Titanium imido complexes stabilised by bis(iminophosphoranyl)methanide ligands: the influence of N-substituents on solution dynamics and reactivity

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Terminal titanium imido complexes of the general formula [Ti(N’Bu)Cl(CH2P(NR)2)3] 4 (R = Ph, tPr, tBu) are reported. These compounds were synthesized from the corresponding Li adducts 3 of BIPMH (bis(iminophosphoranyl)methanide) and Mountford’s complex [Ti(N’Bu)Cl(PPh3)2]. The crystal structures of two of the Ti complexes (R = Ph, tBu) and two of the Li compounds (R = Pr, tBu) are reported. Dynamic solution NMR spectroscopy reveals a dynamic isomerisation process in the case of the Ti complex 4c (R = tBu). DFT studies showed that this dynamic process comes from steric repulsion between the imido ligand and the tBu N-substituents on the BIPMH ligand. Complexes 4 were tested in alkyne hydroamination; 4a (R = Ph) displayed modest catalytic activity in the reaction of aniline with phenylacetylene.

Introduction

The coordination chemistry of bis(iminophosphoranyl)methanide and bis(iminophosphoranyl)methanediide ligands (hereafter referred to as BIPMH and BIPM respectively) has been thoroughly studied and reviewed.1–6 Whilst BIPM complexes are best described as pincer carbene complexes,4 BIPMHs are analogous to L2X ligands such as the cyclopentadienyl (Cp) or 1,3-diketiminate (nacnac) ligands.7,8 However, this analogy is of limited use in order to understand the structure and reactivity of BIPMH complexes. Indeed, negative hyperconjugation plays an important part in BIPMH ligands.5 Most BIPMH complexes display σ-donor fragments12,13 and most BIPMH complexes display π-acceptor coordination6 as a result of the considerable electron density localised on the methine bridge. However, the extent of the interaction between the carbon atom and the metal centre varies widely, ranging from the covalent bond14 to almost no interaction at all.15 A striking illustration of this somewhat unpredictable variability was reported by Stephan in the shape of a chromium-BIPMH dimer for which the crystal structure revealed two isomers with very different Cr–C bond lengths.16 Thus, BIPMH complexes represent a fascinating class of coordination compounds for the study of the influence of steric, electronic and stereoelectronic factors on the structure and reactivity.

Despite the large (and growing) number of BIPMH and BIPM complexes reported to date, titanium complexes of such ligands remain rare. In 1999, Cavell reported the only known example of a Ti-BIPM complex (Fig. 2).17 To the best of our knowledge, a Ti-BIPMH complex is yet to be reported, although Hf (Ia) and Zr (Ib) complexes obtained from the reaction of the corresponding carbene complexes with Brønsted acids are known.20

σ- and π-donor fragments,12,13 most BIPMH complexes display κ2N,N,κC coordination (Fig. 1),5 as a result of the considerable electron density localised on the methine bridge. However, the extent of the interaction between the carbon atom and the metal centre varies widely, ranging from the covalent bond14 to almost no interaction at all.15 A striking illustration of this somewhat unpredictable variability was reported by Stephan in the shape of a chromium-BIPMH dimer for which the crystal structure revealed two isomers with very different Cr–C bond lengths.16 Thus, BIPMH complexes represent a fascinating class of coordination compounds for the study of the influence of steric, electronic and stereoelectronic factors on the structure and reactivity.

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form A, which is more favourable with electron-donating groups on the nitrogens. It is noteworthy that the newly synthesized ligand 2c gives a mixture of both forms (as evidenced by its $^1$H and $^{31}$P NMR spectra in CD$_2$Cl$_2$ and d$_6$-THF) despite the highly electron-donating nature of the tertiary alkyl groups, whilst 2a and 2b are present almost exclusively in D and A forms, as previously reported.$^{10}$

Reaction of 2 with [Ti(N^Bu)Cl$_3$(Py)$_3$] (Scheme 2) invariably afforded BIPMH complexes 4, together with pyridine hydrochloride and monocation 5, which was identified notably by the appearance of a new signal in the $^{31}$P NMR spectrum (5a: 24.3 ppm; 5b: 31.3 ppm; 5c: 26.8 ppm). Comparison of the reaction mixtures with independently prepared 4 (vide infra) confirmed the concomitant formation of those species. Addition of one equivalent of potassium hexamethyldisilazane (KHMD) to the reaction mixture enabled clean and complete conversion of the BIP to the Ti imido species for 2a and 2b (see ESI, Fig. S4 to S10;† a complex mixture was observed in the case of 2c). Although the formation of the BIPMH complexes 4 is likely driven by the presence of pyridine in the reaction mixture, it is worth noting that Caulton reported a similar formation of a Ru BIPMH complex in the absence of a base (i.e. HCl was released).$^{14}$

Since the formation of BIPMH-stabilised Ti imido complexes 4 appeared to be thermodynamically favoured over that of Ti-BIP species,$^{33}$ we turned our attention to their study. We initially envisaged the sequential one-pot reaction of 1 with 3 equivalents of n-BuLi and one equivalent of [Ti(N^Bu)Cl$_3$(Py)$_3$], however, the material obtained following this procedure appeared to contain considerable amounts of coordinated Br, as evidenced by the isolation of crystals of [TiBr(BIPMH$^{Ph}$)-(μ-O)$_2$] after workup.$^{34}$ This compound probably results from the hydrolysis of [Ti(N^Bu)Br(BIPMH$^{Ph}$)] and suggest that a Br-free route would be more practical. For this purpose, the use of alkaline metal complexes as BIPMH transfer agents – a strategy already employed by one of us,$^{31,35,36}$ and others$^{3,37-44}$ – seemed particularly attractive (Scheme 3). Synthesis of lithium compounds 3 was achieved by deprotonation of the corresponding BIP ligands with 1 equiv. of n-BuLi. Complexes 3 were obtained as extremely air-sensitive solids; possibly due to their moisture sensitivity, they decomposed over time when the reaction mixtures were left at room temperature for too long (>30 min).

Once in the solid state, they could be stored in a glovebox at −18 °C for months without decomposition. $^1$H and $^{31}$P NMR spectra were consistent with those reported for similar monomeric structures.$^{10,15,45-47}$ Interestingly, only one set of signals was observed for the four P-substituents, suggesting a rapid
equilibrium between the two boat conformations. Single crystals suitable for X-ray diffraction were obtained in the case of 3b and 3c by slow diffusion of n-pentane into a THF solution of each compound at −18 °C. The putative monomeric solution structures were thus confirmed in the solid state (Fig. 3).

