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FULL PAPER

Binuclear doubly cyclometallated platinum-(II) and -(IV) compounds †

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Doubly cyclometallated binuclear platinum-(II) and -(IV) complexes, as well as their non-cyclometallated platinum(II) precursors, were prepared from the reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with imine ligands derived from terephthalaldehyde. All compounds were characterized by NMR and UV/VIS spectroscopy and the reactivities of the cyclometallated platinum complexes towards phosphines were studied. Electrochemical and spectroelectrochemical (UV/VIS/NIR and EPR) studies were carried out and indicated that while the oxidation of the platinum(II) complexes leads to unstable platinum(III) species, the reduction of the platinum compounds leads to an uptake of an electron into a MO mainly centred on the bridging ligand and is followed by either scission of the bridging ligand for the platinum(II) compounds or scission of the axial ligands for the platinum(IV) compounds.

Cyclometallated complexes of the Group 10 elements have generated considerable interest in recent decades due to their numerous applications in organic synthesis (stoichiometric and catalytic)[1] and in the design of compounds with interesting properties, including liquid crystals or non-linear optics materials.[2] However, investigations to elucidate the electronic structures of cyclometallated compounds are scarce.[3]

On the other hand, binuclear platinum complexes with nitrogen donor bis-bidentate ligands have been described and their reactivity as well as their electrochemical properties compared with those of mononuclear analogues.[4] Binuclear compounds arising from double cyclometallation of nitrogen donor ligands can be considered to be analogues of complexes containing binucleating bis(diimine) ligands in which a nitrogen donor is replaced by a carbon σ donor. Such a replacement has been reported to increase the metal–metal coupling in diruthenium complexes.[5] Besides the high intermetallic electronic contact,[6] interest in these compounds is related to their usefulness as building blocks for supramolecular architectures[7] and to the liquid crystal behaviour recently reported for a dicyclopalladated Schiff base.[8] However, relatively few examples of double cyclometallation on a single arene have been reported for palladium,[9] while only one analogous diplatinum compound has recently been described.[10],‡

Since intramolecular C–H or C–X (X = halogen) activation at $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ **1** readily produces [C,N,N′]-tridentate[11] or [C,N]-bidentate[12] mononuclear complexes, a similar strategy, using ligands derived from terephthalaldehyde, was attempted for the synthesis of binuclear platinum-(II) or -(IV) complexes by double cyclometallation of a single benzene ring. As a result, we report here the preparation of several compounds in which two metal fragments are linked by bridging ligands containing two [N,N′] (**2a**,**2b**), two [C,N,N′] (**3a**,**3b**) or two [C,N′] co-ordination moieties (**3c**–**3e**). Electrochemical and spectroelectrochemical measurements (UV/VIS/NIR and EPR), which provide insights into the electronic properties and reactivity of such cyclometallated compounds,[13] are also presented. In particular, the spectroelectrochemical experiments allow the odd-electron species prepared by oxidation or reduction to be characterized spectroscopically even if they are transient,[14] and provide information on the reactivity pathways, when subsequent decomposition reactions lead to detectable species.

Results and discussion

Double cyclometallation in [C,N,N′] systems

Ligands containing two [C,N,N′] co-ordination moieties such as **Ia** and **Ib** were prepared from the reaction of 2,5-dichloroterephthalaldehyde or terephthalaldehyde with two equivalents of *N*,*N*-dimethylethylenediamine and were characterized by ^{1}H NMR and mass spectra.

Binuclear compounds **2a** and **2b** were readily obtained upon reaction of **Ia** and **Ib** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ **1** in acetone at room temperature, as shown in Scheme 1. Incorporation of two $PtMe_2$ fragments is achieved through the co-ordination of each moiety to both nitrogen donor atoms. Compounds **2a** and **2b** were characterized by elemental analysis, FAB-MS and ^{1}H and ^{13}C (**2b**) NMR. In the ^{1}H NMR of both compounds two resonances due to non-equivalent methylplatinum groups appear. The one at higher field with a larger coupling to ^{195}Pt is assigned to the methyl *trans* to the NMe_2. The co-ordination of the ligand through the nitrogen atoms is confirmed by the coupling of both amine and imine protons to platinum.

Compounds **2a** and **2b** are stable in solution at room temperature; however, double cyclometallation processes occur in refluxing toluene to yield **3a** and **3b**, which contain a five fused ring system and a *para*-diplatinated benzene ring. Both compounds were characterized by elemental analysis, FAB-MS and ^{1}H and ^{13}C (**3a**) NMR. Binuclear platinum(IV) compound **3a** is produced, as a very slightly soluble yellow solid, by intramolecular C–Cl bond activation. As reported for mononuclear compounds,[11a] a higher reactivity of C–Cl bonds, when compared to C–H bonds, is expected in view of the greater bond

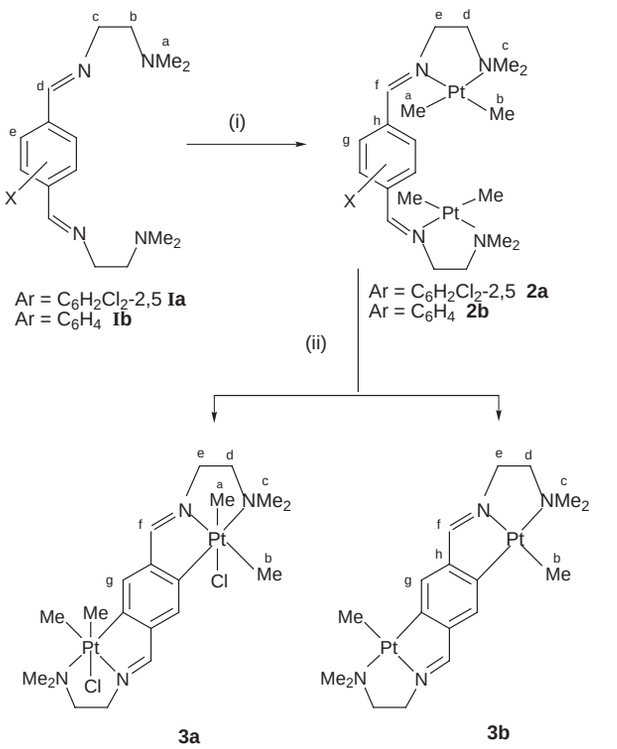
† *Supplementary data available*: electrochemical and absorption spectral data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/1629/, otherwise available from BLDSC (No. SUP 57526, 5 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

‡ Ref. 10, published when the present manuscript was in preparation, describes the synthesis of compound **4b**.

Table 1 Selected ^{1}H NMR data for compounds **2** and **3**[a]

Compound	δ(Me[a]) [^2J(Pt–H)]	δ(Me[b])- [^2J(Pt–H)]	δ(CHN)- [^3J(Pt–H)]
2a	0.08 (90.8)	0.65 (84.6)	9.20 (43.6)
2b	0.17 (90.0)	0.62 (84.6)	9.00 (44.4)
3a	0.61 (74.0)	1.00 (63.5)	8.43 (46.0)
3b		0.90 (78.4)	8.53 (60.8)
3c	0.96 (68.8)	1.22 (67.4)	8.18 (45.4)
3d		0.97 (81.0)	8.63 (56.0)
3e		1.01 (81.4)	8.64 (55.6)

[a] δ in parts per million and J in hertz; solvent $CDCl_3$, referenced to TMS; Me[a] *trans* to Cl or NMe_2, Me[b] *trans* to CHN.



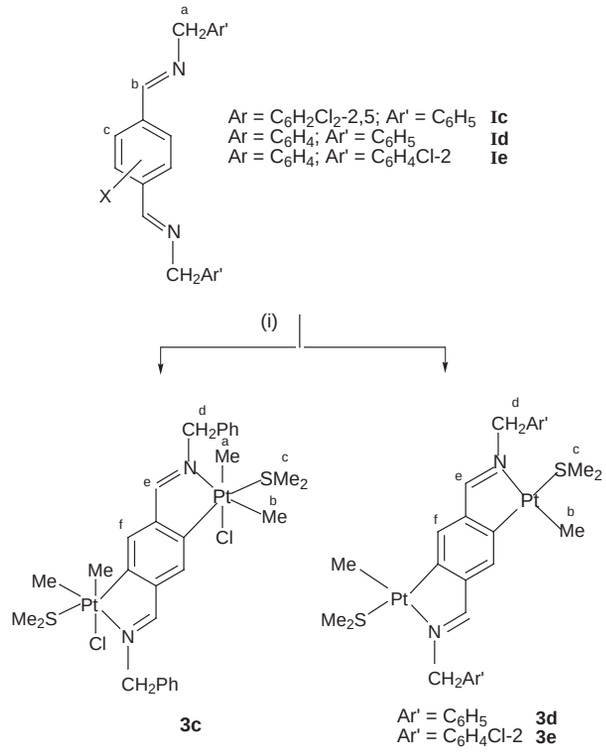
Scheme 1 (i) $+[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, $-SMe_2$, acetone solution, room temperature, 16 h; (ii) toluene solution, under reflux, 4 h, $-CH_4$ for **3b**.

energy of the latter. Regioselective activation of C–H bonds in the 2,5 positions, followed by methane elimination, yields binuclear platinum(II) compound **3b** as a red solid, soluble in most common organic solvents. The fact that double metallation at mutually *ortho* positions is not observed may be due to the steric crowding that would result from the presence of two metal fragments in adjacent positions.

