Syntheses and Coordination Chemistry of Aminomethylphosphine Derivatives of Adenine

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Two aminomethylphosphane derivatives of adenine 9-(2-{bis[(diphenylphosphanyl)methyl]amino}ethyl)adenine (**La**) and 9-(3-{bis[(diphenylphosphanyl)methyl]amino}propyl)-adenine (**Lb**) were synthesised. Oxidation of **La** and **Lb** with H_2O_2, elemental sulfur or elemental selenium led to the corresponding oxidized products **4a/b**–**6a/b**. Both **La** and **Lb** behave as didentate ligands towards late transition metals. Reaction of **La** or **Lb** with [MX_2(cod)] (M = Pd, Pt; X = Cl, Me) gave chelate complexes **7a/b**–**10a/b**. Reaction of **La** or **Lb** with [AuCl(tht)] or [{RuCl(μ-Cl)(*p*-MeC_6H_4*i*Pr)}$_2$] gave the didentate bridging complexes **11a/b** and **12a**. All compounds have been fully characterised by microanalysis, IR, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and EI/CI/FAB mass spectrometry. ^{1}H{^{31}P} NMR and ^{1}H-^{13}C correlation experiments were used to confirm the spectral assignments where necessary. Two compounds were structurally characterised by X-ray crystallographic analysis.

Introduction

Owing to their resemblance to the structure of adenosine and their broad-spectrum of antiviral or anticancer activity, adenine derivatives substituted at the 9-position constitute an important class of pharmacologically active compounds.[1] Among them 9-[2-(phosphonomethoxy)ethyl]adenine and its analogues have been extensively studied.[2,3] In bioinorganic chemistry, metal complexes capable of forming complementary hydrogen bonds occupy an increasingly important position in the development of biochemically active molecules. Houlton et al.[4] have prepared some interesting bifunctional complexes that combine the covalent bond-forming capabilities of the metal ion and a ligand surface capable of recognizing nucleotide bases by means of hydrogen bonding. The same group developed the concept of *directed metallation* and reported a series of nucleoside analogues in which the ribose group is replaced by a dimethylene/trimethylene tethered ethylenediamine [5−8] or 1,2-dithioethane.[9] Interaction of such chelate-tethered nucleoside analogues with metal ions gave interesting A−N^3-bound or A−C^8-bound mono- or polynuclear complexes. In an approach which combines the antitumour activities of diphosphanes and their gold complexes[10,11] and our experience in the synthesis coordination chemistry of P−C−N compounds,[12] we have incorporated the aminomethylphosphane unit into adenine through an aminodi/trimethylene linkage at the 9-position. The adenine analogues prepared in this way possess two functions: an excellent coordination tendency toward transition metals and the capacity for base-pair or complementary hydrogen-bonding interactions. Some enhanced biological activities are expected from the new combination of the bioactive adenine and aminophosphane as well as the corresponding complexes.

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Results and Discussion

Preparation and Oxidation of La and Lb

Scheme 1 shows the synthesis of **La** and **Lb** and the corresponding oxidized compounds. Precursor **1a** was prepared using 1-bromo-2-chloroethane and the sodium salt of adenine, formed from adenine and sodium hydride in anhydrous DMF by a literature method,[13,14] while **1b** was prepared following a modified literature method using adenine and 1-bromo-3-chloropropane in the presence of anhydrous K_2CO_3 in anhydrous DMF, which proved to be milder than NaH and gave a higher yield of the target product.[15−17] Compounds **2**[18] and **3**[19] were also prepared according to the literature method, with slight modification.

Due to the low solubility of **3a** and **3b** in common organic solvents at room temperature, the condensation reactions with Ph_2PCH_2OH were carried out in refluxing acetonitrile. Monitoring by ^{31}P{^{1}H} NMR spectroscopy indicated that the reaction of **3a** or **3b** with a slight excess of Ph_2PCH_2OH (**3**: $Ph_2PCH_2OH \approx$ 1:2 molar ratio) gave **La**

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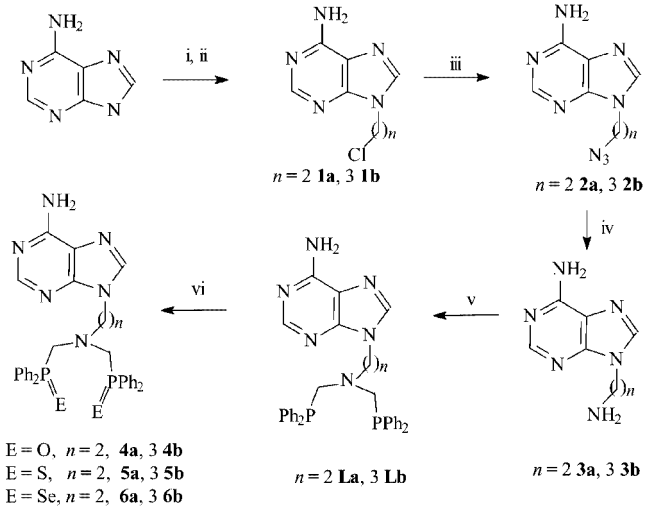


Scheme 1. Preparation and oxidation of **La** and **Lb**; i) NaH (60% in mineral oil) or K_2CO_3, anhydrous DMF, room temp.; ii) $ClCH_2CH_2Br$ or $ClCH_2CH_2CH_2Br$, room temp., 48 h; iii) NaN_3, DMF, 80 °C, 24 h; iv) H_2, 1 atm, Pd/C (10%), MeOH; v) Ph_2PCH_2OH, CH_3CN, reflux, overnight; vi) H_2O_2 (30%), 0 °C, THF, room temp., 2 h; or S_8/Se, THF, reflux, overnight

and **Lb** overnight. Workup by simple concentration and washing with Et_2O removes the excess Ph_2PCH_2OH, and recrystallisation from CH_3CN gave the air- and moisture-stable white solids **L** in good yields. The successful selectivity of N−C bond formation at the dangling alkylamino group rather than the aryl C^6-NH_2 at the purine ring can be attributed to the difference in basicities of the two primary amino groups. The alkylamino group at the 9-position is much more electron-rich than the amino group at the 6-position, whose lone pair is highly delocalised in the electron-withdrawing purine ring. Attempts to get 9-{2-[(diphenylphosphanyl)methylamino]ethyl}adenine and 9-{3-[(diphenylphosphanyl)methylamino]propyl}adenine by using a 1:1 molar ratio of reagents failed; double condensation always occurred under these conditions.

Oxidation of **La** and **Lb** with excess elemental sulfur or selenium in THF gave the corresponding sulfides and selenides. As shown by $^{31}P\{^1H\}$ NMR spectroscopy, however, there is always a trace of unidentified impurities ($\delta_P \approx 40.6$, 37.7 and 36.5 ppm for sulfides; $\delta_P \approx 27.0$ ppm for selenides) in the reaction mixture, implying that the P−C−N bond is not very robust under oxidation conditions. Attempts to get rid of the impurities were not successful by either chromatography or recrystallisation. Oxidation of **La** and **Lb** with aqueous H_2O_2 (30%) needs to be performed with caution. The oxidizing agent can only be used stoichiometrically or slightly in excess, otherwise oxidation at the N1 position of the purine ring occurs as described previously[20,21] and as observed in the mass spectrum. Even so, using our method there are still some unidentified impurities ($\delta_P \approx 30.9$, 27.0 and 26.0 ppm) in the reaction mixture that are very difficult to remove. Oxidation of **La** and **Lb** by air proved too slow to be useful as a preparative technique. Stirring a solution of **La** or **Lb** in THF in air at room temperature for four days only gives about 20% oxidation of the starting material.

Characterization of La, Lb and 1a/b−6a/b

La, **Lb** and compounds **1b, 2b, 3b, 4a/b−6a/b** were fully characterised by multinuclear NMR spectroscopy, EI/CI/FAB mass spectrometry, infrared spectrometry and microanalysis. All the compounds gave reasonable microanalysis results apart from **4a** and **4b**, which showed slightly lower carbon percentages than the calculated value due to the impurities described above. Their mass spectra show the molecular ions and the expected fragmentation pattern with appropriate isotope distributions. The sulfur and selenium species **5a/b−6a/b** show the $[M - S]^+$ and $[M - Se]^+$ fragment ions in their EIMS spectra. The corresponding $[M - O]^+$ ion was not observed for **4a/b**. In the IR spectra, all compounds display two broad medium intensity ν_{N-H} bands between 3349 and 3106 cm^{-1}. The strong N−H bending absorption of the NH_2 group and the stretching absorption of the C=N bond of the purine ring were observed at around 1655 cm^{-1} and 1598 cm^{-1}, respectively. Compounds **2a/b** show an $\nu_{N\equiv N}$ band at 2100 cm^{-1}. Compounds **4a** and **4b** display the $\nu_{P=O}$ absorption at ca. 1178 and 1176 cm^{-1}; the $\nu_{P=S}$ and $\nu_{P=Se}$ bands could not be assigned unambiguously for **5a/b** and **6a/b**.