It is worth mentioning that despite their synthetic utility, there are only a limited number of structurally characterized group 1 BIPMH complexes,10,15,45–49 of which only 5 have monomeric Li structures (Fig. 4). The most salient feature of these solid-state structures is the high variability of the Li–C1 bond distance between the metal and the methine bridge, ranging from 2.543 (3c) to 3.196 Å (3g).

These distances are well above the sum of van der Waals radii (3.89 Å), a common structural feature of BIPMH complexes.5 Table 1 gives selected bond distances and angles for 3b–c and relevant literature compounds.

For BIPMH ligands with aryl substituents at the nitrogens, increasing steric bulk results in an opening of the 6-membered metallacycle along the Li–C1 axis, whilst in the case of alkyl substituents (e.g. 3b and 3c), the opposite trend is observed. As a result of the poorer interaction between Li and C1 in “open boat” structures, the interaction between Li and N becomes stronger and Li–N bond distances are shortened (compare 3b and 3c). Other notable features are (i) the trigonal planar geometry around N (sum of angles close to 360°) and (ii) the sp2 hybridization of C1 suggested by P1 values close to 134.6° (3e). Again, these features are commonplace for BIPMH complexes, and they are also observed in Ti complexes 4 (vide infra). Reaction of Li compounds 3 with [Ti(N’Bu)2Cl2(Py)3] afford complexes 4 in moderate to good yield (Scheme 3). The presence of the terminal Ti-imido group is suggested by the IR spectra of 4, with medium bands in the 1200–1260 cm−1 region and strong bands in the 520–550 cm−1 region, as reported by Mountford.51

Upon coordination to Ti, the four phenyl substituents on the phosphorus atoms give rise to two sets of signals in the 1H NMR spectra, consistent with the now diastereotopic relationship of those groups. In the case of 4b, the CH3 groups of the ‘Pr substituent are also diastereotopic and resonate as two doublets at 1.77 and 0.91 ppm (JHH = 7.2 Hz). Complexes 4a and 4c gave crystals suitable for X-ray diffraction by slow diffusion of n-pentane into CH2Cl2 solutions of the complexes at −18 °C (Fig. 5).52 Relevant structural parameters are given in Table 2, together with those of 1a and 1la (Fig. 2) for comparison.

The metallacycles in both complexes exhibit the same boat conformation with the Cl ligand located in the axial position. At 2.599(2) (4a) and 2.557(2) Å (4c), the Ti–C1 distances are longer than the sum of covalent radii for Ti and sp2 C (2.33(8) Å),50 and considerably smaller than the sum of van der Waals radii (4.23 Å).53

This contrasts with BIPMH-Hf complex 1a, which features an elongated covalent Hf–C1 bond (2.438(6) vs. 2.48(10) Å). As expected, the Ti–C1 distance in BIPM complex 1a (2.008(4) Å) is much shorter than in 4a and 4c. One notable variation when comparing 4a and 4c with their Li analogues 3a and 3c is the somewhat shorter P–N bond distances in the latter (−0.03 Å for Ph and −0.04 Å for ‘Bu). This difference could originate from higher ligand-to-metal charge transfer in Ti complexes, hence decreased charges on the nitrogens and a weaker interaction between N and P.11 Steric factors also seem to play an important part in the differences between Ti complexes and Li adducts. For instance, one could expect the presence of the ‘Bu imido group in Ti complexes to impact the geometry of the BIPMH ligand itself. Consistent with this view, P–N–C angles are narrower in 4a and 4c compared to 3a and 3c, and the effect is more pronounced for 4c than 4a (−1.2°), in line with the considerably more bulky nature of ‘Bu compared to Ph. Further comparison between both complexes shows that the presence of the ‘Bu group causes a small but noticeable

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**Table 1**

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<th>Compound</th>
<th>Bond Distance (Å)</th>
<th>Angle (°)</th>
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<td>3b</td>
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<tr>
<td>3c</td>
<td>3.196</td>
<td>134.6</td>
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<tr>
<td>4a</td>
<td>2.599</td>
<td>134.3</td>
</tr>
<tr>
<td>4c</td>
<td>2.557</td>
<td>134.6</td>
</tr>
</tbody>
</table>

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**Fig. 3** POVRAY depiction of 3b and 3c (thermal ellipsoids drawn at the 50% probability level).

**Fig. 4** Structurally characterised monomeric Li compounds.10,15,45–47
distortion of the boat metallacycle, principally by widening the N–Ti–N angle (+3.60°). Finally, a combination of steric and electronic factors can be invoked to explain the shorter Ti-imido bond distance in 4a (1.670(2) Å) compared to 4c (1.715(2) Å); indeed, the steric repulsion between tBu groups, as well as the greater electron density of the [TiCl(BIPMHtBu)] fragment (due to the more electron-donating tBu compared to Ph), both mitigate against a short Ti-imido bond.

In light of the rather similar solid-state structures of 4a and 4c, it might seem surprising that, unlike 4a and 4b, 4c would exist as a mixture of two isomers in solution. Indeed, we invariably observed a small amount (∼10%) of additional product by NMR for the latter. By 31P NMR spectroscopy, a signal at 15.6 ppm was observed, and several additional signals are also present in the 1H NMR spectrum, most notably a triplet at 2.49 ppm (2JPH = 3.8 Hz) ascribed to a bridging methine group, and tBu signals at 1.30 and 1.24 ppm;13C NMR spectroscopy also reveals a pattern of signals paralleling that of the main product. Crucially, an EXSY NMR experiment revealed that both species are involved in a chemical exchange (Fig. 6).

Altogether, these observations suggest a rapid dynamic equilibrium between two boat forms 4c-ax and 4c-eq, (Scheme 4; in the following discussion, both isomers will be distinguished by the axial or equatorial position of the Cl ligand).55

Variable temperature NMR spectroscopy experiments enabled us to determine the values of the equilibrium distortion of the boat metallacycle, principally by widening the N–Ti–N angle (+3.60°). Finally, a combination of steric and electronic factors can be invoked to explain the shorter Ti-imido bond distance in 4a (1.670(2) Å) compared to 4c (1.715(2) Å); indeed, the steric repulsion between tBu groups, as well as the greater electron density of the [TiCl(BIPMHtBu)] fragment (due to the more electron-donating tBu compared to Ph), both mitigate against a short Ti-imido bond.

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Variable temperature NMR spectroscopy experiments enabled us to determine the values of the equilibrium
constant at different temperatures in the 273–333 K range by integration of the CH bridge signal intensity in 4c-ax and 4c-eq. Using the relationship $\ln K = -\Delta G^0/RT$, values of $\Delta H^0 = 12.6 \pm 1.4$ kJ mol$^{-1}$ and $\Delta S^0 = 24.9 \pm 4.7$ J mol$^{-1}$ K$^{-1}$ were obtained (see ESI, Fig. S3†).

