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Direct Synthesis of Titanium Complexes with Chelating *cis*-9,10-Dihydrophenanthrenediamide Ligands through Sequential C–C Bond-Forming Reactions from *o*-Metalated Arylimines

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Abstract: A series of new titanium(IV) complexes with *o*-metalated arylimine and/or *cis*-9,10-dihydrophenanthrenediamide ligands, [*o*-C_6H_4(CH=NR)$TiCl_3$] (R = 2,6-*i*$Pr_2C_6H_3$ (**3a**), 2,6-$Me_2C_6H_3$ (**3b**), *t*Bu (**3c**)), [*cis*-9,10-PhenH_2(NR)$_2TiCl_2$] (PhenH_2 = 9,10-dihydrophenanthrene; R = 2,6-*i*$Pr_2C_6H_3$ (**4a**), 2,6-$Me_2C_6H_3$ (**4b**), *t*Bu (**4c**)), [{*cis*-9,10-PhenH_2(NR)$_2$}{*o*-C_6H_4(HC=NR)}TiCl] (R = 2,6-*i*$Pr_2C_6H_3$ (**5a**), 2,6-$Me_2C_6H_3$ (**5b**), *t*Bu (**5c**)), have been synthesised from the reactions of $TiCl_4$ with *o*-C_6H_4(CH=NR)Li (R = 2,6-*i*$Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$, *t*Bu). Complexes **4** and **5** were formed unexpectedly from the reactions of $TiCl_4$ with two or three equivalents of the corresponding *o*-C_6H_4(CH=NR)Li followed by sequential intramolecular C–C bond-forming reductive elimination and oxidative coupling reactions. Attempts to isolate the intermediates, [{*o*-C_6H_4(CH=NR)}$_2TiCl_2$] (**2**), were unsuccessful. All complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy, and the molecular structures of **3a**, **4a–c**, **5a**, and **5c** were determined by X-ray crystallography.

Keywords: C–C coupling · diamines · domino reactions · synthetic methods · titanium

Introduction

Carbon–carbon bond-forming reactions have been one of the most active research areas in organic and organometallic chemistry.[1] In particular, transition-metal-mediated carbon–carbon bond-forming reactions have been studied extensively for construction of the basic carbon backbone of small organic molecules and extended polymeric structures.[2] Mechanistic studies of such reactions indicate that the stoichiometric and catalytic C–C bond-forming reactions mediated by mid- and late-transition metals can follow several pathways, such as reductive elimination, oxidative coupling, migratory insertion, and σ-bond or π-bond metathesis,[3] whereas reactions mediated by Group 4 metals go mainly through the migratory insertion pathway, which does not require redox changes at the metal centre such as those that happen in Ziegler–Natta polymerisation reactions.[4] The Group 4 metals also mediate C–C bond-forming reactions through the reductive elimination process, although the coupling of alkyl, acyl, and 1-alkenyl groups is the most commonly observed C–C bond-forming reductive elimination involving Group 4 metal complexes.[5] Very few examples of aryl–aryl bond-forming reductive eliminations mediated by Group 4 metals have been reported so far,[6] although the analogous process is well documented for Group 10 metals.[7] Yet the oxidative coupling of unsaturated organic compounds to low-valent Group 4 metals is an efficient pathway for construction of carbon–carbon bonds.[8] In oxidative coupling reactions, the compounds of low-valent Group 4 metals such as Ti^{II} or Zr^{II} are usually generated by treatment of Ti^{IV} or Zr^{IV} complexes with Grignard or organolithium reagents, followed by a reductive elimination process.[9] In principle, both the reductive elimination and oxidative coupling processes can be used to construct carbon–carbon bonds. However, there are no examples of formation of two C–C bonds in one molecule by means of the sequential reductive elimination and oxidative coupling reactions. Recently, in an attempt to synthesise [{*o*-C_6H_4(CH=NR)}$_2TiCl_2$] complexes as potential olefin polymerisation catalysts, some new titanium complexes with a *cis*-9,10-dihydrophenanthrenediamide ligand were obtained in high yields. Clearly the latter complexes are produced through sequential C–C bond-forming reductive elimination and oxidative coupling from the originally formed [{*o*-C_6H_4(CH=

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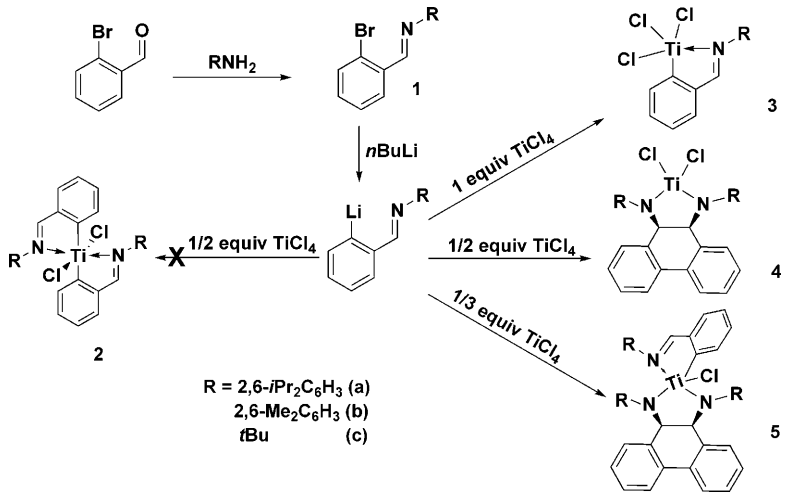
NR)}$_2$TiCl$_2$]. To the best of our knowledge, this is the first time that such a sequential C–C bond-forming process has been used to synthesise complexes of this type. The new chemistry may supply a simple and efficient method of synthesizing complexes with various diamide ligands directly from easily obtained imine compounds. The rare titanium-mediated aryl–aryl bond-forming reductive elimination involved in the process makes this chemistry especially interesting.

