

# Preparation, structural studies, and magnetic properties of coordination complexes of bimetallic arylplatinum compounds and pyridyl nitronyl nitroxide radicals

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Received 23rd May 2001, Accepted 10th September 2001

First published as an Advance Article on the web 14th November 2001

Treatment of 1,3-C<sub>6</sub>H<sub>4</sub>I<sub>2</sub> with Pt(PEt<sub>3</sub>)<sub>4</sub> in toluene leads to the isolation of [1,3-(Pt(PEt<sub>3</sub>)<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] (**2**). This complex has been characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR and elemental analysis. The structure of **2** as well as that of [1,4-(Pt(PEt<sub>3</sub>)<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] (**1**) have been determined by single crystal X-ray analysis. As expected, the platinum centers of these derivatives adopt a square planar coordination geometry with the phosphine ligands in a *trans* arrangement. Treatment of compounds **1** and **2** with AgPF<sub>6</sub> and subsequent addition of two equivalents of NITpPy (NITpPy = [2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide]) results in the formation of [1,4-(Pt(PEt<sub>3</sub>)<sub>2</sub>(NITpPy))<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sup>2+</sup>[PF<sub>6</sub>]<sup>-</sup><sub>2</sub> (**3**) and [1,3-(Pt(PEt<sub>3</sub>)<sub>2</sub>(NITpPy))<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sup>2+</sup>[PF<sub>6</sub>]<sup>-</sup><sub>2</sub> (**4**), respectively. Compounds **3** and **4** have been characterized by +ESI/TOF, IR, UV and elemental analysis. Their structures have been determined by X-ray crystallography which confirmed the coordination of a NITpPy ligand at each platinum center. As in **1** and **2**, the platinum centers adopt a square planar coordination geometry with the phosphine ligands in a *trans* arrangement. As shown by EPR spectroscopy and SQUID magnetometry, intramolecular magnetic coupling of the coordinated NITpPy moieties does not occur.

## Introduction

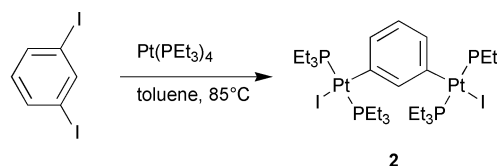
Bifunctional Lewis acids are an emerging class of supramolecular building blocks. Such compounds can be regarded as the charge reverse analogs of Lewis basic spacers such as 4,4'-bipyridyl or pyrazine. They usually feature diverging Lewis acidic sites accessible to coordination by incoming Lewis basic substrates. In addition to a few main group systems,<sup>1–3</sup> a variety of dinuclear organometallic complexes of late transition metals have been investigated. In most cases, these complexes are cationic and incorporate palladium or platinum as binding sites. Previous investigations have shown the potential of such species for the preparation of self-assembled macrocycles,<sup>4</sup> dendrimers<sup>5</sup> and polymers.<sup>6</sup> It occurred to us that such species could also be useful for the preparation of materials with unusual magnetic properties. In particular, we became intrigued by the possible use of these derivatives for the modular assembly of polyradical species. Thus, in the initial steps of an investigation aimed at discovering new motifs for the mediation of magnetic superexchange interactions, we have probed the ability of dinuclear platinum phenylene complexes to serve as linkers between organic nitroxide radicals.

The study of magnetic properties of nitroxide free radicals and their coordination complexes is of current interest owing to their potential utility as molecular magnetic materials.<sup>7</sup> Due to their ease of preparation and stability, nitronyl nitroxides<sup>8,9</sup> have often been used as ligands to transition metals.<sup>10,11</sup> In this contribution, we report the synthesis and properties of diradical derivatives obtained by coordination of NITpPy molecules (NITpPy = [2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide])<sup>12</sup> to the metallic centers of 1,3- and 1,4-diplatinum phenylene complexes.<sup>13</sup>

## Results and discussion

### Syntheses and structures of the bis(iodobis(triethylphosphine)-platinum)phenylene complexes

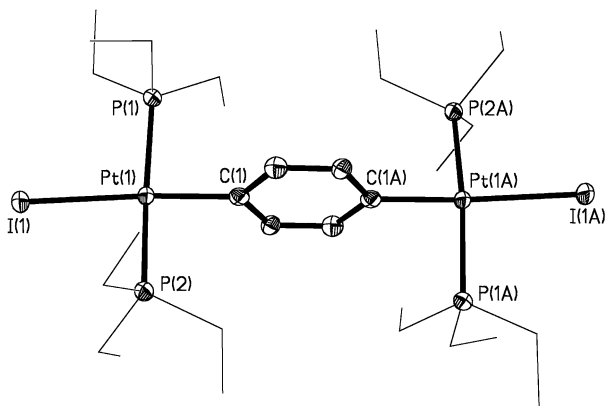
1,3-Bis(iodobis(triethylphosphine)platinum)phenylene (**2**) was prepared by adapting the published procedure used for the synthesis of the 1,4-isomer (**1**).<sup>14</sup> Thus, treatment of 1,3-diiodobenzene with Pt(PEt<sub>3</sub>)<sub>4</sub> in toluene at 85 °C afforded **2** (Scheme 1). Due to the high solubility of **2** in Et<sub>2</sub>O, separation



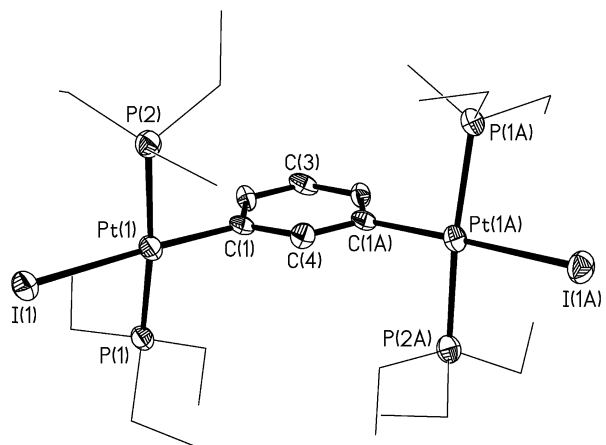
Scheme 1

of this compound from reaction by-products required repeated fractional crystallization from hexanes to afford a 53% yield of analytically pure **2**. The NMR spectroscopic features of **2** are in agreement with a solution structure of C<sub>2v</sub> symmetry. The <sup>31</sup>P NMR spectrum of **2** consists of a single resonance line with a pair of platinum satellites. Furthermore, the <sup>1</sup>H NMR spectrum of **2** exhibits one set of resonances for the triethylphosphine protons. Accordingly, the aromatic protons give rise to resonances whose multiplicity is in agreement with a symmetrically *meta*-disubstituted phenylene ring.

