Aromatic interactions in hydrotris(3-methylindazolyl)borate organoniobium complexes: control of an alkyne ligand orientation in the crystal†

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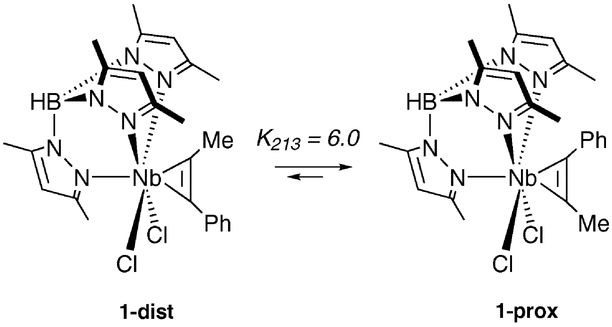
Received (in Montpellier, France) 3rd February 2006, Accepted 5th April 2006
First published as an Advance Article on the web 19th April 2006
DOI: 10.1039/b601652a

Reaction of $NbCl_3(MeOCH_2CH_2OMe)(PhC{\equiv}CMe)$ with $KTp^{4Bo,3Me}$ in THF produces a 68% yield of the dichloro–phenylpropyne complex $Tp^{4Bo,3Me}NbCl_2(PhC{\equiv}CMe)$ [$Tp^{4Bo,3Me}$ = hydrotris(3-methylindazol-1-yl)borate]. As observed by solution NMR spectroscopy, the four-electron donor alkyne sits in the molecular mirror plane and restricted rotation of the alkyne ligand allows the observation of an equilibrium between two rotamers. The conformation of the alkyne ligand in the major isomer is such that the phenyl group is proximal to $Tp^{4Bo,3Me}$. Unexpectedly, the minor rotamer in solution, that with the distal phenyl group, is observed in the crystal. Analysis of the possible interactions suggest that aromatic interactions are responsible for this unusual observation.

Introduction

Among the numerous examples of scorpionate ligands, tris(indazolyl)borates have received little attention despite the relative ease of their preparation.[1]‡ Among advantages on the related hydrotris(pyrazolyl)borate they secure the substitution pattern at positions 4 and 5 (and consequently at position 3) on the pyrazolyl ring (Scheme 1).[1] They may serve as surface anchors for single molecule motors,[2] a concept that could be used for supporting organometallic catalysts. Supramolecular assembly has also been realized thanks to combined π–π and C–H···π interactions, or so-called aromatic interactions.[3] Clearly, there are potentially large differences between seamingly closely related ligands. Thanks to a delicate balance between electronic and steric effects operating intramolecularly, we have been able to observe an unprecented equilibrium between α- and β-C–H agostic rotamers of secondary alkyl groups in $Tp^{Me2}Nb$ complexes,[4] and to characterise a rare case of α-C–C agostic interaction.[5] A C–C bond metathesis reaction of a coordinated alkyne, occuring *via* a reversible migratory insertion/β-alkyl elimination, is a direct consequence of the presence of α-C–H agostic interactions.[6] Also, similar competing effects have led to structure–activity relationships during ethylene polymerisation by these complexes[7] with a rare alkyl cation of a group 5 metal being fully characterised.[8]



1-dist **1-prox**

Scheme 1

We report herein a new hydrotris(3-methylindazolyl)borate complex of niobium [$Tp^{4Bo,3Me}NbCl_2(PhC{\equiv}CMe)$] (**2**) in which aromatic interactions dictate ancillary alkyne ligand orientation in the solid state. Indeed the equilibrium of two interconverting alkyne rotamers in solution is driven to the minor form in the crystal. This unexpected result suggests that organometallic complexes, in addition to more classical coordination species, may be used as building blocks in crystal engineering.