The $^{31}P\{^1H\}$ NMR signals (Table 1 and 2) of **La/b** at around $\delta_P = -27$ ppm are similar to other bis[(diphenylphosphanyl)methyl]amine compounds.[22] The dichalcogenides **4a/b-6a/b** show signals shifted to higher frequency at ca. $\delta_P = 29$, 35 and 25 ppm compared with that of **La/b**. Interestingly, the $^{31}P\{^1H\}$ NMR spectra of the selenium species **6a/b** not only show a central singlet of 92% intensity with selenium satellites ($^1J_{P,Se} = 730$ Hz)[23] but also a small P−P coupling ($^4J_{P,P} = 9$ Hz) in the satellites. The latter is due to the inequivalence of the two phosphorus atoms arising from the $Ph_2P(Se)CH_2NCH_2P(^{77}Se)Ph_2$ isotopomer. Similar P−P couplings in the selenium satellites were also observed in $Ph_2P(Se)NHP(Se)Ph_2$ ($^2J_{P,P} = 29$ Hz)[24] and $Ph_2P(Se)OP(Se)Ph_2$ ($^2J_{P,P} = 44$ Hz).[25]

The ^1H NMR spectra of **1b**[14,26] and **3b**[27] in $[D_6]$DMSO or $[D_6]$DMSO + D_2O have been reported previously. In order to compare the NMR spectra of the precursors and the aminomethylphosphanes **La** and **Lb**, the same solvent should be employed. However, catalytic oxidation (with either catalyst or irradiation) of P^{III} compounds by DMSO has been reported[21,28−30] and we have also observed the gradual oxidation of some aminophosphane compounds in $[D_6]$DMSO during spectral acquisition, therefore the employment of $[D_6]$DMSO for **La** and **Lb** was precluded. For comparative purposes, in addition to the spectra in $[D_6]$DMSO, the ^1H NMR spectroscopic data of **1−3** in $CDCl_3$ containing a few drops of $[D_6]$DMSO were acquired. The data of **1a**, **2a** and **3a** will be reported elsewhere, and those of **1b**, **2b**, **3b** are listed in Table 3. In the ^1H NMR spectra the chemical shifts of the C^6-NH_2 group and one of the CH groups of the purine ring (C^2-H or C^8-H) vary with solvent ($[D_6]$DMSO, $CDCl_3$ or $CDCl_3$/$[D_6]$DMSO). On the other hand, in the $^{13}C\{^1H\}$ NMR

Table 1. NMR spectroscopic data for compounds **La** and **4a−6a**

Entry	$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P (ppm)	J (Hz)	^1H NMR ($CDCl_3$) δ_H (ppm)	J (Hz)	$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C (ppm)	J (Hz)
					155.89 (C^6)	
					152.98 (C^2)	
			8.32 (s, 1 H, C^2-H)		150.10 (C^4)	
			7.10 (s, 1 H, C^8-H)		141.29 (C^8)	
			7.37−7.28 (m, 20 H, ArH)		137.65 (d, ArC^i)	$^1J_{P,C}$ = 13
L_a	−26.71 (s)		5.55 (br. s, 2 H, NH_2)		133.43 (d, ArC^o)	$^2J_{P,C}$ = 18
			4.05 (t, 2 H, AdeC$H_2$$CH_2$)	$^3J_{CH,CH}$ = 6	129.03 (d, ArC^m)	$^3J_{P,C}$ = 22
			3.61 (d, 4 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 5	128.81 (s, ArC^p)	
			3.27 (t, 2 H, C$H_2$$NPCH_2$)	$^3J_{CH,CH}$ = 6	119.54 (C^5)	
					59.71 (dd, PCH_2)	$^1J_{P,C}$ = 6, $^3J_{P,C}$ = 8
					56.00 (t, CH_2NPCH_2)	$^3J_{P,C}$ = 9
					42.16 (s, AdeCH_2CH_2)	
					154.20 (C^6)	
			8.24 (s, 1 H, C^2-H)		152.22 (C^2)	
			7.60 (s, 1 H, C^8-H)		150.19 (C^4)	
			7.70−7.31 (m, 20 H, ArH)		142.24 (C^8)	
4a	29.06 (s)		6.87 (v br. s, 2 H, NH_2)		132.47−128.20 (m, PhC)	
			4.19 (t, 2 H, AdeC$H_2$$CH_2$)	$^3J_{CH,CH}$ = 6	119.15 (C^5)	
			3.82 (d, 4 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 5	57.92 (t, CH_2NPCH_2)	$^3J_{P,C}$ = 6
			3.50 (t, 2H C$H_2$$NPCH_2$)	$^3J_{CH,CH}$ = 6	56.67 (dd, PCH_2)	$^1J_{P,C}$ = 82, $^3J_{P,C}$ = 7
					41.83 (s, AdeCH_2CH_2)	
					154.91 (C^6)	
			8.25 (s, 1 H, C^2-H)		151.98 (C^2)	
			7.85 (s, 1 H, C^8-H)		149.99 (C^4)	
			7.83−7.36 (m, 20 H, ArH)		142.03 (C^8)	
5a	35.37 (s)		5.93 (br. s, 2 H, NH_2)		132.48−128.65 (m, PhC)	
			4.19 (br. s, 4 H, PCH_2)		119.51 (C^5)	
			4.07 (t, 2 H, AdeC$H_2$$CH_2$)	$^3J_{CH,CH}$ = 6	59.34 (d, PCH_2)	$^1J_{P,C}$ = 58
			3.43 (t, 2 H, C$H_2$$NPCH_2$)	$^3J_{CH,CH}$ = 6	56.40 (br. s CH_2NPCH_2)	
					42.58 (s, AdeCH_2CH_2)	
					155.34 (C^6)	
			8.24 (s, 1 H, C^2-H)		152.41 (C^2)	
			7.88 (s, 1 H, C^8-H)		149.80 (C^4)	
			7.78−7.35 (m, 20 H, ArH)		141.61 (C^8)	
6a	25.26 (s)	$^1J_{P,Se}$ = 730	6.10 (br. s, 2 H, NH_2)		132.10−128.74 (m, PhC)	
		$^4J_{P,P'}$ = 9	4.41 (br. s, 4 H, PCH_2)		119.41 (C^5)	
			3.99 (t, 2 H, AdeC$H_2$$CH_2$)	$^3J_{CH,CH}$ = 6	59.34 (d, PCH_2)	$^1J_{P,C}$ = 51
			3.42 (t, 2 H, C$H_2$$NPCH_2$)	$^3J_{CH,CH}$ = 6	56.11 (br. s, CH_2NPCH_2)	
					42.72 (s, AdeCH_2CH_2)	

spectra, the resonance frequencies of the carbons (C^2, C^4, C^5, C^6 and C^8) of the purine ring of compounds **1−3** show little variation in different solvents. To assign the C^2−H and C^8−H protons unambiguously, ^1H-^{13}C heteronuclear correlation spectra (HMQC) were measured. It turned out that the C^8−H appears at lower frequency at around δ_H = 7.8 ppm in $CDCl_3$ or $CDCl_3$/[D_6]DMSO, while in [D_6]DMSO, it is close to the C^2−H resonance at around δ_H = 8.2 ppm. The C^6−NH_2 resonance in $CDCl_3$ or $CDCl_3$ + [D_6]DMSO is observed at around δ_H = 5.6 ppm, while in [D_6]DMSO it appears at around δ_H = 7.2 ppm.

Based on the above observation, we assign the higher frequency singlet at δ_H = 8.32−8.24 ppm to C^2−H and the lower one at δ_H = 7.10−7.88 ppm to C^8 in the ^1H NMR spectra of **La/b** and **4a/b−6a/b**. The ^1H-^{13}C heteronuclear correlation experiment confirmed the assignments. Like their precursors **1−3**, the broad singlet of C^6−NH_2 of **La**, **Lb** and **4−6** appears at around δ_H = 6 ppm. Among them, the resonance of C^6−NH_2 of the oxygen species **4a/b** appears at relatively higher frequency. The proton signals of the dangling chain of **La** and **4a/6a** are as easy to assign as their precursors **1a−3a**, which will be reported elsewhere, with the triplet of AdeC$H_2$$CH_2$ at higher frequency between δ_H = 4.48 and 4.05 ppm and the triplet of CH_2N(CH_2PPh_2) at lower frequency between δ_H = 3.61 and 3.42 ppm. For **Lb** and **4b/6b**, the triplet of AdeC$H_2$$CH_2$ between δ_H = 3.95 and 3.76 ppm and that of CH_2N(CH_2PPh_2) between δ_H = 3.09 and 2.79 ppm are at slightly lower frequency than in **La** and **4a/6a**, but still follow the tendency AdeC$H_2$$CH_2$ > CH_2N(CH_2PPh_2). The triplet of CH_2N(CH_2PPh_2) seems always less-well resolved and slightly broader than that of AdeC$H_2$$CH_2$, which may be attributed to the long-distance coupling of these methylene protons with phosphorus atoms. The AdeCH_2C$H_2$$CH_2$ signal in **Lb** and **4b−6b** appears as a well-resolved quintet at an even lower frequency, between δ_H = 1.87 and 1.69 ppm. The signal of C$H_2$$PPh_2$ of the above compounds appears between δ_H = 4.47 and 3.60 ppm as a doublet or

