Synthesis and Reactivity of Bis(*o*-nitrophenyl)platinum. *X*-Ray Crystal and Molecular Structure of [Pt{*o*-C₆H₄N(O)O}(*o*-C₆H₄NO₂)(PPh₃)] †

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Reaction of [Hg(*o*-C₆H₄NO₂)₂] with K₂[PtCl₄] or PtCl₂ (2:1) yields the complex [Pt{*o*-C₆H₄N(O)O}₂]. It reacts (*i*) with monodentate ligands L (PPh₃, AsPh₃, or pyridine) (1:1) to give complexes of the type [Pt{*o*-C₆H₄N(O)O}(*o*-C₆H₄NO₂)L] or (*ii*) with monodentate L (PPh₃, AsPh₃, pyridine, or CO) (1:2) or bidentate ligands L₂ [cyclo-octa-1,5-diene, 1,10-phenanthroline, 2,2'-bipyridine, 1,2-bis(diphenylphosphino)ethane, or bis(diphenylphosphino)methane] (1:1) to give complexes [Pt(*o*-C₆H₄NO₂)₂L₂]. The crystal structure of [Pt{*o*-C₆H₄N(O)O}(*o*-C₆H₄NO₂)(PPh₃)] shows both chelating and monodentate *o*-nitrophenyl groups. They show no significant differences in the bond lengths Pt–C [2.018(9) and 1.983(8) Å, respectively] and N–C [1.446(11) and 1.468(12) Å, respectively]. The co-ordinated oxygen atom has a longer N–O bond length [1.273(10) Å] than the unco-ordinated one [1.221(10)], *cf.* those in the unco-ordinated *o*-nitrophenyl group [1.220(10) and 1.230(11) Å].

We are looking for new uses of organomercury compounds as transmetallating agents in the synthesis of organo complexes that are not accessible, or not easily prepared, using Grignard or organolithium reagents.[1,2] The mercury derivative is a candidate for the transfer of the *o*-nitrophenyl group; the corresponding lithium derivative is very unstable[3] and, probably for this reason, scarcely used[4] as a transmetallating reagent, although a recent paper cites its use to prepare *cis*-[Pt(*o*-C₆H₄NO₂)₂L₂] [L = PPh₃, cyclo-octa-1,5-diene (cod), or Me₂N(CH₂)₂NMe₂],[5] in which the nitrophenyl ligands are monodentate. The interest in preparing these aryl complexes is well documented. Thus *o*-nitrophenyl compounds of silicon[6] have been prepared by reacting the appropriate organic halides with Si₂R₆ (R = alkyl) derivatives or by nitration of arylsilanes. The first transition-metal derivative, [Pd(*o*-C₆H₄NO₂)Cl(PPh₃)₂], was prepared[7] by an oxidative addition reaction. Finally, an electrochemical synthesis has been used to prepare some zinc and cadmium derivatives.[8] Because of the limited synthetic utility of these reactions and also because only a few types of products can be obtained [*e.g.* monoaryl(halogeno) derivatives of some transition elements] we thought it of interest to investigate whether bis(*o*-nitrophenyl)mercury can be used as an arylating agent to prepare *o*-nitrophenyl complexes of different metals, with different bonding and structural characteristics.

Structural data on nitrophenyl derivatives may provide information concerning electron-withdrawing behaviour of the nitro group, about which there has been some recent controversy.[9] The *o*-nitrophenyl group can act as a mono- or bidentate ligand. Infrared spectra suggest that the gold complexes we have described[1] possess monodentate *o*-nitrophenyl groups.

In a recent communication we reported a rhodium (III) complex with two chelating *o*-nitrophenyl groups.[10]

Arylmercury derivatives have been used to prepare platinum(II) complexes through transmetallation or redox transmetallation reactions;[11,12] here we report the synthesis, using bis(*o*-nitrophenyl)mercury, of bis(*o*-nitrophenyl)-platinum, its reactivity towards neutral ligands, and the *X*-ray crystal structure of the first example of a complex in which both types of co-ordinating *o*-nitrophenyl groups are present.

