vironments 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.

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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)

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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 β = 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 β = 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 α = 95.97 (2), β = 91.31 (3), and γ = 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

Table I. Crystal Data

	$PdCl_2(dpm)$	$PdCl_2(dpe)\cdot CH_2Cl_2$	$PdCl_2(dpp)$
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a, A	11.372 (3)	12.290 (8)	10.633 (3)
b, A	12.273 (3)	15.495 (9)	11.525 (2)
c, A	17.498 (8)	15.403 (12)	14.461 (5)
α, deg			95.97 (2)
β, deg	100.27 (3)	104.70 (5)	91.31 (3)
γ, deg			134.90 (1)
Vol, A^3	2402.8	2837.1	1236.7
Mol wt	561.7	660.6	589.8
Z	4	4	2
ρ(calcd), g/cm³	1.553	1.547	1.584
ρ(measd), g/cm³	1.556	1.566	1.578
Crystal size, mm³	0.33 × 0.31 × 0.26	0.35 × 0.19 × 0.10	0.54 × 0.39 × 0.21
Recrystallizn solvent	Acetonitrile	CH_2Cl_2/hexane	Chloroform
Method of data collection	Moving crystal, moving counter	Moving crystal, moving counter	Moving crystal, moving counter
Radiation used	Mo Kα	Mo Kα	Mo Kα
μ, cm^{-1}	11.2	11.4	10.9
2θ range, deg	0–45	0–45	0–45
No. of unique reflections	3159	3750	3251
No. of obsd reflections	2855	2885	2954

the $PdCl_2[Ph_2PN(C_2H_5)PPh_2]$[6] complex suggested that the electronic factors might vary as a function of the P–Pd–P angle. Therefore, we undertook a study of the corresponding $PdCl_2[Ph_2P(CH_2)_nPPh_2]$ complexes so that changes in the diphosphine ligand could be studied with a constant group opposite the phosphorus atoms. Our results suggest that although there are small, nonsystematic changes in the Pd–P distances, our earlier conclusions remain valid.

Experimental Section

Materials. The three diphosphines were obtained from Pressure Chemical Corp. and were used as supplied. The other chemicals were all reagent grade or equivalent.

Preparation of the Complexes $Cl_2Pd[Ph_2P(CH_2)_nPPh_2]$, *n* = 1, 2, and 3. The bis(benzonitrile)palladium chloride complex was prepared by the published method[7] and then reacted with a stoichiometric amount of the diphosphine ligand.[8] The microanalyses of all three compounds were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The melting points were taken in open capillaries with a Mel-temp apparatus and are uncorrected. Crystals suitable for diffraction studies were grown by slow cooling and evaporation, using the solvents given in Table I.

Anal. Calcd for $PdCl_2(dpm)$, $PdC_{25}H_{22}P_2Cl_2$: C, 53.46; H, 3.95; Cl, 12.62. Found: C, 53.25; H, 3.95; Cl, 12.82; mp 310 °C. Calcd for $PdCl_2(dpe)$, $PdC_{26}H_{24}P_2Cl_2$: C, 54.24; H, 4.20; Cl, 12.32. Found: C, 53.98; H, 4.14; Cl, 12.42; mp >360 °C. Calcd for $PdCl_2(dpp)$, $PdC_{27}H_{26}P_2Cl_2$: C, 54.99; H, 4.44; Cl, 12.02. Found: C, 54.79; H, 4.57; Cl, 11.86; mp 335 °C.

Data Collection and Reduction. Preliminary precession and Weissenberg photographs were taken of all three compounds to determine the space groups and approximate unit cell dimensions. A different crystal was selected for the determination of precise cell constants and the measurement of the intensity data. A Syntex $P\bar{1}$ diffractometer was utilized for these measurements. The pertinent crystal data and details of the intensity measurements are summarized in Table I. The abbreviations used in Table I and in the remainder of the paper are dpm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$, dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, and dpp = $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$. These abbreviations and the experimental details of the data collection are identical with those previously reported.[3] The criteria for "reliable" reflections were $I > 2.0\sigma(I)$ for the dpm and dpe complexes and $I > 1.8\sigma(I)$ for the dpp case. The space group $P\bar{1}$ for the dpp complex was chosen on the basis of the intensity statistics.[9] No absorption corrections were applied because of the relatively small value of μ.

Table II. Scheme of Refinement

	$PdCl_2$-(dpm)	$PdCl_2(dpe)\cdot CH_2Cl_2$	$PdCl_2$-(dpp)
R index with all atoms from Fourier syntheses	0.14	0.18	0.21
Refinement with isotropic thermal parameters	3 cycles	3 cycles	3 cycles
R index	0.070	0.110	0.074
Refinement with anisotropic thermal parameters	3 cycles	3 cycles	3 cycles
R index	0.042	0.066	0.044
Refinement with hydrogen atoms included but not refined	6 cycles	6 cycles	6 cycles
R index (final)	0.024	0.047	0.027
F_{low} for weighting scheme	12.0	25.0	30.0
F_{high} for weighting scheme	48.0	75.0	100.0

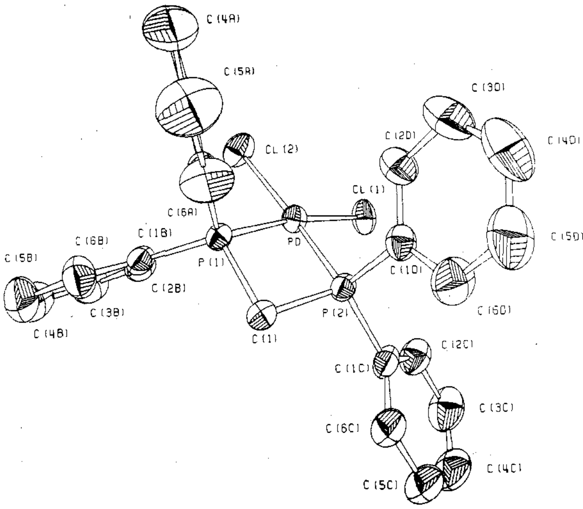

Figure 1. View of the $PdCl_2(dpm)$ molecule, showing the atomic numbering and thermal ellipsoids.