The ^{1}H NMR spectra of compounds **3a** and **3b** display analogous features to those obtained for mononuclear cyclometallated compounds[11] and are summarized in Table 1. In particular, two methylplatinum resonances are observed for the platinum(IV) compound and the one at higher field with a larger coupling to platinum is assigned to the axial methyl; for **3b**, one single methylplatinum resonance is observed. Reduced coupling constants to platinum are obtained for methyl, amine, and imine hydrogens in **3a** when compared to **3b**, as expected for the different oxidation state of the metal centre. For **3b** the aromatic protons appear as a singlet with J(Pt–H) = 63 Hz; this value indicates a three-bond coupling and can be taken as evidence for the formation of the *para*-diplatinated regioisomer.

Double cyclometallation in [C,N] systems

In order to explore the possibility of double cycloplatination in greater depth, the reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ **1** with ligands **Ic**, **Id** and **Ie** were also studied (see Scheme 2). These ligands



Scheme 2 (i) $+[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, $-SMe_2$, acetone solution, room temperature, 16 h, $-CH_4$ for **3d** and **3e**.

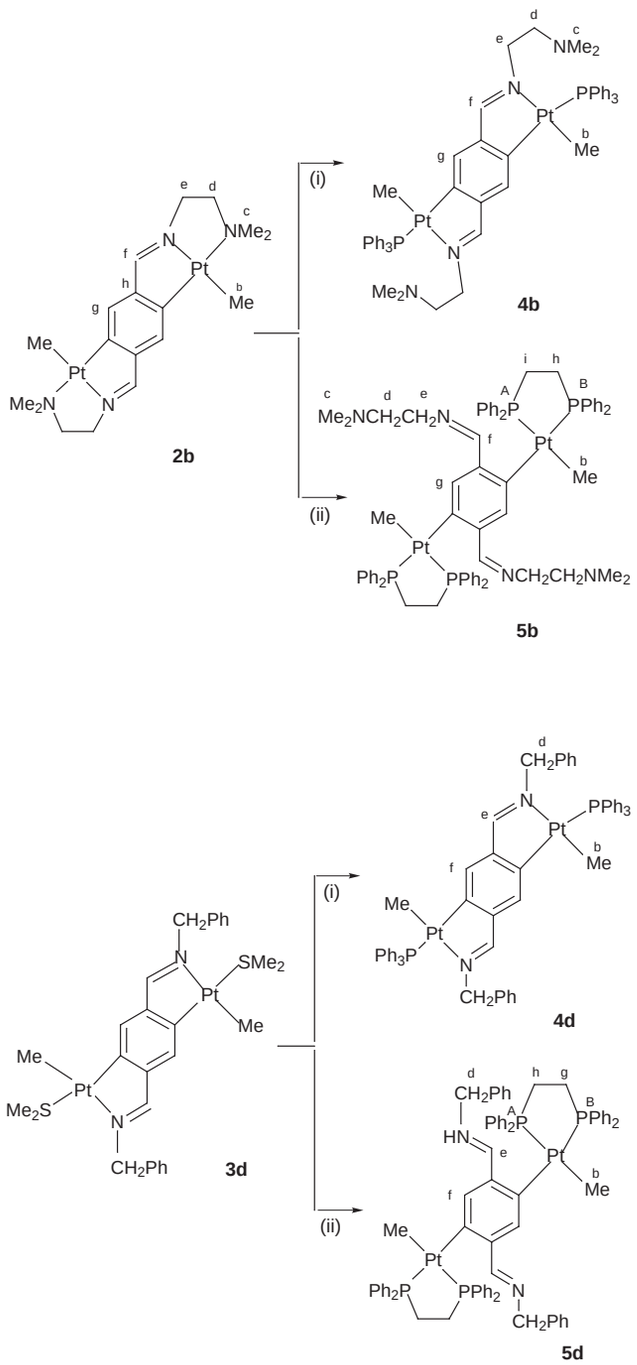
were prepared by reaction of 2,5-dichloroterephthalaldehyde or terephthalaldehyde with amines containing one single nitrogen donor such as benzylamine or 2-chlorobenzylamine, and were characterized by ^{1}H NMR and mass spectra. The reactions of these ligands with platinum substrates may lead to the formation of either *endo*- (containing the C=N group) or *exo*-cycles. For monometallated compounds the formation of *endo*-cycles has been reported as being preferred, due, among other factors, to the stability associated with the electronic delocalization into the two fused rings.[12]

The reaction of ligands **Ic**, **Id** and **Ie** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ **1** in acetone at room temperature in a 1 : 1 ratio produces, in all cases, tricyclic systems due to double metallation at *para* positions of the terephthalylidene group, either by C–Cl bond activation (**3c**) or by C–H bond activation, followed by methane elimination (**3d**, **3e**). Formation of *exo*-metallacycles was not observed, not even for ligand **Ie**, in spite of the fact that, in this case, this process could be achieved by activation of a weaker C–Cl bond. However, activation of C–Cl bonds to yield *endo*-cycles is preferred over C–H bond activation for ligand **Ic**. These results suggest the following reactivity order for C–X bond activation: C–Cl(*endo*) > C–H(*endo*) > C–Cl(*exo*) as reported for the formation of monocyclometallated complexes.

Co-ordination compounds of type **2**, analogous to those obtained for [C,N,N′] systems, have not been detected for ligands **Ic**–**Ie**, which indicates that cyclometallation reactions occur more readily for [C,N] systems.

In an attempt to produce monomer compounds, the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ **1** with ligand **Id** in a 1 : 2 ratio was tested. This yields doubly cyclometallated compound **3d**, along with unchanged ligand, which suggests a high stability of the tricyclic unit. Similar arguments to those used to explain the stability of *endo*-cycles[15] can be used since a strong delocalization is to be expected for the three fused ring unit.

Compounds **3c**, **3d** and **3e** were characterized by elemental analysis, FAB and ^{1}H NMR spectra. The spectra show similar patterns to those observed for mononuclear cyclometallated platinum complexes with [C,N] ligands.[12] In particular, reduced coupling constants to ^{195}Pt are observed for methyl and imine



Scheme 3 (i) $+PPh_3$, toluene solution, room temperature, 2 h, $-SMe_2$ for **4d**; (ii) +dppe, toluene solution, room temperature, 2 h, $-SMe_2$ for **5d**.

resonances for platinum(IV) complex **3c** when compared to analogous platinum(II) compounds **3d** and **3e**. As indicated for the [C,N,N′] systems, the J(Pt–H) value for the aromatic proton is typical for a three-bond coupling to platinum-(II) (59) or to -(IV) (46 Hz), thus suggesting that the platinum fragments are in mutually *para* positions.

Reactivity with phosphines

According to previous results for cyclometallated palladium compounds,[16] the reactions with phosphines can be taken as a criterion for the stability of metallacycles. For instance, it has been reported that the reactions of *exo*-palladacycles with PPh_3 lead to cleavage of the Pd–N bond, while for the more stable *endo* derivatives this process does not take place. Moreover, it has been shown that steric crowding in the co-ordination sphere of the metal favours the cleavage of platinacycles upon reaction with phosphines.[17]

Table 2 Selected ^{1}H and ^{31}P NMR data for compounds **4** and **5**[a]

Compound	δ(Me)[^2J(Pt–H)][^3J(P–H)]	δ(CHN)-[^3J(Pt–H)]	δ(P)[^1J(Pt–H)]
4b	0.74(82.0)(8.0)	8.57(56.8)	30.53(2160.4)
4d	0.71(82.6)(7.8)	8.37(56.0)	30.55(2166.7)
5b[b]	0.64(73.0)(7.5)	8.58	41.56(1760.6) P^B
			44.02(1780.3) P^A
	0.60(73.0)(7.5)	8.45	40.09(1724.9) P^B
			45.67(1789.1) P^A
5d[b]	0.64(73.0)(7.5)	8.67	43.00(1758.8) P^B
			47.70(1794.5) P^A
	0.65(73.0)(7.0)	8.75	41.15(1724.0) P^B
			45.74(1782.5) P^A

[a] δ in parts per million and J in hertz; solvent $CDCl_3$, referenced to TMS (^{1}H) or H_3PO_4 (^{31}P). [b] P^A *trans* to Me, P^B *trans* to aryl; two isomers (see text).