Table 2. NMR spectroscopic data for compounds $\mathbf{L_b}$ and **4b−6b**

Entry	$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P (ppm)	J (Hz)	^1H NMR ($CDCl_3$) δ_H (ppm)	J (Hz)	$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C (ppm)	J (Hz)
					155.45 (C^6)	
			8.30 (s, 1 H, C^2-H)		152.82 (C^2)	
			7.25 (s, 1 H, C^8-H)		150.19 (C^4)	
			7.44−7.25 (m, 20 H, ArH)		141.33 (C^8)	
$\mathbf{L_b}$	−28.12 (s)		5.74 (br. s, 2 H, NH_2)		137.94 (d, ArC^i)	$^1J_{P,C} = 12$
			3.81 (t, 2 H, Ade$CH_2$$CH_2$)	$^3J_{CH,CH} = 6$	133.38 (d, ArC^o)	$^2J_{P,C} = 19$
			3.60 (d, 4 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH} = 3$	128.80 (d, ArC^m)	$^3J_{P,C} = 21$
			2.79 (t, 2 H, $CH_2$$NCH_2P$)	$^3J_{CH,CH} = 6$	128.74 (s, ArC^p)	
			1.83 (quint, 2 H, AdeCH_2CH_2)		119.97(C^5)	
					59.01 (dd, PCH_2)	$^1J_{P,C} = 6$ or 9 $^3J_{P,C} = 6$ or 9
					53.18 (t, $CH_2$$NCH_2P$)	$^3J_{P,C} = 9$
					41.70 (s, Ade$CH_2$$CH_2$)	
					17.30 (s, Ade$CH_2$$CH_2$)	
					154.48 (C^6)	
			8.29 (s, 1 H, C^2-H)		150.31 (C^2)	
			7.58 (s, 1 H, C^8-H)		149.67 (C^4)	
			7.85−7.36 (m, 20 H, ArH)		141.80 (C^8)	
4b	29.43(s)		6.78 (v br. s, 2 H, NH_2)		132.79−128.19 (m, PhC)	
			3.76 (d + t, 6 H, PCH_2+ AdeCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH} = 5$	119.65 (C^5)	
			3.09 (t, 2 H, $CH_2$$NCH_2P$)	$^3J_{CH,CH} = 6$	56.07 (dd, PCH_2)	$^1J_{P,C} = 83$, $^3J_{P,C} = 7$
			1.87 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH} = 6$	55.75 (t, $CH_2$$NCH_2P$)	$^3J_{P,C} = 7$
					42.27 (s, Ade$CH_2$$CH_2$)	
					27.46 (s, Ade$CH_2$$CH_2$)	
					155.25 (C^6)	
			8.30 (s, 1 H, C^2-H)		152.38 (C^2)	
			7.70 (s, 1 H, C^8-H)		150.12 (C^4)	
			7.87−7.32 (m, 20 H, ArH)		141.36 (C^8)	
5b	35.27 (s)		5.84 (br. s, 2 H, NH_2)		132.76−128.74 (m, PhC)	
			4.29 (br. s, 4 H, PCH_2)		119.87 (C^5)	
			3.95 (t, 2 H, Ade$CH_2$$CH_2$)	$^3J_{CH,CH} = 7$	57.96 (d, PCH_2)	$^1J_{P,C} = 62$
			2.95 (t, 2 H, $CH_2$$NCH_2P$)	$^3J_{CH,CH} = 7$	53.56 (br. t, $CH_2$$NCH_2P$)	$^3J_{P,C} = 4$
			1.76 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH} = 7$	41.74 (s, Ade$CH_2$$CH_2$)	
					27.02 (s, Ade$CH_2$$CH_2$)	
					155.22 (C^6)	
			8.29 (s, 1 H, C^2-H)		152.42 (C^2)	
			7.72 (s, 1 H, C^8-H)		150.15 (C^4)	
			7.88−7.30 (m, 20 H, ArH)		141.16 (C^8)	
6b	24.64 (s)	$^1J_{P,Se} = 730$	5.88 (br. s, 2 H, NH_2)		132.18−128.80 (m, PhC)	
		$^4J_{P,P'} = 9$	4.47 (br. s, 4 H, PCH_2)		119.99 (C^5)	
			3.95 (t, 2 H, Ade$CH_2$$CH_2$)	$^3J_{CH,CH} = 7$	57.67 (d, PCH_2)	$^1J_{P,C} = 52$
			2.92 (t, 2 H, $CH_2$$NCH_2P$)	$^3J_{CH,CH} = 7$	53.13 (t, $CH_2$$NCH_2P$)	$^3J_{P,C} = 4$
			1.69 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH} = 7$	41.69 (s, Ade$CH_2$$CH_2$)	
					27.26 (s, Ade$CH_2$$CH_2$)	

broad singlet arising from the two-bond or four-bond couplings of CH and phosphorus. This resonance can appear at a higher or lower frequency than, and sometimes even overlapped with, that of Ade$CH_2$$CH_2$.

In the $^{13}C\{^1H\}$ NMR spectra, **La/Lb** and their oxidized compounds show very similar purine ring carbon signals (Table 1 and 2) to their precursors and other reported adenine analogues.[31] However, as revealed by a ^1H-^{13}C heteronuclear correlation experiment, the ^{13}C signal of $CH_2NCH_2PPh_2$ is shifted to higher frequency between $\delta_C = 57.92$ and 53.13 ppm and appears as a triplet or broad singlet due to coupling with the phosphorus atoms, while the signal of AdeCH_2CH_2 remains as a singlet between $\delta_C = 42.58$ and 41.69 ppm. The CH_2PPh_2 signal, which appears as a doublet of doublets, doublet or broad singlet due to the $^1J_{P,C}$ and/or $^3J_{P,C}$ couplings, appears at the highest frequency in the alkyl region. **La** and **Lb** exhibit neat signals in the aromatic carbon region and the coupling constants $^nJ_{P,C}$ (n = 1, 2, 3) are available in Table 1 and 2. The coupling constants $^nJ_{P,C}$ (n = 1, 2, 3) in **4a/b-6a/b**, however, are very difficult to observe due to the trace impurities that cause small overlapping signals in the aromatic carbon resonance region in **4a/b-6a/b**.

Compound **2b** was also characterised by X-ray crystallography (Figure 1 and Table 4). Two typical types of hydrogen bonding for the purine system are observed between adjacent molecules (Figure 1, bottom), they are the Watson−Crick type between N(6)−H of one molecule and N(1) of a second molecule, [N(6)−H(6A)···N(1A), d(D···A) 3.056(4) Å, d(H···A) 2.10 Å, ∠(DHA) 164(2)°], and the

Table 3 NMR spectroscopic data for compounds **1b**−**3b**

Entry	^{1}H NMR ([D$_6$]DMSO)		^{1}H NMR ($CDCl_3$ for **1b**, **2b**; $CDCl_3$ + [D$_6$]DMSO for **3b**)		^{13}C{^{1}H} NMR ([D$_6$]DMSO)	^{13}C{^{1}H} NMR ($CDCl_3$ for **1b**, **2b**; $CDCl_3$ + [D$_6$]DMSO for **3b**)
	δ_H (ppm)	J (Hz)	δ_H (ppm)	J (Hz)	δ_C (ppm)	δ_C (ppm)
					155.96 (C^6)	155.30 (C^6)
	8.16 (s, 1 H, C^8-H)		8.38 (s, 1 H, C^2-H)		152.41 (C^2)	153.49 (C^2)
	8.15 (s, 1 H, C^2-H)		7.85 (s, 1 H, C^8-H)		149.52 (C^4)	150.08 (C^4)
	7.22 (br. s, 2 H, NH_2)		5.55 (br. s, 2 H, NH_2)		140.78 (C^8)	141.20 (C^8)
1b	4.30 (t, 2 H, AdeCH_2CH$_2$)	$^3J_{CH,CH}$ = 6	4.43 (t, 2 H, AdeCH_2CH$_2$)	$^3J_{CH,CH}$ = 6	118.76 (C^5)	119.82 (C^5)
	3.65 (t, 2 H, CH_2Cl)	$^3J_{CH,CH}$ = 6	3.53 (t, 2 H, CH_2Cl)	$^3J_{CH,CH}$ = 6	42.33 (AdeCH$_2$CH$_2$)	41.67 (AdeCH$_2$CH$_2$)
	2.31 (quint, 2 H, AdeCH$_2$CH_2)	$^3J_{CH,CH}$ = 6	2.40 (quint, 2 H, AdeCH$_2$CH_2)	$^3J_{CH,CH}$ = 6	40.58 (CH_2Cl)	41.33 (CH_2Cl)
					31.99 (AdeCH$_2$CH$_2$)	32.19 (AdeCH$_2$CH$_2$)
					155.91 (C^6)	155.73 (C^6)
			8.37 (s, 1 H, C^2-H)		152.92 (C^2)	153.35 (C^2)
	8.16 (s, 2 H, C^8-H + C^2-H)		7.81 (s, 1 H, C^8-H)		149.53 (C^4)	150.33 (C^4)
	7.21 (br. s, 2 H, NH_2)		5.91 (br. s, 2 H, NH_2)		140.73 (C^8)	140.77 (C^8)
2b	4.27 (t, 2 H, AdeCH_2CH$_2$)	$^3J_{CH,CH}$ = 7	4.32 (t, 2 H, AdeCH_2CH$_2$)	$^3J_{CH,CH}$ = 7	118.74 (C^5)	120.05 (C^5)
	3.39 (t, 2 H, CH_2Cl)	$^3J_{CH,CH}$ = 7	3.36 (t, 2 H, CH_2N_3)	$^3J_{CH,CH}$ = 7	48.12 (CH_2N_3)	48.38 (CH_2N_3)
	2.08 (quint, 2 H, AdeCH$_2$CH_2)	$^3J_{CH,CH}$ = 7	2.18 (quint, 2 H, AdeCH$_2$CH_2)	$^3J_{CH,CH}$ = 7	40.53 (AdeCH_2CH$_2$)	41.24 (AdeCH_2CH$_2$)
					28.63 (AdeCH$_2$CH$_2$)	29.26 (AdeCH$_2$CH$_2$)
					155.92 (C^6)	155.64 (C^6)
			8.21 (s, 1 H, C^2-H)		152.29 (C^2)	152.91 (C^2)
	8.14 (s, 2 H, C^2-H + C^8-H)		7.73 (s, 1 H, C^8-H)		149.54 (C^4)	150.14 (C^4)
3b	7.20 (br. s, 2 H, NH_2)		5.85 (br. s, 2 H, NH_2)		140.88 (C^8)	140.58 (C^8)
	4.21 (t, 2 H, AdeCH_2CH$_2$)	$^3J_{CH,CH}$ = 7	4.20 (t, 2 H, AdeCH_2CH$_2$)	$^3J_{CH,CH}$ = 7	118.70 (C^5)	119.60 (C^5)
	2.48 (t, 2 H, CH_2NH$_2$)	$^3J_{CH,CH}$ = 7	2.57 (t, 2 H, CH_2NH$_2$)	$^3J_{CH,CH}$ = 7	40.54 (AdeCH_2CH$_2$)	40.91 (AdeCH_2CH$_2$)
	1.86 (quint, AdeCH$_2$CH_2)	$^3J_{CH,CH}$ = 7	1.89 (quint, AdeCH$_2$CH_2)	$^3J_{CH,CH}$ = 7	38.43 (CH_2NH_2)	38.52 (CH_2NH_2)
	1.54 (br. s, 2 H, NH_2)		1.13 (br. s, NH_2)		33.27 (AdeCH$_2$CH$_2$)	33.48 (AdeCH$_2$CH$_2$)

Hoogsteen type between the other N(6)−H of this molecule and N(7) of a third molecule [N(6)−H(6B)···N(7B), d(D···A) 3..082(3) Å, d(H···A) 2.11 Å, ∠(DHA) 174(4)°].