Structure Determination and Refinement. All three structures were solved by the heavy-atom method and refined by least-squares techniques. The details are summarized in Table II; the procedures are similar to those previously reported.[3] The scattering factor for Pd was taken from Cromer, Larson and Waber's compilation,[10] while the factors for Cl, P, and C were from Hanson, Herman, Lea, and Skillman.[11] The hydrogen scattering curve was from Stewart, Davidson, and Simpson.[12] The final atomic parameters for the nonhydrogen atoms are given in Table III–V. The hydrogen atom parameters are presented in Tables VI–VIII. The tables of observed and calculated structure amplitudes are available.[13]

Results and Discussion

The three complexes are illustrated in Figures 1–3 and are discrete molecular species. The Pd atom is in the center of the approximately square-planar arrangement of the two phosphorus and two chlorine atoms. The chlorine atoms are cis as required by the geometry of the bidentate chelating diphosphine ligand. Individual bond distances and angles in the three complexes are given in Tables IX and X, except for the bond distances and C–C–C bond angles in the four phenyl rings, not included but available.[13]

The three complexes differ only in the length of the alkyl chain between the two phosphorus atoms of the diphosphine ligand. There is no reason to expect the Lewis basicity of the phosphorus atoms in the three ligands to differ in the absence of steric factors. Therefore, the variations in Pd–P distances in the three complexes were somewhat surprising. The Pd–P distances are significantly different in the dpm complex (t_0

Table III. Final Parameters of Nonhydrogen Atoms in $PdCl_2(dpm)$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	56 369 (2)	37 850 (2)	27 431 (1)	450 (2)	492 (2)	249 (1)	47 (3)	127 (2)	51 (2)
Cl(1)	5 273 (1)	5 235 (1)	1 845 (1)	60 (1)	62 (1)	43 (0)	6 (1)	18 (1)	40 (1)
Cl(2)	4 168 (1)	4 363 (1)	3 444 (1)	77 (1)	81 (1)	40 (0)	63 (1)	52 (1)	16 (1)
P(1)	6 092 (1)	2 278 (1)	3 451 (0)	43 (1)	44 (1)	19 (0)	0 (1)	17 (1)	1 (1)
P(2)	7 244 (1)	3 032 (1)	2 366 (0)	44 (1)	49 (1)	20 (0)	−7 (1)	18 (1)	−1 (1)
C(1)	7 058 (3)	1 711 (3)	2 815 (2)	62 (3)	47 (2)	25 (1)	0 (4)	31 (3)	−4 (3)
C(1a)	6 960 (3)	2 444 (3)	4 414 (2)	61 (3)	45 (2)	21 (1)	−9 (4)	10 (3)	6 (3)
C(2a)	6 496 (3)	3 073 (3)	4 941 (2)	86 (3)	68 (3)	29 (1)	12 (5)	22 (3)	−12 (3)
C(3a)	7 137 (4)	3 216 (3)	5 688 (2)	143 (5)	75 (3)	33 (1)	−16 (7)	26 (4)	−26 (4)
C(4a)	8 240 (4)	2 733 (4)	5 893 (2)	133 (5)	103 (4)	28 (1)	−44 (7)	−16 (4)	−8 (4)
C(5a)	8 700 (4)	2 106 (4)	5 385 (3)	95 (4)	133 (5)	41 (2)	32 (7)	−19 (4)	3 (5)
C(6a)	8 070 (3)	1 958 (3)	4 626 (2)	78 (3)	94 (4)	33 (1)	36 (6)	−6 (4)	−8 (4)
C(1b)	4 909 (3)	1 323 (3)	3 504 (2)	60 (3)	62 (3)	22 (1)	−23 (4)	27 (3)	−7 (3)
C(2b)	3 768 (3)	1 517 (3)	3 092 (2)	63 (3)	82 (3)	29 (1)	−28 (5)	18 (3)	−10 (3)
C(3b)	2 877 (4)	758 (4)	3 090 (2)	77 (4)	116 (4)	43 (2)	−67 (6)	26 (4)	−28 (4)
C(4b)	3 112 (4)	−181 (4)	3 499 (3)	113 (4)	126 (5)	52 (2)	−135 (8)	64 (5)	−37 (5)
C(5b)	4 235 (5)	−390 (4)	3 922 (3)	167 (6)	78 (4)	51 (2)	−80 (8)	53 (5)	16 (4)
C(6b)	5 151 (4)	369 (3)	3 925 (2)	98 (4)	69 (3)	39 (2)	−43 (6)	19 (4)	16 (4)
C(1c)	7 450 (3)	2 783 (3)	1 382 (2)	60 (3)	78 (3)	21 (1)	−37 (5)	28 (3)	−7 (3)
C(2c)	7 007 (3)	3 505 (3)	796 (2)	83 (3)	98 (4)	28 (1)	−14 (6)	23 (3)	7 (4)
C(3c)	7 214 (4)	3 304 (4)	41 (2)	126 (5)	138 (5)	27 (1)	−34 (8)	27 (4)	22 (4)
C(4c)	7 857 (4)	2 408 (4)	−106 (2)	137 (5)	142 (4)	32 (2)	−67 (8)	68 (5)	−37 (5)
C(5c)	8 295 (4)	1 685 (4)	475 (3)	124 (5)	107 (4)	45 (2)	−37 (7)	82 (5)	−39 (5)
C(6c)	8 100 (4)	1 858 (3)	1 225 (2)	98 (4)	83 (3)	33 (1)	−21 (6)	50 (4)	−9 (4)
C(1d)	8 615 (3)	3 624 (3)	2 887 (2)	50 (3)	58 (3)	25 (1)	−11 (4)	9 (3)	7 (3)
C(2d)	8 549 (3)	4 381 (3)	3 470 (2)	75 (3)	58 (3)	33 (1)	−14 (5)	−2 (3)	−1 (3)
C(3d)	9 601 (4)	4 810 (3)	3 896 (2)	118 (4)	70 (3)	42 (2)	−36 (6)	−30 (4)	−10 (4)
C(4d)	10 684 (4)	4 489 (4)	3 746 (3)	84 (4)	92 (4)	62 (2)	−55 (6)	−44 (5)	20 (5)
C(5d)	10 747 (3)	3 744 (4)	3 179 (3)	56 (3)	131 (5)	64 (2)	−33 (7)	10 (4)	4 (5)
C(6d)	9 720 (3)	3 312 (4)	2 746 (2)	55 (3)	107 (4)	45 (2)	−10 (6)	16 (4)	−15 (4)

[a] All values are $\times 10^4$ except those for Pd, which are $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

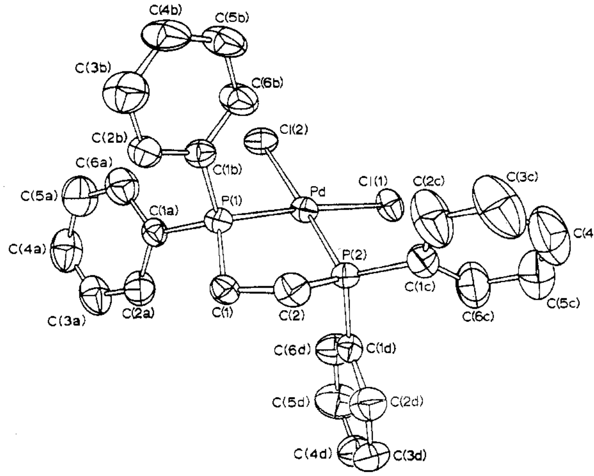

Figure 2. View of the $PdCl_2(dpe)$ molecule, showing the atomic numbering and thermal ellipsoids.

