Table VIII. Valency Angles (deg) at the Phosphorus Atoms in Some Diethyl Phenylphosphonite (L) Complexes

Angles[a]	$[Co(CNR)_3L_2]^+$ [b]	$[Ni(CN)_2L_3]$ [c]	$[H_2FeL_4]$ [d]
O(I)-P-Ph	98.4	97.2	94.6
O(II)-P-Ph	104.6	106.2	100.3
O(I)-P-O(II)	106.0	105.6	101.1
M-P-Ph	118.4	117.3	119.4
M-P-O(I)	116.3	119.8	123.4
M-P-O(II)	111.9	109.2	113.7

[a] The symbols are in accordance with Figure 4. [b] This work. [c] From J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 8, 1085 (1969). [d] L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *J. Am. Chem. Soc.*, 94, 1135 (1972).

σ orbitals used by the oxygen atoms can best be described as sp^2 hybrids, as shown by the close approach of the P–O–C bond angles to 120°. All O–C–C angles are 107°. Some of the CH_2–CH_3 distances, which average 1.50 Å, are somewhat shorter than expected, but this shortening is probably due to vibrational effects. The geometry of the perchlorate anion is essentially tetrahedral. The generally high thermal parameters of the oxygen atoms presumably indicate some disorder, an effect which is also reflected in the wide variation of chlorine–oxygen bond lengths and bond angles. For this reason the atomic sites of the oxygen atoms [particularly O(9) and O(10)] are approximate. No other model was sought for this group.

Acknowledgment. Support of this research from the Consiglio Nazionale delle Ricerche (Rome) is gratefully acknowledged. Thanks are due to Mr. R. Salmaso for ^1H NMR spectra and to Mrs. M. Magnabosco for valuable assistance in the x-ray work. We are also grateful to Dr. J. E. Bercaw for constructive comments.

Registry No. I, 42422-51-5; II, 59492-76-1.

Supplementary Material Available: Table IV, listing structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Università di Padova. (b) On leave of absence from Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Padova, Italy. (c) Università di Venezia.
(2) E. Bordignon, U. Croatto, U. Mazzi, and A. A. Orio, *Inorg. Chem.*, **13**, 935 (1974).
(3) (a) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960); (b) S. Otsuka and M. Rossi, *Bull. Chem. Soc. Jpn.*, **46**, 3411 (1973).
(4) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4**, 318 (1965).
(5) R. Rabinowitz and J. Pellon, *J. Org. Chem.*, **20**, 4623 (1961).
(6) (a) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offerman, *Angew. Chem., Int. Ed. Engl.*, **4**, 672 (1965); (b) I. Ugi and R. Meyer, *Org. Synth.*, **41**, 101 (1961).
(7) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(8) D. T. Cromer, *ibid.*, **18**, 17 (1965).
(9) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, "X-Ray 70 System of Crystallographic Programs", Version of July 1970, University of Maryland, College Park, Md.
(10) R. E. Long, Ph.D. Thesis, Part III, University of California at Los Angeles, 1965.
(11) J. Karle and H. Hauptmann, *Acta Crystallogr.*, **9**, 635 (1956).
(12) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).
(13) G. Albertin, E. Bordignon, A. A. Orio, and G. Troilo, *Inorg. Chem.*, **14**, 238 (1975).
(14) G. Albertin, E. Bordignon, A. A. Orio, and G. Rizzardi, *Inorg. Chem.*, **14**, 944 (1975).
(15) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 7920 (1974).
(16) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 332.
(17) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3**, 1945 (1964).
(18) C. C. Costain, *J. Chem. Phys.*, **29**, 872 (1958).
(19) D. R. Lide, *J. Chem. Phys.*, **21**, 1119 (1953).
(20) M. Atoji and W. N. Lipscomb, *Acta Crystallogr.*, **6**, 770 (1953).
(21) P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, 46 (1950).
(22) S. C. Abrahams, *Acta Crystallogr.*, **3**, 194 (1950).
(23) L. E. Sutton, *Chem. Soc., Spec. Publ.*, **No. 18** (1965).
(24) R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, London, 1972.
(25) H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, **12**, 265 (1973).
(26) J. D. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).

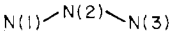
Contribution from the Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Padova, Italy, the Istituto di Chimica delle Macromolecole del CNR, Milano, Italy, and the Istituto di Chimica Generale ed Inorganica, Università di Padova, Padova, Italy

Crystal Structure of Bis(triphenylphosphine)chloro-1,3-di-*p*-tolyltriazenidopalladium(II)

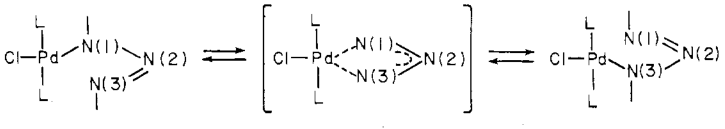
G. BOMBIERI,*[1a] A. IMMIRZI,[1b] and L. TONIOLO[1c]

Received November 20, 1975 AIC50844L

The title compound has square-planar coordination with the phosphine groups trans to each other and the triazenido group acting as monodentate ligand. The



plane contains the metal atom; thus interactions of the N=N π electrons seem to be absent. This and the short Pd···N(3) distance suggest that the fluxional behavior of the compound could be explained as occurring via a σ,σ-chelating intermediate according to the mechanism (L = phopshine)



Introduction

1,3-Diaryl- (or dialkyl-) triazenido ligands R—N—N=N—R (dpt for R = C_6H_5, dtt for R = $C_6H_4CH_3$, dmt for R = CH_3) can form coordination metal complexes in which they act as monodentate or bidentate (chelate or bridging) ligands.

