$Et_2NCH_2CH_2N(CH_2CH_2PPh_2)_2$ apparently induces the trigonal-bipyramidal structure onto cobalt in that case.

Figure 3 is a stereoscopic view showing the molecular packing of the cobalt complex. The hydrogen atoms were refined for the cobalt structure, and they are included in the stereoscopic view. The unit-cell dimensions of the nickel and cobalt complexes are similar except for an elongation of the *c* axis (0.34 Å) in the nickel complex. This elongation of the *c* axis is attributed to the increased metal–halogen bond length in the nickel complex. The positional parameters of comparable atoms in both structures are very similar, even to the position of the boron and phosphorus atoms of the anions. The position of F1 in the cobalt complex is close to the position of F4 in the nickel complex; the anions in both complexes are located above the plane defined by the four donor atoms, near N1 and close to the phenyl rings.

A water molecule is located near amine proton H51 in the cobalt complex. The N2–H51–O angle is 159° with a contact distance of 3.08 Å between N2 and oxygen. The H51–O distance is 2.25 Å, which is sufficiently close for hydrogen bonding. Since only very weak O–H absorption bands were observed in the infrared spectrum of the cobalt complex when it was stored in a dry N_2 atmosphere, we assume that the H_2O molecule became entrapped in the lattice during a long exposure to the laboratory atmosphere before the X-ray data collection began. There was no X-ray evidence, and only very weak infrared evidence, of water in the nickel complex.

Hydrogen bonding of the amine protons appears to be prominent in both the nickel and cobalt complexes. The number of amine stretching vibrations can be explained on the basis of hydrogen-bonding contact distances between the N–H protons and the halogen atoms near them (Table IX).

The sums of the van der Waals radii for the sets of atoms H, F and H, Cl are 2.5 and 3.0 Å, respectively; thus, the $X\cdots H$ distances determined here and reported in Table IX indicate the presence of intermolecular hydrogen bonding in the solid state. The infrared spectrum of the cobalt complex shows two vibrations at 3240 and 3190 cm^{-1} that arise from N–H hydrogen bonding, whereas the nickel complex shows three bands at 3210, 3160, and 3110 cm^{-1} (Figure 1). One possible reason for the difference in the number of absorption bands may be the fact that the N1 proton in the nickel complex is about equidistant from F4 and F5, whereas only one fluorine atom (F1) is near N1 in the cobalt complex. The hydrogen–fluorine contact distance with either F4 or F5 is estimated to be ~2.4 Å, which is within hydrogen-bonding limits. The sharp infrared band at 3290 cm^{-1} that is observed for both metal complexes is assigned to the amine proton H51, which does not participate in any hydrogen bonding.

Acknowledgment. The authors thank Capt. M. Wellman, Air Force Wright Aeronautical Laboratory, WPAFB, and Dr. A. Fratini, University of Dayton Research Institute, for access to and assistance in operating the Picker FACS-1 diffractometer. Dr. D. J. Schaefer, Wright State University Computing Center, is thanked for his help with the X-ray calculations. S.C.C. gratefully acknowledges financial support for this investigation by the National Institutes of Health, Grant HL 15640, from the Heart, Lung and Blood Institute.

Registry No. $[NiCl(3,3,3\text{-}N_2P_2)]PF_6$, 81447-13-4; $[CoCl(3,3,3\text{-}N_2P_2)]BF_4\cdot 0.8H_2O$, 81447-16-7; 3,3,3-$N_2P_2$, 71734-66-2; Ph(H)-$PCH_2CH_2CH_2NH_2$, 13822-50-9; 1,3-dichloropropane, 142-28-9.