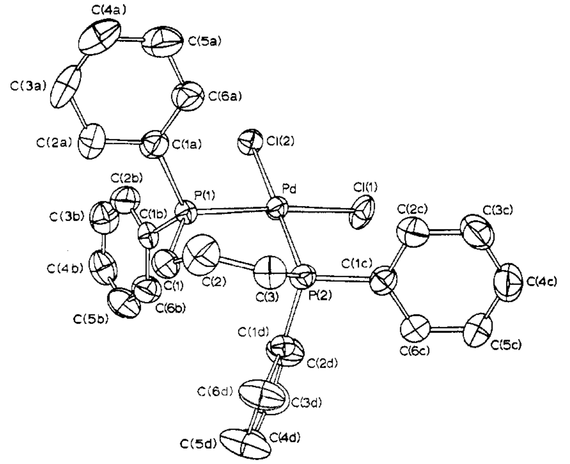

Figure 3. View of the $PdCl_2(dpp)$ molecule, showing the atomic numbering and thermal ellipsoids.

$= (l_1 - l_2)/(\sigma_1^2 - \sigma_2^2)^{1/2} = 11.3$), and the differences are possibly significant ($t_0 = 2.47$ for dpe and 2.23 for the dpp) in the other two complexes. The variations in the Pd–P distances can be rationalized if we consider the steric problems involved in having a cis-bidentate chelating ligand. A view down the C(1)–P(1) bond in $PdCl_2(dpm)$ and down the C(2)–C(3) bond in $PdCl_2(dpp)$ is given in Figure 4. In both the dpm and dpp complexes appreciable eclipsing of bonds is required if both phosphorus atoms are to bond to the same palladium atom. The dpe case where the bonds are staggered has not been shown. The steric strain is also indicated in the bond angles in the alkyl chain which show large deviations from ideality in the dpm and dpp cases while the angles are nearly tetrahedral in the dpe complex. Finally, one can consider the displacements of the two phosphorus atoms from the plane defined by the Pd and the two Cl atoms, which of course would be zero in an ideal square-planar arrangement. The deviations of P(1) and P(2) from the $PdCl_2$ plane are −0.136 and +0.242 Å in the dpm case, −0.070 and +0.087 Å in the dpe complex, and −0.053 and +0.312 Å when dpp is the ligand. In summary we see that the dpe ligand appears to form the least strained complex and the one which is the nearest to an ideal square-planar arrangement.

The two Pd–P distances in the relatively strain-free dpe complex are significantly shorter than the Pd–P bonds in the dpp case. In both complexes, the differences in the individual Pd–P distances are possibly significant but the differences are small and the average value can probably be used. Therefore, we see that there is an increase in the Pd–P distances (average 2.230 Å for dpe and 2.246 Å for dpp) in going from the dpe to dpp complex, in agreement with an increase in strain in the latter case. An analysis of the dpm Pd–P distances is complicated by the fact that the difference in the two Pd–P bond lengths is highly significant. The shorter Pd–P(1) distance

Table IV. Final Parameters of Nonhydrogen Atoms in $PdCl_2(dpe)\cdot CH_2Cl_2$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	22 116 (5)	30 670 (3)	37 299 (3)	618 (4)	267 (2)	260 (2)	49 (7)	215 (4)	26 (5)
Cl(1)	3 130 (2)	3 729 (1)	2 731 (1)	88 (2)	43 (1)	31 (1)	−27 (2)	37 (2)	12 (2)
Cl(2)	438 (2)	3 656 (1)	3 029 (1)	70 (2)	36 (1)	37 (1)	27 (2)	8 (2)	7 (2)
P(1)	1 462 (2)	2 360 (1)	4 701 (1)	59 (2)	24 (1)	25 (1)	4 (2)	24 (2)	1 (1)
P(2)	3 846 (2)	2 512 (1)	4 493 (1)	56 (2)	32 (1)	30 (1)	2 (2)	19 (2)	1 (2)
C(1)	2 517 (6)	1 614 (5)	5 346 (5)	66 (6)	30 (3)	39 (4)	3 (7)	27 (8)	11 (6)
C(2)	3 646 (6)	2 063 (5)	5 548 (5)	73 (6)	45 (4)	31 (4)	14 (9)	14 (8)	16 (7)
C(1a)	220 (6)	1 713 (4)	4 260 (4)	63 (6)	33 (4)	29 (3)	−9 (7)	35 (7)	−1 (5)
C(2a)	305 (7)	862 (6)	4 012 (6)	95 (8)	45 (4)	53 (5)	−24 (10)	61 (10)	−25 (8)
C(3a)	−662 (9)	381 (6)	3 626 (6)	142 (11)	52 (5)	56 (5)	−73 (12)	88 (12)	−37 (8)
C(4a)	−1 691 (8)	741 (7)	3 493 (6)	104 (9)	74 (6)	56 (5)	−75 (12)	47 (11)	−35 (9)
C(5a)	−1 797 (8)	1 587 (7)	3 713 (7)	76 (8)	75 (6)	92 (7)	−29 (12)	19 (12)	−17 (11)
C(6a)	−846 (7)	2 079 (6)	4 108 (6)	86 (8)	46 (5)	78 (6)	−23 (10)	30 (11)	−16 (9)
C(1b)	1 118 (5)	3 084 (5)	5 510 (4)	59 (6)	30 (3)	29 (3)	10 (8)	22 (7)	−4 (6)
C(2b)	744 (7)	2 770 (5)	6 220 (5)	101 (8)	29 (4)	33 (4)	8 (8)	56 (9)	3 (6)
C(3b)	443 (8)	3 334 (6)	6 806 (5)	124 (9)	55 (5)	36 (4)	19 (11)	61 (10)	4 (7)
C(4b)	528 (8)	4 212 (6)	6 712 (5)	151 (11)	41 (4)	35 (4)	30 (11)	60 (11)	−6 (7)
C(5b)	920 (8)	4 524 (5)	6 014 (6)	149 (11)	32 (4)	46 (5)	11 (10)	78 (12)	6 (7)
C(6b)	1 207 (8)	3 965 (5)	5 410 (5)	122 (9)	31 (4)	40 (4)	7 (9)	66 (10)	−3 (6)
C(1c)	5 047 (6)	3 221 (5)	4 815 (5)	70 (6)	39 (4)	44 (4)	−4 (9)	10 (8)	7 (7)
C(2c)	5 138 (10)	3 772 (7)	5 525 (7)	167 (13)	71 (6)	66 (6)	−112 (15)	63 (14)	−42 (10)
C(3c)	6 097 (12)	4 298 (8)	5 795 (8)	234 (18)	86 (8)	71 (7)	−118 (20)	61 (18)	−46 (13)
C(4c)	6 906 (10)	4 299 (8)	5 390 (9)	135 (12)	79 (7)	110 (9)	−83 (16)	−15 (17)	5 (14)
C(5c)	6 789 (10)	3 790 (8)	4 635 (10)	126 (13)	84 (8)	165 (12)	−72 (16)	139 (20)	−23 (16)
C(6c)	5 824 (8)	3 258 (7)	4 332 (7)	112 (10)	66 (6)	96 (7)	−62 (13)	98 (14)	−27 (11)
C(1d)	4 265 (6)	1 605 (5)	3 914 (5)	55 (6)	34 (4)	42 (4)	2 (7)	29 (8)	6 (6)
C(2d)	5 176 (7)	1 096 (6)	4 297 (6)	89 (8)	50 (5)	62 (5)	31 (10)	36 (11)	9 (8)
C(3d)	5 504 (8)	413 (6)	3 873 (7)	90 (9)	49 (5)	100 (7)	48 (11)	80 (13)	28 (10)
C(4d)	4 908 (9)	216 (6)	3 024 (7)	124 (10)	43 (5)	99 (7)	27 (12)	110 (14)	−7 (10)
C(5d)	4 001 (10)	692 (7)	2 613 (6)	168 (12)	61 (6)	55 (5)	29 (14)	46 (13)	−31 (9)
C(6d)	3 651 (8)	1 402 (6)	3 050 (6)	105 (9)	42 (4)	56 (5)	24 (11)	34 (11)	−20 (8)
Cl(3)	6 606 (4)	3 180 (4)	2 066 (3)	167 (4)	208 (5)	131 (3)	117 (8)	36 (6)	65 (7)
C(3)	7 746 (11)	3 038 (13)	1 700 (12)	102 (12)	199 (16)	204 (16)	83 (25)	62 (23)	164 (28)
Cl(4)	7 950 (4)	3 828 (5)	969 (3)	183 (5)	285 (7)	142 (4)	−156 (10)	−72 (7)	139 (8)

