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(Tetraazabutadiene)platinum Complexes. X-ray Crystal and Molecular Structure of the Triethylphosphine Nucleophilic Addition Product $[Pt(1,4\text{-}(4\text{-}NO_2C_6H_4)_2N_4)(\overline{CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2})(PEt_3)]$, a Novel Five-Coordinate Blue Mononuclear Platinum Species

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(Tetraazabutadiene)platinum complexes $[Pt(Ar_2N_4)L_2]$ have been prepared by reacting bis(1,5-cyclooctadiene)platinum or $[Pt_3(t\text{-BuNC})_6]$ with aryl azides (Ar = 4-MeC_6H_4, 4-ClC_6H_4, and $4\text{-NO}_2C_6H_4$). $[Pt(Ar_2N_4)(COD)]$ reacts with ligands L (L = *t*-BuNC or PEt_3) to yield $[Pt(Ar_2N_4)L_2]$ complexes. Spectroscopic measurements indicate these compounds do contain divalent platinum. For Ar = $4\text{-NO}_2C_6H_4$, $[Pt(Ar_2N_4)(COD)]$ reacts with PEt_3 by nucleophilic attack on the coordinated COD ligand to yield the intensely blue five-coordinate platinum(II) complex $[Pt(1,4\text{-}(4\text{-}NO_2C_6H_4)_2N_4)(\overline{CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2})(PEt_3)]$, of which the structure has been determined by a single-crystal X-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 12.824$ (4) Å, $b = 13.392$ (4) Å, $c = 23.963$ (11) Å, and $\beta = 102.97$ (3)°. The final R value is 0.044 for 6919 reflections. The 2-(triethylphosphino)-cyclooct-5-enyl ring is bonded to the platinum atom by an η^2 olefinic bond (C=C = 1.49 (1) Å) and a σ bond (C—Pt = 2.079 (6) Å), the vicinal P–C and C–Pt bonds being mutually trans. This ligand spans equatorial–axial sites in the trigonal-bipyramidal array around the platinum atom. The other axial site is occupied by a neutral PEt_3 ligand (P–Pt = 2.376 (2) Å). The two remaining equatorial sites are taken up by a σ,σ-N,N′ chelate bonded tetraazabutadiene ligand which shows the structural features of the dianionic form, i.e., a short N^β–N^β (1.263 (8) Å) and two longer N^α–N^β distances (1.391 (7) and 1.385 (7) Å). Furthermore both aryl rings and the PtN_4 chelate are coplanar as a result of additional mesomeric resonance forms involving the NO_2 substituents. The intense blue color of this complex ($\epsilon = 5.2 \times 10^4$ at 605 nm) presumably arises from extensive charge transfer in the C–Pt–Ar_2N_4 moiety. ^{31}P NMR data show the large trans influence of the σ-bonded enyl on the axial PEt_3 ligand ($^1J(^{195}Pt\text{–}^{31}P) = 1501$ Hz) and the phosphonium character of the triethylphosphino entity attached to the cyclooct-5-enyl ring ($\delta(^{31}P) = 39.0$ ppm).

Introduction

In a recent paper we reported that reactions of $[Ni(COD)_2]$ with nonactivated aryl azides lead to the formation of $[Ni(Ar_2N_4)_2]$ complexes,[2a] while an aryl azide with strongly electron-withdrawing substituents is known to provide a $[Ni(Ar_2N_4)(COD)]$ complex.[2b] The latter type of complex is a likely intermediate in the formation of $[Ni(Ar_2N_4)_2]$. From the reaction of $[Ni(Cp)_2]$ with a nonactivated aryl azide was isolated a mono(tetraazabutadiene) complex, $[Ni(Ar_2N_4)(\eta^5\text{-}C_5H_5)]$, which we have shown to be a stable intermediate in the formation of $[Ni(Ar_2N_4)_2]$.[3,4]

In this paper we report the results of related reactions with $[Pt(COD)_2]$, which lead to the mono(tetraazabutadiene) complexes $[Pt(Ar_2N_4)(COD)]$. This study reveals two further aspects that have not been observed in the related nickel chemistry. First, $[Pt(Ar_2N_4)(PEt_3)_2]$ complexes can be prepared by substitution of COD when Ar is 4-MeC_6H_4 or 4-ClC_6H_4; second, for Ar = $4\text{-NO}_2C_6H_4$ one coordinated olefinic unit of the COD ligand is highly activated for nucleophilic attack by PEt_3, leading to an unexpected five-coordinate (tetraazabutadiene)platinum(II) complex. The structure of the latter complex was established by a X-ray crystal structure determination. Part of this work was the subject of preliminary communications.[3,5]

Experimental Section

Preparations were carried out in a dry oxygen-free N_2 atmosphere. Solvents were dried and freshly distilled prior to use. Bis(1,5-cyclooctadiene)platinum, $[Pt(COD)_2]$,[6] $[Pt_3(t\text{-BuNC})_6]$,[6] and the organic azides[7] were prepared by methods reported in the literature.

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IR spectra were recorded on Beckman 4250 and Perkin-Elmer 283 spectrophotometers. All spectra were run with KBr disks of the compounds. ^{1}H NMR spectra were recorded on Varian HA 100 and XL 100 and Bruker WM 250 spectrometers at ambient temperature. ^{13}C NMR spectra were recorded on a Bruker WP 80 spectrometer at ambient temperature. ^{31}P NMR spectra were recorded on Varian XL 100 and Bruker WM 250 spectrometers at various temperatures.

Field desorption mass spectra were obtained with a Varian MAT 711 spectrometer. The samples were dissolved in THF and loaded onto the emitter with the dipping technique. In all experiments emission-controlled FD[8] was used at a threshold of 5×10^{-9} A measured between the field anode and the slotted cathode, 1.5 mm apart. The emitter currents, which were used to desorb the samples, were in the range 0–18 mA (see the supplementary material). The source temperature was generally 50 °C.

X-ray photoelectron spectra were collected with an AEI ES 200 spectrometer at a pressure of 10^{-10} torr, obtained with turbomolecular and Ti sublimation pumps. As a source Mg Kα radiation was used. We have used the C(1s) line, set at 285.0 eV, as a reference. The estimated error in the recorded values was ±0.1 eV.

Syntheses of (1,5-Cyclooctadiene)(tetraazabutadiene)platinum Complexes, [Pt(Ar_2N_4)(COD)]. For Ar = 4-ClC_6H_4 (I). A mixture of [Pt(COD)$_2$] (1 g, 2.4 mmol) and 4-$ClC_6H_4N_3$ (5 g, 32 mmol) was stirred at 25 °C for 4 days in the dark. With a change to an ethylene atmosphere, pentane (30 mL) was added to the mixture. The precipitate was filtered off and washed with ethylene-saturated pentane (4 × 30 mL) to remove unreacted [Pt(COD)$_2$] and azide. The atmosphere was changed again to N_2. The residue was washed with toluene (2 × 20 mL) and dissolved in THF, and the solution was filtered through a G_3 glass frit. The complex was precipitated again by addition of pentane and, after the solution was decanted, washed with pentane (3 × 20 mL) and dried in vacuo.

For Ar = 4-MeC_6H_4 (II) or 4-$NO_2C_6H_4$ (III). The compounds were prepared as described for I, but in the case of III the reaction mixture of [Pt(COD)$_2$] (1 g, 2.4 mmol) and 4-$NO_2C_6H_4N_3$ (3 g, 18.3 mmol) in toluene (10 mL) was stirred for 8 h instead of 4 days.

