# SYNTHESIS AND PROPERTIES OF BIS-IMIDO COMPLEXES OF THE TYPE $Pt\{(NH)_2C_6H_3NO_2\}(PR_3)_2$ FROM REACTIONS IN LIQUID AMMONIA. X-RAY STRUCTURE OF $Pt\{(NH)_2C_6H_3NO_2\}(PMePh_2)_2$

# MARY HARMAN, MICHAEL B. HURSTHOUSE and MAJID MOTEVALLI

Department of Chemistry, Queen Mary College, Mile End Road, London El 4NS, U.K.

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# **IVAN P. PARKIN and J. DEREK WOOLLINS\***

Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London SW7 2AY, U.K.

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Abstract—Reaction of o-(NH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-4-NO<sub>2</sub> with PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> in liquid ammonia gives Pt{(NH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NO<sub>2</sub>}(PR<sub>3</sub>)<sub>2</sub> (PR<sub>3</sub> = PEt<sub>3</sub>, PMe<sub>2</sub>Ph, PPh<sub>2</sub>Me, 1/2dppe) in good yield (80% isolated). The new complexes were characterized by <sup>31</sup>P, <sup>1</sup>H NMR, IR, UV-vis, mass spectra, microanalyses and, in the case of PR<sub>3</sub> = PMe<sub>2</sub>Ph, by X-ray crystallography.

Although there are a great number of amine complexes of platinum there are relatively few examples of species containing di-imido ligands. Formally, these ligands are isoelectronic with dithiolenes and may thus be of interest from the point of view of preparing stacking compounds. There have been previous reports of the preparation of bis complexes containing two  $C_6H_4(NH)_2^{2-}$  ligands<sup>1,2</sup> and work is in progress (by other groups) on tris complexes of rhenium.<sup>3</sup> Here we report on the reactivity of *p*nitro-*o*-phenylenediamine (1) with *cis*-PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (2) in liquid ammonia. The products from this reaction (3)–(7) contain the doubly deprotonated dianion [*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>(NH)<sub>2</sub>]<sup>2-</sup> as a ligand in simple platinum(II) complexes.

#### **EXPERIMENTAL**

All solvents were dried prior to use and reactions performed under an inert atmosphere ( $N_2$ , Ar). The bis-phosphine-platinum (palladium) dichlorides were made as previously described.<sup>4</sup> Ammonia (BOC) and 4-nitro-o-phenylenediamine (Aldrich) were used as suplied. <sup>31</sup>P-{<sup>1</sup>H} and <sup>1</sup>H NMR spectra were obtained using a JEOL FX90Q spectrometer operating at 36.21 and 89.55 MHz and are refered to external 85% H<sub>3</sub>PO<sub>4</sub> and internal TMS, respectively. Some <sup>31</sup>P NMR spectra were also run at higher field on a Bruker WM 250 spectrometer at 101.1 MHz and referred to external 85% H<sub>3</sub>PO<sub>4</sub>. IR spectra were recorded as pressed KBr discs using a Perkin–Elmer 1720X instrument. UV–vis spectra were obtained on a PE Lambda 3. Mass spectra were taken on a Varian VG 2020 spectrometer in the E.I. mode. Elemental analyses were performed by the microanalytical service at Imperial College.

In a typical reaction 4-nitro-o-phenylenediamine (0.16 mmol) was dissolved in liquid ammonia at  $-78^{\circ}$ C to generate a red solution, whereupon PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (0.15 mmol) was added. The resultant slurry was stirred for 0.5 h at  $-78^{\circ}$ C and the ammonia allowed to evaporate under a blanket of nitrogen as the solution warmed slowly to room temperature, leaving a black-purple solid. Purification was achieved by extraction with CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>), followed by filtration through a celite/glass wool plug and passage down a Biobead (SX-8) column with CH<sub>2</sub>Cl<sub>2</sub> as the eluent. The product, Pt{(NH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NO<sub>2</sub>}(PR<sub>3</sub>)<sub>2</sub> (3)-(7), was obtained,

<sup>\*</sup> Author to whom correspondence should be addressed.

upon removal of the solvent *in vacuo*, from the first purple band which eluted (0.12 mmol, *ca* 80%). Crystals suitable for X-ray studies were obtained by slow diffusion of hexane into a  $CH_2Cl_2$  solution of 3. Microanalyses, yields, <sup>31</sup>P and <sup>1</sup>H NMR are given in Table 1, mass spectra and selected IR data in Table 2.

