
N2–Ti–N3	96.0(5)	C3–C4–C24	125.7(17)
Ti–O–C42	169.0(11)	C5–C4–C24	121.7(14)
C16–N1–C39	117.1(16)	C4–C5–C6	102.7(12)
Ti–N2–C6	120.8(10)	N2–C6–C2	114.5(12)
Ti–N2–C25	118.5(9)	N2–C6–C5	109.4(11)
C6–N2–C25	120.4(12)	N2–C6–C7	106.3(13)
Ti–N3–C8	102.9(10)	C2–C6–C5	102.3(12)
Ti–N3–C32	136.4(11)	C2–C6–C7	110.2(12)
C8–N3–C32	120.8(12)	C5–C6–C7	114.4(13)
C7–N4–C14	109.4(14)	N4–C7–C6	122.7(17)
C2–C1–C16	117.6(12)	N4–C7–C8	108.1(15)
C1–C2–C3	116.8(13)	C6–C7–C8	128.4(17)
C1–C2–C6	110.4(12)	N3–C8–C7	124.8(17)
C3–C2–C6	99.6(12)	N3–C8–C9	126.8(16)
		C7–C8–C9	106.9(15)



**Fig. 4** Solid state structure of compound **6**.

sible) with a *p*-tolyl group leads to the first fused ring precursor to the indole. The coupling could be envisioned as a nucleophilic attack on the arene, or as a formal insertion of an olefin (within the arene ring) into the Ti–C (azaallyl) bond. This step must necessarily differ from that proposed for an indole construction from a complex pentadienyl–isocyanide coupling reaction,<sup>2‡</sup> and thus raises the likely possibility that the fused ring construction for the previous indole system would also occur in a manner analogous to that proposed here.

‡ The reason a different process is proposed here derives from the fact that in the present case, just prior to the indole construction, the complex must be regarded as involving Ti<sup>IV</sup>, whereas in the previous case it could still be considered Ti<sup>II</sup>.



Scheme 1

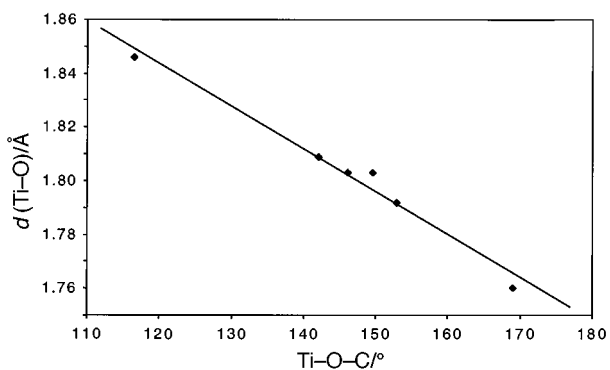
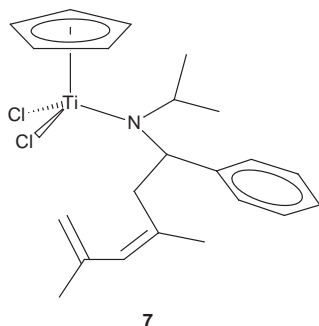


Fig. 5 Variation of the Ti-O bond distances with the Ti-O-C bond angles in related coupling products.

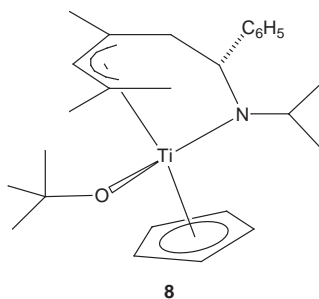
The structure may be considered to be pseudo-tetrahedral with the four co-ordination sites on Ti being occupied by C<sub>5</sub>H<sub>5</sub>, O, N<sub>2</sub>, and N<sub>3</sub>. The N-Ti-(N,O) angles are fairly similar, with that of N<sub>2</sub>-Ti-N<sub>3</sub> [96.0(5)°] being slightly smaller than the others, perhaps due to the presence of a bridge between N<sub>2</sub> and N<sub>3</sub>. The angles about both N<sub>2</sub> and N<sub>3</sub> sum to *ca.* 360°, reflecting a planar arrangement, consistent with 3 electron donation. The Ti-O-C<sub>42</sub> angle of 169.0(11)° is greater than the value of 146.1(2)° in **4**, whose alkoxide interaction appeared to possess some contribution as a five electron donor. In fact, the present Ti-O distance of 1.760(10) Å is even shorter than that of 1.803(2) Å in **4**, again perhaps implicating some contribution as a five electron donor. As can be seen in Fig. 5, there is an excellent correlation ( $R^2 = 0.978$ , with the average deviation in distance from the plot being 0.003 Å, or 1 $\sigma$ ) between Ti-O