Herein we report the synthesis of the new titanium(IV) complexes with *o*-metalated arylimine and/or *cis*-9,10-dihydrophenanthrenediamide ligands, [*o*-C$_6$H$_4$(CH=NR)TiCl$_3$] (R = 2,6-*i*Pr$_2$C$_6$H$_3$ (**3a**), 2,6-Me$_2$C$_6$H$_3$ (**3b**), *t*Bu (**3c**)), [*cis*-9,10-PhenH$_2$(NR)$_2$TiCl$_2$] (PhenH$_2$ = 9,10-dihydrophenanthrene; R = 2,6-*i*Pr$_2$C$_6$H$_3$ (**4a**), 2,6-Me$_2$C$_6$H$_3$ (**4b**), *t*Bu (**4c**)), [{*cis*-9,10-PhenH$_2$(NR)$_2$}{*o*-C$_6$H$_4$(CH=NR)}TiCl] (R = 2,6-*i*Pr$_2$C$_6$H$_3$ (**5a**), 2,6-Me$_2$C$_6$H$_3$ (**5b**), *t*Bu (**5c**)), and the attempted synthesis of intermediate complexes [{*o*-C$_6$H$_4$(CH=NR)}$_2$TiCl$_2$] (**2**) from the reaction of TiCl$_4$ with *o*-C$_6$H$_4$Li-(CH=NR) (R = 2,6-*i*Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$, *t*Bu), as well as their spectroscopic characterisation and crystal structure analysis of complexes **3a**, **4a–c**, **5a**, and **5c**.

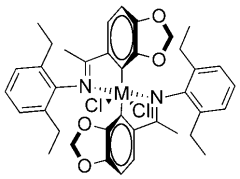
Results and Discussion

Synthesis of imine compounds: The imine compounds *o*-C$_6$H$_4$(CH=NR)Br (**1a–c**) were prepared according to a literature procedure[10] in high yields by condensation of *o*-bromobenzaldehyde with the corresponding amine (1 equiv) in hexane (Scheme 1). Compound **1a** was isolated as yellow crystals, whereas **1b** and **1c** were obtained as pale yellow oils. These compounds are soluble in most common organic solvents. Compounds **1a–c** were characterised by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. Their ^{1}H NMR spectra exhibit resonances in the region of δ = 8.58–8.64 ppm for the C*H*=*N* imine protons, with the corresponding ^{13}C NMR resonances occurring in the range δ = 154.5–162.0 ppm.



Scheme 1. Synthesis of complexes **1**, **3**, **4**, and **5**.

Reaction of TiCl$_4$ with *o*-C$_6$H$_4$(CH=NR)Li: Reactions of the *o*-bromoimine compounds **1a–c** with *n*BuLi (1 equiv) in hexane resulted in formation of the corresponding *o*-lithiated imine derivatives.[11] The reactions were carried out at 0 °C to minimise the formation of by-products, as the lithiation reactions are usually rapid and exothermic. The products were isolated in high yields as air- and moisture-sensitive precipitates, which were washed with hexanes to remove residual *n*BuLi. In toluene, the *o*-lithiated imine derivative from **1b** has good solubility whereas those from **1a** and **1c** are sparingly soluble. Reactions of these derivatives with TiCl$_4$ were studied in detail (Scheme 1): TiCl$_4$ with one equivalent of any of the *o*-lithiated imine reagents in toluene gives the corresponding complex **3** in high yields (ca. 85 %). However, attempts to synthesise complexes **2** by the reactions of TiCl$_4$ with two equivalents of a corresponding *o*-lithiated imine reagent were unsuccessful. Surprisingly, when reactions were investigated in different solvents, such as toluene, diethyl ether, and THF, at different temperatures, unexpected complexes **4** with a *cis*-9,10-dihydrophenanthrenediamide ligand were always isolated instead of **2**. To our knowledge, no similar chemistry has been reported for Group 4 metals. Ti^{IV} and Zr^{IV} complexes with two *o*-metalated acetophenone imine ligands (see Scheme 2) similar to **2** were reported recently.[12] These complexes were found to be stable even when heated to 60 °C in solution and no reductive elimination or oxidative coupling C–C bond-forming process was observed. Why complexes **2** could not be isolated from our reaction system is not very clear. It is possible that the less bulky ligands used in our reaction system facilitate the reductive elimination and oxidative coupling C–C bond-forming processes. It was found that the synthetic yields of complexes **4a–c** (50–70 %) depend on reaction conditions and the solvent system, and the yield for a specific complex decreases with the solvent in the order



Scheme 2. Ti^{IV} and Zr^{IV} complexes with two *o*-metalated acetophenone imine ligands similar to **2**.

toluene > diethyl ether > THF. To examine if the initial C–C coupling reaction is caused by light, the reactions were also tested in the dark; complexes **4** were obtained in similar yields, indicating that the C–C coupling process is not a photochemical reaction. From reactions at molar ratio $TiCl_4$/*o*-lithiated imine = 1:3, complexes **5a** and **5c** were isolated in high yields (> 85%), but **5b** could be obtained only in low yields as an oily crude product. Attempts to synthesise titanium complexes with two 9,10-dihydrophenanthrenediamide ligands by treating $TiCl_4$ with four or more equivalents of an *o*-lithiated imine reagent were not successful, and complexes **5** were always obtained. Complexes **5** could also be formed in the reactions of $TiCl_4$ with two equivalents of an *o*-lithiated imine if the reaction conditions (temperature and concentration) were not properly controlled. Crystallographic analysis of complexes **4a–c**, **5a**, and **5c** indicates that the 9,10-dihydrophenanthrenediamide ligands in these complexes are all in a *cis* configuration.

Complexes **3**, **4** and **5** are all soluble in toluene, CH_2Cl_2, and THF, but less soluble in petroleum ether and hexanes. Complexes **3** are air- and moisture-sensitive in both the solid state and solution, whereas complexes **4** and **5** show relatively good stability to air and moisture, and can be exposed to air for several hours without obvious decomposition. Complexes **3**, **4** and **5** show good thermal stability in solution and can be heated in boiling toluene for hours without decomposition. Complexes **3**, **4**, and **5** were all characterised by elemental analysis and ^1H and ^{13}C NMR spectroscopy, and satisfactory analytical results were obtained.