In this context, we decided to study the reactions of the new doubly metallated binuclear complexes with mono- and bi-dentate phosphines. The reactions of **3b** and **3d** with triphenylphosphine or 1,2-bis(diphenylphosphino)ethane (dppe) were carried out in toluene solution at room temperature and are shown in Scheme 3. The reaction with the monodentate phosphine did not produce cleavage of the metallacycle, and either the dimethylamino moiety (**3b**) or the dimethyl sulfide ligand (**3d**) were displaced by the phosphine. These results suggest the great stability of the tricyclic unit, which could be cleaved, however, upon reaction with the chelating diphosphine dppe. In the resulting binuclear compounds **5b** and **5d** two PtMe(dppe) moieties are bridged by a 1,4-phenylene group.

Compounds **4b**, **4d**, **5b** and **5d** were characterized by elemental analysis, FAB and ^{1}H and ^{31}P NMR spectra. Selected ^{1}H and ^{31}P NMR data are given in Table 2. For **4b** and **4d** the presence of the PPh_3 ligand is seen in the ^{31}P NMR spectra by the single resonance coupled to ^{195}Pt, and in the ^{1}H NMR spectra by the coupling of the methylplatinum to phosphorus. For both compounds, the value of the coupling constant of the imine proton to ^{195}Pt indicates that the metallacycle is not cleaved. For **4b**, dissociation of the NMe_2 fragment is confirmed by the lack of ^{195}Pt satellites for the corresponding resonance.

For both compounds **5b** and **5d** two sets of resonances appear in the ^{1}H and ^{31}P NMR spectra, thus showing the presence of two isomers in an approximately 1:1 ratio for **5d** and in slightly different amounts for **5b**. Both ^{1}H and ^{31}P NMR data disclose the cleavage of the metallacycle and the bidentate co-ordination of the diphosphine. The methylplatinum group appears as a triplet due to coupling with both phosphorus atoms while imine protons are not coupled to ^{195}Pt. In the ^{31}P NMR spectra the resonances of non-equivalent phosphorus atoms show couplings to platinum, and the values are well within the range observed for phosphorus *trans* to methyl or aryl groups.[18]

Compounds **5b** and **5d** are *cis* analogues of the bimetallic platinum and palladium compounds with aryl bridges reported in the literature.[19] The usual orientation of aryl groups co-ordinated to platinum is nearly perpendicular to the co-ordination plane,[20] which implies the existence of isomers **A** and **B**, which differ in the relative orientation of their methylplatinum groups.

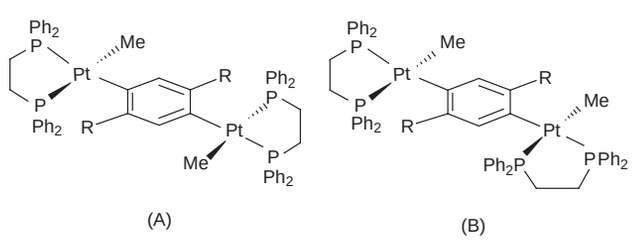


Table 3 Electrochemical data[a]

Compound	E_{pa} oxI[b]	$E_{1/2}$ redI (ΔE_p)[c]	$E_{1/2}$ redII (ΔE_p)[c]	E_{pc}[d] redIII
Ia	0.55	−1.96 (81)[e]	−2.42 irr.	−2.67
Ib	0.33	−2.42 (92)[e]	−2.92 irr.	
Ic	0.55	−1.91 (87)[e]	−2.72 irr.	
Id	0.54	−2.28 (91)[e]	−2.73 irr.	
Ie	0.56	−2.25 (83)[e]	−2.71 irr.	−3.04
2a	0.27	−1.73 (70)	−2.16 irr.	−2.81
2b	0.57	−2.06 (107)	−2.41 (111)	−2.82
3b	0.04	−2.27 (72)	−2.65 irr.	−2.80
3d	0.33	−2.19 (78)	−2.38 irr.	−2.61
3e	0.34	−2.11 (95)	−2.44 irr.	−2.64
3a	—	−1.94 irr.	−2.05 irr.	−2.26
3c	—	−1.90 irr.	−2.21 irr.	−2.38

irr. = Irreversible. [a] From cyclic voltammetry in 0.1 M Bu_4NPF_6–DMF solutions at 100 mV s^{-1} scan rate. Potentials in V *vs.* ferrocene–ferrocenium couple. [b] Anodic potentials E_{pa} for irreversible oxidation. [c] Half-wave potentials $E_{1/2}$, peak potential differences $\Delta E_p = E_{pa} - E_{pc}$ in mV (in parentheses). [d] Cathodic peak potential E_{pc} for irreversible reduction. [e] Measured at 500 mV s^{-1}.

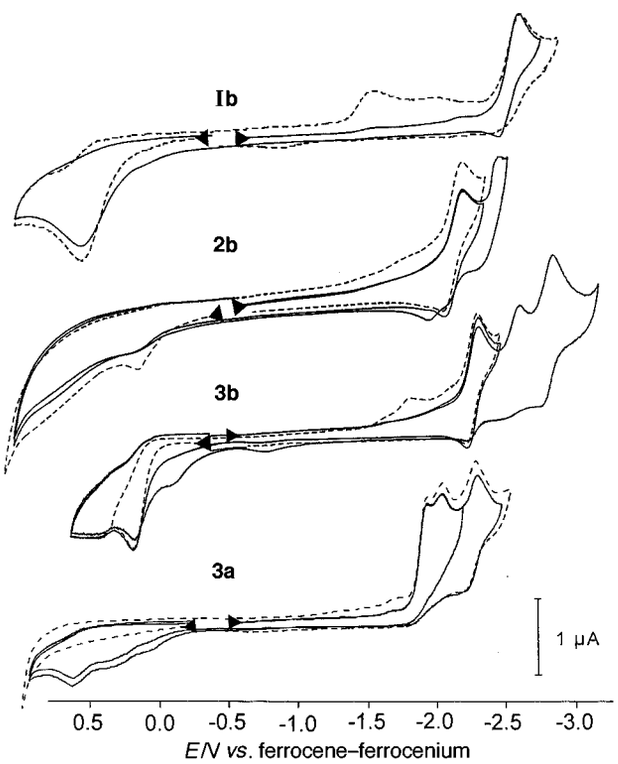


Fig. 1 Cyclic voltammograms of compounds **Ib**, **2b**, **3b** and **3a** in DMF–0.1 M Bu_4NPF_6 at 100 mV s^{-1} scan rate. Solid lines indicate scans with negative first vertex potentials and positive second vertex potentials (reductive scans), dashed lines show oxidative scans in that respect.

Electrochemical measurements

The ability of the complexes to gain or lose electrons was studied by cyclic voltammetry and square wave voltammetry at room temperature. An example of the cyclic voltammograms obtained is shown in Fig. 1 and the results are summarized in Table 3. Further data have been deposited as SUP 57526.

The cyclometallated platinum(II) complexes **3b**, **3d** and **3e** as well as the non-cyclometallated dimethylplatinum complexes **2a** and **2b** are reduced in several closely lying reduction steps. The first reduction involves one electron as determined from experiments with weighed samples of compound and ferrocene. Returning after the first wave gives reasonable reoxidation waves and allows the measurement of the half-wave potentials. Determination of the current ratios is difficult due to the close vicinity of the second reduction processes that are irreversible. The potentials of the first reduction are markedly less negative than those of the corresponding "free" ligands or of comparable mononuclear compounds of the same type.[3a] Oxidations of the platinum(II) compounds occur in an irreversible manner and only for the cyclometallated compounds were well defined oxidation waves found. Interestingly, the decrease observed in the anodic peak potentials in the series **3e** > **3d** ≫ **4b** reflects a stronger influence of the different ligand systems on the oxidation potentials than on the reduction potentials. The oxidation reaction very probably leads to highly unstable platinum(III) species which undergo very fast follow-up reactions that involve the solvents, as has recently been reported for thoroughly investigated dimethylplatinum(II) complexes of the diazabutadienes.[21] When DMF was used as the solvent we found, on the reverse scan after oxidation, reduction waves of species that can be considered to be cationic platinum-(II) and -(IV) molecules, as reported in the aforementioned study. Further investigations, currently underway, including bulk electrolysis experiments, should clarify this. The currents for the oxidation reactions are somewhat higher (1.1 to 1.5 times) compared to those of the reduction reactions but unambiguous determination of the number of electrons involved is hampered by the irreversibility of the process.