Results and Discussion

Synthesis.—By refluxing in EtOH a mixture of K₂[PtCl₄] or PtCl₂ and [Hg(*o*-C₆H₄NO₂)₂] (2—3 h; 1:2) the dark red complex [Pt{*o*-C₆H₄N(O)O}₂] (1) crystallizes in high yield (95%). From the mother-liquor the by-product [HgCl(*o*-C₆H₄NO₂)] can be isolated. As this compound symmetrizes[13] in the presence of NaI (2:3), according to equation (i), complex (1) can be better obtained by reacting K₂[PtCl₄] or PtCl₂ with [Hg(*o*-C₆H₄NO₂)₂] in the presence of NaI (1:1:3).

$$2[HgCl(o\text{-}C_6H_4NO_2)] + 3NaI \longrightarrow$$
$$[Hg(o\text{-}C_6H_4NO_2)_2] + Na[HgI_3] + 2NaCl \quad (i)$$
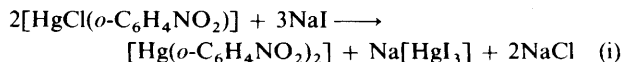
[Hg(*o*-C₆H₄NO₂)₂] reacts with K₂[PtCl₄] (1:1) (in refluxing EtOH; 2 h) to give (1), [HgCl(*o*-C₆H₄NO₂)], and unreacted K₂[PtCl₄]. This is the same behaviour as observed[1] towards [NMe₄][AuCl₄], which could mean that monoarylated complexes are not intermediates in these transmetallation reactions. These reactions show that [HgCl(*o*-C₆H₄NO₂)] has no arylation capability towards K₂[PtCl₄] or [NMe₄][AuCl₄]. We have also found that it does not arylate PtCl₂; PtCl₂ and [HgCl(*o*-C₆H₄NO₂)] do not react until NaI is added. Scheme 1 shows the probable steps involved in the synthesis of (1) when NaI and PtCl₂ are used.

As monoarylated complexes are usually the first compounds obtained in transmetallation reactions using diorganomercury compounds,[11] we have made several attempts to prepare mono-*o*-nitrophenylplatinum complexes. However, well established methods of preparing such compounds failed. Thus, reactions

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between (1) and HgCl$_2$ (refluxing in acetone or MeOH; 2 h) or between [Hg(o-C$_6$H$_4$NO$_2$)$_2$] and [PtCl$_2$(cod)] (refluxing in EtOH: 3 h) or cis-[PtCl$_2$(PPh$_3$)$_2$] (refluxing in EtOH; 3 h) were not observed. In contrast [Pt{(PhCH=CH)$_2$CO}$_2$] reacts with [HgCl(o-C$_6$H$_4$NO$_2$)] (1:1, room temperature, acetone, 24 h) or with o-ClC$_6$H$_4$NO$_2$ (1:1, refluxing in toluene, 6 h) but the expected product, [{Pt[o-C$_6$H$_4$N(O)O](μ-Cl)}$_2$], was not isolated. Instead a mixture of (1), PtCl$_2$ and Hg, or a black product not containing the nitrophenyl group (by i.r.), respectively, results. As reactions between zerovalent platinum and aryl(halogeno)mercury or halogenoarene compounds are well established routes for the preparation of aryl(halogeno)-platinum(II) complexes,[12a] we believe that these reactions can be explained if the initially formed halogeno(o-nitrophenyl)-platinum(II) complex is an unstable compound that symmetrizes to (1) and PtCl$_2$ at room temperature, or decom-

poses in refluxing toluene. If this were so, such a platinum complex could be a non-isolable intermediate in the synthesis of (1), although our recent results with the corresponding palladium(II) complexes[14] indicate a route that leads directly to (1), in agreement with Scheme 1.

The above mentioned symmetrization reaction could be favoured by the great stability of complex (1). It sublimes at around 280 C and in its mass spectrum the largest peak corresponds to the molecular ion (m/z 439).