A chelate structure with square-planar coordination about the metal was proposed for $Ni(dpt)_2$ and a mixed-chelate-bridged structure was proposed for $Ni_2(dpt)_4$[2] on the basis of magnetic susceptibility and molecular weight measurements. Subsequently x-ray diffraction studies proved that in $Ni_2(dpt)_4$ the nickel atoms are bridged by four ligand groups through the terminal nitrogen atoms.[3] Bridged structures were also shown by x-ray diffraction for $Cu_2(dpt)_2$[4] and assigned by spectroscopic and magnetic methods for $Cu_2(dpt)_4$ and $Pd_2(dpt)_4$.[5]

Recently, [(π-methallyl)Pd(dmt)]$_2$[6] and [(1,3-π-allyl)-Pd(dtt)]$_2$[7] were shown to have the bridged structure by x-ray diffraction. An example of a complex containing the chelate structure is the octahedral species Co(dpt)$_3$.[8]

Monodentate structures were proposed for the triazenido ligands in Pd(dpt)$_2$(dpth)$_2$ and Pd(dpt)$_2$(py)$_2$[5] on the basis of magnetic susceptibility and molecular weight measurements. No x-ray diffraction studies were undertaken.

Recently palladium(II) and platinum(II) complexes with the formulas PdCl(PPh$_3$)$_2$dtt, PtH(PPh$_3$)$_2$dtt, and PtCl(PPh$_3$)$_2$dtt, which exhibit fluxional behavior in solution, have been synthetized.

We have undertaken the crystal structure analysis of the above complexes with the aim of elucidating the type of bonding and obtaining indications for the interpretation of the fluxional mechanism. A preliminary account has been given previously.[9] In this paper we give the complete crystallographic information on the PdCl(PPh$_3$)$_2$dtt complex.

X-Ray Diffraction Experiments

Crystals suitable for an x-ray study were crystallized from an ethanol–chloroform mixture. The crystal used was a prism with approximate dimensions of 0.65 × 0.40 × 0.20 mm. All x-ray experiments were performed using a single-crystal PW-1100 Philips diffractometer with graphite-monochromated Cu Kα radiation (λ 1.5418 Å). The unit cell was determined on the basis of 15 strong reflections found by mounting the crystal at random, varying the orientation angles ϕ and χ in ranges of 90 and 45°, respectively, with the detector position varying between $\vartheta = 6°$ and $\vartheta = 12°$.

The unit cell was found to be triclinic and the experimental density (1.36 g cm^{-3} by flotation) is in agreement with that calculated for $Z = 2$ (1.33 g cm^{-3}).

For the determination of precise lattice parameters 30 strong reflections with $30° < \vartheta < 48°$ were considered, and the precise diffraction angles ϑ were evaluated as centers of gravity of their profiles $I = F(\vartheta)$, averaging over positive and negative ϑ values.

Integrated intensities for hkl reflections with $l \geq 0$ and $4° < \vartheta < 64°$ were measured using the ω-scan method with a scan speed of 3° min^{-1}, a scan width of 1.0°, and two background counts of 10 s at each end of the scan. Of the 7363 reflections thus considered, the 6674 having a net intensity greater than 3σ (σ = standard error based on count statistics) were used in structure determination and refinement. Every hour three standard reflections were monitored to check the crystal stability. Only statistical variations were observed. [$\sigma(I) = [\mathrm{CT} + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$, where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time $^1/_2t_b$, and $I = \mathrm{CT} - (t_c/t_b)(B_1 + B_2)$. A value of 0.04 was assigned to the factor p in the formula to calculate $\sigma(I)$ to allow for other error sources.]

Structure Determination and Refinement

Precise lattice parameters and their standard deviations were determined by means of a least-squares calculation, minimizing $\sum(\sin \vartheta_{\mathrm{obsd}} - \sin \vartheta_{\mathrm{calcd}})^2$ for the 30 reflections cited above. They are a = 18.954 (2) Å, b = 11.850 (1) Å, c = 11.143 (1) Å, α = 114.97 (1)°, β = 94.75 (1)°, γ = 97.51 (1)° (V = 2222.8 Å^3).

Integrated intensities were corrected for Lorentz and polarization effects and for absorption.[10]

The Patterson function was in agreement with a centrosymmetric distribution of Pd, P, and Cl atoms. The full $P\bar{1}$ symmetry was confirmed in the subsequent structure refinement. The positions of the light atoms were determined by the standard heavy-atom method. The structure was then refined by the least-squares procedure using anisotropic thermal parameters and blocks of 200 variables (owing to the limited capacity of the memory) and minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1$. Computations were carried out on a CDC 6600 computer using the "X-Ray 70" program package.[11] The scattering factors were those given by Cromer and Waber[12] introducing anomalous dispersion corrections for Pd and Cl.[13] In the final cycles the positions of the 38 aromatic hydrogen atoms were calculated by assuming C–H = 1.08 Å and contributions of these atoms were included in F_c.

The final $R = \sum|\Delta F|/\sum|F_o|$ based on the 6674 observed reflections was 0.060. The ratios of parameter shifts to standard deviations in the last cycle were less than 0.1σ.

The final positional and thermal parameters with their standard deviations are listed in Table I. The list of observed and calculated structure factors is given as supplementary material.

