Synthesis of a tri(organoplatinum) complex *via* the double directed lithiation of a mono(organoplatinum) precursor

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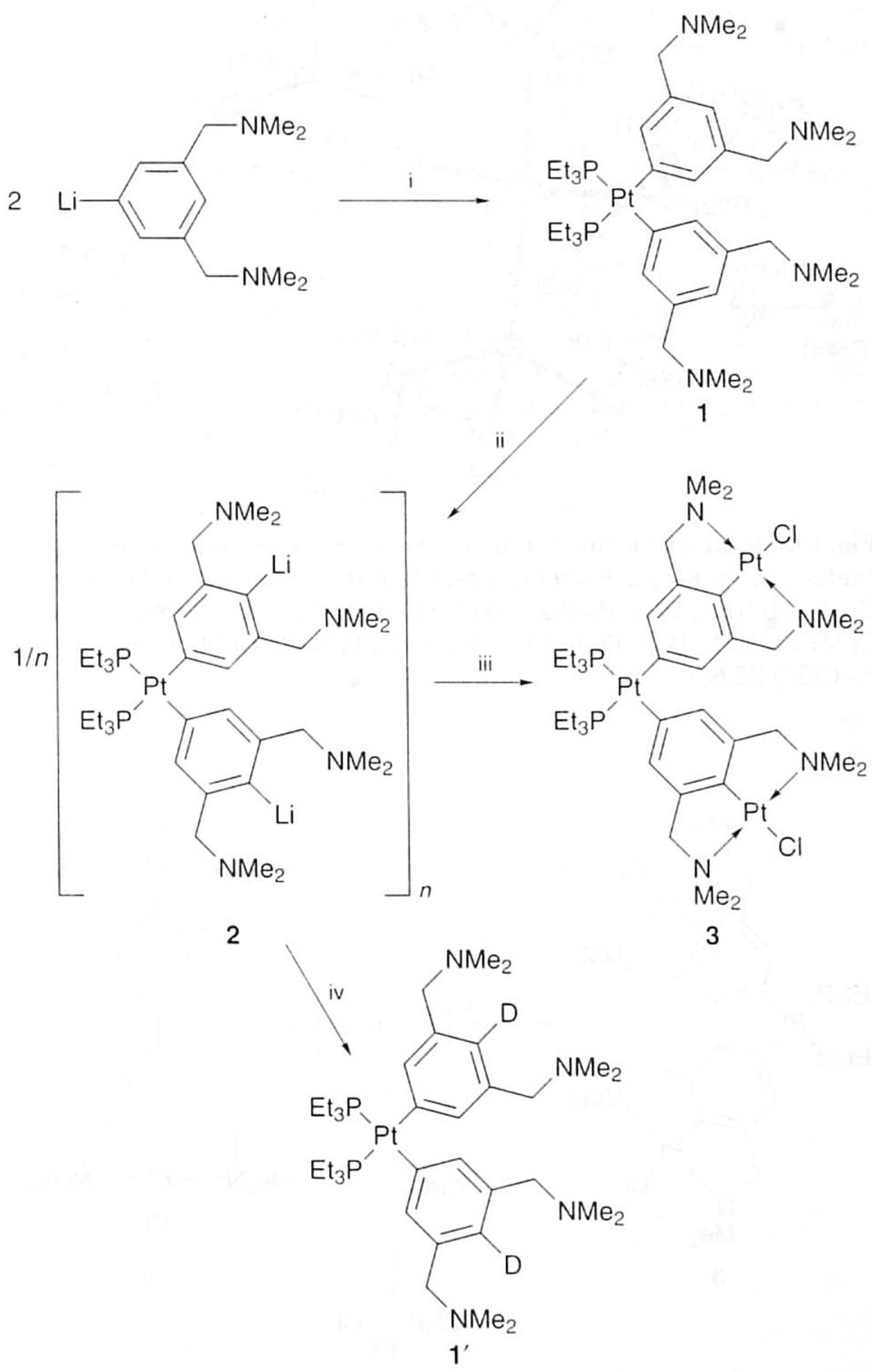
The new diarylplatinum complex *cis*-[Pt(PEt$_3$)$_2$\{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-3,5\}$_2$] 1, containing four free amine coordination sites, undergoes directed lithiation with Bu^{t}Li and subsequent transmetallation with [PtCl$_2$(SEt$_2$)$_2$] to give a triplatinum species 3 which reductively eliminates the diplatinum complex [ClPt\{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_2$–C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6\}PtCl] 4.