Complex (1) reacts with monodentate ligands giving red complexes of the type [Pt{o-C$_6$H$_4$N(O)O}(o-C$_6$H$_4$NO$_2$)L] [L = PPh$_3$ (2), AsPh$_3$ (3), or pyridine (py) (4)] or yellow complexes [Pt(o-C$_6$H$_4$NO$_2$)$_2$L$_2$] [L = PPh$_3$ (5) or AsPh$_3$ (6)] depending on the molar ratios of the reagents. Reaction of (1) with carbon monoxide gives a yellow solution which, upon concentration, yields (1). When pyridine is used in excess a yellow complex can be isolated but slow conversion, even in the solid, to the red complex occurs, preventing us from obtaining an analytically pure sample of the bis(pyridine) complex. As shown in Scheme 2, this dissociative process allows a more convenient synthetic method for preparing complex (4) by the reaction of (1) with the yellow complex. None of the complexes (5) or (6) appears to convert to the corresponding red derivatives; however, in solution such dissociation should occur, since (5) and (6) are converted to (2) and (3), respectively, by reaction with (1) (Scheme 2). Such conversion is incomplete in the case of the PPh$_3$ complex (5), probably because of the smaller equilibrium constant of the dissociation. Complex (1) also reacts (1:1) with bidentate ligands giving yellow complexes of formula [Pt(o-C$_6$H$_5$NO$_2$)$_2$L$_2$] [L$_2$ = cod (7), 1,10-phenanthroline (phen) (8), 2,2'-bipyridine (bipy) (9), 1,2-bis(diphenylphosphino)ethane (dppe) (10), or bis(diphenyl-phosphino)methane (dppm) (11)]. As mentioned above, neither (5) nor (7) could be prepared by reacting [Hg(o-C$_6$H$_4$NO$_2$)$_2$] with the corresponding cis-[PtCl$_2$L$_2$] complexes. Scheme 2 summarizes all these reactions and shows the proposed structures of the complexes. Table 1 gives analytical data and some physical properties of the complexes, all of which, except those not soluble in acetone [(1), (8)—(10)], are non-conducting in this solvent. The mononuclear nature of
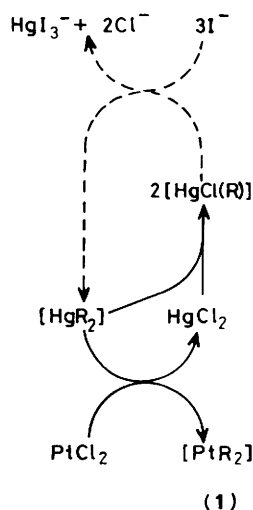
Scheme 1. Probable steps involved in the synthesis of complex (1); R = o-C$_6$H$_4$NO$_2$
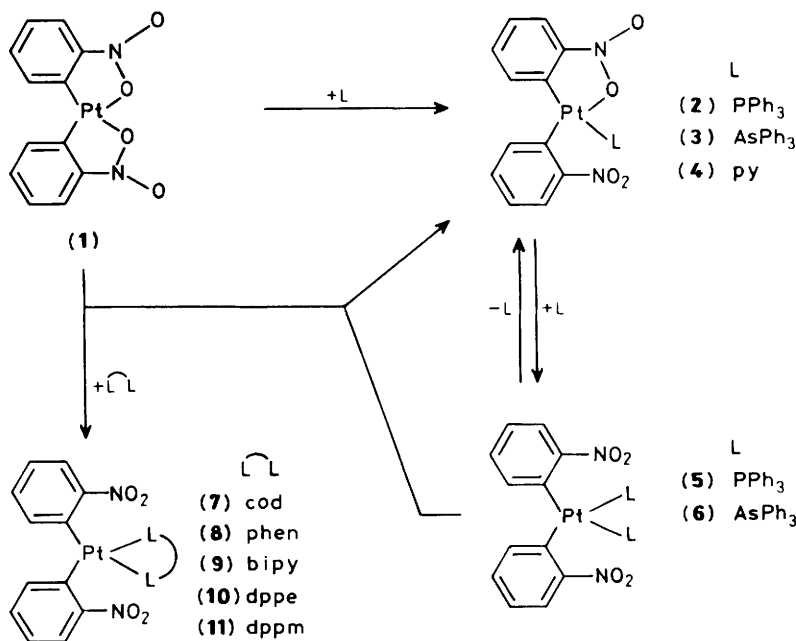
Scheme 2. Syntheses and proposed structures of complexes (2)—(11)