Coordination Chemistry of La/b with Late Transition Metals

As shown in Scheme 2, **La/b** are excellent didentate ligands towards late transition metals. Reaction of **La/b** with [MX$_2$(cod)] gave a series of didentate complexes **7a/b**−**10a/b**. Interaction of **La/b** with two molar equivalents of [AuCl(tht)] gave the didentate bridging bimetallic complexes **11a/b**. The reaction of **La** and [{RuCl$_2$(η^6-*p*-MeC$_6$H$_4$*i*Pr)}$_2$] also gave the bimetallic compound **12a**. All the complexes gave reasonable microanalyses. Their FAB-MS or ES-MS spectra show the expected molecular ion and fragmentation ions, with appropriate isotope distribution. In the IR spectra the anticipated medium intensity ν_{N-H} stretching band at around 3395−3314 cm^{-1} and 3186−3144 cm^{-1}, and the very strong ν_{N-H} bending and $\nu_{C=N}$ stretching at around 1637 cm^{-1} and 1596 cm^{-1}, respectively, were observed as in the free ligands and oxidized compounds. In the complexes, medium intensity ν_{M-Cl} vibrations were also observed at 329−246 cm^{-1}; the two bands in this region for complexes **7a/b**, **8a/b** are in agreement with the *cis*-geometry of the chelate complexes.

The ^{31}P{^{1}H} NMR spectra of **7a/b**−**10a/b** (Table 5) show high-frequency shifts relative to the free ligands. The platinum species gave more information because of the platinum satellites. In complexes **8a/b** and **9a/b** the large $^1J_{Pt,P}$ coupling (3416 Hz) and the relatively small $^1J_{Pt,P}$ coupling (ca. 1782 Hz) are typical of a phosphorus *trans* to a chloride and a methyl group, respectively, and are thus in agreement with the *cis*-geometry. Complex **10a/b** displays two doublets ($^2J_{P,P} \approx 22$ Hz) corresponding to the two inequivalent phosphorus atoms. The doublet at ca. δ_P = 4.0 ppm with a large $^1J_{Pt,P}$ coupling of ca. 4200 Hz was assigned to the phosphorus *trans* to chloride and the signal with a small $^1J_{Pt,P}$ of about 1640 Hz at ca. δ_P = 0.8 ppm to the phosphorus atoms *trans* to the methyl group.

The ^{1}H NMR spectra of the complexes in CD_2Cl_2 or $CDCl_3$ (Table 5) are generally similar to that of the free ligand **La/b**, the chemical shifts of C^2−H ($\delta_H \approx 8.2$ ppm) > C^8−H ($\delta_H \approx 7.0$ ppm) and that of AdeCH_2 ($\delta_H \approx 3.7$ ppm) > CH_2NCH$_2$P ($\delta_H \approx 3.0$ ppm). Like **La/b**, the chelate complexes show a doublets of doublet, a doublet or a broad singlet for CH_2P, arising from $^2J_{P,CH}$ and/or $^4J_{P,CH}$ coupling, between the signals of AdeCH_2 and CH_2NCH$_2$P, except complex **9b**, while the CH_2P signal in the bridging complexes **11a/b** and **12a** appears at higher frequency than that of AdeCH_2. The platinum complexes display satellites for both CH_2P and the coordinated CH_3 groups. The coupling constants $^3J_{PtCH} \approx 38$ Hz for the dichloride compounds **8a/b**, $^3J_{PtCH} \approx 15$ Hz for **9a/b**, and $^3J_{PtCH}$ = 45 and 15 Hz for **10a/b** were obtained unambiguously from the ^{1}H{^{31}P} NMR spectra. The doublet of doublets for CH_3 at δ_H = 0.33 and 0.49 ppm with satellites ($^2J_{Pt,CH}$ = 54 Hz) in **10a/b** can be easily interpreted as being due to the coupling of this group with the two inequivalent phosphorus atoms.

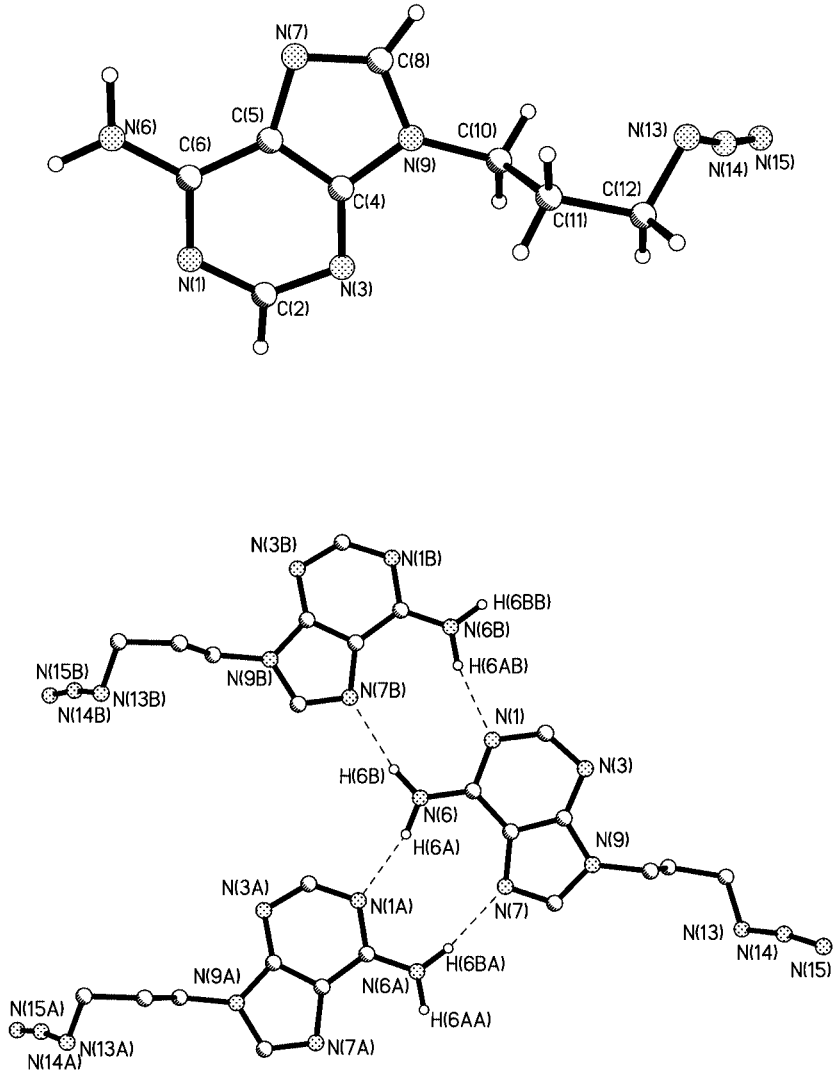


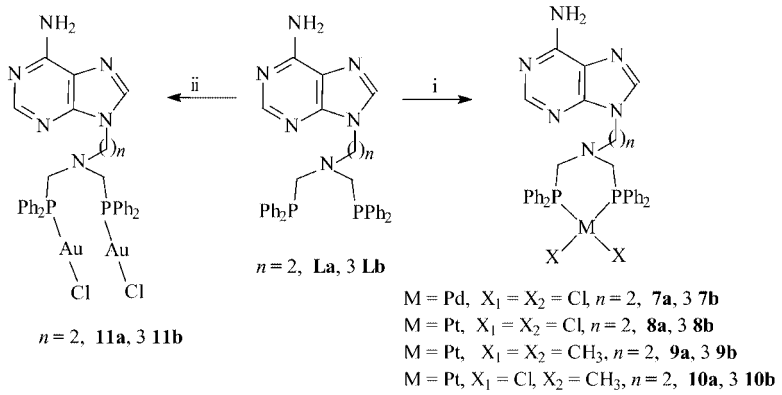
Figure 1. (top) The crystal structure of 9-(3-azidopropyl)adenine (**2b**); (bottom) the crystal structure of **2b** showing part of the hydrogen bonding

Table 4. Selected bond lengths (Å) and angles (°) in compound **2b**

C(2)−N(1)	1.340(3)	N(3)−C(2)	1.318(4)
C(4)−N(3)	1.348(3)	C(5)−C(4)	1.378(4)
C(6)−C(5)	1.395(4)	N(1)−C(6)	1.356(3)
C(6)−N(6)	1.340(3)	N(7)−C(5)	1.399(7)
C(8)−N(7)	1.306(3)	N(9)−C(8)	1.357(3)
N(9)−C(4)	1.373(3)	C(10)−N(9)	1.457(3)
C(11)−C(10)	1.492(4)	C(11)−C(12)	1.503(4)
C(12)−N(13)	1.450(5)	N(13)−N(14)	1.226(4)
N(14)−N(15)	1.117(4)		
C(2)−N(1)−C(6)	118.1(3)	N(3)−C(2)−N(1)	130.5(3)
C(4)−N(3)−C(2)	109.6(2)	N(3)−C(4)−C(5)	127.2(3)
C(6)−C(5)−C(4)	117.4(2)	N(1)−C(6)−C(5)	117.3(3)
N(7)−C(5)−C(4)	110.0(2)	C(8)−N(7)−C(5)	103.2(2)
N(9)−C(8)−N(7)	115.0(2)	C(4)−N(9)−C(8)	105.2(2)
C(5)−C(4)−N(9)	106.5(2)	N(9)−C(10)−C(11)	113.1(2)
C(12)−C(11)−C(10)	113.2(3)	N(13)−C(12)−C(11)	111.8(3)
N(14)−N(13)−C(12)	117.0(3)	N(15)−N(14)−N(13)	170.2(5)

However, the two peaks at δ_H = 0.39 ppm with satellites ($^2J_{Pt,CH} \approx 68$ Hz) in **9a/b** are somewhat confusing. The $^1H\{^{31}P\}$ NMR spectra reveal that the signals are not from the inequivalent CH_3 groups but are a doublet ($^3J_{P,CH} \approx 2$ Hz) due to the coupling of the equivalent methyl groups with either a *trans* or a *cis* phosphorus atom; it is not clear why only one coupling is observed.