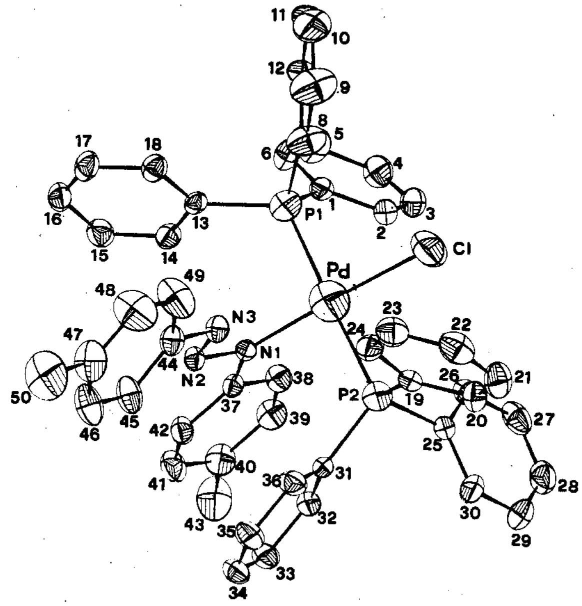


Figure 1. Perspective view of the molecule ((001) projection). Atoms are labeled as in Table I except for carbon atoms C(n) indicated as n. Hydrogen atoms are omitted.

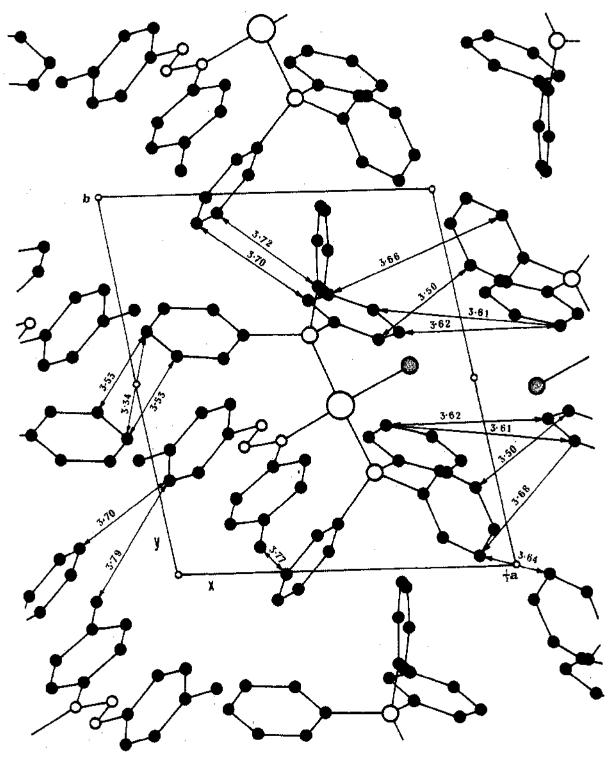


Figure 2. Environment of the molecule in the crystal ((001) projection). The most significant intermolecular distances (Å) are indicated. Hydrogen atoms are omitted.

Molecular Structure

The (001) projection of the structure and the atomic thermal ellipsoids are shown in Figure 1, which reproduces a Calcomp drawing obtained with the program ORTEP.[14] The most significant bond lengths, valence angles, and torsion angles are listed in Table II.

Coordination. The palladium atom exhibits square-planar coordination, with the two PPh$_3$ groups mutually trans and the dtt ligand bonded to the metal through a single terminal nitrogen atom. The coordination angles are only slightly displaced from normal values in spite of the bulkiness of the PPh$_3$ and dtt ligands. Distortions from planarity are small: the mean deviation from the best plane passing through atoms

Table I. Fractional Coordinates and Anisotropic Temperature Factors ($\times 10^4$)[a,b]

