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Contribution from Sterling Chemistry Laboratory,
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Structure and Bonding in 4,4'-Dinitro-*trans*-stilbenebis(triphenylphosphine)platinum, $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

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The crystal and molecular structure of a disubstituted olefin complex of platinum, $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)]$-$[P(C_6H_5)_3]_2$, has been determined from three-dimensional X-ray diffraction data. The complex crystallizes in space group $P\bar{1}$ of the triclinic system, with two molecules in a unit cell of dimensions $a = 12.955$ (3), $b = 15.012$ (3), $c = 11.169$ (3) Å; $\alpha = 96.65$ (1), $\beta = 97.93$ (1), $\gamma = 93.00$ (1)°. No symmetry is crystallographically imposed upon the molecules. The structural parameters were refined by least-squares techniques, the R factor on F converging to 6.6% for the 2785 independent reflections measured using a four-circle diffractometer for which $2\theta \leqslant 35°$. Coordination around platinum is approximately planar, the most significant distortion being the displacement of one olefinic carbon atom by 0.22 (1) Å from the plane defined by the other four atoms; the dihedral angle between the PtP_2 and PtC_2 planes is 8.7 (7)°. The olefinic carbon–carbon separation is 1.416 (15) Å and these carbon atoms are approximately equidistant from platinum, the Pt–C distances being 2.093 (14) and 2.165 (12) Å. The Pt–P bond lengths are 2.261 (4) and 2.298 (4) Å, which differ significantly, the longer being trans to the shorter Pt–C separation. Both 4-nitrophenyl substituents are almost exactly perpendicular to the PtC_2 plane, the dihedral angles being 86.6 (6) and 87.5 (4)°. This perpendicular orientation maximizes electron withdrawal by π-symmetry orbitals of the substituents. So that hydrogen–hydrogen contacts within the olefin do not become impossibly short in this perpendicular orientation, it is necessary for the olefin substituents to be bent away from platinum to different extents, the observed angles being 33 (2) and 5 (2)°; electronic effects stemming from this difference may be the cause of the asymmetry in the bond lengths to platinum.

Introduction

Many olefin-platinum complexes of the general formula $Pt[L][P(C_6H_5)_3]_2$, where L is the olefin, have been prepared[1,2] and X-ray diffraction studies have delineated the overall structural characteristics of this class of compounds.[3-8] The olefinic carbon atoms are approximately equidistant from platinum and the olefinic carbon–carbon separation increases upon coordination to platinum, reported values ranging from 1.42 to 1.62 Å. However, some of the diffraction experiments were of relatively low precision and crystallographic disorder was a problem in other cases: consequently, few of these carbon–carbon separations differ significantly from each other. In order to elucidate the relationships between the electronic effects of the substituents upon the olefin and the changes in olefin geometry that occur upon coordination, we intend to determine the structures of a number of complexes formed by olefins with extreme properties.

The olefins that bind most strongly to platinum have substituents that are electron withdrawing in a π fashion and 4,4'-dinitro-*trans*-stilbene, I, is one of the most strongly bound olefins of all.[1] A study of the complex formed by I has the particular advantage that the olefin must adopt a sterically unfavorable conformation for optimum use to be made of the electron-withdrawing ability of the substituents. The plane of each 4-nitrophenyl ring must be perpendicular to the plane defined by the platinum and two olefinic carbon atoms for maximum overlap of the π-symmetry orbitals. Such an orientation causes the ortho hydrogen atoms of each substituent ring to be at a minimum separation from the hydrogen atoms on the olefinic carbon atoms. Thus the operation of the electron-withdrawing mechanism will be made manifest by the otherwise unfavored orientation of the substituents. Furthermore, the derived olefinic C–C separation will provide a bench-mark value for comparisons with other results, particularly since, as it will be seen, a precise value is obtained.

Experimental Section

Preparation of the Crystals. The literature method[1] was modified slightly in order to obtain crystals of sufficient size (rather than to maximize product yield). The reaction was performed under nitrogen using Schlenk apparatus. $PtCl_2[P(C_6H_5)_3]_2$, 0.20 g dissolved in 7 ml of ethanol, was heated to 60° in the reaction flask, and hydrazine hydrate, 0.3 ml, was added to give a clear, colorless solution. 4,4'-Dinitro-*trans*-stilbene, 0.10 g dissolved in 30 ml of ethanol, was heated to 60° and added slowly to the reaction mixture. The clear orange-red solution was permitted to cool to room temperature very slowly, whereupon thin, platelike crystals of the product, $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$, formed.

Collection and Reduction of X-Ray Diffraction Data. Optical examination and preliminary X-ray photography revealed no symmetry and the crystal was assigned to the triclinic system. Successful refinement of the structure confirmed the initial assumption of $P\bar{1}$ for the space group. The cell constants, obtained by least-squares refinement using the setting angles of 12 reflections centered on a Picker four-circle automatic diffractometer with Mo $K\alpha_1$ X-radiation

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(λ 0.70930 Å), are (at 20°) a = 12.955 (3),[9] b = 15.012 (3), c = 11.169 (3) Å; α = 96.65 (1), β = 97.93 (1), γ = 93.00 (1)°. A Delauney reduction confirmed this choice of cell. For two formula weights of the molecule in the unit cell, the calculated density is 1.56 g/cm^3; the observed density (by flotation) is 1.51 g/cm^3. No symmetry is crystallographically imposed upon the molecules.