The resulting products I, II, and III were often contaminated with [Pt(COD)$_2$], as found in the FD mass spectra, and repeated recrystallizations were required to obtain analytically pure yellow samples. Final yields range from 30 to 45%.

Anal. Calcd for I ($C_{20}H_{20}N_4Cl_2Pt$): C, 41.24; H, 3.46; N, 9.62; Cl, 12.17; Pt, 33.50. Found: C, 41.0; H, 3.6; N, 9.2; Cl, 11.9; Pt, 34.0. Calcd for III ($C_{20}H_{20}N_6O_4Pt$): C, 39.80; H, 3.34; N, 13.93; O, 10.60; Pt, 32.33. Found: C, 39.9; H, 3.4; N, 13.6; O, 10.5; Pt, 32.6.

Syntheses of Bis(*tert*-butyl isocyanide)(tetraazabutadiene)platinum Complexes, [Pt(Ar_2N_4)(*t*-BuNC)$_2$]. For Ar = 4-ClC_6H_4 (IV). Method A. A mixture of I (50 mg, 0.09 mmol) and *t*-BuNC (2 mL, 19 mmol) in toluene (10 mL) was stirred at room temperature for 18 h, during which time the color changed from pale to bright yellow. Pentane was added (30 mL), and the mixture was stored at −20 °C for 24 h. The solution was decanted off and the remaining precipitate washed with pentane (4 × 20 mL), followed by recrystallization from a THF/pentane mixture. The yield was 25 mg (43%) of bright yellow IV. Anal. Calcd for IV ($C_{22}H_{26}N_6Cl_2Pt$): C, 41.25; H, 4.09; N, 13.12. Found: C, 41.6; H, 4.4; N, 12.8.

Method B. A mixture of [Pt$_3$(*t*-BuNC)$_6$] (0.18 g, 0.17 mmol) and 4-$ClC_6H_4N_3$ (1 g, 6.5 mmol) in THF (5 mL) was stirred for 24 h in the dark. Pentane (30 mL) was added, and the mixture was stored for 24 h at −20 °C. After the solution was decanted, the resulting precipitate was washed with pentane (3 × 20 mL). Recrystallization from a THF/pentane mixture yielded 80 mg (25%) of IV.

For Ar = 4-MeC_6H_4 (V) and Ar = 4-$NO_2C_6H_4$ (VI). The reactions of *t*-BuNC with II and III, according to method A, were carried out similarly. However, satisfactory analyses have not been obtained for V (bright yellow) and VI (light orange). The reactions of [Pt$_3$(*t*-BuNC)$_6$] with 4-$MeC_6H_4N_3$ and 4-$NO_2C_6H_4N_3$ proceeded according to method B. Yields via this route were generally lower than via method A, which, moreover, yielded purer products. The complexes IV, V, and VI were identified by IR and FD mass spectra (see the supplementary material).

Table I. Crystal Data and Details of the Structure Analysis

a. Crystal Data

formula	$C_{36}H_{58}N_6O_5P_2Pt$	μ(Mo Kα), cm^{-1}	38
mol wt	1002.60		
cryst syst	monoclinic	cryst size, mm	$(100)\rightarrow(\bar{1}00)$, 0.22; $(001)\rightarrow(00\bar{1})$, 0.34; $(012)\rightarrow(0\bar{1}\bar{2})$, 0.38; $(01\bar{2})\rightarrow(0\bar{1}2)$, 0.44
space group	No. 14, $P2_1/c$		
a, Å	12.824 (4)		
b, Å	13.392 (4)		
c, Å	23.963 (11)	cryst vol, mm^3	0.046
β, deg	102.97 (3)		
V, Å^3	4010 (2)	no. of grid points	832
Z	4		
D(calcd), g/cm^3	1.510	max transmission	0.48
F(000)	1856	min transmission	0.24

b. Data Collection

θ(min), θ(max)	0.1, 28.0
radiation, Å	Mo Kα (Zr-filtered), 0.710 69
$\omega/2\theta$ scan, deg	$0.35 + 0.35 \tan\theta$
horiz and vert aperture, mm	1.30, 2.0
max time/reflctn, s	90
ref reflctn	040
total data	10 022
total unique reflctns	9650
obsd data ($I > 2.5\sigma(I)$)	6919

c. Refinement

no. of refined parameters	444
weighting scheme	$w^{-1} = (\sigma^2(F) + 0.0006F^2)/4.63$
final $R_F = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.044
final $R_{wF} = [(\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2)/(\Sigma w\lvert F_o\rvert^2)]^{1/2}$	0.047
variance (rms dev of a reflctn of unit wt)	2.71

Syntheses of Bis(triethylphosphine)[1,4-bis(4-chlorophenyl)tetraazabutadiene]platinum, [Pt(1,4-(4-$ClC_6H_4)_2N_4$)(PEt$_3$)$_2$] (VII), and Bis(triethylphosphine)[1,4-bis(4-tolyl)tetraazabutadiene]platinum, [Pt(1,4-(4-$MeC_6H_4)_2N_4$)(PEt$_3$)$_2$] (VIII). The reactions of I and II with PEt$_3$ to yield VII and VIII, respectively, follow the same procedure as for the reaction of I with *t*-BuNC (method A). The color of both VII and VIII is orange. The yields are 30–40%. Anal. Calcd for VII ($C_{24}H_{38}N_4P_2Cl_2Pt$): C, 40.57; H, 5.39; N, 7.89; P, 8.72. Found: C, 39.7; H, 5.4; N, 7.5; P, 8.2.

Synthesis of [Pt(1,4-(4-$NO_2C_6H_4)_2N_4$)($\overline{CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2}$)(PEt$_3$)] (IX). To a solution of III (200 mg, 0.33 mmol) in THF (20 mL) was added PEt$_3$ (0.4 mL, 2.7 mmol). The color of the mixture immediately turned deep blue. After 5 min of stirring the mixture was brought onto a silica-60 column (15 cm × 2 cm) and chromatographed with THF. The deep blue fraction was collected and recrystallized from a THF/pentane mixture to yield 173 mg (62%) of IX. Anal. Calcd for IX ($C_{32}H_{50}N_6O_4P_2Pt$): C, 45.76; H, 6.00; N, 10.01; O, 7.62; P, 7.38. Found: C, 46.0; H, 6.2; N, 9.6; O, 7.7; P, 7.0.

Structure Determination and Refinement of $C_{36}H_{58}N_6O_5P_2Pt$ (IX). A dark violet crystal, suitable for data collection, was glued on top of a glass fiber and transferred to an Enraf-Nonius CAD-4 diffractometer. The quality of the crystal was examined on three Laue photographs, prepared on the diffractometer by 30° oscillations about the three unit cell axes. Unit cell dimensions and their standard deviations were determined in the usual and previously described way from the settings of eight carefully centered reflections.[9a] The crystal data and details of the data collection and structure refinement are summarized in Table I. The intensities of a tetarto sphere of the reflections were collected in the $\omega/2\theta$ scan mode, with use of zirco-