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	2985.1 (2)	4355.0 (4)	983.1 (5)	274 (2)	292 (2)	374 (3)	36 (2)	11 (2)	136 (2)
Cl	4148 (1)	5362 (2)	2104 (2)	341 (10)	403 (10)	703 (13)	−44 (8)	−120 (9)	236 (10)
P(1)	2721 (1)	6223 (2)	992 (2)	311 (9)	288 (9)	352 (10)	77 (7)	47 (7)	140 (8)
P(2)	3284 (1)	2503 (2)	942 (2)	261 (8)	272 (9)	374 (10)	46 (7)	36 (7)	140 (8)
N(1)	1981 (3)	3400 (5)	13 (5)	294 (29)	304 (29)	340 (30)	60 (23)	10 (23)	68 (24)
N(2)	1494 (3)	3259 (5)	764 (6)	280 (29)	414 (32)	360 (32)	70 (24)	77 (24)	161 (26)
N(3)	1733 (3)	3837 (6)	2027 (6)	393 (33)	508 (37)	363 (33)	113 (28)	105 (26)	202 (29)
C(1)	3138 (4)	6548 (7)	−279 (7)	393 (40)	357 (38)	444 (42)	54 (31)	97 (32)	158 (33)
C(2)	3768 (4)	6083 (7)	−664 (8)	364 (40)	448 (43)	532 (47)	75 (33)	58 (34)	192 (37)
C(3)	4080 (4)	6271 (8)	−1662 (9)	465 (47)	582 (52)	633 (54)	116 (40)	215 (41)	250 (45)
C(4)	3772 (5)	6874 (9)	−2307 (10)	584 (55)	715 (61)	691 (60)	110 (46)	276 (46)	382 (52)
C(5)	3156 (6)	7388 (10)	−1914 (11)	774 (67)	834 (70)	916 (75)	312 (56)	367 (58)	628 (63)
C(6)	2848 (5)	7223 (9)	−894 (9)	560 (51)	703 (58)	744 (60)	288 (44)	293 (45)	500 (51)
C(7)	3025 (4)	7598 (7)	2587 (8)	368 (40)	473 (44)	471 (44)	116 (34)	35 (33)	169 (36)
C(8)	3077 (6)	7483 (10)	3754 (9)	1096 (85)	637 (61)	490 (54)	268 (58)	47 (53)	205 (47)
C(9)	3271 (8)	8538 (13)	4995 (10)	1530 (125)	924 (92)	456 (60)	370 (86)	−111 (67)	158 (61)
C(10)	3396 (7)	9711 (12)	5073 (12)	1005 (90)	767 (80)	619 (71)	217 (67)	−202 (63)	−80 (61)
C(11)	3360 (6)	9857 (9)	3921 (13)	686 (67)	468 (56)	997 (88)	−22 (48)	96 (61)	−10 (57)
C(12)	3175 (5)	8824 (8)	2662 (9)	542 (51)	364 (43)	692 (58)	24 (37)	125 (43)	104 (41)
C(13)	1772 (4)	6288 (6)	627 (7)	370 (38)	353 (37)	443 (40)	119 (30)	97 (31)	244 (33)
C(14)	1411 (4)	5644 (7)	−671 (8)	445 (43)	452 (43)	465 (44)	128 (35)	65 (34)	199 (44)
C(15)	693 (4)	5725 (8)	−964 (9)	479 (48)	564 (51)	606 (54)	54 (40)	−24 (40)	271 (44)
C(16)	335 (4)	6429 (8)	74 (9)	355 (42)	575 (52)	764 (61)	81 (37)	110 (41)	370 (48)
C(17)	688 (4)	7026 (8)	1368 (9)	448 (46)	639 (54)	743 (61)	215 (41)	293 (44)	398 (49)
C(18)	1407 (4)	6976 (8)	1667 (8)	456 (44)	537 (48)	516 (47)	140 (37)	168 (37)	274 (40)
C(19)	3668 (4)	2804 (6)	2607 (8)	363 (38)	306 (36)	505 (44)	14 (30)	53 (33)	148 (33)
C(20)	4321 (4)	2482 (8)	2908 (8)	390 (42)	657 (54)	580 (51)	129 (38)	55 (37)	329 (44)
C(21)	4601 (5)	2795 (10)	4215 (10)	518 (53)	920 (73)	695 (63)	151 (50)	−44 (46)	462 (58)
C(22)	4230 (6)	3427 (10)	5270 (10)	767 (67)	753 (66)	522 (55)	−40 (53)	−131 (49)	285 (51)
C(23)	3580 (5)	3750 (9)	4978 (9)	698 (61)	593 (56)	455 (50)	72 (46)	25 (44)	108 (42)
C(24)	3309 (4)	3447 (8)	3686 (8)	509 (47)	468 (46)	451 (45)	113 (37)	30 (37)	101 (37)
C(25)	3930 (4)	1881 (6)	−186 (7)	292 (35)	373 (38)	453 (41)	44 (29)	41 (30)	156 (33)
C(26)	4247 (4)	2558 (8)	−806 (8)	484 (46)	483 (46)	515 (48)	−24 (37)	89 (38)	170 (39)
C(27)	4716 (5)	2058 (10)	−1709 (9)	512 (52)	761 (66)	563 (54)	−90 (47)	167 (43)	210 (49)
C(28)	4863 (5)	902 (10)	−1995 (10)	450 (51)	760 (68)	720 (64)	99 (47)	187 (46)	103 (54)
C(29)	4550 (5)	190 (9)	−1392 (10)	539 (54)	647 (59)	805 (67)	272 (46)	230 (49)	216 (52)
C(30)	4085 (4)	688 (8)	−477 (9)	428 (44)	558 (50)	670 (55)	201 (38)	173 (40)	269 (44)
C(31)	2553 (3)	1131 (6)	371 (7)	298 (35)	302 (35)	475 (41)	76 (28)	51 (30)	174 (32)
C(32)	2324 (4)	426 (7)	−989 (8)	376 (40)	405 (41)	494 (45)	58 (32)	28 (33)	195 (36)
C(33)	1751 (4)	−592 (8)	−1445 (8)	473 (46)	448 (45)	559 (50)	17 (37)	−75 (38)	144 (40)
C(34)	1404 (4)	−882 (8)	−528 (9)	428 (45)	436 (45)	739 (60)	−52 (36)	−9 (41)	283 (44)
C(35)	1626 (4)	−182 (8)	801 (9)	503 (49)	564 (52)	693 (59)	−50 (40)	122 (43)	332 (47)
C(36)	2197 (4)	830 (7)	1286 (8)	502 (46)	431 (44)	537 (48)	17 (36)	123 (38)	205 (38)
C(37)	1782 (4)	2733 (6)	−1344 (7)	309 (35)	389 (38)	376 (38)	113 (29)	40 (29)	174 (32)
C(38)	2281 (4)	2866 (8)	−2180 (8)	456 (44)	510 (46)	429 (43)	76 (36)	114 (34)	208 (37)
C(39)	2126 (5)	2165 (9)	−3549 (8)	620 (55)	697 (59)	447 (48)	132 (46)	169 (41)	221 (44)
C(40)	1490 (5)	1291 (9)	−4179 (8)	628 (57)	719 (61)	389 (46)	157 (48)	34 (41)	88 (43)
C(41)	996 (4)	1179 (9)	−3337 (8)	409 (45)	695 (58)	478 (49)	17 (40)	−52 (37)	119 (43)
C(42)	1138 (4)	1869 (8)	−1971 (8)	331 (38)	545 (47)	427 (43)	72 (34)	20 (32)	144 (37)
C(43)	1332 (6)	532 (13)	−5663 (10)	840 (79)	1396 (112)	424 (55)	266 (76)	52 (52)	126 (63)
C(44)	1226 (4)	3614 (8)	2802 (8)	416 (43)	627 (52)	438 (44)	148 (38)	117 (34)	246 (40)
C(45)	655 (4)	2572 (10)	2284 (8)	419 (46)	975 (72)	483 (49)	44 (46)	83 (38)	370 (50)
C(46)	202 (5)	2388 (11)	3151 (10)	494 (53)	1178 (89)	621 (60)	−1 (54)	88 (44)	527 (63)
C(47)	315 (6)	3209 (12)	4496 (11)	740 (70)	1206 (96)	631 (65)	235 (67)	326 (55)	497 (67)
C(48)	901 (8)	4200 (13)	5004 (11)	1217 (107)	1138 (102)	529 (64)	−12 (84)	400 (68)	111 (65)
C(49)	1361 (6)	4433 (12)	4147 (9)	815 (73)	1142 (93)	364 (49)	−126 (65)	162 (48)	76 (54)
C(50)	−188 (8)	2959 (16)	5409 (13)	1192 (109)	1675 (142)	947 (94)	211 (99)	675 (86)	701 (98)