Crystal structures: Crystals of **3a**, **4a–c**, **5a**, and **5c** suitable for X-ray crystal structure determination were grown from CH_2Cl_2/*n*-hexane at room temperature. The ORTEP drawings of their molecular structures are shown in Figure 1, and selected bond lengths and angles are given in Table 1. The X-ray diffraction analysis reveals that the solid-state structure of **3a** has a C_s symmetry and adopts a distorted trigonal bipyramidal geometry around the metal centre with two chlorine atoms and one carbon atom on the equator and the other chlorine atom and the nitrogen atom in the apical positions (Figure 1a; Table 1). The average Ti–Cl bond length (2.214 Å) is close to those reported in the literature.[13,2b] The Ti–C (2.109(2) Å) and Ti–N(imine) bond lengths (2.255 (18) Å) are comparable to those reported for related titanium complexes.[14]

In the molecular structures of **4a** and **4c**, the titanium atom is four-coordinate and the geometry around it can be described as a distorted tetrahedron. Complex **4b** exists in a dimeric form in the solid state, in which titanium atom is five-coordinate and adopts a distorted trigonal bipyramidal geometry. The average Ti–N bond lengths (1.853 Å in **4a**, 1.888 Å in **4b**, and 1.861 Å in **4c**) are all in normal range found in other titanium complexes with a diamide ligand.[15,2b] The Ti–N bond lengths in **4b** are longer than those in **4a** and **4c** because the dimeric structure of **4b** makes the molecule more crowded. The average Ti–Cl bond lengths of 2.231 Å in **4a** and 2.276 Å in **4c** are comparable to those reported for related titanium chloride complexes.[15,2b] The terminal Ti–Cl bond length (2.277 (2) Å) in **4b** is similar to those in **4a** and **4c**, whereas the bridged Ti–Cl bond lengths (2.3946(16) and 2.6059(16) Å) in **4b** are much longer than normal ones. Because of the dimeric structure of **4b**, the bond angles of N1-Ti-N2 in **4a** (88.08(19)°) and **4c** (90.21(9)°) are larger than that (85.60(17)°) in **4b**. For the same reason, the Cl1-Ti-Cl2 bond angles in **4a** (108.56(9)°) and **4c** (113.55(4)°) are also quite different from those in **4b** (78.11 (5), 86.37 (6), and 127.67(7)°). The N1-C1-C14-N2 torsion angle in **4c** (50.4(2)°) is clearly larger than the corresponding ones in **4a** (36.3(5)°) and **4b** (39.66(2)°). Similarly, the C2-C7-C8-C13 torsion angle in **4c** (23.0 (4)°) is also larger than those in **4a** (20.1(9)°) and **4b** (18.25(4)°). These results reveal that the two *t*Bu groups in **4c** impose a greater effect on forcing the molecule to twist than the 2,6-diisopropylphenyl and 2,6-dimethylphenyl groups in **4a** and **4b**. These torsion-angle data agree with ^1H and ^{13}C NMR analyses of these complexes, indicating that the bulky *t*Bu groups in **4c** block the transformation between two different conformations in solution.

In complexes **5a** and **5c** the metal centre is five-coordinate, adopting a distorted square pyramidal geometry. The average Ti–N(amide) bond lengths (1.900 Å in **5a** and 1.906 Å in **5c**) are in the normal range found in other titanium complexes with a diamide ligand.[2b,15] The Ti–N(imine) bond lengths (2.447(3) Å in **5a** and 2.3806(17) Å in **5c**) are close to those in related titanium complexes with imine ligands reported in the literature.[14b] The Ti–Cl bond lengths (2.3218(13) Å in **5a** and 2.3682(8) Å in **5c**) and Ti–C bond lengths (2.178 (4) Å in **5a** and 2.144 (2) Å in **5c**) are comparable to those reported for related titanium complexes, and longer than the corresponding ones in **3a** and **4a–c**. As discussed above for **4a** and **4c**, the torsion angles of N1-C1-C14-N2 (53.88(2)°) and C2-C7-C8-C13 (23.41(4)°) in **5c** are clearly larger than the corresponding ones in **5a** (27.9(4)° and 18.6(6)°) due to the relatively large steric effect of *t*Bu groups in **5c**.

NMR analysis of complexes: All new complexes were characterised by ^1H and ^{13}C NMR spectroscopy; for selected NMR data, see Table 3. For complexes **3a–c**, the resonances for the C*H*=N protons (δ = 8.28–8.40 ppm) in the ^1H NMR spectra shift 0.23–0.31 ppm toward high field compared to their corresponding signals in free imine compounds, while the resonances (δ = 169.5–179.0 ppm) for the *C*H=N carbon atoms in the ^{13}C NMR spectra shift to low field compared with their corresponding signals in free imine compounds.[16] Resonances for other protons and carbon atoms are in normal positions. Complexes **4a–c** could be identified readily by ^1H and ^{13}C NMR spectroscopy. A sharp singlet was observed at δ = 6.18 and 6.39 ppm in the ^1H NMR spectra of complexes **4a** and **4b**, respectively, which is representative of the –C*H*N– protons in the 9,10-dihydrophenanthrene ring. The corresponding –*C*HN– carbon resonances were