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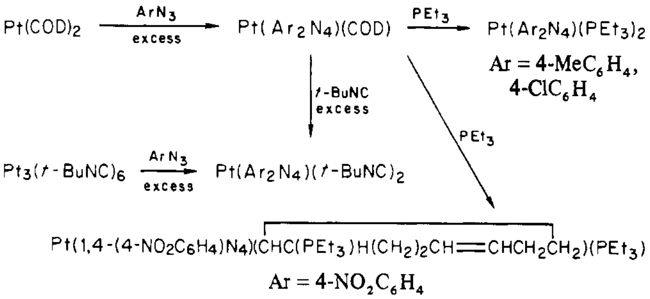
Table II. Positional Parameters and Their Esds in Parentheses for $C_{36}H_{58}N_6O_5P_2Pt$

atom	*x/a*	*y/b*	*z/c*
Pt	0.22699 (2)	0.28016 (2)	0.03817 (1)
P(1)	0.1133 (2)	0.2132 (1)	−0.04558 (8)
P(2)	0.3599 (2)	0.3651 (2)	0.23020 (9)
O(1)	0.6071 (5)	0.3394 (4)	−0.1580 (2)
O(2)	0.6941 (5)	0.2043 (5)	−0.1305 (3)
O(3)	−0.1238 (5)	0.0601 (6)	0.2194 (3)
O(4)	−0.0224 (6)	−0.0674 (6)	0.2484 (3)
O(5)	0.782 (1)	0.425 (1)	0.1400 (7)
N(1)	0.3627 (4)	0.1940 (4)	0.0251 (2)
N(2)	0.3906 (4)	0.1119 (4)	0.0604 (2)
N(3)	0.3255 (4)	0.0850 (4)	0.0900 (2)
N(4)	0.2330 (4)	0.1418 (4)	0.0850 (2)
N(5)	0.6253 (5)	0.2649 (4)	−0.1270 (2)
N(6)	−0.0415 (6)	0.0109 (6)	0.2196 (3)
C(1)	0.5597 (5)	0.2476 (5)	−0.0867 (3)
C(2)	0.4809 (5)	0.3141 (5)	−0.0831 (3)
C(3)	0.4147 (6)	0.2963 (4)	−0.0438 (3)
C(4)	0.4307 (5)	0.2106 (4)	−0.0096 (3)
C(5)	0.5147 (5)	0.1435 (5)	−0.0143 (3)
C(6)	0.5765 (6)	0.1621 (5)	−0.0537 (3)
C(7)	0.0294 (6)	0.0424 (6)	0.1858 (3)
C(8)	0.1202 (6)	−0.0147 (6)	0.1849 (3)
C(9)	0.1885 (6)	0.0178 (5)	0.1517 (3)
C(10)	0.1688 (5)	0.1064 (5)	0.1192 (3)
C(11)	0.0764 (6)	0.1600 (6)	0.1213 (3)
C(12)	0.0084 (6)	0.1283 (6)	0.1551 (3)
C(13)	0.2110 (6)	0.4302 (5)	0.0130 (3)
C(14)	0.1252 (6)	0.4015 (5)	0.0425 (3)
C(15)	0.1068 (6)	0.4422 (6)	0.0973 (3)
C(16)	0.1978 (6)	0.4551 (6)	0.1488 (3)
C(17)	0.2706 (5)	0.3616 (5)	0.1589 (3)
C(18)	0.3290 (5)	0.3413 (5)	0.1098 (3)
C(19)	0.3838 (6)	0.4321 (5)	0.0911 (3)
C(20)	0.3068 (7)	0.4932 (5)	0.0447 (4)
C(21)	0.0685 (7)	0.3060 (6)	−0.1016 (4)
C(22)	−0.0169 (9)	0.2788 (7)	−0.1543 (4)
C(23)	0.1747 (7)	0.1205 (6)	−0.0830 (3)
C(24)	0.1935 (8)	0.0182 (6)	−0.0531 (4)
C(25)	−0.0079 (7)	0.1511 (6)	−0.0367 (4)
C(26)	−0.0912 (7)	0.2202 (7)	−0.0158 (5)
C(27)	0.275 (1)	0.323 (1)	0.2837 (9)
C(28)	0.246 (1)	0.2135 (8)	0.2727 (6)
C(29)	0.383 (1)	0.490 (1)	0.2601 (9)
C(30)	0.443 (1)	0.505 (1)	0.3186 (9)
C(31)	0.462 (2)	0.279 (1)	0.238 (1)
C(32)	0.547 (1)	0.288 (1)	0.223 (1)
C(33)	0.680 (1)	0.423 (1)	0.1139 (7)
C(34)	0.683 (1)	0.329 (1)	0.0876 (8)
C(35)	0.733 (1)	0.257 (1)	0.1191 (7)
C(36)	0.807 (1)	0.327 (1)	0.1577 (8)
Coordinates for the Carbon Atoms in the Disordered $(C_2H_5)_3P$ Moiety (43% Alternative)			
C(27)	0.367 (2)	0.242 (2)	0.256 (1)
C(28)	0.246 (1)	0.2135 (8)	0.2727 (6)
C(29)	0.335 (2)	0.454 (2)	0.274 (1)
C(30)	0.406 (2)	0.457 (2)	0.333 (1)
C(31)	0.518 (2)	0.376 (2)	0.232 (1)
C(32)	0.555 (2)	0.464 (2)	0.233 (1)

Scheme I



nium-filtered Mo Kα radiation. The intensity of one reflection was monitored every 0.5 h of X-ray exposure time. There was no indication for decay during data collection. The data were subsequently corrected for absorption, Lorentz, and polarization effects and averaged into a unique set of data in the previously described way.[9a]

The structure was solved by standard Patterson and Fourier techniques and subsequently refined by blocked full-matrix least-squares techniques. The crystal structure was found to contain one solvated molecule of tetrahydrofuran per asymmetric unit. One of the two $(C_2H_5)_3P$ moieties appeared to be disordered (57%:43%). All non-hydrogen atoms were refined with anisotropic thermal parameters except for those of the disordered carbons that were only allowed to refine isotropically with one overall occupancy factor. Hydrogen atoms were introduced on calculated positions and refined in the riding mode on corresponding non-hydrogen atom positions. Weights based on counting statistics were introduced in the final stages of refinement. Convergence was reached at $R = 0.044$ for 6919 observed reflections. A final difference Fourier showed no significant features. The final values of the refined parameters are given in Table II. Neutral scattering factors were taken from ref 9b and corrected for anomalous dispersion.[9c] All calculations were carried out either on the in-house Eclipse/S230 minicomputer with the program ILIAS[9d] (structure determination and refinement) or on the Cyber-175 computer of the University of Utrecht computer center with the programs of the EUCLID package[9e] (molecular geometry and illustrations).

Results

All reported complexes were identified by a combination of techniques, including ^1H, ^{13}C, and ^{31}P NMR (see Table III), IR, UV, and FD mass spectrometry (see the supplementary material). X-ray photoelectron spectra of $[Pt(Ar_2N_4)(t\text{-}BuNC)_2]$ (Ar = $4\text{-}MeC_6H_4$ (V) or $4\text{-}NO_2C_6H_4$ (VI)) and $[Pt(1,4\text{-}(4\text{-}NO_2C_6H_4)_2N_4)(CHC(PEt_3)H(CH_2)_2CH{=}CH\text{-}CH_2CH_2)(PEt_3)]$ (IX) were recorded (see Table IV). In order to determine the structure and bonding in IX, we undertook an X-ray crystal structure determination.

