

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201**Pt-NO_x Chemistry. Preparation and Structure of
trans-Dinitrobis(tri-*p*-tolylphosphine)platinum(II), Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₃)₂**

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The structure of *trans*-dinitrobis(tri-*p*-tolylphosphine)platinum(II), Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₃)₂, has been determined from three-dimensional x-ray data. The compound was isolated while attempting to grow crystals of Pt(N₂O₂)(P(*p*-C₆H₄CH₃)₃)₂. The complex crystallizes in the space group C_{2h}⁵-P2₁/n with two molecules in a unit cell of dimensions *a* = 11.585 (6) Å, *b* = 18.387 (9) Å, *c* = 10.697 (9) Å, and β = 119.30 (4)°. Least-squares refinement of the 106 variables has led to a value of the conventional *R* index (on *F*) of 0.043 for the 4735 independent reflections having *F*_o² > 3σ(*F*_o²). The complex is a typical square-planar Pt(II) complex. The Pt atom occupies a crystallographic center of symmetry. Important structural parameters include: Pt-P = 2.337 (1) Å, Pt-N = 2.030 (5) Å, N-O(1) = 1.228 (8) Å, N-O(2) = 1.198 (7) Å, N-Pt-P = 88.4 (1)°, N-Pt-P' = 91.6 (1)°, O(1)-N-O(2) = 121.7 (6)°, Pt-N-O(1) = 118.9 (5)°, Pt-N-O(2) = 119.4 (5)°. The angle between the plane of the nitro ligand and the coordination plane is 75°. The structural results provide no evidence of Pt(II)-NO₂ π bonding. Several reactions of Pt(N₂O₂)(PPh₃)₂ and Pt(0) complexes with nitrogen oxides are described, and the production of *trans*-Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₃)₂ from Pt(N₂O₂)(P(*p*-C₆H₄CH₃)₃)₂ is rationalized.

Introduction

In our previous studies of the catalysis of reaction 1 by

$$2\text{NO} + \cdot\text{CO} \rightarrow \text{N}_2\text{O} + \text{CO}_2 \quad (1)$$

complexes of the form M(NO)₂L₂ (M = Co⁺, Rh⁺, Ir⁺, Ru, Os; L = PR₃)^{1,2} we have noted a possible correlation between the solid-state structures of the dinitrosyl complexes and the activity of their solutions in *N,N*-dimethylformamide (DMF) as catalysts for reaction 1. The larger the N-M-N angle and the smaller the M-N-O angle, the more active the catalyst solution. We attribute the bending of these nearly linear nitrosyl groups to an increase of the NO⁻ character of the nitrosyl ligand, indicating increased electron density at the metal atom. Thus, the most electron-rich complexes produce the most active catalyst solutions. This led us to predict that a similar, more electron-rich complex should be the precursor to a better catalyst solution. On intuitive grounds, Pt(Ptol₃)₃ (tol = *p*-C₆H₄CH₃) should be more electron rich than the dinitrosyl complexes. As this complex was at hand, we examined the activity of a solution of Pt(Ptol₃)₃ in DMF as a catalyst for reaction 1 and found that the rate of reaction was about 27 times faster than that produced by our previous best catalyst, a solution of [Rh(NO)₂(PPh₃)₂][PF₆] in DMF.³

A complex of the stoichiometry Pt(NO)₂(PPh₃)₂ is known.⁴ If this were a dinitrosyl complex, it would be formally a "20-electron" complex; unusual chemistry might then be expected. In fact, the infrared spectrum indicates that the complex is a Pt(II) complex of the N₂O₂²⁻ ion. Such a complex might provide a structural model for the "dinitrogen dioxide" complex we had proposed originally as an intermediate in the catalysis of reaction 1 by dinitrosyl complexes.⁵

We therefore synthesized the complex Pt(N₂O₂)(Ptol₃)₂ (in the hope that the increased solubility as compared with Pt(N₂O₂)(PPh₃)₂ would facilitate crystallization), grew crystals, and accomplished the structure determination reported here. The data crystal was shown to be of *trans*-Pt(NO₂)₂(Ptol₃)₂. This structure, together with some chemistry which evolved in our attempts to rationalize the production of nitro ligands and the isomerization from *cis* to *trans* phosphine ligands, is described here.

Experimental Section

Specific conditions are included in the descriptions of the individual reactions. Infrared spectra were taken on a Perkin-Elmer 727B spectrometer. Analyses are by H. Beck of the Analytical Services Laboratory of Northwestern University.