Results and discussion

In solution, two slowly interconverting phenylpropyne rotamers ($\Delta G_{rot}^{\ddagger}$ > 90 kJ mol^{-1}) are observed in the complex [$Tp^{Me2}NbCl_2(PhC{\equiv}CMe)$] (**1**).[9] The alkyne sits in the molecular symmetry plane. The rotamer with the phenyl group proximal to Tp^{Me2} is the more abundant (K_{213} = 6, ΔG^0 = −3.2 kJ mol^{-1}) (Scheme 1). It is this rotamer, **1-prox**, that is observed in the crystal.[9a]

The new related hydrotris(3-methylindazol-1-yl)borato complex [$Tp^{4Bo,3Me}NbCl_2(PhC{\equiv}CMe)$] (**2**), prepared in 68% yield following the same procedure as that for **1** by

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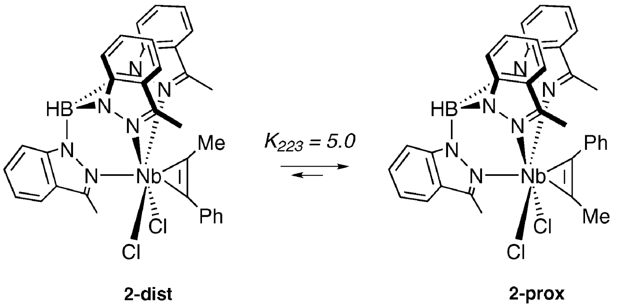
† Electronic supplementary information (ESI) available: A detailed analysis of the aromatic interactions within a crystal of **1-prox**. See DOI: 10.1039/b601652a

‡ The nomenclature proposed by Trofimenko[1a] for the abbreviation of ligands is used throughout: Tp^{Me2} = hydrotris(3,5-dimethylpyrazol-1-yl)borate, $Tp^{4Bo,3Me}$ = hydrotris(3-methylindazol-1-yl)borate.



Scheme 2

reacting KTp^{4Bo,3Me} and $[NbCl_3(MeOCH_2CH_2OMe)(PhC\equiv CMe)]$[10] in THF overnight, exhibits fully similar properties in solution as expected on the similar steric and electronic properties of Tp^{Me2} and Tp^{4Bo,3Me} ligands.§ In the ^{1}H and ^{13}C NMR spectra of **2** at room temperature, just like for **1**, two sets of signals exist due to the presence of two alkyne rotamers, **2-prox** and **2-dist**. For each rotamer, all of the sets of the Tp^{4Bo,3Me} indazolyl groups signals appear in a 2 : 1 intensity pattern, indicating that a plane of symmetry containing the phenylpropyne exists for each rotamer. As ascertained by dynamic ^{1}H NMR spectroscopy, the two sets of signals for **2-prox** and **2-dist** do not coalesce at 363 K in toluene-d_8 ($\Delta G_{rot}^{\ddagger} >$ 90 kJ mol^{-1}), and the ratio **2-prox** : **2-dist** is 5 : 1 at 223 K ($\Delta G^0 = -3.0$ kJ mol^{-1}) (Scheme 2). These data are fully similar to those for **1**. Furthermore, ^{1}H NMR NOE experiments have confirmed the orientation of the four-electron[11] phenylpropyne ligand (^{13}C NMR: δ 267.4, 222.6 in **2-prox**; 249.3, 237.4 in **2-dist**; Nb(PhC≡*C*Me)) in both rotamers. In **2-prox**, the alkyne methyl protons resonate as a ^{1}H NMR singlet at δ 4.06 whereas these protons are highly shielded at δ 1.83 in **2-dist**.

The molecular structure of **2** as determined by X-ray diffraction on a single crystal is shown in Fig. 1. Clearly, and in complete contrast to the case of **1**, it is **2-dist**, where the phenyl group is distal to the Tp^{4Bo,3Me} ligand, that is observed in the solid state despite the fact that **2-dist** is the least stable rotamer in solution. Overall both structures are fully comparable as far as bond lengths and angles are concerned. Key metric parameters for **2-dist,** with those of **1-prox** in brackets for comparison, include Nb–Cl bond lengths of 2.3768(11) and 2.3969(11) Å [2.399(3) and 2.408(3) Å], Nb–C bond lengths of 2.065(4) and 2.082(4) Å [2.050(9) and 2.093(9) Å], and a Cl–Nb–Cl angle of 100.39(4)° [101.96(10°)]. The *trans* influence of the phenylpropyne leads to a slightly longer *trans* Nb–N bond [2.379(3) Å] in **2-dist** as compared to that [2.312(7) Å] in **1-prox**. Similarly, the whole phenylpropyne, including the phenyl ring, lies in the molecular mirror plane that contains the niobium and bisects the Cl–Nb–Cl angle. These observations indicate that changing Tp^{Me2} for Tp^{4Bo,3Me} is not the reason for the change in ground state alkyne orientation when going from solution to the crystal in **2**.