Syntheses and Properties. The (1,5-cyclooctadiene)(tetraazabutadiene)platinum complexes $[Pt(Ar_2N_4)(COD)]$ (I–III) were prepared by reactions of $[Pt(COD)_2]$ with $4\text{-}ClC_6H_4N_3$, $4\text{-}MeC_6H_4N_3$, and $4\text{-}NO_2C_6H_4N_3$, respectively. These complexes are stable in air, and attempted reactions with MeI resulted in recovery of the starting materials. Reactions of I–III with *t*-BuNC produced the $[Pt(Ar_2N_4)(t\text{-}BuNC)_2]$ complexes IV–VI, which could also be obtained in lower yields and purity by the reactions of $[Pt_3(t\text{-}BuNC)_6]$ with the appropriate azides. The $[Pt(Ar_2N_4)(COD)]$ complexes I and II did not react with PPh_3 but did react with PEt_3 to form $[Pt(Ar_2N_4)(PEt_3)_2]$ (VII and VIII). The reaction of $[Pt(Ar_2N_4)(COD)]$ (III, Ar = $4\text{-}NO_2C_6H_4$) with PEt_3 provided the unexpected compound $[Pt(1,4\text{-}(4\text{-}NO_2C_6H_4)_2N_4)(CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2)(PEt_3)]$ (IX), which is intensely blue ($\epsilon = 5.2 \times 10^4$ at 605 nm). The above reactions are summarized in Scheme I. Infrared spectra of the complexes I–IX showed no bands attributable to the N_4 moiety. The $\nu(NC)$ values for the $[Pt(Ar_2N_4)(t\text{-}BuNC)_2]$ complexes (IV–VI) show the isocyanide to be terminally bonded.

^1H NMR spectra of complexes I–XIII showed equivalence of the aryl groups of the tetraazabutadiene ligands and of the symmetrically bonded coligands. ^{13}C NMR spectra of compounds I and III revealed symmetrically bonded COD units.

^{31}P NMR spectra showed the equivalence of the terminally bonded PEt_3 groups in complexes VII and VIII. For complex IX two widely separated signals were found. One, assignable to the P(1) atom (δ −12.3) directly coordinated to the metal, has a rather small $^1J(^{195}Pt\text{–}^{31}P)$ value of 1501 Hz. The other, P(2) (δ 39.0), is found in the region typical for triethylphosphonium centers and, as well as possessing a coupling to the metal ($^3J(^{195}Pt\text{–}^{31}P) = 165$ Hz), also exhibits coupling to P(1) ($^4J(^{31}P\text{–}^{31}P) = 64$ Hz).

Table III. ^1H, ^{13}C,[a] and ^{31}P NMR Data of I–VIII[b]

compd no.	Ar	aryl[c]	COD[d] CH	COD[d] CH$_2$	PEt$_3$[e]	*t*-Bu
			[Pt(Ar$_2$N$_4$)(COD)]			
I	4-ClC$_6$H$_4$	7.0, 7.2 (8) [127.7, 128.7, 131.6, 149.2]	4.4 (60) [86.5 {160}]	2.15 [30.0]		
II	4-MeC$_6$H$_4$	7.0	4.3 (60)	2.20		
III	4-NO$_2$C$_6$H$_4$	7.2, 8.2 (10) [124.5, 125.3][f]	4.90 (60) [90.0 {158}]	2.40 [30.0]		
			[Pt(Ar$_2$N$_4$)(CN-*t*-Bu)$_2$]			
IV	4-ClC$_6$H$_4$	7.5				1.70
V	4-MeC$_6$H$_4$[g]	7.2				1.50
VI	4-NO$_2$C$_6$H$_4$	7.3, 8.0 (9)				1.40
			[Pt(Ar$_2$N$_4$)(PEt$_3$)$_2$]			
VII	4-ClC$_6$H$_4$	7.0, 7.2 (8)			−7.14 (3339)[h]	
VIII	4-MeC$_6$H$_4$[i]	7.2			−6.53 (3330)[h]	
			Title Compound			
IX					−12.3, 39.0 (1501, 165)[j,k]	

[a] ^{13}C NMR data in brackets. [b] ^1H and ^{13}C NMR data of solutions in $CDCl_3$ at room temperature; δ measured from internal Me_4Si. [c] AB patterns; if well observable J_{AB} is also given in parentheses. [d] $J(^{195}Pt-^1H)$ in parentheses; $J(^{195}Pt-^{13}C)$ in braces. [e] δ relative to 85% H_3PO_4 external standard; negative values are upfield and positive values downfield. [f] Not all aryl ^{13}C resonances were observed owing to the low solubility of this complex. [g] $\delta(CH_3)$ 2.40. [h] In $CDCl_3$ at room temperature recorded on a Varian XL 100. [i] $\delta(CH_3)$ 2.20. [j] In THF-d_8 at −50 °C; recorded on a Bruker WM 250. [k] $^nJ(^{195}Pt-^{31}P)$ in which n is 1 and 3, respectively; $^4J(^{31}P-^{31}P)$ = 64 Hz.

Table IV. XPS Binding Energy[a] Results

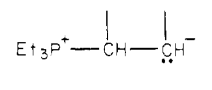
compd	Pt-(4f$_{7/2}$)	N(1s)	O(1s)
[Pt((4-MeC$_6$H$_4$)$_2$N$_4$)(CN-*t*-Bu)$_2$] (V)	74.4	399.0	
[Pt((4-NO$_2$C$_6$H$_4$)$_2$N$_4$)(CN-*t*-Bu)$_2$] (VI)	74.5	400.5	532.9
title compd (IX)	74.0	399.4	532.4

[a] In eV; C(1s) = 285.0 eV.

The Pt(4f) band in the X-ray photoelectron spectra of IV, VI, and IX lies in the platinum(II) range while the N(1s) band exhibited a shake-up satellite.

The FD mass spectra gave correct *m*/*z* values, and the observed isotopic patterns correlated well with those calculated.

Molecular Geometry of [Pt(1,4-(4-NO$_2$C$_6$H$_4$)$_2$N$_4$)(CHC(PEt$_3$)H(CH$_2$)$_2$CH=CHCH$_2$CH$_2$)(PEt$_3$)] (IX). The molecular structure with the adopted numbering scheme is shown in a PLUTO drawing (see Figure 1). Relevant bond distances and angles are given in Table V. A list of relevant torsion angles and least-squares planes, as well as an ORTEP stereodrawing, have been deposited as supplementary material. The unit cell comprises four discrete monomeric units of IX, along with four molecules of THF used as a solvent for the crystallization. Within each molecule there are two inequivalent phosphorus centers, one bonded to the metal center (P(1)) and a second (P(2)) σ bonded to what was originally an olefinic carbon atom of the coordinated COD ligand. This generates a



$$Et_3P^+—CH—\ddot{C}H^-$$

system, and as a result the cyclooct-5-enyl skeleton is now bonded to the metal center by one η^2-C=C bond and a σ carbon-to-platinum donative bond. One PEt$_3$ unit is disordered (see insert in Figure 1).

Analysis of the geometry of the three triethylphosphino moieties (including those of the disordered forms as shown in Figure 1) reveals that they occur in two essentially different conformations. In both cases a pattern trans–gauche–gauche is observed for the X–P–C–C torsion angles (where X stands for the fourth atom bonded to the phosphorus atom). The two conformations differ only with respect to the relative signs of the two gauche torsion angles. A study of the structures that are contained in the files of the Cambridge Crystallographic Database showed that the triethylphosphino moiety is generally observed in one of the above-mentioned conformations.

