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Synthesis of complexes of platinum (II) with *C*,*N*,*N'*-terdentate Schiff base donor ligands. Crystal and molecular structure of [Pt{3-Me-4-MeOC$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)]

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Abstract

Treatment of the potentially terdentate ligands $C_6R_xH_{5-x}C(H)=N-CH_2CH_2NMe_2$ [R: **a** ($x = 2$), 2,4-(MeO)$_2$; **b** ($x = 2$), 3,4-(MeO)$_2$; **c** ($x = 2$), 3-Me-4-MeO; **d** ($x = 3$), 2,3,4-(MeO)$_3$; **e** ($x = 2$), 4,5-(OCH$_2$O); **f** ($x = 1$), 2-NO$_2$] with [PtMe$_2$(COD)] gave the platinated compounds [Pt{$C_6R_xH_{4-x}C(H)=NCH_2CH_2-NMe_2$}(Me)] with two fused five-membered rings at platinum. The crystal and molecular structure of [Pt{3-Me-4-MeOC$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)] has been determined by X-ray crystallography. The reactivity of these complexes was tested by the reactions of [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}–(Me)] with tertiary phosphines and diphosphines. In the latter case, dinuclear and mononuclear platinum complexes were synthesized, with bridging or chelating diphosphine ligands, respectively, depending on the complex/diphosphine molar ratio used. The reaction of the related potentially hexadentate ligand 1,4-[Me$_2$NCH$_2$CH$_2$N=(H)C]$_2$C$_6$H$_4$ with [PtMe$_2$(COD)] gave the metallated compound [(Me)Pt{Me$_2$NCH$_2$CH$_2$N=(H)C}C$_6$H$_2${C(H)=N–CH$_2$CH$_2$NMe$_2$}Pt(Me)] with five fused rings. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Platnium(II) complexes; Schiff base complexes; Metallated compounds

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1. Introduction

Transition metal complexes with C,N-bonded organic ligands have aroused great attention in the past years [1,2]. Many of these complexes are palladium(II) compounds, which are found to be very useful in liquid crystals [3], catalysis [4], and in organic synthesis [5]; recently the term cyclic carbopalladation has been coined [6]. Although platinum(II) complexes have been less studied than their palladium(II) counterparts, their applications are nevertheless important, for example, as compounds with antitumor activity [7]. Also, photophysical and photochemical properties of square-planar platinum(II) complexes have been described [8], and more recently photoluminiscent cyclometallated platinum(II) complexes have been prepared [9]. Following our studies on *C*,*N* and *C*,*N*,*N* metallacycles, lately we have become interested in preparing complexes of platinum with similar ligands [10]. Related cyclometallated compounds of platinum with halogenated multidentate *C*,*N*,*N* ligands have been developed by oxidative addition of C–X bonds or, by orthometallation with loss of methane [11–14], using the platinum complexes [Pt$_2$Cl$_4$(SMe$_2$)$_2$] or [Pt$_2$Me$_4$(SMe$_2$)$_2$]; crystal structures of six-co-ordinate platinum(IV) complexes have also been reported. This paper gives an account of the preparation of platinum complexes using [PtMe$_2$(COD)] as the metallating substrate, which proves to be an excellent

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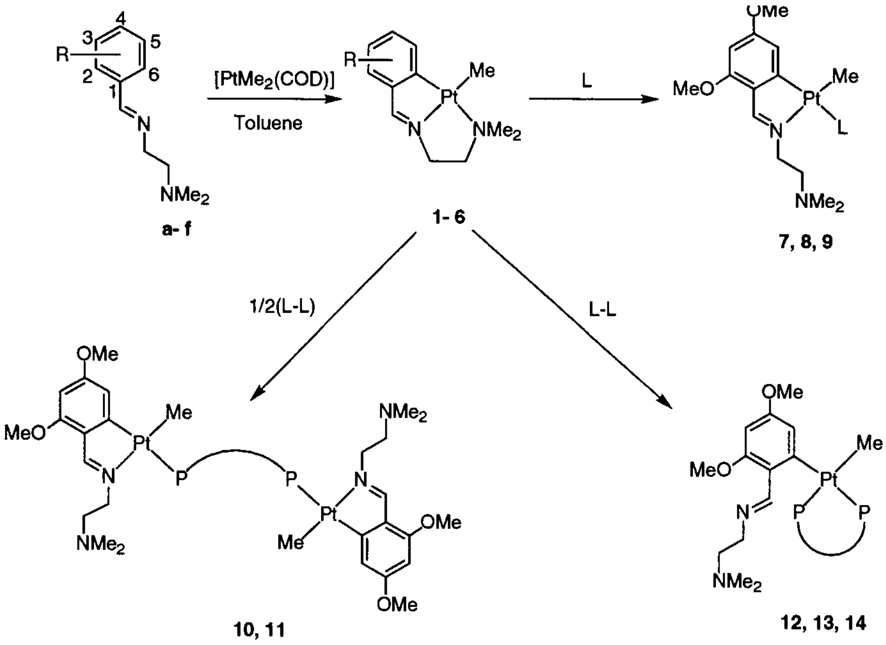


Fig. 1. **a**: 2,4-(MeO)$_2$; **b**: 3,4-(MeO)$_2$; **c**: 3-Me-4-MeO; d: 2,3,4-(MeO)$_3$; e: 4,5-(OCH$_2$O); f: 2-NO$_2$**1**: 2,4-(MeO)$_2$; **2**: 3,4(MeO)$_2$; **3**: 3-Me-4-MeO; 4: 2,3,4-MeO)$_3$; 5: 4,5-(OCH$_2$O); 6: 2-NO$_2$; 7: L = PPh$_3$; 8: L = PMePh$_2$; 9: L = Pet$_2$Ph; 10: L = trans-Ph$_2$PCH=CHPPh$_2$; 12: L = Ph$_2$P(CH$_2$)$_4$PPh$_2$; 13: L = Ph$_2$P(CH$_2$)$_3$PPh$_2$; 14: L = Ph$_2$P(CH$_2$)$_2$PPh$_2$.

material for the synthesis of cycloplatinated complexes via C–H activation, giving metallacycles with *C,N,N* ligands in good yields; the reactivity of one of these compounds has been tested against tertiary phosphines and diphosphines. We also present the crystal structure of a four-coordinate square-planar platinum(II) complex with a *C,N,N* ligand: the first double metallation by platinum of an aryl ring.

2. Results and discussion

2.1. Synthesis of [Pt{$C_6R_xH_{4-x}C(H)$=$NCH_2CH_2NMe_2$}(Me)]

Treatment of the potentially terdentate ligands $C_6R_xH_{5-x}C(H)$=$NCH_2CH_2NMe_2$ (**a**–**f**) with [PtMe$_2$(COD)] in toluene gave the platinated compounds [Pt{$C_6R_xH_{4-x}C(H)$=$NCH_2CH_2NMe_2$}(Me)] (**1**–**6**) (Fig. 1) with two fused five-membered rings at platinum.