While **1** has been previously characterized,<sup>14</sup> its crystal structure was not reported. In the course of this work, we were able to obtain single crystals of this compound that were analyzed



**Fig. 1** Molecular structure of **1**. Selected bond distances [Å] and angles [°]: Pt(1)–C(1) 2.021(5), Pt(1)–P(2) 2.2991(13), Pt(1)–P(1) 2.3002(12), Pt(1)–I(1) 2.7136(6); C(1)–Pt(1)–P(2) 89.11(13), C(1)–Pt(1)–P(1) 87.80(13), P(2)–Pt(1)–P(1) 168.71(4), C(1)–Pt(1)–I(1) 176.32(13), P(2)–Pt(1)–I(1) 88.89(3), P(1)–Pt(1)–I(1) 94.74(3).

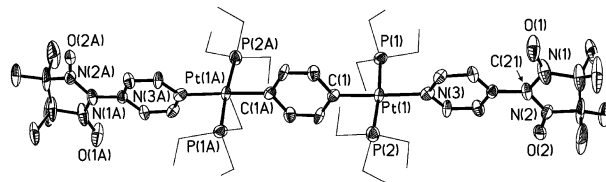


**Fig. 2** Molecular structure of **2**. Selected bond distances [Å] and angles [°]: Pt(1)–C(1) 2.034(8), Pt(1)–P(2) 2.292(2), Pt(1)–P(1) 2.304(2), Pt(1)–I(1) 2.7031(7); C(1)–Pt(1)–P(2) 90.7(2), C(1)–Pt(1)–P(1) 91.5(2), P(2)–Pt(1)–P(1) 172.02(7), C(1)–Pt(1)–I(1) 175.8(2), P(2)–Pt(1)–I(1) 89.30(6), P(1)–Pt(1)–I(1) 89.04(5).

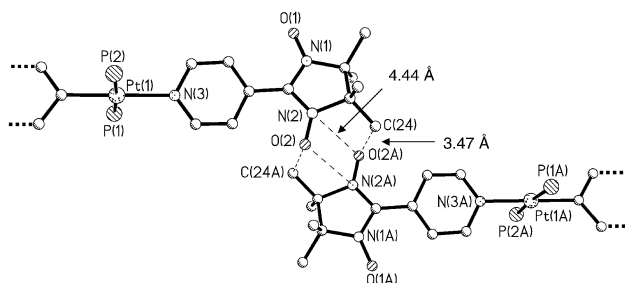
by X-ray diffraction. Compound **1** crystallizes in the monoclinic space group  $P2_1/n$  with two molecules in the unit cell (Fig. 1). Molecules of **1** are centrosymmetric. As expected, the coordination geometry about the platinum is square planar with the two phosphine ligands in a *trans*-arrangement. The platinum square plane forms a dihedral angle of 82.3° with the plane of the phenyl group. Similar deviations from orthogonality have been observed in related platinum aryls.<sup>15</sup> Other bond distances and angles within the platinum square plane are reminiscent of those found in (4,4′-[Pt(PET<sub>3</sub>)<sub>2</sub>(I)]<sub>2</sub>biphenyl)<sup>14</sup> and do not warrant further discussion. Compound **2** crystallizes in the tetragonal space group  $P4_32_12$  with four molecules in the unit cell (Fig. 2). Molecules of **2** contain a crystallographic two-fold axis that bisects the phenylene ring and passes through C(3) and C(4). The dihedral angles formed between the platinum square plane and the phenylene ring is 78.0°. This deviation from orthogonality appears slightly larger than that observed in the case of **1** which possibly reflects the different steric requirements imposed by the *meta*- rather than *para*-substitution of the phenylene ring.

### Syntheses and structures of the diradicals

The diradicals **3** and **4** (Scheme 2) were prepared in good yield by activation of the corresponding platinum iodide complexes with AgPF<sub>6</sub> and subsequent addition of two equivalents of NITpPy. Compounds **3** and **4** are soluble in methylene chloride, insoluble in aliphatic and aromatic solvents, and only slightly



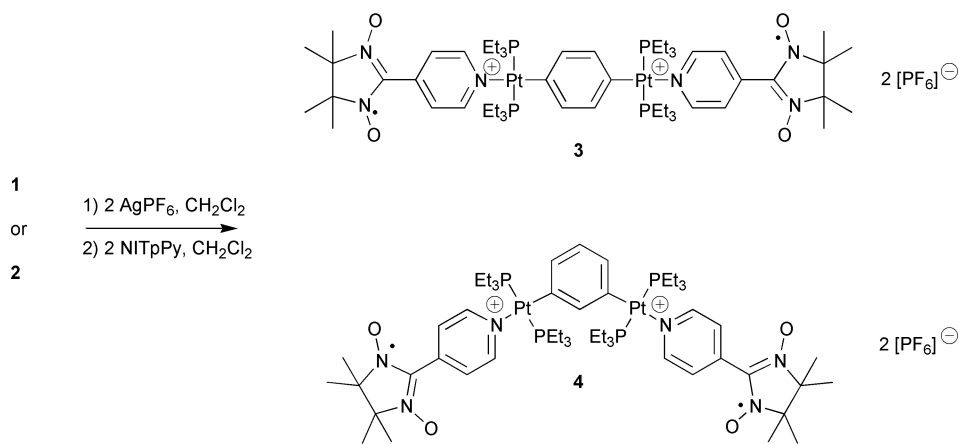
**Fig. 3** Structure of the dication in **3**. Selected bond distances [Å] and angles [°]: Pt(1)–C(1) 2.017(12), Pt(1)–N(3) 2.122(11), Pt(1)–P(1) 2.282(3), Pt(1)–P(2) 2.310(4); C(1)–Pt(1)–N(3) 178.2(5), C(1)–Pt(1)–P(1) 86.6(4), N(3)–Pt(1)–P(1) 91.8(3), C(1)–Pt(1)–P(2) 88.7(4), N(3)–Pt(1)–P(2) 92.9(3), P(1)–Pt(1)–P(2) 175.09(12).