A closer inspection of the crystal packing yields interesting features. A number of so-called close contacts can be identified in the general context of hydrogen bridges[12] or C–H···π interactions or π–π stacking.[13] Essentially, the direction of the stacking is one key parameter. Indeed, face-to-face stacking of hydrogen-based aromatics is repulsive. An attractive interaction is observed only if an offset (or slippage) of the two parallel aromatic planes and/or if an angle between these planes is present. In Table 1, we provide the results of an analysis of such possible intermolecular contacts within the crystal lattice of **2**, based on the reports of ref. 12 and 13.

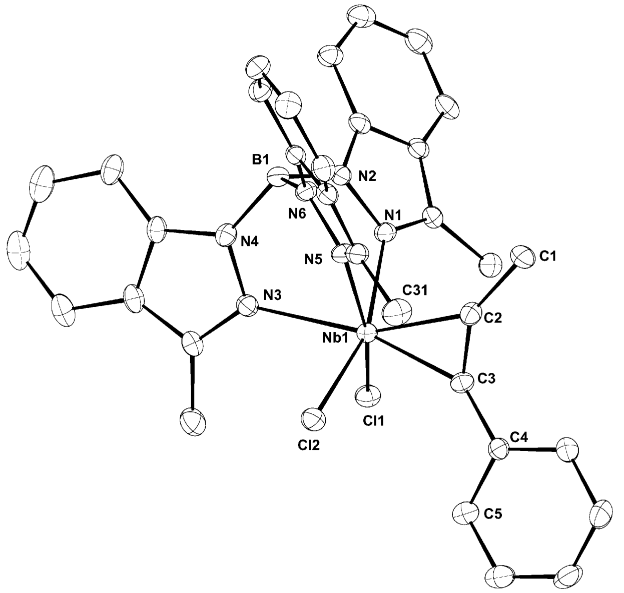


Fig. 1 The molecular structure of **2**.

These interactions, summarized for molecule Unit A (UA) (Fig. 2), involve either indazolyl rings or an alkyne phenyl ring. Attractive interaction (*Ind–Ind*)$_{att}$ (entry A) results from the stacking of the benzo rings of indazolyl groups of two molecules connected by the inversion center. A very similar interaction, albeit between molecules connected by a C2 axis, is present in the crystal of thallium indazolylborate.[9b] It has no consequence on the alkyne orientation. There are attractive interactions, (*Ind–Ph*)$'_{att}$ (Table 1, entry B) and (*Ind–Ph*)$''_{att}$ (Table 1, entry C) that occur between a single alkyne phenyl ring of a given complex and one indazolyl ring of two neighbouring molecules UA′ and UA″. UA′ and UA″ are symmetry related as can be seen from the identical angle between interacting planes (Table 1, entries B and C). In this way, the alkyne phenyl ring of a single complex experiences two interactions from both faces of its plane, a framework

Table 1 Aromatic interactions within a crystal of **2-dist**

Entry	Interaction name	Ctd–Ctd/Å^a	Ctd-plane/Å^b	Angle/deg^c	Offset/Å	Interaction type
A	(*Ind–Ind*)$_{att}$	3.75	3.48	0	1.39	Attractive
B	(*Ind–Ph*)$'_{att}$	3.95	3.34	8	2.11	Attractive
C	(*Ind–Ph*)$''_{att}$	5.65	3.18	8	4.67	Attractive
D	(*Ph–Ph*)$'_{rep}$	5.52	4.86	61	2.63	Repulsive
E	(*Ph–Ph*)$''_{ep}$	6.11	3.08	61	5.28	Repulsive

^{a} Distance between centroids. ^{b} Distance between a centroid and the interacting plane. ^{c} Angle between planes.