distance and the Ti-O-C angle for a variety of species;<sup>2</sup> the correlation roughly suggests formal 1 (sp<sup>3</sup>) and 5 (sp) electron donation limits for the Ti-O distances to be *ca.* 1.86 and 1.75 Å, respectively. Interestingly, data for some other metal systems have been equivocal,<sup>12</sup> perhaps in part due to sizeable steric effects and the poorer  $\pi$ -donating ability of aryl oxide *vs.* alkoxide ligands.<sup>13</sup> However, were both amides to serve as 3 electron donors, and the alkoxide and C<sub>5</sub>H<sub>5</sub> ligands to serve as 5 electron donors, the complex would attain a 20 electron configuration. There is no clear reason to believe any slippage of the C<sub>5</sub>H<sub>5</sub> ligand is occurring, as the Ti-C distances are comparable to those in **4**; however, the Ti-N(2,3) distances average 1.943(8) Å, appearing to be longer than the 1.914(3) Å distance in **4**. It is quite possible if not inevitable, therefore, for **6** and other species as well, that the  $\pi$  donations for the amide, alkoxide, and even Cp ligands represent only partial interactions, as metal orbitals would not be available to accept the electrons from each ligand orbital. In this case a parallel may be drawn with the situation for W(PhCCPh)<sub>3</sub>(CO).<sup>14</sup>

In addition to the above coupling reactions, it was of interest to investigate other modes of reactivity of these complexes. In an attempt to initiate the removal of the coupled fragment from the metal center, a reaction between **2b** and C<sub>2</sub>Cl<sub>6</sub> was attempted. In fact, a change to bright red was observed, but the product could only be isolated as a red oil. Nevertheless, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data (see Experimental section) suggest that the diene has been removed from the metal center, as for example three C-H resonances experience significant downfield shifts, which would be expected for the free diene unit in one possible product **7**. Unfortunately, crystalline material could not be isolated even at -90 °C, preventing definitive characterization through a structural study.



As Bu<sup>t</sup>OH was found to react selectively with an isocyanide coupling product, yielding **6**, a similar reaction was attempted with **2b**. Indeed, a slow color change revealed that a reaction had occurred, but the product could only be isolated as an oil, precluding definitive structural characterization. Nonetheless, relatively clean <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained. Particularly diagnostic was the presence of eight methyl groups, providing a strong indication that protonation did not occur on nitrogen (as happened for **6**) but instead for the uncoupled terminal CH<sub>2</sub> group of the original diene fragment, presumably yielding **8**. However, the product can be expected to be a  $\sigma$ , rather than  $\pi$ , allyl, based upon the precedents demonstrated for other mixed allyl/alkoxide complexes<sup>2</sup> (see below). Support for this assignment can be obtained from the <sup>13</sup>C NMR resonances for the allylic fragment. For the mixed imine/ketone coupling product **4** these were observed at  $\delta$  83.7, 139.6, and 126.7, nearly identical to those of the proposed **8**,  $\delta$  83.6, 144.5, and 121.4.



The fact that a second equivalent of an imine will couple to a pentadienyl ligand much more slowly than the first, presumably as a result of steric influences, has allowed for the tandem couplings of a pentadienyl ligand with an imine and either a ketone, nitrile,<sup>11</sup> other imine, or even isocyanide. In each case the two heteroatoms become joined by a chain of seven carbon atoms. Conceivably, the use of bulkier ketones such as acetophenone could also lead to the selective isolation of mono(coupling) products, thereby allowing for the subsequent incorporation of a second coupling partner. In any event, other tandem couplings involving Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(diene) complexes have also been achieved,<sup>15</sup> and in the cases involving heteroatom-containing multiple bonds the heteroatoms become joined by a chain of six carbon atoms. Certainly one can expect that, with the appropriate choice of metal  $\pi$  complex, similar tandem couplings will be able to lead to related species with other chain lengths separating the heteroatoms. Such possibilities are currently under investigation.

## Experimental

All operations were carried out under a nitrogen atmosphere using either Schlenk techniques or a glove-box. Hydrocarbon, aromatic, diethyl ether and THF solvents were distilled under nitrogen from sodium–benzophenone. Aryl isocyanides<sup>16</sup> and Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(2,4-C<sub>7</sub>H<sub>11</sub>)(PR<sub>3</sub>) (C<sub>7</sub>H<sub>11</sub> = dimethylpentadienyl, R = Me or Et)<sup>1,17</sup> were prepared according to published pro-

cedures. Spectroscopic data were obtained as previously described.<sup>18</sup> The <sup>13</sup>C NMR spectra were not precisely integrated, but numbers of carbon atoms are given in accord with their assignments. Elemental analyses were obtained from E + R Microanalytical Labs, Robertson Microanalytical Labs, or Desert Analytics.