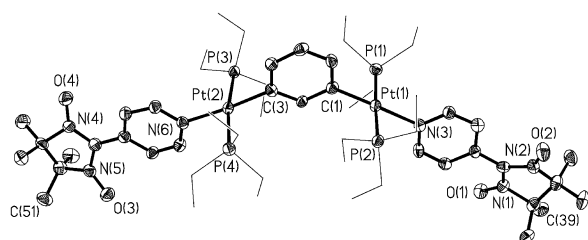
**Fig. 4** View of a portion of the supramolecular structure of **3** showing the short contacts occurring between the nitronyl nitroxide moieties.

soluble in either chloroform or hot methanol. The +ESI/TOF mass spectrum of each compound is characterized by a  $m/z$  peak at 704.7 that can be assigned to the [(Pt(PET<sub>3</sub>)<sub>2</sub>(NITpPy))<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sup>2+</sup> dication. The IR spectra of **3** and **4** exhibit absorption bands at 1374 and 1375 cm<sup>−1</sup>, respectively, which correspond to the N–O stretching vibration. With respect to the free radical, the UV-vis spectra of **3** and **4** are characterized by a bathochromic shift of the NITpPy-centered transitions below 400 nm. Only weak absorption bands were observed in the visible region of the spectra and were assigned to the forbidden  $n \rightarrow \pi^*$  transitions (**3**:  $\epsilon(\lambda = 655 \text{ nm}) = 70$ ; **4**:  $\epsilon(\lambda = 656 \text{ nm}) = 105$ ).<sup>16</sup>

Complex **3** crystallizes in the monoclinic space group  $P2_1/n$  as a bis(methylene chloride) solvate (Fig. 3). The cation is centrosymmetric. As expected, the coordination geometry at platinum is square planar and the atoms that define the square plane form an 81.2° angle with respect to the phenylene ring. The Pt–N (2.12(1) Å), Pt–C (2.02(1) Å) and Pt–P (2.282(3), 2.310(4) Å) bond lengths are comparable to the distances found in related compounds.<sup>17</sup> There is a 15.6° deviation from coplanarity between the pyridyl and phenylene moieties. Furthermore, the planar O(1)–N(1)–C(21)–N(2)–O(2) fragment and the mean plane of the pyridine ring form a 15.1° angle with respect to each other, which is comparable to that found in Zn(hfac)<sub>2</sub>·2NITpPy (15.9°) (Hhfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione).<sup>18</sup> It is of interest to note that metal–NITpPy complexes which are bound solely through the pyridyl nitrogen<sup>19</sup> typically exhibit larger angles which range from 24° for Mn(N<sub>3</sub>)<sub>2</sub>·4NITpPy<sup>20</sup> to 33° for HgBr<sub>2</sub>·NITpPy.<sup>21</sup> An examination of the extended structure of **3**·2CH<sub>2</sub>Cl<sub>2</sub> reveals the existence of linear chains of the dications. In these chains, the shortest intermolecular distance involves a nitroxide oxygen atom (O(2)) and a methyl group (C(24A)) of the neighboring molecule related by the symmetry transformation  $-x + 1, -y + 1, -z$ . The resulting distance O(2) ⋯ C(24A) (3.47 Å) is similar to that observed in the crystal structures of a series HgBr<sub>2</sub>/pyridyl nitronyl nitroxide Lewis adducts<sup>21</sup> and indicates the presence of a short O ⋯ HC contact which can be estimated to range from 2.3 to 2.6 Å based on the calculated position of the hydrogen atoms (Fig. 4).<sup>18</sup> The second shortest intermolecular distance occurs between the neighboring NO moieties and results in a N(2) ⋯ O(2A) distance of 4.44 Å (Fig. 4). Such NO ⋯ NO contacts are prevalent in the solid state structures of nitronyl nitroxides. Typically, however, these contacts are much shorter and fall in the 3.2–3.5 Å range.<sup>9</sup>