The platinum(IV) complexes **3a** and **3c** exhibit an irreversible first reduction. Oxidation waves are not observed up to potentials of about +1.2 V. On the reverse scans returning after the first irreversible reduction wave, defined oxidation waves are observed at +0.57 V for **3a** and +0.62 V for **3c** respectively.

The electrochemical data suggest that the reduction of the platinum(II) complexes might be regarded as being more or less centred on the aromatic ring system. In contrast, the first reduction of the platinum(IV) complexes is probably followed by a fast decomposition reaction. Involvement of the axial ligands and formation of platinum(II) species is assumed. The reoxidation waves observed are consistent with platinum(II) species but not with the platinum(II) compounds **3b** and **3d**. The oxidation reactions on the platinum(II) complexes are considered to take place mainly at the platinum centre yielding very unstable platinum(III) species. In the case of the platinum(IV) complexes, oxidation reactions are consequently not observed.§

UV/VIS/NIR Spectroscopy and spectroelectrochemistry

The spectroelectrochemical method allows one not only to follow the spectroscopic response to electrochemical reactions and to characterize the species thus obtained, but also to obtain information on the reversibility of the electrochemical reactions and the stability of the generated species on a larger timescale. For all the compounds studied here our results showed that the species generated by reduction are more or less unstable. During our experiments we found that within some minutes the parent platinum(II) compounds could be recovered from the reduction products by reoxidation. The reduced species appeared to be stable for 5–10 min under the experimental conditions in the OTTLE cell (see Experimental section) and we could characterize them by UV/VIS/NIR absorption spectroscopy. The platinum(IV) compounds have been reduced under the same conditions giving reproducibly distinct optically detectable species of comparable stability.

The neutral platinum complexes show long-wavelength bands in the visible region. They exhibit slightly negative solvatochromy and are assigned as d Pt–π* or metal-to-ligand charge transfer (MLCT) transitions. Additionally more intense absorptions are observed in the UV region, which are assigned

§ A reinvestigation of the mononuclear platinum(IV) compounds reported in ref. 3(*a*) showed that, as observed for the binuclear compounds, the oxidation waves were only present after a reductive scan.

Table 4 Spectroelectrochemical data. Long wavelength absorption maxima of binuclear platinum complexes and "free" ligands[a]

Compound											
Ia	*279*		*317*		329 (sh)						
	(20.7)		(0.66)		(0.49)						
Ia$^{\bullet -}$	*261*		*366*		450	481	*506*		535	*653*	700 (sh)
	(19.9)		(0.59)		(0.28)	(0.33)	(0.36)		(0.25)	(0.07)	(0.06)
Ib	*278*	284 (sh)									
	(17.6)	(16.3)									
Ib$^{\bullet -}$	*264*			*416*			509	540	*626*	*673*	801
	(8.30)			(0.21)			(0.09)	(0.08)	(0.08)	(0.07)	(0.03)
2a	*224*	*278*	283 (sh)		316 (sh)				*461*		
	(8.6)	(5.04)	(4.70)		(0.51)				(0.2)		
2a$^{\bullet -}$				*403*		*550*				*653*	762
				(0.24)		(0.22)				(0.08)	(0.06)
2b	*243*		334	*447*							
	(1.46)		(0.31)	(0.29)							
2b$^{\bullet -}$	2.38		395 (sh)	*408*		538			634	708	758
	(1.51)		(0.28)	(0.28)		(0.10)			(0.03)	(0.03)	(0.03)
3b	*275*		359	*372*		411	442	*471*		534	581
	(3.47)		(0.7)	(0.80)		(0.44)	(0.53)	(0.66)		(0.14)	(0.11)
3b$^{\bullet -}$	*271*		373	*414*	464	503	*539*		*682*	788	*895*
	(4.20)		(0.63)	(0.64)	(0.35)	(0.27)	(0.33)		(0.39)	(0.20)	(0.51)
3a[b]	*236*	314	*328*		345 (sh)				*411*		*473*
	(0.86)	(0.28)	(0.28)		(0.22)				(0.11)		(0.08)
3a$^{\bullet -}$[b]	*269*	365	*412*		457	*524*		615	*678*	791	*892*
	(0.67)	(0.14)	(0.12)		(0.10)	(0.07)		(0.04)	(0.05)	(0.04)	(0.07)

[a] Absorption maxima in nm, absorption coefficient ε in 10^3 M^{-1} cm^{-1} in parentheses. Anionic species generated by electrolysis in 0.1 M Bu_4NPF_6–THF solution. Italicized maxima represent characteristic bands. [b] Measured in DMF.

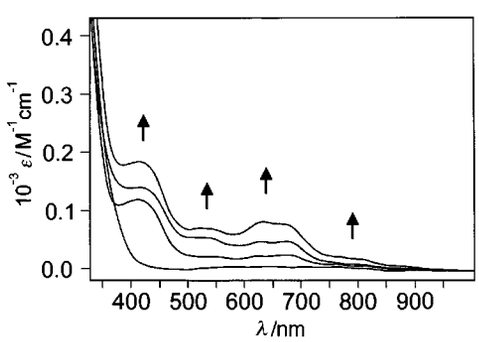


Fig. 2 The UV/VIS/NIR absorption spectra from reductive spectroelectrochemistry of compound **Ib** in THF–0.1 M Bu_4NPF_6. The generation of the monoanion is shown.

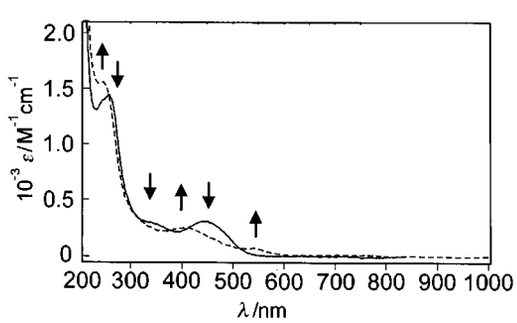


Fig. 3 The UV/VIS/NIR absorption spectra from reductive spectroelectrochemistry of compound **2b** in THF–0.1 M Bu_4NPF_6. The generation of the monoanionic complex is shown.

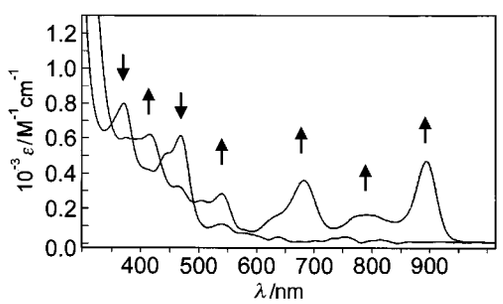


Fig. 4 The UV/VIS/NIR absorption spectra from reductive spectroelectrochemistry of compound **3b** in THF–0.1 M Bu_4NPF_6. The generation of the monoanionic complex is shown.

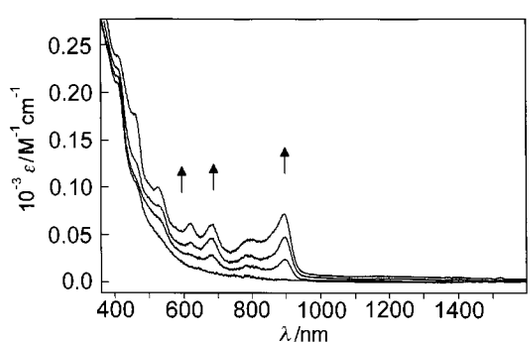


Fig. 5 The UV/VIS/NIR absorption spectra from reductive spectroelectrochemistry of compound **3a** in DMF–0.1 M Bu_4NPF_6. The generation of the monoanionic complex is shown.

to π–π* transitions due to the fact that they also occur for the corresponding "free" ligands. Data have been deposited as SUP 57526.

As shown in Table 4 and Figs. 2 to 5, the species generated by electrochemical reduction from the platinum-(II) and -(IV) complexes show partly structured long-wavelength bands of low intensity between 500 and 800 nm. The fact that they also appear for the reduced "free" ligands leads to the conclusion that they are all of the same character: π*–π* transition from the singly occupied molecular orbital (SOMO), the former LUMO (lowest unoccupied MO), to higher unoccupied molecular orbitals (SLUMO), that are all more or less centred on the bridging ligand. The detected species decompose within a couple of minutes with consequent bleaching of the long-wavelength bands. Electrochemical oxidation of platinum(II) complexes also leads to bleaching of the long-wavelength bands supporting also their assignment to MLCT transitions.