The new compounds were obtained as orange (**1**–**5**) or dark red (**6**) air-stable solids, which were soluble in the common organic solvents, and they were characterised by elemental analysis,^{1}H and ^{13}C-NMR (except **4**) in CDCl$_3$, and the crystal structure determination of complex **3**. The ^{1}H and ^{13}C-NMR spectra were unambiguously assigned by comparison with the free ligands. The ^{1}H-NMR spectra showed the *H*C=N resonance was shifted to lower a field from the free ligand by 0.1–0.3 ppm (except in **6** where the shift is 0.92 ppm), with $^3J_{PtH}$ ca. 60 Hz, while broad deceptively simple triplets for the N(CH_2)$_2$N protons were observed. A singlet at δ 2.78–2.87 ppm was assigned to the NMe$_2$ resonance with $^3J_{PtH}$ 22.5–20.2 Hz; the methyls are equivalent, with the value of $^3J_{PtH}$ in the range 20.4–21.5 Hz, consistent with a three-bond coupling [15]. Coupling of the NMe$_2$ and of the *H*C=N protons to ^{195}Pt (Table 1) clearly indicated that both nitrogen atoms of the ligand were co-ordinated to the metal atom. The PtMe resonance was at δ 1.13–0.84 ppm with $^2J_{PtH}$ 78.6–77.8. The ^{13}C-NMR spectra showed the C=N ($^2J_{PtC}$ ca. 95 Hz), C1 ($^2J_{PtC}$ ca. 95 Hz) and C6 resonances were shifted to lower field from those of the free ligand, confirming that metallation had taken place [16] (Section 3 and Table 1). The methylene carbon resonances, =N*C*H$_2$ and *C*H$_2$NMe$_2$, were shifted to lower and higher field, respectively, with the latter being coupled to ^{195}Pt. In those cases where there are two potential metallation sites, ligands **b**, **c**, and **e**, the NMR data clearly shows that the preferred position for metalation is the C6 carbon atom in compounds **2**, **3**, and **5** [17] (Section 3 and Table 1). Thus, $^1J_{PtC6}$ was 1076.5, 1085.3, and 1092.3 Hz, respectively, whilst $^3J_{PtC2}$ was 52.5, 25.4, and 42.1 Hz, respectively. It has been recently reported that ligand **f** did not undergo metallation when treated with [Pt$_2$Me$_4$(SMe$_2$)$_2$] to give an *ortho* metallated Pt(II) square-planar compound [12]; however, under the reaction conditions used in the present paper the cycloplatinated complex **6** was obtained, which was fully characterised (Section 3 and Table 1). The imine HC=N, H$_3$, and H$_5$ proton resonances were

Table 1
^{31}P[a] and ^{1}H-NMR[b] data[c,d]