Scheme 2

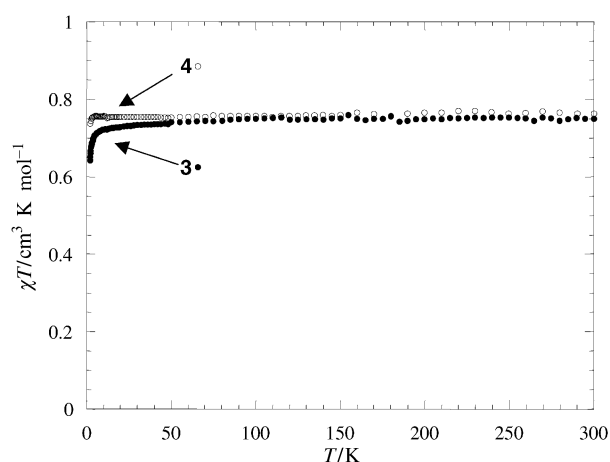


**Fig. 5** Structure of the dication in **4**. Selected bond distances [Å] and angles [°]: Pt(1)–C(1) 2.023(6), Pt(1)–N(3) 2.134(5), Pt(1)–P(1) 2.3081(18), Pt(1)–P(2) 2.3203(18), Pt(2)–C(3) 2.028(7), Pt(2)–N(6) 2.127(5), Pt(2)–P(4) 2.3019(17), Pt(2)–P(3) 2.3065(17); C(1)–Pt(1)–N(3) 178.6(2), C(1)–Pt(1)–P(1) 92.06(19), N(3)–Pt(1)–P(1) 89.30(16), C(1)–Pt(1)–P(2) 88.37(19), N(3)–Pt(1)–P(2) 90.31(16), P(1)–Pt(1)–P(2) 174.56(7), C(3)–Pt(2)–N(6) 175.7(2), C(3)–Pt(2)–P(4) 88.61(18), N(6)–Pt(2)–P(4) 93.72(15), C(3)–Pt(2)–P(3) 86.59(18), N(6)–Pt(2)–P(3) 91.50(15), P(4)–Pt(2)–P(3) 171.91(6).

Complex **4** crystallizes in the monoclinic space group  $P2_1/n$  as a water–methanol solvate (Fig. 5). The average Pt–N (av. 2.12 Å), Pt–C (av. 2.02 Å), Pt–P (av. 2.31 Å) bond distances are similar to those observed in **3**. The mean plane of the phenylene moiety is nearly orthogonal to both platinum coordination square planes (89.7° and 89.8° for Pt(1) and Pt(2), respectively). The angle between the plane of the phenylene group and the pyridyl group bound to Pt(1) is 5.5° whereas the corresponding angle involving Pt(2) is 9.4°. The planar ONCNO fragments of the nitronyl nitroxide five membered rings form a dihedral angle of 20.4° and 25.2° with their corresponding pyridyl group. The cations in  $4 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$  are arranged into zigzagging chains. In these chains, the shortest intermolecular distances are found between neighboring molecules related by the symmetry operation  $x + 1, y - 1, z$ . As in **3**, the shortest distances occur between the nitronyl nitroxide oxygen atoms and methyl groups of neighboring nitronyl nitroxides (O(1)  $\cdots$  C(51A) 3.501 Å and O(3)  $\cdots$  C(39A) 3.566 Å with associated O  $\cdots$  HC distances in the range 2.4–2.6 Å). The next shortest intermolecular distances between the nitronyl nitroxide moieties of neighboring dications in  $4 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$  are those involving the NO groups. In this case, however, the distances separating the paramagnetic moieties are large (N(2)  $\cdots$  N(2A) distance of 5.66 Å).

#### Magnetic properties of the diradicals

The magnetic properties of **3** and **4** are consistent with an isolated two  $S = 1/2$  spin system rather than an interacting (either an  $S = 1$  or  $S = 0$ ) spin system. Thus, the room temperature EPR spectrum of  $10^{-5}$  M  $\text{CH}_2\text{Cl}_2$  solutions of each compound exhibits a five line signal centered at  $g = 2.01$ . The multiplicity of this signal indicates coupling of the electron spin with two equivalent nitrogen nuclei. The magnitude of the hyperfine



**Fig. 6**  $\chi T$  vs.  $T$  plot for compound **3** (●) and **4** (○) at 1 T.

coupling constant  $a_N$  (7.4 G) is comparable to that observed in various nitronyl nitroxide derivatives.<sup>22</sup> The absence of coupling to the  $^{195}\text{Pt}$  nuclei most likely results from the localization of the SOMO on the nitronyl nitroxide part of the NITpPy molecule.<sup>23</sup> The  $\Delta m_s = 2$  transitions associated with the existence of a triplet state were never observed. The magnetic susceptibility of each compound was measured in the range 2–300 K and a plot of  $\chi T$  vs.  $T$  is given in Fig. 6. The  $\chi T$  value of  $0.749 \text{ cm}^3 \text{ K mol}^{-1}$  found for each compound at 300 K is in close agreement with the theoretical value of  $0.75 \text{ cm}^3 \text{ K mol}^{-1}$  for two uncoupled  $S = 1/2$  spins. While the temperature dependence of the magnetic susceptibility of  $4 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$  is very close to a Curie Law between 300 and 2 K, the magnetic data of **3** reflect weak antiferromagnetic interactions ( $\theta = -0.3 \text{ K}$ ).

The HOMO of a square planar  $d^8$  metal complex is largely  $d_{xy}$  in character.<sup>24</sup> As shown by investigations on the non-linear optical properties of complexes such as *p*-nitrophenylbis(triethylphosphine)platinum halides, the  $d^8$  metal readily conjugates with the aromatic  $\pi$ -system.<sup>25</sup> Thus, in compounds **3** and **4**, the  $d_{xy}$  orbitals of the platinum could enable electronic communication between the phenylene and the pyridyl  $\pi$ -systems.<sup>26</sup> However, because of the negligible spin density found at the pyridine nitrogen atom of NITpPy,<sup>23</sup> it is unlikely that intramolecular magnetic interactions occur. In turn, it seems reasonable to assume that the weak antiferromagnetic interactions observed in the case of **3** results from intermolecular interactions between proximal nitronyl nitroxide moieties of neighboring complexes. In particular, since both platinum derivatives were found to possess similar O  $\cdots$  HC contacts, the difference between the magnetic properties of **3** and **4** may be attributed to the shorter NO  $\cdots$  NO distance observed in **3**.