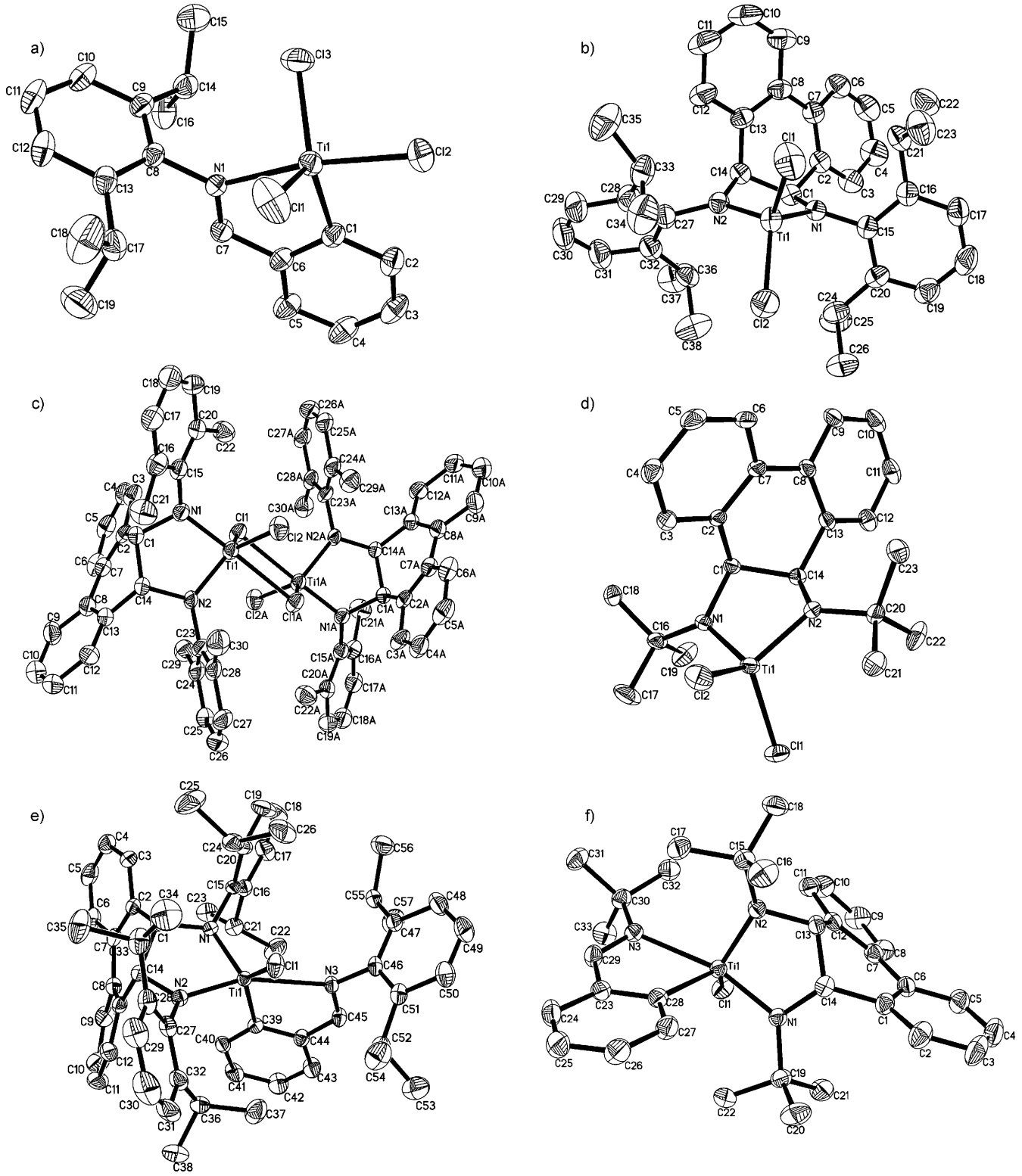


Figure 1. Perspective view of complexes **3a** (a), **4a** (b), **4b** (c), **4c** (d), **5a** (e), and **5c** (f) with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. See Table 2 for a summary of the crystallographic data.

observed at $\delta = 72.6$ and 71.5 ppm in their ^{13}C NMR spectra. Two sets of doublets (at $\delta = 4.95$ and 6.05 ppm) in the ^{1}H NMR spectrum of complex **4c** and two resonances (at $\delta = 66.1$ and 68.9 ppm) in its ^{13}C NMR spectrum were observed, indicating that the two −CHN− groups in the 9,10-dihydrophenanthrene ring of **4c** are inequivalent, probably because the bulky *t*Bu groups at the N atoms block the conformation transformation of the six-membered ring. Com-

Table 1. Selected bond lengths [Å] and angles [°] for **3a**, **4a–c**, **5a**, and **5c**.

	3a	**4a**	**4b**	**4c**	**5a**	**5c**
Ti–Cl	2.203(9)–2.233(8)	2.228(2)–2.233(2)	2.277(2)–2.6059(16)	2.2762(9)	2.3218(13)	2.3682(8)
Ti–C	2.109(2)	–	–	–	2.178(4)	2.144(2)
Ti–N	2.255(18) (imine)	1.842(4), 1.864(4) (amide)	1.875(4), 1.901(4) (amide)	1.852(2), 1.870(2) (amide)	1.882(3), 1.919(3) (amide); 2.447(3) (imine)	1.8963(16), 1.9168(16) (amide); 2.3806(17) (imine)
N-Ti-N	–	88.08(19)	85.60(17)	90.21(9)	83.33(15)–157.10(13)	88.68(7)–164.74(6)
Cl-Ti-Cl	90.37(7)–118.94(4)	108.56(9)	78.11(5)–127.67(7)	113.55(4)	–	–
N-C-C-N	–	36.3(5)	39.66(2)	50.4(2)	27.9(4)	48.27(4)
C2-C7-C8-C13	–	20.1(9)	18.25(4)	23.0(4)	18.6(6)	23.41(4)
C2-C1-C14-C13	–	40.1(6)	44.33(2)	56.2(3)	29.7(4)	53.88(2)

Table 2. Summary of crystallographic data for complexes **3a**, **4a–c**, **5a** and **5c**.

	3a	**4a**	**4b**	**4c**	**5a**	**5c**
formula	$C_{19}H_{22}Cl_3NTi$	$C_{38}H_{38}Cl_2N_2Ti\cdot0.5C_5H_{12}$	$C_{33}H_{35}Cl_2N_2Ti$	$C_{22}H_{28}Cl_2N_2Ti$	$C_{57}H_{66}ClN_3Ti\cdot0.5CH_2Cl_2$	$C_{33}H_{42}ClN_3Ti$
F_w	418.63	683.63	578.43	439.24	918.94	564.05
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P21/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$	Cc	Cc
a [Å]	9.6194(8)	19.139(6)	10.287(2)	8.3734(7)	13.075(4)	10.532(3)
b [Å]	14.0367(11)	17.273(6)	12.568(3)	10.2708(9)	20.681(7)	19.111(5)
c [Å]	15.6617(12)	23.121(5)	13.028(3)	13.9754(12)	19.572(5)	15.133(4)
α [°]	90	90	68.23(3)	99.8470(10)	90	90
β [°]	99.2860(10)	91.48(3)	82.22(3)	101.9480(10)	97.583(11)	96.254(4)
γ [°]	90	90	83.11(3)	105.4350(10)	90	90
V [Å^3]	2087.0(3)	7641(4)	1545.4(5)	1100.39(16)	5246(3)	3027.8(15)
Z	4	8	2	2	4	4
μ [mm^{-1}]	0.795	0.392	0.473	0.641	0.303	0.397
R_{int}	0.0160	0.1227	0.0633	0.0178	0.0415	0.0148
GOOF	1.041	1.016	1.089	1.030	1.027	1.059
$R1$	0.0431	0.1005	0.1030	0.0617	0.0734	0.0295
w$R2$	0.1163	0.2299	0.2869	0.1166	0.2008	0.0728

Table 3. Selected ^{1}H NMR data for complexes **3a–c**, **4a–c**, and **5a–c**.[a]