The crystal used in data collection was a fragment of a larger platelet. The crystal was bounded by the faces 100, $\bar{1}00$, 010, $00\bar{1}$, and $0\bar{4}5$ (the last three of these being only approximate and chosen to best represent the crystal shape); the lengths of the normals to the faces to a convenient origin were 0.00, 0.022, 0.00, 0.28, and 0.00 mm, respectively. The crystal was initially aligned about the a axis of the cell and was misset before data collection. The diffraction intensity data were collected using a Picker four-circle automatic diffractometer in the ω–2θ scan mode with crystal-monochromated Mo Kα X-radiation. A symmetric scan of 1.0° in 2θ was used with a scan rate of 1°/min. Stationary-crystal, stationary-counter background counts of 10 sec were measured at each end of the scan. The intensities of the symmetry-equivalent reflections $\overset{\pm}{h}\overset{\pm}{k}l$ and $\bar{h}\overset{\pm}{k}\overset{\pm}{l}$ were recorded out to a 2θ value of 25° and those of the reflections $h\overset{\pm}{k}\overset{\pm}{l}$ out to a 2θ value of 35°. The intensities of three standard reflections were measured at intervals throughout data collection; these intensities steadily decreased and, at the conclusion of the experiment, the losses averaged about 15% of the original intensity.

The data were corrected for background and the changes in the standard reflections. The linear absorption coefficient is 32.3 cm^{-1} and corrections were applied,[10] the transmission coefficients ranging between 0.54 and 0.74. The equivalent reflections were averaged and the R factor of averaging [$R_{av} = 100(I_1 - I_2)/(I_1 + I_2)$, where I_1 and I_2 are the two corrected intensities] was 4.6% for those 682 reflections classed as observed and measured more than once. The independent reflections were corrected for Lorentz-polarization effects. Individual standard deviations, $\sigma(F^2)$, of the corrected intensities were calculated both from counting statistics and from the range of symmetry-equivalent reflections; the larger of these two estimates was assigned to the reflection. A total of 3777 reflections were measured and processed. There were 2785 independent reflections, of which 1834 could be classed as observed using the criterion that at least one of the measured net intensities be greater than 3 times the estimated standard deviation, calculated from counting statistics, of the total background counts.

Solution and Refinement of the Structure. Initial values of the atomic coordinates of the platinum atom were obtained from a three-dimensional Patterson function.[10] Succeeding applications of least-squares refinement and difference Fourier calculations yielded the coordinates of all nonhydrogen atoms, the carbon atoms of the phenyl and phenylene rings being refined as groups. The scattering factors were calculated using analytical approximations for neutral atoms[11a] and the effects of anomalous dispersion[11b] were included in F_c. The function minimized in refinement was $\Sigma w||F_o| - |F_c||^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Isotropic thermal parameters were used for all atoms, with only one overall thermal parameter for each group, and the R factor (on F) converged to 5.7% for the 1834 reflections classed as observed. The platinum, phosphorus, nitrogen, and oxygen atoms were then refined with anisotropic thermal parameters and the group carbon atoms with individual isotropic thermal parameters, the R factor decreasing to 5.0% after two cycles.

There was a systematic and chemically reasonable variation of the individual thermal parameters of the group atoms: the C(1) atoms had the lowest thermal parameters, the C(2) and C(6) atoms the next lowest, and the C(3), C(4), and C(5) atoms the highest thermal parameters. In order to reduce the number of variables in subsequent cycles of refinement, advantage was taken of this observation. An overall thermal parameter was defined (and subsequently refined) for each group and the differences (not subsequently varied) from this overall parameter for each of the positions around the ring were averaged for all of the rings. The mean values for the differences from the overall thermal parameters, with the estimated standard deviation (esd) of the *sample* given in parentheses, are as follows (Å^2): C(1), −1.1 (4); C(2) and C(6), −0.04 (4); C(3) and C(5), 0.6 (7); C(4), 0.4 (6). This process is equivalent to obtaining an estimate of the average ring librations in this particular crystal and that this is statistically reasonable is shown by comparison of the above sample esd's with the esd's of the individual group atom thermal parameters obtained from the inverse matrix, which averaged 0.7 Å^2.