Computational studies

The isomerisation equilibrium described above is not surprising in itself. Such dynamic solution behaviour has been reported in the case of related bimetallic phosphinoamide Ti/Pt complexes with a PDX$_2$ bridge isoslab to CH.$^{39}$ Also, as mentioned above, two structural isomers of the complex [Cr($\mu$-Cl)]2[HC(PPh$_2$NSiMe$_3$)$_2$]$_2$ with different Cr–C bond lengths (2.26 vs. 2.92 Å) were previously reported by Stephan.$^{16}$ More intriguing is the fact that 4a and 4b do not display a similar behavior.$^{37}$ One possible explanation could be the increased steric repulsion between the three $^1$Bu groups in the axial Cl isomer (4c-ax), which would reduce the energy gap between both isomers and make the energy level of the equatorial Cl isomer (4c-eq) accessible at room temperature. To test this hypothesis, we conducted DFT calculations at the B3LYP level of theory (see the Computational details section) on 4b and 4c, as well as on 4d (the NMe imido analogue of 4c).

Calculated energies for the different isomers of the $^1$Bu and $^1$Pr complexes are in agreement with the fact that the axial-CI isomer is the experimentally preferred one. For 4c, the free energy difference between both isomers is calculated to be 5.1 kJ mol$^{-1}$ at 298.15 K, which corresponds to a 4c-eq/4c-ax ratio of 0.128 (for an experimental value of 0.124(5)). For 4b, comparison between theory and experiment is more difficult since the axial isomer was the only observed species, however, it is possible to assign an upper limit (0.01) to the equilibrium constant, and thus a lower limit (11 kJ mol$^{-1}$) to $\Delta G^0$. The latter is consistent with the calculated value of 22.1 kJ mol$^{-1}$.

Replacing the $^1$Bu group of the imido ligand in complex 4c by a methyl group leads to a higher energy gap between both isomers in complex 4d (18.5 kJ mol$^{-1}$) consistent with the hypothesis that steric repulsion between the N-substituents of the BIPMH and the imido ligands destabilizes the axial isomer of 4c, thus facilitating the isomerisation.

It is quite remarkable that such a seemingly small change of N-substituents should trigger observable isomerisation equilibrium, and this phenomenon highlights the subtle steric interactions at play in BIPMH complexes. Therefore, it is of interest to compare the experimental (4c-ax) and calculated (4c-ax/eq, 4b-ax/eq, 4d-ax/eq) structures, see Table 3.

As is usually the case with DFT methods in general, and the B3LYP functional in particular, the calculated gas-phase geometry of 4c-ax is close to the experimental solid-state structure. The highest relative error (±4%) is the Ti–C$^1$ distance, which corresponds to an absolute error of 0.108 Å. This discrepancy is likely due to crystal packing effects which are more important for bonds with a large electrostatic contribution.$^{28}$ Other bond distances typically fall within 0.03 Å of the experimental values (3° for angles). In the case of 4b, the low quality of the obtained crystals precludes a detailed comparison of structural parameters, however, it is worth noting that the orientation of the $^1$Pr substituents was similar in both cases, with CH$_3$ groups pointing towards the metal, as observed for the Li adduct 3b.

Comparing the calculated gas-phase structures of the axial and equatorial isomers, it appears that the most important difference resides in the global shape of the metallacycles. For axial isomers, the boat has a relatively open structure, with Ti–C$^1$ distances ranging from 2.592 Å (4d-eq) to 2.753 Å (4b-eq). The less favorable equatorial isomers have considerably shorter (∼0.21 to ∼0.296 Å) Ti–C$^1$ distances, thereby increasing ring strain considerably (see Fig. 7 for 4c).

Table 3 Comparison of bond distances (Å) and angles (°) for 4c and calculated isomers of 4b, 4c, and 4d

<table>
<thead>
<tr>
<th></th>
<th>4c$^a$</th>
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$^a$ Experimental structure. $^b$ Gas phase theoretical structures.
case of 4c-eq and 4d-eq, the Ti–C distances are now within the sum of covalent radii (2.33(8) Å).50

The reason for the longer Ti–C bond distance in the axial isomers is somewhat unclear, as this seems to push the imido 4Bu group closer to the BIPMH N-substituents. The same can be said about the shorter Ti–C bond distance in the equatorial isomers, for which there is a priori no obvious reason. One possible explanation could be the greater influence of the imido ligand compared to the chloride.59 Nevertheless, the shapes of the experimental and computational structures are counter-intuitive, and probably result from a subtle interplay of steric and electronic factors.

Whilst our calculations do not point to an obvious reason for the preference of the axial isomer over the equatorial one, they do reveal differences between 4b-ax and 4c-ax; these parallel the experimentally observed trends between 4a and 4c in their crystal structures, and support the hypothesis of a sterically induced destabilisation of the major isomer of 4c. Indeed, upon replacing 4Pr with 4Bu, we observe the opening of the P–C3–P (+3.62°), N–Ti–N (7.04°) and P–N–C angles (+5.8°) on average. The shape of the metallacycle also changes, with a widening of the φ1 (NTIN/PPPN) dihedral angle (+4.72°), and a narrowing of the φ2 (PC1P/PPPN) dihedral angle (–5.93°). By contrast, these differences are much less pronounced between the equatorial isomers (4b-eq vs. 4c-eq), except for the P–N–C angles which remains wider in 4c-eq (+6.8° on average). These data indicate that the presence of 4Bu N-substituents exerts a considerable influence by pushing the P and N substituents of the BIPMH away from each other.60 This brings the 4Bu groups closer to the imido ligand in the axial isomer, thus distorting the boat metallacycle and reducing the energy gap between both isomers; ultimately, the inversion of the boat is facilitated. Therefore, regardless of the exact reasons for the preference of the axial isomer over the equatorial one, our calculations clearly show that steric factors are decisive to explain the different behavior of 4b and 4c, as observed experimentally.

Reactivity and catalysis

In comparison to the number of reports focusing on their coordination chemistry, catalytic applications of BIPMH complexes are rare. Most reports focus on lanthanides, although other metals have been investigated, notably Ca and Mg (ring-opening polymerisation),7 Al (ethylene polymerisation),67 Cr (ethylene oligomerisation),31 Zn (ring-opening polymerisation),68 Y (intramolecular hydroamination of unsaturated substrates),38,40 and Zr (ethylene polymerisation).35 Given the widespread use of terminal Ti imido complexes in allyl hydrogenation,66 it was interesting to evaluate the potential of complexes 4 in this reaction. The results are presented in Table 4. Overall, the catalytic activity of these complexes was disappointing, and in the case of 4b, nonexistent (entry 1). Indeed, aniline and phenylacetylene are rather forgiving substrates.15 Indeed, under forcing conditions and with low selectivity. In light of the mechanistic studies by Bergman,69 and Doye,70 and considering the structure of complexes 4 compared to active hydroamination catalysts such as [CpTi(NBu)Cl(Py)] or [CpTi(NAr)[NHAr]], it appears that a free coordination site is necessary in order to initiate the catalytic cycle.