Table 1. Analytical and other data for complexes

| Complex[a] | M.p. (°C) | Analyses[b] (%) | | | $v(NO_2)$[c]/cm^{-1} | Yield (%) |
		C	H	N		
(1) [PtR$_2$]	280 (sublim.)	32.20 (32.80)	1.85 (1.80)	6.00 (6.40)	1 508, 1 261	95
(2) [PtR$_2$(PPh$_3$)]	192 (decomp.)	51.25 (51.35)	3.40 (3.30)	3.75 (4.00)	1 505, 1 352, 1 255	62
(3) [PtR$_2$(AsPh$_3$)]	192	48.45 (48.35)	3.25 (3.10)	3.45 (3.75)	1 500, 1 352, 1 255	83
(4) [PtR$_2$(py)]	162 (decomp.)	38.95 (39.40)	2.35 (2.55)	7.60 (8.10)	1 500, 1 345, 1 258	84
(5) [PtR$_2$(PPh$_3$)$_2$]	180 (decomp.)	59.45 (59.80)	4.10 (3.95)	3.20 (2.90)	1 508, 1 328	83
(6) [PtR$_2$(AsPh$_3$)$_2$]	169	54.90 (54.80)	3.60 (3.65)	2.40 (2.65)	1 500, 1 328	70
(7) [PtR$_2$(cod)]	169 (decomp.)	43.75 (43.90)	3.75 (3.70)	4.75 (5.10)	1 500, 1 330	80
(8) [PtR$_2$(phen)]	321 (decomp.)	46.15 (46.55)	2.60 (2.60)	8.65 (9.05)	1 515, 1 348	96
(9) [PtR$_2$(bipy)]	>350	43.75 (44.35)	2.80 (2.70)	9.85 (9.40)	1 519, 1 350	93
(10) [PtR$_2$(dppe)]	307 (decomp.)	54.55 (54.45)	3.60 (3.80)	2.95 (3.35)	1 509, 1 345	68
(11) [PtR$_2$(dppm)]	252 (decomp.)	53.35 (53.45)	3.85 (3.65)	3.20 (3.40)	1 505, 1 330	75

[a] R = o-C$_6$H$_4$NO$_2$. [b] Calculated values in parentheses. [c] See text.

complexes (10) and (11) was established by osmometry in CHCl$_3$ [M calc. (found): 838 (849); 824 (833) respectively].

I.r. Spectra.—From i.r. evidence we have postulated that, in any o-nitrophenylgold complex,[1] there is an appreciable O $\cdots$ Au interaction; the bands assignable to $v_{asym}(NO_2)$ and $v_{sym}(NO_2)$ appear in the ranges expected for nitroaromatic groups (1 510—1 495 and 1 345—1 320 cm^{-1}). We assumed that, if interaction took place, some change in N–O bond strength should occur. Subsequently, X-ray molecular structures and i.r. spectra of some nitrophenolato complexes of Cu and Ru have been reported and it was found[15] that the i.r. spectra do not reliably indicate the structural difference between co-ordinated and unco-ordinated nitro groups. In contrast we have reported[10] that in [Rh$\{o$-C$_6$H$_4$N(O)O$\}_2$-Cl(CO)] $v_{asym}(NO_2)$ appears at 1 525 and 1 535 cm^{-1}, and $v_{sym}(NO_2)$ at 1 270 cm^{-1}, and have suggested that the lowering in energy of the last band with respect to that assigned in nitrophenylgold complexes is evidence for a cyclometallated o-nitrophenyl group. Complexes (1)—(11) offer an opportunity to confirm such an assignment. They show $v_{asym}(NO_2)$ as a broad and very strong band in the range 1 520—1 500 cm^{-1}, confirming the low sensitivity of this vibration mode to the type of co-ordination of the nitrophenyl group. Figure 1 shows i.r. spectra in the 1 400—1 200 cm^{-1} region of some of the complexes reported here. Taking the i.r. spectrum of (1) as a reference [Figure 1(*b*)] the i.r. spectra of complexes of general formula [Pt$\{o$-C$_6$H$_4$N(O)O$\}(o$-C$_6$H$_4$NO$_2)$L] [Figure 1(*c*)] show, as the main difference, a new band at around 1 350 cm^{-1} that should be assigned to $v_{sym}(NO_2)$ of the unco-ordinated nitro group.

The i.r. spectra of complexes of formula [Pt(o-C$_6$H$_4$NO$_2)_2$-L$_2$] [Figure 1(*a*)] also show a new band in the region 1 350—1 320 cm^{-1} but lack the band present in (1) at 1 261 cm^{-1} and that at around 1 250 cm^{-1} in the other group of complexes. Therefore we conclude that $v_{sym}(NO_2)$ of chelated o-nitrophenyl ligands occurs in the range 1 250—1 270 cm^{-1}. According to this assignment, the organomercury compounds [Hg(o-C$_6$H$_4$NO$_2)_2$] and [HgCl(o-C$_6$H$_4$NO$_2$)] contain monodentate o-nitrophenyl groups because of the similarity of their i.r. spectra in the 1 400—1 200 cm^{-1} region to those of [Pt(o-C$_6$H$_4$NO$_2)_2$L$_2$].