EPR Spectroelectrochemistry

EPR Spectroscopy of the singly reduced species is highly revealing of the character of the SOMO. In addition, paramagnetic

Table 5 EPR Data of anionic ligands and binuclear organoplatinum complexes[a]

Compound[b]	g_{iso}[c]	g_1	g_2	g_3	Δg[d]	A_H	A_H	A_N
Ia$^{\bullet -}$	2.0037		[e]			1.95	—	1.50
Ib$^{\bullet -}$	2.0042		[e]			3.81	1.50	0.55
Ic$^{\bullet -}$	2.0036		[e]			1.97	—	1.49
Id$^{\bullet -}$	2.0041		[e]			3.87	1.47	0.65
Ie$^{\bullet -}$	2.0036		[e]			—	—	—
2a$^{\bullet -}$ species I	2.0224	2.036	2.026	2.003	33	5.7[f]		
species II	2.0042		[e]			1.95	—	1.50
2b$^{\bullet -}$ species I	2.0195		2.0195			5.7[f]		
species II	2.0039		2.0038			3.81	1.50	0.55
3b$^{\bullet -}$	1.9976	2.052	2.008	1.914	138			
3d$^{\bullet -}$	1.9968	2.035	2.012	1.947	88			
3e$^{\bullet -}$	1.9972	2.035	2.013	1.948	89			
3a$^{\bullet -}$	1.988	2.037	2.004	1.923	114			
3c$^{\bullet -}$	1.9969	2.034	2.009	1.944	90			

[a] Coupling constants A in G (10 G = 1 mT); values are from spectral simulation. [b] Generated by *in situ* electrolysis at ambient temperatures in 0.1 M Bu_4NPF_6–dmf–thf. [c] Measured at room temperature, anisotropic g factors and coupling constants at 110 K. [d] $\Delta g = 10^3(g_1 - g_3)$. [e] Isotropic spectra at 110 K. [f] From experimental spectra.

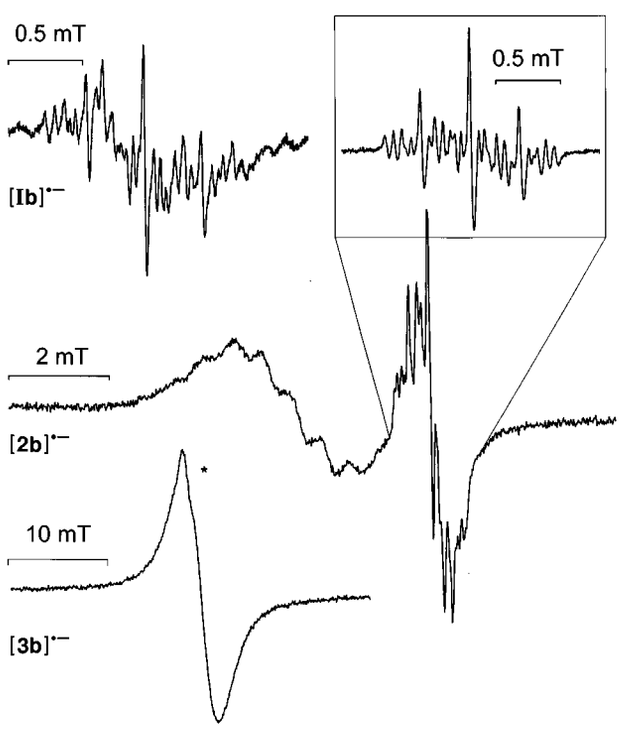


Fig. 6 The EPR spectra of compounds **1b**$^{\bullet -}$ (top), **2b**$^{\bullet -}$ (middle) and **3b**$^{\bullet -}$ (bottom) electrogenerated in THF–DMF–0.1 M Bu_4NPF_6 in fluid solution at 298 K. The asterisk indicates paramagnetic impurities.

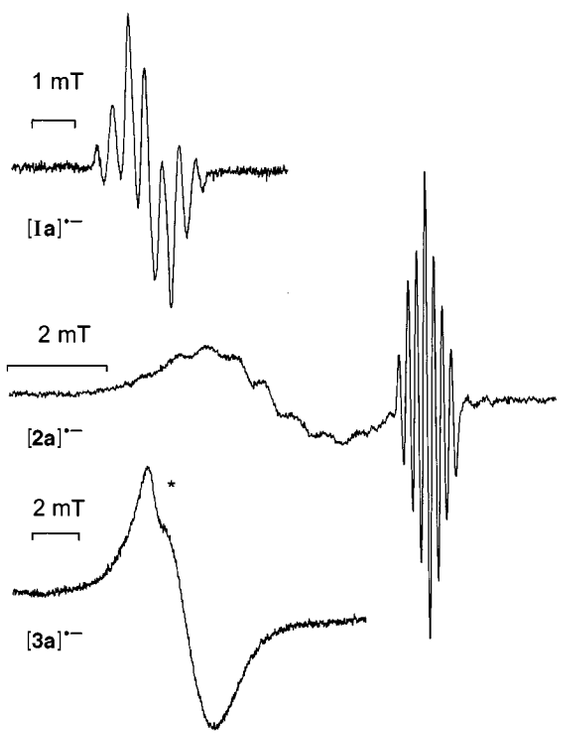


Fig. 7 The EPR spectra of compounds **1a**$^{\bullet -}$ (top), **2a**$^{\bullet -}$ (middle) and **3a**$^{\bullet -}$ (bottom) electrogenerated in THF–DMF–0.1 M Bu_4NPF_6 in fluid solution at 298 K. The asterisk indicates paramagnetic impurities.

products arising from the decomposition reactions may also be observed. The results are summarized in Table 5, and selected spectra are shown in Figs. 6 to 8. The EPR spectra of the reduced ligands all have similar isotropic g values (g_{iso}) that deviate slightly from $g_e = 2.0023$ (value for the free electron). Depending on their substitution pattern, they split either into a septet (**Ia**, **Ic**), probably due to hyperfine interactions (HF) with two ^1H ($I = 1/2$) and two ^{14}N ($I = 1$) nuclei, or appear as complex spectra dominated by a large triplet from a large HF coupling to two ^1H, and with smaller HF coupling to two ^1H and ^{14}N (**Ib**, **Id**). The platinum(II) complexes **2a**$^{\bullet -}$ and **2b**$^{\bullet -}$ show a nine line pattern with coupling constants of 5.7 G and a quite high g_{iso} of about 2.020. In the course of the experiment a second signal appears at higher field and the low-field signal is consumed. Examination of g values and observed splittings show that the secondary signal can be attributed to the "free" ligand radical anion. The cyclometallated platinum-(II) and -(IV) complexes exhibit both unstructured broad isotropic lines at 298 K in fluid solution and rhombic spectra at 110 K in glassy frozen solution with only marginal HF splitting features. The g values are markedly smaller than 2. During the course of the electrolysis only traces of paramagnetic impurities appear as single lines.

Owing to the lack of HF coupling to ^{195}Pt isotopes only the g anisotropy (Δg) of the rhombic spectra can give information on the extent of admixture of platinum orbitals (5d, 6p) to the mainly ligand-centred SOMO. The Δg ranges from 88 to 138 and is comparably small for organometallic platinum complexes.[13,22] The admixture of platinum orbitals can thus be estimated to be smaller than 5%. A different orbital situation with virtually no or only a very small contribution is found for the complexes **2a** ($\Delta g = 33$) and **2b** (isotropic, no Δg).

From the observations made in both kinds of spectroelectrochemical experiments it is reasonable to assume that the observed paramagnetic species are the main products from reduction of the platinum(II) complexes, or from reduction and fast following reaction of the platinum(IV) complexes, respectively, that also have been detected in the optical spectroelectrochemical experiments. It can thus be concluded that

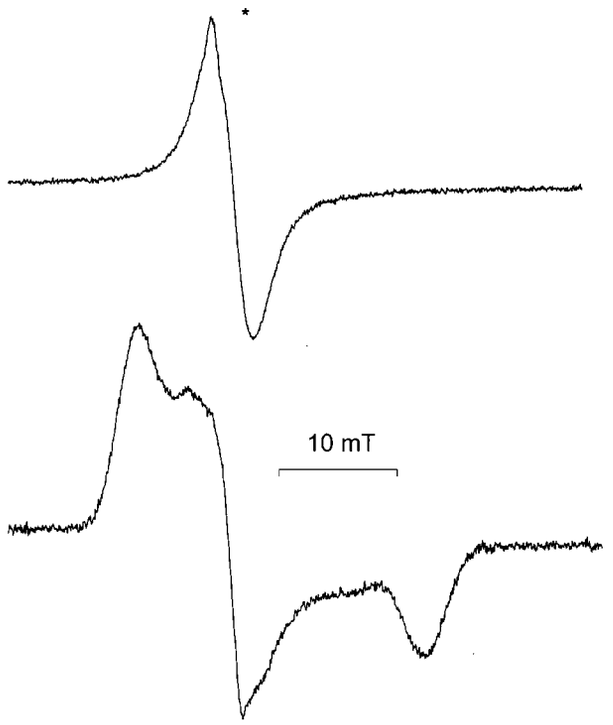


Fig. 8 The EPR spectra of compound $\mathbf{3b}^{\bullet -}$ electrogenerated in THF–DMF–0.1 M Bu_4NPF_6 in fluid solution at 298 K (top) and in glassy frozen solution at 110 K (bottom). The asterisk indicates paramagnetic impurities.

reduction of the cyclometallated platinum(II) complexes leads to radical anions where the electron density of the single unpaired electron is mainly located in the bridging ligand with only small contributions from the platinum metal centres. Reduction of the platinum(IV) complexes **3a** and **3c** followed by a very fast decomposition leads very probably to platinum(II) species that are very similar, but not identical, to the platinum(II) complexes **3b** and **3d**. For the non-cyclometallated species, the metal fragment is cleaved on reduction, yielding the corresponding unco-ordinated radical anionic ligands.