## Conclusion

This work demonstrates that bifunctional cationic aryl-platinum(II) species readily coordinate NITpPy radicals to form diradical species. While the structures of the paramagnetic complexes **3** and **4** have been confirmed by X-ray diffraction methods, magnetic measurements indicate the absence of significant intramolecular magnetic communication, which can be rationalized by invoking the localization of the SOMO on the nitronyl nitroxide part of the NITpPy ligand.<sup>23</sup>

## Experimental

### General

All manipulations involving platinum(0) compounds were carried out either in a nitrogen-filled drybox or by using Schlenk techniques. In these cases, solvents were dried by typical methods and distilled before use.  $\text{K}_2\text{PtCl}_4$ , silver salts, and  $\text{PEt}_3$  were purchased from Strem Chemicals, halogenobenzenes were purchased from Aldrich and all were used as received.  $\text{Pt}(\text{PEt}_3)_4$ <sup>27</sup> and NITpPy were prepared according to published procedures. Atlantic Microlab (Norcross, Georgia) performed elemental analyses. Melting points were measured by using a Mel-Temp II instrument on samples contained in flame sealed capillaries and are uncorrected.  $^1\text{H}$  (300 MHz),  $^{13}\text{C}$  (75.4 MHz),  $^{31}\text{P}$  (121.43 MHz) NMR spectra were acquired on a Varian VXR 300 instrument. All chemical shifts are reported in  $\delta$  (ppm) units and are referenced to  $\text{SiMe}_4$   $\delta$  0.00 ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and to  $\text{CHCl}_3$  at either  $\delta$  7.27 ppm ( $^1\text{H}$ ) or  $\delta$  77.23 ( $^{13}\text{C}$ ) whereas  $^{31}\text{P}$  chemical shifts were externally referenced to 85%  $\text{H}_3\text{PO}_4$  at  $\delta$  0.00. IR spectra (KBr pellets) were obtained by using an ATI Mattson Genesis Series FTIR instrument. UV-vis spectra were acquired by using a HP 8453 spectrophotometer. EPR measurements were recorded at X-band frequencies with a Bruker ESP300 instrument.

### Syntheses

**1,4-[Pt(PEt<sub>3</sub>)<sub>2</sub>(I)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**).** This compound was prepared by an adaptation of the method described in the literature.<sup>14</sup> 1,4-Diiodobenzene (0.21 g, 0.65 mmol) and  $\text{Pt}(\text{PEt}_3)_4$  (0.95 g, 1.43 mmol) were allowed to react in toluene (25 mL) at 80 °C for 30 h. Compound **1** was isolated in an 82% yield (0.64 g) after removing solvent by vacuum distillation and washing the colorless solid with three 2 mL aliquots of  $\text{Et}_2\text{O}$ . Crystals suitable for X-ray structural determinations were obtained either by cooling a concentrated hot toluene solution to –30 °C overnight or after allowing a layer of  $\text{Et}_2\text{O}$  (1 mL) to slowly diffuse (2 d) into a  $\text{CH}_2\text{Cl}_2$  solution (1 mL). Compound **1** is soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , THF, acetone, slightly soluble in benzene, toluene, and hot hexafluorobenzene and insoluble in  $\text{Et}_2\text{O}$ , hexanes and pentane, mp 210 °C decomp. Anal. Calcd. for  $\text{C}_{30}\text{H}_{64}\text{I}_2\text{P}_4\text{Pt}_2$ : C, 30.21; H, 5.41. Found: C, 30.43; H, 5.54%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 6.82 (br, 4H,  $^3J_{\text{HPt}} = 66$  Hz,  $^5J_{\text{HPt}} = 8$  Hz), 1.77 (br, m, 24H), 1.02 (pseudo quint, 36H,  $J_{\text{HH}} = 8$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 136.84 (m), 135.02 (m, *ipso*), 15.30 (pseudo quint,  $J_{\text{CP}} = 17$  Hz), 8.12 (pseudo t,  $J_{\text{CP}} = 13$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) 8.35 (s,  $J_{\text{PP}} = 2787$  Hz).

**1,3-[Pt(PEt<sub>3</sub>)<sub>2</sub>(I)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**2**).** In the drybox, a 50 mL Schlenk flask fitted with a magnetic stirbar was charged with 1,3-diiodobenzene (0.28 g, 0.86 mmol),  $\text{Pt}(\text{PEt}_3)_4$  (1.15 g, 1.72 mmol), and 25 mL toluene. After heating the reaction mixture with an external 85 °C oil bath for 24 h, the volatile components were removed by vacuum distillation at room temperature to leave a sticky light yellow solid. The solid was washed with hexanes (4 mL) and the supernatant was separated from the insoluble portion by cannula filtration. The washing/filtration procedure was repeated twice until the remaining solid was colorless. Recrystallization of the colorless solid by cooling a hot hexane

solution to –30 °C overnight, afforded after drying for 12 hours at 60 °C a 53% yield (0.54 g) of **2** as colorless needles. It should be noted that the drying procedure should be followed since an X-ray structural study revealed that **2** readily crystallizes with  $\frac{1}{2}$  mol hexane molecule per mol **2**. Furthermore, the elemental analytical data performed on several undried samples were consistent with the partial loss of hexane from  $\text{2} \cdot 0.5\text{C}_6\text{H}_{14}$ . X-Ray quality crystals of solvent-free **2** were formed by allowing hot  $\text{C}_6\text{F}_6$  solutions to cool to room temperature and allowing the solutions to stand for several days. Compound **2** is soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , THF, acetone, benzene, and toluene, and slightly soluble in  $\text{Et}_2\text{O}$ , hexanes, pentane, and hot hexafluorobenzene; mp 180–185 °C, melts with decomp. Anal. Calcd. for  $\text{C}_{30}\text{H}_{64}\text{I}_2\text{P}_4\text{Pt}_2$ : C, 30.21; H, 5.41. Found: C, 30.42; H, 5.32%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.20 (s, 1H,  $^3J_{\text{HPt}} = 68$  Hz), 6.79 (d, 2H,  $J_{\text{HH}} = 7$  Hz,  $^3J_{\text{HPt}} = 68$  Hz), 6.53 (t, 1H,  $J_{\text{HH}} = 7$  Hz,  $^4J_{\text{HPt}} = 26$  Hz), 1.86 (br, m, 24H), 1.02 (pseudo quint, 36H,  $J_{\text{HH}} = 8$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 144.76 (m,  $\text{C}_{\text{ipso}}$ ), 142.04 (m,  $\text{C}_2$ ), 132.07 (m,  $\text{C}_{4(6)}$ ), 128.00 (s,  $\text{C}_3$ ), 15.30 (pseudo quint,  $J_{\text{CP}} = 17$  Hz), 8.08 (pseudo t,  $J_{\text{CP}} = 13$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) 9.61 (s,  $J_{\text{PP}} = 2807$  Hz).