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§ Cone angles: Tp^{Me2}, 239°; Tp^{4Bo,3Me}, 235°. Wedge angles: Tp^{Me2}, 67°; Tp^{4Bo,3Me}, 68°.[1] The unsubstituted ligand Tp^{4Bo} has a slightly higher field than the unsubstituted Tp.[3a]

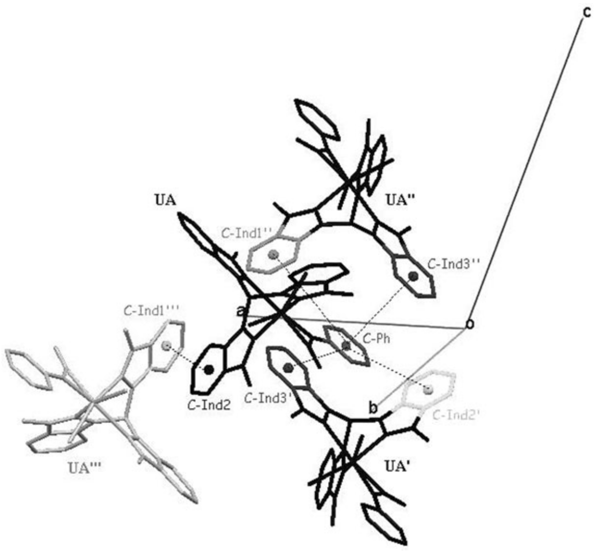

Fig. 2 Partial view of the packing within a crystal of **2**, with labeled interactions.

constituting a "slipped sandwich". According to the parameters in Table 1, interaction (*Ind–Ph*)′$_{att}$ between UA and UA′ is significantly stronger[12,13] and it is depicted in Fig. 2. The same alkyne phenyl ring experiences yet a third type of interaction. Interactions (*Ph–Ph*)′$_{rep}$ (Table 1, entry D) and (*Ph–Ph*)″$_{rep}$ (again related by symmetry) (entry E) are now repulsive, but the metric parameters for these interactions suggest they are considerably weaker and thus cannot have any consequence on alkyne orientation.

The direct analysis of these aromatic interactions in **2-prox**, the major rotamer in solution, is of course not feasible since it does not exist in the solid state. However, we have now analysed the aromatic interactions in the parent Tp^{Me2} complex **1**, for which **1-prox**, the major rotamer in solution, is also observed in the crystal.[9] The relevant data have been retrieved from the CSD under VOKSIX. Basically, there are several aromatic interactions present, but based on the analysis of the metric parameters they are all very weak (see text, Table S1 and Fig. S1 in electronic supplementary information†). The most prominent is an attractive interaction[13] (*Pz–Pz*)$_{att}$ (distance between centroids, 4.72 Å, distance between centroid and plane, 3.88 Å, offset 2.69 Å, angle between plane 0°) that is present between two pyrazolyl rings of neighbouring complexes related by an inversion centre. It is thus similar to (*Ind–Ind*)$_{att}$ (Table 1, entry A) for **2-dist** except that benzo rings, not nitrogen-based rings, interact in **2-dist**. Given the distance and the offset between centroids, this interaction is much weaker in **1-prox** than in **2-dist**.[13] Overall, the compared analysis of aromatic interactions in **2-dist** and **1-prox** strongly suggests that it is the presence of the benzo ring of the indazole involved in the stabilizing interaction (*Ind–Ph*)$_{att}$ in **2-dist** that is controlling alkyne orientation in the crystal.

Having highlighted the characteristics of the packing for **2**, an attempt at justifying this behaviour is desirable. Although a full account of forces that are at play in solution and in the crystal is beyond the scope of this study, an estimate of the possible competing interactions can be made. Stabilising aromatic interactions are typically in the 2 to 5 kJ mol^{-1} range, nitrogen substitution leading to values in the upper range.[13b] Taking into account that two such interactions are at play for a given phenyl group in **2-dist**, this energy could overcome the enthalpy $\Delta H^0 \approx -3.0$ kJ mol^{-1} estimated from the rotamer ratio of 5 : 1 in solution ($\Delta G^0{}_{223} = -3.0$ kJ mol^{-1}, neglecting entropy effects that likely cancel out).

Finally, for either complex **1** or **2**, it could be argued that the crystal that was analysed was simply the nicest looking crystal. Although this cannot be totally excluded, several crystals of **2** yielded the same crystal data. Also, it is worth considering that crystals of the recently reported trifluoropropyne complex [Tp^{Me2}NbCl$_2$(CF$_3$C≡CH)] contain three independent molecules in the asymetric unit showing the two possible alkyne orientations.[6b] Two of these molecules only differ slightly in their metric parameters and the alkyne orientation is such that the CF$_3$ group is distal to Tp^{Me2}. In contrast, the third independent molecule has a CF$_3$ group that is proximal to Tp^{Me2}. Some C–F···H–C interactions seem responsible for this situation, together with a lower barrier to alkyne rotation and an equilibrium ($\Delta G^0{}_{223} = 3.5$ kJ mol^{-1}) favoring the distal rotamer in solution.[6b]