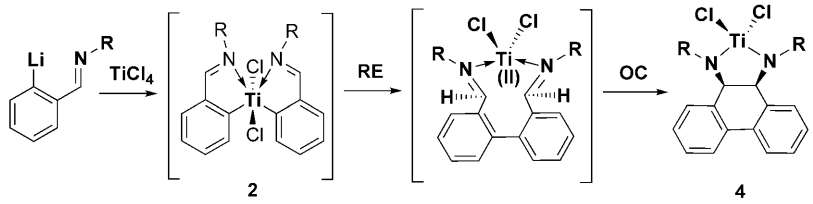
	3a	**3b**	**3c**	**4a**	**4b**	**4c**	**5a**	**5b**	**5c**
−C*H*=*N*−	8.28 (s, 1H)	8.40 (s, 1H)	8.37 (s, 1H)	–	–	–	7.92 (s, 2H)	8.43 (s, 1H)	
−C*H*N−	–	–	–	6.18 (s, 2H)	6.39 (s, 2H)	4.95 (d, ^3J= 3.9 Hz, 1H); 6.05 (d, ^3J= 3.9 Hz, 1H)	6.06 (s, 1H)	6.17 (s, 2H)	4.68 (d, ^3J= 4.2 Hz, 1H); 6.53 (d, ^3J= 4.2 Hz, 1H)
−C*H*$_3$	1.12 (d, ^3J= 6.6 Hz, 6H); 1.34 (d, ^3J= 6.6 Hz, 6H)	2.58 (s, 6H)	1.67 (s, 9H)	1.11 (d, ^3J= 6.6 Hz, 12H); 1.20 (d, ^3J= 6.6 Hz, 12H)	2.42 (s, 12H)	1.09 (s, 9H); 1.61 (s, 9H)	0.44 (d, ^3J=6.6 Hz, 6H); 0.52 (d, ^3J=6.6 Hz, 6H); 0.70 (d, ^3J=6.6 Hz, 6H); 0.90 (d, ^3J=6.6 Hz, 6H); 1.28 (d, ^3J=6.6 Hz, 6H); 1.50 (d, ^3J=6.6 Hz, 6H)	2.19 (s, 12H); 2.60 (s, 6H)	1.17 (s, 9H); 1.43 (s, 9H); 1.75 (s, 9H)
−C*H*(CH$_3$)$_2$	3.52 (sept, ^3J= 6.6 Hz, 2H)	–	–	3.29 (sept, ^3J= 6.6 Hz, 4H)	–	–	2.27 (sept, ^3J=6.6 Hz, 2H); 3.37 (sept, ^3J=6.6 Hz, 2H); 3.65 (sept, ^3J=6.6 Hz, 2H)	–	–

[a] δ values in ppm referred to TMS; measurements were carried out at room temperature.

plexes **5a** and **5c** could also be readily identified by ^{1}H and ^{13}C NMR spectroscopy. The presence of resonances for both the −C*H*N− protons and the C*H*=N protons in their ^{1}H NMR spectra confirms the structures of **5a** and **5c**.[17] The resonance for the C*H*=N proton in complex **5a** (δ= 7.92 ppm) shifts 0.36 ppm toward high field compared to the corresponding signal in complex **3a**, while the resonance for the −C*H*N− protons in complex **5a** (δ=6.06 ppm) shifts 0.12 ppm toward high field compared to the corresponding signal in complex **4a**. The resonances for the *C*H=N and −*C*HN− carbon atoms in complexes **5a** all shift toward high field compared to the corresponding signals in complexes **3a** and **4a**. As observed for complex **4c**, two sets of doublets (δ=4.68 and 6.53 ppm) were observed for the −C*H*N− protons in complex **5c** for the same reason. For complexes **3a**, **4a** and **5a**, two sets of doublets were observed for the two

methyl groups in the isopropyl unit, indicating that the rotation about the *N*-aryl bond is blocked in these complexes, which results in inequivalence of the two methyl groups.

Mechanistic aspects of the coupling reactions: As mentioned above, complexes **4** were always obtained instead of **2** from the reactions of $TiCl_4$ with two equivalents of the corresponding *o*-lithiated imine reagents. On the basis of the known chemistry and the structure of complexes **4**, it can reasonably be speculated that the complexes **2** must be formed first in these reactions and then converted to complexes **4** in situ through the sequential C–C bond-forming reductive elimination and oxidative coupling reactions shown in Scheme 3. Although the Ti^{IV} complexes **2** were not isolated from our reactions, probably because of their low stability, similar Ti^{IV} and Zr^{IV} complexes with two *o*-metalated acetophenone imine ligands (Scheme 2) have been obtained previously from the reaction of $TiCl_4$ or $ZrCl_4$ with two equivalents of bulky *o*-lithiated acetophenone imine ligand, and the crystal structure of the Zr^{IV} complex has been determined.[12] Only a few examples of the Ti^{IV}-mediated aryl–aryl bond-forming reductive elimination have been reported so far.[6,18] One is the formation of biphenyl and $[(C_6H_5)_2Ti^{II}]$ from $[(C_6H_5)_4Ti]$.[18] Another related example is the formation of $[Cp_2Ti^{II}(2,2'\text{-biquinoline})]$ from $[Cp_2Ti^{IV}(2\text{-quinoline})_2]$ (Cp = cyclopentadienyl).[6b] Attempts to isolate the Ti^{II} intermediates from our reactions by lowering the reaction temperature or adding an additional ligand, such as pyridine, to the reaction system to stabilise the intermediates have been unsuccessful so far. Since the titanium(II) intermediates are coordinately unsaturated species with a strong tendency to lose two electrons, the two imine groups in these Ti^{II} intermediates would coordinate to the Ti^{II} atom and undergo oxidative coupling immediately to form the complexes **4** as shown in Scheme 3. The Ti^{II}- and Zr^{II}-mediated C–C bond-forming reactions of alkenes, alkynes, carbonyls, and imines have been well documented.[17a,19] From the proposed mechanism shown in Scheme 3, 9,10-dihydrophenanthrenediamide ligands with both *cis* and *trans* configurations may be formed in the oxidative coupling C–C bond-forming step. However, only the titanium complexes with *cis*-9,10-dihydrophenanthrenediamide ligands have been obtained so far. It is possible that only the intermediate with the two imine bonds in a coplanar position can have the two imine carbon atoms close to each other[19] and the oxidative coupling reaction can therefore take place easily to form the *cis*-diamide ligands. The *cis* selectivity of this reaction system may also be related to the smaller atomic radius of titanium, as *trans*-diamide ligands were obtained in similar imine oxidative couplings mediated by samarium reagents.[20]



Scheme 3. The proposed mechanism for the formation of **4**. RE = reductive elimination, OC = oxidative coupling.

