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The Crystal and Molecular Structures of $[(C_6H_5CH_2)_3P]_2PdX_2$; X = CN, N_3

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The crystal structures of the complexes (I) trans-*$[(C_6H_5CH_2)_3P]_2Pd(N_3)_2$, and (II)* trans-*$[(C_6H_5CH_2)_3P]_2Pd(CN)_2 \cdot 2CHCl_3$ have been determined by Patterson and Fourier methods. Crystal data are: (I), monoclinic, space group $P2_1/a$, Z = 2, a = 13.424(16), b = 18.724(11), c = 7.673(6) Å, β = 91.58(16)°; (II), triclinic, space group $C\bar{1}$, Z = 1, a = 12.301(4), b = 18.516(6), c = 10.347 Å, α = 89.54(5), β = 104.86(5), γ = 88.16(4)°. The structural data illustrate that both of these complexes are* trans *because of the large steric bulk of the tribenzylphosphine. The conformation and cone angle of tribenzylphosphine are very flexible (the cone angle varies from 200° in (I) to 232° in (II)). The phenyl rings in (II) effectively block the fifth and sixth coordination positions about the palladium whereas in (I) the* ortho *hydrogens of the phenyl rings occupy these positions. A sizeable* cis-*influence is manifest in these complexes. In this vein, the Pd–P distance in (I), 2.316 Å is shorter than in (II), 2.331 Å suggesting that cyanide exerts a greater* cis-*influence than azide.*

Introduction

The relative thermodynamic stabilities of *cis* and *trans* isomers of compounds of the type $(R_3P)_2MX_2$ have interested chemists for some time [1]. This interest is intimately related to detailed theoretical consideration of the bonding in complexes of this sort. A knowledge of the bonding, including the effects of steric and electronic perturbations, is in turn important in predicting the reactivity of these species [2]. It is normally found for L_2PdX_2 complexes that the *cis* isomer is thermodynamically more stable than the *trans*, and that the two isomers are often interconvertible by one of three associative processes [3]. The isomeric energy difference, the rate of interconversion, and the general reactivity of these species is highly ligand (R_3P) and anion dependent [4]. For example, equilibrium mixtures of isomers generally exist in solution [5] for $(R_3P)_2Pd(N_3)_2$, the isomer population being temperature dependent, and in this series the *cis* isomer is favored by electronic and the *trans* favored by steric effects. On the other hand, solutions of the $(R_3P)_2Pd(CN)_2$ complexes contain only the *trans* isomer and this was rationalized on the basis of electronic effects [6].

There has been considerable recent interest in chemical reactions which as a class have been termed *ortho-*, internal- or cyclo-metallations [7]. The facility with which these reactions occur has been related to a number of factors, including the metal, the donor atom, the chelate ring size, the nature of the leaving group, and the steric bulk and conformation of the ligand.

In order to obtain accurate structural data and to gain further insight into the factors which control the geometry and reactivity of L_2PdX_2 complexes, the X-ray crystal structures of $[(C_6H_5CH_2)_3P]_2PdX_2$, X = N_3, CN were determined, where the R group in this case is a relatively bulky group.

Experimental

The syntheses of the complexes $[(C_6H_5CH_2)_3P]_2PdX_2$; X = N_3 [5a], X = CN [6] have been previously described. Well-formed crystals were grown from chloroform by slow evaporation.

Crystal Data

(I) $(Bzl_3P)_2Pd(N_3)_2$

Monoclinic, $P2_1/a$, $Z = 2$, yellow, $a = 13.424(16)$, $b = 18.724(11)$, $c = 7.673(6)$ Å, $\beta = 91.58(16)°$, $\rho_c = 1.38$ g cm^{-3}, $\mu = 6.0$ cm^{-1}.

(II) $(Bzl_3P)_2Pd(CN)_2 \cdot 2CHCl_3$

Triclinic, $C\bar{1}$, $Z = 1$, $a = 12.301(4)$, $b = 18.516(6)$, $c = 10.347(4)$ Å, $\alpha = 89.54(5)$, $\beta = 104.86(5)$, $\gamma = 88.16(4)°$, $\rho_c = 1.46$ g cm^{-3}, $\mu = 8.5$ cm^{-1}.

Crystals were mounted in glass capillaries and transferred directly to a four-circle diffractometer.

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TABLE I. Positional Parameters[a] for $[(C_6H_5CH_2)_3]_2Pd(N_3)_2$.