[a] In the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. [b] Esd's are in parentheses.

Pd, Cl, P(1), P(2), and N(1) is 0.017 Å. The Pd–Cl bond length of 2.332 (2) Å is very close to the value 2.331 (3) Å reported for PdCl(Me₃dpma),[15] where a chlorine atom is trans to a nitrogen. The Pd–P bond lengths 2.329 (3) and 2.320 (3) Å have the usual values for trans metal–phosphine complexes.[16]

The dtt Ligand. The dtt ligand has a trans configuration with respect to the double bond N(2)=N(3) and a trans conformation about the N(1)—N(2) single bond, so that the sequence C(37)–N(1)–N(2)–N(3)–C(44) is almost planar. [A cis conformation could allow a larger M···N(3) contact; however it must be ruled out because of an unacceptable N(3)···H (bonded to the C(42) carbon atom; see Figure 1) interaction.[9]]

The tolyl groups are slightly twisted with respect to this plane, by 4.4 and 15.2°, respectively. Similar conformations are observed also in the case of diazoaminobenzene molecule[17] and related *p*-bromo derivative.[18] The above-mentioned plane is roughly perpendicular to the coordination plane (85.1°) and the metal atom is displaced from it by 0.30 Å only. This excludes interaction of the N(2)=N(3) π electrons with the metal atom. On the other hand, the conformation and the orientation of the dtt ligand brings the atom N(3) in close contact with the metal (2.836 (6) Å) and the lone pair of N(3) is in favorable orientation for formation of a five-coordinate species which could explain the fluxional behavior of the compound as occurring via a σ,σ-chelating intermediate according to Scheme I. [The Pd···N(2) contact is 2.897 (6) Å.] The N(1)–C(37) bond (1.368 (8) Å) is shorter than the ordinary C–N bond in aromatic amines (~1.42 Å; see also the values 1.42–1.44 Å found in the above-mentioned diazoaminobenzene and brominated derivative[17,18]). We in-

Table II. Bond Distances (Å), Valence Angles (deg), and Torsion Angles (deg)

Bond Distances

Pd–Cl	2.332 (2)[a]	C(19)–C(20)	1.40 (1)
Pd–P(1)	2.329 (3)	C(20)–C(21)	1.38 (1)
Pd–P(2)	2.320 (3)	C(21)–C(22)	1.40 (2)
Pd–N(1)	2.033 (4)	C(22)–C(23)	1.39 (2)
P(1)–C(1)	1.829 (9)	C(23)–C(24)	1.36 (1)
P(1)–C(7)	1.813 (7)	C(24)–C(19)	1.41 (1)
P(1)–C(13)	1.830 (8)	C(25)–C(26)	1.38 (1)
P(2)–C(19)	1.803 (9)	C(26)–C(27)	1.39 (1)
P(2)–C(25)	1.825 (8)	C(27)–C(28)	1.34 (2)
P(2)–C(31)	1.833 (6)	C(28)–C(29)	1.39 (2)
N(1)–N(2)	1.336 (8)	C(29)–C(30)	1.39 (1)
N(1)–C(37)	1.368 (8)	C(30)–C(25)	1.39 (1)
N(2)–N(3)	1.286 (7)	C(31)–C(32)	1.38 (1)
N(3)–C(44)	1.415 (11)	C(32)–C(33)	1.39 (1)
C(1)–C(2)	1.40 (1)	C(33)–C(34)	1.39 (2)
C(2)–C(3)	1.39 (1)	C(34)–C(35)	1.35 (1)
C(3)–C(4)	1.36 (2)	C(35)–C(36)	1.38 (1)
C(4)–C(5)	1.40 (2)	C(36)–C(31)	1.41 (1)
C(5)–C(6)	1.39 (2)	C(37)–C(38)	1.42 (1)
C(6)–C(1)	1.39 (2)	C(38)–C(39)	1.38 (1)
C(7)–C(8)	1.36 (2)	C(39)–C(40)	1.39 (1)
C(8)–C(9)	1.40 (1)	C(40)–C(41)	1.41 (1)
C(9)–C(10)	1.34 (2)	C(41)–C(42)	1.37 (1)
C(10)–C(11)	1.36 (2)	C(42)–C(37)	1.40 (1)
C(11)–C(12)	1.40 (1)	C(40)–C(43)	1.49 (1)
C(12)–C(7)	1.41 (1)	C(44)–C(45)	1.40 (1)
C(13)–C(14)	1.38 (1)	C(45)–C(46)	1.41 (2)
C(14)–C(15)	1.40 (1)	C(46)–C(47)	1.38 (1)
C(15)–C(16)	1.40 (1)	C(47)–C(48)	1.39 (2)
C(16)–C(17)	1.37 (1)	C(48)–C(49)	1.43 (2)
C(17)–C(18)	1.39 (1)	C(49)–C(44)	1.38 (1)
C(18)–C(13)	1.40 (1)	C(47)–C(50)	1.54 (2)

