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Amidophosphine ligands as constructs for early–late heterobimetallic complexes; the formation of an anisotropic metallocage†

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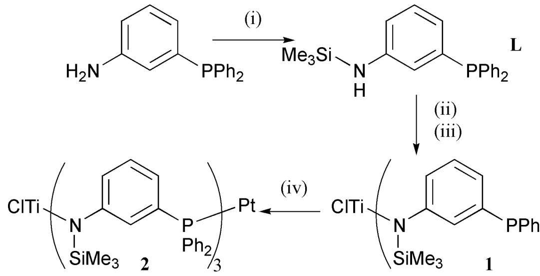
A new amidophosphine ligand has been synthesised and has been shown to support the formation of an early–late mixed metal complex in which the metals are rigidly separated, so creating a metallocage with an anisotropic cavity.

Early–Late HeteroBimetallic (ELHB) compounds have the potential to promote chemical transformations that are not possible with either metal alone.[1] However, in the many examples of such complexes, co-ordinative saturation of the early metal and undesired bridging ligand interactions between the metals often results in poor reactivity. We are interested in the transformation of inert molecules such as N_2, and so are exploring the use of ELHB complexes to effect N–C and N–H bond formation *via* the concomitant activation of the substrates by the different metal moieties. In this context, nitrogen has been shown to be hydrogenated to ammonia by mixing $W(N_2)$ and $Ru(\eta^2\text{-}H_2)$ complexes under an atmosphere of H_2,[2] plus mixtures of $Ti(N_2)$ and Pd^0 species have promoted the arylation of N_2.[3] Here, the activation of N_2 by one metal species and the second substrate (*e.g.* H_2, Ar–X) by the other evidently promotes the desired bond formation.

In order to generate ELHB complexes in which the potential problems of early metal co-ordinative saturation and metal–metal bridging interactions are circumvented, a new amidophosphine ligand that incorporates bulky amido substituents and a *m*-substituted aryl spacer between the donor atoms has been synthesised. The amido moiety should stabilise *reactive*, early metal species (*e.g.* Ti^{II}, V^{II}, Mo^{III}) that are capable of N_2 activation,[4] and the rigid *m*-aryl ring should effectively separate the two metals so that reaction between the activated substrates can occur. Furthermore, amidophosphine ligands have been little utilised in the formation of ELHB complexes.[5] We report here the generation of an unusual TiPt complex that is supported by a ditopic, amidophosphine ligand environment which describes some of the above principles.

The synthesis of the new aminophosphine ligand (**L**) is described in Scheme 1; the reaction of the known,[6] primary aminophosphine with $ClSiMe_3$ in the presence of a strong base generates **L** in moderate yield as a colourless, low melting solid.‡ The *in-situ* lithiation of **L** and subsequent reaction with $TiCl_4(THF)_2$ results in the clean formation of the air and moisture sensitive, triply substituted, amidotitanium complex **1**, which was isolated as a yellow powder. All attempts to crystallise **1** were unsuccessful, which is probably a consequence of the motional freedom of the arylphosphine substituents. Complex **1** was found to react cleanly with $Pt(norbornene)_3$ to yield the novel, orange TiPt heterobimetallic complex **2**. No other products were observed when monitoring the reaction by NMR spectroscopy at 25 °C. The low temperature X-ray crystal structure of **2** was determined and is shown in Fig. 1.§ It is seen that the three amidophosphine ligands provide a ditopic, C_3-symmetric co-ordination environment for the two metals; the Ti^{IV} and Pt^0 centres adopt tetrahedral and trigonal planar geometries, respectively. Both the $TiCl[N(SiMe_3)Ar]_3$ and $Pt(PPh_2Ar)_3$ moieties have almost identical geometric parameters to the monomeric species $TiCl[N(SiMe_3)_2]_3$[7] and $Pt(PPh_3)_3$,[8] which suggests that there is limited torsional strain within the complex. The two parts of the molecule may therefore be expected to act independently and so should show considerable synthetic potential. Close contacts between the unique hydrogen H2 and that of an *o*-H of a phenyl ring (H · · · H 2.895 Å) and the Pt centre (H · · · H 2.916 Å) are observed; similar interactions are seen in the structure of $Pt(PPh_3)_3$.[8] The two metals are well separated by the aryl spacer (Ti–Pt 5.8 Å), so forming a cavity capped at either ends by dissimilar metals. This molecule can therefore be described as an anisotropic metallocage.