Slow diffusion of petroleum ether (b.p. 60−80 °C) into a solution of **10b** in CH_2Cl_2 gave colourless crystals suitable for X-ray analysis (Figure 2 and Table 6). Figure 2 (top) reveals a platinum coordinated in a square plane with a maximum deviation of 0.04 Å for the P(14)−P(15)−C(40A)−Cl(1A)−Pt(1) mean plane. The six-membered chelate ring is chair-like, with the N(13)−C(14)−C(15) plane heavily folded above (72°) and the P(14)−Pt(1)−P(15) plane slightly below (15°) the mean plane P(14)−P(15)−C(14)−C15) (mean deviation 0.03 Å). As shown in Figure 2 (bottom), both the Watson−Crick [N(6)−H(6A)···N(1A); d(D···A) 3.069(10) Å, d(H···A)



Scheme 2. Coordination of **La** and **Lb** to transition metals; i) $[MX_2(cod)]$ (M = Pd, Pt; X = Cl, CH_3), CH_2Cl_2, 2 h; ii) 2[AuCl(tht)], CH_2Cl_2, 2 h

2.12 Å, ∠(DHA) 164 (4)°] and Hoogsteen [N(6)−H(6B)···N(7B); d(D···A) 3.04(10) Å, d(H···A) 2.14 Å, νDHA 152(6)°] types of intermolecular hydrogen bonding between adjacent molecules are found in the crystal. A quarter molecule of solvate hexane was also observed. For clarity, the solvate molecule is omitted from the figure.

Conclusion

We report here two [(diphenylphosphanyl)methyl]amino analogues of adenosine **La/b** and their chalcogenide derivatives. **La** and **Lb** proved to be good didentate ligands towards late transition metals to give a series of didentate chelate complexes and didentate bridging complexes. All the compounds retain a free adenine moiety for complementary hydrogen bonding. Further studies on the interaction of these compounds with DNA and bioactivities are underway.

Experimental Section

General: All solvents and reagents were purchased from either Aldrich or Lancaster. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Diethyl ether and tetrahydrofuran were purified by reflux over sodium/benzophenone and distillation under nitrogen. Ligand preparations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Coordination reactions and workup were performed in dry solvents. Ph_2PCH_2OH,[32] $[MX_2(cod)]$ (M = Pd, Pt; X = Cl; cod = cycloocta-1,5-diene)[33] and [AuCl(tht)] (tht = tetrahydrothiophene)[34] were prepared following literature procedures.

Infrared spectra were recorded as KBr discs on a Perkin−Elmer system 2000 spectrometer. ^1H NMR spectra (300 MHz) were recorded on a Varian Gemini 2000 spectrometer, $^{31}P\{^1H\}$ NMR spectra at 121.4 MHz (referenced to external 85% H_3PO_4) and $^{13}C\{^1H\}$ NMR spectra at 67.9 MHz on a JEOL GSX 270 spectrometer, and $^1H\{^{31}P\}$ NMR and 2D NMR (^1H-^{13}C heteronuclear correlation experiment) on a Bruker Advance 300. Microanalyses were performed by the University Service within this Department and fast atom bombardment (FAB) or chemical ionization (CI) mass spectra by the EPSRC Mass Spectrometer Service (Swansea, UK). Precious metal salts were provided on loan by Johnson Matthey Plc.

9-(3-Chloropropyl)adenine (1b):[15−17] 1-Bromo-3-chloropropane was added to adenine (27 g, 199.8 mmol) and anhydrous K_2CO_3 in anhydrous DMF (300 mL). The mixture was stirred under an atmosphere of nitrogen for 4 days. The resultant suspension was filtered and the residue was washed with CH_2Cl_2 (3 × 30 cm^3). The combined filtrates were evaporated to dryness by rotary evaporation. The crude product was washed by water (600 cm^3) with sonication in an ultrasonic bath. Recrystallisation from ethanol (220 cm^3) gave 28.0 g of the white product. The mother liquor was concentrated and recrystallised three times to give three additional crops (5.92 g). Total yield: 33.92 g, 80.2%. $C_8H_{10}ClN_5$ (211.7): calcd. C 45.40, H 4.76, N 33.09; found C 45.79, H 4.54, N 33.34. IR (KBr disc): $\tilde{\nu}$ = 3289m cm^{-1}, 3114m, 1667vs, 1603vs. CIMS: *m/z* = 212 $[M + H]^+$, 176 $[M - Cl]^+$. EIMS: *m/z* = 211 $[M]^+$, 176 $[M - Cl]^+$, 148 $[M - CH_2CH_2Cl]^+$.

9-(3-Azidopropyl)adenine (2b):[18] Compound **1b** (20 g, 94.5 mmol) and sodium azide (18.4 g, 283 mmol) were mixed in DMF (150 cm^3). The mixture was stirred at 80 °C for 24 h, cooled to room temperature and then filtered. The solid was washed with CH_2Cl_2 (3 × 30 cm^3). The combined filtrates were vacuumed to almost dryness under rotary evaporation. The residue was taken up in H_2O (200 cm^3) with sonication. The crude product was filtered off and washed with water (3 × 30 cm^3). The combined aqueous layer was extracted with CH_2Cl_2 (3 × 600 cm^3). Removal of the solvent from the extracts led to another crop of crude product. The two crops of crude product were recrystallised from EtOH (300 cm^3) to gave 12.17 g of white solid. Further recrystallisation of the mother liquor gave another 3.90 g of product. Total yield: 16.07 g, 77.7%. $C_8H_{10}N_8$ (218.9): calcd. C 44.03, H 4.62, N 51.35; found C 44.13, H 4.44, N 52.06. IR (KBr disc): $\tilde{\nu}$ = 3302m cm^{-1}, 3140s, 2108vs, 1664vs, 1600vs. CIMS: *m/z* = 220 $[M + H]^+$, 219 $[M]^+$, 191 $[M - N_2]^+$, 163 $[M - CH_2N_3]^+$, 136 $[M - CH_2CH_2CH_2N_3]^+$.

9-(3-Aminopropyl)adenine (3b):[19] 9-(3-Azidoproyl)adenine (10 g, 5.76 mmol) was dissolved in methanol (700 cm^3). To this solution was added palladium on carbon (10%, 5.0 g) and hydrogen gas was bubbled in. Monitoring by TLC (SiO_2, CH_2Cl_2/ MeOH = 80:20) showed that the reaction was complete after about 22 h. The catalyst was removed by filtration through celite. Solvent removal from the filtrate by rotary evaporation gave the product as a white solid. Yield: 7.60 g, 83%. $C_8H_{12}N_6$ (192.2): calcd. C 49.99, H 6.29,

Table 5. NMR spectroscopic data in CD_2Cl_2[a] or $CDCl_3$[b] for complexes of **La** and **Lb**

