New Group 5 and 6 transition metal imido complexes with monodeprotonated triazacyclononane ligands

John S. Fletcher,[a] Nigel A. H. Male,[a] Paul J. Wilson,[b] Leigh H. Rees,[a] Philip Mountford *[a] and Martin Schröder [b]

[a] Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR
[b] School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD

The 1,4-dialkyl-1,4,7-triazacyclononanes $HR_2[9]aneN_3$ (R = Me or Pr^i) were smoothly deprotonated with *n*-butyl-lithium to give corresponding lithiated amides $\{Li[R_2[9]aneN_3]\}_x$ **1, 2** which are in turn useful precursors to new transition metal complexes. Reaction of **1** or **2** with the mono(imido) or bis(imido) complexes $[M(NBu^t)Cl_3(py)_2]$ (M = Nb or Ta) or $[Mo_2(NC_6H_3R'-2,6)_2Cl_2(dme)]$ gave $[M(NBu^t)(R_2[9]aneN_3)Cl_2]$ (M = Nb, R = Me **3** or Pr^i **4**; M = Ta, R = Me **5** or Pr^i **6**) or $[Mo(NC_6H_3R'_2-2,6)_2(R_2[9]aneN_3)Cl]$ (R = Me, R' = Pr^i **8**; R = Pr^i, R' = H **9**, Me **10** or Pr^i **11**). The compounds **3–6** are relatives of the d^0 metallocene dichlorides $[M(\eta-C_5R_5)_2Cl_2]$ (M = Group 4 metal). The titanium imido analogue $[Ti(NBu^t)(HPr^i_2[9]aneN_3)Cl_2]$ **7** has been prepared for purposes of comparison and exists as a mixture of isomers in solution. The crystal structure of the bis(imido) compound **11** has been determined and shows that the co-ordination of the amido N-donor of $Pr^i_2[9]aneN_3$ is not greatly distorted from planarity. Examination of the molecular structure suggests that in this compound the $Pr^i_2[9]aneN_3$ ligand acts effectively as a 5-electron donor with the molybdenum d$_\pi$-acceptor orbitals dominated by the strongly π-donating arylimido ligands. Extrapolation to the mono(imido) complexes $[M(NBu^t)(R_2[9]aneN_3)Cl_2]$ **3–6**, in which the amido N-donor of $Pr^i_2[9]aneN_3$ lies *trans* to one of the Cl ligands and *cis* to NBu^t, suggests that the amido N-donor should be able at least partly to π-donate to the metal centres. Hence in **3–6** the $Pr^i_2[9]aneN_3$ ligand can in principle act as up to a 7-electron donor.

Introduction

Transition metal imido compounds of the general formula $[M(NR)_nL_m]$ (R typically = alkyl or aryl; L_m is an ancillary ligand set) have been a focus of considerable interest, particularly over the last 15 years.[1,2] This activity has spanned several fields of interest including unusual molecular and electronic structures, fundamental reactivity,[1,2] and potential applications in industrially relevant areas such as olefin polymerisation and metathesis catalysis.[3] As part of our ongoing studies of early transition metal imido chemistry,[2,4] we have reported a number of neutral, triazacycle-supported Group 4 imido complexes of the types **I–III**.[5] Che and co-workers have reported triazacyclononane-supported imido complexes of Group 6 and 7 transition metals.[6] Our initial interest in compounds of this type stemmed from the isolobal relationship between the cyclopentadienide anion, the imide dianion and the *fac*-L$_3$ (L = neutral, 2-electron donor) ligand sets.[7] One consequence of these relationships is that complexes such as **I–III** are isolobal analogues of the corresponding metallocene derivatives **IV** (and their *ansa*-linked relatives in the case of **III**) which have a rich and diverse reaction chemistry, not least in the areas of organic synthesis and catalysis.[8]

We were interested to extend the Group 4 triazacyclononane imido complexes of type **I** to Group 5 and 6 transition metals. The abbreviations adopted for the key triazacyclononanes discussed herein are given in **V**. We have previously shown that reaction of $Me_3[9]aneN_3$ with $[Nb(NBu^t)Cl_3(py)_2]$[9] gives the cationic complex $[Nb(NBu^t)(Me_3[9]aneN_3)Cl_2]^+$ as either the Cl$^-$ or PF$_6^-$ salt.[5e] These had limited solubility and proved difficult to work with. We thus considered the possibility of using monoanionic derivatives of triazacyclononanes, namely $[R_2[9]aneN_3]^-$ **VI**. The anion **VI** is isoelectronic with the 4,7-diaza-1-thia- and -oxa-cyclononanes, $Me_2[9]aneN_2S$ and Me_2-

R, R'	Abbreviation
H, H	$H_3[9]aneN_3$
Me, Me	$Me_3[9]aneN_3$
Me, H	$HMe_2[9]aneN_3$
Pr^i, H	$HPr^i_2[9]aneN_3$
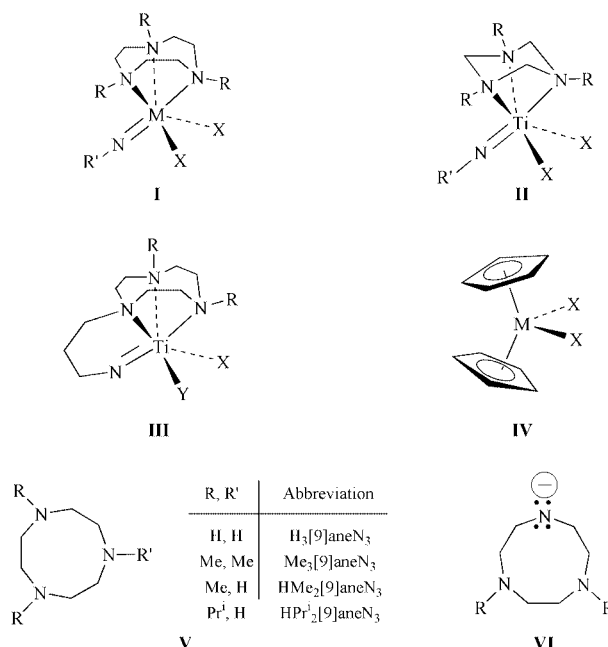
$[9]aneN_2O$,[10] from which we have made the crystallographically characterised titanium imido complexes $[Ti(NBu^t)(Me_2[9]-aneN_2E)Cl_2]$ (E = O or S).[5e] Unsaturated macrocycles (*e.g.* porphyrins and dibenzotetraaza[14]annulenes) with anionic N-donors are very well known,[11] and amido-transition metal chemistry in general is an area of considerable current interest.[1c,12] Saturated macrocycles with anionic donors are less well established.[13] Only one report of complexes of a deprotonated triazacyclononane has appeared, these being bis(imido)-

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rhenium complexes that are formed by loss of a proton from co-ordinated $H_3[9]aneN_3$.[6b] Furthermore, the donor properties of **VI** are potentially interesting: while neutral $R_3[9]aneN_3$ ligands are isolobal and isoelectronic with the cyclopentadienide anion, having 6 electrons to donate, anionic $[R_2[9]aneN_3]^-$ **VI** has an additional amide nitrogen lone pair that could potentially be donated to a metal centre, depending upon the metal–ligand geometry, ancillary ligands and the hybridisation of the macrocyclic amido nitrogen. Here we report the synthesis of lithiated, anionic triazacyclononanes and their application in the synthesis of new Group 5 and 6 transition metal imido complexes.

Experimental

General methods and instrumentation

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or dry-box techniques. All protio-solvents and commercially available reagents were pre-dried over activated molecular sieves and refluxed over an appropriate drying agent under an atmosphere of dinitrogen and collected by distillation. NMR solvents for air- and/or moisture-sensitive compounds were dried over freshly ground calcium hydride at r.t. (CD_2Cl_2) or molten potassium (C_6D_6), distilled under reduced pressure and stored under N_2 in J. Young ampoules. NMR samples of air- and moisture-sensitive compounds were prepared in the dry-box in 5 mm Wilmad tubes, fitted with J. Young Teflon valves.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 500, Mercury 300, or Bruker DPX 300 spectrometer and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0$) in δ (ppm) and coupling constants in hertz. Assignments were confirmed by DEPT-135 and DEPT-90, and two-dimensional ^{1}H–^{1}H and ^{13}C-{^{1}H} NMR experiments as appropriate. Mass spectra were recorded on a AEI MS902 or Micomass Autospec 500 mass spectrometer. Infrared samples were recorded as Nujol mulls between NaCl or KBr plates using a Perkin-Elmer 1710 spectrophotometer. Elemental analyses were carried out by the analysis laboratories of these departments.