The product of the reaction between (1) and carbon monoxide in CH$_2$Cl$_2$ is *cis*-[Pt(o-C$_6$H$_4$NO$_2)_2$(CO)$_2$], as shown by the very strong bands at 2 145 and 2 105 cm^{-1}. Compound (5) shows the same pattern in the i.r. spectrum in the region 490—520 cm^{-1} as described[5] for *cis*-[Pt(o-C$_6$H$_4$NO$_2)_2$-

(PPh$_3)_2$]. Its ^{31}P-$\{^1$H$\}$ n.m.r. spectrum shows a singlet [15.01 p.p.m. (CDCl$_3$) relative to H$_3$PO$_4$] with ^{195}Pt satellites [^1J(Pt–P) 2 241 Hz]. The value of ^1J(Pt–P) is similar to that found[16] for ^1J(Pt–P) *trans* to the phenyl group in *cis*-[Pt(Ph)(SnClPh$_2$)(PPh$_3)_2$] (2 137 Hz).

The only differences in the i.r. spectra of (1) and of [Hg(o-C$_6$H$_4$NO$_2)_2$] in the 500—200 cm^{-1} region are the decrease of the 485 cm^{-1} band of (1) to 468 cm^{-1} $\{$these bands could correspond to the X-sensitive $B_2(y)$ mode[17] at 464, 460 cm^{-1} in [Hg(C$_6$H$_5)_2$][18]$\}$ and the absence of the 280 cm^{-1} band, which could correspond to the Pt–O bond, in the mercury derivative. Related bands appear in complexes (2)—(4) at 273, 268, and 285 cm^{-1} (all w), respectively. For complexes (2)—(11) the $B_2(y)$ mode band cannot be assigned, because of band(s) at *ca.* 500 cm^{-1} from the other ligand.

Structure of Complex [Pt$\{o$-C$_6$H$_4$N(O)O$\}(o$-C$_6$H$_4$NO$_2$)-(PPh$_3$)] (2).—The metal atom displays the usual square-planar geometry (maximum deviation of five atoms 0.06 Å), with Pt–C bonds mutually *cis* (Figure 2). The nitrophenyl ligands differ appreciably in the dihedral angle between the planes of the ring and the nitro group; the chelating ligand, which is almost parallel to the co-ordination plane (dihedral angle to the nitro group 7°), is itself almost planar (dihedral angle 5°), whereas the monodentate ligand shows a 48° rotation of the nitro group. The differing $p\pi$(N)–$p\pi$(C) overlap should then be associated with differing ability to remove electron density from the ring, and thus with observable differences in bond lengths (we have observed this effect in two independent molecules of a p-nitrophenyl ether;[19] see also below). However, all C–C bond distances are similar [1.354(14)—1.403(12) Å] and the main difference is between N–O bond lengths involving co-ordinated and unco-ordinated oxygen [1.273(10), 1.220(10)—1.230(11) Å respectively]; this is presumably due to an interaction $p\pi[O(2)] \longrightarrow d\pi$(Pt), weakening the $p\pi[O(2)]$–$p\pi[N(1)]$ bond. The marginally significant shortening of N(1)–C(1) compared with N(2)–C(8) [1.446(11), 1.468(12) Å respectively] is consistent with the above interpretation.