The scattering of the hydrogen atoms of the phenyl and phenylene groups was calculated by assuming an idealized group geometry with a C–H bond length of 0.95 Å. The thermal parameters of the hydrogen atoms were set to 0.3 Å^2 higher than the carbon atoms to which they are bound. After one cycle of refinement, the R factor was 4.3%. A difference Fourier revealed maxima in the residual electron density at positions appropriate for the olefinic hydrogen atoms, whose scattering was included in subsequent calculations from fixed positions determined as follows: H(1) at 0.95 Å from C(1) with Pt–C(1)–H(1) = 116.5° and C(2)–C(1)–H(1) = 121.4°; H(2) at 0.95 Å from C(2) with Pt–C(2)–H(2) = 109.8° and C(1)–C(2)–H(2) = 125.5° (these angles equal the corresponding angles to the geminal carbon atoms). After two further cycles of refinement, the R factor was 3.8% for the 1834 "observed" reflections. The weighted R factor, $R_w = (\Sigma w(F_o - F_c)^2/wF_o^2)^{1/2}$, was 4.3% and the error in an observation of unit weight was 0.90. Two further cycles of refinement were performed using all 2785 reflections with $F^2 \geqslant 0$. The final values of the R factor and weighted R factor were 6.6 and 4.2% and the error in an observation of unit weight was 0.81. No parameter changed by more than one-tenth of its esd in the final cycle. A final difference Fourier showed no peaks higher than 0.3 e Å^{-3}.

The final values of the positional and thermal parameters for the nongroup atoms and their standard deviations calculated from the inverse matrix are given in Table I. The phenyl and phenylene ring atoms were refined as groups and the parameters are given in Table II. Table III lists the fractional coordinates (derived from the group parameters) and the thermal parameters for the carbon atoms in all groups. Table IV gives the root-mean-square amplitudes of vibration for those atoms refined with anisotropic thermal parameters; for the atoms of the nitro groups the angles made by the principal axes of vibration to vectors structurally significant for those atoms are given.[12]

Description of the Structure

The crystal structure consists of the packing of the monomeric molecular units $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)]$-$[P(C_6H_5)_3]_2$; there are no exceptionally short intermolecular contacts. An important feature of the structure is the C(1)–C(2) internuclear distance of 1.416 (15) Å, which is not exceptionally long for an olefin complex of this type. The C(1)–Pt–C(2) angle is 38.8 (4)° and the P(1)–Pt–P(2) angle is 109.5 (1)°, neither being unusual. An overall view of the molecule is given in Figure 1. Each triphenylphosphine ligand has adopted the customary propellor-like conformation of phenyl rings. The vibrational parameters of the atoms in the coordinated olefin can be seen to be reasonable. The magnitude of vibration increases in going from the atoms nearest the heavy metal atom to the extremities of the olefin moiety. The directions of maximum vibration of the nitrogen and oxygen atoms are given in Table IV. The nitrogen atoms vibrate to a maximum extent normal to their bonds to the phenylene rings. There is an apparent difference between the vibrations of the two nitro groups; the first, N(1), O(1), O(2), vibrates more in the plane of Ph(1), whereas the second, N(2), O(3), O(4), vibrates principally normal to the plane of Ph(2). The calculated N–O bond lengths range from 1.16 (2) to 1.26 (2) Å and average 1.20 Å, and the thermal motion corrections calculated using the riding model average 0.05 Å. The nitro groups in the para positions of the substituent rings are very approximately coplanar with those rings, the calculated internormal angles being 16 (2) and 7 (2)° for substituents 1 and 2, respectively. The geometry of the

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(9) The numbers in parentheses here and elsewhere in this paper are estimated standard deviations in units of the last digit.

(10) Calculations were performed on an IBM 370/158 computer and the programs used included modified versions of Zalkin's FORDAP, Busing, Martin, and Levy's ORFLS (with the Doedens and Ibers subroutines for group refinements) and ORFFE, Johnson's ORTEP, and Coppens and Hamilton's DATTAP.

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(12) See paragraph at end of paper regarding supplementary material.

Table I. Positional and Thermal Parameters for the Nongroup Atoms in $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

Atom	x	y	z	B, Å^2, or β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	−0.15924 (5)	−0.25121 (4)	0.09584 (6)	0.00624 (6)	0.00407 (4)	0.00684 (8)	0.00085 (3)	0.00155 (5)	0.00063 (4)
P(1)	−0.3092 (3)	−0.3447 (3)	0.0628 (4)	0.0084 (4)	0.0045 (3)	0.0088 (5)	0.0013 (3)	0.0032 (4)	0.0014 (3)
P(2)	−0.1951 (3)	−0.1119 (3)	0.1721 (4)	0.0090 (4)	0.0039 (3)	0.0084 (5)	0.0005 (3)	0.0018 (4)	0.0009 (3)
O(1)	0.2036 (15)	−0.2364 (11)	0.6579 (13)	0.0235 (23)	0.0137 (14)	0.0132 (22)	0.0025 (13)	−0.0022 (17)	0.0016 (13)
O(2)	0.3320 (13)	−0.1705 (12)	0.5887 (18)	0.0151 (20)	0.0121 (14)	0.0256 (25)	0.0025 (14)	−0.0105 (21)	−0.0026 (13)
O(3)	−0.1334 (13)	−0.3872 (10)	−0.5372 (11)	0.0263 (20)	0.0139 (14)	0.0069 (17)	−0.0015 (13)	0.0026 (15)	0.0024 (11)
O(4)	−0.1546 (17)	−0.5228 (11)	−0.5039 (14)	0.0393 (29)	0.0083 (12)	0.0154 (21)	0.0022 (16)	−0.0010 (18)	−0.0017 (14)
N(1)	0.2483 (17)	−0.2051 (15)	0.5769 (21)	0.0141 (28)	0.0091 (17)	0.0157 (32)	0.0047 (18)	−0.0047 (26)	0.0009 (17)
N(2)	−0.1306 (16)	−0.4446 (14)	−0.4710 (15)	0.0199 (21)	0.0090 (16)	0.0068 (24)	0.0015 (17)	−0.0005 (17)	0.0011 (16)
C(1)	0.0029 (11)	−0.2497 (9)	0.1005 (12)	4.3 (4)					
C(2)	−0.0386 (10)	−0.3354 (9)	0.0421 (12)	3.6 (3)					
H(1)[b]	0.0335	−0.2070	0.0568	4.6					
H(2)[b]	−0.0406	−0.3888	0.0802	3.9					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] None of the parameters for this atom were varied in the refinement.