The compounds $[Ti(NBu^t)Cl_2(py)_3]$,[14] $[M(NBu^t)Cl_3(py)_2]$ (M = Nb or Ta),[9] $HMe_2[9]aneN_3$,[15] $HPr^i_2[9]aneN_3$,[16] $[Mo(NC_6H_3R_2$-2,6$)_2Cl_2(dme)]$ (R = H, Me or Pr^i)[17,18] were prepared according to published methods.

Preparations

Li[Me$_2$[9]aneN$_3$] 1. n-Butyllithium (1.00 ml, 2.5 M in hexanes, 2.50 mmol) was slowly added dropwise to a stirred solution of 1,4-dimethyl-1,4,7-triazacyclononane (0.398 g, 2.50 mmol) in pentane (40 ml) at −78 °C in the absence of light. After the addition was complete the suspension was allowed slowly to warm to r.t. and then stirred for 2 h. The solution was concentrated to approx. 20 ml and then placed at −80 °C for 14 h which gave compound **1** as translucent colourless crystals which were isolated and then dried under reduced pressure to give a white powder. Yield: 0.265 g (65%). ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 3.53, 3.34, 3.16, 3.12, 2.72, 2.68, 2.46 (7 × m, 7 × 1 H, 7 × CH$_2$), 2.39 (s, 3 H, Me), 2.33, 2.29 (2 × m, 2 × 1 H, 2 × CH$_2$), 2.27 (s, 3 H, Me), 2.23, 2.17, 1.98 (3 × m, 3 × 1 H, 3 × CH$_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 59.2, 59.2, 54.8, 54.4, 54.1, 53.8 (6 × CH$_2$), 46.8, 45.3 (2 × Me). IR (Nujol mull, KBr plates): 2953s, 2852m, 2800w, 1675–1420 series of closely overlapping peaks (m), 1363w, 1313w, 1289w, 1250w, 1022m, 985m, 863w, 791m, 698w, 669–419 series of closely overlapping peaks (m) cm^{-1}. Found (calculated for $C_8H_{18}LiN_3$): C 58.3 (58.9); H 11.1 (11.1); N 25.6 (25.8)%.

Li[Pr$^i_2$[9]aneN$_3$] 2. To a solution of $HPr^i_2[9]aneN_3$ (1.24 g, 6.7 mmol) in pentane (20 ml) at −78 °C was added dropwise ^nBuLi in hexanes (2.7 ml of a 2.5 M solution, 6.7 mmol). The solution was allowed to warm to r.t. and stirred for 0.5 h. A white precipitate formed and the volume was reduced to ca. 8 ml and stored at −25 °C for 16 h. The resulting white crystalline solid **2** was filtered off, washed with pentane and dried in vacuo. Yield: 0.88 g (60%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 3.44 (m, 2 H, 2 × NCH$_2$CH$_2$N), 3.22 (m, 2 H, 2 × NCH$_2$CH$_2$N), 2.94 (app. sept, 2 H, app. $J = 6$, CHMe$_2$), 2.71 (m, 2 H, 2 × NCH$_2$CH$_2$N), 2.38 (m, 2 H, 2 × NCH$_2$CH$_2$N), 2.35 (m, 2 H, 2 × NCH$_2$CH$_2$N), 2.17 (m, 2 H, 2 × NCH$_2$CH$_2$N), 1.19 (d, 6 H, $J = 6.0$, CHMe$_2$) and 0.84 (d, 6 H, $J = 6.0$ Hz, CHMe$_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): δ 55.9 (NCH$_2$CH$_2$N), 54.3 (CHMe$_2$), 53.8 (NCH$_2$CH$_2$N), 45.7 (NCH$_2$CH$_2$N), 21.8, 15.0 (2 × CHMe$_2$). IR (Nujol mull, NaCl plates): 3198m, 3034m, 2603w, 2500w, 2090m, 1630m, 1610m, 1545m, 1524m, 1474m, 1421w, 1364w, 1347w, 1276m, 1241m, 1216w, 1179m, 1160w, 1095m, 1075w, 1056w, 1026m, 994w, 959m, 917s, 902s, 835w, 761m and 633w cm^{-1}. Found (calculated for $C_{12}H_{26}LiN_3$): C 64.7 (65.7); H 11.7 (12.0); N 18.7 (19.2)%.

[Nb(NBu^t)(Me$_2$[9]aneN$_3$)Cl$_2$] 3. Cold benzene (20 ml) was added to a mixture of $[Nb(NBu^t)Cl_3(py)_2]$ (0.47 g, 1.1 mmol) and $Li[Me_2[9]aneN_3]$ (0.18 g, 1.1 mmol) at r.t. with vigorous stirring in the absence of light. The resulting bright orange solution was allowed to warm to r.t. and then stirred for 16 h. The orange cloudy solution was filtered to remove suspended material and then volatiles were removed under reduced pressure to give an orange solid. The product was re-extracted into benzene (15 ml) and cautiously precipitated by slow addition of hexane (30 ml) with vigorous stirring. The resulting orange oil was filtered off and dissolved in benzene. Volatiles were removed under reduced pressure to give compound **3** as an orange powder. Yield: 0.087 g (41%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 4.68 (m, 1 H, 1 × NCH$_2$CH$_2$N), 3.62 (m, 2 H, 1 × NCH$_2$CH$_2$N), 2.66 to 2.50 (series of overlapping m, 4 H, 4 × NCH$_2$CH$_2$N), 2.59 (s, 3 H, cis-NMe), 2.53 (s, 3 H, trans-NMe), 2.41 (m, 1 H, 1 × NCH$_2$CH$_2$N), 2.33 (m, 1 H, 1 × NCH$_2$CH$_2$N), 1.99 (m, 1 H, 1 × NCH$_2$CH$_2$N), 1.99 (m, 1 H, 1 × NCH$_2$CH$_2$N), 1.97 (overlapping 2 × m, 2 H, 2 × NCH$_2$CH$_2$N) and 1.38 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): δ 67.9 (1 × NCH$_2$CH$_2$N), 61.8 (CMe$_3$), 60.9 (1 × NCH$_2$CH$_2$N), 59.5 (1 × NCH$_2$CH$_2$N), 58.2 (1 × NCH$_2$CH$_2$N), 56.9 (1 × NCH$_2$CH$_2$N), 54.2 (1 × NCH$_2$CH$_2$N), 51.2 (cis-NMe), 47.9 (trans-NMe) and 31.6 (CMe$_3$). IR (Nujol mull, NaCl plates): 3549s, 3441s, 2920w, 2362w, 1637m, 1542w, 1508w, 1261m, 1217m, 1066m, 1018m, 801w, 671m br and 446s cm^{-1}. EI-MS: $m/z = 390$ ([M]$^+$, 18%). Found (calculated for $C_{12}H_{27}Cl_2N_4Nb \cdot 0.15C_6H_6$): C 38.4 (38.4); H 7.0 (7.0); N 14.0 (14.3)%.