The above results are unexpected, particularly in comparison with the data[10] for the complex [Rh$\{o$-C$_6$H$_4$N(O)O$\}_2$Cl(CO)] where strong electron delocalization is shown by longer N–O [1.283(5), 1.375(5), and 1.321(4) Å; one short distance of 1.171(6) Å is associated with a disordered oxygen atom] and shorter C–N [1.378(5) and 1.362(5) Å] bonds than observed in the chelated group in complex (2). In addition, the phenyl rings display four long bonds [1.436(5)—1.508(7) Å] and two short bonds [1.233(7)—1.298(8) Å]. It is also unexpected that in the
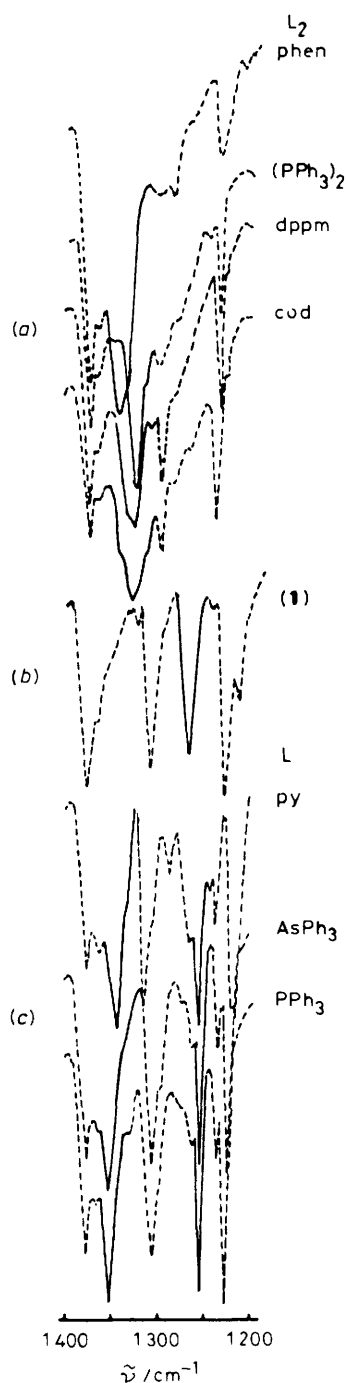
Figure 1. I.r. spectra of some complexes in the 1 400—1 200 cm⁻¹ region. (a) [Pt(o-C$_6$H$_4$NO$_2$)$_2$L$_2$], (b) [Pt{o-C$_6$H$_4$N(O)O}$_2$] (1), (c) Pt{o-C$_6$H$_4$N(O)O}(o-C$_6$H$_4$NO$_2$)L]. The solid lines are our assignment of ν_{asym}(NO$_2$) vibrations (see text)

Figure 2. The molecule of (2) in the crystal, showing the atom numbering scheme

ν_{sym}(NO$_2$) frequency. In contrast, the above mentioned nitro-phenolato complexes [15] of Cu and Ru show similar N–O bond lengths whether they correspond to co-ordinated [1.217(8), 1.225(4) Å] or unco-ordinated [1.202(6)—1.232(8) Å] oxygen atoms, and thus both types show a similar ν(NO$_2$) frequency.

Experimental

Infrared spectra were recorded in the range 4 000—200 cm⁻¹ on a Perkin-Elmer 1430 spectrophotometer. Melting points were determined on a Reichert apparatus and are uncorrected. Carbon, H, and N analyses were carried out by the Instituto de Química Bio-Orgánica, Barcelona (Spain). ³¹P N.m.r. spectra were recorded on a Varian XL-250. Molecular weights were determined with a Knauer vapour-pressure osmometer. The mass spectrum of (1) was recorded on a Hewlett-Packard GC/MS System 5993 at 70 eV.

All reactions were carried out with magnetic stirring and without any special precautions against light, air, or moisture.

[Pt{o-C$_6$H$_4$N(O)O}$_2$] (1).—To a solution of K$_2$[PtCl$_4$] (100 mg, 0.24 mmol) in EtOH (25 cm³, 80%) solid [Hg(o-C$_6$H$_4$NO$_2$)$_2$] [20] (214 mg, 0.48 mmol) was added and refluxed for 2 h. The resulting suspension was filtered off while hot and the dark red solid washed with boiling EtOH (3 × 10 cm³) to give crude (1), a solution of which in CH$_2$Cl$_2$–CH$_3$CN (20:2 cm³) was filtered over MgSO$_4$ and the resulting solution concentrated (3 cm³). By slow addition of diethyl ether (5 cm³) and then n-hexane (15 cm³) analytically pure (1) was obtained. Attempts to prepare single crystals of (1) for X-ray structure analysis always led to extremely thin plates of unsuitable quality.

Syntheses of Complexes (2)—(11).—Most of the complexes were prepared by the following general method. To a suspension of (1) (*ca.* 0.1 mmol) in dichloromethane (15 cm³) the stoicheiometric amount of the ligand was added. After 1 h at room temperature the solution was concentrated (3 cm³) and n-hexane (15 cm³) added to precipitate the complex, which was washed with n-hexane (3 × 4 cm³) and vacuum dried.