Attempted Reaction of Pt(N₂O₂)(PPh₃)₂ and NO. Pt(PPh₃)₄⁶ (0.50 g) was dissolved in 40 mL of N₂-saturated benzene at room tem-

perature. Nitric oxide was bubbled through this solution. The nitric oxide had been passed through traps of H₂SO₄ and KOH (which, in our experience, produces cleaner NO than passing the commercial product through a -78 °C trap). The lemon yellow precipitate of Pt(N₂O₂)(PPh₃)₂⁴ appeared in a few minutes, and the suspension remained unchanged after 90 min of bubbling NO through it. Nitrogen was then bubbled through the suspension for 10 min. The lemon yellow product was filtered, washed with benzene, and dried *in vacuo*. Bands in the infrared spectrum at 1284, 1232, and 1066 cm⁻¹ (Nujol mull) indicate that the Pt(N₂O₂)(PPh₃)₂ produced initially remained unchanged (bands at 1285, 1240, and 1062 cm⁻¹). The N₂O₂ complex is air sensitive and decomposes to an insoluble yellow-orange solid after a few days, even when stored under Ar.

Reaction of Pt(N₂O₂)(PPh₃)₂ and O₂. To a slurry of Pt(N₂O₂)(PPh₃)₂ (0.25 g, 0.32 mmol) in 20 mL of Ar-saturated CH₂Cl₂, 39 mL of air (containing 0.32 mmol of O₂) was added. The pressure in the system dropped, and a clear yellow solution formed at room temperature in about 45 min. The infrared spectrum of the gas above the solution exhibited strong bands at 2230 and 2212 cm⁻¹, indicating the presence of substantial amounts of N₂O. After removing the solvent under vacuum and redissolving the residue in 3 mL of CH₂Cl₂, we added a large excess of Et₂O to produce a tan precipitate. After filtering and drying *in vacuo*, we chromatographed the solid on silica (CH₂Cl₂ eluent). A deep orange band moved with the solvent front, and a large fraction of the material remained on the column. The orange crystalline solid obtained when the solvent was evaporated from the fraction that moved with the solvent front exhibited bands in its infrared spectrum at 1704 and 1660 cm⁻¹ (Nujol mull) and a number of bands in the region around 1450 cm⁻¹ (Beckman fluorocarbon mull). More complete characterization of this material is underway.

Reaction of Pt(N₂O₂)(PPh₃)₂ and NO₂ in CHCl₃. A slurry of Pt(N₂O₂)(PPh₃)₂ (0.18 g) and 15 mL of N₂-saturated CHCl₃ at room temperature was made in a 100-mL Schlenk flask. The flask was evacuated and filled with NO₂. The solid dissolved to produce an orange solution, with effervescence as the color of the NO₂ disappeared. Infrared spectroscopy of the gas above the solution indicated the production of about 1 mol of N₂O/mol of Pt. Most of the solvent was removed and a large quantity of hexane added. The yellow precipitate formed was filtered, washed with hexane, and dried in air. The infrared spectrum of this solid (Nujol mull) exhibited strong bands at 1275, 1265, and 979 cm⁻¹, indicating the presence of O-bound NO₃⁻. When a solution of AgNO₃ in DMF was added to a solution of the product in DMF, a precipitate of AgCl was produced. The product thus is likely to be PtCl(NO₃)(PPh₃)₂. Anal. Calcd for C₃₆H₃₀ClNO₃Pt: C, 52.9; H, 3.7; N, 1.7. Found: C, 48.3; H, 3.3; N, 1.8.

Reaction of Pt(N₂O₂)(PPh₃)₂ and NO₂ in Benzene. Pt(N₂O₂)(PPh₃)₂ (0.21 g) was dissolved in 40 mL of Ar-saturated benzene in a 100-mL Schlenk flask. The flask was evacuated and filled with NO₂. The brown color of the NO₂ disappeared, and a tan precipitate and orange solution were produced. This procedure was repeated several times. The tan precipitate was filtered in air, washed with benzene and Et₂O, and dried *in vacuo*. The infrared spectrum of the

Table I. Positional and Thermal Parameters for the Nongroup Atoms of *trans*-Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₃)₂