**{1,4-[Pt(PEt<sub>3</sub>)<sub>2</sub>(NITpPy)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}[PF<sub>6</sub>]<sub>2</sub> (**3**).** In a typical preparation, a 50 mL Schlenk flask fitted with a magnetic stirring bar was charged with **1** (0.26 g, 0.22 mmol) and  $\text{CH}_2\text{Cl}_2$  (20 mL) in the drybox.  $\text{AgPF}_6$  (0.11 g, 0.43 mmol) was added to the resulting solution. After 30 min, the reaction mixture was filtered and the resulting colorless solution was combined with a solution of NITpPy (0.11 g, 0.45 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). Upon mixing, an emerald green solution formed. After the solution had been stirred for 12 h, the solvent was removed by vacuum distillation at room temperature to leave a dark green oily residue which was subsequently washed with three 10 mL portions of toluene to remove any unreacted NITpPy. From this point forward, all manipulations were carried out in air and care was taken to avoid contact with metal surfaces (such as spatula, aluminium weighing pans) that typically gave rise to trace magnetic impurities. The green product was dissolved in 10 mL of  $\text{CH}_2\text{Cl}_2$  and filtered through a Celite pad three times to remove an unidentified gray insoluble solid thus affording an emerald green solution. Crystalline compound **3** was obtained in a 73% yield (0.27 g) after vapor diffusion of pentane into the  $\text{CH}_2\text{Cl}_2$  solution. Anal. Calcd. (Found) for  $\text{C}_{54}\text{H}_{96}\text{F}_{12}\text{N}_6\text{O}_4\text{P}_6\text{Pt}_2$ : C, 38.21 (38.30); H 5.70 (5.94); N 4.95 (4.80%); mp 192–195 °C decomp. IR (KBr,  $\nu_{\text{N-O}}$ ) 1374  $\text{cm}^{-1}$ . UV [ $10^{-5}$  M  $\text{CH}_2\text{Cl}_2$ ,  $\lambda/\text{nm}(\log \epsilon)$ ] 265 (4.20), 309 (4.27), 369 (4.03), 385 (4.20), 655 (1.84).

**{1,3-[Pt(PEt<sub>3</sub>)<sub>2</sub>(NITpPy)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}[PF<sub>6</sub>]<sub>2</sub> (**4**).** Compound **4** was prepared from **2** (0.43 g, 0.36 mmol),  $\text{AgPF}_6$  (0.18 g, 0.71 mmol) and NITpPy (0.17 g, 0.73 mmol) by following the method used for the synthesis of **3**. Vapor diffusion of pentane into the  $\text{CH}_2\text{Cl}_2$  solution yielded an insoluble green viscous liquid that was dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL) and transferred to a Pasteur pipette containing a 2" column of silica gel. The column was first eluted with  $\text{CH}_2\text{Cl}_2$  (5 mL). The resulting green fraction was set aside. The column was then eluted with methanol (10 mL) to give a second green fraction which after evaporation of the solvent yielded a green solid. The solid was dissolved in the minimal amount of boiling methanol and quickly filtered through a pipette containing a glass wool plug. The resulting solution was allowed to cool to room temperature and yielded after one day a 54% yield (0.34 g) of  $\text{4} \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ . Additional portions of  $\text{4} \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$  were obtained by repeating this procedure with the mother liquor and the  $\text{CH}_2\text{Cl}_2$  fraction collected from the first chromatographic run. A yield of 72% (0.45 g) of crystalline  $\text{4} \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$  was finally obtained. Anal. Calcd. (Found) for  $\text{C}_{55}\text{H}_{102}\text{F}_{12}\text{N}_6\text{O}_6\text{P}_6\text{Pt}_2$ : C, 37.80(37.65); H, 5.88(5.68); N, 4.81(4.80%). mp 181–184 °C decomp. IR (KBr,  $\nu_{\text{N-O}}$ ) 1375  $\text{cm}^{-1}$ . UV [ $10^{-5}$  M  $\text{CH}_2\text{Cl}_2$ ,  $\lambda/\text{nm}(\log \epsilon)$ ] 243 (4.56), 308 (4.26), 371 (4.04), 384 (4.19), 656 (2.02).