This does not seem to be the case with 4, which means that these complexes must find an energetically costly way to accommodate an incoming alkynyl molecule, be it Cl dissociation, BIPMH boat-chair isomerisation or (possibly in the case of 4a) an increase in the coordination number. Thus, further development of BIPMH Ti imido complexes should focus on solutions aimed at creating a free coordination site on Ti, e.g. by replacing Cl by a more labile ligand.

Although the results presented above are only preliminary,71 and show that at the very least, precatalyst design needs to be improved, they indicate that aryl substituents on the BIPMH nitrogen atoms are more likely to give active catalysts. There could be two reasons for this: firstly, aryl groups are less electron-donating and will give rise to more Lewis acidic complexes, a feature which is expected to increase the reactivity of coordinated alkynes; secondly, the increased activity of 4a could also result from the greater steric flexibility of the Ph substituent (compared to 4Pr or 4Bu) which is able to
relieve steric strain around Ti by rotation around the N–C bond. As an illustration of the greater reactivity of 4a, we followed the fate of complexes 4 in the presence of 10 eq. of aniline and phenylacetylene by $^1$H and $^{31}$P NMR spectroscopy. Whilst 4a showed complete imido group exchange at room temperature, $^{31}$ 4b and 4c had to be heated to 105 °C for several hours for the exchange to proceed (Scheme 5). Remarkably, after heating for 13 h at this temperature, virtually no other P-containing products were observed ($^{31}$P NMR: $\delta = 21.6$ (4a$'$), 26.7 (4b$'$), 22.9 (4c$'$) ppm); additionally, 4a$'$ and 4c$'$ (to a lesser extent) showed hydroamination activity (significant amounts of I1 and E2 were observed, see ESI Fig. S11 to S22†). These observations are consistent with the increased catalytic activity of 4a compared to 4b and 4c, which is likely to originate from a combination of steric and electronic factors.

Finally, given the robustness of these complexes even under forcing conditions, it was interesting to probe their reactivity towards water. Indeed, one of the caveats of using oxophilic group 4 metals for hydroamination is that reaction substrates for the reaction to proceed. Clearly, this sensitivity impedes industrial applications of such catalysts.

Interestingly, upon reaction with increasing amounts of water or $^1$PrOH, 4b and 4c showed a rather peculiar behaviour. Indeed, only the starting complexes and monocations 5 were observed. After addition of 2 equivalents of water (or 4 equivalents of $^1$PrOH), the only products observed by $^1$H and $^{31}$P NMR spectroscopy were $^1$BuNH$_2$ and 5 (and [Ti(O$^1$Pr)$_2$]$_2$) in the case of $^1$PrOH. In the case of 4a, intermediate products were observed by $^{31}$P NMR spectroscopy (including 2a), but the global outcome of the reaction was the same as that observed with 4b and 4c (Scheme 6), the only notable difference being the presence of small amounts of 2a, probably due to its lower basicity compared to 2b and 2c (see ESI, Fig. S23 to S30†). Overall, these results highlight the high basicity of the BIPMH ligand in 4, and show that depending on the N-substituents, the Achilles’ heel of these complexes in terms of moisture sensitivity might not be the imido ligand, but the BIPMH.

### Conclusion

We have reported the first examples of Ti imido complexes stabilized by a BIPMH ligand, in addition to new Li adducts of BIPMH. Their structure has been studied both experimentally (X-ray, dynamic solution NMR spectroscopy) and theoretically (DFT). We have shown that these compounds are very sensitive to steric effects, since changing the N-substituents of the BIPMH from $^1$Pr to $^1$Bu brings about a dynamic equilibrium between two isomers of the metallacycle. Finally, we tested complexes 4 in alkyne hydroamination; whilst phenyl substituted complex 4a showed modest catalytic activity, alkyl substituted complexes 4b and 4c were almost completely inactive. This contrasting behavior was mirrored by the rate of imido group exchange in the presence of aniline, with 4a being much more reactive. The globally unsuitable nature of BIPMH as a supporting ligand for Ti in hydroamination could be due to its strong electron-donating nature, or to coordinative saturation at Ti. In any case, improved catalytic activity could be achieved by freeing a coordination site on Ti, or adding electron-drawing substituents on the BIPMH ligand.

### Computational details

The theoretical calculations were performed by using Jaguar v. 5.5.2† using the DFT B3LYP method with a 6-31G** basis for most atoms, 6-311+G** for C and LACV3P** for the titanium atom. The frequencies were checked at the end of the geometry minimizations. The calculations were performed by using HPC resources from DSI-CCUB (Université de Bourgogne).

### Experimental

#### General conditions

All reactions were carried out under Ar using conventional Schlenk techniques or in a N$_2$ glovebox. Toluene, CH$_2$Cl$_2$, Et$_2$O, pentane and THF were dried using an MBRAUN SPS 800 solvent purification system or distilled under Ar from appropriate drying agents and either used directly or stored under N$_2$ in the glovebox. Deuterated solvents were dried by passage through a short column of activated neutral alumina (Brockman grade II) and stored over activated 3 Å molecular sieves in vacuo. Alumina and molecular sieves were activated by overnight heating above 230 °C in vacuo. Salts 1a–c were synthesized according to literature procedures, except hygroscopic 1b which had to be dried by successive azeotropic distillation with toluene. Compounds 2a–b and 3a–b were previously reported but were incompletely characterized, or NMR data were reported in different solvents. All other reagents were commercially available and used as received.

All of the analyses were performed at the “Plateforme d’Analyse Chimique et de Synthèse Moléculaire de l’Université de Bourgogne”, or at the elemental analysis service of London
Metropolitan University. The identity and purity of the compounds were unambiguously established using elemental analysis, high-resolution mass spectrometry, X-ray diffraction, NMR and IR spectroscopy. High resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL ESI-MS spectrometer. NMR spectra (1H, 31P, 13C) were recorded on Bruker 300 Avance III, 500 Avance III, or 600 Avance II spectrometers. Chemical shifts are quoted in parts per million (δ) relative to TMS (for 1H and 13C) or 85% H3PO4 (for 31P). For 1H and 13C spectra, values were determined by using solvent residual signals (e.g. CDCl3 in CD2Cl2 as internal standards. In the case of 31P NMR, a capillary filled with 85% H3PO4 was placed in the NMR tube for the characterization of new compounds.