Table II. Group[a] Parameters[b] in $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

Group	x_c	y_c	z_c	δ	ϵ	η
Ph(1)	0.1251 (5)	−0.2281 (4)	0.3407 (6)	2.401 (7)	−2.759 (7)	1.989 (6)
Ph(2)	−0.0816 (4)	−0.3904 (4)	−0.2168 (6)	−0.210 (5)	2.927 (7)	−1.748 (5)
1A	−0.2434 (4)	−0.5486 (4)	0.0663 (5)	−1.285 (13)	−2.117 (5)	−0.023 (12)
1B	−0.4788 (5)	−0.3243 (4)	0.2488 (5)	0.155 (6)	2.905 (6)	2.284 (6)
1C	−0.4432 (6)	−0.3413 (3)	−0.2048 (6)	−1.554 (7)	2.606 (8)	−1.745 (6)
2A	−0.3152 (5)	−0.1150 (4)	0.4066 (6)	−2.690 (6)	−3.013 (8)	1.084 (6)
2B	−0.3380 (5)	−0.0058 (5)	−0.0182 (6)	2.745 (8)	2.628 (7)	−0.707 (7)
2C	0.0054 (5)	0.0272 (4)	0.2608 (6)	−1.129 (6)	2.803 (8)	−1.253 (6)

[a] The groups are either phenyl or phenylene rings and each set of six parameters applies to the carbon and to the hydrogen atoms of that ring. [b] The parameters have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

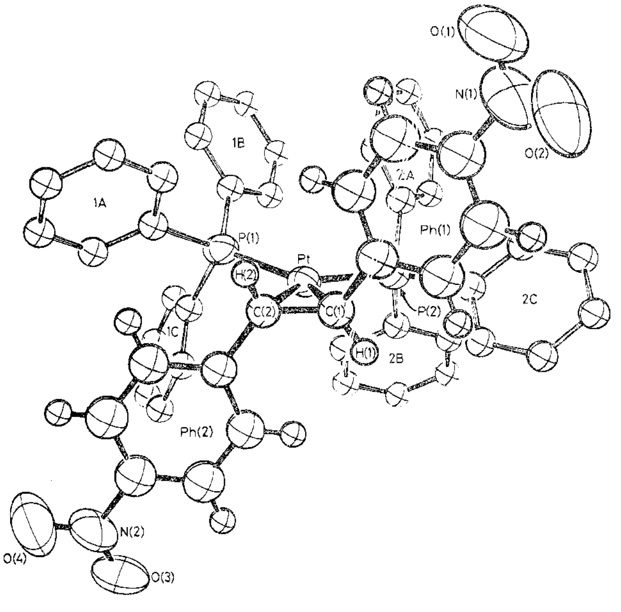

Figure 1. General view of a molecule of $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$. The atoms are represented by 50% probability ellipsoids, except the carbon atoms of the triphenylphosphine ligands and the hydrogen atoms of the olefin which have been assigned artificially low thermal parameters for the purpose of clarity. The hydrogen atoms of the triphenylphosphine ligands are omitted. The ring nomenclature is specified in this figure.

substituents is generally similar to that in 1,1-bis(4-nitrophenyl)ethylene.[13]

The dihedral angle between the Pt, C(1), C(2) and the Pt, P(1), P(2) planes (the PtC_2 and PtP_2 planes) is 8.7 (7)°; an alternative description of this deviation from coplanarity is given by the displacements of C(1) and C(2) from the PtP_2 plane, which are 0.22 (1) and 0.03 (1) Å, respectively, *i.e.*, the distortion is due almost completely to the displacement of C(1) from the essentially coplanar atoms Pt, P(1), P(2), C(2). Such distortions are common in complexes of this general type, but no specific chemical significance can yet be associated with individual variations in these deviations.

