

Synthesis and Reactivity of Bis(*o*-nitrophenyl)platinum. X-Ray Crystal and Molecular Structure of $[\text{Pt}\{\overline{o\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}}\}(o\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)]^\dagger$

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Reaction of $[\text{Hg}(o\text{-C}_6\text{H}_4\text{NO}_2)_2]$ with $\text{K}_2[\text{PtCl}_4]$ or PtCl_2 (2:1) yields the complex $[\text{Pt}\{\overline{o\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}}\}_2]$. It reacts (i) with monodentate ligands L (PPh_3 , AsPh_3 , or pyridine) (1:1) to give complexes of the type $[\text{Pt}\{\overline{o\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}}\}(o\text{-C}_6\text{H}_4\text{NO}_2)\text{L}]$ or (ii) with monodentate L (PPh_3 , AsPh_3 , pyridine, or CO) (1:2) or bidentate ligands L_2 [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 $[\text{Pt}(o\text{-C}_6\text{H}_4\text{NO}_2)_2\text{L}_2]$. The crystal structure of $[\text{Pt}\{\overline{o\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}}\}(o\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)]$ 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 unstable³ and, probably for this reason, scarcely used⁴ as a transmetallating reagent, although a recent paper cites its use to prepare *cis*- $[\text{Pt}(o\text{-C}_6\text{H}_4\text{NO}_2)_2\text{L}_2]$ [$\text{L} = \text{PPh}_3$, cyclo-octa-1,5-diene (cod), or $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$],⁵ in which the nitrophenyl ligands are monodentate. The interest in preparing these aryl complexes is well documented. Thus *o*-nitrophenyl compounds of silicon⁶ have been prepared by reacting the appropriate organic halides with Si_2R_6 (R = alkyl) derivatives or by nitration of arylsilanes. The first transition-metal derivative, $[\text{Pd}(o\text{-C}_6\text{H}_4\text{NO}_2)\text{Cl}(\text{PPh}_3)_2]$, was prepared⁷ 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 described¹ possess monodentate *o*-nitrophenyl groups.

[†] (*o*-Nitrophenyl-*C*¹)(*o*-nitrophenyl-*C*¹O)(triphenylphosphine)-platinum(II).

Supplementary data available: further details of the crystal structure determination have been deposited with the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, whence they may be obtained by quoting the deposition number CSD-51743, the names of the authors, and the journal reference.

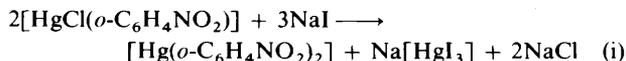
Non-S.I. unit employed: eV $\approx 1.60 \times 10^{-19}$ J.

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

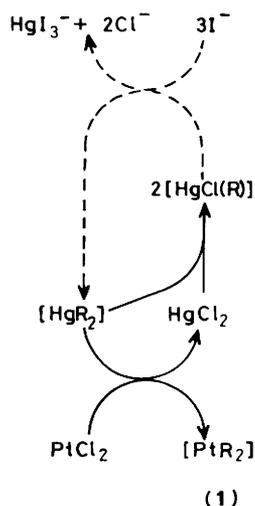
Synthesis.—By refluxing in EtOH a mixture of $\text{K}_2[\text{PtCl}_4]$ or PtCl_2 and $[\text{Hg}(o\text{-C}_6\text{H}_4\text{NO}_2)_2]$ (2–3 h; 1:2) the dark red complex $[\text{Pt}\{\overline{o\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}}\}_2]$ (1) crystallizes in high yield (95%). From the mother-liquor the by-product $[\text{HgCl}(o\text{-C}_6\text{H}_4\text{NO}_2)]$ can be isolated. As this compound symmetrizes¹³ in the presence of NaI (2:3), according to equation (i), complex (1) can be better obtained by reacting $\text{K}_2[\text{PtCl}_4]$ or PtCl_2 with $[\text{Hg}(o\text{-C}_6\text{H}_4\text{NO}_2)_2]$ in the presence of NaI (1:1:3).