IR spectra were recorded on a Bruker Vertex 70v FTIR spectrophotometer fitted with a Globar MIR source, a Ge/KBr (MIR) or silicon (FIR) beam splitter, a DLaTGS detector and a diamond ATR module.

Preparations

**Preparation of ligand 2a.** Salt 1a (5.360 g, 6.880 mmol) was suspended in Et2O (40 mL) at room temperature, and a suspension of KHMD (2.750 g, 13.76 mmol) in Et2O (30 mL) was cannulated onto the suspension. The resulting pale yellow mixture was stirred for 4 h and filtered over Celite®. The filtered solid was rinsed with Et2O. The clear yellow solution thus obtained was evaporated and extensively dried in vacuo to remove hexamethyldisilazane. Compound 2a was isolated in 71% yield (2.78 g). The purity of the material thus obtained (assessed by 1H and 31P NMR spectroscopy) was sufficient for further reaction. An analytically pure sample suitable for elemental analysis was obtained by recrystallization from a THF-n-pentane mixture.

Elemental analysis: calcld for C37H32N2P2: C, 78.43; H, 5.69; N, 4.94. Found: C, 78.34; H, 5.84; N, 5.03. HRMS (ESI-pos): calcld for C37H32N2P2 [M + H]+: 527.27395. Found: 527.27421

Preparation of ligand 2b. Salt 1b (4.95 g, 7.50 mmol) was suspended in Et2O (40 mL) at 0 °C, and a solution of KHMD (2.750 g, 15.0 mmol) in Et2O (30 mL) at room temperature was cannulated onto the suspension. The resulting pale yellow mixture was stirred for 3 h and filtered over Celite®. The filtered solid was rinsed with Et2O. The clear yellow solution thus obtained was evaporated and extensively dried in vacuo to remove hexamethyldisilazane. Compound 2b was isolated in 87% yield (3.25 g). The purity of the material thus obtained (assessed by 1H and 31P NMR spectroscopy) was sufficient for further reaction. An analytically pure sample suitable for elemental analysis was obtained by recrystallization from a THF-n-pentane mixture.

Elemental analysis: calcld for C33H29N2P2: C, 74.68; H, 7.28; N, 5.62. Found: C, 74.56; H, 7.39; N, 5.63. HRMS (ESI-pos): calcld for C33H29N2P2 [M + H]+: 499.24265. Found: 499.24115 (−3.0 ppm). FTIR (ATR): 2962 (m), 1433 (m), 1272 (br, s), 1308 (m), 1103 (br, m), 1047 (m), 770 (br, m), 754 (m), 740 (m), 717 (m), 704 (m), 688 (s), 486 (s), 401 (m) cm−1. 1H NMR (500 MHz, CD2Cl2, 300 K): δ = 7.70 (m, 8H, o-PhP), 7.39−7.27 (m, 12H, p- and m-PhP), 7.04 (br s, 1H, NH), 3.42 (t, 2JPH = 13.2 Hz, 4H, PCH2P of minor D form), 3.24 (d of heptuplet, 3JPH = 16.8 Hz, 3JHH = 6.2 Hz, 2H, C6H(CH3)2, 0.96 (d, 2JHH = 6.2 Hz, 12H, CH(CH3)2), 0.81 (t, 2JPH = 4.1 Hz, 1H, PCH2P), 13C{1H} NMR (126 MHz, d8-THF, 300 K): δ = 138.6 (d, 1JPC = 95.4 Hz, i-PhP), 132.4 (app t, 2JPC = 4.9 Hz, o-PhP), 130.3 (s, p-PhP), 128.2 (app t, 2JPC = 5.7 Hz, m-PhP), 45.5 (s, CH(CH3)2), 27.5 (m, two overlapping CH(CH3)2), 9.5 (t, 2JPC = 134.5 Hz, PCH2P). 31P{1H} NMR (202 MHz, d8-THF, 300 K): δ = 26.2 (major A form, v1/2 = 3 Hz), −4.2 (minor D form, v1/2 = 5 Hz).

Preparation of ligand 2c. Salt 1c (5.16 g, 7.50 mmol) was suspended in Et2O (40 mL) at 0 °C, and a solution of KHMD (2.99 g, 15.0 mmol) in Et2O (30 mL) at room temperature was cannulated onto the suspension. The resulting pale yellow mixture was stirred for 3 h and filtered over Celite®. The filtered solid was rinsed with Et2O. The clear yellow solution thus obtained was evaporated and extensively dried in vacuo to remove hexamethyldisilazane. Compound 2c was isolated as a mixture of alternating dipolar (2c-A, minor) and dipolar (2c-D, major) forms in 79% yield (3.11 g). The purity of the material thus obtained (assessed by 1H and 31P NMR spectroscopy) was sufficient for further reaction. An analytically pure sample suitable for elemental analysis was obtained by recrystallization from a THF-n-pentane mixture.

Elemental analysis: calcld for C31H29N2P2: C, 75.26; H, 7.66; N, 5.32. Found: C, 75.19; H, 7.75; N, 5.37. HRMS (ESI-pos): calcld for C31H29N2P2 [M + H]+: 527.27395. Found: 527.27241 (0.5 ppm). FTIR (ATR): 2962 (m), 1433 (m), 1272 (br, s), 1216 (m), 1106 (m), 1094 (m), 803 (m), 755 (m), 719 (m), 704 (m), 697 (s), 534 (m), 502 (m), 445 (m), 376 (m), 366 (m), 154 (br) cm−1. 1H NMR (500 MHz, CD2Cl2, 300 K): δ = 7.76 (m, 8H, o-PhP of 2c-A), 7.67 (m, 8H, o-PhP of 2c-D), 7.41−7.30 (m, p- and m-PhP of both forms), 7.26 (m, p- and m-PhP of both forms), 6.13 (br s, 1H, NH of 2c-A), 3.35 (t, 2JPH = 13.6 Hz, PCH2P of 2c-D), 1.08 (s, 9H, Bu of 2c-D), 1.06 (s, 9H, Bu of 2c-A), n.o. (PCH2P of 2c-A). 13C{1H} NMR (126 MHz, CD2Cl2, 300 K): δ = 139.3 (d, 2JPC = 97.4 Hz, i-PhP of 2c-A), 131.1 (d, 2JPC = 98.2 Hz, i-PhP of 2c-D), 129.0 (s, m-PhP), 128.8 (app t, 2JPC = 6.1 Hz, m-PhP), 123.3 (m, o-PhP), 117.5 (s, p-PhP), 103.5 (t, 2JPC = 66.3 Hz, PCH2P). 31P{1H} NMR (202 MHz, CD2Cl2, 300 K): δ = −0.9 (v1/2 = 9 Hz).
Preparation of Li compound 3a. Compound 2a (1.00 g, 1.76 mmol) was suspended in THF (10 mL). A solution of n-BuLi (1.61 M in hexanes; 1.20 mL, 1.80 mmol) was prepared by dilution in THF (5 mL). Both vessels were cooled to −80 °C, and n-BuLi was added dropwise by cannulation onto 2a. The resulting mixture was stirred at −80 °C for 15 min, and then the cold bath was removed. After a further 20 min, the solvent was evaporated and the vessel was taken into the glovebox. The residue was triturated with 10 mL pentane, the supernatant was evaporated and the vessel was taken into the glovebox. The resulting mixture was stirred at −80 °C for 15 min, and then the cold bath was removed. After a further 15 min, the solvent was evaporated, affording complex 3a as a white powder in 75% yield (1.04 g). The purity of the material thus obtained (assessed by 1H and 31P NMR spectroscopy) was sufficient for further reaction. An analytically pure sample suitable for elemental analysis was obtained by recrystallization from a THF−n-pentane mixture.