Organometallic complexes containing two or more metal centres (including polymers) linked by conjugated organic groups have received considerable attention due to their optical non-linearity and liquid crystalline behaviour.[1] Many efforts have focussed on the use of alkynyl groups to bridge the metal centres because they are conjugated (allowing communication between metals), rigidly one-dimensional (giving rise to spatially well defined species) and for their synthetic availability. We are interested in developing synthetic routes to multimetallic complexes with aryldiamines as bridging groups (Scheme 1) since these ligands are conjugated and should also give rise to well defined multimetallic complexes.[2]

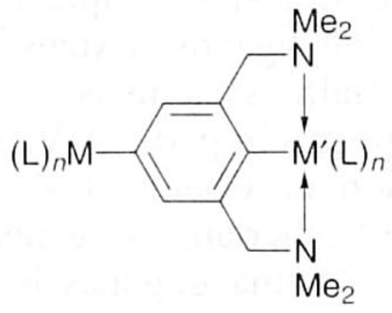
The simplest approach to the construction of these species, which should also allow the synthesis of *heterometallic* complexes, is stepwise attachment of metals to the aryl bridge. A common procedure for attaching a transition metal to an aryldiamine ligand system is *via* directed lithiation of the ligand with Bu^{n}Li or Bu^{t}Li, followed by transmetallation with a transition-metal salt or complex.[3] We now wish to report that this conventional process can also be applied when a transition metal is already attached to the aryl ring.

The new diarylplatinum complex **1** was prepared from the corresponding dichloro complex[4] and aryllithium[5] (Scheme 2) and was characterised by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis.† An X-ray crystal structure determination was conducted‡ which confirms the expected overall structure (see Fig. 1).

Interesting structural features are the two aryl rings which make angles of 71.9(3) and 86.9(3)° with the mean coordination plane of the platinum(II) centre, and the four dimethylaminomethyl arms positioned *meta* to the C$_{ipso}$ bonds. Importantly, **1** is soluble in pentane. The position of lithiation of conventional (purely organic) aryldiamines when treated with Bu^{n}Li or Bu^{t}Li has been found to be dependent on the solvent used: pentane or hexane are required for selective lithiation at the position between the two coordinating arms, whereas coordinating solvents such as diethyl ether or thf give rise to significant amounts of lithiation outside the arms.[6] Addition of 2 equiv. of Bu^{t}Li to a colourless pentane solution of **1** at −78 °C or at ambient temperature give an orange precipitate which, from its subsequent reactions, we assume to be the platinum dilithium species **2** (see Scheme 2). Since related 2,6-bis(dimethylaminomethyl)aryllithium complexes are known to be dimeric both in the solid state and in solution,[7] **2** is most likely a polymer or oligomer. Addition of CD$_3$OD to **2** gives the corresponding deuteriated product **1′** for which the ^{1}H NMR spectrum is identical to that of **1** minus the singlet for H *para* to C$_{ipso}$. Treatment of **2** with 2.2 equiv. of [PtCl$_2$(SEt$_2$)$_2$] in diethyl ether and subsequent work up gives the expected triplatinum complex



Scheme 2 *Reagents and conditions*: i, *cis*-[PtCl$_2$(PEt$_3$)$_2$]; ii, 2 Bu^{t}Li, pentane, iii, 2[PtCl$_2$(SEt$_2$)$_2$], Et$_2$O; iv, excess CD$_3$CD



Scheme 1 Aryldiamines as bridging ligands in multimetallic complexes

3, in 95% overall yield (>95% purity), which contains one central and two 'terminal' platinum centres (Scheme 2). Complex **3** was characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.† However, a satisfactory elemental analysis could not be obtained due to the unexpected instability of **3** in solution at ambient temperature. The attempted purification of **3** by crystallisation always resulted in the formation of a new organoplatinum complex **4**. This decomposition of **3** was monitored by ^{1}H and ^{31}P NMR spectroscopy in $CDCl_3$ solution and found to be due to reductive elimination (aryl coupling) leading to **4** (Scheme 3). The reaction was 95% complete based on **3** after 7 days at ambient temperature, as determined by ^{1}H NMR spectroscopy.