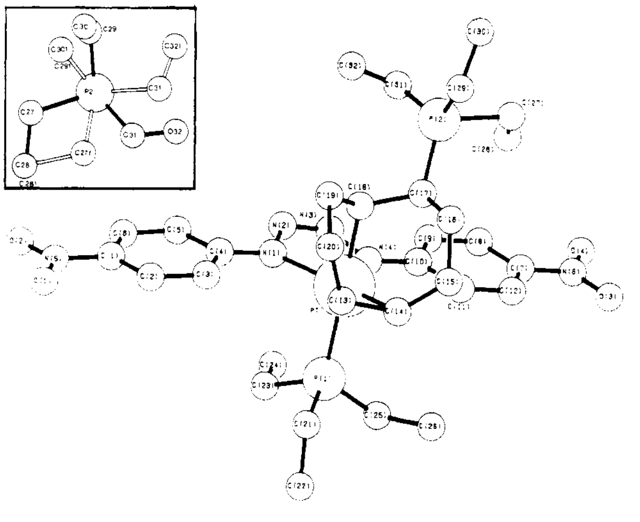


Figure 1. PLUTO drawing of the crystal structure of [Pt(1,4-(4-NO$_2$C$_6$H$_4$)$_2$N$_4$)(CHC(PEt$_3$)H(CH$_2$)$_2$CH=CHCH$_2$CH$_2$)(PEt$_3$)] (IX) showing the adopted numbering scheme and the disorder in the PEt$_3$ moiety.

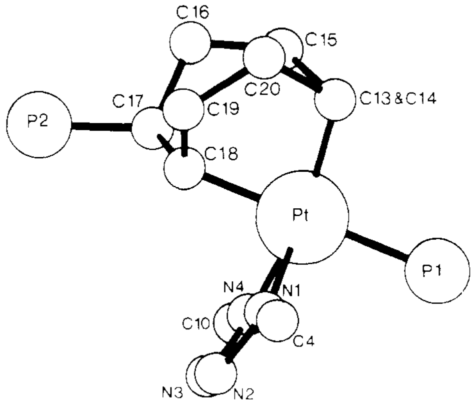


Figure 2. View of the central part of the complex as seen along C(13)–C(14).

The configuration around the platinum center is distorted trigonal bipyramidal. The σ,σ-N,N′-bonded tetraazabutadiene ligand and the η^2-C=C bond (1.49 (1) Å) of the cyclooct-5-enyl unit occupy the equatorial plane. The metal-bonded PEt$_3$

Table V. Bond Distances (Å) and Angles (Deg) for $C_{36}H_{58}N_6O_5P_2Pt$

A. Bond Distances

Pt-P(1)	2.376 (2)	C(2)-C(3)	1.42 (1)
Pt-N(1)	2.169 (5)	C(3)-C(4)	1.398 (9)
Pt-N(4)	2.159 (5)	C(4)-C(5)	1.427 (9)
Pt-C(13)	2.095 (6)	C(5)-C(6)	1.39 (1)
Pt-C(14)	2.101 (7)	C(7)-C(12)	1.36 (1)
Pt-C(18)	2.079 (6)	C(7)-C(8)	1.40 (1)
P(1)-C(21)	1.825 (9)	C(8)-C(9)	1.38 (1)
P(1)-C(23)	1.811 (8)	C(9)-C(10)	1.41 (1)
P(1)-C(25)	1.816 (9)	C(10)-C(11)	1.40 (1)
P(2)-C(17)	1.832 (7)	C(11)-C(12)	1.38 (1)
P(2)-C(27)	1.95 (2)	C(13)-C(14)	1.49 (1)
P(2)-C(29)	1.82 (2)	C(13)-C(20)	1.54 (1)
P(2)-C(31)	1.72 (2)	C(14)-C(15)	1.49 (1)
O(1)-N(5)	1.236 (8)	C(15)-C(16)	1.51 (1)
O(2)-N(5)	1.215 (9)	C(16)-C(17)	1.55 (1)
O(3)-N(6)	1.24 (1)	C(17)-C(18)	1.552 (9)
O(4)-N(6)	1.25 (1)	C(18)-C(19)	1.52 (1)
O(5)-C(36)	1.39 (2)	C(19)-C(20)	1.55 (1)
O(5)-C(33)	1.32 (2)	C(21)-C(22)	1.52 (1)
N(1)-C(4)	1.351 (8)	C(23)-C(24)	1.54 (1)
N(1)-N(2)	1.385 (7)	C(25)-C(26)	1.58 (1)
N(2)-N(3)	1.263 (8)	C(27)-C(28)	1.52 (2)
N(3)-N(4)	1.391 (7)	C(29)-C(30)	1.45 (3)
N(4)-C(10)	1.370 (8)	C(31)-C(32)	1.23 (3)
N(5)-C(1)	1.435 (9)	C(33)-C(34)	1.41 (2)
N(6)-C(7)	1.41 (1)	C(34)-C(35)	1.30 (2)
C(1)-C(2)	1.37 (1)	C(35)-C(36)	1.50 (2)
C(1)-C(6)	1.38 (1)		

Bond Distances within the 43% Disorder Form of the $(C_2H_5)_3P$ Moiety

P(2)-C(17)	1.832 (7)	C(27)-C(28)	1.73 (3)
P(2)-C(27)	1.76 (2)	C(29)-C(30)	1.48 (3)
P(2)-C(29)	1.67 (2)	C(31)-C(32)	1.27 (3)
P(2)-C(31)	2.02 (2)		

B. Bond Angles

P(1)-Pt-N(1)	92.1 (1)	N(5)-C(1)-C(6)	118.6 (6)
P(1)-Pt-N(4)	93.4 (1)	C(1)-C(2)-C(3)	119.5 (6)
P(1)-Pt-C(13)	96.7 (2)	C(2)-C(3)-C(4)	119.7 (6)
P(1)-Pt-C(14)	93.6 (2)	N(1)-C(4)-C(5)	123.2 (6)
P(1)-Pt-C(18)	178.2 (2)	C(3)-C(4)-C(5)	119.1 (6)
N(1)-Pt-N(4)	71.5 (2)	N(1)-C(4)-C(3)	117.7 (6)
N(1)-Pt-C(13)	119.9 (2)	C(4)-C(5)-C(6)	119.8 (6)
N(1)-Pt-C(14)	161.1 (2)	C(1)-C(6)-C(5)	120.0 (6)
N(1)-Pt-C(18)	87.3 (2)	N(6)-C(7)-C(8)	119.4 (7)
N(4)-Pt-C(13)	164.4 (2)	C(8)-C(7)-C(12)	121.3 (7)
N(4)-Pt-C(14)	126.1 (2)	N(6)-C(7)-C(12)	119.3 (7)
N(4)-Pt-C(18)	88.1 (2)	C(7)-C(8)-C(9)	118.3 (7)
C(13)-Pt-C(14)	41.5 (3)	C(8)-C(9)-C(10)	121.8 (7)
C(13)-Pt-C(18)	82.1 (3)	N(4)-C(10)-C(9)	124.3 (6)
C(14)-Pt-C(18)	86.4 (3)	N(4)-C(10)-C(11)	118.3 (6)
Pt-P(1)-C(21)	113.4 (3)	C(9)-C(10)-C(11)	117.4 (6)
Pt-P(1)-C(23)	115.1 (3)	C(10)-C(11)-C(12)	121.0 (7)
Pt-P(1)-C(25)	116.9 (3)	C(7)-C(12)-C(11)	120.2 (7)
C(21)-P(1)-C(23)	101.7 (4)	Pt-C(13)-C(20)	111.5 (5)
C(21)-P(1)-C(25)	105.2 (4)	C(14)-C(13)-C(20)	120.0 (6)
C(23)-P(1)-C(25)	102.9 (4)	Pt-C(13)-C(14)	69.5 (4)
C(17)-P(2)-C(27)	106.4 (6)	Pt-C(14)-C(13)	69.0 (4)
C(17)-P(2)-C(29)	113.8 (7)	C(13)-C(14)-C(15)	127.3 (6)
C(17)-P(2)-C(31)	112.6 (8)	Pt-C(14)-C(15)	123.3 (5)
C(27)-P(2)-C(29)	94.2 (8)	C(14)-C(15)-C(16)	121.2 (6)
C(27)-P(2)-C(31)	105.1 (9)	C(15)-C(16)-C(17)	111.4 (6)
C(29)-P(2)-C(31)	121.4 (9)	P(2)-C(17)-C(18)	113.8 (5)
C(33)-O(5)-C(36)	105 (1)	C(16)-C(17)-C(18)	113.6 (6)
Pt-N(1)-C(4)	130,6 (4)	P(2)-C(17)-C(16)	110.7 (5)
N(2)-N(1)-C(4)	113.2 (5)	Pt-C(18)-C(17)	111.9 (4)
Pt-N(1)-N(2)	116.0 (4)	C(17)-C(18)-C(19)	114.6 (5)
N(1)-N(2)-N(3)	117.3 (5)	Pt-C(18)-C(19)	108.5 (4)
N(2)-N(3)-N(4)	117.0 (5)	C(18)-C(19)-C(20)	111.9 (6)
Pt-N(4)-N(3)	116.4 (4)	C(13)-C(20)-C(19)	112.0 (6)
Pt-N(4)-C(10)	130.6 (4)	P(1)-C(21)-C(22)	119.8 (6)
N(3)-N(4)-C(10)	112.0 (5)	P(1)-C(23)-C(24)	114.8 (6)
O(1)-N(5)-O(2)	122.7 (7)	P(1)-C(25)-C(26)	115.3 (6)
O(1)-N(5)-C(1)	118.4 (6)	P(2)-C(27)-C(28)	108 (1)
O(2)-N(5)-C(1)	118.9 (6)	P(2)-C(29)-C(30)	120 (1)
O(3)-N(6)-C(7)	119.7 (8)	P(2)-C(31)-C(32)	127 (2)
O(4)-N(6)-C(7)	119.8 (7)	O(5)-C(33)-C(34)	96 (1)
O(3)-N(6)-O(4)	120.5 (8)	C(33)-C(34)-C(35)	117 (2)
N(5)-C(1)-C(2)	119.4 (6)	C(34)-C(35)-C(36)	93 (1)
C(2)-C(1)-C(6)	121.9 (6)	O(5)-C(36)-C(35)	110 (1)