Summarizing, a new class of binuclear cyclometallated platinum-(II) and -(IV) compounds based on bridging ligands derived from terephthalaldehyde and primary amines was prepared and thoroughly characterized. The compounds are very stable to air, moisture and light both in solution and in the solid state. Interestingly, they become highly reactive when transformed into an odd-electron species. There is strong evidence from spectroelectrochemical experiments that the electrochemical reduction of the present organometallic platinum-(II) and -(IV) complexes leads to the uptake of an electron into a mainly ligand-centred MO. The reduction is followed by more or less fast reactions leading to scission of the bridging ligand as radical anions (**2a**, **2b**) or neutral ligands (**3b**, **3d**, **3e**). In the case of the platinum(IV) complexes (**3a**, **3c**) the reduction is followed by a very fast chemical reaction most probably involving scission of the axial ligands yielding platinum(II) species. Oxidation of the platinum(II) complexes leads to unstable platinum(III) species (not detectable) and consequently does not occur at potentials up to +1.2 V (*vs.* $FeCp_2^{+/0}$) for the platinum(IV) complexes. Compared to nitrogen containing aromatic bridging ligands, platinum binding to the phenylene unit seems to be much weaker and the ability to transmit metal-to-metal interactions is much smaller in contrast to findings for diruthenium complexes.[5]

Experimental

The ^{1}H and ^{31}P-{^{1}H} NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200 MHz), Varian 500 (^{1}H, 500 MHz) and Bruker 250 (^{31}P, 101.25 MHz) spectrometers, and referenced to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P); δ values are given in ppm and J values in Hz. The IR spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses and mass spectrometry (CI and FAB, 3-nitrobenzyl alcohol matrix) were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona. The UV/VIS/NIR absorption spectra were recorded on a Bruins Instruments Omega 10 instrument. Cyclic voltammetry and square-wave voltammetry were carried out using a three-electrode configuration (glassy carbon working electrode, platinum counter electrode, Ag–AgCl reference) and a PAR 273 potentiostat and function generator with PAR M270/250 software. The ferrocene–ferrocenium couple ($FeCp_2^{+/0}$) was used as internal standard. Spectroelectrochemical measurements were performed using an optical transparent thin-layer electrode (OTTLE) cell[23] for UV/VIS/NIR spectra, a platinum two-electrode capillary for EPR studies and a Bank Elektronik Potentioscan Wenking POS 73 potentiostat and function generator equipped with an XY-plotter PAR RE 0089. The EPR spectra were recorded in the X band on a Bruker ESP 300 system equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. Spectral simulation was achieved by using the Bruker WINEPR SimFonia (version 1.25) program. The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ **1** was prepared as reported.[24]

Synthesis of ligands

Compounds **I** were prepared by the reaction of 5 mmol of the corresponding dialdehyde (terephthalaldehyde or 2,5-dichloroterephthalaldehyde) with 10 mmol of *N*,*N*-dimethylethylenediamine, benzylamine or 2-chlorobenzylamine in toluene. After stirring for 30 min, the reaction mixture was dried over anhydrous Na_2SO_4 and the solvent removed in a rotary evaporator to yield yellow oils (80–85%). 1,4-$(Me_2NCH_2CH_2N{=}CH)_2$-2,5-$Cl_2C_6H_2$ **Ia**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 [s, 12 H, H^a], 2.67 [t, 4 H, ^3J(H^b–H^c) = 7, H^b], 3.80 [td, 4 H, ^3J(H^c–H^b) = 7, ^4J(H^c–H^d) = 1.5, H^c], 8.06 [s, 2 H, H^e] and 8.66 [t, 2 H, ^4J(H^d–H^c) = 1.5 Hz, H^d]; IR (KBr, cm^{-1}) 1639 (C=N); MS (CI, NH_3) *m*/*z* 343 (M + H$^+$). 1,4-$(Me_2NCH_2CH_2N{=}CH)_2C_6H_4$ **Ib**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 [s, 12 H, H^a], 2.67 [t, 4 H, ^3J(H^b–H^c) = 7, H^b], 3.77 [td, 4 H, ^3J(H^c–H^b) = 7, ^4J(H^c–H^d) = 1.1, H^c], 7.77 [s, 4 H, H^e] and 8.33 [t, 2 H, ^4J(H^d–H^c) = 1.1 Hz, H^d]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.7 [s, C^a], 59.8 [s, C^b], 59.9 [s, C^c], 128.2 [s, C^e], 137.9 [s, C^f] and 161.1 [s, C^d]; IR (KBr, cm^{-1}) 1650 (C=N); MS (CI, NH_3) *m*/*z* 275 (M + H$^+$). 1,4-$(C_6H_5CH_2N{=}CH)_2$-2,5-$Cl_2C_6H_2$ **Ic**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.88 [d, 4 H, ^4J(H^a–H^b) = 1.6, H^a], 7.34 [m, 10 H, H^{ar}], 8.14 [s, 2 H, H^c] and 8.76 [t, 2 H, ^4J(H^b–H^a) = 1.6 Hz, H^b]; IR (KBr, cm^{-1}) 1632 (C=N); MS (CI, NH_3) *m*/*z* 381 (M + H$^+$). 1,4-$(C_6H_5CH_2N{=}CH)_2C_6H_4$ **Id**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.84 [d, 4 H, ^4J(H^a–H^b) = 1.2, H^a], 7.34 [m, 10 H, H^{ar}], 7.83 [s, 4 H, H^c] and 8.41 [t, 2 H, ^4J(H^b–H^a) = 1.2 Hz, H^b]; IR (KBr, cm^{-1}) 1637 (C=N); MS (CI, NH_3) *m*/*z* 313 (M + H$^+$). 1,4-$(2\text{-}ClC_6H_4CH_2N{=}CH)_2C_6H_4$ **Ie**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.94 [d, 4 H, ^4J(H^a–H^b) = 1.5, H^a], 7.4 [m, 8 H, H^{ar}], 7.86 [s, 4 H, H^c] and 8.44 [t, 2 H, ^4J(H^b–H^a) = 1.5 Hz, H^b]; IR (KBr, cm^{-1}) 1646 (C=N); MS (CI, NH_3) *m*/*z* 381 (M + H$^+$).

Synthesis of compounds 2

Compounds **2a** and **2b** were obtained by adding a solution of 2.6×10^{-4} mol of the imine in toluene (10 mL) to a solution of 150 mg (2.6×10^{-4} mol) of compound **1** in toluene. The mixture was stirred for 16 h, and the orange solid was filtered off, washed with hexane and dried in vacuum. $[Pt_2Me_4\{1,4\text{-}(Me_2NCH_2CH_2NCH)_2\text{-}2,5\text{-}Cl_2C_6H_2\}]$ **2a** (100 mg, 50%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 [s, 6 H, ^2J(Pt–H) = 90.8, Me^a], 0.65 [s, 6 H, ^2J(Pt–H) = 84.6, Me^b], 2.84 [s, 12 H, ^3J(Pt–H) = 20.2, Me^c], 2.69 [t, 4 H, ^3J(H^d–H^e) = 5.8, H^d], 4.05 [t, 4 H, ^3J(H^e–H^d) = 5.8, H^e], 8.91 [s, 2 H, H^g] and 9.2 [s, 2 H, ^3J(Pt–H^f) = 43.6 Hz, H^f]; IR (KBr, cm^{-1}) 1629 (C=N); MS [FAB(+)]