Supplementary Material Available: Listings of structure factor amplitudes (×10), positional and thermal parameters for the hydrogen atoms, thermal parameters for nonhydrogen atoms, least-squares planes, and bond lengths and angles for the anions (50 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of $[(t\text{-}C_4H_9NC)_2Pd((C_6H_5)_2PCH_2P(C_6H_5)_2)_2][B(C_6H_5)_4]_2$, a Compound with Two Monodentate Diphosphine Ligands

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$[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$ (dpm is bis(diphenylphosphino)methane) has been prepared by the successive addition of *tert*-butyl isocyanide, dpm, and sodium tetraphenylborate to bis(benzonitrile)palladium dichloride, by the addition of *tert*-butyl isocyanide, dpm, and sodium tetraphenylborate to $(dpm)PdCl_2$ and by the addition of *tert*-butyl isocyanide and sodium tetraphenylborate to $[Pd_2(\mu\text{-dpm})_2(\mu\text{-I})(CH_3)I][BF_4]$. The structure of $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$ has been determined by X-ray crystallography. It crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell of dimensions $a = 13.554$ (12) Å, $b = 14.172$ (8) Å, $c = 14.658$ (8) Å, $\alpha = 113.58$ (5)°, $\beta = 111.39$ (5)°, and $\gamma = 97.00$ (6)°. Full-matrix least-squares refinement yielded $R = 7.9\%$. The palladium is planar with trans isocyanide and trans, monodentate dpm ligands.

Introduction

Bis(diphenylphosphino)methane (dpm) has been extensively used as a bridging ligand.[1-3] In this form, it is remarkable for the variability in the metal–metal separation which it spans.[4] Compounds in which this diphosphine acts as a chelating ligand are also known.[5-8] We have recently reported on a case of the bridge to chelate transformation.[9]

Complexes containing monodentate bis(diphenylphosphino)methane ligands are known but are currently less

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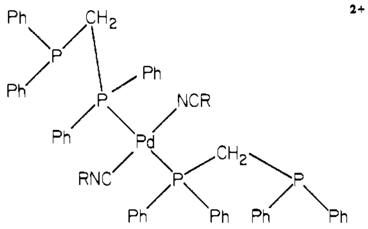
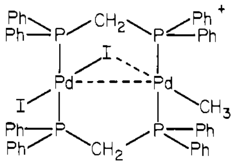
numerous than the preceding two classes. Only three examples, $[Pt_2(\mu\text{-dpm})_2H(dpm)][PF_6]$,[10] $Mo(dpm)_2(CO)_2Cl_2$[11] and $Ru(dpm)_2(TPP)$,[12] where TPP is the dianion of the tetraphenylporphyrin, have been characterized by X-ray crystallography. Here we report the synthesis and structural characterization of another member of this class, $(t\text{-}C_4H_9NC)_2Pd(dpm)_2^{2+}$ (**1**), which contains two monodentate bis(diphenylphosphino)methane ligands.

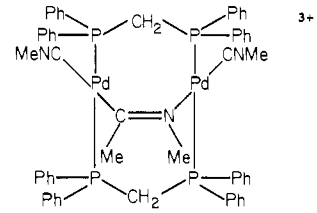


1, R = *t*-C_4H_9



2

This compound was first encountered during our studies of the insertion of small molecules (isocyanides, carbon monoxide, sulfur dioxide) into the Pd–C bonds of the binuclear complexes $[Pd_2(\mu\text{-dpm})_2(\mu\text{-X})(CH_3)_2]X$ (X = I, Br) and $[Pd_2(\mu\text{-dpm})_2(\mu\text{-I})(CH_3)I]BF_4$ (**2**).[13-15] The reaction of methyl isocyanide with $[Pd_2(\mu\text{-dpm})_2(\mu\text{-I})(CH_3)I]BF_4$ produces the white, crystalline complex **3**, the product of isocyanide insertion into the Pd–C bond as well as of isocyanide substitution for the iodo ligands of **2**.[14] Attempts to extend this reaction to other isocyanides led to the formation of different products. With *tert*-butyl isocyanide, the only product we were able to characterize was $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][BPh_4]_2$. Subsequently we developed two rational routes to this complex which makes it available in high yield from readily obtained starting materials.