[Nb(NBu^t)(Pr$^i_2$[9]aneN$_3$)Cl$_2$] 4. To a solution of $[Nb(NBu^t)Cl_3(py)_2]$ (0.43 g, 1.0 mmol) in benzene (25 ml) at r.t. was added dropwise a solution of $Li[Pr^i_2[9]aneN_3]$ (0.22 g, 1.0 mmol) in benzene (25 ml). The mixture was stirred at r.t. for 16 h before filtration through a Celite pad. Volatiles were removed under reduced pressure to give compound **4** as an orange powder. Yield: 0.26 g (58%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 4.51 (m, 1 H, 1 × NCH$_2$CH$_2$N), 3.75 (m, 1 H, 1 × NCH$_2$CH$_2$N), 3.59 (app. sept, 1H, app. $J = 6.5$, cis-CHMe$_2$), 3.44 (m, 1 H, 1 × NCH$_2$CH$_2$N), 3.33 (app. sept, 1 H, app. $J = 6.5$, trans-CHMe$_2$), 2.77 (ddd, 1 H, $J = 13.0$, 7.5, 3.0, 1 × NCH$_2$CH$_2$N), 2.67 (ddd, 1 H, $J = 12.5$, 6.25, 3.0, 1 × NCH$_2$CH$_2$N), 2.59 to 2.69 (overlapping 2 × m, 2 H, 2 × NCH$_2$CH$_2$N), 2.32 (ddd, 1 H, $J = 15.0$, 6.0, 4.0, 1 × NCH$_2$CH$_2$N), 2.02 (ddd, 1 H, $J = 12.0$, 6.5, 2.0, 1 × NCH$_2$CH$_2$N), 1.90 (m, 1 H, 1 × NCH$_2$CH$_2$N), 1.81 (ddd, 1 H, $J = 15.0$, 9.5, 3.5, 1 × NCH$_2$CH$_2$N), 1.70 (ddd, 1 H, $J = 14.0$, 6.25, 3.5, 1 × NCH$_2$CH$_2$N), 1.44 (s, 9 H, Bu^t), 1.34

(d, 3 H, $J = 6.5$, CH*Me*$_2$), 1.29 (d, 3 H, $J = 6.5$, CH*Me*$_2$), 0.97 (d, 3 H, $J = 6.5$, CH*Me*$_2$) and 0.67 (d, 3 H, $J = 6.5$ Hz, CH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): δ 70.0 (*C*Me$_3$), 61.7 (1 × N*C*H$_2$CH$_2$N), 57.5 (1 × N*C*H$_2$CH$_2$N), 56.7 (*cis* *C*HMe$_2$), 56.5 (1 × N*C*H$_2$CH$_2$N), 56.4 (*trans* *C*HMe$_2$), 55.6 (1 × N*C*H$_2$CH$_2$N), 49.3 (1 × N*C*H$_2$CH$_2$N), 48.7 (1 × N*C*H$_2$CH$_2$N), 31.2 (C*Me*$_3$), 22.4, 19.9, 17.7, 16.7 (4 × CH*Me*$_2$). IR (Nujol mull, NaCl plates): 4331w, 4256w, 4061w, 2294w br, 1603m, 1298m br, 1259m br, 1221w, 1164w, 1121w, 1071w, 1039w, 935w, 873w, 800w, 762m, 676w, 590w and 454w cm^{-1}. EI-MS: *m/z* = 446 ([M]$^+$, 7%). Found (calculated for C$_{16}$H$_{35}$Cl$_2$N$_4$Nb·0.2C$_6$H$_6$): C 44.9 (44.6); H 8.0 (7.9); N 11.8 (12.1)%.

[Ta(NBu^t)(Me$_2$[9]aneN$_3$)Cl$_2$] 5. Cold benzene (15 ml) was added to a mixture of [Ta(NBu^t)Cl$_3$(py)$_2$] (0.103 g, 0.20 mmol) and Li[Me$_2$[9]aneN$_3$] (0.033 g, 0.20 mmol) at 5 °C with vigorous stirring in the absence of light. The resulting bright orange solution was allowed to warm to r.t. and then stirred for 19 h. The bright orange cloudy solution was filtered to remove suspended material and then the volatiles were removed under reduced pressure to give an orange solid. The product was re-extracted into benzene (8 ml) and then cautiously precipitated by slow addition of hexane (25 ml) with vigorous stirring. The resulting orange microcrystalline precipitate was filtered off, washed with hexane (5 ml), pentane (5 ml) and dried under reduced pressure to give compound **5** as a bright orange powder. Yield: 0.076 g (79%). ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): δ 4.66, 4.03, 3.49, 2.92, 2.90, 2.69 (6 × m, 6 × 1 H, 6 × 1 × NC*H*$_2$CH$_2$N), 2.68 (s, 3 H, *cis* NMe), 2.68 (s, 3 H, *trans* NMe), 2.54, 2.51, 2.24, 2.04, 1.97, 1.75 (6 × m, 6 × 1 H, 6 × 1 × NC*H*$_2$CH$_2$N) and 1.41 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): δ 69.0 (1 × N*C*H$_2$CH$_2$N), 64.8 (*C*Me$_3$), 59.8 (1 × N*C*H$_2$CH$_2$N), 59.2 (1 × N*C*H$_2$CH$_2$N), 58.4 (1 × N*C*H$_2$CH$_2$N), 56.6 (1 × N*C*H$_2$CH$_2$N), 55.4 (1 × N*C*H$_2$CH$_2$N), 51.3 (*cis*-NMe), 48.2 (*trans*-NMe) and 33.5 (C*Me*$_3$). Satisfactory elemental analysis was not obtained for this compound.

[Ta(NBu^t)(Pr$^i_2$[9]aneN$_3$)Cl$_2$] 6. To a solution of [Ta(NBu^t)Cl$_3$(py)$_2$] (0.24 g, 0.46 mmol) in benzene (20 ml) at r.t. was added dropwise a solution of Li[Pr$^i_2$[9]aneN$_3$] (0.10 g, 0.46 mmol) in benzene (20 ml). The mixture was stirred at r.t. for 16 h before filtration through Celite. Volatiles were removed under reduced pressure to give compound **6** as a yellow powder. Yield: 0.14 g (56%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K): δ 4.45 (dt, 1 H, $J = 12.5$, 8.0, 1 × NC*H*$_2$CH$_2$N), 4.04 (ddd, 1 H, $J = 13.5$, 8.0, 3.0, 1 × NC*H*$_2$CH$_2$N), 3.49 (app. sept, 1 H, app. $J = 7.0$, *cis* C*H*Me), 3.28 (app. sept, 1 H, app. $J = 6.5$, *trans* C*H*Me$_2$), 3.27 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 2.95 (ddd, 1 H, $J = 12.5$, 8.0, 4.0, 1 × NC*H*$_2$CH$_2$N), 2.79 (ddd, 1 H, $J = 13.0$, 7.0, 4.0, 1 × NC*H*$_2$CH$_2$N), 2.69 (ddd, 1 H, $J = 13.0$, 10.0, 7.5, 1 × NC*H*$_2$CH$_2$N), 2.52 (ddd, 1 H, $J = 14.0$, 8.0, 4.0, 1 × NC*H*$_2$-CH$_2$N), 2.38 (ddd, 1 H, $J = 15.0$, 8.0, 4.0, 1 × NC*H*$_2$CH$_2$N), 2.07 (dt, 1 H, $J = 12.0$, 7.5, 1 × NC*H*$_2$CH$_2$N), 1.92 (ddd, 1 H, $J = 12.5$, 7.0, 2.5, 1 × NC*H*$_2$CH$_2$N), 1.87 (ddd, 1 H, $J = 14.5$, 8.0, 3.5, 1 × NC*H*$_2$CH$_2$N), 1.71 (ddd, 1 H, $J = 14.5$, 8.0, 3.5, 1 × NC*H*$_2$CH$_2$N), 1.46 (s, 9 H, Bu^t), 1.37 (d, 3 H, $J = 6.5$, CH*Me*$_2$), 1.37 (d, 3 H, $J = 7.0$, CH*Me*$_2$), 0.82 (d, 3 H, $J = 6.5$, CH*Me*$_2$) and 0.71 (d, 3 H, $J = 7.0$ Hz, CH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): δ 65.8 (*C*Me$_3$), 58.8 (1 × N*C*H$_2$-CH$_2$N), 57.7 (1 × N*C*H$_2$CH$_2$N), 57.4 (1 × N*C*H$_2$CH$_2$N), 57.0 (*cis* *C*HMe$_2$), 56.9 (*trans* *C*HMe$_2$), 54.6 (1 × N*C*H$_2$CH$_2$N), 50.9 (1 × N*C*H$_2$CH$_2$N), 48.9 (1 × N*C*H$_2$CH$_2$N), 33.2 (C*Me*$_3$), 22.4, 20.7, 17.2, 16.9 (4 × CH*Me*$_2$). IR (Nujol mull, NaCl plates): 3176w, 2955s, 2600w, 2516w, 2104w, 1587w, 1352w, 1297w, 1261w, 1238m, 1208w, 1150w, 1064w, 1031w, 1008w, 921w, 890w, 801m, 785m, 741w, 596w, 542w and 446w cm^{-1}. Found (calculated for C$_{16}$H$_{35}$Cl$_2$N$_4$Ta): C 35.5 (35.9); H 6.8 (6.6); N 9.4 (10.5)%.