ATOM	X ^A	Y	Z	B ₁₁ ^B	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
PT	0	0	0	74.34(28)	16.23(7)	70.44(31)	-3.60(14)	30.36(22)	-1.61(16)
P	0.11473(14)	-0.102934(75)	-0.00751(15)	81.2(13)	17.70(34)	72.5(14)	-0.08(58)	34.4(11)	1.66(62)
N	0.12782(61)	0.00644(26)	0.21379(57)	101.4(54)	27.0(18)	67.6(48)	8.3(25)	24.7(41)	-5.4(26)
O(1)	0.11754(56)	-0.03755(32)	0.29418(54)	156.5(71)	40.0(21)	96.2(60)	6.9(32)	62.2(56)	5.9(30)
O(2)	0.21303(53)	0.05173(30)	0.25787(61)	135.5(66)	35.2(19)	145.5(79)	-20.6(29)	10.5(58)	-14.8(31)
C(217)	0.71655(67)	-0.07406(49)	0.36195(93)	93.1(68)	52.5(34)	181.1(13)	-6.7(39)	33.5(74)	-2.4(53)
C(227)	0.0053(10)	-0.18748(58)	-0.60992(90)	195.1(14)	75.3(48)	123.1(10)	-10.0(66)	87.1(10)	-51.4(61)
C(237)	-0.07580(94)	-0.37648(42)	0.1596(11)	250.1(14)	28.8(25)	253.1(18)	-17.3(45)	134.1(14)	32.3(53)

^A ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. ^B THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $\text{EXP}[-(B_{11}H^2 + B_{22}K^2 + B_{33}L^2 + 2B_{12}HK + 2B_{13}HL + 2B_{23}KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^4$.

precipitate (Nujol mull) exhibited strong bands at 1501, 1492, 1280, 1269, and 974 cm⁻¹. The reported infrared spectrum of *cis*-Pt(NO₃)₂(PPh₃)₂⁷ exhibits bands at 1501, 1491, 1272, 1263, and 974 cm⁻¹. The solid produced here melts at 210 °C (in air, uncorrected). The literature value for the melting point of *cis*-Pt(NO₃)₂(PPh₃)₂ is 223–227 °C.⁸ Thin-layer chromatography of the product on silica (CH₂Cl₂ eluent) revealed it to be a mixture. Thus, *cis*-Pt(NO₃)₂(PPh₃)₂ was the principal product of the reaction.

Reaction of Pt(PPh₃)₄ and N₂O₃. Pt(PPh₃)₄⁴ (0.46 g) was placed in a Schlenk flask, cooled in a dry ice bath. Nitric oxide directly from the tank was passed through this flask for about 1 h. A substantial amount of the blue liquid N₂O₃ was produced during this time. While the flask was kept at -78 °C, 20 mL of Ar-saturated toluene was added. The flask was allowed to warm to room temperature, and the contents were filtered under Ar. The pale yellow solid was dried in vacuo while the green solution was discarded. This solid is very air sensitive. The infrared spectrum of the decomposed product contains bands characteristic of both coordinated NO₂⁻ and NO₃⁻. A white solid, only slightly soluble in CH₂Cl₂, can be isolated, whose infrared spectrum (Nujol and Beckman fluorocarbon mulls) exhibits prominent bands at 1482, 1435, 1412, 1337, and 823 cm⁻¹. These bands are identical with those of *cis*-Pt(NO₂)₂(PPh₃)₂,⁹ as is the rest of the spectrum.

Conversion of *cis*-Pt(NO₂)₂(PPh₃)₂ into *trans*-Pt(NO₂)₂(PPh₃)₂. *cis*-Pt(NO₂)₂(PPh₃)₂⁹ (0.15 g) was dissolved in 10 mL of DMF together with a catalytic amount of PPh₃. After refluxing for 20 min, the colorless solution turned yellow. The yellow solid isolated by removing the solvent was shown to be *trans*-Pt(NO₂)₂(PPh₃)₂ on the basis of its infrared spectrum and analogy with the known isomerization reactions of PtCl₂(PPh₃)₂.¹⁰

***trans*-Pt(NO₂)₂(Ptol₃)₂.** Pt(Ptol₃)₃ (0.46 g) was dissolved in 30 mL of Ar-saturated toluene. Nitric oxide was bubbled through the yellow-orange solution (after passing through a -78 °C trap) for about 10 min. Through the lighter yellow solution produced, Ar was bubbled for about 15 min. (The Pt(N₂O₂)(Ptol₃)₂ produced can be isolated here by precipitation with cyclohexane.) Nitrogen-saturated cyclohexane was allowed to diffuse slowly into this solution. Over the course of 4 months, two large, fragile, light yellow crystals formed, along with a quantity of light yellow powder. A fragment of one of the two crystals, of approximate dimensions 0.30 × 0.85 × 1.25 mm, was mounted in a glass capillary. On the basis of x-ray measurements we established that the crystal belongs to the monoclinic system and that the principal faces of this fragment can be described by the planes (110), (230), (111), (150), (120), (231), (101), (371), and (271). Weissenberg photography taken with Cu Kα radiation indicated that the space group is C_{2h}⁵-P2₁/n. The lattice constants at 22 °C, determined¹¹ from the setting angles of 11 strong reflections which had been centered manually on a Picker FACS-I diffractometer using Mo Kα radiation (λ 0.709 300 Å), are a = 11.585 (6) Å, b = 18.387 (9) Å, c = 10.697 (9) Å, and β = 119.30 (4)°. With two formula units per unit cell, the calculated density is 1.53 g cm⁻³, a reasonable value for a complex of this type.