Atom	x	y	z	Atom	x	y	z
Pd	0	0	0	C(35)	–3793(7)	2299(4)	445(1)
P	–1156(1)	8633(9)	707(2)	C(36)	–4137(6)	1829(5)	316(1)
N(1)	–638(4)	–744(3)	1568(8)	C(37)	–3543(5)	1300(4)	2572(9)
N(2)	385(4)	–837(3)	3008(9)	H(11)	–2575	1443	–652
N(3)	–188(5)	–955(4)	448(1)	H(11)	–1583	1339	–2125
C(11)	–2010(4)	1077(3)	–1120(8)	H(13)	–1230	–59	–2870
C(12)	–2534(5)	444(3)	–1934(8)	H(14)	–2124	–1054	–4284
C(13)	–2040(5)	–80(3)	–2820(9)	H(15)	–3962	–1072	–4352
C(14)	–2538(7)	–632(4)	–3644(9)	H(16)	–4880	–159	–2781
C(15)	–3559(9)	–648(5)	–365(1)	H(17)	–3991	841	–1303
C(16)	–4068(7)	–133(7)	–280(1)	H(21)	–675	1835	2632
C(17)	–3572(6)	423(5)	–195(1)	H(21)	256	1658	1081
C(21)	–541(5)	1723(3)	1264(8)	H(23)	–2183	2559	1679
C(22)	–885(5)	2371(3)	206(7)	H(24)	–2698	3625	–44
C(23)	–1732(5)	2736(3)	601(8)	H(25)	–1708	4042	–2461
C(24)	–2033(6)	3338(4)	–37(1)	H(26)	–207	3381	–3282
C(25)	–1477(8)	3568(4)	–172(1)	H(27)	368	2317	–1514
C(26)	–632(7)	3204(4)	–217(1)	H(31)	–1410	459	3634
C(27)	–312(5)	2599(3)	–1188(9)	H(31)	–2385	172	2179
C(31)	–1914(5)	621(3)	2570(8)	H(33)	–1485	1604	5092
C(32)	–2583(5)	1203(3)	3247(8)	H(34)	–2544	2581	6137
C(33)	–2236(5)	1670(4)	4540(8)	H(35)	–4272	2725	4921
C(34)	–2830(8)	2216(4)	5135(9)	H(36)	–4892	1888	2620
				H(37)	–3826	945	1550

*The positional parameters are in fractional unit cell coordinates ($\times 10^4$), except for hydrogens ($\times 10^3$). In this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures.

Initial ω-oscillation photographs were taken and approximate positions of reflections selected from these photographs were input into the automatic indexing program reported by Jacobson [8]. The reduced cell and reduced cell scalars indicated probable crystal symmetry. Subsequent ω-oscillation photographs about each of the three crystal axes verified reciprocal lattice spacing and for (I), the 2/m Laue symmetry as well. Unit cell parameters were obtained by a least squares fit to tuned $\pm 2\theta$ values for several high angle reflections.

Collection and Reduction of X-Ray Intensity Data

Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory and interfaced to a PDP-15 computer in a real-time mode [9]. All data in the hkl and $hk\bar{l}$ octants for (I) and in the hkl, $hk\bar{l}$, $h\bar{k}l$ and $h\bar{k}\bar{l}$ octants for (II) within a sphere of $2\theta \leqslant 45°$ ($\sin\theta/\lambda = 0.539$) were collected using an ω-stepscan technique and graphite monochromated Mo K_α radiation ($\lambda = 0.70954$ Å). Care was taken to limit the use of room lighting when data was collected on (I) because of this particular azide's photosensitivity.

As a general check on crystal and electronic stability, the intensities of three standard reflections were remeasured every 75 reflections. These indicated that some crystal decomposition had occurred during data collection (<20%) and therefore the data were corrected for linear decomposition.

The intensity data were then corrected for Lorentz and polarization effects. Because of the small μ, absorption corrections were not made. The estimated variance in each intensity was calculated by

$$\sigma_I^2 = C_T + K_TC_B + (0.03\,C_T)^2 + (0.03\,C_B)^2$$

where C_T, C_B and K_T represent total count, background count, and counting time factors, respectively, and the factor 0.03 represents an estimate of non-statistical errors. The estimated deviations in the structure factors were calculated by the finite difference method [10]. After correction, 1981 reflections for (I) and 3838 reflections for (II) were considered observed ($>3\sigma_I$) and retained for use in the structural solution and refinement.