3

Experimental Section

Preparation of Compounds. $(C_6H_5CN)_2PdCl_2$,[16] $(dpm)PdCl_2$,[6] and $[Pd_2(\mu\text{-dpm})_2(\mu\text{-I})(CH_3)I]BF_4$[13] were prepared by known routes.

$[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$. 1. From $(C_6H_5CN)_2PdCl_2$. *tert*-Butyl isocyanide was added dropwise to a stirred suspension of 300 mg (0.78 mmol) of $(C_6H_5CN)_2PdCl_2$ in 10 mL of methanol until all of the solid had dissolved. Four additional drops of *tert*-butyl isocyanide were added after dissolution was complete. The solution was filtered, and a solution containing 601 mg (1.56 mmol) of bis(diphenylphosphino)methane in 3 mL of dichloromethane was added to the filtrate. A filtered solution of 535 mg (1.56 mmol) of sodium tetraphenylborate in 2 mL of methanol was added dropwise to the yellow solution. The white, crystalline product was collected by filtration and washed with methanol. Purification was accomplished by recrystallization from dichloromethane/methanol; yield 1190 mg, 90%.

2. From $(dpm)PdCl_2$. *tert*-Butyl isocyanide was added dropwise to a stirred slurry of 300 mg (0.534 mmol) of $(dpm)PdCl_2$ in 10 mL of methanol until all of the solid had dissolved. Four additional drops of *tert*-butyl isocyanide and a solution of 205 mg (0.534 mmol) of bis(diphenylphosphino)methane in 2 mL of dichloromethane were added to the solution. After the mixture was filtered, a filtered solution of 366 mg (1.068 mmol) of sodium tetraphenylborate in 2 mL of methanol was added. The white product was collected by filtration and purified as described above; yield 854 mg, 95%.

3. From $[Pd_2(\mu\text{-dpm})_2(\mu\text{-I})(CH_3)I]BF_4$. *tert*-Butyl isocyanide was added dropwise to a suspension of 300 mg (0.224 mmol) of $[Pd_2(\mu\text{-dpm})_2(\mu\text{-I})(CH_3)I]BF_4$ in 5 mL of methanol until all of the brown crystals had dissolved to give a yellow solution. A filtered solution of 242 mg (0.707 mmol) of sodium tetraphenylborate in 2 mL of methanol was added to the solution after it has been filtered. The pale yellow solid which formed was collected by filtration and recrystallized three times from dichloromethane/methanol; yield 375 mg, 50% based on palladium.

X-ray Data Collection. Crystals of $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$ suitable for X-ray data collection were obtained by diffusion of diethyl ether into a dichloromethane solution of the salt. A colorless needle of dimensions 0.25 × 0.10 × 0.25 mm was mounted along the needle axis on the goniometer head of a Syntex $P2_1$ automated diffractometer. The collection of X-ray data was carried out at 140 K with graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Reflections were initially located with a rotation photograph. A typical reflection had a width at half-height of 0.35° on an ω scan. With the use of 10 reflections and the $P2_1$ automatic indexing program, the lattice was assigned as triclinic *P*. This was confirmed by a series of axial photographs. A density of 1.216 g cm^{-3} was measured by flotation in tetrabromoethane/CCl_4 at room temperature, which agrees with a value of 1.223 g cm^{-3} calculated for $Z = 1$, with the assumption of a slight increase in density at 140 K. A least-squares fit of 12 reflections with $22° < 2\theta < 29°$ yielded cell dimensions a = 13.554 (12) Å, b = 14.172 (8) Å, c = 14.658 (8) Å, α = 113.58 (5)°, β = 111.39 (5)°, and γ = 97.00 (6)°. Data were collected with an ω scan of 1° range and speed ranging from 8 to 60° min^{-1}. Stationary background counts were collected with a 1° offset from the center of the peak. Two check reflections were monitored throughout and showed only random fluctuations. Reflections were collected to 2θ = 45°, yielding 5521 unique data. The data were corrected for Lorentz and polarization effects but not for absorption (μ = 3.18 cm^{-1}). For a crystal of the dimensions given, the absorption correction factors range from 1.06 to 1.14. Reduction of the data to F_o and $\sigma(F_o)$ were as previously described.[17]