Figure 2 shows the coordination sphere around platinum and gives a revealing view of the coordinated olefin moiety; the viewpoint is normal to the PtC_2 plane and above the centroid of the Pt, C(1), C(2) triangle. Clearly the planes of both substituent rings are almost exactly perpendicular to the PtC_2 plane: 86.8 (6) and 87.5 (4)° are the angles between the PtC_2 plane and the Ph(1) and Ph(2) planes respectively. This arrangement must bring the hydrogen atoms on the olefinic carbon atoms to a minimum separation from hydrogen atoms on the phenylene rings. This structure report provides no information about the actual distances between these atoms, since the hydrogen atom positions were not refined. However, the positions assumed for the olefinic hydrogen atoms (see Table I) are at distances greater than 2.0 Å from any phenylene ring atom: the shortest contacts (both ~2.05 Å) are to the C(1) atoms of the geminal substituents and the other closest contacts are ~2.2 Å to the H(2) atoms of the vicinal substituents and ~2.3 Å to the H(6) atoms of the geminal substituents. While these separations are not derived experimentally, they do show that impossibly short contacts can be avoided even with this arrangement of substituent rings.

There is a marked difference in the extent to which the olefin substituents are bent away from the metal, which is apparent in Figure 2. Substituent 1 is bent back to a considerable extent, whereas substituent 2 is scarcely bent back at all; the angles between the olefinic carbon-carbon vector and the normals to the phenylene rings are 57 (2) and 85 (2)°, respectively. This difference can also be expressed by the displacements of the olefinic carbon atoms, C(1) and C(2), from the planes of the phenylene rings, which are 0.03 (2) and 0.75 (3) Å from Ph(1) and 0.06 (3) and 0.07 (2) Å

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[13] G. Cassalone and M. Simonetta, *J. Chem. Soc. B*, 1180 (1971).

Table III. Thermal Parameters and Derived Fractional Coordinates of Phenyl Group Carbon Atoms in $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

Ring	Atom	*B*, Å²	*x*	*y*	*z*
Ph(1)	C(1)	4.3	0.0671	−0.2387	0.2238
	C(2)	5.0	0.0381	−0.2876	0.3129
	C(3)	6.0	0.0958	−0.2769	0.4286
	C(4)	5.8	0.1822	−0.2176	0.4559
	C(5)	6.0	0.2118	−0.1688	0.3685
	C(6)	5.0	0.1546	−0.1791	0.2526
Ph(2)	C(1)	3.8	−0.0580	−0.3628	−0.0914
	C(2)	4.5	−0.0510	−0.3018	−0.1743
	C(3)	5.5	−0.0744	−0.3295	−0.2985
	C(4)	5.3	−0.1049	−0.4176	−0.3405
	C(5)	5.5	−0.1121	−0.4787	−0.2594
	C(6)	4.5	−0.0888	−0.4517	−0.1350
1A	C(1)	3.3	−0.2763	−0.4615	0.0622
	C(2)	4.0	−0.2134	−0.4831	0.1638
	C(3)	5.0	−0.1810	−0.5696	0.1673
	C(4)	4.8	−0.2109	−0.6345	0.0702
	C(5)	5.0	−0.2732	−0.6139	−0.0308
	C(6)	4.0	−0.3061	−0.5277	−0.0353
1B	C(1)	3.6	−0.4051	−0.3348	0.1685
	C(2)	4.3	−0.4563	−0.2564	0.1815
	C(3)	5.3	−0.5293	−0.2463	0.2612
	C(4)	5.1	−0.5516	−0.3140	0.3280
	C(5)	5.3	−0.5015	−0.3919	0.3160
	C(6)	4.3	−0.4283	−0.4026	0.2365
1C	C(1)	4.8	−0.3879	−0.3442	−0.0884
	C(2)	5.5	−0.3358	−0.3416	−0.1883
	C(3)	6.4	−0.3909	−0.3387	−0.3034
	C(4)	6.3	−0.4977	−0.3385	−0.3194
	C(5)	6.4	−0.5502	−0.3411	−0.2214
	C(6)	5.5	−0.4957	−0.3439	−0.1060
2A	C(1)	5.1	−0.2637	−0.1119	0.3046
	C(2)	5.9	−0.2494	−0.1806	0.3766
	C(3)	6.8	−0.3006	−0.1834	0.4775
	C(4)	6.6	−0.3659	−0.1181	0.5071
	C(5)	6.8	−0.3808	−0.0497	0.4367
	C(6)	5.9	−0.3300	−0.0463	0.3355
2B	C(1)	4.9	−0.2747	−0.0507	0.0639
	C(2)	5.6	−0.3379	−0.0981	−0.0355
	C(3)	6.5	−0.4005	−0.0533	−0.1166
	C(4)	6.4	−0.4003	0.0385	−0.0992
	C(5)	6.5	−0.3382	0.0863	−0.0012
	C(6)	5.6	−0.2753	0.0421	0.0804
2C	C(1)	5.0	−0.0836	−0.0320	0.2250
	C(2)	5.7	−0.0110	−0.0217	0.1468
	C(3)	6.7	0.0771	0.0371	0.1826
	C(4)	6.5	0.0931	0.0856	0.2961
	C(5)	6.7	0.0219	0.0760	0.3744
	C(6)	5.7	−0.0664	0.0174	0.3393