Solution and Refinement

The palladium atom in both structures was restricted to sit on a center of symmetry. The phosphorus position (I) was readily obtained by examining a sharpened Patterson. All other non-hydrogen atoms in both structures were found by successive

TABLE II. Thermal Parameters[a] for $[(C_6H_5CH_2)_3P]_2Pd(N_3)_2$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	5.94(5)	2.68(2)	14.2(1)	0.08(2)	−0.64(6)	0.68(4)
P	6.2(1)	2.78(5)	14.0(3)	0(6)	−0.8(1)	0.6(1)
N(1)	9.4(4)	3.5(2)	20(1)	0(2)	0.6(6)	2.1(4)
N(2)	7.1(4)	3.1(2)	26(1)	0.3(2)	2.4(6)	2.1(4)
N(3)	12.8(6)	6.7(3)	22(1)	−0.6(3)	−0.7(7)	5.0(6)
C(11)	6.9(4)	3.0(2)	18(1)	−0(2)	−2.9(6)	0.9(4)
C(12)	7.3(5)	3.7(2)	15(1)	−0.5(3)	−0.9(6)	1.4(4)
C(13)	8.0(5)	4.0(2)	16(1)	−0.6(3)	−1.0(7)	−0.7(4)
C(14)	11.5(7)	5.2(3)	18(1)	−2.0(4)	0.3(8)	−1.8(5)
C(15)	15(1)	6.0(4)	24(1)	−4.8(5)	−1(1)	−2.4(7)
C(16)	8.1(6)	9.8(6)	31(2)	−3.6(5)	−1(1)	−4.6(9)
C(17)	8.3(6)	6.4(3)	26(1)	−0.3(4)	−3.1(8)	−2.0(7)
C(21)	7.3(4)	3.0(2)	19(1)	−0(2)	−0.9(6)	0.7(4)
C(22)	7.7(4)	2.6(2)	15(1)	−0.3(2)	−0.5(6)	−0(4)
C(23)	9.3(5)	3.4(2)	20(1)	0.7(3)	0.6(7)	1.1(5)
C(24)	10.8(6)	3.6(2)	23(1)	1.2(3)	−1.4(8)	−0.6(5)
C(25)	14.9(8)	3.1(2)	27(2)	1.0(4)	−2(1)	0.1(6)
C(26)	13.3(8)	4.1(3)	22(1)	−1.0(4)	0(9)	2.4(6)
C(27)	9.7(5)	3.5(2)	21(1)	−0.6(3)	0.6(7)	0.5(5)
C(31)	8.4(5)	3.0(2)	18(1)	0.8(2)	1.4(6)	1.3(4)
C(32)	7.1(4)	3.4(2)	16(1)	0.5(2)	0.8(6)	2.0(4)
C(33)	9.7(5)	4.2(2)	15(1)	0.9(3)	−0.4(7)	0.4(5)
C(34)	13.5(8)	4.4(3)	20(1)	0(4)	2.7(9)	−0.2(5)
C(35)	11.5(7)	5.1(3)	27(2)	2.9(4)	4(1)	2.3(7)
C(36)	8.2(3)	5.7(3)	25(1)	1.4(4)	0.7(8)	2.0(7)
C(37)	6.2(4)	4.5(3)	23(1)	0.5(3)	0.6(7)	0.1(5)

[a] The β_{ij} are $\times 10^3$ and defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$. For all hydrogen atoms an isotropic thermal parameter of 7.0 Å^2 was assigned.

TABLE III. Bond Distances (Å) for $[(C_6H_5CH_2)_3P]_2Pd(N_3)_2$

Pd–N(1)	2.045(6)	C(21)–C(22)	1.524(9)
N(1)–N(2)	1.161(8)	C(22)–C(23)	1.367(9)
N(2)–N(3)	1.180(9)	C(23)–C(24)	1.403(10)
Pd–P	2.316(2)	C(24)–C(25)	1.357(11)
P–C(11)	1.831(7)	C(25)–C(26)	1.374(12)
P–C(21)	1.854(7)	C(26)–C(27)	1.421(11)
P–C(31)	1.834(7)	C(27)–C(22)	1.402(9)
C(11)–C(12)	1.505(9)	C(31)–C(32)	1.512(9)
C(12)–C(13)	1.376(10)	C(32)–C(33)	1.393(9)
C(13)–C(14)	1.376(10)	C(33)–C(34)	1.381(11)
C(14)–C(15)	1.370(13)	C(34)–C(35)	1.390(12)
C(15)–C(16)	1.362(14)	C(35)–C(36)	1.394(12)
C(16)–C(17)	1.391(13)	C(36)–C(37)	1.357(11)
C(17)–C(12)	1.393(10)	C(37)–C(32)	1.388(9)