Bond Angles within the 43% Disorder Form of the $(C_2H_5)P$ Moiety

C(17)-P(2)-C(27)	106.0 (8)	C(29)-P(2)-C(31)	105 (1)
C(17)-P(2)-C(29)	116.2 (8)	P(2)-C(27)-C(28)	108 (1)
C(17)-P(2)-C(31)	116.1 (8)	P(2)-C(29)-C(30)	117 (2)
C(27)-P(2)-C(29)	117 (1)	P(2)-C(31)-C(32)	116 (2)
C(27)-P(2)-C(31)	94.8 (9)		

ligand (P(1)–Pt = 2.376 (2) Å) and the σ-bonded sp^3 carbon atom (C(18)) of the cyclooct-5-enyl unit (C18)–Pt = 2.079 (6) Å) reside on axial positions with a linear (178.2 (2)°) lineup of the C(18)–Pt–P(1) atoms (see Figure 2). The bite angle of 71.5 (4)° for the tetrazabutadiene ligand results in a considerable distortion of the angles in the equatorial plane from ideal trigonal bipyramidal.

The central N–N bond of the tetraazabutadiene ligand is short (1.263 (8) Å) while the adjacent N–N bonds are significantly longer (1.385 (7) and 1.391 (7) Å). The N–C bond lengths between the N_4 moiety and the aryl groups are shorter than those found in other known tetraazadiene complexes (N(1)–C(4) = 1.351 (8) Å, N(4)–C(10) = 1.370 (8) Å). The PtN_4 chelate ring is planar (deviations of atoms from the least-squares plane: Pt, 0.071 (11); N(1), –0.089 (13); N(2), 0.056 (13); N(3), 0.046 (12); N(4), –0.084(11) Å). C(4) and C(10) deviate from this plane –0.218 (15) and –0.073 (12) Å, respectively (see Figure 2), and the aryl rings (deviations of atoms from the least-squares planes: C(1), 0.005 (27); C(2), 0.001 (26); C(3), –0.000 (25); C(4), –0.006 (23); C(5), 0.012 (24); C(6), –0.012 (26) Å) are coplanar with it (see Figure 1; angle between these planes 8.6 (3)°).

Discussion

The reactions of $[Pt(COD)_2]$ with aryl azides show a sharp contrast to the reactions of $[Ni(COD)_2]$ with the same azides.[2a,3] The latter reactions are violently exothermic and give products whose nature is dependent on the electronic properties of the substituent on the aryl rings Ar. Such reactions lead to $[Ni(Ar_2N_4)_2]$ products for electron-donating and mildly electron-withdrawing substituents. For Ar = 4-$NO_2C_6H_4$ no products have been identified[2a] though for Ar = C_6F_5 $[Ni(Ar_2N_4)(COD)]$ has been prepared.[2b]

In the case of platinum (i) the reactions are slow (4 days for Ar = 4-MeC_6H_4, 8 h for Ar = 4-$NO_2C_6H_4$) and (ii) $[Pt(Ar_2N_4)L_2]$ was the only type of product isolated from reaction of aryl azides with either $[Pt(COD)_2]$ or $[Pt_3(t\text{-}BuNC)_6]$. In our platinum system the influence of the aryl substituents is only recognized in the reaction times. However reaction of $[Pt(PPh_3)_4]$ with 4-$MeC_6H_4SO_2N_3$ led to $[Pt(Ar_2N_4)(PPh_3)_2]$ while azides which were not activated by electron-withdrawing substituents failed to produce tetraazabutadiene complexes.[10]

Our attempts to prepare such triphenylphosphine complexes by substitution of COD from $[Pt(Ar_2N_4)(COD)]$ (I–III) were also unsuccessful. The substitution of the COD in $[Pt(Ar_2N_4)(COD)]$ by t-BuNC or PEt_3 is dependent on the aryl substituents, and the rate follows the same order as the reactivity of $[Pt(COD)_2]$ toward the aryl azides, i.e., 4-NO_2 > 4-Cl > 4-Me.

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(10) Beck, W.; Bauder, M.; La Monica, G.; Cenini, S.; Ugo, R. *J. Chem. Soc. A* **1971**, 113.

The most striking example of the influence of the substituent on Ar is provided by the reaction of $[Pt((4\text{-}NO_2C_6H_4)_2N_4)(COD)]$ (III) with PEt_3 to yield IX. To date several nucleophilic addition reactions have been reported, including addition of tertiary phosphines to the η^2-coordinated hydrocarbons in cationic metal complexes.[11a–d] Furthermore, addition of the conjugate bases of alcohols, aliphatic primary and secondary amines, carboxylic acids, keto esters, malonic esters, and β-diketones to neutral platinum and palladium complexes of the type $[MCl_2(\eta^2\text{-diene})]$ has been shown to give dimeric species containing carbon–metal σ bonds.[11e–m]

In one case the addition of (*S*)-(1-aminoethyl)benzene to $[PtCl_2(\text{hexa-1,5-diene})]$ is reported to yield a monomeric (aminohexadienyl)platinum dichloride species.[11n] An X-ray crystal structure determination of this compound showed a square-planar four-coordinate geometry with a presumed zwitterionic structure containing the positive charge on nitrogen and the negative charge on platinum.