## Preparations

**Ti(C<sub>5</sub>H<sub>5</sub>)(NPr<sup>i</sup>CHPhCH<sub>2</sub>CMe=CHCMe=CH<sub>2</sub>) 2b.** To a stirred solution of Ti(C<sub>5</sub>H<sub>5</sub>)(2,4-C<sub>7</sub>H<sub>11</sub>)(PEt<sub>3</sub>) (0.50 g, 1.4 mmol) in 50 mL THF under nitrogen at –78 °C was added PhC(H)NPr<sup>i</sup> (0.42 mL, 2.8 mmol). After warming to room temperature with stirring overnight, a dark red color appeared. The solvent was then removed *in vacuo*, leaving behind a red oily residue which was in turn extracted with three 50 mL portions of pentane. These extracts were filtered through a Celite pad on a coarse frit. The dark red filtrate was concentrated *in vacuo* to ca. 20 mL and placed in a –90 °C freezer for 2 d. Removal of the supernatant *via* syringe and drying *in vacuo* gave 0.40 g (74%) of the product as an air-sensitive, dark red solid (mp 81–82 °C) (Found: C, 74.51; H, 8.08; N, 3.89. Calc. for C<sub>22</sub>H<sub>29</sub>N<sub>1</sub>Ti: C, 74.36; H, 8.08; N, 3.89%). <sup>1</sup>H NMR (benzene-d<sub>6</sub>, ambient):  $\delta$  7.5–7.4 (m, 5 H, Ph), 5.67 (s, 5 H, Cp), 4.50 (d, 1 H,  $J = 6$ , H-5<sub>exo</sub>), 3.65 (s, 1 H, H-3), 3.14 [septet,  $J = 6.6$ , NCH(CH<sub>3</sub>)<sub>2</sub>], 2.98 (dd, 1 H,  $J = 6$ , 1.4, H-1), 2.67 (dd, 1 H,  $J = 6$ , 1.5, H-5<sub>endo</sub>), 2.52 (dd, 1 H,  $J = 14$ , 7, CHPh), 2.24 (d, 1 H,  $J = 14$ , H-1'), 1.58 (s, 3 H, CH<sub>3</sub>C=), 1.56 (s, 3 H, CH<sub>3</sub>C=), 0.86 [d, 3 H,  $J = 6.5$ , CH(CH<sub>3</sub>)<sub>2</sub>] and 0.65 (d, 3 H,  $J = 6.6$ , CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, ambient):  $\delta$  151.7 (s, 1 C), 128–126 (5 C), 115.9 (d, 1 C,  $J = 154$ , C-3), 108.5 (d of quintets, 5 C,  $J = 172$ , 7, Cp), 95.9 (s, 1 C, C-2 or 4), 67.6 (d, 1 C,  $J = 132$ , CHPh), 61.1 (t, 1 C,  $J = 150$ , C-5), 52.9 [d, 1 C,  $J = 131$ , CH(CH<sub>3</sub>)<sub>2</sub>], 43.9 (t, 1 C,  $J = 128$ , C-1), 32.2 (q, 1 C,  $J = 132$ , CH<sub>3</sub>C=), 30.4 (q, 1 C,  $J = 132$ , CH<sub>3</sub>C=), 24.4 [qt, 1 C,  $J = 126$ , 4, NCH(CH<sub>3</sub>)<sub>2</sub>] and 23.6 [qt, 1 C,  $J = 126$ , 5, NCH(CH<sub>3</sub>)<sub>2</sub>].