structure factor and electron density map calculations [11]. The hydrogen positions were calculated with the C–H distance set to 1.09 Å. The isotropic thermal parameters for hydrogen were fixed at 7.0 Å^2. The cycle of varying non-hydrogen parameters followed by calculation of new hydrogen positions was repeated until convergence of the non-hydrogen parameters.

Refinement of the positional and anisotropic thermal parameters of all non-hydrogen atoms by a full matrix least squares procedure minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma_F^2$, yielded final crystallographic residual factors $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$ of 0.057 for (I) and 0.062 for (II). The final weighted residuals $R_w = \{\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega|F_o|^2\}^{1/2}$ were 0.075 for (I) and 0.076 for (II). The weights (ω) were adjusted so that $\omega(|F_o| - |F_c|)^2$ was a constant function of $\sin\theta/\lambda$.

The final positional and thermal parameters are listed in Tables I and II for (I) and V and VI for (II). Bond lengths and bond angles are listed in Tables III and IV for (I) and VII and VIII for (II). ORTEP [12] drawings of the molecules are given in Figs. 1 and 2. A list of calculated and observed structure factors is available from the authors upon request.

Discussion

Both the azide (I) and cyano (II) complexes are *trans* in the solid state (Figs. 1 and 2) as they are in

TABLE IV. Bond Angles (°) for $[(C_6H_5CH_2)_3P]_2Pd(N_3)_2$.

Pd–N(1)–N(2)	123.1(5)	C(16)–C(17)–C(12)	119.4(9)
N(1)–N(2)–N(3)	175.4(7)	C(21)–C(22)–C(23)	121.4(6)
P–Pd–N(1)	92.5(2)	C(22)–C(23)–C(24)	120.2(7)
Pd–P–C(11)	112.5(2)	C(23)–C(24)–C(25)	121.1(8)
Pd–P–C(21)	111.3(2)	C(24)–C(25)–C(26)	119.9(8)
Pd–P–C(31)	113.6(2)	C(25)–C(26)–C(27)	120.2(7)
P–C(11)–C(12)	114.9(4)	C(26)–C(27)–C(22)	118.9(7)
P–C(21)–C(22)	116.2(4)	C(31)–C(32)–C(33)	120.5(6)
P–C(31)–C(32)	116.0(4)	C(32)–C(33)–C(34)	121.0(7)
C(11)–C(12)–C(13)	122.8(6)	C(33)–C(34)–C(35)	119.9(8)
C(12)–C(13)–C(14)	121.9(8)	C(34)–C(35)–C(36)	118.9(8)
C(13)–C(14)–C(15)	119.6(8)	C(35)–C(36)–C(37)	120.7(8)
C(14)–C(15)–C(16)	119.7(8)	C(36)–C(37)–C(32)	121.3(7)
C(15)–C(16)–C(17)	121.2(9)		

TABLE V. Positional Parameters[a] for $[(C_6H_5CH_2)_3P]_2Pd(CN)_2$.