## X-ray crystallography

All X-ray measurements were made on a CAD4 diffractometer operating in the  $\omega$ -2 $\theta$  scan mode with graphite monochromated Mo- $K_a$ , following procedures previously described in detail.<sup>5</sup> The structure was solved and refined by the heavy atom method and full-matrix least-squares in a routine manner. All non-hydrogen atoms were refined anisotropically. Phosphine phenyl rings were treated as rigid bodies with hydrogens included in idealized positions with group  $U_{iso}$  values. Methyl hydrogens and those on the phenylene-diimine were freely refined with individual  $U_{iso}$  values.

Crystal data.  $C_{22}H_{27}N_3O_2P_2Pt$ , M = 622.512, monoclinic, a = 12.817(3), b = 14.262(2), c = 13.013(2) Å,  $\beta = 96.17(1)^{\circ}$ , U = 2364.9 Å<sup>3</sup>, space group  $P_{21}/n$ , Z = 4,  $D_c = 1.75$  g cm<sup>-3</sup>,  $\mu$ (Mo- $K_x$ ) = 61.5 cm<sup>-1</sup>,  $\lambda = 0.71069$  Å.

Data collection.  $(1.5\theta \le 25^\circ)$ , graphite monochromated Mo- $K_{\alpha}$  radiation; 4547 independent measured reflections, 2906 observed  $[|F_o| > 1.5\sigma(|F_o|)]$ , corrected for Lorentz and polarization factors; empirical absorption correction.

Refinement. 281 parameters, weighting scheme  $1/[F_o + 0.001431F_o] R = 0.042$ ,  $R_g = 0.0527$ . Phenyl rings refined as rigid groups. All non-hydrogens anisotropic; hydrogens fixed. Computations were carried out on an VAX 11.750 computer using the SHELX76 program system. Final atomic positional and thermal parameters, full lists of bond lengths and angles and  $F_o/F_c$  values have been deposited as supplementary material with the Editor, from whom copies are available on request. Atomic coordinates have also been submitted to the Cambridge Crystallographic Data Centre.

## **RESULTS AND DISCUSSION**

Upon dissolving 1 in liquid ammonia, an intense red coloured solution is observed. If this solution is reacted with 2 the new complexes 3-7 are obtained [Eq. (1)]:

$$O_{2}NC_{6}H_{3}(NH_{2})_{2} + PtCl_{2}(PR_{3})_{2} \xrightarrow{\text{liq NH}_{3}} (1) (2)$$