[Ti(NBu^t)(HPr$^i_2$[9]aneN$_3$)Cl$_2$] 7. [Ti(NBu^t)Cl$_2$(py)$_3$] (0.40 g, 0.94 mmol) was slurried in dry benzene (25 ml) and stirred for the addition of Pr$^i_2$[9]aneN$_3$ (0.20 g, 0.94 mmol). The solution rapidly homogenised before depositing a yellow precipitate. The mixture was stirred for 4 h and then filtered. The solid was dried *in vacuo* to give the product, 0.30 g (80%), as a mixture of *cis* (major) and *trans* isomers (*cis* and *trans* refer to the position of the macrocycle N–H group with respect to NBu^t) in a *ca.* 4:1 ratio (by ^{1}H NMR integration). ^{1}H NMR (CD$_2$Cl$_2$, 500.0 MHz, 298 K): *cis* (major) isomer, δ 4.78 (br s, 1 H, NH), 4.07 (app. sept, 1 H, $J = 6.5$, C*H*Me$_2$), 3.88 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 3.59 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 3.50 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 3.40 (app. sept, 1 H, $J = 6.5$, C*H*Me$_2$), 3.03–3.09 (2 × m, 2 H, 2 × NC*H*$_2$CH$_2$N), 2.96 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 2.73–2.85 (3 × m, 3 H, 3 × NC*H*$_2$CH$_2$N), 2.63 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 2.45 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 2.33 (m, 1 H, 1 × NC*H*$_2$CH$_2$N), 1.52 (d, 3 H, $J = 6.5$, CH*Me*$_2$), 1.45 (d, 3 H, $J = 6.5$, CH*Me*$_2$), 1.16 (d, 3 H, $J = 6.5$, CH*Me*$_2$), 1.13 (s, 9 H, NC*Me*$_3$) and 1.11 (d, 3 H, $J = 6.5$ Hz, CH*Me*$_2$); *trans* (minor) isomer, δ 4.14 (app. sept, 2 H, $J = 6.5$, C*H*Me$_2$), 1.96 (br s, 1 H, N*H*), 1.55 (d, 6 H, $J = 6.5$, CH*Me*$_2$), 1.45 (d, 6 H, $J = 6.5$ Hz, CH*Me*$_2$) and 1.13 (s, 9 H, NC*Me*$_3$) (all macrocyclic CH$_2$ groups obscured by major isomer). ^{13}C-{^{1}H} NMR for *cis* (major) isomer only (CD$_2$Cl$_2$, 125.7 MHz, 298 K): δ 70.28 (N*C*Me$_3$), 59.57 (*C*HMe$_2$), 55.29 (*C*HMe$_2$), 50.82 (N*C*H$_2$CH$_2$N), 49.86 (N*C*H$_2$CH$_2$N), 48.99 (N*C*H$_2$CH$_2$N), 48.71 (N*C*H$_2$CH$_2$N), 48.58 (N*C*H$_2$CH$_2$N), 46.26 (N*C*H$_2$CH$_2$N), 30.82 (NC*Me*$_3$), 20.28 (CH*Me*$_2$), 18.95 (CH*Me*$_2$), 18.76 (CH*Me*$_2$) and 17.71 (CH*Me*$_2$). IR (Nujol mull, KBr plates): 3255 [w, *v*(N–H) minor isomer], 3235 [mw, *v*(N–H) major isomer], 1246s, 1208w, 1164w, 1104mw, 1038m, 983mw, 963w, 800w, 824w, 736w, 682w, 600w and 527w cm^{-1}. EI-MS: *m/z* (%) = 402 (10) ([M]$^+$), 387 (36) ([M − Me]$^+$), 367 (15) ([M − Cl]$^+$) and 330 (100) ([M − NCMe$_3$ + H]$^+$). Found (calculated for C$_{16}$H$_{36}$Cl$_2$N$_4$Ti): C 48.3 (47.7); H 9.1 (9.0); N 12.8 (13.9)%.

[Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(Me$_2$[9]aneN$_3$)Cl] 8. To a solution of [Mo(N-C$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2$(dme)] (0.23 g, 0.37 mmol) in benzene (20 ml) at r.t. was added dropwise a solution of Li-[Me$_2$[9]aneN$_3$] (0.061 g, 0.37 mmol) in benzene (20 ml). The mixture was stirred at r.t. for 16 h before filtration through a Celite pad. Volatiles were removed under reduced pressure to give a dark red solid. The solid was dissolved in diethyl ether (8 ml), pentane (15 ml) added and the mixture stored at −25 °C for 2 days. The resulting red precipitate was filtered off. The filtrate was stored at −25 °C for 13 days. The resulting red crystals were filtered off, washed with pentane and dried *in vacuo*. Yield: 0.040 g (17%). ^{1}H NMR (C$_6$D$_6$, 500.0 MHz, 298 K): δ 7.06 (d, 4 H, $J = 13.5$, *m*-C$_6$H$_5$), 6.90 (t, 2 H, $J = 12$, *p*-C$_6$H$_5$), 4.26 (overlapping 2 × app. sept, 4 H, C*H*Me$_2$), 4.07 (m, 2 H, 2 × NC*H*$_2$CH$_2$N), 2.83 (overlapping 2 × m, 4 H, 4 × NC*H*$_2$CH$_2$N), 2.60 (s, 6 H, NMe), 2.39 (m, 2 H, 2 × NC*H*$_2$-CH$_2$N), 2.07 (m, 2 H, 2 × NC*H*$_2$CH$_2$N), 1.69 (m, 2 H, 2 × NC*H*$_2$CH$_2$N), 1.30, 1.27 (2 × d, 2 × 12 H, $J = 11$ Hz, 2 × CH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): δ 154.2 (*ipso*-C of C$_6$H$_3$), 142.1 (*o*-C of C$_6$H$_3$), 124.2 (*p*-C of C$_6$H$_3$), 123.8 (*m*-C of C$_6$H$_3$), 60.7 (N*C*H$_2$CH$_2$N), 60.3 (*C*HMe$_2$), 56.5 (N*C*H$_2$CH$_2$N), 49.6 (N*C*H$_2$CH$_2$N), 27.3 (NMe), 25.2, 24.8 (2 × CH*Me*$_2$). IR (Nujol mull, NaCl plates): 2955s, 2672w, 1733w, 1337w, 1262m, 1224w, 1154w, 1003w, 1073w, 1059w, 1021w, 958w, 862w, 845w, 799m br, 766w, 752w, 563w, 513w and 424w cm^{-1}. EI-MS: 639 ([M]$^+$, 7%). Satisfactory elemental analysis was not obtained.

[Mo(NPh)$_2$(Pr$^i_2$[9]aneN$_3$)Cl] 9. To a solution of [Mo(NPh)$_2$-Cl$_2$(dme)] (0.33 g, 0.75 mmol) in benzene (15 ml) at r.t. was added dropwise a solution of Li[Pr$^i_2$[9]aneN$_3$] (0.17 g, 0.75 mmol) in benzene (15 ml). The mixture was stirred at r.t. for 16 h before filtration through a Celite pad. Volatiles were removed under reduced pressure to give a dark red oil. The oil

was dissolved in dichloromethane (10 ml), mixed with hexane (10 ml) and stored at $-25\,^{\circ}$C for 10 days. The resulting brown precipitate was filtered off. Volatiles were removed from the filtrate under reduced pressure and the resulting brown solid was dissolved in ether (5 ml) and stored at $-25\,^{\circ}$C for 8 days. The brown microcrystalline solid was filtered off and dried *in vacuo*. Yield: 0.047 g (12%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 7.20 (d, 4 H, $J = 8$, *o*-C of C_6H_5), 6.98 (m, 4 H, *m*-C of C_6H_5), 6.68 (t, 2 H, $J = 8$, *p*-C of C_6H_5), 4.18 (m, 2 H, $2 \times$ N*CH*$_2$-CH$_2$N), 3.49 (app. sept, 2 H, app. $J = 6$, C*H*Me$_2$), 3.03 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 2.90 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 2.56 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 1.80 (overlapping $2 \times$ m, 4 H, $4 \times$ NC*H*$_2$CH$_2$N), 1.46, 0.72 ($2 \times$ d, 2×6 H, $J = 6.5$ Hz, $2 \times$ CH*Me*$_2$). ^{13}C-$\{^1$H$\}$ NMR (C_6D_6, 125.7 MHz, 298 K): δ 158.0 (*ipso*-C of C_6H_5), 128.5 (*o*-C of C_6H_5), 123.6 (*p*-C of C_6H_5), 122.9 (*m*-C of C_6H_5), 62.8 (N*C*H$_2$CH$_2$N), 55.3 (*C*HMe$_2$), 52.4 (N*C*H$_2$CH$_2$N), 48.5 (N*C*H$_2$CH$_2$N), 21.3, 16.2 ($2 \times$ CH*Me*$_2$). IR (Nujol mull, NaCl plates): 3549s br, 3441s br, 2962w, 2362w, 1637m, 1502w, 1385s, 1261m, 1217w, 1066w, 1018w, 801w, 671s br and 446s cm^{-1}. Found (calculated for $C_{24}H_{36}ClMoN_5$): C 54.7 (54.8); H 6.9 (6.9); N 13.3 (13.3)%.