The tendency for nucleophilic attack is generally dominated by the strength of the attacking nucleophile and the ability of the metal center to form stable metal–carbon σ bonds.[11o–q]

Our complex IX, while clearly a product of a nucleophilic addition, shows a number of very marked differences from the above-mentioned systems. (i) It is the first time a tertiary phosphine has been added to a neutral platinum–diene system. (ii) As the PtN_4 metallacycle is retained, the complex does not, and cannot, become a four-coordinate dimeric species. (iii) Since the product IX results from attack by two nucleophiles, it contrasts with normally observed competition between attack at the metal and at the olefinic bond, giving products including only one nucleophile.[11m,q]

In studies concerned with the stereochemical pattern of these nucleophilic additions it has been pointed out that trans addition to coordinated dienes arises from intermolecular attack of the nucleophile to the η^2-C=C unit.[11r–u] The alternative mechanism, involving coordination of the nucleophile to the metal followed by intramolecular attack at the olefin, would lead to the cis product. It is therefore important that although there is a metal-coordinated PEt_3 group in IX the trans geometry of the nucleophilic addition suggests that it is an inter- rather than intramolecular mechanism that is operative.

The activation of coordinated olefins toward nucleophilic attack has been attributed to electron withdrawal from the olefin by the metal and the coligands.[11v,w] The olefin would then be more susceptible when the metal is a reluctant π back-donor and the coligands are strongly π accepting.

Table VI. ν(NC) Stretching Frequencies for $M(Ar_2N_4)(CN\text{-}t\text{-}Bu)_2$ Complexes[a]

M	Ar	ν(NC)	M	Ar	ν(NC)
Ni	$4\text{-}MeC_6H_4$	2168, 2146	Pt	$4\text{-}MeC_6H_4$ (V)	2214, 2186
	$4\text{-}ClC_6H_4$	2195, 2173		$4\text{-}ClC_6H_4$ (IV)	2219, 2188
				$4\text{-}NO_2C_6H_4$ (VI)	2228, 2204

[a] KBr pellets; in cm^{-1}.

In contrast, Eisenstein and Hoffmann[11x] argued that application of the Dewar–Chatt–Duncanson model for metal–olefin bonding should lead to a decreased sensitivity of the olefin toward nucleophilic attack on coordination. These authors proposed that olefin slipping plays the dominant role in nucleophilic activation. Although we have no way of evaluating the contribution of slipping modes in the activation of the η^2-C=C of the COD in $[Pt(Ar_2N_4)(COD)]$, the observation that nucleophilic attack by PEt_3 in the series Ar = $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}NO_2C_6H_4$ only occurs for the latter ligand indicates that an electronic effect dominates. The results from CNDO-S calculations[11y] on three $1,4\text{-}(4\text{-}XC_6H_4)_2N_4$ ligands (X = H, Cl, or NO_2), with the tetraazabutadiene geometry as found in IX, confirmed this pattern. Not only was the calculated affinity for one electron larger for NO_2 (4.87 eV) than for Cl (3.77 eV) and H (3.76 eV) but only the 4-NO_2 ligand showed a positive affinity for a second electron 1.51 eV).

Bonding in $[Pt(Ar_2N_4)L_2]$ Complexes. It has been pointed out that the isocyanide stretching frequencies in $[M(L)_n(RNC)_m]$ complexes can be used as a measure of electron transfer from the metal center to the coligands L.[12] In a series of related compounds ν(NC) will increase with increasing positive charge on the metal. The different electronic properties of nickel and platinum are reflected in the isocyanide stretching frequencies of their $[M(Ar_2N_4)(t\text{-}BuNC)_2]$ complexes (see Table VI). Although the $[Ni(Ar_2N_4)_2]$ complexes are best considered as Ni^0 species,[2a,3] the ν(NC) values of the corresponding isocyanide complexes are fairly high, indicating an appreciable electron transfer to the Ar_2N_4 system.[12c,d]

For the analogous platinum isocyanide complexes the values for ν(NC) are found to be considerably higher. By comparison with the data from other known bis(*tert*-butyl isocyanide)platinum complexes (ranging from 2030 cm^{-1} for $[(t\text{-}BuNC)_2Pt(PPh_3)_2]$ to 2270 cm^{-1} for $[(t\text{-}BuNC)_2Pt(CN)_2]$; see supplementary material)[12g–j] the $[Pt(Ar_2N_4)(t\text{-}BuNC)_2]$ complexes (IV–VI) are best described as approaching divalent platinum, with Ar_2N_4 as a formally dianionic ligand according to canonical form B (see Figure 3).

The validity of this description is clearly illustrated by the observed nucleophilic attack of PEt_3 on the COD ligand in III (vide supra).

Whereas separation of σ and π effects on the value of ν(NC) is not practicable,[13] there seem to be two ranges for the ^{13}C

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NMR shifts of the olefinic carbon atoms of the COD unit in symmetrically bonded [Pt(COD)L_2] complexes[14] (supplementary material).

One range, from 73.3 ppm (for [Pt(COD)$_2$] representing the platinum(0) extreme) to 91 ppm (for [Pt(COD)(1,4-diquinone)]) comprises complexes in which the chelate-bonded ligand has a strong π interaction with the metal. Within this range the shift reflects the electron-accepting properties of L_2. The other range starts at 98.8 ppm with [Pt(COD)Me$_2$] and features coligands L which bind to the metal without π interaction being an important factor. All compounds in this range contain formally platinum(II). With use of this sort of comparison both I and III can be seen to fall to the high end of the first range, their shift values of 86.5 and 90.0 ppm demonstrating high ligand electronegativity. The shift difference resulting from the change in aryl ring substituent from Cl (I) to NO_2 (III) is not large, $\Delta\delta(C) = 2.5$ but does parallel a significant change in chemical reactivity since only III is subject to nucleophilic attack. In this respect it is worth noting that $\Delta\delta$(C) between [Pt(COD)Me$_2$] and [Pt(COD)Cl$_2$] is only 1.8 yet nucleophilic attack on the olefin has only been reported for the latter. Although use of such ^{13}C NMR data to predict reactivity is premature, we note that a $\Delta\delta$(C) value of 5.9 ppm between I and its 1,4-diazabuta-1,3-diene analogue [Pt(R-DAB)(COD)] (R = 4-ClC$_6$H$_4$) parallels a large difference in chemical behavior, the tetraazabutadiene compound being air stable while [Pt(R-DAB)(COD)] shows extreme air sensitivity.[4,15]

XPS measurements of platinum compounds are known to give a very good indication of the oxidation state of the metal, with little or no overlap between the ranges for platinum in formal oxidation states 0, 2, and 4. Our results place complexes V, VI, and IX high up among platinum(II) complexes whose Pt(4f$_{7/2}$) binding energies (BE) normally range from ca. 72.3 to 74.8 eV.[16] Table IV shows a very small increase in BE on going from V (Ar = 4-MeC$_6$H$_4$) to VI (Ar = 4-NO$_2$C$_6$H$_4$). This observation illustrates that transfer of electron density from the coligands via the metal to the tetraazabutadiene moiety is probably the main effect, leaving the metal nearly unaffected. The lower figure for the Pt(4f$_{7/2}$) BE of IX probably reflects the presence of two PEt$_3$ groups and their electron-donating effect.

The fact that in the N(1s) band of IX a shake-up satellite was recorded +10 eV from the principal peak parallels similar observations in the spectra of [Ni(Ar$_2$N$_4$)(η^5-C$_5$H$_5$)][4] and metal–azo complexes.[16h]

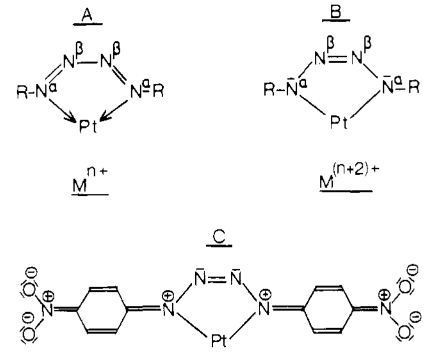

Figure 3. Two canonical forms A and B for the formal valence structure of the coordinated tetraazabutadiene ligand as well as one of the mesomeric structures of B involving the *p*-NO$_2$ substituents (C).