Scheme 1 Synthesis of the TiPt complex **2**. Reagents and conditions: (i) $ClSiMe_3$, DABCO, Et_2O; (ii) Bu^nLi, Et_2O, 0 °C; (iii) $TiCl_4(THF)_2$, Et_2O, 0 °C; (iv) $Pt(norbornene)_3$, PhMe, −78 °C.

The NMR data for **2** show that the solid state structure is retained in solution.† The $^{31}P\{^1H\}$ [51.9 (s, J_{PtP} 4468 Hz)] and $^{195}Pt\{^1H\}$ NMR spectra [−4606 ppm (q, J_{PtP} 4468 Hz)] both suggest equivalent phosphines. Close inspection of the crystal structure of **2** shows that the phenyl rings of each PPh_2 group are different and orthogonal to each other; the $N–SiMe_3$ groups on the Ti centre are arranged in a staggered conformation to the PPh_2 groups. This arrangement is also observed in CD_2Cl_2 solution in both the ^1H and ^{13}C NMR spectra (300 MHz) of **2** at 25 °C; two *ipso* carbons [144.0 ($^1J_{PC}$ 34.6, $^3J_{PC}$ 6.0 Hz) and 139.6 ppm ($^1J_{PC}$ 34.6, $^3J_{PC}$ 6.0 Hz)] and two sets of *o*-aryl carbons [135.4 (m) and 134.3 ppm (m)], plus two sets of *o*-aryl protons (7.37 and 6.78 ppm) were observed. These assignments were corroborated by $^1H–^{13}C$ HETCOR experiments. The close contact of H2 to the *o*-H50 observed in the solid state structure is also evident in solution, as a strong, positive NOE was recorded between these two protons, plus a weaker interaction to another *o*-H was seen. Spin saturation NMR experiments confirmed that no exchange between the *o*-protons occurred at 25 °C, with exchange only becoming apparent at temperatures approaching 100 °C (*i.e.* the phenyl rings on each P become equivalent). In order to equilibrate the phenyl rings, the $N(SiMe_3)$ groups must rotate past an eclipsed conformation with the PPh_2 groups, which is evidently a high

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† Electronic supplementary information (ESI) available: full NMR and mass spectroscopic data. See http://www.rsc.org/suppdata/dt/b1/b105698k/

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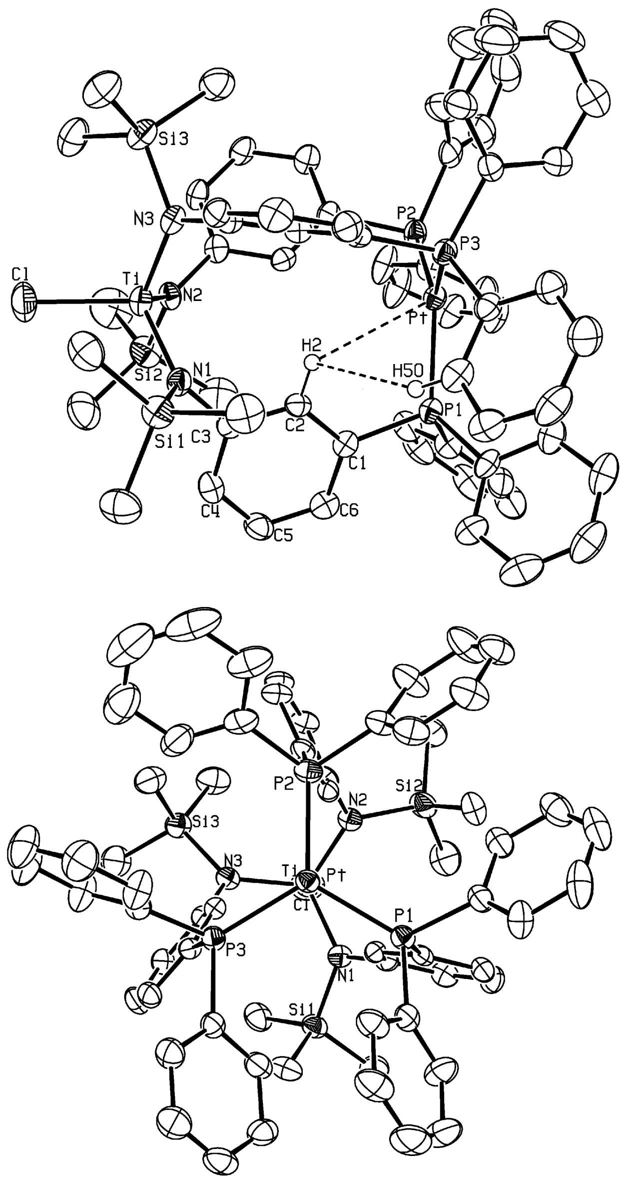