For data collection Mo Kα radiation was used, prefiltered by a 2-mil Zr foil. The intensities were measured at a takeoff angle of 3.0°. At this angle the intensity of a reflection was about 90% of its maximum value. A receiving counter aperture 4.5 mm wide and 4 mm high was positioned 35 cm from the crystal. Symmetric scans in 2θ, 1.2° below the Kα₁ peak to 1.2° above the Kα₂ peak, were used. Stationary-counter, stationary-crystal background counts of 10 s were

measured at the beginning and end of each scan. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts s⁻¹.

The data set having $k \geq 0$, $l \geq 0$, and $2\theta \leq 64^\circ$ was gathered; the intensities of 7836 reflections were recorded. The intensities of the four standard reflections remained constant within counting statistics.

All data processing was carried out as previously described.¹¹ The value of p was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. The 4735 unique reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. The linear absorption coefficient, μ , for this dinitro compound using Mo Kα radiation is 36.8 cm⁻¹. An absorption correction was made,¹² and transmission coefficients ranged from 0.098 to 0.325.

The structure of Pt(N₂O₂)(Ptol₃)₂ cannot be an ordered one with two formula units in space group P2₁/n. In order to determine unambiguously the identity of the compound that actually had crystallized, we proceeded with the structure determination. The Pt atom was fixed at the origin. A least-squares refinement on F was computed. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, in which $w = 4F_o^2/\sigma^2(F_o^2)$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. Values of the atomic scattering factors and anomalous terms were taken from the usual source.¹³ Only the overall scale factor and the isotropic thermal parameter of the Pt atom were varied. This refinement led to the agreement indices $R = 0.32$ and $R_w = 0.39$, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum F_o^2)^{1/2}$. A difference Fourier map computed on the basis of this model revealed trans phosphorus atoms. Successive difference Fourier maps revealed all three independent tolyl groups and provided evidence that the two other positions of the coordination sphere of the Pt atom were occupied by trans NO₂ ligands. The Pt, P, N, O, and methyl C atoms were refined anisotropically; the phenyl rings were treated as rigid groups¹⁴ and restricted to their known geometry (6/*mmm* symmetry, $d(\text{C}-\text{C}) = 1.392$ Å). Each ring carbon atom was assigned an individual isotropic thermal parameter. All hydrogen atoms were located and were included in later structure factor calculations in calculated idealized positions ($d(\text{C}-\text{H}) = 0.95$ Å) which were not refined.

The final refinement of 106 variables using 4735 observations resulted in the values $R = 0.043$ and $R_w = 0.067$. A structure factor calculation for the 2280 reflections omitted from the refinements because $F_o^2 < 3\sigma(F_o^2)$ revealed that $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$ for 34 of them. Agreement of $|F_o|$ and $|F_c|$ is poorest for the weakest reflections and for those in the general direction of [011]. We attribute this to difficulty in describing the shape of one end of the crystal correctly, as it is a fragment of a larger one. Errors in the absorption correction are thus a likely source of this poor agreement. Slight errors in the optical centering of the large irregularly shaped crystal could also account for these trends. The largest peak in the final difference Fourier map is 2.8 e Å⁻³, near the Pt atom. The error in an observation of unit weight is 2.48 electrons. When it became clear that the data crystal was not of the hoped-for Pt(N₂O₂) complex, the second crystal was "sacrificed" for an infrared spectrum. Bands consistent with the formulation as *trans*-Pt(NO₂)₂(Ptol₃)₂ were found.