Atom	x	y	z	Atom	x	y	z
C(4)	7497(4)	9414(2)	9571(5)	C(33)	9302(4)	3503(3)	6264(5)
Cl(1)	7270(1)	8550(1)	8867(2)	C(34)	9481(4)	3854(3)	5166(6)
Cl(2)	6196(1)	9866(1)	9395(2)	C(35)	8591(5)	4002(3)	4093(6)
Cl(3)	8361(1)	9902(9)	8810(1)	C(36)	7502(4)	3808(2)	4086(4)
Pd	5000	5000	5000	H(4)	7915	9352	10633
P	5401(8)	3872(5)	6063(9)	H(1α)	5928	4328	8301
C	5278(3)	5473(2)	6777(4)	H(1β)	7079	3868	7877
N	5442(3)	5729(2)	7807(3)	H(12)	5136	3817	9824
C(1)	6185(3)	3848(2)	7834(4)	H(13)	4794	2769	11129
C(11)	6021(3)	3192(2)	8644(3)	H(14)	5508	1549	10728
C(12)	5443(4)	3280(2)	9632(4)	H(15)	6562	1385	9021
C(13)	5257(4)	2694(3)	10369(4)	H(16)	6884	2425	7688
C(14)	5656(4)	2012(3)	10146(5)	H(2)	3805	3638	6930
C(15)	6239(4)	1921(2)	9192(4)	H(2)	4264	2854	6206
C(16)	6240(4)	2506(2)	8445(4)	H(22)	2724	4621	5460
C(2)	4090(3)	3434(2)	6083(4)	H(23)	1235	4887	3394
C(21)	3163(3)	3568(2)	4837(4)	H(24)	767	3985	1639
C(22)	2543(3)	4222(2)	4671(5)	H(25)	1849	2845	1852
C(23)	1700(4)	4369(3)	3516(6)	H(26)	3379	2554	3908
C(24)	1448(5)	3871(4)	2530(6)	H(3α)	5649	3194	4176
C(25)	2043(5)	3234(3)	2656(5)	H(3β)	6213	2713	5711
C(26)	2909(4)	3069(2)	3813(5)	H(32)	8098	3016	7137
C(3)	9302(4)	3237(2)	5207(4)	H(33)	10324	3382	7131
C(31)	7315(3)	3457(2)	5191(4)	H(34)	10324	4014	5154
C(32)	7315(3)	3302(2)	6267(4)	H(35)	8733	4278	3219
				H(36)	6805	3932	3216

[a] As in Table I.

solution [5a, 6]. The large steric effect of the tribenzylphosphine ligand (average cone angle = 200° in (I) and 232° in (II)) doubtlessly contributes to the relative stability of the *trans* isomers. Both of these cone angles are substantially larger than Tolmans' minimum cone angle [2] of 165° for tribenzylphosphine illustrating the flexibility of the ligand cone angle [13].

Comparison of these two structures gives us direct information on the relative *cis*-influence of the azide and cyano ligands and allows us to speculate on the electronic factors involved. The Pd–P bond distance of 2.316 Å in (I) is shorter than the 2.331(1) Å distance in (II). This fact coupled with the ^{31}P chemical shift [(I) δ 15.7 ppm and (II) δ 15.1 ppm] which indicate that the phosphorus in (I) is less shielded

TABLE VI. Thermal Parameters* for $[(C_6H_5CH_2)_3P]_2Pd(CN)_2$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(4)	7.2(3)	3.4(1)	12.5(5)	−0.1(1)	2.0(3)	1.1(2)
Cl(1)	10.8(1)	4.48(6)	28.1(3)	−1.40(7)	4.4(1)	−3.0(1)
Cl(2)	13.4(1)	5.21(7)	31.1(3)	3.18(9)	12.2(2)	5.1(1)
Cl(3)	9.3(1)	4.75(5)	15.8(1)	−0.62(6)	3.4(1)	2.45(8)
Pd	4.77(3)	1.90(1)	5.73(4)	−0.06(1)	1.38(2)	0.41(1)
P	5.01(7)	1.86(2)	6.40(9)	−0.05(3)	1.38(6)	0.45(4)
C	5.7(2)	2.3(1)	8.7(4)	0(1)	1.6(2)	0.9(1)
N	10.4(3)	3.4(1)	6.9(3)	0.1(1)	1.4(2)	−0.5(1)
C(1)	6.9(3)	2.3(1)	6.9(3)	−0.1(1)	0.9(2)	0.4(1)
C(11)	5.6(2)	2.6(1)	6.4(3)	0(1)	0.4(2)	0.6(1)
C(12)	7.1(3)	3.6(1)	8.1(4)	0.4(1)	1.7(3)	0.8(2)
C(13)	8.4(4)	4.9(2)	8.4(4)	−0(2)	2.5(3)	1.4(2)
C(14)	9.5(4)	3.7(1)	9.0(5)	−1.6(2)	0.2(3)	1.7(2)
C(15)	9.3(4)	2.9(1)	9.3(5)	−0.7(1)	0.2(3)	0.9(2)
C(16)	7.7(3)	2.5(1)	8.5(4)	0.1(1)	1.4(3)	0.8(1)
C(2)	6.0(3)	2.7(1)	9.7(4)	−0.6(1)	2.2(3)	1.0(2)
C(21)	5.5(2)	2.7(1)	8.7(4)	−1.0(1)	2.1(2)	0.4(1)
C(22)	5.3(3)	3.5(1)	12.4(5)	−0.8(1)	2.4(3)	0.2(2)
C(23)	5.4(3)	4.6(2)	16.7(7)	−0(2)	1.3(4)	2.3(3)
C(24)	8.1(4)	5.4(2)	13.1(6)	−2.0(2)	−0.8(4)	1.9(3)
C(25)	11.6(5)	4.9(2)	11.2(6)	−3.3(3)	1.4(4)	−1.1(3)
C(26)	9.4(4)	3.0(1)	10.9(5)	−1.3(2)	2.3(3)	−0.2(2)
C(3)	6.3(3)	2.1(1)	8.4(4)	0(1)	2.4(2)	−0.3(1)
C(31)	6.2(3)	2.3(1)	8.7(4)	0.2(1)	2.5(2)	−0.1(1)
C(32)	7.0(3)	3.1(1)	9.0(4)	−0(1)	2.2(3)	0.5(2)
C(33)	6.8(3)	4.6(2)	12.0(6)	−0.6(2)	2.2(3)	−0.2(2)
C(34)	8.1(4)	4.6(2)	15.7(7)	−1.0(2)	5.3(4)	−0.5(3)
C(35)	9.3(4)	4.8(2)	13.5(6)	0(2)	5.7(4)	1.7(3)
C(36)	7.7(3)	3.4(1)	10.3(5)	0.6(1)	3.7(3)	0.9(2)