$$Pt\{(NH)_{2}C_{6}H_{3}NO_{2}\}(PR_{3})_{2} + 2NH_{4}Cl. (1) (3)-(7)$$

	Table I. I	Microanaly	tical (calcu	lated val	ues in parenth	eses), yield	is and NM	R data	
PR3	С	Н	z	Yield	Ś	<sup>1</sup> J <sub>a</sub>	<sup>۱</sup> ۳ ۲ <sup>۱</sup>	$^{2}J_{ab}$	H
PMe <sub>2</sub> Ph (3)	42.2(42.5)	4.0(4.3)	6.5(6.7)	82	-21.8	2916	2983	22	7.38m(13H), 6.15d(2H), 1.6m(12H)
PMePh <sub>2</sub> (4)	51.0(51.4)	4.1(4.1)	5.6(5.6)	80	-4.7, -5.2	2959	3010	22	7.43m(23H), 6.05d(2H), 1.81m(6H)
PEt <sub>3</sub> (5)	37.9(37.9)	4.1(4.1)	7.4(7.4)	75	9.2, 9.5	2910	2983	23	7.5s(2H), 7.3s(1H), 6.35d(2H) 1.92m(12H), 1.15m(18H)
PPh <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> 1/2CDCl <sub>3</sub> (6)	48.1(48.4)	3.9(3.8)	6.0(5.3)	71	39.8	2965	3070	12	7.82(8H), 7.45m(14H), 7.28s(1H) 6.3d(2H), 2.4m(4H)
Palladium PPh <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> CDCl <sub>3</sub> (7)	51.6(51.1)	4.1(4.0)	5.3(5.4)	<b>5</b>	56.5	I	ļ	I	7.64m(8H), 7.35m(14H), 7.3s(1H) 6.35d(2H), 2.5m(4H)

Compound	, ₩	M + - NO,	M <sup>+</sup> – PR,	$M^+ - NO, Ph(NH),$	(H—-N)v	v(NO.)	v(CN)	x	Ύ (ε ×	( <sub>f</sub> - 01	
4			C	7/		14				`	
3	606	560	468	471	3405m, 3381s	1250vs	1567m	232	351	385	547
								(16.0)	(2.74)	(2.11)	(1.32)
4	746	700	546	595	3389s, 3381m	1248vs	1557m	232	350	384	546
								(19.2)	(2.90)	(2.38)	(1.63)
S	582	536	463	427	3407m, 3389m	1248vs	l 568m	230	344	382	552
								(4.84)	(2.15)	(1.61)	(06.0)
9	744	869		593	3397m	1258vs	1560m	232	351	379	544
								(32.3)	(3.21)	(2.24)	(1.40)
7	656	624		504	3394m	1254vs	1560m				
M + - nareni	t ion Derce	nto ao chindon			1 11 /036 6	Ē	-		1,1,1		

The colour changes during the course of the reaction suggest that 1 is deprotonated by liquid ammonia to form an anionic species. However, we have no strong evidence for this. At best a monoanion would be formed and we presume that this forms an (unobserved) intermediate which eliminates HCl to give the desired product. Compounds 3-7 were characterized by NMR, mass spectra, IR and, in the case of  $PR_3 = PMe_2Ph$ , Xray crystallography.

The <sup>31</sup>P NMR of 3-7 (Fig. 1, Table 1) consist at low field (36.21 MHz) of a central resonance with complex satellites due to coupling to <sup>195</sup>Pt. The magnitude of the  ${}^{1}J {}^{31}P - {}^{195}Pt$  coupling constants show an inequivalence and are typical of the pattern normally observed in AX spectra. The substituted NO<sub>2</sub> group of 4-nitro-1,2-diaminobenzene makes the two nitrogen donor atoms slightly different. Thus, although the chemical shift for the phosphorus atoms are essentially the same at 36.21 MHz, the  $^{1}J$  coupling constants are of sufficiently different magnitude (40 Hz) to be seen. On going to higher field (101.1 MHz) the small chemical shift difference between the phosphorus atoms is enough for the individual resonances to be seen. The magnitude of the  ${}^{1}J {}^{31}P - {}^{195}Pt$  coupling constant of ca 2940 Hz is typical of square-planar cis-phosphine platinum(II) species with nitrogen donor ligands<sup>6,7</sup>  $({}^{1}J {}^{31}P - {}^{195}Pt \text{ in } Pt(NSO)_{2}(PR_{3})_{2} \text{ is } 3100 \text{ Hz and}$ in  $Pt(S_2N_2)(PR_3)_2$  is 2800 Hz). The chemical shift variation between 3-7 is due to the variation of the phosphine group. The  ${}^{2}J{}^{31}P-{}^{31}P$  coupling constant of 22 Hz is as expected for cis-phosphine groups on platinum(II). The lower  ${}^{2}J {}^{31}P - {}^{31}P$  coupling constant for 6 of 12 Hz could be due to contributions of  ${}^{2}J(P--Pt--P)$  combined with a contribution directed via a  ${}^{3}J(P--CH_{2}--CH_{2}--P)$ pathway.