For the syntheses of (8) and (9) the ligands (phen and bipy) were added to a solution of complex (1) in dichloromethane–acetonitrile (10:1 cm³), when the complexes precipitated. After 1 h at room temperature they were filtered off and washed with dichloromethane (2 × 5 cm³).

almost planar nitrophenyl groups in *cis*-[Pt(o-C$_6$H$_4$NO$_2$)$_2$-(PPh$_3$)$_2$] [5] the C–N and N–O bond lengths [1.474(9), 1.482(9); 1.220(9)—1.233(9) Å respectively] are very similar to those of complex (2). It thus seems that several types of bonding can be found in o-nitrophenyl complexes, but more structural data are needed before the picture becomes clear.

The lengthening of the N–O bond in the chelating o-nitro-phenyl ligands is responsible for the observed lowering in the
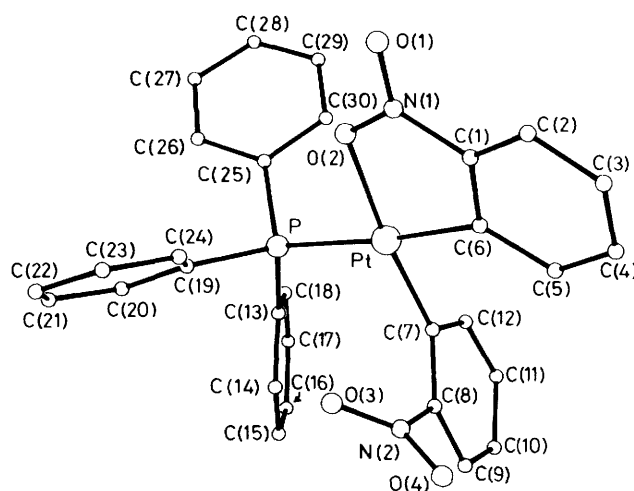
Table 2. Atom co-ordinates ($\times 10^4$) for (2)

Atom	x	y	z
Pt	1 024.6(0.4)	2 388.7(0.1)	4 661.9(0.2)
P	2 584(2)	3 326(1)	4 920(1)
N(1)	−1 724(8)	2 634(3)	3 682(4)
N(2)	3 440(8)	1 285(4)	3 921(5)
O(1)	−2 775(7)	2 918(3)	3 307(4)
O(2)	−659(6)	2 994(2)	4 010(3)
O(3)	3 495(7)	1 825(3)	3 520(4)
O(4)	3 421(9)	718(4)	3 566(4)
C(1)	−1 675(9)	1 896(4)	3 801(5)
C(2)	−2 775(10)	1 499(4)	3 394(5)
C(3)	−2 704(11)	809(5)	3 505(6)
C(4)	−1 574(11)	532(4)	4 006(6)
C(5)	−460(10)	932(4)	4 396(5)
C(6)	−450(9)	1 649(4)	4 298(5)
C(7)	2 424(8)	1 752(4)	5 278(5)
C(8)	3 417(9)	1 306(4)	4 873(5)
C(9)	4 395(9)	869(4)	5 291(6)
C(10)	4 413(11)	860(4)	6 178(7)
C(11)	3 424(11)	1 264(4)	6 627(6)
C(12)	2 507(10)	1 701(4)	6 179(5)
C(13)	4 278(8)	3 194(4)	5 586(5)
C(14)	5 416(9)	2 784(4)	5 267(5)
C(15)	6 677(9)	2 651(4)	5 757(6)
C(16)	6 825(10)	2 920(5)	6 594(5)
C(17)	5 735(11)	3 322(5)	6 903(6)
C(18)	4 458(11)	3 465(4)	6 415(5)
C(19)	3 268(9)	3 695(4)	3 921(5)
C(20)	4 465(11)	4 158(5)	3 917(6)
C(21)	4 893(12)	4 453(5)	3 144(7)
C(22)	4 175(13)	4 284(5)	2 369(7)
C(23)	3 023(12)	3 822(5)	2 366(6)
C(24)	2 568(9)	3 530(4)	3 134(5)
C(25)	1 613(9)	4 008(3)	5 476(5)
C(26)	2 004(11)	4 700(4)	5 430(6)
C(27)	1 244(12)	5 190(5)	5 914(7)
C(28)	122(13)	4 993(6)	6 427(6)
C(29)	−291(12)	4 322(6)	6 472(6)
C(30)	438(10)	3 826(4)	6 003(5)

Table 3. Selected bond lengths (Å) and angles (°) for (2)