Entry	NMR δ_P (ppm) & J (Hz)	δ_H (ppm)	J (Hz)	Entry	NMR δ_P (ppm) & J (Hz)	δ_H (ppm)	δ_H (ppm)
		8.22 (br. s, 1 H, C^2-H)				8.20 (br. s, 1 H, C^2-H)	
		7.79−7.39 (m, 20 H, PhH)				7.89−7.46 (m, 20 H, PhH)	
		6.52 (br. s, 1 H, C^8-H				7.37 (br. s, 1 H, C^8-H)	
7a[a]	9.37 (s)	5.67 (br. s, 2 H, NH_2)		**7b**[a]	9.01 (s)	5.46 (br. s, 2 H, NH_2)	
		3.90 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 6			3.79 (t, 2 H,AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
		3.46 (dd, 4 H, PCH_2)	$^2J_{P,CH}$ = 3 or 5 $^4J_{P,CH}$ = 3 or 5			3.42 (dd, 4 H, PCH_2)	$^2J_{P,CH}$ = 3 or 5 $^4J_{P,CH}$ = 3 or 5
		3.08 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 6			2.61 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 7
						1.85 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
						8.28 (br. s, 1 H, C^2-H)	
		8.02 (s, 1 H, C^2-H)				7.91−7.44 (m, 20 H, PhH)	
		7.81−7.33 (m, 20 H, PhH)				7.25 (br. s, 1 H, C^8-H)	
		6.37 (s, 1 H, C^8-H)				5.51 (br. s, 2 H, NH_2)	
8a[a]	−7.07 (s) $^1J_{Pt,P}$ = 3416	5.61 (br. s, 2 H, NH_2)		**8b**[b]	−7.13 (s) $^1J_{Pt,P}$ = 3416	3.74 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
		3.90 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 6			3.48 (d, 4 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 3, $^3J_{Pt,CH}$ = 37
		3.51 (d, 4 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 3			2.57 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 7
		3.01 (t, 2 H, CH_2NCH_2P)	$^3J_{Pt,PCH}$ = 38			1.86 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
						8.28 (s, 1 H, C^2-H)	
		8.02 (s, 1 H, C^2-H)				7.77−7.69 (m, 20 H, PhH)	
		7.62−7.33 (m, 20 H, PhH)				6.83 (s, 1 H, C^8-H)	
		5.90 (s, 1 H, C^8-H)				5.47 (br. s, 2 H, NH_2)	
9a[b]	2.21 (s) $^1J_{Pt,P}$ = 1782	5.68 (br. s, 2 H, NH_2)		**9b**[b]	1.70 (s) $^1J_{Pt,P}$ = 1784	3.57 (d, 2 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 3 $^3J_{Pt,CH}$ = 16
		3.83 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 6			3.38 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
		3.51 (br. s, 4 H, PCH_2)	$^3J_{Pt,CH}$ = 14			2.41 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 7
		2.88 (t, 2 H, CH_2NCH_2P)	$^3J_{P,H}$ = 2			1.68 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
		0.39 (d, 6 H, CH_3)	$^2J_{Pt,H}$ = 68			0.39 (d, 6 H, CH_3)	$^3J_{P,CH}$ = 2, $^2J_{Pt,CH}$ = 69
						8.19 (s, 1 H, C^2-H)	
		8.20 (s, 1 H, C^2-H)				7.82−7.38 (m, 20 H, PhH)	
		7.72−7.20 (m, 20 H, PhH)				7.11 (s, 1 H, C^8-H)	
		6.22 (s, 1 H, C^8-H)				5.42 (br. s, 2 H, NH_2)	
		5.86 (br. s, 2 H, NH_2)				3.57 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
10a[a]	3.97 (d) $^1J_{Pt,P}$ = 4169	3.85 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 6	**10b**[a]	4.47 (d) $^1J_{Pt,P}$ = 4211	3.52 (d, 2 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 3 $^3J_{Pt,PCH}$ = 45
	0.96 (d) $^1J_{Pt,P}$ = 1648, $^2J_{P,P}$ = 23	3.57 (d, 2 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 4, $^3J_{Pt,PCH}$ = 45		0.69(d) $^1J_{Pt,P}$ = 1637, $^2J_{P,P}$ = 21	3.49 (d, 2 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 3 $^3J_{Pt,PCH}$ = 16
		3.52 (d, 2 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 4, $^3J_{Pt,PCH}$ = 15			2.45 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 7
		2.57 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 6			1.71 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
		0.33 (dd, 3 H, CH_3)	$^3J_{P,CH}$ = 4, $^3J_{P'CH}$ = 7 $^2J_{Pt,CH}$ = 54			0.32 (dd, 3 H, CH_3)	$^3J_{P,CH}$ = 4, $^3J_{P'CH}$ = 7, $^2J_{PtCH}$ = 54
						8.25 (s, 1 H, C^2-H)	
		8.25 (s, 1 H, C^2-H)				7.76 (s, 1 H, C^8-H)	
		7.60 (s, 1 H, C^8-H)				7.71−7.41(m, 20 H, PhH)	
		7.56−7.43 (m, 20 H, PhH)				5.63 (br. s, 2 H, NH_2)	
11a[b]	17.41 (s)	5.76 (br. s, 2 H, NH_2)		**11b**[b]	17.34 (s)	4.29 (d, 4 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 1
		4.29 (d, 4 H, PCH_2)	$^2J_{P,CH}$ or $^4J_{P,CH}$ = 1			4.01 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
		3.94 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 6			2.90 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 7
		3.42 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 6			1.79 (quint, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 7
		8.11 (s, 1 H, C^2-H)					
		7.81−7.39 (m, 20 H, PhH + C^8-H)					
		5.47 (br. s, 2 H, NH_2)					
		5.03 (d, 4 H, ArH of Cy)	$^3J_{CH,CH}$ = 6				
		4.94 (d, 4 H, ArH of Cy)	$^3J_{CH,CH}$ = 6				
12a[a]	20.10 (s)	3.71 (br. s, 4 H, PCH_2)					
		3.59 (t, 2 H, AdeCH_2CH_2)	$^3J_{CH,CH}$ = 6				
		2.37 [sept, 2 H, $CH(CH_3)_2$]	$^3J_{CH,CH}$ = 6				
		2.07 (t, 2 H, CH_2NCH_2P)	$^3J_{CH,CH}$ = 6				
		1.67 (s, 6 H, CH_3)					
		0.85 [d, 12 H, $CH(CH_3)_2$]	$^3J_{CH,CH}$ = 6				

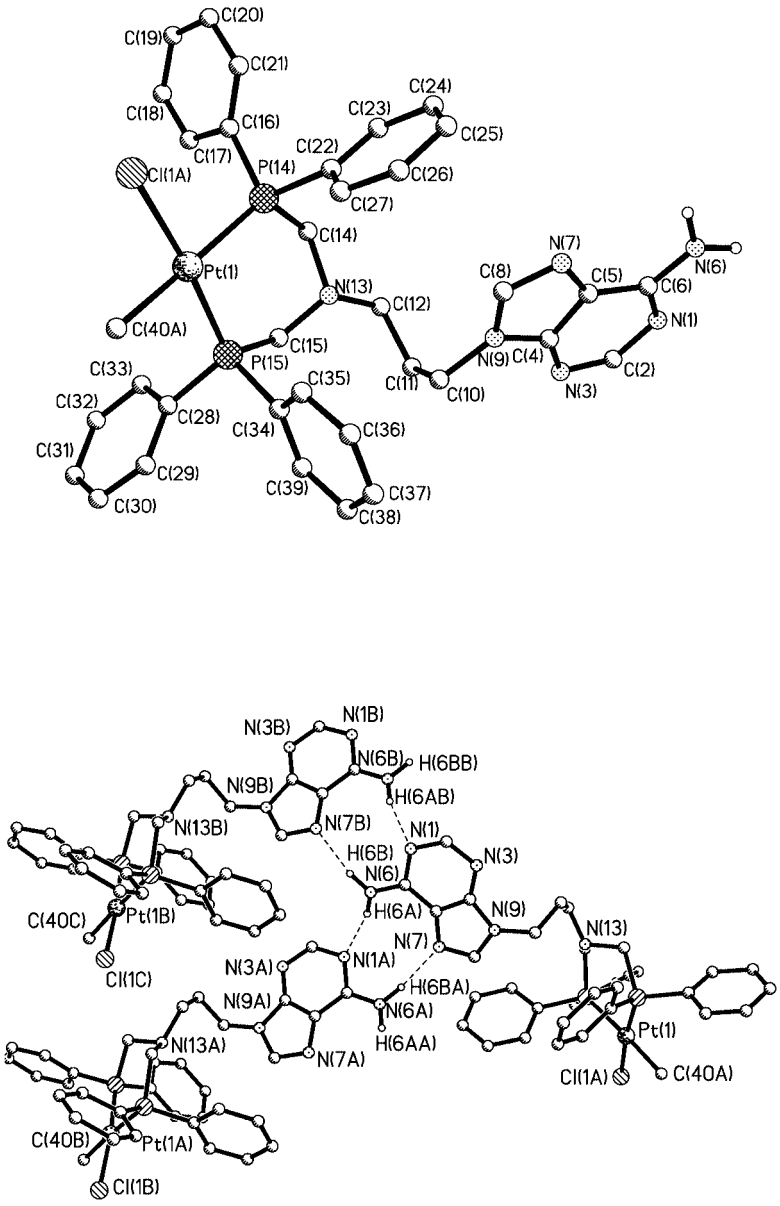


Figure 2. (top) Molecular structure of complex **10b**; (bottom) crystal structure of complex **10b** showing part of the hydrogen bonding

N 43.72; found C 49.37, H 6.28, N 42.73. IR (KBr disc): $\tilde{\nu}$ = 3349 m cm^{-1}, 3282s, 3112s, 1684vs, 1607vs. EIMS: *m*/*z* = 192 $[M]^+$.

9-(2-{Bis[(diphenylphosphanoyl)methyl]amino}ethyl)adenine (La): To a solution of 9-(2-aminoethyl)adenine (1.150 g, 6.45 mmol) in acetonitrile (150 cm^3) was added Ph_2PCH_2OH (2.79 g, 12.90 mmol). The mixture was refluxed overnight and then concentrated in vacuo until the solution became opaque (ca. 20 cm^3). Cooling in a fridge overnight led to the precipitation of the product. Subsequent filtration, and washing of the precipitate with cold acetonitrile (3 × 5 cm^3) and cold Et_2O (3 × 30 cm^3) gave the product as a white solid. Yield: 2.14 g, 57.9%. $C_{33}H_{32}N_6P_2$ (574.6): calcd. C 68.98, H 5.61, N 14.63; found C 67.54, H 5.47, N 13.90. IR (KBr disc): $\tilde{\nu}$ = 3315m cm^{-1}, 3136m, 1648vs, 1598vs, 742s, 696vs. ESMS$^+$: *m*/*z* = 613 $[M + K]^+$, 597 $[M + Na]^+$, 575 $[M + H]^+$.