*As in Table II.

TABLE VII. Bond Distances (Å) for $[(C_6H_5CH_2)_3P]_2Pd(CN)_2$.

C(4)–Cl(1)	1.764(6)	C(16)–C(11)	1.384(6)
C(4)–Cl(2)	1.749(6)	C(2)–C(21)	1.499(6)
C(4)–Cl(3)	1.745(5)	C(21)–C(22)	1.394(7)
Pd–C(3)	1.998(5)	C(22)–C(23)	1.386(8)
Pd–P	2.331(1)	C(23)–C(24)	1.363(9)
C–N	1.143(6)	C(24)–C(25)	1.356(10)
P–C(1)	1.839(4)	C(25)–C(26)	1.407(8)
P–C(2)	1.832(4)	C(26)–C(21)	1.392(7)
P–C(3)	1.833(4)	C(3)–C(31)	1.513(6)
C(1)–C(11)	1.518(6)	C(31)–C(32)	1.383(6)
C(11)–C(12)	1.394(6)	C(32)–C(33)	1.386(7)
C(12)–C(13)	1.380(7)	C(33)–C(34)	1.374(8)
C(13)–C(14)	1.384(8)	C(34)–C(35)	1.364(9)
C(14)–C(15)	1.369(8)	C(35)–C(36)	1.396(7)
C(15)–C(16)	1.382(7)	C(36)–C(31)	1.384(6)

than in (II) imply that there is a larger σ-component in the Pd–P bond in (I) than in (II). These bond lengths also imply that cyanide exerts a greater influence on distances *cis* to it than does azide and is consistent with previous suggestions [14]. This is not unexpected as cyanide also exerts a greater *trans*-influence [15] than azide. One might attribute the difference in Pd–P bond lengths to azide being a better π-acceptor [16] than cyanide but this interpretation is seemingly refuted by the symmetric nature of the azide in (I), N_1–N_2, 1.161(8) Å ≈ N_2–N_3, 1.180(9) Å. One would anticipate that significant π-bonding would result in a lengthening of the N_1–N_2 bond relative to the N_2–N_3 bond as is the case in many coordinated azides [17]. It seems then that the difference in *cis*-influences must be explained by a larger σ-contribution from cyanide than from azide.

The Pd–N distance 2.045(6) Å in (I) is significantly larger than that in [18] $[Pd_2(N_3)_6]^{2-}$, 2004(5) Å, implying a greater *cis* influence for Bzl_3P than for azide. It is interesting to note that for $[N_3Pd(Et_4\text{-}dien)]^+$ the Pd–N distance 2.077(12) Å [16] is also significantly longer than in $[Pd_2(N_3)_6]^{2-}$ and that for both this complex and (I), the azide is symmetric while for $[Pd_2(N_3)_6]^{2-}$ the azide ligand is

TABLE VIII. Bond Angles (°) for $[(C_6H_5CH_2)_3P]_2Pd(CN)_2$.