The <sup>1</sup>H NMR spectra of 3–7 show the phosphine protons often overlapping the aromatic protons of the NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(NH)<sub>2</sub> ring. The N—H protons are observed at *ca* 6.2 ppm as a doublet ( ${}^{3}J {}^{31}P{}^{-1}H$ , *ca* 5 Hz). This indicates coupling to the *trans*-phosphorus. No  ${}^{2}J {}^{19}$ Pt–<sup>1</sup>H coupling is observed.

The mass spectra of 3-7 show the parent ion with the expected isotopic correlation (principally due to the platinum isotopes). Fragment ions mainly consist of loss of phosphine to form  $[Pt\{(NH)_2 C_6H_3NO_2\}(PR_3)]^+$ , loss of  $(NH)_2C_6H_4NO_2$  to leave  $[Pt(PR_3)_2]^+$  and loss of  $NO_2$  to form  $Pt\{(NH)_2C_6H_3\}(PR_3)_2$ . In the case of the bidentate derivatives (6, 7) the  $M-(PR_3)$  peak is not observed, a peak due to loss of  $(O_2)$  is seen.

The IR spectra of 3-7 show the expected phosphine and  $\{(NH)_2C_6H_3NO_2\}$  ligand vibrations. Two intense v(NH) vibrations at *ca* 3405 and 3380



Fig. 1. <sup>31</sup>P NMR of **4** at 36.21 MHz, with the insert showing the central resonances measured at 101.1 MHz.

 $cm^{-1}$  are observed for 3-5 and one for 6, 7 at 3395 cm<sup>-1</sup>. The free ligand 4-nitro-1,2-phenylinediamine has four distinguishable v(NH) vibrations and the loss of two vibrations is consistent with the ligand having been doubly deprotonated on complexation. The observed v(NH) vibrations are higher than that observed in the homoleptic rhenium compounds<sup>3</sup> at 3264 cm<sup>-1</sup> and normal aromatic v(NH)vibrations at 3250 cm<sup>-1</sup>. The most intense band in the spectrum is the  $v(NO_2)$  stretching vibration at 1250 cm<sup>-1</sup>. This is lower than its assigned value in the free ligand at 1293 cm<sup>-1</sup>. An assignable v(CN) vibration is observed at  $1567 \text{ cm}^{-1}$ , as this vibration does not exist in either starting material. Typically in the homoleptic analogues v(CN) occurs at ca 1594 cm<sup>-1</sup>.

The UV-vis spectra of **3-6** show four main bands at ca 230, 350, 385 and 547 nm. The high energy band at 230 nm is associated with aromatic ring transitions and is of higher intensity in **3**, **4** and **6** due to the aromatic groups also present on the phosphine ligand. The bands at 350 and 385 nm are due to the nitro group. Whilst the weak band at 547 nm, responsible for the purple colour in solution, is due to the complexed ligand.

The X-ray crystal structure of 3 (Table 3, Fig. 2) reveals the expected square-planar geometry at platinum. The Pt—P and Pt—N bond lengths are

normal, whilst the C—N bond lengths are, as expected, consistent with formal C—N bond lengths. There are no short contacts in the crystal structure which would indicate any significant intermolecular interactions.