[a] All values are $\times 10^4$ except those for Pd, which are $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. Final Parameters of Nonhydrogen Atoms in $PdCl_2(dpp)$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	6555 (4)	40 143 (4)	24 529 (2)	1059 (5)	848 (4)	371 (1)	1348 (8)	286 (4)	302 (4)
Cl(1)	1548 (1)	6 522 (1)	2 329 (1)	164 (2)	92 (2)	89 (1)	183 (4)	24 (2)	50 (2)
Cl(2)	3674 (1)	5 413 (1)	2 724 (1)	95 (2)	105 (2)	59 (1)	128 (3)	23 (2)	37 (2)
P(1)	−113 (1)	1 741 (1)	2 791 (1)	110 (2)	84 (2)	38 (1)	138 (3)	37 (2)	42 (2)
P(2)	−2251 (1)	2 592 (1)	2 162 (1)	105 (2)	97 (2)	33 (1)	146 (3)	19 (2)	19 (2)
C(1)	−2506 (5)	−131 (5)	2 675 (3)	137 (9)	89 (7)	62 (3)	135 (14)	53 (8)	54 (7)
C(2)	−3463 (6)	−590 (5)	1 720 (3)	167 (10)	114 (8)	65 (3)	165 (16)	−3 (9)	−3 (8)
C(3)	−3735 (6)	480 (5)	1 485 (3)	155 (9)	127 (7)	45 (3)	181 (15)	1 (8)	2 (7)
C(1a)	707 (5)	1 057 (5)	2 072 (3)	127 (8)	102 (7)	43 (2)	166 (13)	23 (7)	19 (6)
C(2a)	483 (7)	−221 (6)	2 299 (4)	329 (14)	207 (10)	65 (3)	453 (22)	75 (11)	75 (9)
C(3a)	988 (8)	−823 (7)	1 719 (4)	352 (14)	226 (11)	95 (4)	507 (24)	2 (13)	14 (11)
C(4a)	1734 (7)	−167 (7)	940 (4)	256 (13)	228 (11)	82 (4)	380 (22)	5 (11)	−58 (10)
C(5a)	1951 (7)	1 091 (7)	712 (4)	272 (13)	189 (10)	73 (4)	297 (21)	120 (11)	19 (10)
C(6a)	1432 (6)	1 699 (5)	1 278 (3)	194 (10)	126 (8)	54 (3)	218 (16)	66 (8)	29 (7)
C(1b)	730 (5)	2 130 (5)	4 008 (3)	149 (8)	95 (6)	44 (2)	170 (13)	40 (7)	53 (6)
C(2b)	2352 (6)	2 661 (6)	4 258 (3)	186 (10)	180 (9)	49 (3)	270 (17)	30 (8)	42 (8)
C(3b)	3017 (6)	3 055 (6)	5 194 (4)	182 (10)	178 (9)	64 (3)	248 (18)	−13 (9)	42 (9)
C(4b)	2119 (7)	2 951 (6)	5 883 (3)	252 (12)	183 (9)	50 (3)	289 (19)	9 (9)	64 (8)
C(5b)	494 (7)	2 424 (7)	5 646 (3)	293 (14)	252 (12)	44 (3)	377 (23)	75 (10)	78 (9)
C(6b)	−202 (6)	2 003 (6)	4 708 (3)	187 (10)	216 (10)	47 (3)	289 (18)	66 (8)	84 (8)
C(1c)	−2679 (5)	3 542 (5)	1 469 (3)	117 (8)	131 (7)	39 (2)	168 (14)	13 (7)	32 (6)
C(2c)	−2253 (6)	3 725 (6)	563 (3)	199 (10)	196 (9)	48 (3)	292 (18)	52 (8)	54 (8)
C(3c)	−2570 (7)	4 446 (6)	17 (3)	224 (11)	234 (11)	45 (3)	317 (20)	59 (9)	97 (9)
C(4c)	−3260 (7)	4 999 (7)	389 (4)	205 (11)	233 (11)	84 (4)	332 (20)	51 (10)	142 (10)
C(5c)	−3671 (7)	4 848 (6)	1 291 (4)	222 (11)	232 (10)	76 (3)	378 (20)	71 (10)	109 (10)
C(6c)	−3391 (6)	4 102 (6)	1 825 (3)	177 (9)	174 (8)	50 (3)	277 (16)	52 (8)	57 (8)
C(1d)	−3139 (5)	2 399 (5)	3 259 (3)	108 (7)	113 (7)	41 (2)	164 (13)	40 (7)	40 (6)
C(2d)	−2062 (6)	3 677 (6)	3 996 (3)	169 (10)	142 (8)	51 (3)	150 (16)	47 (8)	2 (8)
C(3d)	−2693 (7)	3 558 (7)	4 850 (3)	274 (13)	208 (10)	46 (3)	314 (21)	35 (10)	−11 (9)
C(4d)	−4332 (8)	2 182 (7)	4 979 (4)	320 (14)	254 (12)	60 (3)	446 (24)	156 (11)	111 (10)
C(5d)	−5422 (8)	886 (7)	4 242 (4)	212 (13)	236 (12)	89 (4)	188 (22)	175 (12)	87 (12)
C(6d)	−4847 (7)	991 (6)	3 386 (4)	163 (10)	176 (10)	64 (3)	137 (18)	65 (9)	9 (9)

[a] All values are $\times 10^4$ except those for Pd, which are $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table VI. Final Parameters of Hydrogen Atoms in $PdCl_2(dpm)^a$

Atom	*x*	*y*	*z*	*B*, Å²	Dist, Å
H1(1)	781	123	303	3.9	1.06
H2(1)	651	124	243	3.9	1.02
H(2a)	565	337	479	4.9	1.01
H(3a)	675	378	607	6.0	1.10
H(4a)	860	289	649	6.1	1.07
H(5a)	969	188	546	6.7	1.14
H(6a)	836	137	422	5.7	1.10
H(2b)	357	219	279	4.7	0.98
H(3b)	203	87	280	6.0	1.01
H(4b)	239	−68	353	6.7	1.03
H(5b)	447	−115	421	6.6	1.07
H(6b)	596	23	422	5.6	0.99
H(2c)	657	416	92	5.3	1.00
H(3c)	678	389	−34	6.6	1.05
H(4c)	803	215	−69	6.6	1.11
H(5c)	887	101	35	6.4	1.10
H(6c)	843	134	167	5.4	1.03
H(2d)	767	466	353	4.9	1.08
H(3d)	948	539	431	6.2	1.05
H(4d)	1146	473	410	6.6	1.03
H(5d)	1153	363	299	6.6	1.01
H(6d)	976	280	230	5.6	1.01

[a] The positional parameters are $\times 10^3$. The number in parentheses is the number of the carbon atom to which the hydrogen is bonded at a distance given in the last column.