In addition to the biaryl **4**, a second product was formed which was *cis*-$[PtCl_2(PEt_3)_2]$, identified from its ^{1}H and ^{31}P NMR spectra, which presumably arises from reaction of an initially formed unsaturated zero-valent complex '$[Pt(PEt_3)_2]$' with the chloroform solvent. We are unaware of any preceding reports dealing specifically with the reaction between zero-valent platinum phosphine complexes with chloroform. However, complexes of type $[PtX_2(PEt_3)_2]$ (X = halide) have been observed as major final products in reactions between $[Pt(PEt_3)_3]$ with excess of a reactive alkyl halide.[8] Radical mechanisms have been shown to operate in such cases. The formation of **4** from complex **3** was also observed in non-chlorinated solvents, *e.g.* benzene, at approximately the same rate, but the identity of the other reaction products was not established in these cases. The diplatinum complex [ClPt{2,6-$(Me_2NCH_2)_2C_6H_2$–$C_6H_2(CH_2NMe_2)_2$-2,6}PtCl] **4** could be separated from *cis*-$[PtCl_2(PEt_3)_2]$ by washing with thf and was characterised by ^{1}H NMR spectroscopy, FABMS and elemental analysis.† The poor solubility of **4** precluded the measurement of its ^{13}C NMR spectrum. Although the reductive elimination of biaryls from $[Pt(PR_3)_2(Ar)_2]$ complexes is known,[9] its rate is highly dependent upon the nature of PR_3. Whilst PPh_3 complexes are found to undergo elimination at ambient temperature ($t_{1/2}$ = 3.89 h at 50 °C in toluene solution), PPh_2Me complexes are far less labile, and $[Pt(PEt_3)_2Ph_2]$ appears to be indefinitely stable.[4] We were therefore surprised at the instability of the PEt_3 complex **3**. Indeed, its monoplatinum precursor **1** shows no evidence of biaryl elimination after two weeks at room temperature in $CDCl_3$, as monitored by ^{1}H NMR spectroscopy. The reason for the observed difference in lability between complexes **1** and **3** is unlikely to be steric, since although the conformation of the dimethylaminomethyl arms will be very different in the two complexes, they are sufficiently far apart not to interfere strongly with each other. As for an electronic explanation, although a considerable number of complexes of type $[PtL_2(C_6H_4X\text{-}4)_2]$ (X = electron donor/acceptor) have been studied,[10] the electronic effect of the substituent X on reductive elimination is not clear; both complexes where X is a donor and where X is an acceptor give stable, isolable products. It has been shown, however, that complexes of type $[PtL_2(C_6H_4X\text{-}4)(C_6H_4Y\text{-}4)]$ (X = electron donor, Y = electron acceptor) are extremely susceptible to reductive elimination.[10b] Given the limited stability of complex **3**, a subtle donor–acceptor relationship may therefore exist between the two aryl rings, through the central platinum centre, in the sense that through covalent σ- and π-interactions with the terminal platinum(II) centres, the bridging aryl groups become more polarisable. This may be sufficient to stabilise the hypothesised donor–acceptor interaction in the transition state of reductive biphenyl elimination.