[Mo(NC$_6$H$_3$Me$_2$-2,6)$_2$(Pr$^i_2$[9]aneN$_3$)Cl] 10. To a solution of [Mo(NC$_6$H$_3$Me$_2$-2,6)$_2$Cl$_2$(dme)] (0.22 g, 0.44 mmol) in benzene (15 ml) at r.t. was added dropwise a solution of Li[Pr$^i_2$[9]aneN$_3$] (0.097 g, 0.44 mmol) in benzene (15 ml). The mixture was stirred at r.t. for 16 h before filtration through a Celite pad. Volatiles were removed under reduced pressure to give a dark red solid. The product was dissolved in ether (10 ml) and stored at $-25\,^{\circ}$C. The resulting red-brown solid was filtered off and washed with pentane (10 ml). The filtrate was reduced to 15 ml, causing a red precipitate to form. The suspension was stored at $-25\,^{\circ}$C for 5 days. The resulting red crystals were filtered off, washed with pentane (10 ml) and dried *in vacuo* to give compound **10** as a red powder. Yield: 0.018 g (7%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 6.81 (d, 4 H, $J = 13$, *m*-C of C_6H_3), 6.56 (t, 2 H, $J = 12.5$, *p*-C of C_6H_3), 4.00 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 3.62 (app. sept, 2 H, C*H*Me$_2$), 2.93 (overlapping $2 \times$ m, 4 H, $4 \times$ NC*H*$_2$CH$_2$N), 2.71 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 2.66 (s, 12 H, C$_6$H$_3$*Me*$_2$), 1.77 (overlapping $2 \times$ m, 4 H, $4 \times$ NC*H*$_2$-CH$_2$N), 1.40, 0.73 ($2 \times$ d, 2×6 H, $J = 11$ Hz, $2 \times$ CH*Me*$_2$). ^{13}C-$\{^1$H$\}$ NMR (C_6D_6, 125.7 MHz, 298 K): δ 157.5 (*ipso*-C of C_6H_3), 134.8 (*o*-C of C_6H_3), 127.7 (*m*-C of C_6H_3), 123.2 (*p*-C of C_6H_3), 61.4 (N*C*H$_2$CH$_2$N), 55.4 (*C*HMe$_2$), 52.7 (N*C*H$_2$-CH$_2$N), 46.8 (N*C*H$_2$CH$_2$N), 20.9, 19.4 ($2 \times$ CH*Me*$_2$) and 16.4 (C$_6$H$_3$*Me*$_2$). IR (Nujol mull, NaCl plates): 1733m br, 1286s br, 1246w, 1175w, 1152m, 1120w, 1098w, 1070w, 1046w, 964m, 918w, 892w, 876w, 850w, 802w and 763m cm^{-1}. Found (calculated for $C_{28}H_{44}ClMoN_5 \cdot 0.1C_6H_6$): C 58.2 (58.0); H 7.4 (7.6); N 11.8 (12.0)%.

[Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(Pr$^i_2$[9]aneN$_3$)Cl] 11. To a solution of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2$(dme)] (0.30 g, 0.49 mmol) in benzene (15 ml) at r.t. was added dropwise a solution of Li[Pr$^i_2$[9]aneN$_3$] (0.11 g, 0.49 mmol) in benzene (15 ml). The mixture was stirred at r.t. for 16 h before filtration through a Celite pad. Volatiles were removed under reduced pressure to give a dark red solid. The product was dissolved in dichloromethane (15 ml), layered with hexane (10 ml) and stored at $-25\,^{\circ}$C for 6 days. The resulting red crystals were filtered off, washed with hexane and volatiles removed under reduced pressure to give compound **11** as a red powder. Yield: 0.31 g (62%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 7.00 (d, 4 H, $J = 12.5$, *m*-C of C_6H_3), 6.86 (t, 2 H, $J = 12.5$, *p*-C of C_6H_3), 4.09 (app. sept, 2 H, C$_6$H$_3$-(C*H*Me$_2$)$_2$), 3.58 (app. sept, 2 H, app. $J = 11$, C$_6$H$_3$(C*H*Me$_2$)$_2$), 3.04 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 2.91 (m, 2 H, NC*H*Me$_2$), 2.91 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 2.30 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 2.18 (m, 2 H, $2 \times$ NC*H*$_2$CH$_2$N), 1.91 (overlapping $2 \times$ m, 4 H, $4 \times$ NC*H*$_2$CH$_2$N), 1.38 (d, 6 H, $J = 11$, NCH*Me*$_2$), 1.19 (d, 12 H, $J = 10.5$, C$_6$H$_3$(CH*Me*$_2$)$_2$), 1.02 (d, 12 H, $J = 10.5$,

C$_6$H$_3$(CH*Me*$_2$)$_2$) and 0.81 (d, 6 H, $J = 11$ Hz, NCH*Me*$_2$). IR (Nujol mull, NaCl plates): 2672w, 1606m, 1573w, 1300w, 1259m, 1240m, 1213w, 1153w, 1083m, 1033w, 1016m, 985w, 943m, 830s, 801w, 758w, 742w, 691w, 678w, 645w, 634w, 569w, 556w and 443w cm^{-1}. EI-MS: $m/z = 695$ ([M]$^+$, 72) and 652 ([M $-$ Pr^i]$^+$, 76%).

Crystal structure determination of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$-(Pr$^i_2$[9]aneN$_3$)Cl] 11
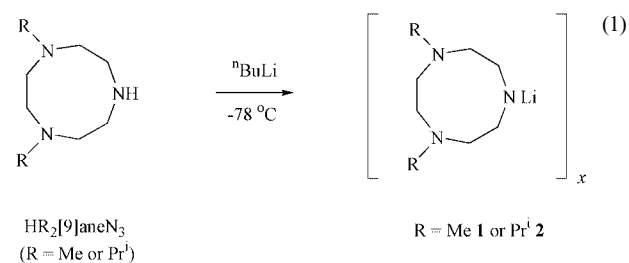
Crystal data collection and processing parameters are given in Table 1. A crystal of compound **11** was immersed in a film of perfluoropolyether oil on a glass fibre and transferred to an Enraf-Nonius DIP2000 image plate diffractometer equipped with an Oxford Cryosystems low-temperature device.[19] Data were collected at 150 K using Mo-Kα radiation; equivalent reflections were merged and the images processed with the DENZO and SCALEPACK programs.[20] Corrections for Lorentz-polarisation effects and absorption were performed and the structures solved by direct methods using SIR 92.[21] Subsequent Fourier difference syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed geometrically and their positions allowed to vary using a riding model. Examination of the refined extinction parameters and agreement analyses suggested that no extinction correction was required. All crystallographic calculations were performed using SIR 92 and CRYSTALS PC.[22]

CCDC reference number 186/2196.

See http://www.rsc.org/suppdata/dt/b0/b006177h/ for crystallographic files in .cif format.