Fig. 1 The solid state structure of the TiPt complex **2**. Selected bond lengths (Å) and angles (°): Ti–N1 1.907(3), Ti–N2 1.900(4), Ti–N3 1.904(4), Ti–Cl 2.2565(14), Pt–P1 2.2696(12), Pt–P2 2.2631(12), Pt–P3 2.2677(12); P1–Pt–P2 120.09(4), P1–Pt–P3 117.95(4), P2–Pt–P3 121.35(4), N1–Ti–N2 109.84(15), N1–Ti–N3 109.15(15), N1–Ti–Cl 111.27(12), N2–Ti–N3 108.44(16), N2–Ti–Cl 109.68(11), N3–Ti–Cl 108.40(11).

energy process; a space filling model of **2** shows severe steric interaction between the $N(SiMe_3)$ groups and the associated bridging aryl rings. Furthermore, the unique aryl-proton on the bridging phenyl group of L (H2) was found to be *deshielded*, occurring at 8.7 ppm as a broad singlet (in C_6D_6); this resonance correlated to a complex multiplet at 134.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum. No such resonance was observed for the Ti-only complex **1** and is therefore a consequence of the formation of the metallocage **2**. Selective decoupling of the remaining bridging phenyl protons simplified the unique proton into the multiplet shown in Fig. 2 (bottom), containing ^{31}P and ^{195}Pt contributions only. Simulation of this resonance was possible by assuming the P–P coupling was large (300 Hz) [Fig. 2 (top)], and revealed coupling of the unique proton to both phosphorus and platinum, with J_{PH} 13.7 and J_{PtH} 4.8 Hz. Similar J_{PtH} coupling constants and chemical shifts to high frequency have been observed for platinum and palladium complexes in which a hydrogen, generally from an associated ligand, sits apically above the trigonal or square plane of the metal.[9] These interactions have been classified as *weakly agostic*, as the J_{PtC} coupling constant is relatively unchanged. This is also the case in **2**, where no reduction in the C–H2 coupling constant is observed (J_{CH} 160 Hz). The observation of this interaction in **2** is a result of the combination of the proximity of H2 to the Pt centre and the rigidity of the cage architecture.[9]

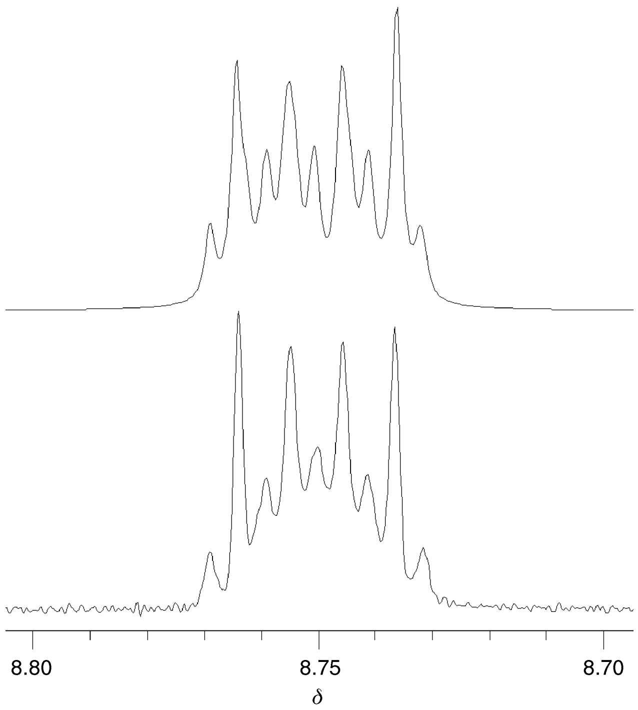

Fig. 2 ^1H NMR spectrum (500 MHz, selective ^1H decoupled) of the unique aryl H (bottom); simulated (top).

Platinum and palladium metallocryptands have been shown to act as hosts for Pb^{II} and Tl^{I} ions in which the guest ions are bound *via* metal–metal interactions; the filled Pt/Pd d_{z^2} can overlap significantly with empty guest p_z orbitals.[10] The interaction of the unique hydrogen with the platinum metal centre in **2** suggests that this molecule may be able to act as a host to small molecules and ions; we are currently probing the reactivity of the metallocage **2** towards such species.