Elemental analysis: calculated for C41H39LiN2OP2: C, 76.27; H, 6.10; N, 4.39. Found: C, 76.27; H, 6.00; N, 4.39. HRMS (ESI−neg): calcld for C41H39LiN2OP2 [M − Li − THF]: 556.2397. Found: 556.2397 (0.99 ppm). 1H NMR (500 MHz, CD2Cl2, 300 K): δ = 7.53 (m, 5H, o-Ph2P), 7.24 (m, 4H, p-Ph2P), 7.10 (m, 8H, m-Ph2P), 6.88 (m, 4H, m-PhN), 6.53 (m, 6H, overlapping o- and p-PhN), 3.91 (m, 4H, OCH2), 1.90 (m, 4H, CH2), 1.28 (br s, 1H, PCHP). 31P{1H} NMR (126 MHz, CD2Cl2, 300 K): δ = 151.9 (s, i-Ph2P), 134.8 (d, JPC = 91.0 Hz, i-Ph2P), 132.2 (app t, JPC = 4.6 Hz, o-Ph2P), 130.2 (s, p-Ph2P), 128.7 (s, m-PhN), 128.1 (app t, JPC = 5.4 Hz, m-PhN), 122.7 (br s, o-PhN), 116.6 (s, p-PhN), 69.0 (s, OCH2), 26.0 (s, CH2), 19.0 (t, JPC = 137.5 Hz, PCHP). 31P{1H} NMR (202 MHz, CD2Cl2, 300 K): δ = 16.5 (ν/2 = 184 Hz).

Preparation of Li compound 3b. Compound 2b (0.93 g, 1.90 mmol) was suspended in THF (10 mL). A solution of n-BuLi (1.61 M in hexanes; 1.20 mL, 1.93 mmol) was prepared by dilution in THF (5 mL). Both vessels were cooled to −80 °C, and n-BuLi was added dropwise by cannulation onto 2b. The resulting mixture was stirred at −80 °C for 15 min, and then the cold bath was removed. After a further 30 min, the solvent was evaporated and the vessel was taken into the glovebox. The residue was triturated with 10 mL pentane, the supernatant solution was discarded and the remaining solid was dried in vacuo, affording complex 3b as a white powder in 76% yield (1.53 g). The purity of the material thus obtained (assessed by 1H and 31P NMR spectroscopy) was sufficient for further reaction. An analytically pure sample suitable for elemental analysis was obtained by recrystallization from a THF−n-pentane mixture. Single crystals suitable for X-ray diffraction were grown by slow diffusion of n-pentane into a THF solution of 3c at −18 °C.

Elemental analysis: calculated for C41H39LiN2OP2·THF: C, 73.49; H, 7.83; N, 4.63. Found: C, 73.31; H, 7.78; N, 4.71. HRMS (ESI−neg): calcld for C41H39LiN2OP2 [M − Li − THF]: 525.2583. Found: 525.26019 (1.55 ppm). 1H NMR (500 MHz, CD2Cl2, 300 K): δ = 7.62 (m, 8H, o-Ph2P), 7.28 (m, 4H, p-Ph2P), 7.20 (m, 8H, m-Ph2P), 3.95 (m, 4H, OCH2), 1.92 (m, 4H, CH2), 1.09 (s, 18H, Bu), 0.47 (t, JPH = 4.9 Hz, 1H, PCHP). 31P{1H} NMR (126 MHz, CD2Cl2, 300 K): δ = 142.7 (d, JPC = 81.2 Hz, i-Ph2P), 132.4 (app t, JPC = 4.9 Hz, o-Ph2P), 128.9 (s, p-Ph2P), 127.4 (app t, JPC = 5.1 Hz, m-PhP), 68.8 (s, OCH2), 51.4 (t, JPC = 3.9 Hz, C(CH3)2), 35.2 (t, JPC = 5.2 Hz, C(CH3)2), 26.0 (s, CH2), 23.8 (s, JPC = 146.6 Hz, PCHP). 31P{1H} NMR (202 MHz, CD2Cl2, 300 K): δ = 10.4 (ν/2 = 17 Hz).

Preparation of Ti complex 4a. Compound 3a (1.00 g, 1.55 mmol) and Ti precursor (0.71 g, 1.55 mmol) were placed in a Schlenk vessel at −15 °C, and Et2O (25 mL) was added by a syringe. The heterogeneous reaction mixture was stirred for 2 h, after which the cold bath was removed. The yellow suspension was stirred for another 20 min and filtered over Celite®. The insoluble solids deposited on the Celite® cake were rinsed with toluene, and the resulting yellow solution was evaporated. The crude product was taken into the glovebox and dissolved in THF (2 mL). The resulting solution was layered with n-pentane (25 mL) and stored at −18 °C for over two days. Complex 4a was isolated as pale yellow crystals in 63% yield (0.45 g), which decomposes slowly (months) upon storage under N2 at −18 °C. The material thus obtained contained 20 mol% of THF (assessed by 1H NMR spectroscopy). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of n-pentane into a CH2Cl2 solution of 4a at −18 °C.