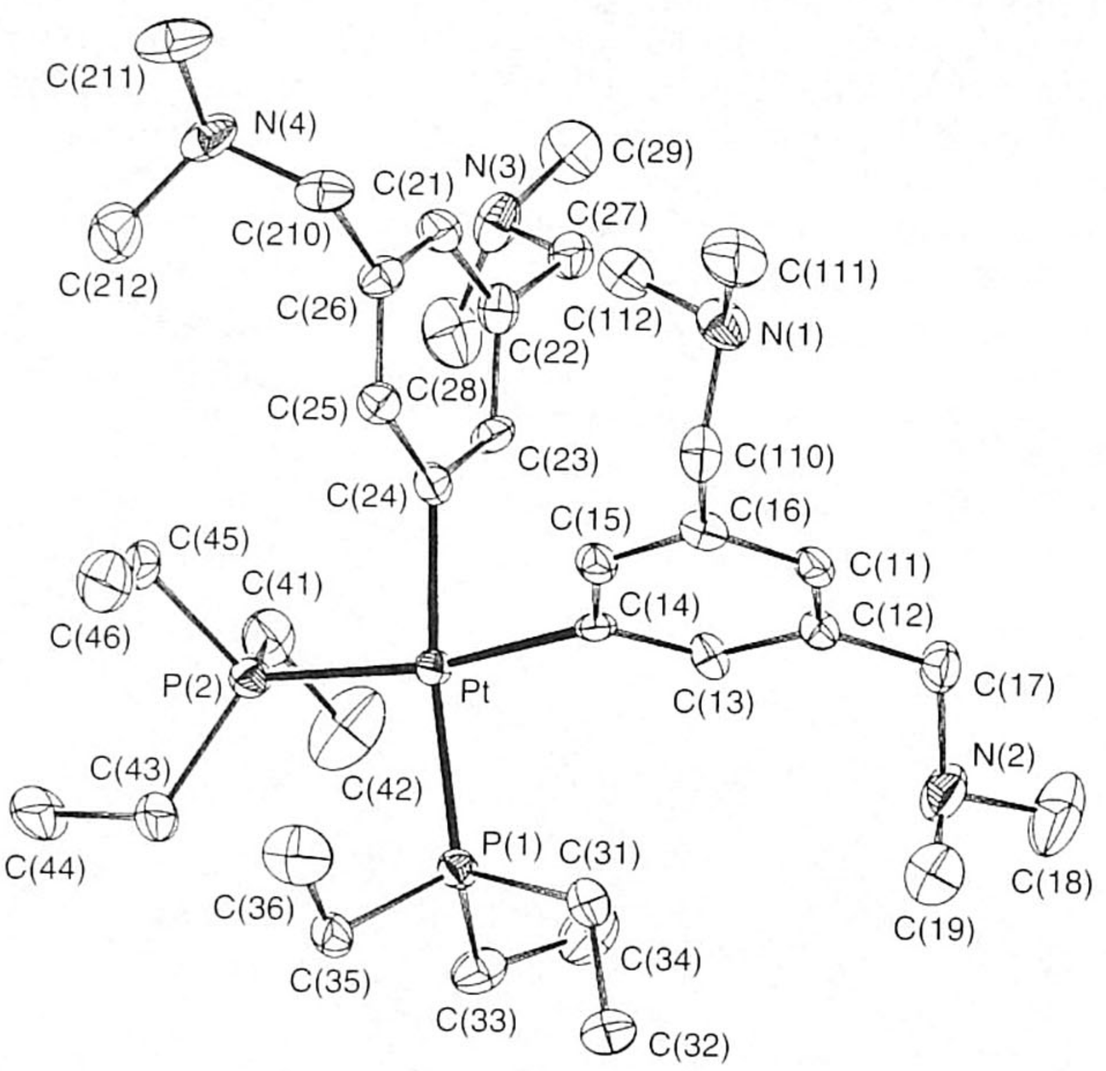
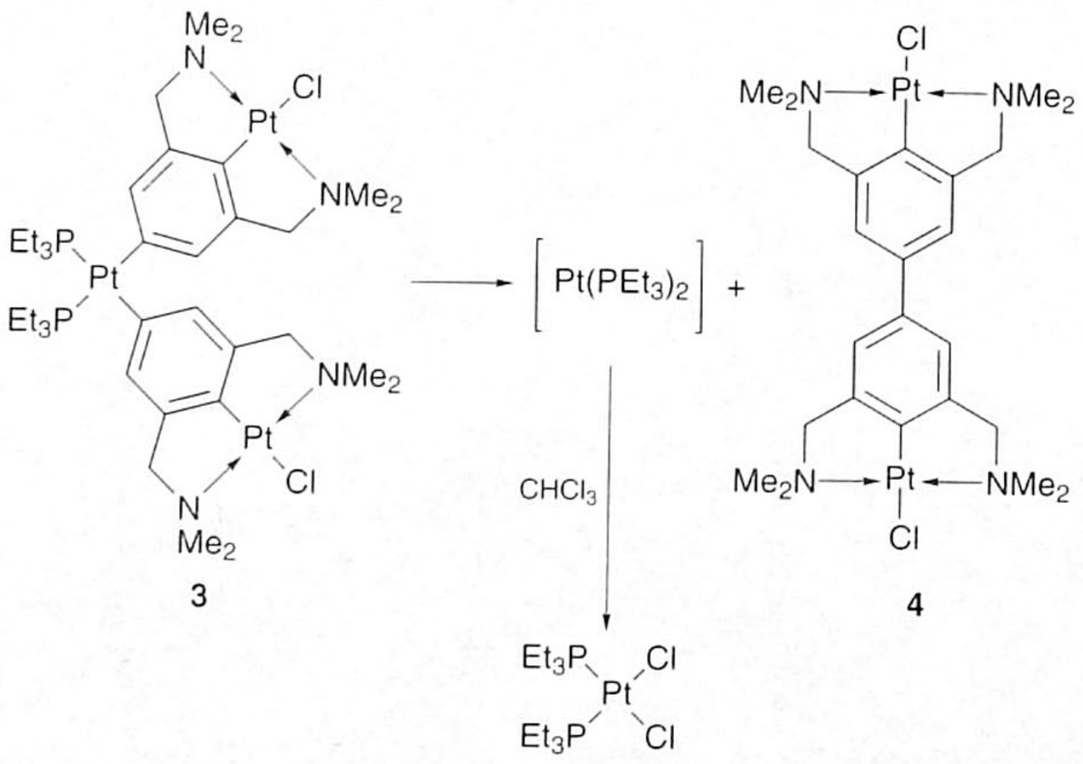