Results and discussion

The ligand precursors HR$_2$[9]aneN$_3$ (R = Me or Pr^i) were pepared according to the literature methods.[15,16] Treatment of HR$_2$[9]aneN$_3$ with *n*-butyllithium in cold pentane or hexanes afforded the lithiated triazacyclononanes $\{$Li[Me$_2$[9]aneN$_3$]$\}_x$ **1** and $\{$Li[Pr$^i_2$[9]aneN$_3$]$\}_x$ **2** as air-sensitive, white solids in 60–65% isolated yield (eqn. 1). The new compounds were characterised by NMR spectroscopy and elemental analysis. The NMR spectra of **1** reveal two inequivalent N–Me groups and 6 inequivalent ring CH$_2$ groups indicating that it possesses at least a dimeric (and possibly a higher oligomeric) structure in the solution state, as is quite typical of lithium amides in general.[23] The NMR spectra of **2** suggest an apparently more simple structure in solution with three sets of ring CH$_2$ resonances and one set of diastereotopic isopropyl group resonances (*i.e.* with the methyl group resonances appearing as a pair of doublets). These data do not preclude an aggregated solution or solid state structure.

$$\text{HR}_2[9]\text{aneN}_3 \quad \xrightarrow[\,-78\,^{\circ}\text{C}\,]{^n\text{BuLi}} \quad \text{R = Me } \mathbf{1} \text{ or Pr}^i \mathbf{2} \tag{1}$$

Attempts to prepare titanium or zirconium imido complexes [M(NR′)(R$_2$[9]aneN$_3$)Cl(L)$_n$] by reaction of **1** and **2** with imido-supported precursors gave mixtures of unidentified compounds. However, reactions of these lithiated macrocycles with niobium and tantalum *tert*-butylimido precursors [M(NBu^t)Cl$_3$(py)$_2$] (M = Nb or Ta)[9] gave the desired products [M(NBu^t)(R$_2$[9]aneN$_3$)Cl$_2$] (M = Nb, R = Me **3** or Pr^i **4**; M = Ta, R = Me **5** or Pr^i **6**) in 41–79% isolated yields. These compounds are very air- and moisture-sensitive in the solution

phase, and form yellow or orange solids that are insoluble in pentane or hexanes but dissolve readily in aromatic solvents such as benzene or toluene. The synthesis and proposed structures of **3–6** are shown in Scheme 1.
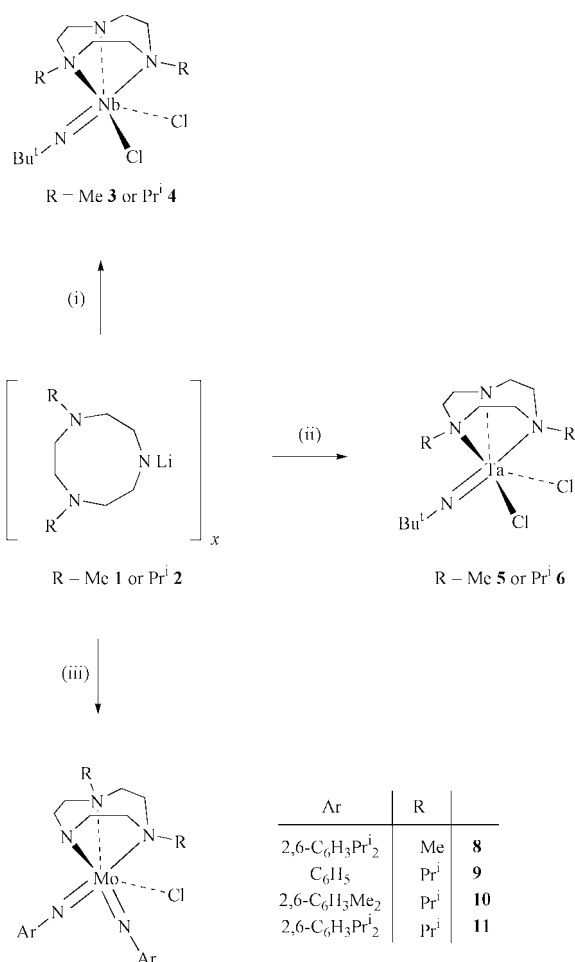

Scheme 1 Synthesis and structures of new early transition metal imido complexes with monodeprotonated triazacyclononane ligands. Reagents and conditions: (i) [Nb(NBu^t)Cl$_3$(py)$_2$], benzene, 5 °C to r.t., 16 h, 41 (**3**) or 58% (**4**); (ii) [Ta(NBu^t)Cl$_3$(py)$_2$], benzene, 5 °C to r.t. or r.t., 16–19 h, 79 (**5**) or 56% (**6**); (iii) [Mo(NAr)$_2$Cl$_2$(dme)], r.t., 16 h, 7–62%.

Ar	R	
2,6-C$_6$H$_3$Pr$^i_2$	Me	**8**
C$_6$H$_5$	Pr^i	**9**
2,6-C$_6$H$_3$Me$_2$	Pr^i	**10**
2,6-C$_6$H$_3$Pr$^i_2$	Pr^i	**11**

The new compounds have been fully characterised by spectroscopic methods and elemental analysis as far as possible. Repeated attempts to obtain diffraction-quality crystals were unsuccessful and the structures are assigned on the basis of the spectroscopic data, and in particular one- and two-dimensional ^{1}H and ^{13}C-{^{1}H} NMR. The NMR spectra for **3–6** show resonances attributed to a *tert*-butylimido ligand and 6 inequivalent R$_2$[9]aneN$_3$ methylene groups, the H atoms of which are all chemically inequivalent. In addition, the ^{1}H NMR spectra of the dimethyltriazacyclononane complexes [M(NBu^t)(Me$_2$[9]-aneN$_3$)Cl$_2$] **3**, **5** show two additional singlets for inequivalent ring N–Me groups while the two ring N–Pr^i groups of [M-(NBu^t)(Pr$^i_2$[9]aneN$_3$)Cl$_2$] **4**, **6** appear as two apparent septets and four doublets for the methine and methyl protons respectively. These data are consistent with the pseudo-octahedral, C_1-symmetrical structures for **3–6** shown in Scheme 1 in which the triazacyclononane amido nitrogen lies *cis* to the imido nitrogen. There was no evidence from the NMR spectra for the formation of alternative C_s-symmetrical isomers with the amido nitrogen *trans* to the imido group. The spectra of these isomers would be comparatively simpler, featuring, for example, one ring N–Me or N–Pr^i environment.

The preference for formation of the *cis* isomers of compounds **3–6** warrants further discussion as it provides some insight into the electronic structures of the complexes since statistically **3–6** would be expected to form in a 2:1 *cis*:*trans* ratio. Electronic (*e.g.* p$_\pi \longrightarrow$ d$_\pi$ donor effects from the R$_2$[9]-aneN$_3$ amido nitrogen) and steric considerations should be taken into account; comparisons can be also made with isoelectronic imido complexes of cyclononane-derived ligands. For example, the crystallographically characterised titanium imido complex [Ti(NBu^t)(Me$_2$[9]aneN$_2$S)Cl$_2$] exists exclusively as the *cis* isomer (with respect to the [9]aneN$_2$S sulfur donor and the imido nitrogen), whereas the 1-oxa-4,7-diazacyclo-nonane analogue forms exclusively *trans*-[Ti(NBu^t)(Me$_2$[9]-aneN$_2$O)Cl$_2$] (with respect to the O- and imido N-donors).[5e] It is not apparent why these two complexes should have different structures but the different nature of the donor atoms (O, S, N) complicates any interpretation. To gain better insight into the co-ordination preferences for asymmetrically ring-substituted N$_3$-donor cyclononanes we prepared a titanium imido complex of HPr$^i_2$[9]aneN$_3$, namely [Ti(NBu^t)(HPr$^i_2$[9]-aneN$_3$)Cl$_2$] **7** (eqn. 2). Compound **7** is free of any macrocycle amide π-donor effects having only 3 σ-donor tertiary amines.