The positional, thermal, and group parameters derived from the last cycle of least-squares refinement are given in Table I, along with the standard deviations as estimated from the inverse matrix. The positional parameters of the ring carbon atoms which may be derived from the data in Table I are presented in Table II, together with their thermal parameters. The final values of $10|F_o|$ and $10|F_c|$ in electrons

Table II. Derived Parameters for the Rigid Group Atoms of *trans*-Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₃)₂

ATOM	X	Y	Z	B _i A ²	ATOM	X	Y	Z	B _i A ²
C(211)	0.29436(26)	-0.09565(23)	0.09966(37)	3.25(9)	C(224)	0.03750(48)	-0.16799(24)	-0.45749(39)	4.57(13)
C(212)	0.35438(35)	-0.09950(24)	0.24846(39)	4.09(11)	C(225)	0.03255(53)	-0.22055(17)	-0.36652(53)	5.79(19)
C(213)	0.49098(37)	-0.09178(26)	0.33147(30)	4.28(13)	C(226)	0.05500(48)	-0.20102(19)	-0.23070(47)	4.80(14)
C(214)	0.56756(27)	-0.08022(26)	0.26568(41)	4.14(12)	C(231)	0.06765(36)	-0.18174(18)	0.05860(46)	3.04(9)
C(215)	0.50754(35)	-0.07636(25)	0.11688(43)	4.50(13)	C(232)	-0.06534(33)	-0.18770(20)	0.02070(48)	3.87(11)
C(216)	0.37095(36)	-0.08408(24)	0.03387(30)	3.92(11)	C(233)	-0.11170(29)	-0.25084(23)	0.05365(50)	4.68(13)
C(221)	0.08239(39)	-0.12893(22)	-0.18586(34)	3.28(9)	C(234)	-0.02506(41)	-0.30801(19)	0.12329(51)	4.21(12)
C(222)	0.08734(39)	-0.07637(16)	-0.27683(41)	3.43(10)	C(235)	0.10792(38)	-0.30205(19)	0.16119(49)	4.45(13)
C(223)	0.06489(41)	-0.09590(21)	-0.41265(39)	3.72(10)	C(236)	0.15428(28)	-0.23891(22)	0.12885(46)	4.10(11)

RIGID GROUP PARAMETERS

GROUP	X _C ^A	Y _C	Z _C	DELTA ^B	EPSILON	ETA
R(21)	0.43096(26)	-0.08793(14)	0.18267(30)	1.6732(26)	-3.2232(21)	-1.4607(27)
R(22)	0.05994(26)	-0.14846(16)	-0.32167(33)	-0.5633(84)	-1.8609(23)	-1.9745(82)
R(23)	0.02129(27)	-0.24488(16)	0.09095(31)	-0.3835(23)	2.6889(27)	-3.1823(29)

^AX_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^BTHE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIAN) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

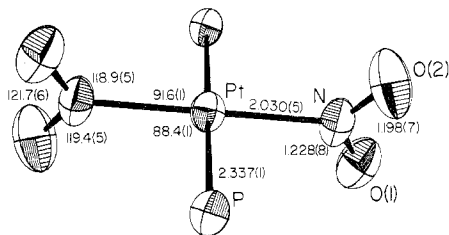


Figure 1. A perspective view of the coordination sphere of *trans*-Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₃)₂. The platinum atom occupies a crystallographic center of symmetry. The shapes of the atoms in this and the following drawings represent 50% contours of thermal motion.

are given in Table III.¹⁵ Table IV presents the root-mean-square amplitudes of vibration.¹⁵ The calculated idealized positions of the hydrogen atoms are given in Table V.¹⁵

Description of the Structure

The data crystal, grown from a sample of Pt(N₂O₂)(Ptol₃)₂, consists of discrete, neutral molecules of *trans*-Pt(NO₂)₂(Ptol₃)₂. Each molecule has a crystallographically imposed center of symmetry. The geometry of the coordination sphere is shown in Figure 1, a stereoview of the complete molecule is presented in Figure 2, and a packing diagram is presented in Figure 3. A selection of distances and angles is given in Table VI.

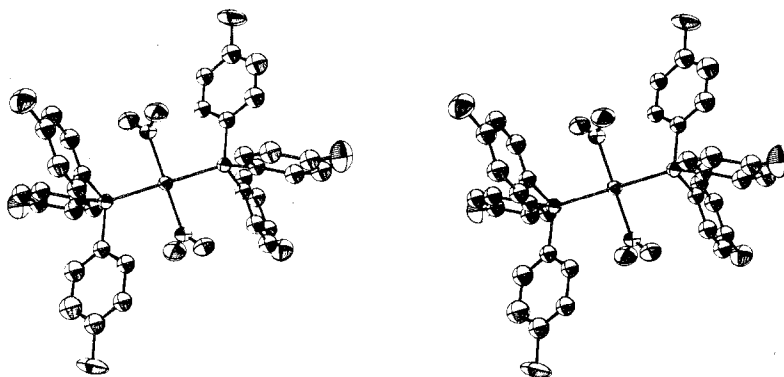


Figure 2. A stereoview of the complete molecule. The view is approximately down [110]. Hydrogen atoms are omitted for clarity.