Fig. 1 Molecular structure of **1**, in the crystal. Selected bond lengths (Å) and angles (°): Pt–P(1) 2.3045(19), Pt–P(2) 2.317(2), Pt–C(14) 2.058(7), Pt–C(24) 2.071(7), P(1)–Pt–P(2) 100.17(7), P(1)–Pt-C(14) 89.8(2), P(1)–Pt–C(24) 172.4(2), P(2)–Pt–C(14) 170.01(19), P(2)–Pt–C(24) 87.5(2), C(14)–Pt–C(24) 82.6(3).



Scheme 3 Reductive elemination reaction of **3** in chloroform solution

The reductive elimination product, diplatinum complex **4**, is of interest in its own right since it is the second example of a complex containing the formally dianionic biphenyl bridging ligand $\{2,6\text{-}(Me_2NCH_2)_2C_6H_2\text{–}C_6H_2(CH_2NMe_2)_2\text{-}2,6\}^{2-}$. This bridging ligand system has been found to give rise to exceptionally strong metal–metal communication in the diamagnetic bis-ruthenium(III) complex [(terpy)Ru{2,6-$(Me_2NCH_2)_2C_6H_2$–$C_6H_2(CH_2NMe_2)_2$-2,6}Ru(terpy)]$^{4+}$ (terpy = 2,2′:6,2″ terpyridine) with the two aryl rings of the bridging ligand being coplanar in the solid state.[2] The diplatinum complex **4** has recently been independently synthesised in this laboratory§ *via* the free ligand and will be the subject of a future publication.

In conclusion, we have found that a conventional procedure for the introduction of a metal to an aryldiamine ligand (*i.e.* directed lithiation, followed by transmetallation with a transition-metal salt/complex), can also be applied when a metal is already attached to the aryl ring of the ligand. This observation opens up the way to multimetallic complexes and polymers with aryldiamines as bridging ligands. Extension of this methodology to other multimetallic systems is in progress.

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Centre of Biomolecular Research, University of Utrecht, for the FABMS analysis of **4**. This work is part of the COST-D4 chemistry action D4/04/92 'Towards Organometallic Polymers Containing Bis-cyclometallating Bridging Ligands'.

Footnotes

†*Characterising data for* **1**; ^{1}H NMR (300 MHz, $CDCl_3$, *J*/Hz) δ 7.05 [4H, d 3.8 $^4J(^{31}P–^1H)$, $^3J(^{195}Pt–^1H)$ 54.0, aromatic], 6.47 (2 H, s aromatic), 3.19 (8 H, s, NCH_2), 2.09 (24 H, s, NCH_3), 1.52 (12 H, m, PCH_2), 1.04 (18 H, m, CH_2CH_3). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) 163.63 [dd, $^2J(^{31}P–^{13}C)$ 109.8 (*trans*), 13.0 (*cis*), PtC, $^1J(^{195}Pt–^{13}C)$ not resolved], 136.4 [s, $^2J(^{195}Pt–^{13}C)$ 34.1], 135.5 [s, $^3J(^{195}Pt–^{13}C)$ 62.8], 123.1 [s, $^1J(^{195}Pt–^{13}C)$ not resolved], 65.0 (s, NCH_2), 45.1 (s, NCH_3), 15.9 (m, PCH_2), 8.2 [s, ^{2}J(^{195}Pt–^{13}C) 17.0, PCH_2CH_3]. ^{31}P-{^{1}H} NMR (80 MHz, $CDCl_3$) δ 3.95 [s, $^1J(^{195}Pt–^{31}P)$ 1784].