***trans*-7** (Minor product)

***cis*-7** (Major product)
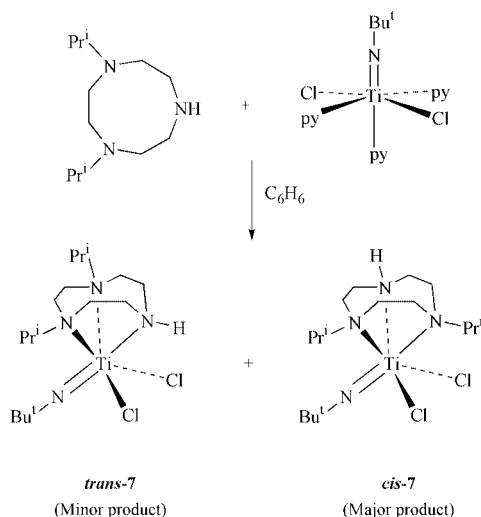
Compound **7** was characterised by NMR and IR spectroscopy, EI mass spectrometry, and elemental analysis. It is analogous to the Group 4 compounds [Ti(NR′)(Me$_3$[9]aneN$_3$)-Cl$_2$] (**I**, R′ = Bu^t or aryl) that we have reported previously.[5a,c,e] Examination of the ^{1}H and ^{13}C-{^{1}H} NMR spectra show that it exists as a mixture of isomers, ***cis*-7** (major product, 80%) and ***trans*-7** (minor product, 20%) where *cis* and *trans* refer to the relative co-ordination sites of the macrocycle N–H and imido N groups. On statistical grounds the product distribution should be ***cis*-7**:***trans*-7** = 2:1. The non-statistical preference of **7** for the *cis* isomer presumably reflects steric effects of alternative neighbouring groups.

Returning again to consider the Group 5 compounds [M(NBu^t)(R$_2$[9]aneN$_3$)Cl$_2$] **3–6**, it would be expected that, for these larger metals, inter-ligand steric interactions would be reduced relative to those in **7**, and so the expected *cis*:*trans* product distribution should be closer to the statistical ratio of 2:1 on steric grounds at least. That compounds **3–6** form exclusively the *cis* isomers shown is therefore attributed to electronic factors. Both the *tert*-butylimido and macrocycle amido nitrogens are strong σ and π donors.[1c] By adopting mutually *cis* arrangements the competition between these two strong σ and π donors for metal d$_\pi$ acceptor orbitals is presumably reduced. The extents of possible p$_\pi \longrightarrow$ d$_\pi$ donation from the amido nitrogen of the R$_2$[9]aneN$_3$ ligands in **3–6** is discussed in further detail later on in the context of the crystal structure of **11**.

A number of attempts to make Group 6 mono(imido) complexes of R$_2$[9]aneN$_3$ from {Li[R$_2$[9]aneN$_3$]}$_x$ **1**, **2** and suitable
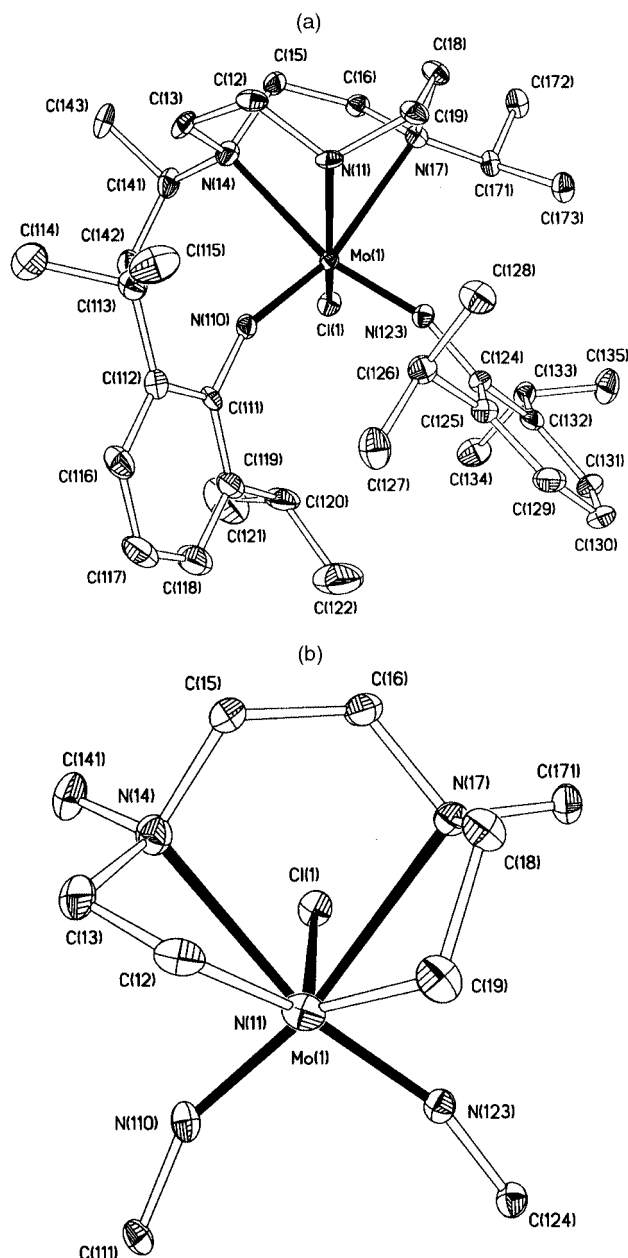
Fig. 1 Displacement ellipsoid (35%) plots of one of the two crystallographically independent molecules of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(Pr$^i_2$-[9]aneN$_3$)Cl] **11**. (a) General view with H atoms omitted. (b) Viewed along the N(11)–Mo(1) bond with H atoms, aryl groups (except for the *ipso* C atoms) and ring isopropyl methyl group C atoms omitted.

imido precursors were all unsuccessful. Nonetheless we were able to make bis(imido) derivatives of the type [Mo(NC$_6$H$_3$R$'_2$-2,6)(R$_2$[9]aneN$_3$)Cl] (R = Me, R′ = Pr^i **8**; R = Pr^i, R′ = H **9**, Me **10** or Pr^i **11**) as shown in Scheme 1 from {Li[R$_2$[9]aneN$_3$]}$_x$ **1**, **2** and the appropriate [Mo(NC$_6$H$_3$R$'_2$-2,6)$_2$Cl$_2$(dme)] complexes.[17,18] The new compounds formed as brown or red solids in poor to good yields. They are moderately air and moisture sensitive in solution and the solids dissolve easily in aromatic and polar solvents. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of all four compounds are broadly similar showing resonances for N–Ar groups and co-ordinated R$_2$[9]aneN$_3$. Overall the spectra indicate products with C_s symmetry in which the macrocycle amide N-donor lies *trans* to the chloride ligand, as illustrated in Scheme 1.

Single crystals of [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(Pr$^i_2$[9]aneN$_3$)Cl] **11** were grown from diethyl ether at −25 °C. Data collection and processing parameters are given in Table 1 and selected bond lengths and angles are listed in Table 2. There are two crystal-

Table 1 X-Ray data collection and processing parameters for [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)$_2$(Pr$^i_2$[9]aneN$_3$)Cl] **11**

Formula	C$_{36}$H$_{60}$ClMoN$_5$
Formula weight	694.31
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	13.658(4)
b/Å	15.846(6)
c/Å	19.138(7)
α/°	111.07(2)
β/°	105.09(2)
γ/°	96.08(2)
V/Å^3	3639.2
Z	4
μ(Mo-Kα)/mm^{-1}	0.46
Total reflections	13859
Observed reflections ($I > 3\sigma(I)$)	9214
Final R, R_w	0.0475, 0.0564

Table 2 Selected bond distances (Å) and angles (°) for [Mo(NC$_6$H$_3$-Pr$^i_2$-2,6)$_2$(Pr$^i_2$[9]aneN$_3$)Cl] **11**. The corresponding values for the other crystallographically independent molecule are given in brackets

Mo(1)–N(11)	2.003(4) [1.997(4)]
Mo(1)–N(14)	2.530(4) [2.520(4)]
Mo(1)–N(17)	2.635(2) [2.644(5)]
Mo(1)–N(110)	1.779(4) [1.779(4)]
Mo(1)–N(123)	1.767(4) [1.777(4)]
Mo(1)–Cl(1)	2.4223(11) [2.4036(11)]
N(110)–Mo(1)–N(123)	102.46(17) [103.11(17)]
Mo(1)–N(110)–C(111)	154.6(3) [160.5(3)]
Mo(1)–N(123)–C(124)	161.5(3) [156.2(3)]
C(12)–N(11)–C(19)	114.1(4) [114.2(4)]
Mo(1)–N(11)–C(12)	120.9(3) [120.5(3)]
Mo(1)–N(11)–C(19)	114.8(3) [115.1(3)]
Cl(1)–Mo(1)–N(11)	148.58(11) [147.47(12)]

lographically independent molecules in the asymmetric unit. There are no significant differences between the two molecules. Two views of the molecular structure of one of them are shown in Fig. 1.