Solution and Refinement of the Structure. Neutral atom scattering factors and corrections for anomalous dispersion for Pd and P were from common sources.[18] The structure was solved by assuming $P\bar{1}$ to be the correct space group and placing palladium at (0.0, 0.0, 0.0). Two phosphorus atoms were found on the first Fourier map. Refinement of these three atoms brought R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ to 0.33. A second Fourier map revealed the remaining nonhydrogen atoms; full-matrix least-squares refinement of all 59 atoms with isotropic thermal parameters and the 3932 reflections for which $I > 3\sigma(I)$ brought R to 0.089. The quantity minimized during refinement was $\sum w(|F_o| - k|F_c|)^2$, where k is a scale factor and w is given by a Hughes weighting scheme. At this stage the large thermal motion of the methyl groups of the isocyanide ligand was noted, and a difference map was computed to check for possible disorder. No separate atoms could be found on this map. Judging from the distribution of

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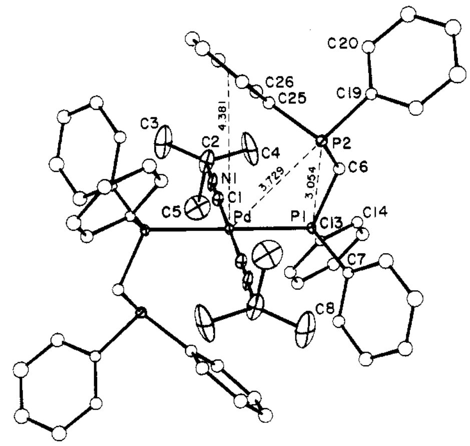

Figure 1. Perspective view of the complex cation **1** showing some interatomic distances and the numbering scheme.

electron density, the methyl carbon atoms have a tendency to rotate around the N–C bond. This is also evident in the drawings (Figures 1 and 2) showing anisotropic thermal ellipsoids for these atoms. Three additional cycles of full-matrix least-squares refinement with anisotropic thermal parameters for palladium, phosphorus, and the atoms of the isocyanide ligand brought *R* to 0.079. In the final cycle of refinement, the last shift in any parameter was less than one-tenth of its esd except for those of the methyl carbon atoms, which shifted as much as half their esd. No feature corresponding to atoms larger than hydrogen atoms was found in the final differnce map. Final positional parameters are given in Table I. Tables of structure factor amplitudes and thermal parameters are available as supplementary material. Calculations were performed on a Data General Eclipse computer using local crystallographic programs developed by Professor H. Hope.

Physical Measurements. Infrared spectra were recorded from Nujol mulls on a Perkin-Elmer 180 infrared spectrometer. Proton-decoupled ^{31}P NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer at 81 MHz. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra and the high-frequency-positive convention, recommended by IUPAC, has been used in reporting chemical shifts.

Results

Synthesis and Spectroscopic Characterization. $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2]^{2+}$ is readily synthesized in high yield by using either $(C_6H_5CN)_2PdCl_2$ or $(dpm)PdCl_2$ as starting materials. Treatment of $(C_6H_5CN)_2PdCl_2$ with an excess of *tert*-butyl isocyanide in methanol results in the formation of a colorless solution which probably contains $[(t\text{-}C_4H_9NC)_4Pd]^{2+}$.[19] Addition of bis(diphenylphosphino)methane followed by sodium tetraphenylborate results in the formation of crystals of $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$. Similarly, successive additions of *tert*-butyl isocyanide, bis(diphenylphosphino)methane, and sodium tetraphenylborate to $(dpm)PdCl_2$ result in the formation of the same crystalline salt.