Conclusions

In attempts to synthesise the titanium complexes $[\{o\text{-}C_6H_4(CH{=}NR)\}_2TiCl_2]$ (**2**), chelating *cis*-9,10-dihydrophenanthrenediamide complexes of titanium (**4** and **5**) have been obtained by the reactions of $TiCl_4$ with two or three equivalents of the corresponding *o*-$C_6H_4(CH{=}NR)Li$, followed by sequential intramolecular C–C bond-forming reductive elimination and oxidative coupling. Attempts to isolate the intermediates **2** were unsuccessful. No *trans*-9,10-dihydrophenanthrenediamide complex has been obtained from these reactions. The synthetic yields of complexes **4** were found to change in the order **4a** > **4c** > **4b**. The *cis* configurations of complexes **4a–c**, **5a** and **5c** were confirmed by X-ray crystallographic analysis. ^1H and ^{13}C NMR spectroscopic analysis revealed asymmetric structures for complexes **4c** and **5c** in solution, probably because the bulky *t*Bu groups at the N atoms block the transformation between different conformations. A possible reaction mechanism was proposed, based on the structures of complexes **4** and **5**.

Experimental Section

General: All manipulations of air- and water-sensitive compounds were performed under an inert atmosphere of nitrogen by using standard Schlenk-line or glove-box techniques. Solvents were dried and purified by known procedures and distilled under nitrogen before use. *n*BuLi and $TiCl_4$ were purchased from Aldrich and used as received without further purification. ^1H and ^{13}C NMR spectra were measured on either a Varian Mercury-300 or a Bruker Avance-500 NMR spectrometer. Elemental analysis was performed on a Perkin-Elmer 2400 analyzer.

Synthesis of *o*-$C_6H_4(CH{=}NC_6H_3iPr_2\text{-}2,6)Br$ (1a): A mixture of *o*-bromobenzaldehyde (8.71 g, 47.1 mmol), 2,6-diisopropylaniline (8.9 mL, 47.1 mmol) and $MgSO_4$ (1.0 g) in *n*-hexane (30 mL) was stirred for 2 h. The mixture was filtered and the filtrate was evaporated to dryness in vacuo to give the crude product as a yellow solid. Pure product (13.8 g, 40.1 mmol, 85%) was obtained as yellowish-green crystals by recrystallisation from ethanol at −20 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.20$ (d, $^3J(H,H) = 6.9$ Hz, 12H; $CH(CH_3)_2$), 2.98 (sept, $^3J(H,H) = 6.9$ Hz, 2H; $CH(CH_3)_2$), 7.16–7.21 (m, 3H; Ph–H), 7.39 (t, 1H; Ph–H), 7.45 (t, 1H; Ph–H), 7.65 (d, 1H; Ph–H), 8.29 (d, 1H; Ph–H), 8.59 ppm (s, 1H; CH=NAr); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 23.5$-(CH_3),27.9 ($CH(CH_3)_2$), 123.1,124.4,125.7, 127.7, 128.8, 132.3, 133.1,

134.6, 137.5, 148.9, 161.3 ppm (*C*H=NAr); elemental analysis calcd (%) for $C_{19}H_{22}NBr$: C 66.28, H 6.44, N 4.07; found: C 66.17, H 6.49, N 4.11.

Synthesis of *o*-C_6H_4(CH=$NC_6H_3Me_2$-2,6)Br (1b): Compound **1b** was prepared in the same manner as **1a** with 2,6-dimethylaniline (5.8 mL, 47.1 mmol) as starting material. Pure product (11.5 g, 39.9 mmol, 79%) was obtained as a yellowish oil by distillation under reduced pressure at 82–83 °C/10 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.18 (s, 6H; CH_3), 6.96–7.11 (m, 3H; Ph−H), 7.37(t, 1H; Ph−H), 7.45 (t, 1H; Ph−H), 7.64 (d, 1H; Ph−H), 8.28 (d, 1H; Ph−H), 8.63 ppm (s, 1H; C*H*=*N*Ar); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.5(*C*H_3) 124.2, 125.8, 127.0, 127.8, 128.3, 128.8, 132.4, 133.2, 134.8, 151.0, 162.0 ppm (*C*H=NAr); elemental analysis calcd (%) for $C_{15}H_{14}NBr$: C 62.52, H 4.90, N 4.86; found: C 62.54, H 4.93, N 4.82.

Synthesis of *o*-C_6H_4(CH=N*t*Bu)Br (1c): Compound **1c** was prepared in the same manner as **1a** with *tert*-butylaniline (5.9 mL, 56.5 mmol) as starting material. Pure product (11.1 g, 46.2 mmol, 89%) was obtained as a light yellow oil by distillation under reduced pressure at 54–55 °C/ 10 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.31 (s, 9H; C-(CH_3)$_3$), 7.20 (t, 1H; Ph−H), 7.30 (t, 1H; Ph−H), 7.52 (d, 1H; Ph−H), 7.99 (d, 1H; Ph−H), 8.60 ppm (s, 1H; C*H*=*N*Ar); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 29.6 (*C*H_3), 57.9 (*C*(CH$_3$)$_3$), 125.0, 127.4, 128.5, 131.2, 132.6, 135.3, 154.5 ppm (*C*H=NAr); elemental analysis calcd (%) for $C_{11}H_{14}NBr$: C 55.0, H 5.88, N 5.83; found: C 55.1, H 5.86, N 5.84.

Synthesis of [{*o*-C_6H_4(CH=NC_6H_3iPr$_2$-2,6)}$TiCl_3$] (3a): A solution of *n*BuLi (2.2 mmol) was added dropwise to a solution of **1a** (760 mg, 2.2 mmol) in *n*-hexane (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The lithium salt of **1a** formed was collected on a frit, washed with *n*-hexane (2×5 mL), and dried under vacuum. The lithium salt (570 mg, 2.1 mmol) obtained was dissolved in toluene (20 mL) and added to a solution of $TiCl_4$ (398 mg, 2.1 mmol) in toluene (10 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The precipitate was filtered off, and the solvent was removed to leave a red solid. Recrystallisation from CH_2Cl_2/hexane gave the pure **3a** as red crystals (810 mg, 1.9 mmol, 87%), m.p. 109–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.12 (d, ^3J(H,H) = 6.6 Hz, 6H; CH(CH_3)$_2$), 1.34 (d, ^3J(H,H) = 6.6 Hz, 6H; CH(CH_3)$_2$), 3.52 (sept, ^3J(H,H) = 6.6 Hz, 2H; C*H*-(CH$_3$)$_2$), 7.24–7.56 (m, 6H; Ph−H), 8.15 (d, 1H; Ph−H), 8.28 ppm (s, 1H; C*H*=*N*Ar); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 23.1 (*C*H_3), 26.2 (*C*H_3), 29.0 (*C*H(CH$_3$)$_2$), 123.0, 124.1, 127.4, 128.5, 131.9, 135.9, 140.4, 141.5, 142.6, 146.3, 177.8 ppm (*C*H=NAr); elemental analysis calcd (%) for $C_{19}H_{22}NCl_3Ti$: C 54.51, H 5.30, N 3.35; found: C 54.49, H 5.32, N 3.37.