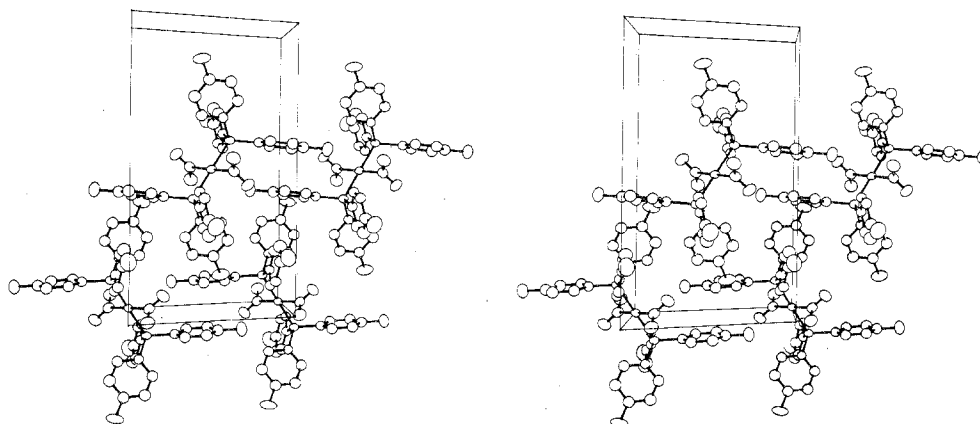


Figure 3. A stereodrawing illustrating the packing in *trans*-Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₃)₂. The view is approximately down the z axis, with the y axis going from bottom to top and the x axis from left to right. The contents of two unit cells are illustrated. Hydrogen atoms are omitted.

Table VI. Distances and Angles in *trans*-Pt(NO₂)₂(P(*p*-C₆H₄CH₃)₂)₂^a

Intramolecular Distances, Å			
Pt-P	2.337 (1)	P-C(221)	1.819 (4)
Pt-N	2.030 (5)	P-C(231)	1.810 (5)
N-O(1)	1.228 (8)	C(214)-C(217)	1.521 (7)
N-O(2)	1.198 (7)	C(224)-C(227)	1.527 (11)
P-C(211)	1.824 (3)	C(234)-C(237)	1.518 (11)
Angles, Deg			
N-Pt-P	88.4 (1)	Pt-P-C(211)	114.3 (1)
N-Pt-P'	91.6 (1)	Pt-P-C(221)	114.8 (1)
O(1)-N-O(2)	121.7 (6)	Pt-P-C(231)	110.5 (2)
Pt-N-O(1)	118.9 (5)	C(211)-P-C(221)	105.3 (2)
Pt-N-O(2)	119.4 (5)	C(211)-P-C(231)	106.4 (2)
		C(221)-P-C(231)	104.6 (2)
Intramolecular Nonbonded Contacts, Å ^b			
Pt-O(1)	2.835 (6)	N-H(212)	2.71
Pt-O(2)	2.818 (6)	O(1)-O(2)	2.119 (8)
Pt-H(232)	2.98	O(1)-H(212)	2.41
Pt-H(222)	3.41	O(2)-H(235)	2.22
Intermolecular Contacts, Å ^b			
C(215)-H(225)	2.72	H(233)-H2(227)	2.16
C(235)-H(213)	2.77	H2(217)-H1(227)	2.38

^a In the labels of the carbon atoms C(2xy), x denotes the number of the tolyl group to which the carbon atom belongs, and y designates the position of the atom in the phenyl ring, with y = 7 denoting the methyl carbon atom. ^b In the calculation of these distances, the hydrogen atoms were placed in calculated idealized positions with d(C-H) = 1.08 Å. The methyl hydrogen positions were obtained by a least-squares fit of an idealized methyl group to the observed methyl hydrogen positions.

The molecules are separated by van der Waals contacts, and this is reflected in the fragility of the crystals and the absence of good cleavage planes. The packing is an efficient one, as evidenced by the several examples of "graphitic" packing of phenyl rings. The efficient packing undoubtedly is reflected by relatively low solubility, resulting in the isolation of this particular compound from the starting material.

The complex is a typical square-planar Pt(II) complex. The Pt-P bond length of 2.337 (1) Å is unexceptional, as are the P-C and C(phenyl)-C(methyl) distances. The tolyl groups show no signs of distortion as a result of packing forces. The coordination geometries of the carbon atoms in the 1 and 4 positions of the phenyl rings do not differ significantly from planar. There is no tendency to fill vacant coordination sites, as the closest calculated Pt-H contacts are 2.98 and 3.41 Å. The deviations of the angles in the coordination sphere from the ideal square-planar values are small and unimportant.