For **3**, ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 [4 H, d, $^4J(^{31}P–^1H)$ 4.5 $^3J(^{195}Pt–^1H)$ 56.0, aromatic], 3.87 [8 H, s, $^3J(^{195}Pt–^1H)$ 48.0 NCH_2], 3.02 [24 H, s, $^3J(^{195}Pt–^1H)$ 32.2, NCH_3], 1.42 (12 H, m, PCH_2), 1.03 (18 H, m, PCH_2CH_3). ^{13}C-{^{1}H} NMR (75 MHz) δ 159.1 [dd, $^2J(^{31}P–^{13}C)$ 112.0 (*trans*), 12.8 (*cis*), PtC], 144.2 [s, $^3J(^{195}Pt–^{13}C)$ 68.8], 137.9 [s, C_{ipso}, $^1J(^{195}Pt–^{13}C)$ not resolved], 128.4 [s, $J(^{195}Pt–^{13}C)$ 37.7], 79.9 [s, $^2J(^{195}Pt–^{13}C)$ 53.8], 54.3 (s). ^{31}P-{^{1}H} NMR (80 MHz, $CDCl_3$) δ 4.07 [s, $^1J(^{195}Pt–^{31}P)$ 1752]. Complex **1′** was identified by its ^{1}H NMR spectrum which was identical to that of **1**, except for the absence of a singlet at δ 6.47.

For **4**, ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.95 (4 H s, aromatic), 4.07 [8 H, s, $^3J(^{195}Pt–^1H)$ 45.2, NCH_2], 3.12 [24 H, s, $^3J(^{195}Pt–^1H)$ 36.3, NCH_3]. FABMS (positive-ion mode) shows a most intense pseudomolecular ion cluster centred around *m/z* 805, having an isotope distribution corresponding precisely to that expected for $[\mathbf{4}-Cl]^+$, and a less intense cluster, centred around *m/z* 841 and having a isotope distribution as expected for $[\mathbf{4}]^+$.

‡ *Crystal data* for **1**, $C_{36}H_{68}N_4P_2Pt$, M_r = 813.99, transparent, colourless (after irradiation yellowish), cut to shape crystal (0.10 × 0.30 × 0.45 mm), monoclinic, space group $P2_1/c$ (no. 14), a = 10.4237(9), b = 22.1591(12), c = 17.9442(14) Å, β = 106.388(6)°, U = 3976.4(5) Å^3, Z = 4, D_c = 1.360 g cm^{-3}, $F(000)$ = 1680, μ(Mo-Kα) = 36.4 cm^{-1}, 9306 reflections measured, 9029 independent, R_{int} = 0.0432 (1.5 < θ < 27.5°, ω scan, T = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.7103 Å) on an Enraf-Nonius CAD4-T diffractometer on rotating anode. Data were corrected for *Lp* effects and for a linear decay of 6% of the reference reflections, empirical absorption correction applied (PLATON, transmission range 0.505–1.000). The structure was solved by automated Patterson methods (DIRDIF92). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criterion was applied during refinement, nine reflections were omitted because of distinct background problems. Refinement converged at $wR2$ = 0.1039, $R1$ = 0.0518 [for 5988 reflections with $F_0 > 4\sigma(F_0)$], S = 1.008, for 402 parameters. Weights were optimized in the final refinement cycles. A final difference Fourier showed no residual density outside −0.96 and 1.21 e Å^{-3} (near Pt). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The synthesis involves dilithiation of the parent biaryl derivative 1,3-$(Me_2NCH_2)_2C_6H_3C_6H_3(CH_2NMe_2)_2$-1,3 with Bu^{n}Li followed by transmetallation with $[PtCl_2(SEt_2)_2]$ in diethyl ether.

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