Valence Angles

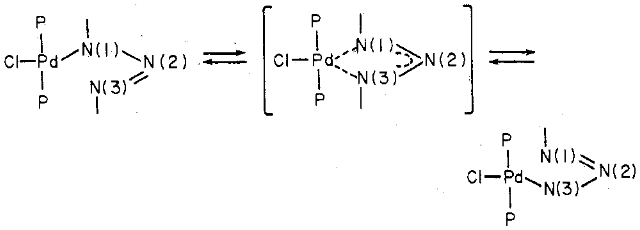
P(1)–Pd–Cl	91.39 (8)[a]	C(7)–C(8)–C(9)	121.7 (12)
P(2)–Pd–Cl	87.39 (8)	C(8)–C(9)–C(10)	120.6 (12)
P(1)–Pd–N(1)	91.4 (2)	C(9)–C(10)–C(11)	119.2 (9)
P(2)–Pd–N(1)	89.8 (2)	C(10)–C(11)–C(12)	121.9 (11)
Pd–P(1)–C(1)	110.6 (3)	C(11)–C(12)–C(7)	118.7 (10)
Pd–P(1)–C(7)	113.5 (3)	P(1)–C(13)–C(14)	120.0 (6)
Pd–P(1)–C(13)	117.3 (2)	P(1)–C(13)–C(18)	120.1 (5)
C(1)–P(1)–C(7)	107.5 (4)	C(14)–C(13)–C(18)	119.9 (7)
C(1)–P(1)–C(13)	103.9 (4)	C(13)–C(14)–C(15)	120.3 (7)
C(7)–P(1)–C(13)	103.1 (3)	C(14)–C(15)–C(16)	119.5 (7)
Pd–P(2)–C(19)	109.1 (2)	C(15)–C(16)–C(17)	119.9 (8)
Pd–P(2)–C(25)	113.1 (3)	C(16)–C(17)–C(18)	121.1 (8)
Pd–P(2)–C(31)	117.1 (2)	C(17)–C(18)–C(13)	119.2 (7)
C(19)–P(2)–C(25)	108.4 (4)	P(2)–C(19)–C(20)	123.9 (6)
C(19)–P(2)–C(31)	106.3 (4)	P(2)–C(19)–C(24)	118.7 (6)
C(25)–P(2)–C(31)	102.3 (3)	C(20)–C(19)–C(24)	117.4 (8)
Pd–N(1)–C(37)	126.1 (4)	C(19)–C(20)–C(21)	120.8 (8)
Pd–N(1)–N(2)	117.1 (4)	C(20)–C(21)–C(22)	120.8 (10)
N(2)–N(1)–C(37)	116.1 (4)	C(21)–C(22)–C(23)	118.8 (10)
N(1)–N(2)–N(3)	113.0 (5)	C(22)–C(23)–C(24)	120.2 (9)
N(2)–N(3)–C(44)	112.2 (5)	C(23)–C(24)–C(19)	122.1 (8)
P(1)–C(1)–C(2)	119.0 (7)	P(2)–C(25)–C(26)	120.8 (6)
P(1)–C(1)–C(6)	122.4 (6)	P(2)–C(25)–C(30)	120.2 (7)
C(2)–C(1)–C(6)	118.6 (8)	C(26)–C(25)–C(30)	118.9 (8)
C(1)–C(2)–C(3)	120.3 (9)	C(25)–C(26)–C(27)	120.7 (9)
C(2)–C(3)–C(4)	120.6 (8)	C(26)–C(27)–C(28)	120.4 (11)
C(3)–C(4)–C(5)	120.4 (11)	C(27)–C(28)–C(29)	120.4 (10)
C(4)–C(5)–C(6)	119.1 (12)	C(28)–C(29)–C(30)	119.5 (10)
C(5)–C(6)–C(1)	120.8 (9)	C(29)–C(30)–C(25)	120.1 (10)
P(1)–C(7)–C(8)	120.9 (7)	P(2)–C(31)–C(32)	118.8 (6)
P(1)–C(7)–C(12)	121.0 (7)	P(2)–C(31)–C(36)	121.4 (5)
C(8)–C(7)–C(12)	118.0 (7)	C(32)–C(31)–C(36)	119.7 (6)
C(31)–C(32)–C(33)	119.8 (8)	C(39)–C(40)–C(43)	122.0 (9)
C(32)–C(33)–C(34)	119.9 (7)	C(41)–C(40)–C(43)	121.7 (8)
C(33)–C(34)–C(35)	120.1 (7)	N(3)–C(44)–C(45)	123.3 (6)
C(34)–C(35)–C(36)	121.4 (10)	N(3)–C(44)–C(49)	115.4 (7)
C(35)–C(36)–C(31)	119.1 (7)	C(45)–C(44)–C(49)	121.0 (9)
N(1)–C(37)–C(38)	118.0 (5)	C(44)–C(45)–C(46)	119.2 (7)
N(1)–C(37)–C(42)	124.7 (7)	C(45)–C(46)–C(47)	120.9 (9)
C(38)–C(37)–C(42)	117.2 (6)	C(46)–C(47)–C(48)	119.1 (12)
C(37)–C(38)–C(39)	120.5 (7)	C(47)–C(48)–C(49)	121.3 (9)
C(38)–C(39)–C(40)	122.6 (9)	C(48)–C(49)–C(44)	118.2 (9)
C(39)–C(40)–C(41)	116.3 (7)	C(46)–C(47)–C(50)	119.1 (10)
C(40)–C(41)–C(42)	122.1 (7)	C(48)–C(47)–C(50)	121.7 (10)
C(41)–C(42)–C(37)	121.2 (8)		