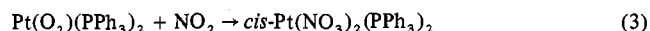
The geometry of the nitro ligand is likewise unremarkable. The Pt-N distance of 2.030 (5) Å is solidly in the middle of the range of observed Pt(II)-N distances. The ligand geometry at first glance seems to differ from that of the nitrite ion in NaNO₂¹⁶ (N-O = 1.240 (3) Å, O-N-O = 114.9 (5)°, determined by neutron diffraction), but if the oxygen atoms are assumed to ride on the nitrogen atom the observed distances of 1.228 (8) and 1.198 (7) Å increase to 1.25 and 1.24 Å. It seems clear that the geometry of the coordinated nitrite ion observed here does not differ greatly from the free nitrite ion. The plane of the nitro ligand makes an angle of 75° with the coordination plane. The Pt-NO₂ group is nearly planar; the distance of the Pt atom from the plane of the nitro ligand is 0.05 Å. Examination of the nonbonded contacts listed in Table VI suggests that the observed angle between the plane of the nitro ligand and the coordination plane is in part a result of steric effects.

There is a dearth of recent reports of structures containing the Pt(II)-NO₂ linkage; a comparison can be made between the present structure and that of *trans*-Pt(NO₂)₂(PEt₃)₂.¹⁷ The Pt-P distances are equal within experimental error (2.337 (1) Å here, and 2.32 (1) and 2.30 (1) Å in *trans*-Pt(NO₂)₂-

(PEt₃)₂). At first glance the Pt-N distances seem to be longer in the triethylphosphine complex (2.11 (2) and 2.09 (2) Å vs. 2.030 (5) Å here), but the large errors of these values make detailed comparisons between these two structures risky. The N-O distances in the triethylphosphine structure (1.42 (4), 1.39 (4), 1.41 (4), and 1.40 (4) Å) are probably actually longer than the distances in this structure (1.228 (8) and 1.198 (7) Å). Graziani et al.¹⁷ conclude that this apparent lengthening of the N-O bonds is a reflection of dπ → π* charge transfer, lowering the formal N-O bond order. This conclusion is in agreement with arguments made on the basis of spectroscopic data by Burmeister and Timmer.⁹ We find little evidence for such bond lengthening relative to the values of the free nitrite ion in this structure and therefore conclude that any arguments for the presence of π bonding between the Pt atom and the nitro ligand are best not based on structural data.

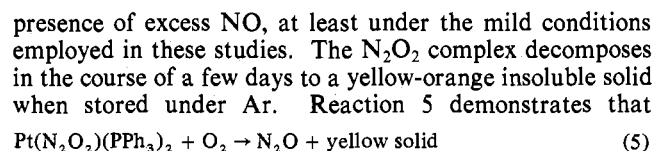
Discussion

It is clearly of interest to rationalize the production of the title complex from the starting material, Pt(N₂O₂)(PtO₃)₂. The known reactions eq 2¹⁸ and 3⁷ indicate that *cis*-Pt(O₂)(PPh₃)₂ + NO → *cis*-Pt(NO₂)₂(PPh₃)₂ (2)



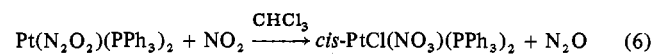
(NO₂)₂L₂ and Pt(NO₃)₂L₂ complexes might be expected products from systems in which Pt, PR₃, and NO_x are present. We carried out reactions 4-9 in attempts to gain a feeling for what sorts of reactions might take place in such systems. We hoped to rationalize the production of the *trans* dinitro complex from Pt(N₂O₂)L₂ by considering the effects that possible contaminants (as O₂, NO, and excess PR₃) might have on this complex.

Reaction 4 indicates that Pt(N₂O₂)L₂ is stable in the presence of excess NO, at least under the mild conditions employed in these studies. The N₂O₂ complex decomposes in the course of a few days to a yellow-orange insoluble solid when stored under Ar. Reaction 5 demonstrates that

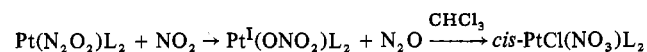


Pt(N₂O₂)L₂ is sensitive to oxygen, products of the reaction being N₂O and a complex mixture of Pt-containing species. The production of N₂O is of interest and seems to be a common reaction of group 8 nitrosyl-phosphine complexes.