m/z 794 (M^+), 779 ($[M - Me]^+$), 764 ($[M - 2Me]^+$), 749 ($[M - 3Me]^+$), 733 ($[M - 4Me]^+$), 713 ($[M - 3Me - Cl]^+$) and 664 ($[M - 4Me - 2Cl]^+$) (Found: C, 30.3; H, 4.7; N, 7.1. $C_{10}H_{18}ClN_2Pt$ requires C, 30.27; H, 4.57; N, 7.06%). $[Pt_2Me_4\{1,4\text{-}(Me_2NCH_2CH_2NCH)_2C_6H_4\}]$ **2b** (100 mg, 51%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.17 [s, 6 H, ^2J(Pt–H) = 90, Me^a], 0.62 [s, 6 H, ^2J(Pt–H) = 84.6, Me^b], 2.83 [s, 12 H, ^3J(Pt–H) = 20.8, Me^c], 2.69 [t, 4 H, ^3J(H^d–H^e) = 5.2, H^d], 4.05 [t, 4 H, ^3J(H^e–H^d) = 5.2, H^e], 8.30 [s, 4 H, H^g] and 9.0 [s, 2 H, ^3J(Pt–H^f) = 44.4 Hz, H^f]; ^{13}C NMR (75 MHz, $CDCl_3$) δ {−24.8 [s], −18.7 [s], C^{a,b}}, 48.8 [s, C^c], 65.5 [s, C^d], 66.1 [s C^e], 128.9 [s, C^g], 136.4 [s, C^h] and 161.3 [s, C^f]; IR (KBr, cm^{-1}) 1616 (C=N); MS [FAB(+)] *m/z* 724 (M^+), 710 ($[M - Me]^+$), 695 ($[M - 2Me]^+$), 680 ($[M - 3Me]^+$) and 664 ($[M - 4Me]^+$) (Found: C, 33.3; H, 5.3; N, 7.6. $C_{10}H_{19}N_2Pt$ requires C, 33.15; H, 5.29; N, 7.73%).

Cyclometallation reactions

Compounds **3a** and **3b** were obtained by heating under reflux for four hours solutions of **2a** and **2b** (50 mg) in toluene (10 ml). The solvent was removed under vacuum, until yellow (**3a**) or red (**3b**) crystals were obtained. $[Pt_2Me_4Cl_2\{1,4\text{-}(Me_2NCH_2CH_2N{=}CH)_2C_6H_2\}]$ **3a** (46 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.61 [s, 6 H, ^2J(Pt–H) = 74, Me^a], 1.00 [s, 6 H, ^2J(Pt–H) = 63.5, Me^b] {2.54 [s, 6 H, ^3J(Pt–H) = 15], 2.95 [s, 6 H], Me^c}, 3.9–4.2 [m, 8 H, H^{d,e}], 7.24 [s, 2 H, H^g] and 8.43 [s, 2 H, ^3J(Pt–H^f) = 46 Hz, H^f]; IR (KBr, cm^{-1}) 1631 (C=N); MS [FAB(+)] *m/z* 793 (M^+), 768 ($[M - Me]^+$), 753 ($[M - 2Me]^+$), 742 ($[M - Me - Cl]^+$), 727 ($[M - 2Me - Cl]^+$), 712 ($[M - 3Me - Cl]^+$), 697 ($[M - 4Me - Cl]^+$) and 664 ($[M - 4Me - 2Cl]^+$) (Found: C, 30.4; H, 4.6; N, 6.9. $C_{10}H_{18}ClN_2Pt$ requires C, 30.27; H, 4.57; N, 7.06%). $[Pt_2Me_2\{1,4\text{-}(Me_2NCH_2CH_2\text{-}N{=}CH)_2C_6H_2\}]$ **3b** (36 mg, 72%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 [s, 6 H, ^2J(Pt–H) = 78.4, Me^b], 2.83 [s, 12 H, ^3J(Pt–H) = 19.4, Me^c], 3.13 [t, 4 H, ^3J(H^d–H^e) = 5.9, H^d], 3.98 [t, 4 H, ^3J(H^e–H^d) = 5.9, H^e], 7.45 [s, 2 H, ^3J(Pt–H^g) = 62.8, H^g] and 8.53 [s, 2 H, ^3J(Pt–H^f) = 60.8, H^f]; ^{13}C NMR (75 MHz, $CDCl_3$) δ −13.6 [s, ^1J(Pt–C) = 791.3, C^b], 48.8 [s, C^c], 52.1 [s, ^2J(Pt–C) = 30.7, C^d], 67.7 [s, C^e], 133.3 [s, ^2J(Pt–C) = 98.7, C^g], 133.6 [s, C^h], 153 [s, C^i] and 168.6 [s, ^2J(Pt–C^f) = 96 Hz, C^f]; IR (KBr, cm^{-1}) 1611 (C=N); MS [FAB(+)] *m/z* 692 (M^+), 677 ($[M - Me]^+$), 662 ($[M - 2Me]^+$), 647 ($[M - 3Me]^+$) and 632 ($[M - 4Me]^+$) (Found: C, 31.2; H, 4.3; N, 7.8. $C_9H_{15}N_2Pt$ requires C, 31.21; H, 4.37; N, 8.09%). Compounds **3c**, **3d** and **3e** were obtained from the reaction of 150 mg (2.6×10^{-4} mol) of **1** with 2.6×10^{-4} mol of the corresponding imines in acetone or toluene (25 ml) at room temperature for 15 h. The solvent was removed in a rotary evaporator and, on addition of hexane, yellow or orange solids, which were washed with hexane, were obtained. $[Pt_2Me_4Cl_2\{1,4\text{-}(C_6H_5CH_2N{=}CH)_2C_6H_2\}(SMe_2)_2]$ **3c** (150 mg, 59%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 [s, 6 H, ^2J(Pt–H) = 68.8, Me^a], 1.22 [s, 6 H, ^2J(Pt–H) = 67.4, Me^b], 1.96 [s, 12 H, ^3J(Pt–H) = 13.8, Me^c], 5.28 [s, 4 H, H^d], 7.4–7.5 [m, 10 H, H^{ar}], 7.29 [s, 2 H, ^3J(Pt–H^f) = 46, H^f] and 8.18 [s, 2 H, ^3J(Pt–H^e) = 45.4, H^e]; IR (KBr, cm^{-1}) 1611 (C=N); MS [FAB(+)] *m/z* 954 (M^+), 939 ($[M - Me]^+$), 919 ($[M - Cl]^+$), 858 ($[M - Cl - SMe_2]^+$), 826 ($[M - Cl - CH_2Ph]^+$), 796 ($[M - Cl - 2SMe_2]^+$), 780 ($[M - Cl - Me - 2SMe_2]^+$), 764 ($[M - Cl - 2Me - 2SMe_2]^+$), 750 ($[M - Cl - 3Me - 2SMe_2]^+$) and 735 ($[M - Cl - 4Me - 2SMe_2]^+$) (Found: C, 37.9; H, 4.5; N, 3.0. $C_{15}H_{21}ClNPtS$ requires C, 37.70; H, 4.43; N, 2.93%). $[Pt_2Me_2\{1,4\text{-}(C_6H_5CH_2N{=}CH)_2C_6H_2\}(SMe_2)_2]$ **3d** (130 mg, 60%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 [s, 6 H, ^2J(Pt–H) = 81, Me^b], 2.08 [s, 12 H, ^3J(Pt–H) = 26.2, Me^c], 5.19 [s, 4 H, ^3J(Pt–H^d) = 13.2, H^d], 7.3–7.4 [m, 10 H, H^{ar}], 7.79 [s, 2 H, ^3J(Pt–H^f) = 59, H^f] and 8.63 [s, 2 H, ^3J(Pt–H^e) = 56 Hz, H^e]; IR (KBr, cm^{-1}) 1613 (C=N); MS [FAB(+)] *m/z* 854 (M^+), 839 ($[M - Me]^+$), 822 ($[M - 2Me]^+$), 807 ($[M - 3Me]^+$), 792 ($[M - SMe_2]^+$), 777 ($[M - Me - SMe_2]^+$), 761 ($[M - 2Me - SMe_2]^+$), 746 ($[M - 3Me - SMe_2]^+$), 731 ($[M - 2SMe_2]^+$) and 715 ($[M - Me - 2SMe_2]^+$) (Found: C, 39.5; H, 4.1; N, 3.1. $C_{14}H_{18}NPtS$ requires C, 39.34; H, 4.24; N, 3.28%). $[Pt_2Me_2\{1,4\text{-}(2\text{-}ClC_6H_4CH_2N{=}CH)_2C_6H_2\}(SMe_2)_2]$ **3e** (70 mg, 30%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.01 [s, 6 H, ^2J(Pt–H) = 81.4, Me^b], 2.07 [s, 12 H, ^3J(Pt–H) = 26.4, Me^c], 5.12 [s, 4 H, H^d], 7.2–7.5 [m, 8 H, H^{ar}], 7.81 [s, 2 H, ^3J(Pt–H^f) = 58.6, H^f] and 8.64 [s, 2 H, ^3J(Pt–H^e) = 55.6 Hz, H^e]; IR (KBr, cm^{-1}) 1617 (C=N); MS [FAB(+)] *m/z* 923 (M^+), 908 ($[M - Me]^+$), 891 ($[M - 2Me]^+$), 861 ($[M - SMe_2]^+$), 846 ($[M - Me - SMe_2]^+$), 831 ($[M - 2Me - SMe_2]^+$), 799 ($[M - 2SMe_2]^+$), 784 ($[M - Me - 2SMe_2]^+$) and 769 ($[M - 2Me - 2SMe_2]^+$) (Found: C, 36.5; H, 3.8; N, 3.0. $C_{14}H_{17}ClNPtS$ requires C, 36.41; H, 3.71; N, 3.03%).