Torsion Angles

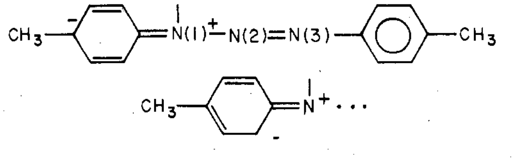
Pd–P(1)–C(1)–C(2)	−27	N(1)–Pd–P(1)–C(1)	−76
Pd–P(1)–C(7)–C(8)	−29	N(1)–Pd–P(1)–C(7)	136
Pd–P(1)–C(13)–C(14)	76	N(1)–Pd–P(1)–C(13)	15
Pd–P(2)–C(19)–C(24)	48	N(1)–Pd–P(2)–C(19)	−130
Pd–P(2)–C(25)–C(26)	7	N(1)–Pd–P(2)–C(25)	70
Pd–P(2)–C(31)–C(36)	83	N(1)–Pd–P(2)–C(31)	−8
N(2)–N(1)–C(37)–C(42)	−4	N(2)–N(3)–C(44)–C(45)	21

[a] Esd's are in parentheses. [b] The angles A–B–C–D are defined as zero when the bonds A–B and C–D are cis planar. They are counted positive when looking along the central B–C bond the far bond is rotated clockwise with respect to the near bond. The average esd is 2°.

Scheme I



terpret this as indicative of a strong contribution of quinone structures of the types



favored by the strong polarity of the Pd–N(1) bond and consequent excess of negative charge onto N(1) atom. The quinone structures could explain the shortening of the N(1)–N(2) (1.336 (8) Å) single bond due to conjugation (see for comparison the value 1.35 Å for N–N in tetrazolate ion[19]) and the value 1.287 Å for the N(2)–N(3) double bond, somewhat longer than an ordinary N=N (~1.22 Å).

The quinone forms, with N(1) lacking its lone pair, could also explain the small angular deviation (8°) of the Pd–N(1) bond from the C(37)–N(1)–N(2) plane also if other factors, like steric hindrance of the ligands, must be taken in account.

Phosphines. All bond lengths and angles in the phenyl rings have expected values: for C–C bonds the values are in the range 1.34–1.41 Å (average 1.386 (18) Å); for C–C–C angles the values are in the range 118.0–122.1° (average 120.0 (1.0)°). The Pd–P–C angles have rather scattered values; the largest values occur for P(1)–C(13) and P(2)–C(31) which are roughly eclipsed with respect to Pd–N(1) (see Table II).

It is worthwhile noting that the two observed conformations are considerably different from those observed for free PPh_3 in the solid state.[20] The conformation of P(1) is roughly similar to that obtained by conformational analysis.[21] Since there are no significant interactions between phosphines and dtt within a single molecule, the different conformations should be caused by intermolecular packing forces. In fact (see below) the crystal packing is very different for the two phosphines.

Crystal Packing

As can be seen in Figure 2, showing the crystal structure projected along (001), the shortest intermolecular distances in the crystal involve the phosphine groups. There are some very short C···C distances, which are close to the C···C distance in graphite.[22] The two phosphines have quite different environments which might be responsible for the different conformations observed. For the dtt group the nonbonded interactions are weaker (no aromatic C···C distances below 3.70 Å) and thus we believe that the dtt geometry is scarcely influenced by the crystal packing.

Conclusions

The essential results of this structural investigation are (i) in transition metal square-planar complexes of 1,3-diaryltriazenido acting as a monodentate ligand, there is no interaction between the π electrons of the ligand and the metal, and (ii) the most likely intramolecular mechanism responsible for the fluxional behavior is through an intermediate five-coordinate 18-electron structure formed by a σ interaction between the lone pair belonging to the terminal nonbonded nitrogen atom and the metal (see Scheme I). The short Pd···N(3) distance (2.836 Å) and the planarity of the Pd–N(1)–N(2)–N(3) system make possible the formation of the intermediate species with a moderate rearrangement of the ligand.

Registry No. $PdCl(PPh_3)_2dtt$, 59671-96-4.