Compound	^{31}P	Aromatic	Others
1		6.79[d, J_{HH} = 2.2, 1H, H^5, 72.0[e]] 6.01[d, J_{HH} = 2.2, 1H, H^3]	8.76[s, 1H, HC=N, 62.2[e]], 3.83[s, 3H, MeO], 3.74[s, 3H, MeO], 3.95[br t, N = 12.0, 2H, $N(CH_2)_2N$], 3.12[br t, N = 12.0, 2H, $N(CH_2)_2N$], 2.81[s, 6H, NMe_2,20.4[e]], 0.88[s, 3H, PtMe, 77.8[e]]
2		7.12[s, 1H, H^5, 70.3[e]] 6.88[s, 1H, H^2, 11.0[e]]	8.42[s, 1H, HC=N, 60.3[e]], 3.92[s, 3H, MeO], 3.80[s, 3H, MeO], 3.99[br t, N = 12.1, 2H, $N(CH_2)_2N$], 3.13[br t, N = 12.1, 2H, $N(CH_2)_2N$], 2.83[s, 6H, NMe_2, 20.8[e]], 0.92[s, 3H, PtMe, 78.4[e]]
3		7.07[s, 1H, H^5, 71.0[e]] 7.03[s, 1H, H^2, 12.8[e]]	8.36[s, 1H, HC=N, 60.1[e]], 3.86[s, 3H, MeO], 3.93[br t, N = 12.1, 2H, $N(CH_2)_2N$], 3.11[br t, N = 12.1, 2H, $N(CH_2)_2N$], 2.81[s, 6H, NMe_2, 20.2[e]], 2.04[s, 3H, Me], 0.89[s, 3H, PtMe, 78.6[e]]
4		6.88[s, ^{1}H, H^5, 72.8[e]]	8.68[s, ^{1}H, HC=N, 61.5[e]], 3.90[s, 3H, MeO], 3.86[s, 3H, MeO], 3.72[s, 3H, MeO], 3.08[br t, N = 12.0, 2H, $N(CH_2)_2N$], 2.78[s, 6H, NMe_2, 20.5[e]], 0.84[s, 3H, PtMe, 78.1[e]]
5		6.95[d, J_{HH} = 7.8, 1H, H^2, 7.7[e]] 6.47[d, J_{HH} = 7.8, 1H, H^3]	8.48[s, 1H, HC=N, 60.3[e]], 5.92[s, 2H, $O(CH_2)O$], 3.96[br t, N = 11.9, 2H, $N(CH_2)_2N$], 3.15[br t, N = 11.9, 2H, $N(CH_2)_2N$], 2.82[s, 6H, NMe_2,22.5[e]], 1.13[s, 3H, PtMe, 76.8[e]]
6		7.97[dd, J_{HH} = 7.8, 1.2, 1H, H^5, 64.7[e]] 7.71[dd, J_{HH} = 7.8, 1.2, ^{1}H, H^3] 7.35[t, J_{HH} = 7.8, 1H, H^4]	9.62[s, 1H, HC=N, 61.0[e]], 4.22[br t, N = 11.8, 2H, $N(CH_2)_2N$], 3.23[br t, N = 11.8, 2H, $N(CH_2)_2N$], 2.87[s, 6H, NMe_2, 21.5[e]], 1.07[s, 3H, PtMe, 77.6[e]]
7	28.1s (2219)[g]	7.04[d, J_{PH} = 5.1, 1H, H^5, 57.0[e]] 6.13[s,1H, H^3]	8.82[s, 1H, HC=N, 58.0[e]], 3.85[s, 3H, MeO], 3.78[s, 3H, MeO], 3.24[br t, N = 6.7, 2H, $N(CH_2)_2N$], 1.84[s, 6H, NMe_2], 0.70[d, J_{PH} = 7.4, 3H, PtMe, 81.2[e]]
8	9.3s (2157)[g]	7.02[d, J_{PH} = 5.2, 1H, H^5, 56.4[e]] 6.13[s,1H, H^3]	8.75[s, 1H, HC=N, 57.2[e]], 3.86[s, 3H, MeO], 3.76[s, 3H, MeO], 3.18[br t, N = 6.7, 2H, $N(CH_2)_2N$], 1.94[s, 6H, NMe_2], 0.78[d, J_{PH} = 7.6, 3H, PtMe, 80.2[e]]
9	12.3s (2165)[g]	7.06[dd, J_{PH} = 6.1, 2.0[f] 1H, H^5, 54.4[e]] 6.09[d, J_{HH} = 2.0,1H, H^3]	8.74[s, 1H, HC=N, 56.0[e]], 3.87[s, 3H, MeO], 3.75[s, 3H, MeO], 3.30[br t, N = 7.2, 2H, $N(CH_2)_2N$], 2.01[s, 6H, NMe_2], 2.01[s, 6H, NMe_2], 0.93[d, J_{PH} = 6.8, 3H, PtMe, 81.2[e]]
10	17.0s (2196)[g]	7.02[dd, J_{PH} = 6.1, 2.0[f] 1H, H^5, 55.2[e]] 6.11[d, J_{HH} = 2.0, H, H^3]	8.75[s, 1H, HC=N, 56.6[e]], 3.88[s, 3H, MeO], 3.77[s, 3H, MeO], 3.20[br t, N = 7.0, 2H, $N(CH_2)_2N$], 2.04[br t, N = 7.0, 2H, $N(CH_2)_2N$], 1.84[s, 6H, NMe_2], 1.84[s, 6H, NMe_2], 0.82[d, J_{PH} = 7.1, 3H, PtMe, 81.0[e]]
11	21.7s (2170)[g]	7.00[dd, J_{PH} = 4.0, 1.9[f] 1H, H^5, 56.4[e]] 6.12[d, J_{HH} = 1.9, H, H^3]	8.69[s, 1H, HC=N, 58.2[e]], 3.88[s, 3H, MeO], 3.78[s, 3H, MeO], 3.01[br t, N = 6.5, 2H, $N(CH_2)_2N$], 1.94[br t, N = 6.5, 2H, $N(CH_2)_2N$], 1.81[s, 6H, NMe_2], 0.74[d, J_{PH} = 7.3, 3H, PtMe, 80.0[e]]
12	25.6d, 10.6d, (2015)[g], (1927)[g], (13.2)[h]	6.41[d, J_{PH} = 6.0, 1H, H^5, 62.0[e]], 5.75[s,1H, H^3]	8.86[s, 1H, HC=N]3.62[s, 3H, MeO], 3.52[s, 3H, MeO], 2.33[s, 6H, NMe_2], 0.30[t, J_{PH} = 6.5, 3H, PtMe, 61.6[e]]
13	4.4d, 2.9d, (1922)g, (1908)[g], (17.3)[h]	6.29[d, J_{PH} = 5.9, 2.0[f] 1H, H^5, 64.4[e]], 5.82[d, J_{HH} = 2.0, 1H, H^3]	8.94[s, 1H, HC=N], 3.64[s, 3H, MeO], 3.46[s, 3H, MeO], 2.36[s, 6H, NMe_2], 2.63[br t, N = 7.6, 2H, $N(CH_2)_2N$], 0.34[dd, J_{PH} = 7.4, 5.6 3H, PtMe, 69.8[e]]
14	51.5d, 45.8d, (1903)[g](3515)(19.4)[hg]	6.50[d, J_{PH} = 6.4, 1H, H^5, 65.0[e]], 6.01[s,1H, H^3]	8.83[s, 1H, HC=N], 3.74[s, 3H, MeO], 3.43[s, 3H, MeO], 2.16[s, 6H, NMe_2], 0.54[t, J_{PH} = 7.3, 3H, PtMe, 71.2[e]]
15		7.45[s, 2H, $H^{2,5}$, 62.0[e]]	8.52[s, 2H, HC=N, 60.4[e]], 3.97[br t, N = 11.8, 4H, $N(CH_2)_2N$], 3.12[br t, N = 11.8, 4H, $N(CH_2)_2N$], 2.82[s, 12H, NMe_2, 9.8[e]], 0.89[s, 6H, PtMe, 74.8[e]]

[a] In $CDCl_3$. Measured at 100.6 MHz (ca. 20°C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4.

[b] In $CDCl_3$, unless otherwise stated. Measured at 250 MHz (ca. 20°C); chemical shifts (δ) in ppm (± 0.01) to high frequency of $SiMe_4$.

[c] Coupling constants in Hz. [d] s, singlet; d, doublet; dd, doublet of doublets; t, triplet; br, broad. [e] J_{PtH}. [f] J_{HH}. [g] J_{PtP}. [h] J_{PP}.

shifted to lower field from the free ligand, owing to the presence of the strong electron-withdrawing $-NO_2$ group.

2.2. Molecular Structure of **Complex 3**

The crystal structure has been determined (Fig. 2) and confirms the geometry predicted from spectroscopic studies. Crystallographic data and bond lengths and angles are listed in Tables 2 and 3, respectively.

The crystal structure consists of discrete molecules separated by van der Waals distances. The platinum atom is bonded in a slightly distorted square planar co-ordination to the *ortho* carbon of the phenyl ring, to the carbon atom of the methyl group, and to the iminic and amine nitrogen atoms. The nitrogen atoms adopt a *cis* arrangement. The deviations from the mean plane (plane 1) are as follows: Pt −0.0165, C(9) 0.0481, N(2) −0.0454, N(1) 0.0433 Å. The angles between adjacent atoms in the co-ordination sphere are close to the expected value of 90°, in the range 99.4(7) to 80.0(7)°, with the distortions being most noticable in the tridentate ligand. The angles C(9)–Pt–N(12), 80.0(7)°, and N(1)–Pt–N(2), 82.4(6)° are less than 90° and the angles C(9)–Pt–C(12), 99.4(7)°, and C(12)–Pt–N(1), 98.3(6)°, are thus >90°. All bond distances are within the expected range, with allowance for the strong *trans* influence of the carbon donor ligands. The Pt–C(9) bond length (1.97(2) Å) is similar to the platinum-aryl carbon bond length found earlier [12,18,19]. The Pt–NMe_2 bond length of 2.162(14) Å is longer than the imine Pt–N bond length of 2.04(2) Å; the former is expected to be weakened by the *trans* aryl group which has a high *trans* influence, the longer Pt–N bond is also consistent with the weak ligating ability of tertiary amines for platinum [12]. The metallacycle Pt, N(2), C(3), C(4), and C(9) (plane 2) is planar with mean deviations from the plane in the range ±0.0126 Å. The metallated phenyl ring C(4)–C(9) (plane 3, mean deviations ±0.0076 Å) is also planar. The ring defined by Pt, N(2), C(2), C(1), and N(1) (plane 4) shows mean deviations of ±0.1207 Å, with the largest deviations on the C1 and C2 atoms, 0.21 and 0.16 Å, respectively, with angles between planes 1–4 as follows: plane 1/plane 2, 4.4°, plane 1/plane 3, 7.1°, plane 1/plane 4, 13.6°, plane 2/plane 3, 2.6°, plane 2/plane 4, 9.2°, plane 3/plane 4, 6.5°.