Table IV. Root-Mean-Square Amplitudes and Directions of Vibration (Å) along Principal Axes for $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

Pt	0.197 (1)	0.211 (1)	0.233 (1)	
P(1)	0.208 (8)	0.217 (7)	0.279 (7)	
P(2)	0.206 (7)	0.224 (7)	0.273 (7)	
O(1)	0.27 (2)	0.39 (2)	0.46 (2)	[40 (6),^{i} 18 (10)^{ii}]^{a}
O(2)	0.24 (3)	0.35 (2)	0.52 (2)	[49 (4),^{i} 22 (9)^{ii}]
O(3)	0.20 (3)	0.38 (2)	0.48 (2)	[75 (7),^{i} 77 (8)^{ii}]
O(4)	0.27 (2)	0.35 (2)	0.58 (2)	[77 (4),^{i} 102 (9)^{ii}]
N(1)	0.22 (4)	0.31 (3)	0.43 (4)	[87 (8),^{iii} 19 (11)^{iv}]
N(2)	0.20 (4)	0.32 (3)	0.41 (2)	[89 (6),^{iii} 108 (13)^{iv}]

[a] Angles (deg) between axis of maximum amplitude of vibration and (i) N–O bond axis, (ii) O–O vector of nitro-group, (iii) axis of bond from N to C(4) of phenylene group, and (iv) plane of phenylene ring.

from Ph(2), respectively. The essential coplanarity of C(1) and C(2) with Ph(2) is further emphasized in Figure 3, for which the direction of view is the C(1)-C(2) vector. The torsion angles Pt-C(1)-C(2)-Ph(2)C(1) and Pt-C(2)-C(1)-Ph(1)C(1) are 99 (1) and 111 (1)°, respectively. It is, therefore, clear that there are differences of high statistical significance between arrangements of the olefin substituents, and to determine whether there are other statistically significant differences, it is convenient to make comparisons between the halves of the molecule related by a (approximate) twofold axis passing through Pt and the midpoint of the C(1)-C(2) vector. Table V lists bond lengths and angles selected in this context and gives the difference between comparable parameters along with the esd of the difference.

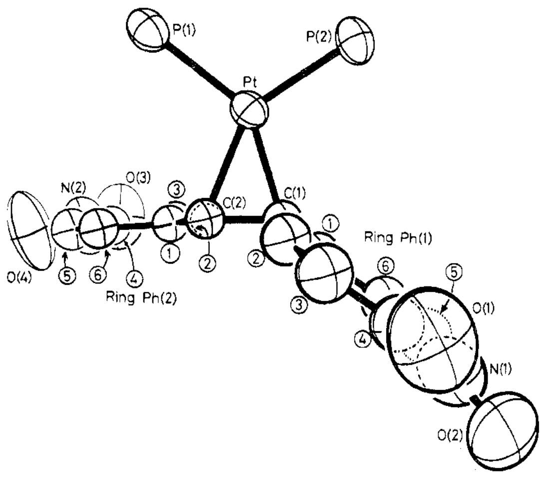

Figure 2. $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$ from a viewpoint normal to the PtC_2 plane and above the centroid of the Pt, C(1), C(2) triangle. The carbon atoms of the triphenylphosphine ligands and all of the hydrogen atoms have been omitted. The other atoms are represented by 50% probability ellipsoids. The atoms obscured by O(1) and C(2) are indicated by noncontinuous outlines; this is not done for other obscurations. The atom nomenclature is specified in this figure and that of the carbon atoms around rings Ph(1) and Ph(2) is indicated by the circled numbers.

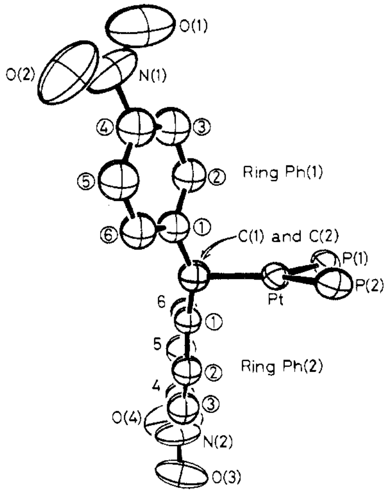

Figure 3. $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$ viewed along the C(1)-C(2) vector, including the same atoms as in Figure 2.

The Pt-C(1) separation is significantly shorter than the Pt-C(2) separation. As has been observed before in related systems,[6,14] the bond trans to a relatively long bond is relatively short: the Pt-P(2) bond length is shorter than the Pt-P(1) bond length, the difference being of very high statistical significance.

The directions of the principal axes of vibration of the platinum and two phosphorus atoms are indicated in Figures 1-3. None of these atoms vibrate with great anisotropy and the corrections to the Pt-P bond lengths calculated using the riding model are small, 0.003 Å for Pt-P(1) and 0.006 Å for Pt-P(2), and do not alter the conclusion that Pt-P(1) is

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[14] J. A. McGinnety, *J. Chem. Soc., Dalton Trans.*, 1038 (1974).