Supplementary Material Available: Listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR. (b) Istituto di Chimica delle Macromolecole del CNR. (c) Istituto di Chimica Generale ed Inorganica, Università di Padova.
(2) P. F. Dwyer and D. P. Mellor, *J. Am. Chem. Soc.*, **63**, 81 (1941).
(3) M. Corbett, B. F. Hoskins, and N. J. McLeod, *Chem. Commun.*, 1602 (1968).
(4) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **14**, 480 (1961).
(5) C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959).
(6) P. Hendricks, K. Olie, and K. Vrieze, submitted for publication.
(7) S. Candeloro de Sanctis, N. V. Pavel, L. Toniolo, *J. Organometal. Chem.*, **108**, 409 (1976).
(8) M. Corbett and B. F. Hoskins, *J. Am. Chem. Soc.*, **89**, 1530 (1967).
(9) L. Toniolo, A. Immirzi, U. Croatto, and G. Bombieri, *Inorg. Chim. Acta*, **19**, 209 (1976).
(10) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).
(11) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, "X-Ray 70 System" crystallographic program, version of July 1970, University of Maryland.
(12) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(13) D. T. Cromer and D. Libermann, *J. Chem. Phys.*, **53**, 1891 (1970).
(14) C. K. Johnson, "ORTEP", Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(15) M. G. B. Drew, M. J. Riede, and J. Rodgers, *J. Chem. Soc., Dalton Trans.*, 234 (1972).
(16) G. Beran, A. J. Carty, P. C. Chieh, and H. A. Patel, *J. Chem. Soc., Dalton Trans.*, 488 (1973), and references therein.
(17) (a) V. F. Gladkova and Yu. D. Kondrashev, *Kristallografiya*, **17**, 33 (1972); (b) *ibid.*, **16**, 929 (1971).
(18) Yu. A. Omel'chenko and Yu. D. Kondrashev, *Kristallografiya*, **17**, 947 (1972).
(19) G. J. Palenik, *Acta Crystallogr.*, **16**, 596 (1963).
(20) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).
(21) C. P. Brock and J. A. Ibers, *Acta Crystallogr., Sect. B*, **29**, 2426 (1973).
(22) R. W. G. Wyckoff "Crystal Structures", Vol. I, Interscience, New York, N.Y., 1963, p 26.

Contribution from the Center for Molecular Structure,
Department of Chemistry, University of Florida, Gainesville, Florida 32611

Crystal and Molecular Structures of Dichloro[bis(diphenylphosphino)methane]palladium(II), Dichloro[bis(diphenylphosphino)ethane]palladium(II), and Dichloro[1,3-bis(diphenylphosphino)propane]palladium(II)

W. L. STEFFEN[1] and GUS J. PALENIK*

Received January 7, 1976 AIC60004M

The synthesis and crystal structure determination of three palladium chloride–diphosphine complexes are reported. The $PdCl_2(dpm)$ complex (dpm is bis(diphenylphosphino)methane) forms monoclinic crystals with unit cell dimensions of $a = 11.372$ (3), $b = 12.273$ (3), and $c = 17.498$ (8) Å, with $\beta = 100.27$ (3)° and space group $P2_1/n$. The $PdCl_2(dpe)$ complex (dpe is bis(diphenylphosphino)ethane) forms monoclinic crystals with one molecule of CH_2Cl_2 incorporated in the lattice. The space group is $P2_1/c$ and the cell dimensions are $a = 12.290$ (8), $b = 15.495$ (9), and $c = 15.403$ (12) Å, with $\beta = 104.70$ (5)°. The $PdCl_2(dpp)$ complex (dpp is bis(diphenylphosphino)propane) forms triclinic crystals of space group $P\bar{1}$ with cell dimensions of $a = 10.633$ (3), $b = 11.525$ (2), and $c = 14.461$ (5) Å and $\alpha = 95.97$ (2), $\beta = 91.31$ (3), and $\gamma = 134.90$ (1)°. The structures were solved by the heavy-atom method and refined by least-squares techniques to unweighted R values of 0.024 for dpm, 0.047 for dpe, and 0.027 for dpp. The three complexes differ in the number of CH_2 groups between the two phosphorus atoms of the ligand, causing the P–Pd–P angle to change from 72.68 (3)° (dpm complex) to 85.82 (7)° (dpe complex) to 90.58 (5)° (dpp complex). The Pd–P distances [2.234 (1) and 2.250 (1) Å in dpm, 2.233 (2) and 2.226 (2) Å in dpe, and 2.244 (1) and 2.249 (2) Å in dpp] neither are equal nor vary systematically with the alkyl chain length. Similarly, the Pd–Cl distances [2.362 (1) and 2.352 (1) Å, 2.361 (2) and 2.357 (2) Å, 2.351 (1) and 2.358 (2) Å in the dpm, dpe, and dpp complexes respectively] are not equal in the three complexes. The results of the three structure determinations are discussed in terms of the steric problems inherent in a bidentate chelating ligand.

Introduction

The relative importance of steric vs. electronic effects in coordination complexes is difficult to determine. Changes in the electronic properties of ligands invariably involve altering the steric requirements and vice versa. For example, in the series of $M(CNS)L_2$ complexes, where M = Pd or Pt, CNS is used for the thiocyanate ion without specifying the mode of coordination, and L is PPh_3, $AsPh_3$, or $SbPh_3$, the steric and electronic factors operate in the same direction.[2] Therefore, changes in the mode of thiocyanate coordination in the above series of complexes could be interpreted as either an electronic or a steric effect depending on one's preference.

We attempted to separate the steric from electronic factors in thiocyanate coordination by considering the series $Pd(CNS)_2[Ph_2P(CH_2)_nPPh_2]$, where $n = 1$, 2, or 3.[3] We observed that the coordination changed from S,S when $n = 1$ to N,S for $n = 2$ and N,N in the $n = 3$ case and seemed to parallel the steric influence. Although we assumed that the electronic properties of the diphosphine would be approximately constant, the fact that the P–Pd–P angle changed from 73.3 to 89.3° raised the question of whether our assumption was valid.[4,5] Furthermore, the very short Pd–P distance in