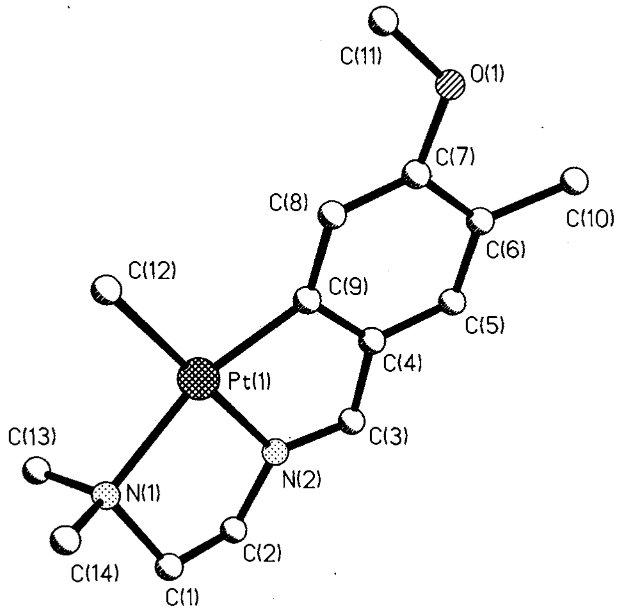


Fig. 2. Molecular structure of **complex 3**.

Table 2
Crystal data for compound 3

Formula	$C_{14}H_{22}N_2OPt$
Formula weight	429.43
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal color	Orange
Crystal size(mm)	$0.65 \times 0.41 \times 0.28$
Crystal system	Orthorombic
Space group	$P2_12_12_1$
Unit cell dimensions	a(Å) = 7.389(2)
	b(Å) = 11.066(3)
	c(Å) = 18.522(3)
	α(°) = 90°
	β(°) = 90°
	γ(°) = 90°
Volume (Mg m^{-3})	1514.5(6)
Z	4
$D_{calc.}$ Mg m^{-3}	1.883
Absorption coefficient (mm^{-1})	9.256
$F(000)$	824
θ range (°)	2.14–25.00
Index ranges	$-1<h<8$, $-1<k<13$, $-1<l<22$
Reflections collected	2099
Independent reflections	1938 ($R_{int} = 0.0372$)
Absorption correction	None
Refinement method	Full-matrix-block least suares on F^2
Data/restraints/parameters	1938/0/163
GOF on F^2	1.045
Final R indices [$I > 2.0\sigma(I)$]	$R_1 = 0.0467$, $wR_2 = 0.0840$
R indices (all data)	$R_1 = 0.0828$, $wR_2 = 0.0965$
Absolute structure parameter	0.02(4)
Largest diff. peak and hole	0.684 and -0.772 eÅ^{-3}

2.3. Synthesis of [Pt{2,4-$(MeO)_2C_6H_2C(H)$=$NCH_2CH_2NMe_2$}(L)(Me)] (L = Phosphine)

The reaction of [Pt{2,4-$(MeO)_2C_6H_2C(H)$=$NCH_2CH_2NMe_2$}–(Me)] with tertiary phosphines gave the mononuclear complexes [Pt{2,4-$(MeO)_2C_6H_2C(H)$=N-$CH_2CH_2NMe_2$}(L)(Me)] (L = PPh_3 (**7**), $PMePh_2$ (**8**), PEt_2Ph (**9**), respectively, as air-stable solids, soluble in the common organic solvents, which were fully characterised (Section 3 and Table 1). Coupling of the *H*5 resonance to the ^{31}P nucleus was observed in the range 5.1–6.1 ppm, but not of the HC=N and =NCH_2 resonances. The NMe$_2$ resonance was shifted to higher field from its value in the free ligand (cf. δ NMe$_2$ in **a**, 2.29 ppm, and in **1**, 1.84 ppm) probably due to shielding of a phosphine phenyl ring. However, no similar shielding effect was observed at the C(4)-methoxy group as would be expected from a *trans* N–Pt–P geometry [20]. Futhermore, no significant high-field shift of the aromatic protons of the phenyl ring was observed, as expected for a *cis* arrangement of the phosphine and the metallated ring [21]. These findings are in accordance with a *trans* C–Pt–P geometry. The complexes showed singlet resonances in the ^{31}P{^{1}H} NMR spectra, with satellites due to ^{195}Pt, and the value of J_{PtP} in the range 2218.8–2165.2 Hz is consistent with a phoshorus *trans* to a phenyl carbon atom [15].

2.4. Synthesis of [{Pt[2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$](Me)}$_2$(μ-L)] (L = Diphosphine)

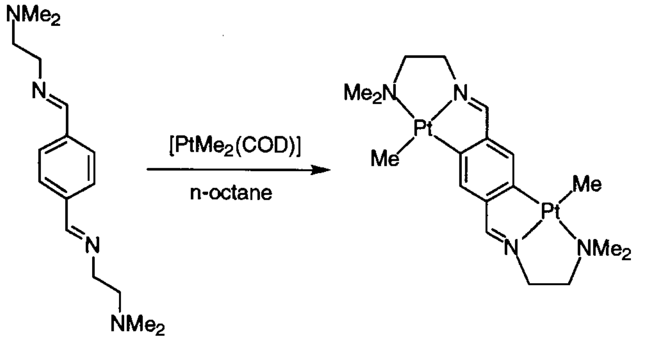
The reaction of [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$–CH$_2$NMe$_2$}(Me)] with *tertiary* diphosphines, in a 2:1 molar ratio, in acetone at room temperature (r.t.) gave the dinuclear complexes [{Pt[2,4-(MeO)$_2$C$_6$H$_2$C–(H)=NCH$_2$CH$_2$NMe$_2$](Me)}$_2$(μ-L)] (L = Ph$_2$P(CH$_2$)$_4$PPh$_2$ (**10**), L = *trans*-Ph$_2$PCH=CHPPh$_2$ (**11**), respectively, as air-stable solids, soluble in the common organic solvents, which were fully characterised (Section 3 and Table 1). The ^{1}H-NMR spectra of the compounds have been fully assigned. Detailed analysis of the proton resonances in the ^{1}H-NMR spectra, and of the value of J_{PtP}, showed that the phosphorus nuclei were in a *trans*-C–Pt–P geometry (vide supra). There was only one set of resonances for each cycloplatinated moiety in the ^{1}H-NMR spectra and only one singlet for the two ^{31}P nuclei in the ^{31}P{^{1}H}-NMR spectra, which suggests the compounds to be centrosymmetric, as we have shown before in related compounds [22]. In the ^{1}H-NMR spectrum of **11** the expected deceptively simple triplet of the PCH=CHP resonances (AA′XX′ spin system) was occluded by the phosphine resonances.