$[\text{Hg}(o\text{-C}_6\text{H}_4\text{NO}_2)_2]$ reacts with $\text{K}_2[\text{PtCl}_4]$ (1:1) (in refluxing EtOH; 2 h) to give (1), $[\text{HgCl}(o\text{-C}_6\text{H}_4\text{NO}_2)]$, and unreacted $\text{K}_2[\text{PtCl}_4]$. This is the same behaviour as observed¹ towards $[\text{NMe}_4][\text{AuCl}_4]$, which could mean that monoarylated complexes are not intermediates in these transmetallation reactions. These reactions show that $[\text{HgCl}(o\text{-C}_6\text{H}_4\text{NO}_2)]$ has no arylation capability towards $\text{K}_2[\text{PtCl}_4]$ or $[\text{NMe}_4][\text{AuCl}_4]$. We have also found that it does not arylate PtCl_2 , PtCl_2 and $[\text{HgCl}(o\text{-C}_6\text{H}_4\text{NO}_2)]$ do not react until NaI is added. Scheme 1 shows the probable steps involved in the synthesis of (1) when NaI and PtCl_2 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

between (1) and HgCl_2 (refluxing in acetone or MeOH; 2 h) or between $[\text{Hg}(o\text{-C}_6\text{H}_4\text{NO}_2)_2]$ and $[\text{PtCl}_2(\text{cod})]$ (refluxing in EtOH; 3 h) or $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ (refluxing in EtOH; 3 h) were not observed. In contrast $[\text{Pt}\{(\text{PhCH}=\text{CH})_2\text{CO}\}_2]$ reacts with $[\text{HgCl}(o\text{-C}_6\text{H}_4\text{NO}_2)]$ (1:1, room temperature, acetone, 24 h) or with $o\text{-ClC}_6\text{H}_4\text{NO}_2$ (1:1, refluxing in toluene, 6 h) but the expected product, $[\text{Pt}\{o\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}\}(\mu\text{-Cl})_2]$, 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-

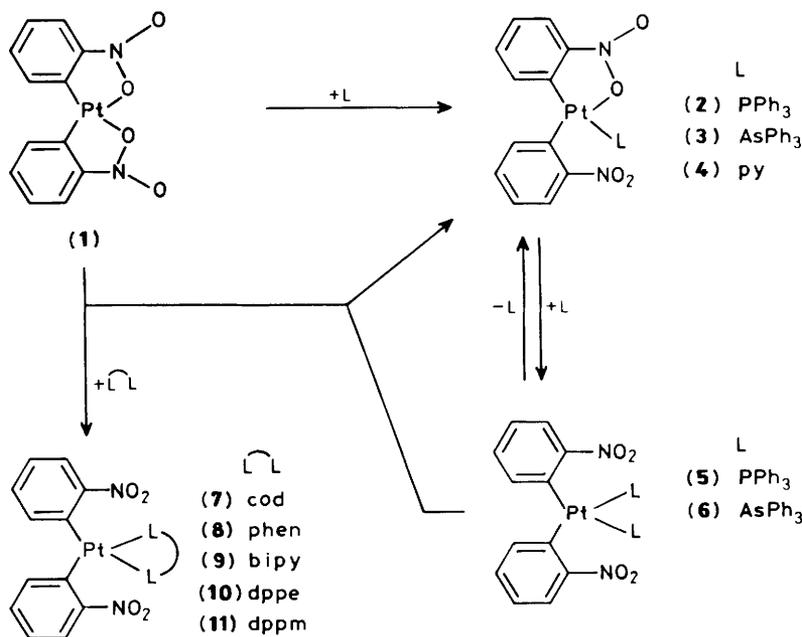


Scheme 1. Probable steps involved in the synthesis of complex (1); R = $o\text{-C}_6\text{H}_4\text{NO}_2$

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) complexes¹⁴ 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 $[\text{Pt}\{o\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}\}(o\text{-C}_6\text{H}_4\text{NO}_2)\text{L}]$ [L = PPh_3 (2), AsPh_3 (3), or pyridine (py) (4)] or yellow complexes $[\text{Pt}(o\text{-C}_6\text{H}_4\text{NO}_2)_2\text{L}_2]$ [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 $[\text{Pt}(o\text{-C}_6\text{H}_5\text{NO}_2)_2\text{L}_2]$ [L₂ = cod (7), 1,10-phenanthroline (phen) (8), 2,2'-bipyridine (bipy) (9), 1,2-bis(diphenylphosphino)ethane (dppe) (10), or bis(diphenylphosphino)methane (dppm) (11)]. As mentioned above, neither (5) nor (7) could be prepared by reacting $[\text{Hg}(o\text{-C}_6\text{H}_4\text{NO}_2)_2]$ with the corresponding $\text{cis-}[\text{PtCl}_2\text{L}_2]$ 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 2. Syntheses and proposed structures of complexes (2)–(11)

Table 1. Analytical and other data for complexes

Complex ^a	M.p. (°C)	Analyses ^b (%)			$\nu(\text{NO}_2)^c/\text{cm}^{-1}$	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 (dppc)]	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*-C₆H₄NO₂. ^b Calculated values in parentheses. ^c See text.