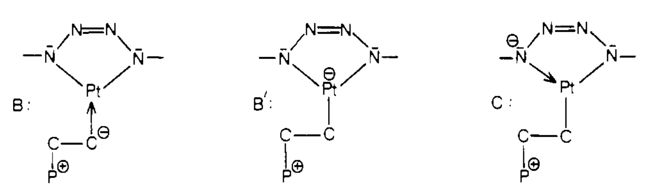

Figure 4. Canonical structures of the zwitterionic center. Forms A and A′ were reported in the literature.[11m,n]

Structure and Bonding in [Pt(1,4-(4-NO$_2$C$_6$H$_4$)$_2$N$_4$)-(CHC(PEt$_3$)H(CH$_2$)$_2$CH=CHCH$_2$CH$_2$)(PEt$_3$)] (IX). In the last decade several five-coordinate platinum–olefin complexes of general formula [PtCl$_2$(η^2-olefin)L$_2$] have been reported.[17] X-ray crystal structure determinations reveal generally a distorted-trigonal-bipyramidal configuration around the platinum with the chlorine atoms in the axial positions and the olefin and L$_2$ (bidentate N donor ligand) in the equatorial plane. Since five-coordinate species have been proposed as intermediates in associative ligand-exchange processes in the chemistry of platinum(II), the study of these complexes may lead to a better understanding of such processes.[18]

The five-coordinate platinum(II) complex IX differs from the complexes mentioned above in that the donor groups now occupy axial positions and the strongly electron-accepting grouping is in the equatorial plane. The reason for considering the tetraazabutadiene ligand as formally dianionic comes not only from the spectroscopic data and chemical reactivity (vide supra) of this and other Ar$_2$N$_4$ systems but also from the crystallographic data.

In the course of our investigations into (tetraazabutadiene)metal complexes we have advocated the description of these complexes according to canonical forms A and B (see Figure 3) for the formal valence structure of the tetraazabutadiene ligand.[2a] While the [Ni(Ar$_2$N$_4$)$_2$] complexes represent mainly form A (neutral ligand), IX is a representative of type B (dianionic ligand); this is evident from a short N$^\beta$–N$^\beta$ distance (1.263 (8) Å) and two long N$^\alpha$–N$^\beta$ distances (1.385 (7) and 1.391 (7) Å), making IX the most pronounced example of type B to date. The observed N–C(aryl) distances (1.351 (8) and 1.370 (8) Å against 1.427 (3) Å in [Ni(1,4-(3,5-

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$Me_2C_6H_3)_2N_4)_2]$) show the importance of additional mesomeric resonance structures involving the para NO_2 substituents (see Figure 3C), and this is the explanation that the aryl rings are found to be coplanar with the PtN_4 system. This finding contrasts with that reported for $[Ir(1,4\text{-}(4\text{-}FC_6H_4)_2N_4)(CO)(PPh_3)_2]BF_4$,[23] another example of tetraazabutadiene-metal bonding according to form B, in which the aryl rings were twisted out of the IrN_4 plane. As coplanarity of the rings is not primarily expected in canonical form B, this feature is only encountered if additional conjugation can occur. In the above-mentioned iridium complex the aryl substituent F only exerts an inductive effect, whereas the NO_2 in IX has a mesomeric effect. It should be noted that in this description it is the lone pairs of the N^α atoms and their interaction with the aryl systems that is important (as found in *N*,*N*-dimethyl-*p*-nitroaniline[19]) and not electron delocalization involving the MN_4 system.

A novel feature for platinum chemistry is the addition of a PEt_3 unit to a coordinated alkenic carbon atom in $[Pt(Ar_2N_4)(COD)]$, giving rise to a zwitterion: a phosphonium center and a carbanionic center, C(18), which upon coordination assumes a tetrahedral configuration (see Figure 2). Although it is obvious that the positive charge of the zwitterion resides at P(2), there are various possibilities for the location of the negative charge (see Figure 4). In systems so far studied the negative charge can be formally concentrated as shown in the canonical forms A and A′, which directly correspond to B and B′ for IX.[11m,n] However, in the present system a further possibility arises: C, in which the negative charge can be dissipated over both N^α–$C_6H_4NO_2$ systems.

The phosphonium type center is evident from the ^{31}P chemical shift of P(2) (δ 39.0; free PEt_3 δ −20[24]). This value is typical for cationic $(PEt_3R)^+$, as is illustrated by $\delta(^{31}P)$ of $(PEt_4)^+$ (40) as well as of $Me_3AuCH_2P^+Me_3$ (24)[20] vs. free PMe_3 (−62).[24]

The extreme donative C(18)–Pt bonding is clearly reflected by the two interconnected results arising from the corresponding large trans influence, i.e., the long Pt–P(1) bond of 2.376 (2) Å and the small value of $^1J(^{195}Pt-^{31}P)$ (1501 Hz). Their values fit very well into the correlation diagram given by Mather et al.[21] for a series of platinum–phosphine complexes. The Pt–C(18) distance (2.079 (6) Å) is not unusual and falls in the range normally encountered for this type of platinum–carbon sp^3 bond[11] (around 2.05 Å).

The η^2-C=C moiety is slightly twisted (14.9 (2)°) out of the PtN_4 plane; this may be due to the fact that C(13) and C(14) are bonded to the apically positioned C(18) via five- and six-membered rings, respectively (see Figures 1 and 2). It is interesting that the C–C olefinic distance (1.49 (1) Å) is comparable to the values found in other platinum(II)–olefin complexes,[11,17] confirming that the bonding is dominated by the ligands in the equatorial plane.[17a]

The Blue Color of IX. Judged by its color and extreme value of ϵ (5.2×10^4 at 605 nm) we orginally anticipated that IX would be a member of the "platinum blues".[22] This class of compounds has attracted considerable interest in recent years because of the potent antitumor activity exhibited by some of them.[22a,g] To date the "blues" have been shown to exist in oligomeric chains resulting from metal–metal interaction. However, complex IX illustrates the fact that strongly blue monomeric platinum(II) complexes are very well possible. In Figure 4 is already indicated a possible reason for the coloration since charge transfer in such species can be easily visualized. Current research shows that reactions of III with some other neutral or charged nucleophiles can likewise yield intensely colored products.

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Registry No. I, 78665-91-5; II, 78665-90-4; III, 78677-39-1; IV, 78665-92-6; V, 78665-88-0; VI, 78665-93-7; VII, 82080-88-4; VIII, 82080-89-5; IX, 82112-67-2; $Pt(COD)_2$, 12130-66-4; $Pt_3(t\text{-}BuNC)_6$, 60674-52-4.

Supplementary Material Available: Tables of structure factor amplitudes, thermal parameters, some relevant torsion angles, least-squares planes with deviations of atoms and dihedral angles between planes, IR spectroscopic and field desorption (FD) mass spectrometric data, NC stretching frequencies for Pt(*t*-BuNC) complexes, and ^{13}C NMR shifts of the olefinic carbon atoms in symmetrical $(COD)PtL_2$ complexes and an ORTEP stereodrawing of the structure of IX showing the thermal ellipsoids (50%) and a view of the central part of the complex IX as seen along P(1)–Pt (60 pages). Ordering information is given on any current masthead page.

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