Table 3
Bond distances (Å) and angles (°) for compound **3**

Bond distance (Å)			
Pt(1)–C(9)	1.97(2)	Pt(1)–N(2)	2.04(2)
Pt(1)–C(12)	2.154(13)	Pt(1)–N(1)	2.162(14)
N(1)–C(13)	1.42(3)	N(1)–C(14)	1.42(2)
N(1)–C(1)	1.55(3)	N(2)–C(3)	1.30(2)
N(2)–C(2)	1.45(2)	O(1)–C(11)	1.37(3)
O(1)–C(7)	1.38(2)	C(1)–C(2)	1.40(3)
C(3)–C(4)	1.39(2)	C(4)–C(5)	1.38(2)
C(4)–C(9)	1.42(2)	C(5)–C(6)	1.39(2)
C(6)–C(7)	1.42(2)	C(6)–C(10)	1.56(2)
C(7)–C(8)	1.37(2)	C(8)–C(9)	1.39(2)
Bond angle (°)			
C(9)–Pt(1)–N(2)	80.0(7)	C(9)–Pt(1)–C(12)	99.4(7)
N(2)–Pt(1)–C(12)	178.7(5)	C(9)–Pt(1)–N(1)	162.0(8)
N(2)–Pt(1)–N(1)	82.4(6)	C(12)–Pt(1)–N(1)	98.3(6)
C(13)–N(1)–C(14)	112(2)	C(13)–N(1)–C(1)	109(2)
C(14)–N(1)–C(1)	106(2)	C(13)–N(1)–Pt(1)	109.2(13)
C(14)–N(1)–Pt(1)	115.5(13)	C(1)–N(1)–Pt(1)	104.8(13)
C(3)–N(2)–C(2)	130(2)	C(3)–N(2)–Pt(1)	116.3(13)
C(2)–N(2)–Pt(1)	113.3(13)	C(11)–O(1)–C(7)	116(2)
C(2)–C(1)–N(1)	114(2)	C(1)–C(2)–N(2)	114(2)
N(2)–C(3)–C(4)	114(2)	C(5)–C(4)–C(3)	122(2)
C(5)–C(4)–C(9)	121(2)	C(3)–C(4)–C(9)	118(2)
C(4)–C(5)–C(6)	123(2)	C(5)–C(6)–C(7)	116(2)
C(5)–C(6)–C(10)	121(2)	C(7)–C(6)–C(10)	123(2)
C(8)–C(7)–O(1)	127(2)	C(8)–C(7)–C(6)	121(2)
O(1)–C(7)–C(6)	113(2)	C(7)–C(8)–C(9)	123(2)
C(8)–C(9)–C(4)	116(2)	C(8)–C(9)–Pt(1)	132(2)
C(4)–C(9)–Pt(1)	111.9(14)		

2.5. Synthesis of [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)(L–P,P)] (L = Diphosphine)

The reaction of [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$–CH$_2$NMe$_2$}(Me)] with *tertiary* diphosphines, in a 1:1 molar ratio, in acetone at r.t. gave the mononuclear complexes [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)(L–P,P)] (L = Ph$_2$P(CH$_2$)$_4$PPh$_2$ (**12**), L = Ph$_2$P(CH$_2$)$_3$PPh$_2$ (**13**), L = Ph$_2$P(CH$_2$)$_2$PPh$_2$ (**14**), respectively, as air-stable solids, soluble in the common organic solvents, which were fully characterised (Section 3 and Table 1). In these complexes the Pt(PP)Me moiety may rotate about the Pt–C vector so that the platinum co-ordination plane should be at 90° to the metallated phenyl ring, in analogy with related palladium complexes [21]; nevertheless the H5 proton resonance is still coupled to one phosphorus nucleus. The ^{31}P{^{1}H}-NMR spectra showed two doublets for the two inequivalent phosphorus nuclei; the one at lower field was assigned to the ^{31}P nucleus *trans* to the methyl group, and the one at higher field was assigned to the ^{31}P nucleus *trans* to the phenyl carbon atom, on the basis of a higher *trans* influence of the methyl group [23] (vide infra). The PtMe resonance was shifted to higher field when compared to complexes **1–11**, and appeared in the range 0.54–0.30 ppm, due to the greater *trans* influence of the phosphorus atom with respect to the C=N nitrogen atom [24]; accordingly $^2J_{\mathrm{Pt}Me}$ was smaller than the mean value of ca. 80 Hz, for complexes **1–11** (Table 1). Surprisingly, the δ P chemical shift values for **14** where strongly shifted to lower field, with one very high J_{PtP} coupling constant, probably due to the change in ring size of the chelating diphosphine, that gives a stable five-membered ring. Similar strong shifts have been observed before by Canty [25] and co-workers, where the change in ring size is from a four-membered to a five membered ring. Garrou [26] has proposed that the



g **15**

Fig. 3. Synthesis of [(Me)Pt{$Me_2NCH_2CH_2N$=(H)C}C_6H_2{C(H)=N–$CH_2CH_2Nme_2$}Pt(Me)] (**15**).

^{31}P chemical shift is influenced by ring size. The ring contribution Δ_R was defined as the difference between the co-ordination shift of a chelated phosphine complex, Δ ($\Delta = A\delta + B$, A and B are constants and δ is the shift for the free ligand), minus the co-ordination shift of an equivalent phosphorus in a nonchelated analogue. Each complex was compared to an analogous compound where the phosphorus atom of the chelated diphosphine was a triphenylphosphine ligand. We have calcualted [27] Δ_R for compounds **12–14**, for both phosphorus atoms *trans* to methyl ($\Delta_R = +2.5$, **12**; -18.72, **13**; $+28.38$, **14**) and *trans* to phenyl ($\Delta_R =$ -13.55, **12**; -21.23, **13**; $+21.63$, **14**); compound **14** shows a large positive Δ_R as expected. Also, in the five-membered ring compound, **14**, the absolute value of Δ_R is smaller when the ^{31}P nucleus is *trans* to methyl in comparison to when it is *trans* to phenyl; the reverse is true for the six- and seven-membered ring compouds **12** and **13**.