Cl(1)–C(4)–Cl(2)	108.8(3)	C(13)–C(14)–C(15)	119.7(4)
Cl(1)–C(4)–Cl(3)	110.7(3)	C(14)–C(15)–C(16)	120.3(5)
Cl(2)–C(4)–Cl(3)	111.1(3)	C(15)–C(16)–C(11)	121.0(5)
P–Pd–C	90.0(1)	C(2)–C(21)–C(22)	119.4(4)
Pd–C–N	178.5(4)	C(21)–C(22)–C(23)	120.8(5)
Pd–P–C(1)	117.5(1)	C(22)–C(23)–C(24)	120.4(6)
Pd–C–C(2)	109.9(1)	C(23)–C(24)–C(25)	120.2(5)
Pd–P–C(3)	113.6(1)	C(24)–C(25)–C(26)	120.7(5)
P–C(1)–C(11)	116.0(3)	C(25)–C(26)–C(21)	119.7(5)
P–C(2)–C(21)	113.8(3)	C(3)–C(31)–C(32)	121.1(4)
P–C(3)–C(31)	114.3(3)	C(31)–C(32)–C(33)	121.6(4)
C(1)–C(11)–C(12)	119.1(4)	C(32)–C(33)–C(34)	119.8(5)
C(11)–C(12)–C(13)	120.7(5)	C(33)–C(34)–C(35)	119.2(5)
C(12)–C(13)–C(14)	120.1(5)	C(34)–C(35)–C(36)	121.6(5)
		C(35)–C(36)–C(31)	119.6(5)

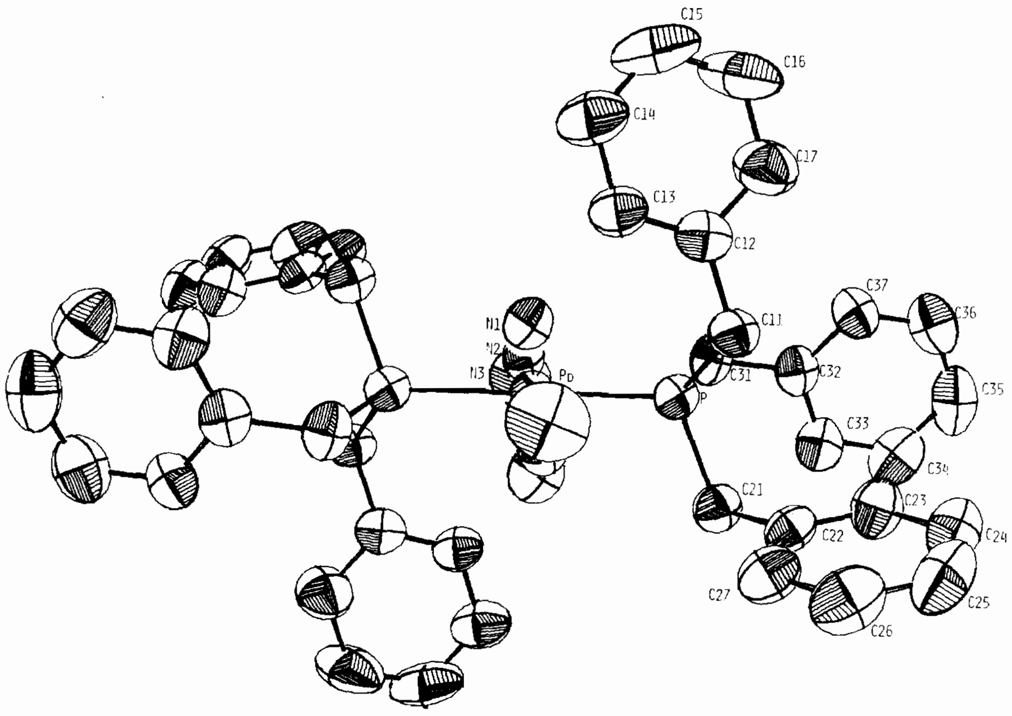

Fig. 1. The $[(C_6H_5CH_2)_3P]_2Pd(N_3)_2$ molecule showing 50% probability ellipsoids.

asymmetric. The bond angle involving the metal and the linear (175.4(7)°) N_3 group, which may not be very sensitive to electronic factors, is 123.1(5)° indicative of an sp^2 hydridized N_1 atom. The dihedral angle between the Pd–N_3 plane and the coordination plane defined by Pd, P and N_1 is 88°.