Conclusion

The selective crystallisation of **2-dist** is a direct consequence of the use of Tp^{4Bo,3Me}. Although no steric or electronic properties of similar ligands such as Tp^{4Bo,3Me} and Tp^{Me2} impart unique behaviour to the complexes in solution, the opportunity to develop secondary interactions thanks to remote substitutions allows the crystallisation of a given alkyne rotamer. Such aromatic interactions would open the field of the synthesis of extended networks to organometallic compounds[14] that are otherwise utilized for their reactivity properties. The successful efficient synthesis of **2** widens the range of available group 5 scorpionate complexes. Research aimed at grafting such ligands or complexes is in progress.

Experimental

General procedures

All experiments were carried out under a dry argon atmosphere using either Schlenck tube or glovebox techniques. THF was obtained after refluxing purple solutions of Na/benzophenone under argon. Toluene, pentane and dichloromethane were dried by refluxing over CaH$_2$ under argon. Deuterated NMR solvents were dried over molecular sieves, degassed by freeze–pump–thaw cycles, and stored under argon. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX 500 spectrometer. Due to the complexity of the aromatic areas, some signals may be obscured at some temperatures, especially in the ^{1}H NMR spectra. Proposed assignments have been secured thanks to NOE, COSY, HMQC and HMBC sequences. The indazolyl hydrogens and carbons are numbered with 'for the in-plane indazole and without' for the two equivalent indazolyl rings. Elemental analyses were performed in the Analytical Service of our Laboratory. [NbCl$_3$(MeOCH$_2$CH$_2$OMe)(PhC≡CMe)] was prepared according to the published procedure.[10]