Synthesis of [{*o*-C_6H_4(CH=$NC_6H_3Me_2$-2,6)}$TiCl_3$] (3b): Complex **3b** was synthesised in the same manner as **3a** with **1b** (630 mg, 2.2 mmol), *n*BuLi (2.2 mmol), and $TiCl_4$ (398 mg, 2.1 mmol) as starting materials or reagents. Pure **3b** was obtained as a red crystalline solid (650 mg, 1.8 mmol, 82%), m.p. 95–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.58 (s, 6H; CH_3), 7.15–7.65 (m, 6H; Ph−H), 8.24 (d, 1H; Ph−H), 8.40 ppm (s, 1H; C*H*=*N*Ar); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.6 (*C*H_3), 124.1, 125.3, 126.8, 127.6, 128.2, 129.0, 131.7, 132.9, 135.8, 142.4, 179.0 ppm (*C*H=NAr); elemental analysis calcd (%) for $C_{15}H_{14}NCl_3Ti$: C 49.70, H 3.89, N 3.86; found: C 49.08, H 3.82, N 3.78.

Synthesis of [{*o*-C_6H_4(CH=N*t*Bu)}$TiCl_3$] (3c): Complex **3c** was synthesised in the same manner as **3a** with **1c** (530 mg, 2.2 mmol), *n*BuLi (2.2 mmol) and $TiCl_4$ (398 mg, 2.1 mmol) as starting materials or reagents. Pure **3c** was obtained as a red crystalline solid (592 mg, 1.9 mmol, 85%), m.p. 89–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.67 (s, 9H; CH_3), 7.26 (t, 1H; Ph−H), 7.68 (t, 1H; Ph−H), 7.80 (d, 1H; Ph−H), 7.98 (d, 1H; Ph−H), 8.37 ppm (s, 1H; C*H*=*N*Ar); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 31.8 (*C*H_3), 63.1 (*C*(CH$_3$)$_3$), 124.2, 127.9, 128.8, 132.4, 133.7, 140.4, 169.5 ppm (*C*H=NAr); elemental analysis calcd (%) for $C_{11}H_{14}NCl_3Ti$: C 42.01, H 4.49, N 4.45; found: C 42.11, H 4.39, N 4.37.

Synthesis of [{*cis*-9,10-(NC_6H_3iPr$_2$-2,6)$_2$-9,10-dihydrophenanthrene}$TiCl_2$] (4a): Complex **4a** was synthesised in the same manner as **3a** with **1a** (760 mg, 2.2 mmol), *n*BuLi (2.2 mmol), and $TiCl_4$ (209 mg, 1.1 mmol) as starting materials or reagents. Pure **4a** was obtained as red crystals (521 mg, 0.79 mmol, 68%), m.p. 207–209 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.11 (d, ^3J(H,H) = 6.6 Hz, 12H; CH_3), 1.20 (d, ^3J(H,H) = 6.6 Hz, 12H; CH_3), 3.29 (sept, ^3J(H,H) = 6.6 Hz, 4H; C*H*(CH$_3$)$_2$), 6.18 (s, 2H; C*H*N), 6.88 (d, 2H; Ph−H), 7.00–7.40 (m, 10H; Ph−H), 7.85 ppm (d, 2H; Ph−H); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 25.0 (*C*H_3), 27.0 (*C*H_3), 29.4 (*C*H(CH$_3$)$_2$), 72.6 (*C*HN), 123.8, 124.9, 125.1, 127.3, 128.5, 129.3, 129.4, 132.3, 134.7, 140.4 ppm; elemental analysis calcd (%) for $C_{38}H_{44}N_2Cl_2Ti$: C 70.48, H 6.85, N 4.33; found: C 70.45, H 6.83, N 4.31.

Synthesis of [{*cis*-9,10-($NC_6H_3Me_2$-2,6)$_2$-9,10-dihydrophenanthrene}$TiCl_2$] (4b): Complex **4b** was synthesised in the same manner as **3a** with **1b** (630 mg, 2.2 mmol), *n*BuLi (2.2 mmol) and $TiCl_4$ (209 mg, 1.0 mmol) as starting materials or reagents. Pure **4b** was obtained as red crystals (273 mg, 0.54 mmol, 54%), m.p. 190–191 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.42 (s, 12H; CH_3), 6.39 (s, 2H; C*H*N), 6.84 (d, 2H; Ph−H), 7.00–7.40 (m, 10H; Ph−H), 7.85 ppm (d, 2H; Ph−H); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.9 (*C*H_3), 71.5 (*C*HN), 123.3, 127.7, 128.3, 128.9, 129.2, 129.3, 129.5, 131.0, 132.3, 134.7 ppm; elemental analysis calcd (%) for $C_{30}H_{28}N_2Cl_2Ti$: C 67.31, H 5.27, N 5.23; found: C 67.30, H 5.26, N 5.21.

Synthesis of [{*cis*-9,10-(N*t*Bu)$_2$-9,10-dihydrophenanthrene}$TiCl_2$] (4c). Complex **4c** was synthesised in the same manner as **3a** with **1c** (530 g, 2.2 mmol), *n*BuLi (2.2 mmol), and $TiCl_4$ (209 mg, 1.1 mmol) as starting materials or reagents. Pure **4c** was obtained as red crystals (334 mg, 0.81 mmol, 65%), m.p. 185–186 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.09 (s, 9H; CH_3), 1.61 (s, 9H; CH_3), 4.95 (d, ^3J(H,H) = 3.9 Hz, 1H; C*H*N), 6.05 (d, ^3J(H,H) = 3.9 Hz, 1H; C*H*N), 7.20–7.80 ppm (m, 8H; Ph−H); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.0 (*C*H_3), 29.4 (*C*H_3), 63.1 (*C*(CH$_3$)$_3$), 63.7 (*C*(CH$_3$)$_3$), 66.1 (*C*HN), 68.9 (*C*HN), 123.7, 124.6, 127.5 128.3, 130.3, 130.9, 131.3, 132.5, 135.4, 136.4, 137.6, 139.1 ppm; elemental analysis calcd (%) for $C_{22}H_{28}N_2Cl_2Ti$: C 60.16; H 6.43; N 6.38; found: C 60.15; H 6.42; N 6.39.