Table VII. Final Parameters of Hydrogen Atoms in $PdCl_2(dpe)\cdot CH_2Cl_2{}^a$

Atom	*x*	*y*	*z*	*B*, Å²	Dist, Å
H1(1)	247	106	501	4.3	1.00
H2(1)	208	140	581	4.3	1.06
H3(2)	428	169	577	4.6	0.97
H4(2)	365	268	599	4.6	1.17
H(2a)	119	57	414	5.7	1.14
H(3a)	−60	−34	346	6.6	1.16
H(4a)	−237	31	320	6.5	1.08
H(5a)	−260	200	361	7.1	1.16
H(6a)	−77	274	429	6.4	1.06
H(2b)	71	215	632	4.3	0.97
H(3b)	13	307	726	5.7	0.97
H(4b)	28	464	714	5.8	1.03
H(5b)	58	522	585	5.6	1.15
H(6b)	153	429	486	4.8	1.14
H(2c)	460	362	592	7.3	1.03
H(3c)	578	468	632	8.2	1.14
H(4c)	812	450	583	8.6	1.50
H(5c)	734	381	422	8.1	1.04
H(6c)	589	306	368	6.8	1.07
H(2d)	538	127	485	6.0	0.87
H(3d)	622	2	422	6.4	1.09
H(4d)	502	−37	264	7.1	1.12
H(5d)	372	84	207	6.8	0.85
H(6d)	307	182	281	6.1	0.96

[a] The positional parameters are $\times 10^3$. The number in parentheses is the number of the carbon atom to which the hydrogen is bonded at a distance given in the last column.

Table VIII. Final Parameters of Hydrogen Atoms in $PdCl_2(dpp)^a$

Atom	*x*	*y*	*z*	*B*, Å²	Dist, Å
H1(1)	−282	−114	281	4.5	1.00
H2(1)	−301	−3	314	4.5	0.92
H3(2)	−288	−56	124	5.5	0.93
H4(2)	−475	−182	162	5.5	1.06
H5(3)	−362	65	85	4.8	0.96
H6(3)	−500	−17	154	4.8	0.99
H(2a)	1	−65	295	5.9	1.07
H(3a)	84	−168	191	6.5	0.95
H(4a)	186	−82	56	6.5	0.97
H(5a)	267	167	13	6.5	1.07
H(6a)	155	269	106	5.0	1.14
H(2b)	286	266	368	5.1	1.00
H(3b)	426	363	539	5.8	0.99
H(4b)	271	322	663	5.9	1.13
H(5b)	−17	237	618	6.4	1.03
H(6b)	−148	159	456	5.4	1.08
H(2c)	−175	335	28	5.3	0.97
H(3c)	−229	446	−66	6.0	1.03
H(4c)	−334	565	7	6.0	0.97
H(5c)	−404	541	158	5.8	1.03
H(6c)	−379	388	246	4.6	1.00
H(2d)	−078	475	395	5.5	1.01
H(3d)	−174	460	537	6.4	1.04
H(4d)	−467	209	566	6.2	1.06
H(5d)	−659	−9	444	7.4	1.00
H(6d)	−569	−4	288	6.4	1.02

[a] The positional parameters are $\times 10^3$. The number in parentheses is the number of carbon atom to which the hydrogen is bonded at a distance given in the last column.

Table IX. Bond Lengths (Å) for $PdCl_2(dpm)$, $PdCl_2(dpe)\cdot CH_2Cl_2$, and $PdCl_2(dpp)$ with Their Estimated Standard Deviations in Parentheses

	dpm	dpe	dpp
Pd–Cl(1)	2.362 (1)	2.361 (2)	2.351 (1)
Pd–Cl(2)	2.352 (1)	2.357 (2)	2.358 (2)
Pd–P(1)	2.234 (1)	2.233 (2)	2.244 (1)
Pd–P(2)	2.250 (1)	2.226 (2)	2.249 (2)
P(1)–C[a]	1.834 (3)	1.830 (8)	1.820 (5)
P(2)–C[a]	1.830 (3)	1.840 (7)	1.840 (4)
C(1)–C(2)		1.512 (11)	1.499 (7)
C(2)–C(3)			1.517 (9)
P(1)–C(1a)	1.806 (3)	1.809 (7)	1.817 (7)
P(1)–C(1b)	1.800 (3)	1.806 (7)	1.815 (4)
P(2)–C(1c)	1.805 (3)	1.806 (8)	1.822 (6)
P(2)–C(1d)	1.812 (4)	1.808 (8)	1.817 (5)

[a] Carbon atom directly bonded to the phosphorus atom is given.

in the dpm complex involves the phosphorus atom which is closer to the $PdCl_2$ plane. Apparently, the large steric constraints in the dpm ligand prevent appropriate orbital overlap when the two Pd–P bonds are equal and coplanar with the $PdCl_2$ unit. Consequently, while a priori we might have expected the three diphosphine ligands to be identical electronically, the steric constraints imposed by chelation alter the interaction between the phosphorus and palladium atoms.