$[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$ is a 1:2 electrolyte. Its molar electrical conductivity in acetonitrile solution is 200 $cm^2\ mol^{-1}\ \Omega^{-1}$. The infrared spectrum of the solid complex in a Nujol mull shows an intense absorption at 2233 cm^{-1}, which is indicative of the presence of terminal isocyanide ligands. The increase in the isocyanide stretching frequency, relative to free *tert*-butyl isocyanide (2143 cm^{-1}),[18] is consistent with the presence of Pd(II) in the complex. The ^1H NMR spectrum exhibits a singlet at 0.98 ppm (relative intensity, 18 protons) from the *tert*-butyl isocyanide ligands, a broad resonance at 3.55 ppm (4 protons) from the methylene protons, and a broad, phenyl multiplet in the region 7–9 ppm. The breadth of the methylene proton resonance suggests that a dynamic process is occurring. Otherwise we would expect to see a sharp resonance with well-defined proton–proton and proton–phosphorus coupling.[9,13,17] The ^{31}P NMR spectrum confirms the occurrence of a dynamic process. Only a single broad resonance at ca. −23 ppm is observed. The position of the resonance can vary by ±2 ppm depending on concentration and temperature. Lowering the temperature down to −80 °C did not result in freezing out of the individual resonances of the complex; only a broad singlet is observed in the ^{31}P NMR from −80 to +35 °C.

Table I. Positional Parameters for $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$