Preparation of $[\mathrm{Tp}^{4Bo,3Me}\mathrm{NbCl_2(PhC{\equiv}CMe)}]$ 2

$\mathrm{KTp}^{4Bo,3Me}$ (0.44 g, 1.0 mmol) was suspended in THF (50 mL) and a solution of $[\mathrm{NbCl_3(MeOCH_2CH_2OMe)(PhC{\equiv}CMe)}]$ (0.49 g, 1.2 mmol) in THF (10 mL) was added. The solution was stirred for 16 h during which time it had turned orange-red. Toluene (20 mL) was added and all volatiles were removed *in vacuo* to yield a brown solid. This was extracted in toluene (20 mL), filtered over celite and rinsed with pentane (30 mL). An orange solid precipitated in the red filtrate when pentane was added. All volatiles were removed under reduced pressure to yield an orange solid which was recrystallized from a mixture of $\mathrm{CH_2Cl_2}$–pentane (1 : 1). After 24 h at room temperature, the desired product **2** (0.47 g, 68%) was recovered as red crystals. Anal. (Found: C, 58.1; H, 4.3; N, 12.3. Calc. for $\mathrm{C_{33}H_{30}BCl_2N_6Nb}$: C, 57.8; H, 4.4; N, 12.3). ^{1}H NMR δ_H (500 MHz, toluene-d$_8$, T = 223 K). Major rotamer **2-prox**: 8.02 (1H, d, J = 9 Hz, $\mathrm{Tp}^{4Bo,3Me}H7'$), 7.92 (2H, d, J = 9 Hz, $\mathrm{Tp}^{4Bo,3Me}H7$), 7.34 (1H, t, J = 8 Hz, $\mathrm{Tp}^{4Bo,3Me}H6'$), 7.19 (obsc m, $\mathrm{Tp}^{4Bo,3Me}H6$), 6.90 (2H, d, J = 8 Hz, $\mathrm{Tp}^{4Bo,3Me}H4$), 6.78 (2H, t, J = 8 Hz, $\mathrm{Tp}^{4Bo,3Me}H5$), 4.06 (3H, s, $\equiv$CH_3), 3.23 (3H, s, $\mathrm{Tp}^{4Bo,3Me}CH'_3$), 2.06 (6H, s, $\mathrm{Tp}^{4Bo,3Me}CH_3$). Minor rotamer **2-dist**: 8.38 (2H, br d, J = 7 Hz, o-C$_6H_5$), 7.42 (2H, t, J = 7 Hz, m-C$_6H_5$), 7.29 (1H, d, $\mathrm{Tp}^{4Bo,3Me}H4'$), 7.25 (1H, br t, J = 7 Hz, p-C$_6H_5$), 7.05 (2H, d, $\mathrm{Tp}^{4Bo,3Me}H4$), 3.28 (3H, s, $\mathrm{Tp}^{4Bo,3Me}CH'_3$), 2.11 (6H, s, $\mathrm{Tp}^{4Bo,3Me}CH_3$), 1.83 (3H, s, $\equiv$CH_3). Isomer ratio: 1 : 5. ^{13}C{^{1}H} NMR δ_C (125.8 MHz, toluene-d$_8$, T = 223 K). Major rotamer: 267.4 ($\equiv C$Ph), 222.6 ($\equiv C$CH$_3$), 147.6 ($\mathrm{Tp}^{4Bo,3Me}C3'$), 146.9 ($\mathrm{Tp}^{4Bo,3Me}C3$), 143.5 ($\mathrm{Tp}^{4Bo,3Me}C7a'$), 142.7 ($\mathrm{Tp}^{4Bo,3Me}C7a$), 123.4 ($\mathrm{Tp}^{4Bo,3Me}C3a'$), 122.4 ($\mathrm{Tp}^{4Bo,3Me}C3a$), 120.7 ($\mathrm{Tp}^{4Bo,3Me}C5$), 120.6 ($\mathrm{Tp}^{4Bo,3Me}C4$), 112.3 ($\mathrm{Tp}^{4Bo,3Me}C7$), 111.6 ($\mathrm{Tp}^{4Bo,3Me}C6$), 25.6 ($\equiv$C$CH_3$), 14.3 ($\mathrm{Tp}^{4Bo,3Me}C'H_3$), 13.7 ($\mathrm{Tp}^{4Bo,3Me}CH_3$). Minor rotamer: 249.3 ($\equiv C$CH$_3$), 237.4 ($\equiv C$Ph), 147.2 ($\mathrm{Tp}^{4Bo,3Me}$C3), 143.1 ($\mathrm{Tp}^{4Bo,3Me}C7a'$), 142.6 ($\mathrm{Tp}^{4Bo,3Me}$C7a), 133.4 (o–$C_6H_5$), 22.8 ($\equiv$C$CH_3$), 14.4 ($\mathrm{Tp}^{4Bo,3Me}C'H_3$), 13.8 ($\mathrm{Tp}^{4Bo,3Me}CH_3$).

X-ray analysis

Data were collected on a Xcalibur Oxford diffraction diffractometer using graphite MoKα radiation (λ = 0.710 73 Å). The final unit cell parameters have been obtained by means of a least-squares refinement performed on a set of 6958 well-measured reflections. The structure has been solved by direct methods using SIR92[15] and refined by means of least-squares procedures with SHELXL97.[16] The atomic scattering factors were taken from International Tables for X-ray crystallography.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic parameter. It was not possible to resolve diffuse electron density residuals (unidentified enclosed solvent molecules). Treatment with the Squeeze facility from PLATON[18] with a localized void of about 270 Å^3 and 12 recovered electrons resulted in a smooth refinement. Since a few low order reflections are missing from the data set, the electron count will be underestimated. The reported values for ρ_calc, $F(000)$ and molecular weight are only valid for the ordered part of the structure. A weighting scheme of the form $w = 1/[\sigma^2(Fo^2) + (0.0472P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$ was used. Drawings were performed with either Cameron[19] or Mercury[20] with 30% probability displacement ellipsoids for non-hydrogen atoms. Crystal data for $\mathrm{C_{33}H_{30}BCl_2N_6Nb}$: M = 685.25, monoclinic, $P2_1/n$, a = 11.1301(14), b = 19.875(2), c = 16.4137(16) Å, β = 109.858(10)°, V = 3415.0(6) Å^3, Z = 4, ρ_calc = 1.333 Mg m^{-3}, μ = 0.540 mm^{-1}, 25 314 reflections collected, 6958 unique (R_int = 0.0779), final $R1$ = 0.0475, $wR2$ = 0.0983 [$I > 2\sigma(I)$], final $R1$ = 0.0894, $wR2$ = 0.1105 (all data).

CCDC reference number 604264. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601652a

Acknowledgements

M. E. and C. D. thank the CNRS for a postdoctoral grant.

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