The Pd–Cl bond distances in the three complexes should provide some indications of the electronic differences in the three ligands resulting from the steric constraints. The Pd–Cl bond is obviously sensitive to the nature of the trans atom as can be seen by the data in Table XI. The Pd–Cl bond is shortest when Cl or N is the trans atom while the longest Pd–Cl bonds are found when P or σ-bonded C ligands are the trans group. The variations of Pd–Cl distances shown in Table XI are in agreement with the trans-effect orderings obtained by other methods.[33] Similar trends have also been reported for Pt–Cl bonds.[34] In general the Pd–Cl or Pt–Cl bond length decreases as the electronegativity of the trans atom increases. Whether these changes are related to σ- or π-bonding effects (or a combination) is still controversial. We see that in the dpe case the two Pd–Cl bonds are not significantly different (as might be expected from the strain-free nature of the complex) and average 2.359 Å. The Pd–Cl distances are in the region expected for a Pd–Cl bond trans to a Pd–P bond. Furthermore, the two Cl–Pd–P angles are virtually identical. In the dpp complex the two Pd–Cl distances [2.351 (1) and 2.358 (2) Å] are significantly different ($t_0 = 3.13$) as are the various Cl–Pd–P angles (see Table X). However, the two Pd–Cl distances are sufficiently close to each that an average value of 2.354 Å can be used for further discussion. We see that in going from the dpe to the dpp complex the average Pd–Cl distances decreases from 2.359 to 2.354 Å while the Pd–P distances increase from 2.230 to 2.246 Å. Although the

Table X. Bond angles (deg) for $PdCl_2$(dpm), $PdCl_2$(dpe)·CH_2Cl_2, and $PdCl_2$(dpp) with Their Estimated Standard Deviations in Parentheses

	dpm	dpe	dpp
Cl(1)-Pd-Cl(2)	93.63 (3)	94.19 (7)	90.78 (5)
Cl(1)-Pd-P(1)	171.26 (3)	175.14 (7)	171.88 (5)
Cl(1)-Pd-P(2)	99.78 (3)	89.73 (7)	91.10 (5)
Cl(2)-Pd-P(1)	94.39 (3)	90.33 (7)	87.74 (5)
Cl(2)-Pd-P(2)	165.21 (3)	175.48 (7)	177.68 (5)
P(1)-Pd-P(2)	72.68 (3)	85.82 (7)	90.58 (5)
Pd-P(1)-C^{α}	94.7 (1)	108.5 (2)	115.9 (2)
Pd-P(1)-C(1a)	117.3 (1)	118.2 (2)	115.1 (2)
Pd-P(1)-C(1b)	117.8 (1)	111.5 (2)	109.3 (2)
C^{α}-P(1)-C(1a)	108.8 (1)	105.5 (3)	102.9 (2)
C^{α}-P(1)-C(1b)	108.6 (1)	106.0 (3)	105.2 (2)
C(1a)-P(1)-C(1b)	108.3 (1)	106.3 (3)	107.6 (2)
Pd-P(2)-C^{α}	94.3 (1)	107.9 (2)	115.5 (2)
Pd-P(2)-C(1c)	126.8 (1)	118.4 (3)	114.4 (2)
Pd-P(2)-C(1d)	111.0 (1)	111.8 (2)	110.1 (2)
C^{α}-P(2)-C(1c)	107.8 (1)	105.6 (4)	102.3 (2)
C^{α}-P(2)-C(1d)	107.1 (1)	105.1 (3)	107.0 (2)
C(1c)-P(2)-C(1d)	107.6 (1)	107.0 (4)	106.7 (2)
P(1)-C^{α}-P(2)	93.0 (1)		
P(1)-C^{α}-C		107.9 (5)	112.9 (4)
C-C^{α}-P(2)		108.2 (5)	118.1 (4)
C-C-C			117.0 (5)

[a] Carbon atom directly bonded to the phosphorus atom is given.

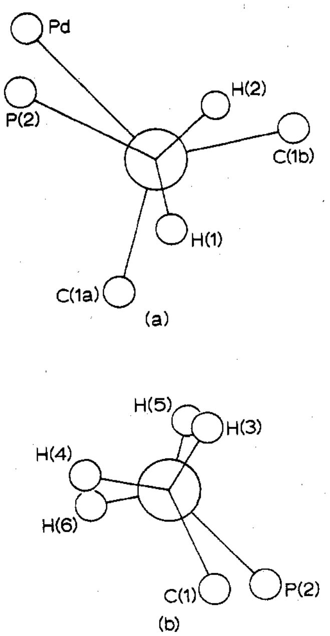

Figure 4. Views down the diphosphine ligand bonds, illustrating the eclipsed nature of various bonds: (a) down the C(1)–P(1) bond in $PdCl_2$(dpm); (b) down the C(2)–C(3) bond in $PdCl_2$(dpp).

changes in the Pd–Cl distances are not significant, the slight decrease is consistent with the increase in the Pd–P distances. The Pd–Cl distances in the dpm complex present much the same dilemma that the Pd–P distances did, namely, the differences are highly significant (t_0 = 7.1). The longer Pd–Cl(1) bond of 2.362 (1) Å is trans to the shorter Pd–P(1) bond of 2.234 (1) Å, in agreement with a trans effect. Strictly speaking, the opposite effect is seen in the dpp complex; however, the differences between the individual values are so small that the assumption of equal Pd–P and Pd–Cl distances appears more reasonable. In summary, we could say that the dpe ligand exerts a stronger trans influence than the dpp ligand and that the dpm case is much more complicated. Certainly, the maximum interaction between the phosphorus and palladium atoms occurs with the relatively strain-free dpe ligand.

An important question is how the present results relate to our earlier study of the palladium thiocyanate complexes with

Table XI. Comparison of Pd–Cl Bond Distances as a Function of the Trans Atom

Pd–Cl dist, Å	Atom trans to Cl	Coordination sphere	Compd[a]	Ref
2.24	Cl	Cl, Cl, N, N	$PdCl_2$(cyclohexanone oxime)$_2$	14
2.266 (9)	Cl	Cl, Cl, Se, Se	$PdCl_2(Et_2Se)_2$	15
2.28	Cl	Cl, Cl, N, N	$PdCl_2(C_{10}H_9NF_6)_2$	16
2.287 (2)	Cl	Cl, Cl, S, S	$PdCl_2$(DMSO)$_2$	17
2.295 (1)	Cl	Cl, Cl, N, N	$PdCl_2$(nitrosobenzene)$_2$	18
2.30 (2)	Cl	Cl, Cl, N, N	$PdCl_2$(acetoxime)$_2$	19
2.30 (1)	N	Cl, Cl, N, N	$PdCl_2$(tetrahydrogen ethylenediaminetetraacetate)·$5H_2O$	20
2.305 (4)	N	Cl, Cl, N, S	$PdCl_2$(*S*-methyl-L-cysteine)·H_2O	21
2.307 (4)	N	Cl, Cl, N, S	$PdCl_2$(*S*-methyl-L-cysteine)·H_2O	21
2.309 (5)	N	Cl, N, N, N	PdCl(cpm)(cpmH)	22
2.31	N	Cl, Cl, N, S	$PdCl_2$(methionine)	23
2.310 (1)	C=C	Cl, Cl, C=C, C=C	$PdCl_2$(norbornadiene)	24
2.311 (4)	P	Cl, Cl, P, P	$PdCl_2[Ph_2PCH_2CH_2P(CF_3)_2]$	25
2.312 (7)	S	Cl, Cl, S, N	$PdCl_2$(*S*-methyl-L-cysteine)·H_2O	21
2.323 (1)	C=C	Cl, Cl, C=C, C=C	$PdCl_2$(norbornadiene)	24
2.324 (3)	S	Cl, Cl, S, N	$PdCl_2$(*S*-methyl-L-cysteine)·H_2O	21
2.327 (7)	S	Cl, Cl, S, C=C	$PdCl_2[C_3H_5NHC(OMe)S]$	26
2.331 (3)	N	Cl, N, N, N	$PdCl(Me_2dpma)^+Cl^-$	27
2.342 (6)	C=C	Cl, Cl, S, C=C	$PdCl_2[C_3H_5NHC(OMe)S]$	26
2.35	S	Cl, Cl, N, S	$PdCl_2$(methionine)	23
2.351 (1)	P	Cl, Cl, P, P	$PdCl_2$(dpp)	This work
2.352 (1)	P	Cl, Cl, P, P	$PdCl_2$(dpm)	This work
2.357 (2)	P	Cl, Cl, P, P	$PdCl_2$(dpe)·CH_2Cl_2	This work
2.358 (2)	P	Cl, Cl, P, P	$PdCl_2$(dpp)	This work
2.361 (2)	P	Cl, Cl, P, P	$PdCl_2$(dpe)·CH_2Cl_2	This work
2.362 (3)	P	Cl, Cl, P, P	*cis*-$PdCl_2(PPhMe_2)_2$	28
2.362 (1)	P	Cl, Cl, P, P	$PdCl_2$(dpm)	This work
2.367 (3)	P	Cl, Cl, P, P	$PdCl_2[Ph_2PN(C_2H_5)PPh_2]$	29
2.370 (4)	P	Cl, Cl, P, P	$PdCl_2[Ph_2PCH_2CH_2P(CF_3)_2]$	25
2.38	σ-C	Cl, P, σ-C, C=C	$PdCl(PPh_3)$(methallyl)	30
2.381 (5)	σ-C	Cl, P, P, σ-C	*trans*-$PdCl(PEt_3)_2(C_{12}H_9N_2)$	31
2.45	σ-C	Cl, N, N, σ-C	PdCl(2-mdp)(mba)	32