Syntheses of phosphine derivatives

Compounds **4** and **5** were obtained by the reaction of 50 mg of **3** with PPh_3 or $Ph_2PCH_2CH_2PPh_2$ (dppe) in a 1:2 ratio in toluene or acetone under N_2 for two hours. The solvent was removed under vacuum, and hexane was added to the residue. The solid was filtered off, washed with diethyl ether and dried under vacuum. $[Pt_2Me_2\{1,4\text{-}(Me_2NCH_2CH_2N{=}CH)_2C_6H_2\}\text{-}(PPh_3)_2]$ **4b** (80 mg, 90%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.74 [d, 6 H, ^2J(Pt–H) = 82, ^3J(P–H) = 8, Me^b], 1.81 [t, 4 H, ^3J(H^d–H^e) = 6.4, H^d], 1.86 [s, 12 H, Me^c], 3.23 [t, 4 H, ^3J(H^e–H^d) = 6.4, H^e] {7.1–7.4 [m], 7.65–7.75 [m], 30 H, H^{ar}}, 7.9 [s, 2 H, H^g] and 8.57 [s, 2 H, ^3J(Pt–H^f) = 56.8 Hz, H^f]; ^{31}P NMR (101 MHz, $CDCl_3$) δ 30.53 [s, ^1J(Pt–P) = 2160.4 Hz]; IR (KBr, cm^{-1}) 1610 (C=N); MS [FAB(+)] *m/z* 1217 (M^+), 1202 ($[M - Me]^+$), 939 ($[M - Me - PPh_3]^+$) and 924 ($[M - 2Me - PPh_3]^+$) (Found: C, 53.2; H, 5.1; N, 4.5. $C_{27}H_{30}N_2PPt$ requires C, 53.29; H, 4.97; N, 4.60%). $[Pt_2Me_2\{1,4\text{-}(C_6H_5CH_2N{=}CH)_2C_6H_2\}(PPh_3)_2]$ **4d** (60 mg, 85%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.71 [d, 6 H, ^2J(Pt–H) = 82.6, ^3J(P–H) = 7.8, Me^b], 4.28 [s, 4 H, H^d] {6.7–6.9 [m], 7.1–7.4 [m], 7.5–7.7 [m], 40 H, H^{ar}}, 7.85 [d, 2 H, ^3J(Pt–H^f) = 45.6, H^f] and 8.37 [s, 2 H, ^3J(Pt–H^e) = 56, H^e]; ^{31}P NMR (101 MHz, $CDCl_3$) δ 30.55 [s, ^1J(Pt–P) = 2166.7]; IR (KBr, cm^{-1}) 1600 (C=N); MS [FAB(+)] *m/z* 1255 ($[M]^+$), 1240 ($[M - Me]^+$), 1225 ($[M - 2Me]^+$), 990 ($[M - PPh_3]^+$), 975 ($[M - Me - PPh_3]^+$), 960 ($[M - 2Me - PPh_3]^+$) and 900 ($[M - CH_2Ph - PPh_3]^+$) (Found: C, 57.5; H, 4.4; N, 2.1. $C_{30}H_{27}NPPt$ requires C, 57.41; H, 4.34; N, 2.23%). $[Pt_2Me_2\{1,4\text{-}(Me_2\text{-}NCH_2CH_2N{=}CH)_2C_6H_2\}(Ph_2PCH_2CH_2PPh_2)_2]$ **5b** (70 mg, 69%): ^{1}H NMR (500 MHz, $CDCl_3$) major isomer, δ 0.64 [t, 6 H, ^2J(Pt–H) = 73.0, ^3J(P–H) = 7.5, Me^b], 2.18 [s, 12 H, Me^c], 1.8–2.6 [m, 8 H, H^{h,i}] {3.0–3.1 [m], 3.2–3.3 [m], 8 H, H^{d,e}} {6.2–6.4 [m], 6.8–8.0 [m], 22 H, H^{g,ar}} and 8.58 [s, 2 H, H^f]; minor isomer, δ 0.60 [t, 6 H, ^2J(Pt–H) = 73.0, ^3J(P–H) = 7.5 Hz, Me^b], 2.18 [s, 12 H, Me^c], 1.8–2.6 [m, 8 H, H^{h,i}] {2.9–3.0 [m], 3.4–3.5 [m], 8 H, H^{d,e}} {6.2–6.4 [m], 6.8–8.0 [m], 22 H, H^{g,ar}} and 8.45 [s, 2 H, H^f]; ^{31}P NMR (101 MHz, $CDCl_3$) major isomer, δ 41.56 [s, ^1J(Pt–P) = 1760.6, P_B] and 44.02 [s, ^1J(Pt–P) = 1780.3, P_A]; minor isomer, δ 40.09 [s, ^1J(Pt–P) = 1724.9, P_B] and 45.67 [s, ^1J(Pt–P) = 1789.1 Hz, P_A]; IR (KBr, cm^{-1}) 1632 (C=N); MS [FAB(+)] *m/z* 1488 (M^+), 1473 ($[M - Me]^+$), 1458 ($[M - 2Me]^+$), 1419 ($[M - CH_2CH_2NMe_2]^+$), 1388 ($[M - CHNCH_2CH_2NMe_2]^+$), 881 ($[M - PtMe(dppe)]^+$) and 866 ($[M - Me - PtMe(dppe)]^+$) (Found: C, 56.3; H, 5.4; N, 3.8. $C_{35}H_{39}N_2P_2Pt$ requires C, 56.45; H, 5.28; N, 3.76%). $[Pt_2Me_2\text{-}\{1,4\text{-}(C_6H_5CH_2N{=}CH)_2C_6H_2\}(Ph_2PCH_2CH_2PPh_2)_2]$ **5d** (60 mg, 57%): ^{1}H NMR (500 MHz, $CDCl_3$) δ {0.64 [t, 6 H, ^2J(Pt–H) = 73.0, ^3J(P–H) = 7.5], 0.65 [t, 6 H, ^2J(Pt–H) = 73.0, ^3J(P–H) = 7.0], Me$^{b,b'}$}, 1.7–2.7 [m, 8 H, H$^{g,g',h,h'}$] {4.06 [d, 1H, ^2J(H–H) = 14.0], 4.12 [d, 1H, ^2J(H–H) = 14.0], 4.40 [d, 1H, ^2J(H–H) = 14.0], 4.61 [d, 1H, ^2J(H–H) = 14.0], AB system, H$^{d,d'}$} {6.1–6.2 [m], 6.7–7.9 [m], 45 H, H^{ar}} {7.97 [d, 2 H, ^3J(Pt–H^f) = 61.0, ^4J(H^f–H^e) = 7.0], 8.21 [d, 2 H, ^3J(Pt–H^f) = 60.5, ^4J(H^f–H^e) = 6.5 Hz], H$^{f,f'}$} {8.67 [s, 2 H], 8.75 [s, 2 H], H$^{e,e'}$}; ^{31}P NMR (101 MHz, $CDCl_3$) δ {43.00 [s, ^1J(Pt–P) = 1758.8], 41.15 [s, ^1J(Pt–P) = 1724.0], $P_{B,B'}$} {45.74 [s, ^1J(Pt–P) = 1782.5],

47.70 [s, ^1J(Pt–P) = 1794.5 Hz], $P_{A,A'}$}; IR (KBr, cm^{-1}) 1632 (C=N); MS [FAB(+)] *m/z* 1528 (M^+), 1513 ([M − Me]$^+$), 1497 ([M − 2Me]$^+$), 1435 ([M − CH_2Ph]$^+$), 1421 ([M − CH_2Ph − Me]$^+$), 1406 ([M − CH_2Ph − 2Me]$^+$), 920 ([M − Me − dppe]$^+$), 904 ([M − 2Me − dppe]$^+$), 609 ([PtMe(dppe)]$^+$) and 592 ([Pt(dppe)]$^+$) (Found: C, 59.7; H, 4.7; N, 1.7. $C_{38}H_{36}NP_2Pt$ requires C, 59.76; H, 4.75; N, 1.83%).

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Paper 9/01028I