Complex (II) exhibits the expected coordination of the cyanide linear to the metal (Pd–C–N, 178.5(4)°) with Pd–C and C–N distances of 1.998(5) and 1.143(6) Å. These bond distances are in accord with those previously reported for palladium cyanides [19].

Considerable interest has recently [7] been expressed in reactions known as cyclometallations and the factors that govern the facility of these reactions. In this light, Bzl_3P is readily metallated by platinum [20]. The complex *trans*-$(PMe_2Ph)_2$ PdI_2 exists in two isomeric forms [21], a red isomer with an average Pd–P distance of 2.629 Å and a yellow isomer with a Pd–P distance of 2.333(7) Å. The red isomer has the phenyl rings situated such that the fifth coordination site on palladium is effectively occupied by the *ortho* hydrogen. It has been demonstrated that the anion in complexes of the

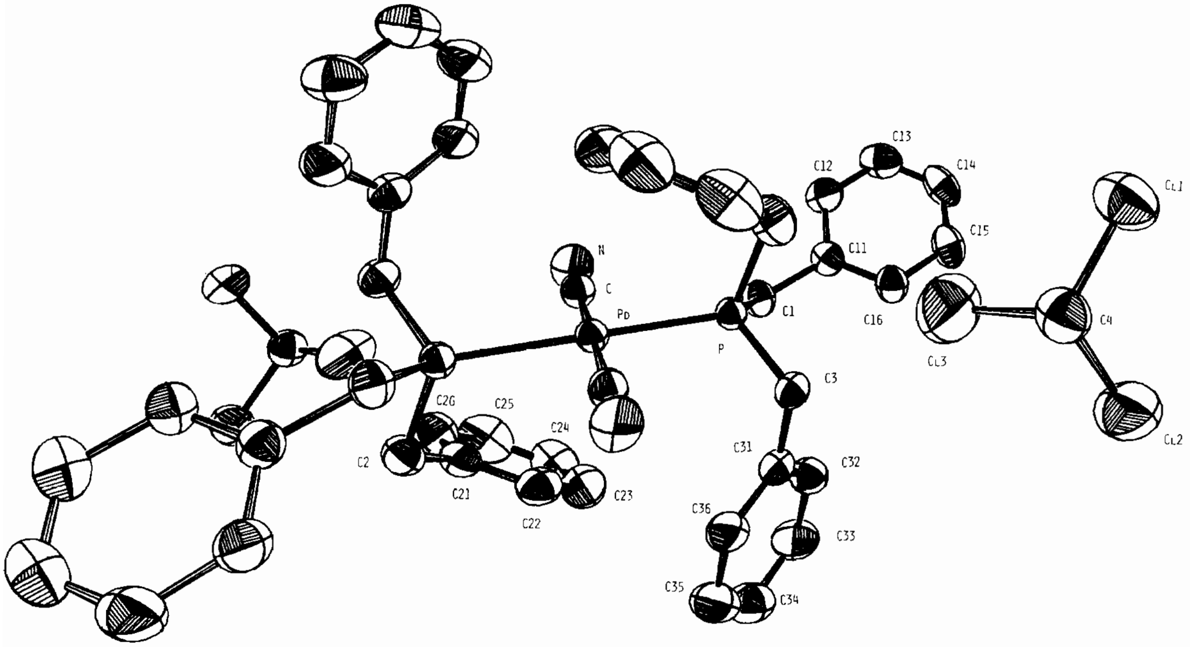

Fig. 2. The $[(C_6H_5CH_2)_3P]_2Pd(CN)_2$ molecule showing 50% probability ellipsoids.

type L_2MX_2 has a considerable influence on the ability of these complexes to undergo cyclometallation reactions. As can be seen in Figs. 1 and 2, the fifth and sixth coordination positions are effectively blocked by the phenyl rings of the Bzl_3P ligands. But, in (II) the rings are oriented in a nearly π-bonding fashion whereas in (I) the *ortho* hydrogens occupy the fifth and sixth coordination positions. It would seem then that (I) has a more favorable orientation for cyclometallation than (II).

It is interesting to note that even though Bzl_3P has a much greater cone angle than Me_2PPh, the Pd–P distances in both (I) and (II) are shorter than they are in either isomer of *trans* $(Me_2PPh)_2PdI_2$. This could simply reflect the smaller steric bulk of N_3^- and CN^- relative to I^-.

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