Table V. Comparison of Parameters in $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

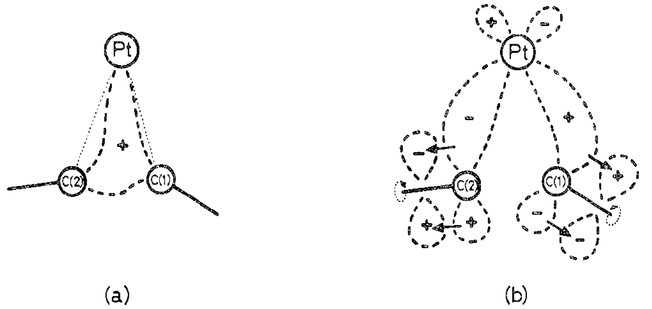
Parameter 1		Parameter 2		Difference (parameter 1 – parameter 2)
		(a) Bond Lengths, Å		
Pt-P(1)	2.298 (4)	Pt-P(2)	2.261 (4)	0.037 (6)
Pt-C(2)	2.165 (12)	Pt-C(1)	2.093 (14)	0.073 (20)
C(2)-Ph(2)C(1)	1.483 (14)	C(1)-Ph(1)C(1)	1.494 (15)	−0.011 (21)
		(b) Bond Angles, Deg		
P(1)-Pt-C(2)	105.0 (4)	P(2)-Pt-C(1)	106.9 (4)	−1.9 (5)
Pt-C(2)-C(1)	67.8 (8)	Pt-C(1)-C(2)	73.4 (8)	−5.6 (15)
Pt-C(2)-Ph(2)C(1)	109.8 (8)	Pt-C(1)-Ph(1)C(1)	116.5 (9)	−6.6 (13)
C(1)-C(2)-Ph(2)C(1)	125.5 (12)	C(2)-C(1)-Ph(1)C(1)	121.4 (12)	4.2 (15)

significantly longer than Pt-P(2). The bond lengths from P to C(1) of the phenyl rings range from 1.82 (1) to 1.85 (1) Å and average 1.83 Å, and the angles subtended to phosphorus by these carbon atoms are in the range 101.7 (7)-106.0 (7)° and average 103.6°.

Bonding in $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

It has been recognized[1] that the olefin is bound strongly to the metal in this compound and its structure was determined to reveal to what extent the substituents on the olefin utilize their electron-withdrawing ability and how this affects the overall metal-olefin geometry, including the separation of the olefinic carbon atoms. A three-center molecular orbital scheme (similar to that proposed for dioxygen[15] and acetylene[14] complexes) can be used to describe the basic metal-olefin interaction and the effects of substituents upon the olefin can then be rationalized by seeing how the three-center orbitals would be affected by the substituents. The three bonds (occupied molecular orbitals) comprising the basic metal-olefin interaction can be simplistically described as donation from the olefin π bond to the metal (X, Figure 4a), a modified σ bond linking the olefinic carbon atoms (Y), and back-donation from an occupied metal d orbital to the olefin π^* orbital (Z, Figure 4b). The substituents withdraw electrons using π-symmetry orbitals and, among the above three bonds, only Z is of correct symmetry to interact. Both substituents are found to be perpendicular to the PtC_2 plane and thus they interact to the maximum extent possible with Z; Figure 4b illustrates how rotation of a substituent ring is hindered by interaction of its π-symmetry orbitals with Z and how the perpendicular orientation would optimize this interaction.

The substituents are bent back from the metal to different degrees; it is in this way that the molecule achieves a configuration in which the hydrogen-hydrogen contacts are not impossibly short. The substituents must be powerful electron-withdrawing groups for the energy gained in achieving the perpendicular orientation to be sufficient to cause this asymmetric olefin geometry. In $Ni[(C_6H_5)CHCH(C_6H_5)][P(C_6H_4CH_3)_3]_2$,[16] the olefin substituents are less electron withdrawing in character and they adopt an alternative way of avoiding close H-H contacts, in that the substituents are significantly twisted away from being perpendicular to the NiC_2 plane. This facile way of relieving the steric strain is not utilized in the nitrostilbeneplatinum complex in order to maximize withdrawal of electrons from orbital Z. Since Z is bonding with respect to the platinum to olefinic carbon directions, this should result in long Pt-C internuclear distances and these distances in the nitrostilbene complex are indeed relatively long: the average value of 2.13 Å can be compared with averages of 2.04 and 2.11 Å for the analogous tetrachloroethylene[5] and tetracyanoethylene[4] complexes, respectively. It can be deduced that considerable back-donation from platinum to the olefin π^* orbitals has occurred and that much of this electron density does not remain in the region between the platinum and two olefinic carbon atoms but is removed to more remote parts of the olefin substituents. It is important to distinguish between the total electron transfer from the metal to the olefin (back-donation) and the occupancy of orbital Z (in the PtC_2 region), because the strength of the total metal-olefin interaction is a function of the former and the extent to which the substituents are bent back is a function of the latter (in sterically unhindered cases).