complexes (10) and (11) was established by osmometry in CHCl₃ [*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...Au interaction; the bands assignable to $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ 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 found¹⁵ that the i.r. spectra do not reliably indicate the structural difference between co-ordinated and unco-ordinated nitro groups. In contrast we have reported¹⁰ that in [Rh{*o*-C₆H₄N(O)O}Cl(CO)] $\nu_{\text{asym}}(\text{NO}_2)$ appears at 1 525 and 1 535 cm⁻¹, and $\nu_{\text{sym}}(\text{NO}_2)$ 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 $\nu_{\text{asym}}(\text{NO}_2)$ 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*-C₆H₄N(O)O}{*o*-C₆H₄NO₂}L] [Figure 1(c)] show, as the main difference, a new band at around 1 350 cm⁻¹ that should be assigned to $\nu_{\text{sym}}(\text{NO}_2)$ of the unco-ordinated nitro group.

The i.r. spectra of complexes of formula [Pt(*o*-C₆H₄NO₂)₂-L₂] [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 $\nu_{\text{sym}}(\text{NO}_2)$ of chelated *o*-nitrophenyl ligands occurs in the range 1 250—1 270 cm⁻¹. According to this assignment, the organomercury compounds [Hg(*o*-C₆H₄NO₂)₂] and [HgCl(*o*-C₆H₄NO₂)] 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*-C₆H₄NO₂)₂-L₂].

The product of the reaction between (1) and carbon monoxide in CH₂Cl₂ is *cis*-[Pt(*o*-C₆H₄NO₂)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 described⁵ for *cis*-[Pt(*o*-C₆H₄NO₂)₂-

(PPh₃)₂]. Its ³¹P-¹H} n.m.r. spectrum shows a singlet [15.01 p.p.m. (CDCl₃) relative to H₃PO₄] with ¹⁹⁵Pt satellites [¹J(Pt—P) 2 241 Hz]. The value of ¹J(Pt—P) is similar to that found¹⁶ for ¹J(Pt—P) *trans* to the phenyl group in *cis*-[Pt(Ph)(SnClPh₂)(PPh₃)₂] (2 137 Hz).

The only differences in the i.r. spectra of (1) and of [Hg(*o*-C₆H₄NO₂)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 B₂(y) mode¹⁷ at 464, 460 cm⁻¹ in [Hg(C₆H₅)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 B₂(y) mode band cannot be assigned, because of band(s) at ca. 500 cm⁻¹ from the other ligand.

*Structure of Complex [Pt{*o*-C₆H₄N(O)O}{*o*-C₆H₄NO₂}(PPh₃)₂] (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 $\pi\pi(\text{N})-\pi\pi(\text{C})$ 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 $\pi\pi[\text{O}(2)] \rightarrow d\pi(\text{Pt})$, weakening the $\pi\pi[\text{O}(2)]-\pi\pi[\text{N}(1)]$ 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 data¹⁰ for the complex [Rh{*o*-C₆H₄N(O)O}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

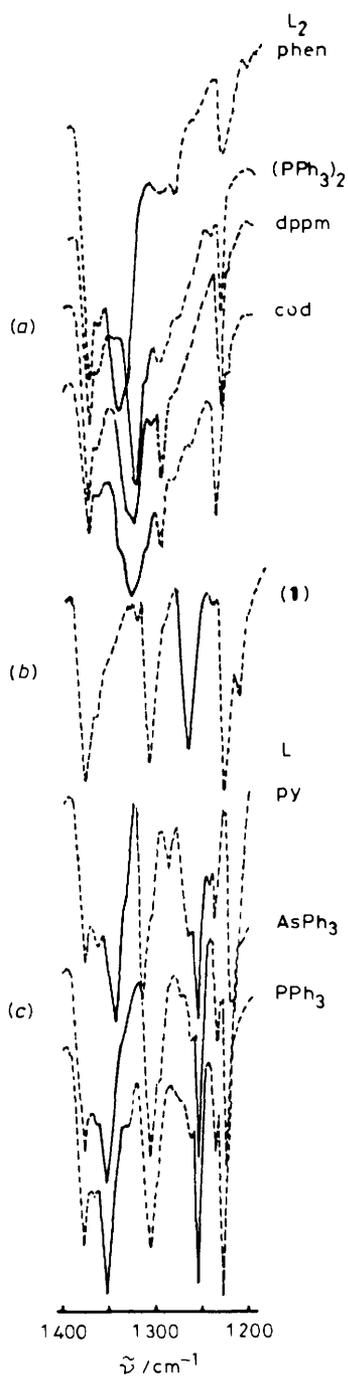


Figure 1. I.r. spectra of some complexes in the 1400–1200 cm^{-1} region. (a) $[\text{Pt}(\text{o-C}_6\text{H}_4\text{NO}_2)_2\text{L}_2]$, (b) $[\text{Pt}\{\text{o-C}_6\text{H}_4\text{N}(\text{O})\text{O}\}_2]$ (1), (c) $\text{Pt}\{\text{o-C}_6\text{H}_4\text{N}(\text{O})\text{O}\}(\text{o-C}_6\text{H}_4\text{NO}_2)\text{L}$. The solid lines are our assignment of $\nu_{\text{asym}}(\text{NO}_2)$ vibrations (see text)