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Notes and references

‡ Full NMR and mass spectroscopic data are available as ESI. Synthesis of *m*-$(Me_3Si)HN(C_6H_4)PPh_2$ (**L**). To a stirred solution of *m*-$H_2N(C_6H_4)PPh_2$ (0.5 g, 1.80 mmol) and DABCO (0.30 g, 2.70 mmol) in Et_2O (15 mL) was added dropwise a solution of chlorotrimethylsilane (0.29 g, 2.70 mmol) in Et_2O (10 mL). After the addition was complete, the reaction mixture was left to stir for 16 h at room temperature. The reaction mixture was then filtered by cannula and the solvents were removed under vacuum, yielding **L** as a pale yellow oil that solidified on standing at room temperature (0.24 g, 44%). Found: C, 72.22; H, 6.87; N, 4.13. $C_{21}H_{24}NPSi$ requires: C, 72.17; H, 6.92; N, 4.01%.

Synthesis of $[TiCl(\mathbf{L})_3]$, **1**. A solution of Bu^nLi in hexanes (2.5 M, 1.55 mL) was added dropwise to a stirred solution of **L** (1.35 g, 3.868 mmol) in Et_2O (30 mL) at 0 °C. The resultant orange solution was stirred at room temperature for 0.5 h, cooled to 0 °C and added dropwise to a stirred slurry of $TiCl_4(THF)_2$ (0.43 g, 1.289 mmol) in Et_2O at 0 °C. The resultant orange slurry was stirred at room temperature for 3 h, and then the solvents were evaporated under vacuum. The brown residues were extracted into hot (*ca.* 50 °C) hexane (2 × 30 mL), filtered through Celite and the yellow filtrate evaporated to dryness under vacuum yielding **1**, (0.903 g, 62%) as a fluffy yellow solid. Found: C, 66.76; H, 6.24; N, 3.58. $C_{63}H_{72}ClN_3P_3Si_3Ti$ requires: C, 66.90; H, 6.37; N, 3.71%.

Synthesis of $[\mathrm{TiCl}(\mathbf{L})_3\mathrm{Pt}]$, **2**. To a stirred mixture of solid **1** (0.25 g, 0.222 mmol) and $\mathrm{Pt(norbornene)_3}$ (0.106 g, 0.222 mmol) was added toluene (10 mL) at −78 °C. The resultant yellow solution was allowed to warm to room temperature and stirred at this temperature for 16 h. After this time, the solvents were evaporated to *ca.* **1** mL volume and cooled to −20 °C, causing **2** to precipitate as a microcrystalline, orange solid. A further crop of **2** could be isolated by the addition of pentane to the toluene washings (total yield 0.201 g, 80%). Orange prisms suitable for X-ray diffraction were grown by the slow evaporation of a C_6D_6 solution of **2** in the glove box. Found: C, 57.04; H, 5.19; N, 3.09. $\mathrm{C_{63}H_{69}ClN_3P_3PtSi_3Ti}$ requires: C, 57.16; H, 5.25, N, 3.17%.

§ Crystal data: $[\mathrm{TiCl}(\mathbf{L})_3\mathrm{Pt}]\cdot 3.5(\mathrm{C_6D_6})$, orange prisms, 0.15 × 0.10 × 0.10 mm, $\mathrm{C_{63}H_{69}ClN_3P_3PtSi_3Ti\cdot 3.5(C_6D_6)}$, monoclinic, $a = 19.7739(3)$, $b = 26.2764(6)$, $c = 31.3507(6)$ Å, $\beta = 103.886(1)°$, $U = 15813.4(5)$ Å^3, space group $C2/c$ (no. 15), $Z = 8$, $\mu = 2.05\ \mathrm{mm}^{-1}$, $F(000) = 6552$, 46295 collected reflections, 13842 unique ($R_{\mathrm{int}} = 0.068$). Data were collected at 173(2) K on a Kappa CCD diffractometer, $\lambda = 0.71073$ Å, $\theta = 3.72$ to 25.01°, absorption correction applied using MULTISCAN, solved by direct methods and refined using SHELXL-97.[11] Of the three C_6D_6 molecules, one was disordered and refined as 50 : 50 occupancy; half a molecule of C_6D_6 lies on a two-fold rotational axis. Final full-matrix least-squares refinement on F^2 converged at $R_1 = 0.043$ for 10181 reflections with $I > 2\sigma(I)$, $wR_2 = 0.087$, $S = 1.001$ for all data and 895 parameters. CCDC reference number 167766. See http://www.rsc.org/suppdata/dt/b1/b105698k/ for crystallographic data in CIF or other electronic format.

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