(a) (b)

Figure 4. Two of the three-center molecular orbitals used, as a first approximation, to describe the olefin-metal interaction in $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$. The shapes of the orbitals are indicated by broken lines. (a) Construction from three σ-symmetry atomic orbitals, one from each atom. The direction of each carbon atomic orbital is defined by the bond vector from the substituent to that atom. The molecular orbital is asymmetric because the substituents are bent back to a different extent on the two carbon atoms; this asymmetry is emphasized by the straight dotted lines drawn from platinum to the two carbon atoms. (b) Construction from a platinum d orbital and a p orbital from each of the carbon atoms. The degree of electron withdrawal from this molecular orbital by a π-symmetry orbital of a substituent (indicated here simply by a p-orbital shape) is dependent upon the orientation of the substituent orbital. Rotation about the carbon-substituent bond axis (indicated by the dotted elliptical arrow) is hindered by this interaction.

The asymmetry induced within coordinated nitrostilbene by adoption of the energetically favored orientation of the substituents and the necessity to maintain reasonable H-H contacts also results in asymmetry in the interaction between the olefin and the metal. The three-center orbital X is constructed from σ-symmetry orbitals, the directions of which are determined by the positions of the substituents upon the olefin and the other ligands coordinated to platinum. In Figure 4a, the positions of the platinum and olefinic carbon atoms are to scale for the nitrostilbene complex; the solid lines emanating from C(1) and C(2) are the projections

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[15] J. A. McGinnety, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One,* 1, 5, 229 (1972).

[16] S. D. Ittel and J. A. Ibers, *J. Organometal. Chem.,* 74, 121 (1974).

of the bond vectors linking these atoms to the substituent rings. X is asymmetric with respect to the PtC_2 triangle, the greater portion lying nearer the Pt-C(1) vector, and it is this that causes the Pt-C(1) separation to be significantly shorter than the Pt-C(2) separation.

The Pt-P bond lengths observed in this compound can be considered in terms of the lengths of all Pt-P bonds in four-coordinate planar platinum complexes (including complexes of the type $\mathrm{Pt[un][P(C_6H_5)_3]_2}$, where un is an unsaturated species such as carbon disulfide or an olefin) that have been determined by X-ray diffraction to a reasonable degree of precision (the criterion adopted here is that the esd in the Pt-P bond length be <0.01 Å).[17] There are 23 compounds included in this analysis with 47 crystallographically independent Pt-P bond lengths. The mean bond length is 2.283 Å and the standard deviation in the sample is 0.026 Å; the third and fourth moments of the sample are not significantly different from zero, providing evidence that the distribution is approximately normal. Important reference points in the sample are given by the compounds *trans*-$\mathrm{Pt(ISO_2)(CH_3)[P(C_6H_5)_3]_2}$[18] and $\mathrm{\overline{PtCH_2CH_2CH_2CH_2}[P(C_6H_5)_3]_2}$[19] for which the mean Pt-P bond lengths are 2.305 and 2.282 Å, respectively. In the former compound, the two phosphine ligands are mutually trans and the mean Pt-P bond length is longer than in the latter compound (which is very close to the mean of the sample), in which each phosphine is trans to a normal Pt-C σ bond; this is consistent with the observation that phosphine ligands are better trans-labilizing groups than alkyl ligands.[20] From an observed Pt-P bond length, information can be gained about the electron density in the region trans to that bond by utilizing the perception of the nature of the Pt-P interaction in which the predominant contribution is σ donation to the metal.[21] In the nitrostilbene complex, the longer Pt-P bond length is 2.298 Å, somewhat longer than the mean of the sample, indicating an electron density in the Pt-C(1) region slightly greater than in a single Pt-C σ bond; the converse holds true for the shorter Pt-P bond. This is consistent with the bonding model illustrated in Figure 4 and discussed above.

The olefinic carbon-carbon separation is 1.416 (15) Å, which can be compared with values of 1.49 (5) and 1.62 (3) Å for the analogous tetracyanoethylene[4] and tetrachloroethylene[5] complexes, respectively. The olefins with substituents electron withdrawing in a π sense have relatively short olefinic carbon-carbon separations and it is these olefins that are bound most strongly to platinum in these complexes; considerable back-donation from platinum to the olefin has occurred, but the electrons do not remain in Z (which is antibonding with respect to the two carbon atoms); they are withdrawn from this orbital by the substituents, thereby increasing the order of the C-C linkage. The tetrachloroethylene substituents are electron donating in a π sense and thus there is considerable electron density in Z, localized in the PtC_2 region, which will lower the order of, and hence lengthen, the C-C linkage.

Registry No. $\mathrm{Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2}$, 52760-70-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2864.

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(17) A convenient compilation of references, from which this sample was partially obtained, is that of I. D. Brown, *et al.*, Bond Index to the Determination of Inorganic Crystal Structures, Institute for Materials Research, McMaster University, 1969-1972.

(18) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, 12, 224 (1973).

(19) C. G. Biefeld, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, 12, 2166 (1973).

(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(21) L. M. Venanzi, *Chem. Brit.*, **4**, 162 (1968).