atom	*x*	*y*	*z*	*B*, Å^2
Pd	0.0000	0.0000	0.0000	1.47 (5)[a]
P(1)	−0.0711 (2)	0.0404 (2)	0.1311 (2)	1.6 (1)[a]
P(2)	−0.2102 (2)	−0.1990 (2)	−0.0032 (2)	2.0 (1)[a]
N(1)	0.1520 (8)	−0.1108 (7)	0.1069 (7)	2.9 (4)[a]
C(1)	0.0960 (8)	−0.0704 (8)	0.0684 (8)	2.0 (4)[a]
C(2)	0.2260 (11)	−0.1667 (11)	0.1543 (11)	4.8 (7)[a]
C(3)	0.2992 (15)	−0.1837 (19)	0.1043 (19)	10 (2)[a]
C(4)	0.2386 (17)	−0.1357 (20)	0.2631 (16)	11 (2)[a]
C(5)	0.1387 (17)	−0.2962 (14)	0.0877 (17)	9 (1)[a]
C(6)	−0.2075 (7)	−0.0568 (7)	0.0737 (8)	2.1 (2)
C(7)	0.0179 (7)	0.0439 (7)	0.2593 (7)	1.8 (2)
C(8)	−0.0110 (9)	−0.0304 (9)	0.2927 (9)	3.2 (2)
C(9)	0.0616 (9)	−0.0242 (9)	0.3934 (10)	3.7 (2)
C(10)	0.1631 (9)	0.0580 (9)	0.4618 (9)	3.1 (2)
C(11)	0.1937 (9)	0.1318 (8)	0.4274 (9)	2.9 (2)
C(12)	0.1209 (8)	0.1239 (8)	0.3272 (8)	2.2 (2)
C(13)	−0.0906 (7)	0.1728 (7)	0.1733 (7)	1.6 (2)
C(14)	−0.1738 (8)	0.1946 (8)	0.2051 (8)	2.2 (2)
C(15)	−0.1831 (8)	0.2992 (8)	0.2420 (9)	2.8 (2)
C(16)	−0.1078 (8)	0.3807 (8)	0.2500 (8)	2.7 (2)
C(17)	−0.0236 (8)	0.3594 (8)	0.2195 (8)	2.6 (2)
C(18)	−0.0143 (8)	0.2559 (8)	0.1816 (8)	2.4 (2)
C(19)	−0.3336 (7)	−0.2692 (7)	−0.0040 (8)	2.0 (2)
C(20)	−0.4424 (8)	−0.3007 (8)	−0.0857 (8)	2.4 (2)
C(21)	−0.5306 (9)	−0.3522 (9)	−0.0782 (9)	3.5 (2)
C(22)	−0.5116 (9)	−0.3709 (9)	0.0118 (10)	3.6 (2)
C(23)	−0.4033 (10)	−0.3411 (10)	0.0946 (10)	4.1 (2)
C(24)	−0.3141 (9)	−0.2895 (9)	0.0858 (9)	3.0 (2)
C(25)	−0.2648 (8)	−0.2261 (7)	−0.1481 (8)	2.1 (2)
C(26)	−0.3154 (8)	−0.1630 (8)	−0.1893 (8)	2.6 (2)
C(27)	−0.3615 (8)	−0.1961 (8)	−0.3038 (9)	2.9 (2)
C(28)	−0.3580 (9)	−0.2929 (9)	−0.3761 (9)	3.1 (2)
C(28)	−0.3070 (9)	−0.3584 (9)	−0.3372 (9)	3.1 (2)
C(30)	−0.2599 (8)	−0.3229 (8)	−0.2215 (8)	2.6 (2)
C(31)	0.3321 (8)	−0.1579 (8)	0.6370 (8)	2.2 (2)
C(32)	0.4025 (8)	−0.1494 (8)	0.7404 (8)	2.4 (2)
C(33)	0.4492 (9)	−0.0498 (9)	0.8390 (9)	3.1 (2)
C(34)	0.4265 (9)	0.0432 (9)	0.8385 (9)	3.2 (2)
C(35)	0.3596 (10)	0.0369 (10)	0.7392 (10)	4.0 (2)
C(36)	0.3113 (9)	−0.0626 (9)	0.6393 (9)	3.4 (2)
C(37)	0.3564 (8)	−0.2682 (8)	0.4516 (8)	2.4 (2)
C(38)	0.4347 (8)	−0.1713 (8)	0.4831 (8)	2.6 (2)
C(39)	0.5004 (9)	−0.1707 (9)	0.4270 (9)	3.5 (2)
C(40)	0.4869 (10)	−0.2663 (10)	0.3394 (10)	3.9 (2)
C(41)	0.4114 (10)	−0.3637 (10)	0.3064 (10)	4.0 (2)
C(42)	0.3466 (8)	−0.3630 (8)	0.3641 (9)	2.9 (2)
C(43)	0.1501 (8)	−0.2789 (8)	0.4399 (8)	2.6 (2)
C(44)	0.0813 (9)	−0.2472 (9)	0.4923 (9)	3.2 (2)
C(45)	−0.0330 (10)	−0.2634 (10)	0.4283 (10)	3.9 (2)
C(46)	−0.0811 (10)	−0.3127 (10)	0.3143 (11)	4.4 (3)
C(47)	−0.0142 (11)	−0.3433 (10)	0.2592 (11)	4.5 (3)
C(48)	0.1002 (9)	−0.3276 (9)	0.3233 (9)	3.1 (2)
C(49)	0.2711 (7)	−0.3789 (7)	0.5346 (8)	2.0 (2)
C(50)	0.1714 (8)	−0.4514 (8)	0.5029 (8)	2.3 (2)
C(51)	0.1674 (8)	−0.5394 (8)	0.5244 (8)	2.6 (2)
C(52)	0.2666 (8)	−0.5545 (8)	0.5827 (9)	2.8 (2)
C(53)	0.3686 (8)	−0.4827 (8)	0.6141 (8)	2.6 (2)
C(54)	0.3688 (7)	−0.3982 (7)	0.5883 (8)	2.0 (2)
B	0.2783 (9)	−0.2693 (9)	0.5166 (9)	2.0 (2)

[a] Equivalent value of the anisotropic temperature factor.

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(20) The analogous complex $[(CH_3NC)_4Pd]^{2+}$ forms under these conditions: Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069.