almost planar nitrophenyl groups in $\text{cis-}[\text{Pt}(\text{o-C}_6\text{H}_4\text{NO}_2)_2(\text{PPh}_3)_2]$ 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*-nitrophenyl ligands is responsible for the observed lowering in the

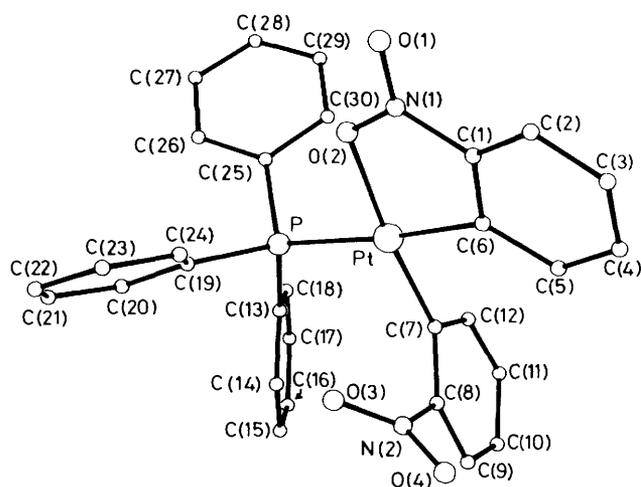


Figure 2. The molecule of (2) in the crystal, showing the atom numbering scheme

$\nu_{\text{sym}}(\text{NO}_2)$ frequency. In contrast, the above mentioned nitrophenolato complexes¹⁵ 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 $\nu(\text{NO}_2)$ frequency.

Experimental

Infrared spectra were recorded in the range 4000–200 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.

$[\text{Pt}\{\text{o-C}_6\text{H}_4\text{N}(\text{O})\text{O}\}_2]$ (1).—To a solution of $\text{K}_2[\text{PtCl}_4]$ (100 mg, 0.24 mmol) in EtOH (25 cm^3 , 80%) solid $[\text{Hg}(\text{o-C}_6\text{H}_4\text{NO}_2)_2]$ 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 ($3 \times 10 \text{ cm}^3$) to give crude (1), a solution of which in CH_2Cl_2 – CH_3CN (20:2 cm^3) was filtered over MgSO_4 and the resulting solution concentrated (3 cm^3). By slow addition of diethyl ether (5 cm^3) and then *n*-hexane (15 cm^3) 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 cm^3) the stoichiometric amount of the ligand was added. After 1 h at room temperature the solution was concentrated (3 cm^3) and *n*-hexane (15 cm^3) added to precipitate the complex, which was washed with *n*-hexane ($3 \times 4 \text{ cm}^3$) 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 cm^3), when the complexes precipitated. After 1 h at room temperature they were filtered off and washed with dichloromethane ($2 \times 5 \text{ cm}^3$).

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)

To prepare complex (4) the general method was followed to prepare $[\text{Pt}(o\text{-C}_6\text{H}_4\text{NO}_2)_2(\text{py})_2]$ 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. $\text{C}_{30}\text{H}_{23}\text{N}_2\text{O}_4\text{PPt}$, $M = 701.6$, monoclinic, space group $P2_1/n$, $a = 8.932(2)$, $b = 19.417(4)$, $c = 15.418(4)$ Å, $\beta = 91.52(2)^\circ$, $U = 2 673$ Å³, Mo- K_α radiation ($\lambda = 0.710 69$ Å), $Z = 4$, $D_c = 1.74$ g cm⁻³, crystal size $0.35 \times 0.15 \times 0.055$ mm, $\mu = 5.4$ mm⁻¹, $F(000) = 1 368$.

Data collection and processing. Stoe-Siemens four-circle diffractometer, 6 262 profile-fitted reflections²¹ ($2\theta_{\text{max}}$, 50° , $-h + k \pm l$), 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 $\pm 2\theta$ 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, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$, 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.

Table 3. Selected bond lengths (Å) and angles ($^\circ$) 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)		

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