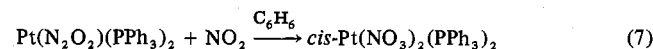
If both excess NO and traces of O₂ were present in a system, NO₂ would also be present. It therefore seemed reasonable to investigate the reaction of this molecule with Pt(N₂O₂)(PPh₃)₂. When the reaction (eq 6) is carried out in CHCl₃,



a high yield of PtCl(NO₃)(PPh₃)₂ (presumably the *cis* isomer, by analogy with reaction 7) is produced, along with an equimolar quantity of N₂O. A reasonable route for this reaction can be postulated

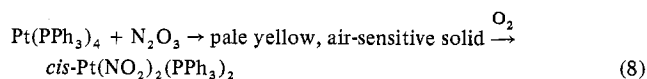


By a redox process, an unstable Pt(I) intermediate can be produced, which would immediately abstract a Cl atom from CHCl₃ to produce the observed Pt(II) chloride complex. Kinetic studies of this reaction might be of interest. The reaction (eq 7) of Pt(N₂O₂)(PPh₃)₂ with NO₂ was then carried

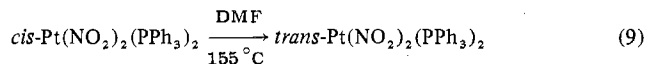


out in a more innocent solvent. Benzene was chosen, and in this case *cis*-Pt(NO₃)₂(PPh₃)₂ was observed as the major product. A pathway similar to that in CHCl₃ can be imagined.

The reaction (eq 8) of a Pt(0) complex with the blue liquid



produced from NO and NO₂ at -78 °C and described as N₂O₃ might possibly be relevant to the production of the trans dinitro complex from Pt(N₂O₂)L₂. When the reaction is carried out, an air-sensitive and as yet uncharacterized pale yellow solid is produced. Exposure of this solid to air results in a mixture of products, one of which is cis-Pt(NO₂)₂L₂. We observe that this complex seems to be a common product in reactions involving compounds of the type discussed here, leading us to conclude that it might be a likely intermediate in the production of trans-Pt(NO₂)₂L₂ from Pt(N₂O₂)L₂. In complexes of the type PtX₂L₂ (X = halide ion), the trans isomer is generally found to be more stable than the cis isomer in solution.¹⁰ The conversion cis → trans is, however, an endothermic process; the greater stability of the trans isomer appears to be a result of entropy effects in the solvation shell. The conversion is catalyzed by excess PR₃,¹⁰ which is present in the system from which the title compound was isolated. The conversion can be carried out for the dinitro complexes, as illustrated by reaction 9. It therefore seems that a reasonable



path to account for the production of the observed product is Pt(N₂O₂)L₂ + O₂ → cis-Pt(NO₂)₂L₂ → trans-Pt(NO₂)₂L₂

The production of the cis dinitro complex is favored kinetically (O₂ is the most likely contaminant to be found in the system), and over the time period involved and in the presence of a known catalyst it seems reasonable that the thermodynamically more stable trans isomer would be produced in solution. This isomer packs very efficiently in the solid state, indicating that, once formed, it would tend to crystallize preferentially. While this path is speculative, it seems reasonable. Our studies of Pt-NO_x systems have led us to observe several mechanistically interesting reactions which deserve to be investigated further.

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Note Added in Proof. Sheldrick et al. (*J. Chem. Soc., Chem. Commun.*, 354 (1977)) have successfully crystallized Pt-(N₂O₂)(PPh₃)₂ and determined its structure. The compound is a Pt(II) complex of the cis hyponitrite ligand, which is bound to the Pt atom through O atoms. This makes the production of the present title compound from Pt(N₂O₂)(Ptol₃)₂ even more surprising, as several rearrangements must take place.

Registry No. Pt(N₂O₂)(PPh₃)₂, 36669-44-0; Pt(PPh₃)₄, 14221-02-4; Pt(Ptol₃)₃, 33937-28-9; trans-Pt(NO₂)₂(PPh₃)₂, 64024-02-8; trans-Pt(NO₂)₂(Ptol₃)₂, 63977-19-5; PtCl(NO₃)(PPh₃)₂, 64024-03-9; N₂O₃, 10544-73-7; cis-Pt(NO₂)₂(PPh₃)₂, 14409-51-9; NO₂, 10102-44-0; NO, 10102-43-9; cis-Pt(NO₃)₂(PPh₃)₂, 17611-57-3.

Supplementary Material Available: Table III, the list of structure amplitudes, Table IV, the root-mean-square amplitudes of vibration, and Table V, the idealized positions of the hydrogen atoms (35 pages). Ordering information is given on any current masthead page.

References and Notes

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