**Ti(C<sub>5</sub>H<sub>5</sub>)(NMeCHPhCH<sub>2</sub>CMe=CH=CMeCH<sub>2</sub>CHPhNMe) 3.** To a stirred solution of Ti(C<sub>5</sub>H<sub>5</sub>)(2,4-C<sub>7</sub>H<sub>11</sub>)(PMe<sub>3</sub>) (1.00 g, 3.52 mmol) in 50 mL THF under nitrogen at –78 °C was added PhC(H)NMe (1.00 mL, 8.11 mmol, 2.2 equivalents). Upon warming with stirring to room temperature overnight a dark green color appeared. The solvent was then removed *in vacuo* leaving a green oily residue which was in turn extracted with three 50 mL portions of pentane. The extracts were filtered through a Celite pad on a coarse frit. The emerald green filtrate was then concentrated *in vacuo* to ca. 20 mL and placed in a –20 °C freezer for 2 d. Removal of the supernatant *via* syringe and drying *in vacuo* gave 0.74 g (45%) of the product as an air-sensitive dark green solid (mp 118–120 °C). The C<sub>5</sub>H<sub>4</sub>Me analogue was also prepared in the same way in 40% yield (Found: C, 75.08; H, 7.74; N, 6.12. Calc. for C<sub>28</sub>H<sub>34</sub>N<sub>2</sub>Ti: C, 75.32; H, 7.68; N, 6.27%). <sup>1</sup>H NMR (benzene-d<sub>6</sub>, ambient):  $\delta$  7.3–7.1 (m, 10 H, Ph), 5.83 (s, 5 H, Cp), 4.85 (d, 2H,  $J = 8$ , H-1,5), 4.07 (s, 1 H, H-3), 3.60 (dd, 2 H,  $J = 14$ , 8, CHPh), 3.01 (s, 6 H, NCH<sub>3</sub>), 2.15 (d, 2 H,  $J = 14$ , H-1,5') and 1.68 (s, 6 H, CH<sub>3</sub>C=). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, ambient):  $\delta$  147.6 (s, 2 C, Ph), 128.5–127.7 (m, 10 C, Ph), 116.7 (s, 2 C, C-2,4), 111.1 (d of quintets, 5 C,  $J = 171$ , 6, Cp), 109.1 (d, 1 C,  $J = 170$ , C-3), 82.2 (d, 1 C,  $J = 135$ , CHPh), 44.1 (q, 2 C,  $J = 130$ , NCH<sub>3</sub>), 40.5 (t, 2 C,  $J = 127$ , C-1,5) and 32.2 (q, 2 C,  $J = 127$  Hz, CH<sub>3</sub>C=). Mass spectrum (EI, 25 eV): *m/z* (relative intensity) 327 (9), 218 (9), 217 (61), 216 (77), 215 (10), 214 (23), 208 (31), 207 (10), 206 (43), 198 (15), 184 (20), 160 (19), 121 (35), 120 (100), 119 (34), 118 (60), 104 (9), 91 (14), 77 (8) and 42 (21).

**Ti(C<sub>5</sub>H<sub>5</sub>)(NPr<sup>i</sup>CHPhCH<sub>2</sub>CMeCH=CMeCH<sub>2</sub>CMe<sub>2</sub>O) 4.** To a stirred solution of compound **2b** (0.92 g, 2.6 mmol) in 50 mL diethyl ether under nitrogen at –78 °C was added acetone (0.23 mL, 3.1 mmol, 1.1 equivalents). The mixture was warmed with

stirring to 0 °C, changing from dark to light red. At 0 °C, the solvent was removed *in vacuo*, leaving a red solid, which was in turn extracted with three 50 mL portions of pentane. The extracts were filtered through a Celite pad on a coarse frit. The bright red filtrate was concentrated *in vacuo* to ca. 20 mL. Placement of the filtrate in a -90 °C freezer for 2 d gave a red solid. The supernatant was removed *via* syringe, and the solid dried *in vacuo* to give 0.42 g (41%) of the product as an air-sensitive bright red solid (mp 112–115 °C) (Found: C, 72.43; H, 8.63; N, 3.29. Calc. for C<sub>25</sub>H<sub>35</sub>NOTi: C, 72.63; H, 8.53; N, 3.39%). <sup>1</sup>H NMR (benzene-d<sub>6</sub>, ambient): δ 7.33–7.10 (m, 5 H, Ph), 6.16 (s, 1 H, H-3), 6.13 (s, 5 H, Cp), 4.39 (dd, 1 H, *J* = 8, 12), 2.63 [septet, 1 H, *J* = 6.4, CH(CH<sub>3</sub>)<sub>2</sub>], 2.31 (dd, 1 H, *J* = 12, 15), 2.11 (dd, 1 H, *J* = 8, 15), 1.98 (d, 1 H, *J* = 12, H-1), 1.98 (s, 3 H, CH<sub>3</sub>C=), 1.33 [2 s, 6 H, (CH<sub>3</sub>)<sub>2</sub>CO], 1.30 (d, 1 H, *J* = 12, H-1'), 1.18 (s, 3 H, CH<sub>3</sub>C=), 1.17 [d, 3 H, *J* = 6.1, CH(CH<sub>3</sub>)<sub>2</sub>] and 0.91 [d, 3 H, *J* = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>]. <sup>13</sup>C NMR (benzene-d<sub>6</sub>, ambient): δ 146.5 (s, 1 C, Ph), 139.6 (d, 1 C, *J* = 146, C-3), 126.7–129.9 (m, 4 C, Ph), 126.7 (s, 1 C, C-4), 112.6 (d of quintets, 5 C, *J* = 171, 6, Cp), 90.3 (s, 1 C, C-O), 83.7 (s, 1 C, C-2), 61.6 (d, 1 C, *J* = 136, CHPh), 53.4 [d, 1 C, *J* = 135, CH(CH<sub>3</sub>)<sub>2</sub>], 50.5 (t, 1 C, *J* = 124, C-1 or 5), 48.1 (tq, 1 C, *J* = 128, 6, C-1 or 5), 31.5 (q, 1 C, *J* = 124, CH<sub>3</sub>C=), 30.7 (q, 1 C, *J* = 128, CH<sub>3</sub>C=), 29.3 (q, 1 C, *J* = 123, CH<sub>3</sub>CO), 27.8 (q, 1 C, *J* = 125, CH<sub>3</sub>CO), 24.9 [q, 1 C, *J* = 125, CH(CH<sub>3</sub>)<sub>2</sub>] and 20.2 [q, 1 C, *J* = 124 Hz, CH(CH<sub>3</sub>)<sub>2</sub>]. Mass spectrum (EI, 33 eV): *m/z* (relative intensity) 413 (16), 356 (11), 355 (36), 266 (30), 210 (14), 209 (41), 208 (100), 207 (43), 206 (91), 205 (15), 204 (14), 169 (17), 148 (56), 147 (32), 132 (61), 106 (9), 105 (16), 104 (13) and 91 (11).