2.6. Synthesis of [(Me)Pt{$Me_2NCH_2CH_2N$=(H)C}C_6H_2{C(H)=N–$CH_2CH_2NMe_2$} Pt(Me)] (15)

The reaction of 1,4-[$Me_2NCH_2CH_2N$=(H)C]$_2C_6H_4$ with [$PtMe_2$(COD)] in boiling octane gave the metallated compound [(Me)Pt{$Me_2NCH_2CH_2N$=(H)C} C_6H_2{C(H)=$NCH_2CH_2NMe_2$}Pt(Me)], **15**, which was fully characterised (Section 3 and Table 1Fig. 3). The ^1H-NMR spectrum contains only one set of signals in accordance with the presence of only one isomer in solution, i.e. the isomer with the two platinum atoms in *cis* positions on the phenyl ring is discarded. There was a singlet resonance at δ 7.45 ppm (2H) assigned to the H3 and H6 protons, and a singlet resonance at δ 8.52 ppm (2H) assigned to the *H*C=N protons. Thus, the compound is centrosymmetric, and it is the first example of a dimetallated platinum(II) complex with a hexadentate organic ligand. A noticeable feature of this complex is the presence of five fused rings: two sets of two fused five-membered rings at each platinum center symmetrically attatched to a six-membered aryl ring.

3. Experimental section

3.1. Materials and instrumentation

All reactions were carried out in an atmosphere of dry argon. Solvents were purified by standard methods [28]. Chemicals were reagent grade (1,5-cyclooctadiene)dimethylplatinum(II) was purchased from Alfa Products. The diphosphines $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb), were purchased from Aldrich-Chemie; *trans*-Ph_2PCH=$CHPPh_2$ (*trans*-1,2-dppe) was prepared according to procedures described elsewhere [29]. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo Erba Elemental Analyser, Model 1108. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 ($^{31}P\{^1H\}$) and were recorded on Bruker WM250, AMX-300 and AC-200 spectrometers. All chemical shifts were reported downfield from standards.

The synthesis of the Schiff bases 2,4-(MeO)$_2C_6H_3C(H)$=$NCH_2CH_2NMe_2$ (**a**), 3,4-(MeO)$_2C_6H_3$ C(H)=$NCH_2CH_2NMe_2$ (**b**), 3-Me-4-$MeOC_6H_3C$–(H)=$NCH_2CH_2NMe_2$ (**c**) 2,3,4-(MeO)$_3C_6H_2C(H)$=NCH_2 CH_2NMe_2 (**d**) 4,5-(OCH_2O)$C_6H_3C(H)$=NCH_2CH_2N-Me_2 (**e**) 2-$NO_2C_6H_4C(H)$=$NCH_2CH_2NMe_2$ (**f**) and 1,4-[$Me_2NCH_2CH_2N$=(H)C]$_2C_6H_4$ (**g**) was performed by heating a chloroform solution of the appropriate quantities of 2,4-dimethoxybenzal-dehyde, 3,4-dimethoxybenzaldehyde, 3-methyl-4-methoxybenzaldehyde, 2,3,4-trimethoxybenzaldehyde, piperonal, 2-nitrobenzaldehyde or terephtal-aldehyde, respectively, and *N*,*N*-dimethylethylenediamine in a Dean-Stark apparatus under reflux. The ligands were characterized by their NMR spectra.

3.2. ^1H-NMR spectra

Complex **a**, 8.62[s, 1H, HC=N], 7.86[d, $J_{HH} = 8.6$, 1H, H^6], 6.49[dd, $J_{HH} = 8.6$, 2.4, 1H, H^5], 6.41[d, $J_{HH} =$ 2.4, 1H, H^3], 3.83[s, 3H, MeO], 3.82[s, 3H, MeO], 3.70[br t, N = 14.2, 2H, $N(CH_2)_2N$], 2.61[br t, N = 14.2, 2H, $N(CH_2)_2N$], 2.29[s, 6H, NMe_2]; **b**, 8.22[s, 1H, HC=N], 7.41[d, $J_{HH} = 1.8$, 1H, H^2], 7.15[dd, $J_{HH} = 8.6$, 1.8, 1H, H^6], 6.87[d, $J_{HH} = 8.6$, 1H, H^5], 3.91[s, 3H, MeO], 3.94[s, 3H, MeO], 3.74[br t, N = 14.2, 2H, $N(CH_2)_2N$], 2.63[br t, N = 14.2, 2H, $N(CH_2)_2N$], 2.31[s, 6H, NMe_2]; **c**, 8.21[s, 1H, HC=N], 7.58[d, $J_{HH} = 2.2$, 1H, H^2], 7.46[dd, $J_{HH} = 8.4$, 2.2, 1H, H^6], 6.82[d, $J_{HH} =$ 8.4, 1H, H^5], 3.85[s, 3H, MeO], 3.70[br t, N = 14.2, 2H, N(CH$_2$)$_2$N], 2.63[br t, N = 14.2, 2H, N(CH$_2$)$_2$N], 2.31[s, 6H, NMe$_2$], 2.22[s, 3H, Me]; **d**, 8.54[s, 1H, HC=N], 7.64[d, $J_{\mathrm{HH}} = 8.8$, 1H, H^6], 6.68[d, $J_{\mathrm{HH}} = 8.8$, 1H, H^5], 3.90[s, 3H, MeO], 3.86[s, 3H, MeO], 3.85[s, 3H, MeO], 3.70[br t, N = 14.1, 2H, N(CH$_2$)$_2$N], 2.60[br t, N = 14.1, 2H, N(CH$_2$)$_2$N], 2.28[s, 6H, NMe$_2$]; **e**, 8.18[s, 1H, HC=N], 7.33[d, $J_{\mathrm{HH}} = 1.6$, 1H, H^6], 7.09[dd, $J_{\mathrm{HH}} = 8.0$, 1.6, 1H, H^3], 6.81[d, $J_{\mathrm{HH}} = 8.0$, 1H, H^2], 5.98[s, 2H, O(CH$_2$)O], 3.69[br t, N = 14.0, 2H, N(CH$_2$)$_2$N], 2.61[br t, N = 14.0, 2H, N(CH$_2$)$_2$N], 2.30[s, 6H, NMe$_2$]; **f**, 8.70[s, 1H, HC=N], 7.76[m, 4H, H$^{3-6}$], 3.78[br t, N = 13.5, 2H, N(CH$_2$)$_2$N], 2.65[br t, N = 13.5, 2H, N(CH$_2$)$_2$N], 2.29[s, 6H, NMe$_2$]; **g**, 8.32[s, 2H, HC=N], 7.75[s, 4H, H^{2,3,5,6}], 3.74[br t, N = 13.8, 4H, N(CH$_2$)$_2$N], 2.64[br t, N = 13.8, 4H, N(CH$_2$)$_2$N], 2.29[s, 12H, NMe$_2$].