The solid state structure of complex **11** is consistent with that shown in Scheme 1 based on solution NMR data. The co-ordination sphere of the pseudo-octahedral Mo comprises two arylimido, one chloride and a *fac*-co-ordinated Pr$^i_2$[9]aneN$_3$ ligand. A number of bis(imido) complexes of Mo have been described previously, as have complexes of neutral R$_3$[9]aneN$_3$ ligands.[1,24] The structurally characterised bis-(imido) molybdenum complexes that are most similar to **11** are: [Mo(NBu^t)$_2$(Tp*)Cl] (Tp* = hydrotris(3,5-dimethyl-pyrazolyl)borate),[9] [Mo(NC$_6$H$_2$Me$_3$-2,4,6)$_2${(η-C$_5$H$_5$)Co{P(O)-(OEt)$_2$}$_3$}Cl],[25] and [Mo(NBu^t)$_2$(H$_3$[9]aneN$_3$)Cl]ClO$_4$.[6c] The metric parameters and geometry of **11** warrant further discussion.

The Mo–Cl, Mo–N(imide), Mo–N(amide) and Mo–N-(amine) distances are generally all at the long end of ranges of values reported previously.[24] As discussed below, this certainly at least reflects the very crowded nature of complex **11**, and most likely the competing presence of three very good σ and π donors (two imido and one amido ligand). The Mo=N–Ar angles lie in the range that is consistent with the imido ligand acting as up to a four-electron donor to molybdenum.[1a] However, it is well established that orbital restrictions limit the number of electrons donated by each mutually *cis* imide in octahedral complexes such as **11** to three (*i.e.* a Mo=NR bond order of 2.5).[26] The Mo–N(amine) distances of between 2.520(4) and 2.644(5) Å in **11** are longer than for any molybdenum triazacyclononane complexes (for 32 archived examples:[24] range for Mo–N(amine) = 2.177(11)–2.475(4) Å, mean = 2.287(11) Å). The corresponding Mo–N(amine) values

for the related cation $[Mo(NBu^t)_2(H_3[9]aneN_3)Cl]^+$ are 2.367(3), 2.381(3) and 2.201(3) Å (*trans* to Mo–Cl),[6c] with the variation in values being attributable to the large *trans* influence of strong donor ligands such as imides.[1b,4b,27] It is also relevant to comment on the origin of the long Mo–N(amine) distances in **11**. The *trans* influence of the arylimido ligands would certainly help lengthen the Mo–N(amine) bonds, but not perhaps as much as is observed in comparison with $[Mo(NBu^t)_2(H_3-[9]aneN_3)Cl]^+$ (even after the effect of charge has been considered). As expected, the amido nitrogen of the $Pr^i_2[9]aneN_3$ ligand is considerably more tightly bound than the amino donors with Mo–N(amido) 2.003(4) and 1.997(4) Å; these values are not out of line with the mean value of 1.97(6) Å for Mo–NR_2 (R = alkyl or aryl) distances in general.[24] Note that the mean value cited is for a range of amidomolybdenum complexes with differing co-ordination numbers and oxidation states. The difference between the Mo–N(amide) and Mo–N(amine) distances in **11** of 0.517(6)–0.647(6) Å is significantly greater than between the corresponding Re–N(amido) and Re–N(amino) distances in $[Re(NBu^t)_2(H_2[9]aneN_3)(O_3SCF_3)]^+$ (*ca.* 0.345(7) Å).[6b] Thus it does not appear that the tighter binding of the $R_2[9]aneN_3$ amido nitrogen leads *a priori* to substantial lengthening of the M–N(amino) distances. It would appear that for **11** the origin of the long Mo–N(amine) is likely to be predominantly steric in nature and not an intrinsic feature of the metal to $R_2[9]aneN_3$ ligand bonding.

Finally we turn again to the possibility of $p_\pi \longrightarrow d_\pi$ donation from the amido nitrogen of the $R_2[9]aneN_3$ ligand in these complexes. Amido ligands, when possessing an approximately trigonal planar geometry at N, can act as 3-electron donors (*via* $1\sigma + 2\pi$ electrons). In principle $R_2[9]aneN_3$ can therefore act as a 7-electron donor to the metal centre in complexes **3**–**6** and **8**–**11**. By comparison, an η^5-cyclopentadienyl ligand can donate only a maximum of 5 electrons to a transition metal centre, so one would have to avoid any casual analogy drawn between a deprotonated triazacyclononane and a cyclopentadienyl (or Tp* or similar) ligand.

The question of $p_\pi \longrightarrow d_\pi$ donation can be addressed by examination of the structure of $[Mo(NC_6H_3Pr^i_2-2,6)_2-(Pr^i_2[9]aneN_3)Cl]$ **11**. The sums of the angles around the macrocyclic amido nitrogens in **11** are *ca.* 350° (with the nitrogen atoms lying *ca.* 0.30 Å out of the trigonal plane containing their bonded neighbours). In terms of apparent hybridisation, therefore, the N(amido) lone pair resides in a 2p π-donor type orbital. The view of **11** given in Fig. 1(b) helps us to visualise the orientation of the amide nitrogen 2p π-donor orbital with respect to the metal centre. The compound is viewed along the N(11, amide)–Mo(1) vector which can be defined for our purposes as the molecular *z* axis; the corresponding *x* and *y* axes can be defined as approximately coinciding with the projections of the N(14)–Mo(1)–N(123) and N(17)–Mo(1)–N(110) vectors. The $2p_\pi$ donor orbital of the amido nitrogen thus approximately bisects these *x* and *y* axes. The d_π acceptor orbitals required at molybdenum for N(amide) $p_\pi \longrightarrow d_\pi$ donation are a linear combination of the $4d_{yz}$ and $4d_{xz}$ orbitals. However, theoretical studies of pseudo-octahedral *cis*-bis-(imido) complexes[26] have shown that all of the metal d_π orbitals (*i.e.* the t_{2g} set in O_h symmetry) are assigned to N(imido) p_π–d_π bonding. These will generally take precedence over N(amido) $p_\pi \longrightarrow d_\pi$ donation in any given compound based on M–N-(amido/imido) bond length and (hence) π-overlap criteria.[1b,28] Therefore the complexes $[Mo(NAr)_2(R_2[9]aneN_3)Cl]$ **8**–**11** (and also $[Re(NBu^t)_2(H_2[9]aneN_3)(O_3SCF_3)]^+$ by analogy) feature effectively 5-electron donor $R_2[9]aneN_3$ ligands with negligible N(amide) p_π–d_π bonding.

The molecular structure of complex **11** and our qualitative bonding interpretation can be used to comment on the extent of N(amide) p_π–d_π bonding in the mono(imido) complexes $[M(NBu^t)(R_2[9]aneN_3)Cl_2]$ **3**–**6**. In these compounds only two of the three d_π acceptor orbitals of the pseudo-octahedral

metal are involved in N(imido) p_π–d_π bonding.[1b,26] The extent of N(amide) $p_\pi \longrightarrow d_\pi$ donation will therefore depend on the relative orientation of the $2p_\pi$ donor and d_π acceptor orbitals; it is clear from the structure of **11** that the monoanionic triazacyclononane ring can adjust its conformation to allow a near-trigonal planar N(amide) donor. Complexes therefore possess a metal valence electron count of between 16 (5-electron donor $R_2[9]aneN_3$) and 18 (7-electron donor $R_2[9]aneN_3$).

Conclusion

We have reported the first Group 5 and 6 complexes of mono-anionic triazacyclononane ligands $R_2[9]aneN_3$, along with the lithiated derivatives of these ligands. These have proven to be useful entry points to new *fac*-co-ordinated amido-diamine complexes. Examination of the molecular structure of $[Mo(NC_6H_3Pr^i_2-2,6)_2(Pr^i_2[9]aneN_3)Cl]$ **11** suggests that the $R_2[9]aneN_3$ ligands are in principle able to act as up to 7-electron donors to transition metal centres. However, as with many π complexes, a careful consideration of the competing demands of the different π donors is required before comments can be passed with regard to the bonding.[29]

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