[a] Me_2dpma = methyldi-[(6-methyl-2-pyridyl)methyl]amine; 2-mdp = 2-methoxy-3-*N*,*N*-dimethylaminopropyl; Mba = (*S*)-α-methylbenzylamine; cpmH = 3,4′-bis(ethoxycarbonyl)-5-chloro-3′,4,5′-trimethyldipyrromethene.

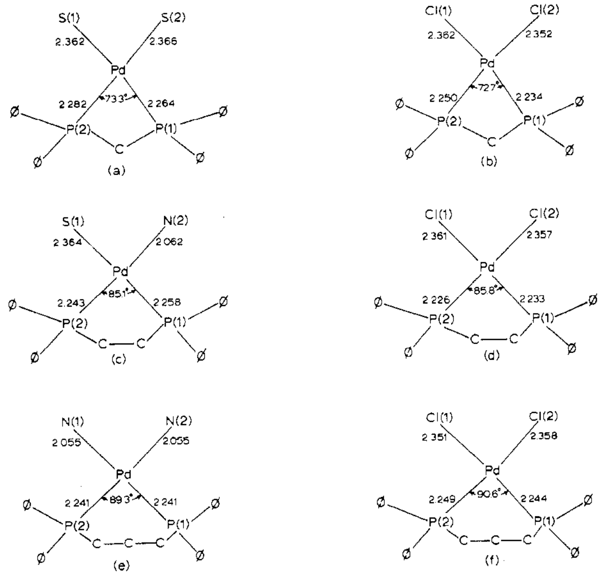

Figure 5. Comparison of the geometry about the central Pd atom in six related diphosphine complexes: (a) $Pd(SCN)_2$(dpm), (b) $PdCl_2$(dpm), (c) Pd(SCN)(NCS)(dpe), (d) $PdCl_2$(dpe), (e) $Pd(NCS)_2$(dpp), (f) $PdCl_2$(dpp).

the three ligands.[3] The pertinent distances and angles in the six complexes are presented in Figure 5. We see that the P–Pd–P angle is dependent only on the ligand and the angles are virtually identical in the appropriate pairs. In addition, the asymmetry in the Pd–P bonds found in $PdCl_2$(dpm) of 0.016 Å is very close to the difference of 0.018 Å found in $Pd(SCN)_2$(dpm), in agreement with steric constraints on the dpm ligand. Furthermore, the Pd–N and Pd–P distances are required by symmetry to be equal in the $Pd(NCS)_2$(dpp) complex and for all practical purposes, the Pd–P and Pd–Cl bonds are equivalent in the $PdCl_2$(dpp) case. Finally, although the strongest Pd–P interaction occurs with the dpe ligand, the thiocyanate coordination is mixed with dpe as the ligand. Consequently, we conclude that our original observations regarding the role of steric effects on thiocyanate coordination in palladium complexes were indeed correct.

The data in Figure 5 also illustrate the fact that the net electron density on the central palladium atom remains essentially constant, in essence, the electroneutrality principle.[35] The two Pd–P distances in the dpp complexes are virtually the same and, of course, Cl and N have very similar trans-effect properties. The introduction of S-bonded thiocyanate in the dpe complex introduces the expected asymmetry in the Pd–P bonds but also causes both Pd–P bonds to increase relative to the $PdCl_2$ case. Finally, in $Pd(SCN)_2$(dpm) the Pd–P bonds are the longest found in any of the six complexes. Furthermore, since the Pd–S and Pd–Cl bond lengths are very similar, the longer Pd–P bonds in $Pd(SCN)_2$(dpm) are probably not due to steric interactions. Presumably as the "better" or softer S donors are introduced into the coordination sphere, the Pd–P bond lengths increase to maintain an approximately constant charge density on the central Pd atom.

There has been some discussion of the change in the endocyclic angle with a change in the electronegativity of the substituent.[36,37] The average angles in the three complexes [120.0 (6)° for dpm, 118.7 (7)° for dpe, and 118.8 (5)° for dpp] are not significantly different from each other or from the average of 118.50 (9)° found in a large number of phosphorus–phenyl compounds.[37] The average P–C(ring) bonds [1.806 (5) Å for dpm, 1.807 (2) Å for dpe, and 1.818 (3) Å for dpp] are all slightly smaller than the average of 1.828 (1) Å found in 13 different compounds. The dpe value is significantly shorter than for the dpp case which is in agreement with slight differences in the two ligands. In summary, the P–C distances and endocyclic angles are consistent with the three ligands having about equal donor properties, with perhaps the dpe ligand having the best steric fit.

A survey of the intermolecular distances less than 4.5 Å in all cases did not reveal any short contacts which might influence the molecular dimensions. Similarly, a scan of intramolecular distances less than 4.0 Å in the three complexes indicated that the majority of the shorter contacts involved the various hydrogen atoms and were not abnormally short. Therefore, the various results discussed above are not a direct consequence of any unusual inter- or intramolecular contact.

Acknowledgment. We wish to thank the Center for Instructional and Research Activities, University of Florida, for a grant of computer time.

Registry No. $PdCl_2$(dpm), 38425-01-3; $PdCl_2(dpe){\cdot}CH_2Cl_2$, 59831-01-5; $PdCl_2$(dpp), 59831-02-6.