**Ti(C<sub>2</sub>H<sub>5</sub>)(NBu<sup>i</sup>CH<sub>2</sub>CH<sub>2</sub>CMe=CHCMeCH<sub>2</sub>CHPhNPr<sup>i</sup>)(Bu<sup>i</sup>-NC) 5.** To a stirred solution of compound **2b** (0.50 g, 1.4 mmol) in 50 mL ether under a nitrogen atmosphere at -78 °C was added *tert*-butyl isocyanide (0.32 mL, 2.8 mmol). A rapid change from dark to bright red occurred upon the addition. The reaction mixture was then warmed with stirring to 0 °C and the solvent removed *in vacuo* to leave behind a dark red solid. The solid was in turn extracted with three 50 mL portions of ether-pentane (50:50) and the extracts were filtered through a Celite pad on a coarse frit. The resulting bright red filtrate was concentrated *in vacuo* to ca. 20 mL and placed into a -30 °C freezer for one week. The supernatant was removed *via* syringe, and the solid dried *in vacuo* yielding 0.31 g (42%) of the product as air-sensitive dark red crystals (mp 117–119°) (Found: C, 73.43; H, 9.08; N, 8.05. Calc. for C<sub>32</sub>H<sub>47</sub>N<sub>3</sub>Ti: C, 73.68; H, 9.08; N, 8.05%). <sup>1</sup>H NMR (benzene-d<sub>6</sub>, ambient): δ 7.42–7.01 (m, 5 H, Ph), 6.09 (s, 5 H, Cp), 5.77 (s, 1 H, H-3), 5.72 (dd, 1 H, (*J* = 5, 8), 3.33 (d, 1 H, *J* = 16, H-5), 3.30 [septet, 1 H, *J* = 6.6, CH(CH<sub>3</sub>)<sub>2</sub>], 2.52 (dd, 1 H, *J* = 8, 14), 2.00 (dd, 1 H, *J* = 5, 14), 1.86 (s, 3 H, CH<sub>3</sub>C=), 1.70 (d, 1 H, *J* = 16, H-5'), 1.44 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>CNC], 1.20 (s, 3 H, CH<sub>3</sub>C=), 1.10 [d, 3 H, *J* = 6.8, CH(CH<sub>3</sub>)<sub>2</sub>], 0.92 [d, 3 H, *J* obscure, CH(CH<sub>3</sub>)<sub>2</sub>] and 0.91 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>CNC]. <sup>13</sup>C NMR (toluene-d<sub>8</sub>, -40 °C): δ 151.6 (s, 1 C, CN), 141.0 (s, 1 C, C-4), 140.0 (s, 1 C, Ph), 109.8 (d, 1 C, *J* = 170, C-3), 108.0 (d of quintets, 5 C, *J* = 170, 6, Cp), 88.4 (s, 1 C, C-6), 67.5 (d, 1 C, *J* = 135, CHPh), 61.0 (d, 1 C, obscured, CH(CH<sub>3</sub>)<sub>2</sub>), 59.8 (s, 1 C, C(CH<sub>3</sub>)<sub>3</sub>), 56.5 (s, 1 C, C-2), 53.0 [s, 1 C, C(CH<sub>3</sub>)<sub>3</sub>], 47.6 (t, 1 C, *J* = 125, C-5), 43.0 (t, 1 C, *J* = 126, C-1), 34.0 [q, 3 C, *J* = 129, C(CH<sub>3</sub>)<sub>3</sub>], 33.8 (q, 1 C, *J* = 129, CH<sub>3</sub>C=), 29.0 (q, 1 C, *J* = 131, CH<sub>3</sub>C=), 28.8 [q, 3 C, *J* = 131, C(CH<sub>3</sub>)<sub>3</sub>], 26.6 [q, 1 C, *J* = 127, CH(CH<sub>3</sub>)<sub>2</sub>] and 24.4 [q, 1 C, *J* = 127 Hz, CH(CH<sub>3</sub>)<sub>2</sub>]. Mass spectrum (EI, 70 eV): *m/z* (relative intensity) 521 (3), 520 (2), 357 (12), 208 (29), 206 (27), 188 (29), 169 (10), 166 (11), 165 (100), 148 (14), 147 (14), 132 (16), 109 (19), 57 (21), 43 (15) and 41 (15). IR (Nujol mull): 3000–2800vs, 2172vs, 1600vw, 1460vs, 1376vs, 1370w, 1261vs, 1240m, 1095s, 1063m, 1019vs, 910w, 798vs and 701s.