P–Pt	2.319(3)	N(1)–O(1)	1.221(10)
N(1)–O(2)	1.273(10)	N(2)–O(3)	1.220(10)
N(2)–O(4)	1.230(11)	O(2)–Pt	2.138(6)
C(1)–N(1)	1.446(11)	C(1)–C(2)	1.385(12)
C(1)–C(6)	1.403(12)	C(2)–C(3)	1.354(14)
C(3)–C(4)	1.365(15)	C(4)–C(5)	1.387(13)
C(5)–C(6)	1.400(12)	C(6)–Pt	2.018(9)
C(7)–Pt	1.983(8)	C(7)–C(8)	1.398(12)
C(8)–N(2)	1.468(12)	C(8)–C(9)	1.368(12)
C(10)–C(9)	1.369(15)	C(10)–C(11)	1.381(14)
C(11)–C(12)	1.355(13)	C(12)–C(7)	1.393(12)
Pt ⋯ O(3)	3.06		

P–Pt–O(2)	93.5(2)	P–Pt–C(6)	172.1(3)
O(2)–Pt–C(6)	79.3(4)	P–Pt–C(7)	92.2(3)
O(2)–Pt–C(7)	174.0(4)	C(6)–Pt–C(7)	95.0(4)
O(1)–N(1)–O(2)	119.9(8)	O(1)–N(1)–C(1)	121.9(8)
O(2)–N(1)–C(1)	118.2(7)	O(3)–N(2)–O(4)	123.0(8)
O(3)–N(2)–C(8)	119.0(8)	O(4)–N(2)–C(8)	118.0(8)
Pt–O(2)–N(1)	113.2(5)	N(1)–C(1)–C(2)	118.3(8)
N(1)–C(1)–C(6)	115.4(7)	C(2)–C(1)–C(6)	126.2(8)
C(1)–C(2)–C(3)	117.6(9)	C(2)–C(3)–C(4)	119.5(10)
C(3)–C(4)–C(5)	122.4(9)	C(4)–C(5)–C(6)	121.1(9)
Pt–C(6)–C(1)	113.7(6)	Pt–C(6)–C(5)	133.1(7)
C(1)–C(6)–C(5)	113.0(8)	Pt–C(7)–C(8)	124.8(7)
Pt–C(7)–C(12)	122.6(7)	C(8)–C(7)–C(12)	112.6(8)
N(2)–C(8)–C(7)	119.4(8)	N(2)–C(8)–C(9)	115.3(8)
C(7)–C(8)–C(9)	125.3(8)	C(8)–C(9)–C(10)	118.0(9)
C(9)–C(10)–C(11)	120.2(9)	C(10)–C(11)–C(12)	119.1(9)
C(7)–C(12)–C(11)	124.6(9)		

To prepare complex (4) the general method was followed to prepare [Pt(o-C$_6$H$_4$NO$_2$)$_2$(py)$_2$] which was then reacted (1:1) with (1), also following the general method.

X-Ray Structure Determination of (2).—Violet-red plates were obtained by liquid diffusion of n-hexane into a dichloromethane solution.

Crystal data. C$_{30}$H$_{23}$N$_2$O$_4$PPt, M = 701.6, monoclinic, space group $P2_1/n$, a = 8.932(2), b = 19.417(4), c = 15.418(4) Å, β = 91.52(2)°, U = 2 673 Å^3, Mo-K_α radiation (λ = 0.710 69 Å), Z = 4, D_c = 1.74 g cm^{-3}, crystal size 0.35 × 0.15 × 0.055 mm, μ = 5.4 mm^{-1}, $F(000)$ = 1 368.

Data collection and processing. Stoe-Siemens four-circle diffractometer, 6 262 profile-fitted reflections[21] ($2\theta_{max.}$ 50°, $-h$ + k ± l), 4 700 unique, 3 463 with $F > 4\sigma(F)$ used for all calculations [program system SHELXTL (written by G.M.S.)]. Absorption correction based on ψ-scans; transmissions 0.42—0.62. Cell constants refined from ± 2θ values of 54 reflections in the range 20—23°.

Structure solution and refinement. Heavy-atom method; refinement on F to R 0.046, R' 0.038 [all non-H atoms anisotropic; H atoms included using a riding model with C–H 0.96 Å, U(H) = 1.2 U_{eq}(C), weighting scheme w^{-1} = $\sigma^2(F)$ + 0.000 25 F^2; 343 parameters]. Final atomic co-ordinates and derived parameters are given in Tables 2 and 3.

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