Supplementary Material Available: A comparison of observed and calculated structure factor amplitudes together with tables of the C–C distances and angles in the various phenyl rings (43 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the 1:1 Uranyl Nitrate Tetrahydrate–18-Crown-6 Compound, $UO_2(NO_3)_2(H_2O)_2 \cdot 2H_2O \cdot$(18-Crown-6). Noncoordination of Uranyl by the Crown Ether

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Received February 3, 1976 AIC60084U

The synthesis and crystal structure of $UO_2(NO_3)_2(H_2O)_2 \cdot 2H_2O \cdot$(18-crown-6), which forms from the reaction of uranyl nitrate hexahydrate and the cyclic polyether 18-crown-6, are reported. The uranyl group is *not* located within the crown ether group. Rather, the structure consists of neutral $UO_2(NO_3)_2(H_2O)_2$ units and separate crown ether molecules connected by hydrogen bonding through intermediary water molecules. The oxygens of the linear uranyl group are coordinated only to uranium; the eight-coordination of uranium is completed by six equatorial oxygen donors, two from waters and two from symmetrically bidentate nitrates. The uranium and the six equatorial oxygens are coplanar within 0.06 Å. Pertinent distances are U–O(uranyl) = 1.693 (6) Å, U–O(water) = 2.434 (5) Å, U–O(nitrate) = 2.482 (6) and 2.486 (6) Å. The cyclic ether molecule exists in the customary crown conformation with normal distances and angles. Crystal data are as follows: space group $P\bar{1}$, $Z = 1$, $a = 7.526$ (7) Å, $b = 11.27$ (1) Å, $c = 7.802$ (4) Å, $\alpha = 97.51$ (6)°, $\beta = 93.22$ (6)°, $\gamma = 105.95$ (6)°, $R_F = 0.058$ for 2453 diffractometer-collected reflections with $I \geq 3\sigma(I)$.

Introduction

Crown ethers (cyclic polyethers) provide a cavity or cage which can be engineered to accommodate metal ions of different charge and size.[1–6] Resulting complexes are of great synthetic interest since enhanced solubilities and reactivities of ionic materials in nonplar solvents often result. The complexes are also of considerable interest in regard to solvent extraction, isotope separation, and biological transport of metal ions. As a result, the synthesis and characterization of crown ether compounds are the subjects of intense interest in many laboratories.

We have recently turned our attention to the possible utilization of crown ethers as a means of stabilizing unusual oxidation states and geometries in actinide complexes. The chelating ability of crown ethers with respect to alkali and alkaline earth metal ions is well documented, both crystallographically and chemically.[4–6] In contrast, syntheses of only a few lanthanide[7,8] and actinide[9,10] complexes have been reported, and structural verification of polyether complexation to these metals has hitherto been lacking.

In this paper we report the synthesis and structure determination of a 1:1 compound containing uranyl nitrate tetrahydrate and 18-crown-6.[26] While this work was under way, the synthesis of the identical compound by a different method was reported.[9] In that preliminary report, spectroscopic data were interpreted to indicate that the nitrate groups were uncoordinated and the uranyl group lay within the ring of the six crown oxygen atoms. The x-ray structure determination described herein was undertaken to test the hypothesis of crown ether ligation.

Experimental Section

Preparation of $UO_2(NO_3)_2(H_2O)_2 \cdot 2H_2O \cdot$(18-crown-6). Excellent crystals of the title compound were prepared in good yield by dissolving 2.70 g (5.4 mmol) of $UO_2(NO_3)_2 \cdot 6H_2O$ and 1.50 g (5.7 mmol) of 18-crown-6 in 90 ml of warm acetonitrile. The solution was allowed to stand overnight at 10 °C, filtered, washed with a few milliliters of acetonitrile, and then vacuum-dried overnight at 25 °C to give 2.64 g (67% yield) of bright yellow needles of the title compound. The x-ray powder pattern, infrared spectrum, and decomposition point of the compound prepared by this method are indistinguishable from material prepared in ethanol.[9]

Anal. Calcd for $UO_{18}N_2C_{12}H_{32}$: C, 19.73; H, 4.42; N, 3.84. Found: C, 20.22; H, 4.08; N, 3.67.

The compound is stable for days at 100 °C under 1 atm of N_2. In an open capillary, the compound melts at 140–147 °C with effervescence to a yellow liquid which resolidifies to a yellow powder by 160 °C and then gradually darkens above 265 °C. From a mixture of neat 18-crown-6 and $UO_2(NO_3)_2 \cdot 6H_2O$ at 150 °C, the compound $UO_3 \cdot {}^1/_2$(18-crown-6) forms, with properties identical with those of the above yellow powder.

Anal. Calcd: N, 0.00; C, 17.23; H, 2.89. Found: N, 0.00; C, 17.34; H, 2.91.

X-Ray Data Collection. Optical examination and precession photographs failed to reveal any symmetry higher than triclinic. A parallelepiped of dimensions 0.06 × 0.08 × 0.14 mm was mounted approximately parallel to the long dimension of the crystal and 12 reflections with 2θ in the range 33–44° were centered using an automated diffractometer and graphite-monochromatized Mo radiation (λ 0.709 30 Å). Least-squares refinement of the setting angles and orientation matrix gave the following cell: $a = 7.526$ (7) Å, $b = 11.27$ (1) Å, $c = 7.802$ (4) Å, $\alpha = 97.51$ (6)°, $\beta = 93.22$ (6)°, $\gamma = 105.95$ (6)°. The unit cell thus chosen contains one formula unit ($\rho_{calcd} = 1.93$ g cm^{-3}) and the large, medium, and small faces are of the forms {001}, {100}, and {010}, respectively. A data set was collected within the limiting hemisphere $1 \leq 2\theta \leq 60°$ by the θ–2θ scan technique using a Picker FACS-I automated diffractometer equipped with a graphite monochromator (λ 0.709 30 Å). A scan range of 2° plus a θ-dependent dispersion term and background counts of 20 s each were used. Of the 3143 unique reflections examined, 2453 were judged to be above background on the basis that $I \geq 3\sigma(I)$ where $\sigma(I) = [T + B + [0.015(T - B)]^2]^{1/2}$, T being the total count for each scan and B being the estimated background. The intensities of two standard reflections, measured after every 50 reflections, were found to decrease by ca. 8% during data collection, apparently due to crystal decomposition. An appropriate correction was applied using a polynomial determined by least-squares fitting the standard reflection curves. Lorentz and polarization corrections were applied in the usual way. Absorption corrections were applied[11,12] ($\mu = 194.3$ cm^{-1}; transmission coefficients 0.21–0.35). Otherwise, the data collection and reduction were as previously described.[13]

Solution and Refinement of the Structure. The centric space group ($P\bar{1}$) was initially chosen, an assumption supported by the successful refinement of the structure. With one formula unit per cell, the uranyl and crown ether groups each are required to possess $\bar{1}$ symmetry. The uranium atom was placed at the origin, and the carbon, nitrogen, and oxygen atoms were easily located with a difference Fourier synthesis. Neutral atom scattering factors were used for the light atoms and hexavalent scattering factors for uranium.[14] Anomalous dispersion terms were included for uranium.[15] A conventional anisotropic refinement of the 17 nonhydrogen atoms plus an overall scale factor