3.3. ^{13}C{^{1}H} NMR spectra

Complex **a,** phenyl: 118.0 (C1), 163.1 (C2), 128.5 (C3), 160.1(C4), 105.4 (C5), 90.0 (C6). Others: 157.5 (C=N), 60.3 (MeO), 59.8 (MeO), 55.4 (N(CH$_2$)$_2$N), 55.3 (N(CH$_2$)$_2$N), 45.7 (NMe$_2$); **b**, phenyl: 129.3 (C1), 123.0, 110.3, 108.6 (C2; C5; C6), 151.2, 149.2 (C3; C4). Others: 161.4 (C=N), 59.5 (MeO), 55.8 (MeO), 60.1 (N(CH$_2$)$_2$N), 59.5 (N(CH$_2$)$_2$N), 45.7 (NMe$_2$); **c**, phenyl: 126.9, 128.4 (C1; C3), 129.7, 127.8, 109.4 (C2; C5; C6), 159.8 (C4). Others: 161.6 (C=N), 55.3 (MeO), 60.1 (N(CH$_2$)$_2$N), 59.6 (N(CH$_2$)$_2$N), 45.7 (NMe$_2$), 16.1 (Me); **d**, phenyl: 122.7 (C1), 157.3, 155.7, 141.6 (C2; C3; C4), 122.9, 107.6 (C5; C6). Others: 157.3 (C=N), 60.9 (MeO), 60.8 (MeO), 56.0 (MeO), 60.2 (N(CH$_2$)$_2$N), 59.9 (N(CH$_2$)$_2$N), 45.7 (NMe$_2$); **e**, phenyl: 130.9 (C1), 149.7, 148.1 (C4; C5), 124.3, 107.9, 106.5 (C2; C3; C6). Others: 160.9 (C=N), 101.3 (OCH$_2$O), 60.1 (N(CH$_2$)$_2$N), 59.4 (N(CH$_2$)$_2$N), 45.7 (NMe$_2$); **f**, phenyl: 131.0 (C1), 148.6 (C2), 133.3, 130.5, 129.6, 124.1, (C3; C4; C5; C6). Others: 157.5 (C=N), 59.6 (N(CH$_2$)$_2$N), 59.5 (N(CH$_2$)$_2$N), 45.6 (NMe$_2$); **g**, phenyl: 138.0 (C1, C4), 128.2 (C2, C3, C5, C6). Others: 161.1 (C=N), 59.9 (N(CH$_2$)$_2$N), 59.8 (N(CH$_2$)$_2$N), 45.7 (NMe$_2$).

3.4. Synthesis of [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)] ***(1)***

A pressure tube containing 2,4-(MeO)$_2$C$_6$H$_3$C(H)=NCH$_2$CH$_2$NMe$_2$ (75 mg, 0.32 mmol), (1,5-cyclooctadiene)dimethylplatinum(II) (100 mg, 0.29 mmol) and 10 cm^3 of dry toluene was sealed under argon. The light-yellow solution was heated at 100°C for 24 h. After cooling to r.t. the orange solution was filtered through celite to remove the small amount of black platinum formed. The solution was concentrated until an orange crystalline precipitate appeared. The solid was filtered off and washed with *n*-hexane. Yield > 95%. Anal. Found, C, 37.6; H, 5.1; N, 6.2. C$_{14}$H$_{22}$N$_2$O$_2$Pt requires: C, 37.7; H, 5.0; N, 6.3. ^{13}C{^{1}H} NMR data: phenyl, 131.9 (C1, J_{PtC} 39.5), 160.5 (C2, J_{PtC} 70.2), 92.7 (C3),164.4 (C4, J_{PtC} 103.0), 110.3 (C5, J_{PtC} 97.5), 147.6 (C6, J_{PtC} 1162.0). Others, 163.4 (C=N, J_{PtC} 98,2), 55.8 (MeO), 55.5 (MeO), 68.6 (N(CH$_2$)$_2$N), 52.1 (N(CH$_2$)$_2$N, J_{PtC} 32.0), 49.1 (NMe$_2$), –11.6 (PtMe, J_{PtC} 792.3). Compounds **2**, **3** and **5** were obtained following a similar procedure as orange solids.

3.5. Synthesis of [Pt{3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)] ***(2)***

Yield 85%. Anal. Found: C, 37.5; H, 5.3; N, 6.3. C$_{14}$H$_{22}$N$_2$O$_2$Pt requires: C, 37.7; H, 5.0; N, 6.3. ^{13}C{^{1}H} NMR data: phenyl, 142.5 (C1, J_{PtC} 37.8), 112.4 (C2, J_{PtC} 52.5), 137.1 (C3),151.7(C4, J_{PtC} 77.0), 116.2 (C5, J_{PtC} 106.6), 145.0 (C6, J_{PtC} 1076.5). Others, 167.0 (C=N, J_{PtC} 95.2), 56.5 (MeO), 56.1 (MeO), 68.4 (N(CH$_2$)$_2$N), 52.1 (N(CH$_2$)$_2$N, J_{PtC} 30.5), 49.1 (NMe$_2$), –12.1 (PtMe, J_{PtC} 794.4).

3.6. Synthesis of [Pt{3-Me-4-MeOC$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)] ***(3)***

Yield 80%. Anal. Found: C, 39.3; H, 5.3; N, 6.3. C$_{14}$H$_{22}$N$_2$OPt requires: C, 39.2; H, 5.2; N, 6.5. ^{13}C{^{1}H} NMR data: phenyl, 143.2 (C1), 130.9 (C2, J_{PtC} 25.4), 119.7 (C3), 160.4(C4, J_{PtC} 66.3), 115.2 (C5, J_{PtC} 106.0), 143.0 (C6, J_{PtC} 1085.3). Others, 167.1 (C = N, J_{PtC} 96.1), 55.7 (MeO), 68.0 (N(CH$_2$)$_2$N), 51.7 (N(CH$_2$)$_2$N, J_{PtC} 31.3), 49.0 (NMe$_2$), –12.3 (PtMe, J_{PtC} 766.9).

Synthesis of [Pt{4,5-(OCH$_2$O)C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)] **(5)**. Yield 60%. Anal. Found: C, 36.3; H, 4.4; N 6.7. C$_{13}$H$_{18}$N$_2$O$_2$Pt requires: C, 36.4; H, 4.2; N 6.5. ^{13}C{^{1}H} NMR data: phenyl, 129.4 (C1), 125.3 (C2, J_{PtC} 42.1), 102.7 (C3), 146.8 (C4, J_{PtC} 13.2), 150.4 (C5, J_{PtC} 62.9), 154.1 (C6, J_{PtC} 1092.3). Others, 167.2 (C = N, J_{PtC} 92.9), 100.0 (OCH$_2$O), 68.8 (N(CH$_2$)$_2$N), 52.0 (N(CH$_2$)$_2$N, J_{PtC} 31.9), 49.1 (NMe$_2$), –19.6 (PtMe, J_{PtC} 732.9).