The compounds 3–7 are sensitive to hydrolysis and weak acids. Dichloromethane solutions of 3–7 show gradual deterioration to the free ligand and PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (detected by both <sup>31</sup>P NMR and UV– vis). This is presumably due to residual HCl from the CH<sub>2</sub>Cl<sub>2</sub> reacting with 3–7 [eq. (2)]:

$$Pt\{(NH)_{2}C_{6}H_{3}NO_{2}\}(PR_{3})_{2}+2HCl \rightleftharpoons$$

$$(NH_{2})_{2}C_{6}H_{3}NO_{2}+PtCl_{2}(PR_{3})_{2}. (2)$$

The complexes 3–7 show no change in the NMR spectrum on adding excess CH<sub>3</sub>OD. Similarly, the



Fig. 2. The X-ray structure of 3.

Table 3. Selected bond lengths and angles for 3

P(1)—Pt 2	2.236(4)	P(2)—Pt	2.243(4)
N(1)—Pt 2	2.036(10)	N(2)—Pt	2.024(9)
C(1)—P(1) 1	.826(13)	C(2) - P(1)	1.807(13)
C(3)—P(2) 1	.810(16)	C(10) - P(1)	1.805(9)
C(16)—P(2) 1	.800(10)	C(4)P(2)	1.829(17)
N(1)—C(18) 1	.347(12)	N(2)—C(17)	1.345(13)
C(17)C(18) 1	.413(14)	C(22)-C(17)	1.408(13)
C(19)—C(18) 1	.394(14)	C(19)C(20)	1.377(16)
C(20)—C(21) 1	.412(16)	C(21)C(22)	1.397(15)
C(21)—N(3) 1	.417(13)	O(1)—N(3)	1.262(13)
O(2)—N(3) 1	.228(14)		
P(2)PtP(1)	97.2(2)	C(17)PtP(1)	118.9(3)
C(17)—Pt—P(2)	143.7(2)	N(1)— $Pt$ — $P(1)$	172.2(2)
N(1)— $Pt$ — $P(2)$	90.1(3)	N(2) - Pt - P(2)	169.2(2)
N(2) - Pt - P(1)	93.6(3)	N(2) - Pt - N(1)	79.1(4)
C(1)—P(1)—Pt	113.9(5)	C(2)—P(1)—Pt	116.5(6)
C(2) - P(1) - C(1)	103.7(7)	C(10)-P(1)-Pt	114.9(3)
C(10) - P(1) - C(1)	100.6(7)	C(10) - P(1) - C(2)	2) 105.5(6)
C(3)—P(2)—Pt	110.8(6)	C(4)P(2)Pt	112.3(7)
C(4) - P(2) - C(3)	100.2(9)	C(16)P(2)Pt	122.0(4)
C(16) - P(2) - C(3)	104.0(7)	C(16)-P(2)-C(4	) 105.2(7)
C(9) - C(10) - P(1)	117.1(3)	C(5)-C(10)-P(1	) 122.9(3)
C(15)-C(16)-P(2)	121.7(3)	C(11)C(16)P(	(2) 118.3(3)
C(18)-C(17)-Pt	77.0(6)	C(22)C(17)Pt	: 164.4(7)
C(22)C(17)C(17)	8) 118.3(10)	N(2)-C(17)-C(2	22) 124.3(10)
N(2)-C(17)-C(18	) 117.4(9)	N(1)-C(18)-C(	17) 114.1(9)
C(19)-C(18)-C(1	7) 120.9(10)	C(20)C(19)C	(18) 121.3(11)
N(1)-C(18)-C(19	) 125.0(10)	C(22)C(21)C	(20) 121.8(10)
C(21)-C(20)-C(1	9) 118.1(11)	N(3)-C(21)-C(2	22) 119.0(11)
N(3)-C(21)-C(20	) 119.2(11)	C(18)N(1)Pt	115.2(7)
C(21)-C(22)-C(1	7) 119.6(10)	O(1)-N(3)-C(2	1) 119.0(12)
C(17)—N(2)—Pt	113.8(7)	O(2)—N(3)—O(1)	) 121.9(11)
O()—N(3)—C(21)	119.1(10)		

IR spectrum obtained by pumping down a solution of 5, which has been treated with  $CH_3OD$ , shows no deuterium/proton exchange.

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