**Compound 6.** To a stirred solution of compound **2b** (0.50 g, 1.4 mmol) in 50 mL THF under nitrogen at -78 °C was added a

3:1 mixture of *p*-tolyl isocyanide-*tert*-butyl alcohol (0.61 mL, 4.2 mmol:0.13 mL, 1.4 mmol). A rapid change from dark to bright red occurred upon the addition. The mixture was warmed with stirring to room temperature and then stirred at room temperature for an additional hour. Next the solvent was removed *in vacuo* leaving a dark red sticky solid. This was extracted with three 50 mL portions of ether-pentane (50:50). Then the extracts were filtered through a Celite pad on a coarse frit. The bright red filtrate was concentrated *in vacuo* to ca. 20 mL, placed into a -90 °C freezer for 2 d, then transferred to a -30 °C freezer for 3 d during which dark red crystals emerged. Removal of the supernatant *via* syringe and drying of the crystals *in vacuo* yielded 0.67 g (61%) of the product as air-stable dark red cube-shaped crystals (mp 129–133 °C) (Found: C, 76.58; H, 8.01; N, 6.93. Calc. for C<sub>50</sub>H<sub>60</sub>N<sub>4</sub>OTi: C, 76.82; H, 7.74; N, 7.17%). <sup>1</sup>H NMR (benzene-d<sub>6</sub>, ambient; some resonances obscured): δ 7.34 (s, 1 H), 7.30–6.96 (Ph), 5.77 (s, 5 H, Cp), 5.62 (s, 1 H, H-3), 3.81 (dd, 1 H, *J* = 6, 16), 2.96 (dd, 2 H, *J* = 7, 15), 2.51 [septet, 2 H, *J* = 3.3, CH(CH<sub>3</sub>)<sub>2</sub>], 2.45 (d, 1 H, *J* = 16), 2.31 (d, 1 H, *J* ≈ 16), 2.28 (s, 3 H, CH<sub>3</sub>), 2.22 (s, 3 H, CH<sub>3</sub>), 2.16 (s, 3 H, CH<sub>3</sub>), 2.02 (dd, 1 H, *J* = 6, 15), 1.27 (s, 3 H, CH<sub>3</sub>C=), 1.17 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 0.99 [d, 3 H, *J* = 6.0, CH(CH<sub>3</sub>)<sub>2</sub>], 0.82 [d, 3 H, *J* = 6.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>] and 0.65 (s, 3 H, CH<sub>3</sub>C=). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, ambient): δ 150.5 (s, 1 C), 150.4 (s, 1 C), 147.0 (s, 1 C), 135.0–121.5 (22 C), 118.6 (d 1 C, *J* = 153), 113.3 (s, 1 C), 111.8 (d, 1 C, *J* = 157, C-3), 109.7 (d of quintets, 5 C, *J* = 171, 7, Cp), 84.6 (s, 1 C, C-6), 79.0 [s, 1 C, C(CH<sub>3</sub>)<sub>3</sub>], 65.9 (t, 1 C, *J* = 140, C-5), 58.8 (s, 1 C, C-2), 58.5 (d, 1 C, *J* = 132, CHPh), 45.2 (t, 1 C, *J* = 132, C-1), 42.6 [d, 1 C, *J* = 127, CH(CH<sub>3</sub>)<sub>2</sub>], 32.1 [q, 3 C, *J* = 125, C(CH<sub>3</sub>)<sub>3</sub>], 24.7 (q, 1 C, *J* = 128, CH<sub>3</sub>C=), 24.2 (q, 1 C, *J* = 125, CH<sub>3</sub>C=), 21.9 (q, 1 C, *J* = 126, CH<sub>3</sub>), 21.6 (q, 1 C, *J* = 126, CH<sub>3</sub>), 21.0 (q, 1 C, *J* = 125, CH<sub>3</sub>), 16.2 [q, 1 C, *J* = 124, CH(CH<sub>3</sub>)<sub>2</sub>] and 15.6 [q, 1 C, *J* = 125 Hz, CH(CH<sub>3</sub>)<sub>2</sub>]. Mass spectrum (EI, 25 eV): *m/z* (relative intensity) 782 (8), 781 (20), 780 (34), 779 (14), 778 (16), 738 (9), 737 (17), 706 (15), 634 (18), 633 (49), 632 (100), 631 (25), 630 (27), 596 (10), 594 (14), 578 (9), 577 (24), 576 (47), 520 (12), 489 (13), 392 (14), 328 (16) and 148 (9). IR (Nujol mull): 3332m br, 3000–2800vs, 1608w, 1502m, 1460vs, 1377s, 1303w, 1261m, 1096w, 1020w and 806vs.