Compounds **4** and **6** were obtained following a similar procedure to that for **1a** but the solvent was removed from the final solutions and the products recrystallised from dichlorometane/hexane to give the desired complexes as orange and dark-red solids for **4** and **6**, respectively. [Pt{2,3,4-(MeO)$_3$C$_6$HC(H)=NCH$_2$CH$_2$NMe$_2$}(Me)] **(4)**. Yield 80%. Anal. Found: C, 37.8; H, 5.0; N 5.9. C$_{15}$H$_{24}$N$_2$O$_3$Pt requires: C, 37.9; H, 5.1; N, 5.9. [Pt{2-NO$_2$C$_6$H$_3$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)] **(6)**. Yield 70%. Anal. Found: C, 31.9; H, 4.1; N 9.8. C$_{12}$H$_{17}$N$_3$O$_2$Pt requires: C, 31.6; H, 4.1; N, 10.0. ^{13}C{^{1}H} NMR data: phenyl, 143.5 (C1, J_{PtC} 52.4), 147.8 (C2, J_{PtC} 42.1) 118.7 (C3), 131.8 (C4, J_{PtC} 79.5), 139.8 (C5, J_{PtC} 88.9), 146.8 (C6, J_{PtC} 1180). Others, 165.1 (C = N, J_{PtC} 93.0), 68.3(N(CH$_2$)$_2$N), 53.6 (N(CH$_2$)$_2$N, J_{PtC} 30.8), 49.3 (NMe$_2$), –10.0 (PtMe, J_{PtC} 795.2).

3.7. Synthesis of [Pt{2,4(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}–(PPh$_3$)(Me)] ***(7)***

A sample of PPh_3 (18 mg, 0.068 mmol) was added to a solution of **1** (30 mg, 0.067 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the solvent removed and the product recrystallised from dichloromethane/hexane to give the desired complex as an orange solid. Yield 89%. Anal. Found: C, 54.0; H, 5.5; N, 4.1. $C_{32}H_{37}N_2O_2PPt$ requires: C, 54.3; H, 5.3; N, 4.0. Compounds **8** and **9** were obtained following a similar procedure as orange solids. [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(PMePh$_2$)(Me)] (**8**). Yield 77%. Anal. Found: C, 50.4; H, 5.4; N, 4.2. $C_{27}H_{35}N_2O_2PPt$ requires: C, 50.2; H, 5.5; N, 4.3. [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(PEt$_2$Ph)(Me)] (**9**). Yield 86%. Anal. Found: C, 47.2; H, 6.3; N, 4.7. $C_{24}H_{37}N_2O_2PPt$ requires: C, 47.1; H, 6.1; N, 4.6.

3.8. Synthesis of [{Pt[2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$](Me)}$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)] ***(10)***

A sample of $Ph_2P(CH_2)_4PPh_2$ (15 mg, 0.035 mmol) was added to a suspension of **1** (30 mg, 0.67 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the solvent removed and the product recrystallized from dichloromethane/hexane to give the desired complex as a yellow solid. Yield 88%. Anal. Found: C, 51.4; H, 5.7; N, 4.3. $C_{56}H_{72}N_4O_4P_2Pt_2$ requires: C, 51.1; H, 5.5; N, 4.2. Compound **11** was synthesized following a similar procedure.

3.9. Synthesis of [{Pt[2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$](Me)}$_2$(μ-trans-Ph$_2$PCH=CHPPh$_2$)] ***(11)***

Yield 92%. Anal. Found: C, 50.3; H, 5.3; N, 4.1. $C_{54}H_{66}N_4O_4P_2Pt_2$ requires: C, 50.4; H, 5.2; N, 4.3. Compounds **12**, **13** and **14** were obtained following a similar procedure to that for **10** but using a **1**/diphosphine 1:1 molar ratio. [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)(Ph$_2$P(CH$_2$)$_4$PPh$_2$–*P*, *P*)] (**12**). Yield 85%. Anal. Found: C, 57.7; H, 5.8; N, 3.3. $C_{42}H_{50}N_2O_2P_2Pt$ requires: C, 57.9; H, 5.8; N, 3.2. [Pt{2,4 - (MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)(Ph$_2$P(CH$_2$)$_3$PPh$_2$–*P*, *P*)] (**13**). Yield 87%. Anal. Found: C, 57.2; H, 5.6; N, 3.3. $C_{41}H_{48}N_2O_2P_2Pt$ requires: C, 57.4; H, 5.6; N, 3.3. [Pt{2,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Me)(Ph$_2$P(CH$_2$)$_2$PPh$_2$-*P*,*P*)] (14). Yield 84%. Anal. Found: C, 57.0; H, 5.5; N, 3.1. $C_{40}H_{46}N_2O_2P_2Pt$ requires: C, 56.9; H, 5.5; N, 3.3.

3.10. Synthesis of [(Me)Pt{Me$_2$NCH$_2$CH$_2$N=(H)C}C$_6$H$_2${C(H)=N–CH$_2$CH$_2$NMe$_2$}Pt(Me)] ***(15)***

A sample of 1,4-[Me$_2$NCH$_2$CH$_2$N=(H)C]$_2$C$_6$H$_4$ (40 mg, 0.156 mmol) and (1,5-cyclooctadiene)dimethylplatinum(II) (100 mg, 0.29 mmol) were added to 25 cm^3 of n-octane to give a pale-yellow solution which was heated under reflux for 3 h. After cooling to r.t. the dark-orange precipitate formed was filtered off and washed with *n*-hexane. Yield 60%. Anal. Found: C, 31.0; H, 4.4; N, 8.0. $C_{18}H_{30}N_4Pt_2$ requires: C, 31.1; H, 4.4; N, 8.1.

3.11. Single-crystal X-ray diffraction analysis

Three-dimensional, r.t. X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Siemens P4 diffractometer by the omega scan method. Of the 2099 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 1358 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by blocked cascade least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R_1 = 0.0467$, ($wR_2 = 0.0965$ for all 1938 unique data; 163 parameters, mean and maximum δ/σ 0.000, 0.006), with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.772 and 0.684 eÅ^{-3}. A weighting scheme $w = 1/[\sigma^2(F_0^2) + (0.0287P)^2 + 1.900P]$ where $P = (F_0^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93 [30] as implemented on a 486dx computer.

4. Supplementary information

Tables of atomic positional and isotropic displacement parameters, anisotropic displacement parameters, and hydrogen co-ordinates and isotropic displacement parameters for the crystal structure of **complex 3** availible on request from author.

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