Elemental analysis: calculated for C31H35N2P2Ti0.2·THF: C, 67.64; H, 5.71; N, 5.72. Found: C, 67.65; H, 5.47; N, 5.74. FTIR (ATR): 2958 (w), 1592 (m), 1485 (m), 1435 (m), 1264 (m), 7.52; N, 4.86. Found: C, 71.57; H, 8.25; N, 4.85 (unsatisfactory, probably due to hydrolysis of the sample). HRMS (ESI−neg): calculated for C31H35N2P2: [M − Li − THF]: 497.22700. Found: 497.22810 (2.2 ppm). 1H NMR (500 MHz, CD2Cl2, 300 K): δ = 7.75 (m, 8H, o-Ph2P), 7.10 (m, 12H, overlapping m- and p-PhP), 3.76 (m, 4H, OCH2), 3.47 (d of heptuplet, JPH = 21.7 Hz, JHH = 184 Hz), View Article Online
Preparation of Ti complex 4b. Compound 3b (0.50 g, 0.867 mmol) and Ti precursor (0.395 g, 0.867 mmol) were placed in a Schlenk vessel at −15 °C, and Et2O (15 mL) was added by a syringe. The heterogeneous reaction mixture was stirred for 2 h, after which the cold bath was removed. The yellow suspension was stirred for another 30 min, filtered over Celite®, and the resulting yellow solution was evaporated. The crude product was taken into the glovebox and dissolved in THF (2 mL). The resulting solution was layered with n-pentane (25 mL) and stored at −18 °C overnight. Complex 4c was isolated as pale yellow crystals in 44% yield (0.53 g). A mixture of conformers was observed in solution (4c-ax and 4c-eq), with 4c-ax representing 88% of the mixture at 300 K in CD2Cl2. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of n-pentane into a CH2Cl2 solution of 4c at −18 °C.

Elemental analysis: calec for C32H38ClN3P2Ti: C, 65.35; H, 6.18; N, 6.44. Found: C, 64.32; H, 6.92; N, 6.34. FTIR (ATR): 3065 (w), 2960 (w), 2895 (m), 1434 (m), 1317 (m), 1274 (m), 1174 (m), 1129 (m), 1074 (m), 1064 (m), 989 (m), 897 (m), 827 (m), 811 (s), 800 (m), 741 (m), 716 (m), 689 (s), 565 (m), 558 (m), 523 (br s), 502 (s), 489 (m), 319 (m) cm−1. 1H NMR (500 MHz, CD2Cl2, 300 K): δ = 7.86 (m, 4H, o-Ph2P), 7.52 (t, 7JHH = 7.1 Hz, 2H, p-Ph2P), 7.43 (t, 7JPC = 4.5 Hz, 2H, p-Ph2P), 7.20 (t, 7JHH = 7.1 Hz, 2H, p-Ph2P), 7.14 (m, 4H, m-Ph2P), 7.09 (t, 7JHH = 7.2 Hz, 4H, m-Ph2P), 3.32 (m, 2H, CH(CH3)2), 1.77 (d, 7JPC = 7.2 Hz, 6H, CH(CH3)2), 1.49 (br s, 1H, PCH2), 1.25 (s, 9H, TiNPh2), 0.91 (d, 7JHH = 7.2 Hz, 6H, CH(CH3)2), 1.31(1H) NMR (126 MHz, CD2Cl2, 300 K): δ = 133.0 (dd, 7JPC = 92.8 Hz, 9JPC = 1.7 Hz, i-Ph2P), 132.1 (app t, 7JPC = 5.0 Hz, o-Ph2P), 132.1 (s, p-Ph2P), 132.0 (app t, 7JPC = 5.4 Hz, o-Ph2P), 131.1 (s, p-Ph2P), 129.1 (dd, 7JPC = 94.8 Hz, 9JPC = 7.2 Hz, i-Ph2P partially hidden under m-Ph2P), 128.7 (app t, 7JPC = 6.0 Hz, m-Ph2P), 128.4 (app t, 7JPC = 6.1 Hz, m-Ph2P), 68.7 (s, TiN(CH2)3), 48.7 (s, CH(CH3)2), 32.8 (s, TiN(CH3)2), 27.4 (s, CH(CH3)2), 27.2 (app t, 7JPC = 5.5 Hz, CH(CH3)2), 4.9 (t, 7JPC = 120.1 Hz, PCH2). 31P{1H} NMR (202 MHz, CD2Cl2, 300 K): δ = 26.4 (ν/2 = 36 Hz).

Preparation of Ti complex 4c. Compound 3c (1.07 g, 1.77 mmol) and Ti precursor (0.806 g, 1.77 mmol) were placed in a Schlenk vessel at −15 °C, and Et2O (30 mL) was added by a syringe. The heterogeneous reaction mixture was stirred for 2 h, after which the cold bath was removed. The yellow suspension was stirred for another 20 min, filtered over Celite®, and the resulting yellow solution was evaporated. The crude product was taken into the glovebox and dissolved in THF (2 mL). The resulting solution was layered with n-pentane (25 mL) and stored at −18 °C overnight. Complex 4c was isolated as pale yellow crystals in 44% yield (0.53 g). A mixture of conformers was observed in solution (4c-ax and 4c-eq), with 4c-ax representing 88% of the mixture at 300 K in CD2Cl2. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of n-pentane into a CH2Cl2 solution of 4c at −18 °C.

Elemental analysis: calec for C32H38ClN3P2Ti: C, 65.35; H, 6.18; N, 6.44. Found: C, 64.32; H, 6.92; N, 6.34. FTIR (ATR): 3065 (w), 2960 (w), 2895 (m), 1434 (m), 1317 (m), 1274 (m), 1174 (m), 1129 (m), 1074 (m), 1064 (m), 989 (m), 897 (m), 827 (m), 811 (s), 800 (m), 741 (m), 716 (m), 689 (s), 565 (m), 558 (m), 523 (br s), 502 (s), 489 (m), 319 (m) cm−1. 1H NMR (500 MHz, CD2Cl2, 300 K): δ = 7.86 (m, 4H, o-Ph2P), 7.52 (t, 7JHH = 7.1 Hz, 2H, p-Ph2P), 7.43 (t, 7JPC = 4.5 Hz, 2H, p-Ph2P), 7.20 (t, 7JHH = 7.1 Hz, 2H, p-Ph2P), 7.14 (m, 4H, m-Ph2P), 7.09 (t, 7JHH = 7.2 Hz, 4H, m-Ph2P), 3.32 (m, 2H, CH(CH3)2), 1.77 (d, 7JPC = 7.2 Hz, 6H, CH(CH3)2), 1.49 (br s, 1H, PCH2), 1.25 (s, 9H, TiNPh2), 0.91 (d, 7JHH = 7.2 Hz, 6H, CH(CH3)2), 1.31(1H) NMR (126 MHz, CD2Cl2, 300 K): δ = 133.0 (dd, 7JPC = 92.8 Hz, 9JPC = 1.7 Hz, i-Ph2P), 132.1 (app t, 7JPC = 5.0 Hz, o-Ph2P), 132.1 (s, p-Ph2P), 132.0 (app t, 7JPC = 5.4 Hz, o-Ph2P), 131.1 (s, p-Ph2P), 129.1 (dd, 7JPC = 94.8 Hz, 9JPC = 7.2 Hz, i-Ph2P partially hidden under m-Ph2P), 128.7 (app t, 7JPC = 6.0 Hz, m-Ph2P), 128.4 (app t, 7JPC = 6.1 Hz, m-Ph2P), 68.7 (s, TiN(CH2)3), 48.7 (s, CH(CH3)2), 32.8 (s, TiN(CH3)2), 27.4 (s, CH(CH3)2), 27.2 (app t, 7JPC = 5.5 Hz, CH(CH3)2), 4.9 (t, 7JPC = 120.1 Hz, PCH2). 31P{1H} NMR (202 MHz, CD2Cl2, 300 K): δ = 26.4 (ν/2 = 36 Hz).
Representative procedure for the catalytic hydroamination of alkynes