9-(2-{Bis[(diphenylphosphanyl)methyl]amino}ethyl)adenine (4a): Aqueous hydrogen peroxide (92 μL, 811 μmol, 30%) was added to a solution of **La** (231 mg, 402 μmol) in THF (40 cm^3). The reaction mixture was stirred at 0−5 °C for 2 h, dried over molecular sieves and then passed through a short celite pad. The filtrate was concentrated to ca. 1 cm^3 by rotary evaporation. Et_2O (20 cm^3) was then added to precipitate the product, and filtration, washing with Et_2O (3 × 1 cm^3) and drying in vacuo gave a white solid. Yield: 222 mg, 92%. $C_{33}H_{32}N_6O_2P_2$ (606.6): calcd. C 65.34, H 5.32, N 13.85; found C 62.49, H 5.90, N 12.02. IR (KBr disc): $\tilde{\nu}$ = 3326m cm^{-1}, 3179m, 1648vs, 1599s, 1178vs, 718vs, 696vs. FABMS$^+$: *m*/*z* = 629 $[M + Na]^+$, 607 $[M + H]^+$.

9-(2-{Bis[(diphenylthiophosphanoyl)methyl]amino}ethyl)adenine (5a): Elemental sulfur (35 mg, 1.06 mmol) was added to a solution of **La** (300 mg, 522 μmol) in THF (20 cm^3). The reaction mixture was refluxed for 2 h and then concentrated to ca. 1 cm^3 by rotary evaporation. Et_2O (20 cm^3) was added to precipitate the product, and filtration, washing with Et_2O (3 × 1 cm^3) and drying in vacuo gave a white solid. Yield: 300 mg, 88%. $C_{33}H_{32}N_6P_2S_2$ (638.7): calcd. C 62.05, H 5.05, N 13.16; found C 59.76, H 5.09, N 14.41.

Table 6. Selected bond lengths (Å) and angles (°) in compound **10b**

Pt(1)−Cl(1A)	2.337(4)	Pt(1)−C(40A)	2.017(5)
Pt(1)−P(14)	2.286(2)	Pt(1)−P(15)	2.219(2)
P(14)−C(14)	1.840(9)	P(15)−C(15)]	1.830(9)
C(14)−N(13)	1.470(10)	C(15)−N(13)	1.453(9)
C(12)−N(13)	1.468(10)	C(11)−C(12)	1.511(11)
C(11)−C(10)	1.496(11)	C(10)−N(9)	1.483(10)
N(9)−C(4)	1.376(10)	N(9)−C(8)	1.356(10)
C(8)−N(7)	1.317(10)	N(7)−C(5)	1.360(10)
C(6)−N(6)	1.333(11)	N(1)−C(6)	1.370(11)
C(6)−C(5)	1.431(12)	C(5)−C(4)	1.389(11)
C(4)−N(3)	1.310(10)	N(3)−C(2)	1.315(10)
C(2)−N(1)	1.363(10)		

C(40A)−Pt(1)−P(15)	86.9(8)	C(40A)−Pt(1)−Cl(1A)	88.0(8)
Cl(1A)−Pt(1)−P(14)	89.88(15)	P(14)−Pt(1)−P(15)	95.27(9)
Pt(1)−P(14)−C(14)	116.6(3)	P(14)−C(14)−N(13)	112.0(6)
C(14)−N(13)−C(15)	110.1(7)	N(13)−C(15)−P(15)	112.0(6)
C(15)−P(15)−Pt(1)	115.6(3)	N(13)−C(12)−C(11)	113.3(8)
N(13)−C(12)−C(11)	113.3(8)	N(9)−C(10)−C(11)	112.3(8)
C(4)−N(9)−C(8)	106.4(7)	N(9)−C(8)−N(7)	114.3(9)]
C(8)−N(7)−C(5)	102.6(8)	N(9)−C(4)−C(5)	103.7(8)
N(7)−C(5)−C(4)	112.9(8)	C(4)−N(3)−C(2)	112.7(8)
N(3)−C(4)−C(5)	127.5(8)	C(2)−N(1)−C(6)	117.2(8)
N(3)−C(2)−N(1)	128.8(9)	C(6)−C(5)−C(4)	115.8(8)
N(1)−C(6)−C(5)	117.9(8)		

IR (KBr disc): $\tilde{\nu}$ = 3320m cm^{-1}, 3170w, 1638vs, 1597s, 705s, 692s. FABMS$^+$: *m*/*z* = 661 [M + Na]$^+$, 639 [M + H]$^+$.

9-(2-{Bis[(diphenylselenophosphanoyl)methyl]amino}ethyl)adenine (6a): Elemental selenium (55 mg, 696 μmol) was added to a solution of **La** (200 mg, 340 μmol) in THF (20 cm^3). The reaction mixture was refluxed for 2 h. After cooling, the mixture was passed through celite. The filtrate was concentrated to ca. 1 cm^3 by rotary evaporation. Et_2O (20 cm^3) was added to precipitate the product, and filtration, washing with Et_2O (3 × 1 cm^3) and drying in vacuo gave a white solid. Yield: 190 mg, 74.5%. $C_{33}H_{32}N_6P_2Se_2$ (732.5): calcd. C 54.11, H 4.40, N 11.47; found C 53.87, H 3.82, N 12.50. IR (KBr disc): $\tilde{\nu}$ = 3333m cm^{-1}, 3188m, 1654vs, 1595vs, 746m, 690s. FABMS$^+$: *m*/*z* = 757 [M + Na]$^+$, 735 [M + H]$^+$.

9-(3-{Bis[(diphenylphosphanoyl)methyl]amino}propyl)adenine (Lb): Ph_2PCH_2OH (3.566 g, 16.5 mmol) was added to a solution of 9-(2-aminoethyl)adenine (1.46 g, 7.60 mmol) in acetonitrile (300 cm^3). The mixture was refluxed overnight and then concentrated in vacuo to ca. 20 cm^3 until a white solid precipitated. The solvent was then pipetted off. The solid was washed with CH_3CN (2 × 20 cm^3) and Et_2O (2 × 50 cm^3). Drying in vacuo gave the product as a white solid. Yield: 3.25 g, 55%. $C_{34}H_{34}N_6P_2$ (588.6): calcd. C 69.38, H 5.82, N 14.28; found C 67.96, H 5.83, N 15.01. IR (KBr disc): $\tilde{\nu}$ = 3297m cm^{-1}, 3134m, 1667vs, 1599vs, 743s, 697vs. ESMS$^+$: *m*/*z* = 611 [M + Na]$^+$, 589 [M + H]$^+$.

9-(3-{Bis[(diphenylphosphanoyl)methyl]amino}propyl)adenine (4b): Aqueous hydrogen peroxide (77 μL, 679 μmol, 30%) was added to a solution of **Lb** (200 mg, 340 μmol) in THF (40 cm^3). The reaction mixture was stirred at 0−5 °C for 2 h, dried over molecular sieves and then passed through a short celite pad. The filtrate was concentrated to ca. 1 cm^3 by rotary evaporation. Et_2O (20 cm^3) was added to precipitate the product, and filtration, washing with Et_2O (3 × 1 cm^3) and drying in vacuo gave a white solid. Yield: 182 mg, 86%. $C_{34}H_{34}N_6O_2P_2$ (620.6): calcd. C 65.80, H 5.52, N 13.54; found C 62.87, H 5.94, N 11.42. IR (KBr disc): $\tilde{\nu}$ = 3324m cm^{-1}, 3180m, 1648vs, 1599vs, 1573m, 1176s, 718s, 695s. FABMS$^+$: *m*/*z* = 643 [M + Na]$^+$, 621 [M + H]$^+$.

9-(3-{Bis[(diphenylthiophosphanoyl)methyl]amino}propyl)adenine (5b): Elemental sulfur (22 mg, 688 μmol) was added to a solution of **Lb** (200 mg, 340 μmol) in THF (20 cm^3). The reaction mixture was refluxed for 2 h and concentrated to ca. 1 cm^3 by rotary evaporation. Et_2O (20 cm^3) was added to precipitate the product, and filtration, washing with Et_2O (3 × 1 cm^3) and drying in vacuo gave a white solid. Yield: 191 mg, 86%. $C_{34}H_{34}N_6P_2S_2$ (652.8): calcd. C 62.56, H 5.25, N 12.87; found C 60.77, H 4.71, N 13.70. IR (KBr disc): $\tilde{\nu}$ = 3315m cm^{-1}, 3173w, 1638vs, 1597vs, 705, 692s. FABMS$^+$: *m*/*z* = 675 [M + Na]$^+$, 653 [M + H]$^+$.

9-(3-{Bis[(diphenylselenophosphanoyl)methyl]amino}propyl)adenine (6b): Elemental selenium (54 mg, 684 μmol) was added to a solution of ligand **2** (200 mg, 340 μmol) in THF (20 cm^3). The reaction mixture was refluxed for 2 h and passed through a short celite pad. The filtrate was concentrated to ca. 1 cm^3 by rotary evaporation. Et_2O (20 cm^3) was added to precipitate the product, and filtration, washing with Et_2O (3 × 1 cm^3) and drying in vacuo gave a white solid. Yield: 176 mg, 69%. $C_{34}H_{34}N_6P_2Se_2$ (746.6): calcd. C 54.70, H 4.59, N 11.26; found C 54.31, H 4.46, N 11.67. IR (KBr disc): $\tilde{\nu}$ = 3312m cm^{-1}, 3162m, 1638vs, 1597s, 746m, 691vs. FABMS$^+$: *m*/*z* = 769 [M + Na]$^+$, 747 [M + H]$^+$.

[PdCl$_2$(La)] (7a): [PdCl$_2$(cod)] (48 mg, 169 μmol) was added to a solution of **La** (100 mg, 169 μmol) in CH_2Cl_2. The reaction mixture was stirred at room temperature for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as a yellow solid. Yield: 102 mg, 80%. $C_{33}H_{32}Cl_2N_6P_2Pd$ (751.9): calcd. C 52.78, H 4.29, N 11.19; found C 54.71, H 5.00, N 9.81. IR (KBr disc): $\tilde{\nu}$ = 3387m cm^{-1}, 3203w, 1637vs, 1594s, 740s, 691s. ESMS$^+$: *m*/*z* = 790 [M + K]$^+$, 774 [M + Na]$^+$, 715 [M − HCl]$^+$, 697 [M − NH$_3$ − HCl]$^+$, 679 [M − HCl − Cl]$^+$.