Synthesis of [{*cis*-9,10-(NC_6H_3iPr$_2$-2,6)$_2$-9,10-dihydrophenanthrene}{*o*-C_6H_4(CH=NC_6H_3iPr$_2$-2,6)}TiCl] (5a): Complex **5a** was synthesised in the same manner as **3a** with **1a** (760 mg, 2.2 mmol), *n*BuLi (2.2 mmol), and $TiCl_4$ (133 mg, 0.7 mmol) as starting materials or reagents. Pure **5a** was obtained as red crystals (561 mg, 0.62 mmol, 89%), m.p. 135–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.44 (d, ^3J(H,H) = 6.6 Hz, 6H; CH(CH_3)$_2$), 0.52 (d, ^3J(H,H) = 6.6 Hz, 6H; CH(CH_3)$_2$), 0.70 (d, ^3J(H,H) = 6.6 Hz, 6H; CH(CH_3)$_2$), 0.90 (d, ^3J(H,H) = 6.6 Hz, 6H; CH-(CH_3)$_2$), 1.28 (d, ^3J(H,H) = 6.6 Hz, 6H; CH(CH_3)$_2$), 1.50 (d, ^3J(H,H) = 6.6 Hz, 6H; CH(CH_3)$_2$), 2.27 (sept, ^3J(H,H) = 6.6 Hz, 2H; C*H*(CH$_3$)$_2$), 3.37 (sept, ^3J(H,H) = 6.6 Hz, 2H; C*H*(CH$_3$)$_2$), 3.65 (sept, ^3J(H,H) = 6.6 Hz, 2H; C*H*(CH$_3$)$_2$), 6.06 (s, 2H; C*H*N), 6.30 (d, 2H; Ph−H), 6.72–7.39 (m, 18H; Ph−H), 7.88 (d, 1H; Ph−H), 7.92 ppm (s, 1H; C*H*=*N*Ar–); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 22.3 (*C*H_3), 23.0 (*C*H_3), 25.4 (*C*H_3), 25.9 (*C*H_3), 26.2 (*C*H_3), 26.4 (*C*H_3), 28.1 (*C*H(CH$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 72.2 (*C*HN), 122.8, 123.6, 123.7, 125.7, 126.1, 126.5, 126.9, 127.3, 128.4, 128.7, 130.1, 130.9, 132.8, 137.0, 137.9, 140.9, 141.1, 145.5, 148.9, 178.1, 191.3 ppm (*C*H=NAr); elemental analysis calcd (%) for $C_{57}H_{66}N_3ClTi$: C78.11, H7.59, N4.79; found: C78.13, H7.57, N4.81.

Synthesis of [{*cis*-9,10-($NC_6H_3Me_2$-2,6)$_2$-9,10-dihydrophenanthrene}{*o*-C_6H_4(CH=$NC_6H_3Me_2$-2,6)}TiCl] (5b): Complex **5b** was synthesised in the same manner as **3a** with **1b** (630 mg, 2.2 mmol), *n*BuLi (2.2 mmol), and $TiCl_4$ (133 mg, 0.7 mmol) as starting materials or reagents. Complex **5b** was obtained as an oily crude product. Pure product has not been obtained yet. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.19 (s, 12H; CH_3), 2.60 (s, 6H; CH_3), 6.17 (s, 2H; C*H*N), 6.90–7.60 (m, 20H; Ph−H), 8.00 (d, 1H; Ph−H), 8.43 ppm (s, 1H; C*H*=*N*Ar).

Synthesis of [{*cis*-9,10-(N*t*Bu)$_2$-9,10-dihydrophenanthrene}{*o*-C_6H_4(CH=N*t*Bu)}TiCl] (5c): Complex **5c** was synthesised in the same manner as **3a** with **1c** (530 mg, 2.2 mmol), *n*BuLi (2.2 mmol), and $TiCl_4$ (133 mg, 0.7 mmol) as starting materials or reagents. Pure **5c** was obtained as red crystals (362 mg, 0.61 mmol, 87%), m.p. 127–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.17 (s, 9H; C(CH_3)$_3$), 1.43 (s, 9H; C(CH_3)$_3$), 1.75 (s, 9H; C(CH_3)$_3$), 4.68 (d, ^3J(H,H) = 4.2 Hz, 1H; C*H*N), 6.53 (d, ^3J(H,H) = 4.2 Hz, 1H; C*H*N), 7.20–7.65 (m, 8H; Ph−H), 7.76 (t, 2H; Ph−

H), 7.86 (t, 2H; Ph−H), 8.49 ppm (s, 1H; C*H*=*N*Ar); ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.0 (*C*H_3), 29.2 (*C*H_3), 31.6 (*C*H_3), 59.9 (*C*$(CH_3)_3$), 60.3 (*C*$(CH_3)_3$), 62.0 (*C*$(CH_3)_3$), 64.9 (*C*HN), 75.1 (*C*HN), 122.4, 124.6, 125.9, 125.7, 127.5, 127.7, 127.9, 128.1, 128.5, 129.5, 129.8, 129.9, 130.7, 131.2, 137.3, 137.8, 141.7, 142.2, 171.1, 190.2 ppm (CH=NAr); elemental analysis calcd (%) for $C_{33}H_{42}N_3ClTi$: C 70.27, H 7.51, N 7.45; found: C 70.28, H 7.52, N 7.44.

X-ray structure determinations of 3a, 4a–c, 5a and 5c: Single crystals of **3a**, **4a–c, 5a** and **5c** suitable for X-ray structural analysis were obtained from the CH_2Cl_2/hexane mixture. The data were collected at 293 K on a Bruker SMART CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) for **3a**, **4c,** and **5c**, and on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) for **4a**, **4b** and **5a**. The structures were solved by direct methods[21] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealised positions. All calculations were performed using the SHELXTL[22] crystallographic software packages. Details of the crystal data, data collections, and structure refinements are summarised in Table 2. CCDC-739019 (**3a**), 739020 (**4a**), 739021 (**4b**), 739022 (**4c**), 739023 (**5a**), and 739024 (**5c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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