**Table 1** Crystal data, data collection, and structure refinement for **1**, **2**, **3** and **4**

|   | <b>1</b>  | <b>2</b>  | <b>3</b> ·2CH <sub>2</sub> Cl <sub>2</sub>  | <b>4</b> ·H <sub>2</sub> O·CH <sub>3</sub> OH   |
|---|---|---|---|---|
| Formula   | C <sub>30</sub> H <sub>64</sub> I <sub>2</sub> P <sub>4</sub> Pt <sub>2</sub> | C <sub>30</sub> H <sub>64</sub> I <sub>2</sub> P <sub>4</sub> Pt <sub>2</sub> | C <sub>56</sub> H <sub>100</sub> Cl <sub>4</sub> F <sub>12</sub> N <sub>6</sub> O <sub>4</sub> P <sub>6</sub> Pt <sub>2</sub> | C <sub>55</sub> H <sub>102</sub> F <sub>12</sub> N <sub>6</sub> O <sub>6</sub> P <sub>6</sub> Pt <sub>2</sub> |
| <i>M</i> <sub>r</sub>   | 1192.67   | 1192.67   | 1867.22   | 1743.43   |
| Crystal size/mm   | 0.40 × 0.27 × 0.13  | 0.19 × 0.17 × 0.10  | 0.19 × 0.11 × 0.06  | 0.19 × 0.08 × 0.07  |
| Crystal system  | Monoclinic  | Tetragonal  | Monoclinic  | Monoclinic  |
| Space group   | <i>P</i> 2 <sub>1</sub> / <i>n</i>  | <i>P</i> 4 <sub>2</sub> /2  | <i>P</i> 2 <sub>1</sub> / <i>n</i>  | <i>P</i> 2 <sub>1</sub> / <i>n</i>  |
| <i>a</i> /Å   | 7.4670(15)  | 10.2652(15)   | 11.634(2)   | 13.772(3)   |
| <i>b</i> /Å   | 15.906(3)   | 10.2652(15)   | 23.791(5)   | 14.307(3)   |
| <i>c</i> /Å   | 16.692(3)   | 38.177(8)   | 14.159(3)   | 36.198(7)   |
| $\beta$ /°  | 100.37(3)   | —   | 107.15(3)   | 93.30(3)  |
| <i>V</i> /Å <sup>3</sup>  | 1950.2(7)   | 4022.9(12)  | 3745.0(13)  | 7121(2)   |
| <i>Z</i>  | 2   | 4   | 2   | 4   |
| $\rho_{\text{calc}}$ /g cm <sup>−3</sup>  | 2.031   | 1.969   | 1.656   | 1.630   |
| $\mu$ (Mo- <i>K</i> $\alpha$ )/mm <sup>−1</sup>   | 8.931   | 8.659   | 4.077   | 4.139   |
| <i>T</i> /K   | 150(2)  | 110(2)  | 110(2)  | 110(2)  |
| <i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.0254, 0.0618 <sup>a</sup>   | 0.0310, 0.0755 <sup>a</sup>   | 0.0809, 0.1513 <sup>b</sup>   | 0.0440, 0.1055 <sup>a</sup>   |

$$^a R1 = \Sigma(F_o - F_c)/\Sigma F_o, ^b wR2 = \{\Sigma w(F_o^2 - F_c^2)/[\Sigma w(F_o^2)]\}^{1/2}.$$

### Crystal structure determination

Data were collected on a Siemens SMART-CCD area detector diffractometer with Mo-*K* $\alpha$  radiation ( $\lambda = 0.71069$  Å). Specimens of suitable size and quality were selected and mounted onto a glass fiber with Apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on *F*<sup>2</sup> using the SHELXTL/PC package<sup>28</sup> allowed location of the remaining non-hydrogen atoms. Further crystallographic details can be found in Table 1.

CCDC reference numbers 171201–171204.

See <http://www.rsc.org/suppdata/dt/b1/b104579m/> for crystallographic data in CIF or other electronic format.

### Magnetometry

The magnetic susceptibility data were measured with the use of a Quantum Design SQUID magnetometer MPMS-XL. Measurements were performed in the temperature range 2–300 K at 1 T on finely divided polycrystalline samples. Data were corrected for the sample holder, and diamagnetic contributions were calculated from Pascal constants.

### Acknowledgements

We thank the Texas A&M Energy Resource Program (Grant 99–29 and 2000–08) and the Robert A. Welch Foundation (Grant A-1423) and the Department of Chemistry at Texas A&M University for generous financial support. The purchase of the X-ray diffractometer was made possible by a grant from the National Science Foundation (CHE-98 07975). R. C. thanks the Conseil Regional d'Aquitaine and the Centre National de Recherche Scientifique for financial support as well as for providing access to the SQUID magnetometer. We thank Dr Reibenspies for his expert insights regarding part of the crystallography.