**Ti(C<sub>2</sub>H<sub>5</sub>)(NPr<sup>i</sup>CHPhCH<sub>2</sub>CMe=CHCMe=CH<sub>2</sub>)Cl<sub>2</sub> 7.** Into a NMR tube was added compound **26** (60 mg, 0.20 mmol) and C<sub>2</sub>Cl<sub>6</sub> (40 mg, 0.20 mmol) followed by 0.60 mL of deuteriated benzene. After sealing the tube the mixture was shaken during which a bright red color was observed. Isolation of the compound using the same general procedure as that for the above complex gave a red oil. <sup>1</sup>H NMR (benzene-d<sub>6</sub>, ambient): δ 7.51–6.89 (m, 5 H, Ph), 6.21 (s, 5 H, Cp), 5.63 (s, 1 H, H-3), 5.01 (s, 1 H), 4.78 (s, 1 H), 4.76 (d, 1 H, *J* = 11, H-5), 3.97 (dd, 1 H, *J* = 11, 15, CHPh), 3.30 [septet, 1 H, *J* = 6.3, CH(CH<sub>3</sub>)<sub>2</sub>], 2.26 (d, 1 H, *J* = 15, H-5'), 1.75 (s, 3 H, CH<sub>3</sub>), 1.63 (s, 3 H, CH<sub>3</sub>C=), 1.20 (d, 3 H, *J* = 6.4, CH<sub>3</sub>) and 1.15 (d, 3 H, *J* = 6.1 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, ambient): δ 157.6 (s, 1 C), 144.4 (s, 1 C), 142.1 (s, 1 C), 134.9–128.0 (m, 5 C), 118.2 (d of quintets, 5 C, *J* = 177, 6, Cp), 114.9 (t, 1 C, *J* = 156, C-1), 65.3 (d, 1 C, *J* = 132, CHPh), 51.3 [d, 1 C, *J* = 127, CH(CH<sub>3</sub>)<sub>2</sub>], 41.3 (t, 1 C, *J* = 128, C-5), 23.9 (q, 1 C, *J* = 126, CH<sub>3</sub>C=), 23.2 (q, 1 C, *J* = 125, CH<sub>3</sub>C=), 20.7 [q, 1 C, *J* = 127, CH(CH<sub>3</sub>)<sub>2</sub>] and 19.9 [q, 1 C, *J* = 128 Hz, CH(CH<sub>3</sub>)<sub>2</sub>].

**Ti(C<sub>2</sub>H<sub>5</sub>)(NPr<sup>i</sup>CHPhCH<sub>2</sub>CMeCHCMe<sub>2</sub>)(Bu<sup>i</sup>O) 8.** To a stirred solution of compound **2b** (0.50 g, 1.4 mmol) in 50 mL ether under an atmosphere of nitrogen at -78 °C was added *tert*-butyl alcohol (0.13 mL, 1.4 mmol). A slow change from dark to light red occurred upon warming to room temperature. The mixture was stirred at room temperature for 1 h. The solvent was next removed *in vacuo*, leaving a dark red sticky oil which was extracted with three 50 mL portions of pentane. These extracts were filtered through a Celite pad on a coarse