In the glovebox, aniline (46 µL, 0.5 mmol) and phenylacetylene (55 µL, 0.5 mmol) were added to 1 mL of 4a in C₆D₆ solution prepared freshly by dissolving 45.0 mg of 4a into 2.5 mL of C₆D₆. The reaction mixture was placed in a pressure tube closed by a Teflon® coated silicon seal, and heated to 105 °C. Upon cooling, the mixture was transferred into the glovebox, the seal was removed and the mixture was analyzed by ¹H NMR spectroscopy. A stock solution of 1,3,5-trimethoxybenzene in C₆D₆ (0.0102 M) was used throughout to enable quantitative analysis of reaction mixtures by ¹H NMR spectroscopy. To this end, spectra were recorded at 300 K on a Bruker 300 Avance III spectrometer (30° pulse, 50 s relaxation time, 4 scans). Reactions were run in duplicate, and relevant NMR signals were compared to the original samples (starting materials) or to those reported in the literature (products).

X-ray diffraction analysis

Intensity data were collected on a Bruker APEX II at 115 K. The structures were solved by direct methods (SHELXS) and refined with a full-matrix least-squares method based on F² (SHELXL). All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms were included in their calculated positions.

Table 5 Crystal data and structure refinement for 3b, 3c, 4a and 4c

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<tr>
<td>ρcalc./mg mm⁻³</td>
<td>1.178</td>
<td>1.157</td>
<td>1.308</td>
<td>1.168</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.163</td>
<td>0.155</td>
<td>0.428</td>
<td>0.401</td>
</tr>
<tr>
<td>f(000)</td>
<td>616.0</td>
<td>648.0</td>
<td>1504.0</td>
<td>720.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.25 × 0.25 × 0.1</td>
<td>0.6 × 0.5 × 0.4</td>
<td>0.25 × 0.25 × 0.2</td>
<td>0.25 × 0.25 × 0.2</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα</td>
<td>MoKα</td>
<td>MoKα</td>
<td>MoKα</td>
</tr>
<tr>
<td>2θ range for data collection</td>
<td>5.78 to 61.63°</td>
<td>4.64 to 55.13°</td>
<td>4.54 to 54.96°</td>
<td>4.67 to 54.97°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>−15 ≤ h ≤ 16</td>
<td>−14 ≤ h ≤ 13</td>
<td>−12 ≤ h ≤ 27</td>
<td>−13 ≤ h ≤ 13</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>62708</td>
<td>12733</td>
<td>26450</td>
<td>16536</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9351</td>
<td>7798</td>
<td>8303</td>
<td>8795</td>
</tr>
<tr>
<td>Rint</td>
<td>0.0335</td>
<td>0.0137</td>
<td>0.0313</td>
<td>0.0172</td>
</tr>
<tr>
<td>Rsigma</td>
<td>0.0315</td>
<td>0.0231</td>
<td>0.0261</td>
<td>0.0261</td>
</tr>
<tr>
<td>Goodness-of-ﬁt on F²</td>
<td>1.040</td>
<td>1.076</td>
<td>1.059</td>
<td>1.060</td>
</tr>
<tr>
<td>Final R indexes [I ≥ 2σ(I)]</td>
<td>R₁ = 0.0505</td>
<td>R₁ = 0.0404</td>
<td>R₁ = 0.0317</td>
<td>R₁ = 0.0404</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>wR₂ = 0.1188</td>
<td>wR₂ = 0.1023</td>
<td>wR₂ = 0.0658</td>
<td>wR₂ = 0.1132</td>
</tr>
<tr>
<td>Largest diff. peak/hole/e Å⁻³</td>
<td>1.25/−0.68</td>
<td>0.47/−0.29</td>
<td>0.22/−0.25</td>
<td>0.34/−0.37</td>
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<tr>
<td>Flack parameter</td>
<td>987356</td>
<td>987357</td>
<td>987358</td>
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</tr>
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</table>

Table 30 Crystal data and structure refinement for 3b, 3c, 4a and 4c.
culated positions and refined with a riding model. In 3c, two carbon atoms of the THF ligand were found disordered and refined in two positions with occupation factors of 0.60/0.40. In 4c, residual electron densities were found close to an inversion center, no attempts to model a solvent molecule were successful and the SQUEEZE procedure in PLATON was used to remove this contribution to the electron density in the final stages of refinement (void of 247 Å² and electron count of 62). Crystallographic data are reported in Table 5.

Acknowledgements

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Notes and references

18 Only Ia and IIa were structurally characterized.
32 Despite the somewhat misleading character of the P=N double bond depiction considering theoretical evidence gathered so far (see ref. 9–11), we decided to keep this widely used formalism for the sake of homogeneity. Obviously, the downside is that the choice of the terms alternating dipolar and dipolar becomes less intuitive with respect to the way structures are drawn. However, we feel they reflect more accurately the nature of the bonding in BIP ligands.
33 Similar metallation reactions have been reported by others, see ref. 19a–c and: (a) G. Aharonian, K. Feghali, S. Gambarotta and G. P. A. Yap, Organometallics, 2001, 20, 2616; (b) C. Bibal, M. Pink, Y. D. Smurnyy, J. Tomaszewski and K. G. Caulton, J. Am. Chem. Soc., 2004, 126, 2312.
34 See ESI, Fig. 51;† the quality of the X-ray diffraction data is insufficient for a detailed discussion of bond distances and angles.
In addition, replacing the N′Bu imido by a less bulky NMe group does not decrease the \(\text{P–N–C}\) angles in \(4\text{d-ax}\) compared to \(4\text{c-ax}\) (in fact it becomes slightly wider), but it does make the \(\text{N–Ti–N}\) angle about 4° smaller, consistent with the notion that steric repulsion is responsible for the opening of this angle.


In particular the fate of the substrates would need to be more rigorously investigated considering the difference between conversion values and the sum of products yields.