### References

- M. Austin, K. Gebreyes, H. G. Kuivila, K. Swami and J. A. Zubieta, *Organometallics*, 1987, **6**, 834.
- F. P. Gabbaï, A. Schier and J. Riede, *Angew. Chem., Int. Ed.*, 1998, **37**, 622.
- M. Fontani, F. Peters, W. Scherer, W. Wachter, M. Wagner and P. Zanello, *Eur. J. Inorg. Chem.*, 1998, 1453.
- B. Olenyuk, A. Fechtenkötter and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1998, 1707; P. J. Stang, *Chem. Eur. J.*, 1998, **4**, 19; P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature (London)*, 1999, **398**, 796; J. R. Hall, S. J. Loeb, G. K. H. Shimizu and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 1998, **37**, 121.
- B.-H. Huisman, H. Schonherr, W. T. S. Huck, A. Friggeri, H.-J. Van Manen, E. Menozzi, G. J. Vancso, F. C. J. M. Van Veggel and D. N. Reinhoudt, *Angew. Chem., Int. Ed.*, 1999, **38**, 2248; W. T. S. Huck, L. J. Prins, R. H. Fokkens, N. M. M. Nibbering, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1998, **120**, 6240; W. T. S. Huck, F. C. J. M. van Veggel and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1213.
- M.-C. Lagunas, R. A. Gossage, A. L. Spek and G. van Koten, *Organometallics*, 1998, **17**, 731; P. Steenwinkel, H. Kooijman, W. J. J. Smeets, A. L. Spek, D. M. Grove and G. van Koten, *Organometallics*, 1998, **17**, 5411.
- See for example: V. I. Ovcharenko and R. Z. Sagdeev, *Russ. Chem. Rev. (Engl. Transl.)*, 1999, **68**, 345; P. M. Lahti, *Magnetic Properties of Organic Materials*, Marcel Dekker, New York, 1999; O. Kahn, *Magnetism: A Supramolecular Function*, Kluwer Publishing Co., Dordrecht, 1996; E. Coronado, P. Delhaes, D. Gatteschi and J. S. Miller, *Molecular Magnetism: From Molecular Assemblies to the Devices*, Kluwer Academic Publishers, Dordrecht, 1996, vol. 321; O. Kahn, *Molecular Magnetism*, VCH, New York, 1993; D. Gatteschi, *Molecular Magnetic Materials*, Kluwer Academic Publishers, Amsterdam, 1991.
- E. F. Ullman and J. H. Osieckie, *J. Am. Chem. Soc.*, 1968, **90**, 1078.
- M. Deumal, J. Cirujeda, J. Veciana and J. J. Novoa, *Chem. Eur. J.*, 1999, **5**, 1631.
- A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, *Acc. Chem. Res.*, 1989, **22**, 392; P. Rey and D. Luneau, *NATO ASI Ser., Ser. C*, 1999, **518**, 145; C. Lescop, D. Luneau and P. Rey, *Mater. Res. Soc. Symp. Proc.*, 2000, 598.
- A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli and C. Zanchini, *J. Am. Chem. Soc.*, 1988, **110**, 2795; C. Benelli, A. Caneschi, D. Gatteschi and L. Pardi, *Inorg. Chem.*, 1992, **31**, 741; T. Mallah, C. Auberger, M. Verdager and P. Veillet, *J. Chem. Soc., Chem. Commun.*, 1995, 61; H. Oshio, T. Watanabe, A. Ohto, T. Ito and H. Masuda, *Inorg. Chem.*, 1996, **35**, 472; K. Takeda and K. Awaga, *Phys. Rev. B: Condens. Matter*, 1997, **56**, 14560; K. Fey, D. Luneau, T. Ohm, C. Paulsen and P. Rey, *Angew. Chem., Int. Ed.*, 1998, **37**, 1270; C. Rancurel, J.-P. Sutter, T. Le Hoerff, L. Ouahab and O. Kahn, *New. J. Chem.*, 1999, **23**, 1333; A. Marvilliers, Y. Pei, J. Cano, K. E. Vostrikova, C. Paulsen, E. Rivière, J.-P. Audièrre and T. Mallah, *Chem. Commun.*, 1999, 1951; M. G. F. Vaz, L. M. M. Pinehiro, H. O. Stumpf, A. F. C. Alcantara, S. Goleen, L. Ouahab, O. Cador, C. Mathonière and O. Kahn, *Chem. Eur. J.*, 1999, **5**, 1486; D. Ruiz-Molina, C. Sporer, K. Wurst, P. Jaitner and J. Veciana, *Angew. Chem., Int. Ed.*, 2000, **39**, 3688.
- R. Sayre, *J. Am. Chem. Soc.*, 1955, **77**, 6689.
- For complexes involving platinum and organic radicals, see: F. Hintermaier, S. Holding, L. B. Volodarsky, K. Suenkel, K. Polborn and W. Beck, *Z. Naturforsch., Teil B*, 1998, **53**, 101; S. Hasenzahl, H.-D. Hausen and W. Kaim, *Chem. Eur. J.*, 1995, **1**, 95; J. M. Rawson, A. J. Banister and I. May, *Magn. Reson. Chem.*, 1994, **32**, 487; R. Weissgerber and K. E. Schwarzahns, *Z. Naturforsch., Teil B*, 1976, **31**, 208.
- J. Manna, C. J. Kuehl, J. A. Whiteford and P. J. Stang, *Organometallics*, 1997, **16**, 1897.
- W. Conzelmann, J. D. Koola, U. Kunze and J. Strahle, *Inorg. Chim. Acta*, 1984, **89**, 147; A. L. Rieger, G. B. Carpenter and P. H. Rieger, *Organometallics*, 1993, **12**, 842.
- A. Caneschi and D. Gatteschi, *Prog. Inorg. Chem.*, 1991, **39**, 331.

- 17 A. Albinati, F. Lianza, P. S. Pregosin and B. Muller, *Inorg. Chem.*, 1994, **33**, 2522; J. Depriest, G. Y. Zheng, C. Woods, D. P. Rillema, N. A. Mikirova and N. A. Zandler, *Inorg. Chim. Acta*, 1997, **264**, 287.
- 18 C.-J. Lee and H.-H. Wei, *Inorg. Chim. Acta*, 2000, **310**, 89.
- 19 For examples of compounds with both N- and O-coordination, see A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, *Inorg. Chim. Acta*, 1991, **184**, 67; A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey and R. Sessoli, *Inorg. Chem.*, 1991, **30**, 3162; C. A. Benelli, A. Caneschi, D. Gatteschi and L. Pardi, *Inorg. Chem.*, 1992, **31**, 741.
- 20 M. Fettesouhi, M. Khaled, A. Waheed, S. Golhen, L. Ouahab, J.-P. Sutter and O. Kahn, *Inorg. Chem.*, 1999, **38**, 3967.
- 21 C.-J. Lee, C.-H. Huang, H.-H. Wei, Y.-H. Liu, G.-H. Lee and Y. Wang, *J. Chem. Soc., Dalton Trans.*, 1998, 171.
- 22 E. F. Ullman, J. H. Osiecki, D. G. B. Boocock and R. Darcy, *J. Am. Chem. Soc.*, 1972, **94**, 7049.
- 23 K. Awaga, T. Inabe and Y. Maruyama, *Chem. Phys. Lett.*, 1992, **190**, 349.
- 24 L. T. Cheng, W. Tam, G. R. Meredith and S. R. Marder, *Mol. Cryst. Liq. Cryst.*, 1990, **189**, 137.
- 25 W. Tam and J. C. Calabrese, *Chem. Phys. Lett.*, 1988, **144**, 79.
- 26 H. Oshio, A. Ohto and T. Ito, *Chem. Commun.*, 1996, 1541.
- 27 T. Yoshida, T. Matsuda and S. Otsuka, *Inorg. Synth.*, 1990, **28**, 122.
- 28 G. M. Sheldrick, SHELXTL/PC, Version 5.1, Siemens Analytical X-ray Instruments, Madison, WI, 1996.