**Table 5** X-Ray data parameters for compounds **3**, **4**, **5** and **6**

	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Formula	C <sub>28</sub> H <sub>34</sub> N <sub>2</sub> Ti	C <sub>25</sub> H <sub>35</sub> NOTi	C <sub>32</sub> H <sub>47</sub> N <sub>3</sub> Ti	C <sub>54</sub> H <sub>70</sub> N <sub>4</sub> O <sub>2</sub> Ti
<i>M</i>	446.50	413.46	521.63	855.09
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
<i>T</i> /K	193	193	193	295
<i>a</i> /Å	8.620(3)	13.650(3)	12.626(3)	11.286(1)
<i>b</i> /Å	23.051(9)	8.995(2)	14.766(4)	10.940(4)
<i>c</i> /Å	23.771(7)	19.006(6)	64.305(3)	41.288(7)
$\beta$ /°		105.33(2)	97.71(2)	90.00(1)
<i>V</i> /Å <sup>3</sup>	4723.5	2250.6	3012.4	5098.1
<i>Z</i>	8	4	4	4
Crystal dimensions/mm	0.49 × 0.25 × 0.15	0.25 × 0.25 × 0.09	0.36 × 0.29 × 0.22	0.22 × 0.18 × 0.07
$\mu$ /cm <sup>-1</sup>	3.74	3.89	3.08	2.04
Data collected	4253	3959	5527	8813
Unique data with <i>I</i> > $n\sigma(I)$ ; <i>n</i>	2272; 3	2300; 3	5274; 2	2128; 3
<i>R</i> ( <i>F</i> )	0.046	0.038	0.041	0.096
<i>R'</i> ( <i>F</i> )	0.054	0.047	0.088 <sup>a</sup>	0.098
Maximum difference peak/e Å <sup>-3</sup>	0.30	0.24	0.29	0.57

<sup>a</sup> SHELXS definition.

frit. The bright red filtrate was concentrated *in vacuo* to ca. 20 mL and placed into a -90 °C freezer for 2 weeks during which a red oil was formed. The supernatant was removed *via* syringe, and the oil pumped on for several hours with no apparent change. <sup>1</sup>H NMR (benzene-d<sub>6</sub>, ambient):  $\delta$  7.35–7.06 (m, 5 H, Ph), 6.13 (s, 5 H, Cp), 5.60 (s, 1 H, H-3), 4.31 (dd, 1 H, *J* = 7, 12, H-5), 2.66 [septet, 1 H, *J* = 6.6, CH(CH<sub>3</sub>)<sub>2</sub>], 2.60 (dd, 2 H, *J* = 12, 15, H-5'), 2.09 (dd, 1 H, *J* = 7, 15, CHPh), 2.00 (s, 3 H, CH<sub>3</sub>), 1.78 (s, 3 H, CH<sub>3</sub>), 1.65 (s, 3 H, CH<sub>3</sub>), 1.39 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>C], 1.25 [d, 3 H, *J* = 6.1, (CH<sub>3</sub>)<sub>2</sub>CH] and 0.82 [d, 3 H, *J* = 6.9 Hz, CH<sub>3</sub>CH]. <sup>13</sup>C NMR (benzene-d<sub>6</sub>, ambient):  $\delta$  147.1 (s, 1 C, Ph), 144.5 (d, 1 C, *J* = 142, C-3), 128.7–126.7 (m, 5 C, Ph), 121.4 (s, 1 C, C-4), 113.0 (d of quintets, 5 C, *J* = 171, 7, Cp), 83.6 (s, 1 C, C-2), 83.0 [s, 1 C, C(CH<sub>3</sub>)<sub>3</sub>], 61.5 (d, 1 C, *J* = 135, CHPh), 53.9 [d, 1 C, *J* = 132, CH(CH<sub>3</sub>)<sub>2</sub>], 49.4 (t, 1 C, *J* = 128, C-1), 32.8 [q, 3 C, *J* = 126, C(CH<sub>3</sub>)<sub>3</sub>], 27.2 (q, 1 C, *J* = 127, CH<sub>3</sub>C=), 26.6 (q, 1 C, *J* = 127, CH<sub>3</sub>C=), 25.0 (q, 1 C, *J* = 126), 20.8 [q, 1 C, *J* = 122, CH(CH<sub>3</sub>)<sub>2</sub>] and 19.7 [q, 1 C, *J* = 125 Hz, CH(CH<sub>3</sub>)<sub>2</sub>].

### X-Ray crystallography

Single crystals of compounds **3**, **4**, **5**, and **6** were grown by slowly cooling their concentrated solutions in hydrocarbon solvents (ether for **6**) to -30 °C. These were then mounted in glass capillaries under a nitrogen atmosphere, and transferred to a Nonius CAD-4 diffractometer for data collection. Pertinent data collection and refinement parameters are contained in Table 5. Initial structural solutions were obtained using direct methods, which located the titanium and most other non-hydrogen atoms. The remaining non-hydrogen atoms, including for **6** those of a molecule of ether which was present in the lattice, were thereafter obtained from Fourier-difference maps. Hydrogen atoms were then included in idealized positions, but their atomic coordinates not refined. The SHELXS program was utilized for **5**, MOLEN for the other structures.<sup>19</sup> CCDC reference number 186/1411.

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