[PdCl$_2$(Lb)] (7b): [PdCl$_2$(cod)] (69 mg, 242 μmol) was added to a solution of **Lb** (143 mg, 243 μmol) in CH_2Cl_2 (10 cm^3). A yellow precipitate appeared immediately. The reaction mixture was stirred at room temperature for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as a yellow solid. Yield: 177 mg, 95%. $C_{34}H_{34}Cl_2N_6P_2Pd$ (765.9): calcd. C 53.32, H 4.47, N 10.97; found C 49.74, H 4.03, N 10.81. IR (KBr disc): $\tilde{\nu}$ = 3314m cm^{-1}, 3144m, 1637vs, 1603s, 737s, 670s, 305w, 291m. ESMS$^+$: *m*/*z* = 789 [M + Na]$^+$, 767 [M + H]$^+$, 729 [M − Cl]$^+$, 694 [M − HCl − Cl]$^+$.

[PtCl$_2$(La)] (8a): [PtCl$_2$(cod)] (65 mg, 171 μmol) was added to a solution of **La** (102 mg, 177 μmol) in CH_2Cl_2 (20 cm^3). The reaction mixture was stirred for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as a white solid. Yield: 156 mg, 91%. $C_{33}H_{32}Cl_2N_6P_2Pt$ (840.6): calcd. C 47.15, H 3.84, N 10.00; found C 47.01, H 3.10, N 9.74. IR (KBr disc): $\tilde{\nu}$ = 3386m cm^{-1}, 3185w, 1637vs, 1596s, 741s, 692s, 313w, 286w. ESMS$^+$: *m*/*z* = 804 [M − HCl]$^+$.

[PtCl$_2$(Lb)] (8b): [PtCl$_2$(cod)] (78 mg, 208 μmol) was added to a solution of **Lb** (124 mg, 211 μmol) in CH_2Cl_2 (20 cm^3). A white precipitate appeared immediately. The reaction mixture was stirred for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as a white solid. Yield: 166 mg, 93%. $C_{34}H_{34}Cl_2N_6P_2Pt$ (854.6): calcd. C 47.34, H 3.46, N

10.32; found C 47.78, H 4.01, N 9.83. IR (KBr disc): $\tilde{\nu}$ = 3338m cm^{-1}, 3163m, 1632vs, 1601s, 740s, 691vs, 314w, 292m. FABMS$^+$: m/z = 819 [M − Cl]$^+$, 783 [M − 2Cl]$^+$.

[Pt(CH$_3$)$_2$(La)] (9a): [Pt(CH$_3$)$_2$(cod)] (56 mg, 168 μmol) was added to a solution of **La** (100 mg, 174 μmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as a white solid. Yield: 124 mg, 62%. $C_{35}H_{38}N_6P_2Pt$ (799.8): calcd. C 52.56, H 4.79, N 10.51; found C 51.64, H 4.24, N 10.19. IR (KBr disc): $\tilde{\nu}$ = 3323m cm^{-1}, 3179w, 1638vs, 1594s, 737m, 696s. ESMS$^+$: m/z = 825 [M + Na]$^+$, 800 [M]$^+$, 783 [M − CH_3]$^+$.

[Pt(CH$_3$)$_2$(Lb)] (9b): [Pt(CH$_3$)$_2$(cod)] (77 mg, 234 μmol) was added to a solution of **Lb** (138 mg, 234 μmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as a white solid. Yield: 154 mg, 82%. $C_{36}H_{40}N_6P_2Pt$ (813.8): calcd. C 53.13, H 4.95, N 10.33; found C 52.41, H 4.52, N 10.66. IR (KBr disc): $\tilde{\nu}$ = 3328m cm^{-1}, 3163w, 1637vs, 1598s, 737m, 695vs. FABMS$^+$: m/z = 798 [M − CH_3]$^+$, 783 [M − H − 2CH_3]$^+$.

[PtCl(CH$_3$)(La)] (10a): [PtCl(CH$_3$)(cod)] (90 mg, 254 μmol) was added to a solution of **La** (147 mg, 254 μmol) in CH_2Cl_2 (20 cm^3). A white solid precipitated out gradually. The reaction mixture was stirred for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as an off-white solid. Yield: 190 mg, 91%. $C_{34}H_{35}ClN_6P_2Pt$ (820.2): calcd. C 49.79, H 4.30, N 10.25; found C 51.18, H 4.13, N 9.86. IR (KBr disc): $\tilde{\nu}$ = 3320w cm^{-1}, 3163w, 1638vs, 1595s, 739s, 694vs. FABMS$^+$: m/z = 804 [M − CH_3]$^+$, 785 [M − Cl]$^+$.

[PtCl(CH$_3$)(Lb)] (10b): [PtCl(CH$_3$)(cod)] (70 mg, 230 μmol) was added to a solution of **Lb** (117 mg, 230 μmol) in CH_2Cl_2 (10 cm^3). A white solid precipitated out gradually. The reaction mixture was stirred for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with light petroleum ether (3 × 1 cm^3) and Et_2O (3 × 1 cm^3) gave the product as an off-white solid. Yield: 149 mg, 91%. $C_{35}H_{37}ClN_6P_2Pt$ (834.2): calcd. C 50.39, H 4.47, N 10.07; found C 49.70, H 4.01, N 10.44. IR (KBr disc): $\tilde{\nu}$ = 3323m cm^{-1}, 3158m, 1636vs, 1600s, 738s, 694vs, 296m. FABMS$^+$: m/z = 798 [M − Cl]$^+$, 784 [M − Cl − CH_3]$^+$.

[(AuCl)$_2$(La)] (11a): [AuCl(tht)] (80 mg, 250 μmol) was added to a solution of **La** (74 mg, 129 μmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred for 2 h and a solid precipitated out after ca. 10 min. The resulting mixture was concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with Et_2O (3 × 1 cm^3) gave the product as a white solid. Yield: 124 mg, 96%. $C_{33}H_{32}Au_2Cl_2N_6P_2$ (1039.4): calcd. C 38.13, H 3.10, N 8.09; found C 38.14, H 2.53, N 8.25. IR (KBr disc): $\tilde{\nu}$ = 3321m cm^{-1}, 3181w, 1639vs, 1596vs, 744s, 692s, 329m. FAB$^+$: m/z = 1003 [M − Cl]$^+$, 967 [M − 2Cl − H]$^+$.

[(AuCl)$_2$(Lb)] (11b): [AuCl(tht)] (80 mg, 250 μmol) was added to a solution of **Lb** (75 mg, 127 μmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred for 2 h and a solid precipitated out after ca.10 - min. The resulting mixture was concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with Et_2O (3 × 1 cm^3) gave the product as a white solid. Yield: 120 mg, 92%. $C_{34}H_{34}Au_2Cl_2N_6P_2$ (1053.5): calcd. C 39.18, H 3.25, N 7.98; found C 38.76, H 3.08, N 7.98. IR (KBr disc): $\tilde{\nu}$ = 3317m cm^{-1}, 3161m, 1638vs, 1595s, 744s, 691vs, 326s. FABMS$^+$: m/z = 1017 [M − Cl]$^+$, 982 [M − 2 Cl − H]$^+$.

[RuCl$_2$(η^6-*p*-CH$_3$C$_6$H$_4$*i*Pr)(La)] (12a): [RuCl(μ-Cl)(*p*-CH$_3$-C$_6$H$_4$*i*Pr)]$_2$ (52 mg, 85 μmol) was added to a solution of **La** (50 mg, 87 μmol) in CH_2Cl_2 (20 cm^3). The reaction mixture was stirred for 2 h and then concentrated to ca. 0.5 cm^3. Addition of Et_2O (10 cm^3), filtration and washing with Et_2O (3 × 1 cm^3) gave the product as an orange solid. Yield: 85 mg, 83%. $C_{53}H_{60}Cl_4N_6P_2Ru_2$ (1187.0): calcd. C 53.63, H 5.09, N 7.08; found C 52.22, H 5.11, N 6.96. IR (KBr disc): $\tilde{\nu}$ = 3338m cm^{-1}, 3187w, 3054m, 1631vs, 1595s, 1474s, 1437s, 746s, 696vs. FABMS$^+$: m/z = 1188 [M + H]$^+$, 1212 [M + Na]$^+$.

Table 7. Details of the X-ray data collections and refinements for compounds **2b** and **10b**

Compound	**2b**	**10b**·1/4C_6H_{14}
Empirical formula	$C_8H_{10}N_8$	$C_{36.50}H_{40.50}ClN_6P_2Pt$
Crystal colour, habit	Colourless, block	Colourless, block
Crystal dimensions/mm	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.01
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a/Å	15.2288(17)	7.9955(9)
b/Å	8.7153(10)	19.312(2)
c/Å	15.4248(16)	46.857(5)
U/Å^3	2047	7235
Z	8	8
M	218.24	855.73
Dc/g cm^{-3}	1.416	1.571
μ/mm^{-1}	0.100	4.076
F(000)	912	3412
Measured reflections	9475	29689
Independent reflections (R_{int})	1419(0.0876)	5187(0.1341)
Final *R*1, ω*R*2[$I > 2\sigma(I)$]	0.0456, 0.1036	0.0409, 0.0664

X-ray Crystallography: Table 7 lists details of data collections and refinements for **2b** and **10b**. Data were collected at room temperature using Mo-K_α radiation with a SMART system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy-atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least-squares based on F^2 using SHELXTL.[35] In complex **10b**, there is disorder of the chlorine and the methyl atoms attached to the platinum atom. The diagram in Figure 2 shows the major (70%) occupancy. CCDC-200672 (**2b**) and -200673 (**10b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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