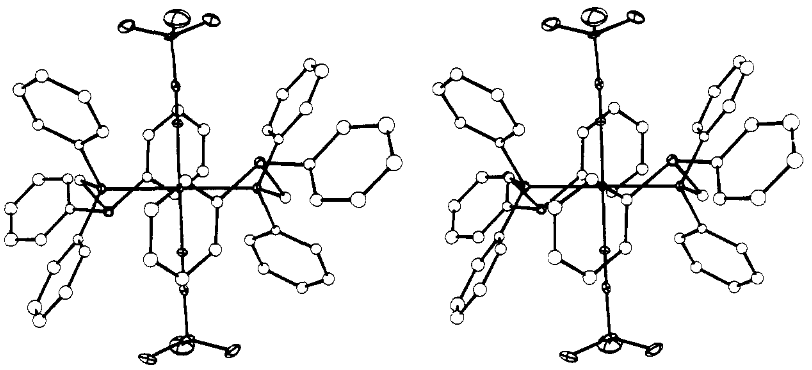

Figure 2. Stereoscopic view of $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2]^{2+}$.

Table II. Bond Distances (Å) and Angles (Deg) for $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$

Pd–P(1)	2.357 (3)	P(2)–C(6)	1.863 (11)
Pd···P(2)	3.729 (3)	P(2)–C(19)	1.832 (11)
Pd–C(1)	1.965 (11)	P(2)–C(25)	1.828 (10)
P(1)–C(6)	1.828 (11)	P(1)···P(2)	3.054 (4)
P(1)–C(7)	1.802 (10)	C(1)–N(1)	1.13 (2)

P(2)···Pd–P(1)	54.8 (1)	C(6)–P(2)–C(25)	103.4 (5)
C(1)–Pd···P(2)	79.5 (3)	C(19)–P(2)–C(25)	101.5 (5)
C(1)–Pd–P(1)	91.6 (3)	Pd–C(1)–N(1)	179.0 (10)
Pd–P(1)–C(6)	111.7 (3)	C(1)–N(1)–C(2)	178.1 (11)
Pd–P(1)–C(7)	114.3 (4)	P(1)–C(6)–P(2)	111.7 (6)
Pd–P(1)–C(13)	111.6 (3)	P(1)–C(7)–C(8)	123.4 (8)
C(6)–P(1)–C(7)	107.3 (5)	P(1)–C(7)–C(12)	117.9 (8)
C(6)–P(1)–C(13)	106.3 (5)	P(1)–C(13)–C(14)	121.2 (8)
C(7)–P(1)–C(13)	105.1 (4)	P(1)–C(13)–C(18)	118.4 (8)
Pd···P(2)–C(6)	67.6 (3)	P(2)–C(19)–C(24)	116.1 (8)
Pd···P(2)–C(19)	164.3 (4)	P(2)–C(25)–C(26)	125.5 (8)
Pd···P(2)–C(25)	75.4 (4)	P(2)–C(25)–C(30)	114.9 (8)
C(6)–P(2)–C(19)	98.7 (5)		

X-ray Crystallographic Results. $[(t\text{-}C_4H_9NC)_2Pd(dpm)_2][B(C_6H_5)_4]_2$ crystallizes with half of the complex cation and one tetraphenylborate in the asymmetric unit. The cation sits on a center of symmetry and so the *tert*-butyl isocyanide ligands are trans to each other as are the two bis(diphenylphosphino)methane ligands. Figure 1 shows the numbering scheme used for the complex cation along with some interatomic distances. Figure 2 shows a stereoscopic view of the cation. The tetraphenylborate has its usual geometry and will not be discussed further. Fractional atomic coordinates are given in Table I. Selected interatomic distances and angles are given in Table II.

The palladium ion is four-coordinate and planar. The Pd–C distance of 1.965 (11) Å is similar to other Pd–C distances involving trans $M(CNR)_2$ units. These include $(CH_3NC)_4Pd^{2+}$ (Pd–C = 1.975 (7) and 1.993 (7) Å),[21] $(CH_3NC)_6Pd_2^{2+}$ (Pd–C(equatorial) = 1.963 (5)),[22] $(t\text{-}C_4H_9NC)_2PdI_2$ (Pd–C = 1.92 (4)),[23] and $(CH_3NC)_2Pt(C(SEt)NHCH_3)_2^{2+}$ (Pt–C = 1.968 (9)).[24] The isocyanide ligands in **1** are clearly linear as expected. The Pd–P(1) distance of 2.357 (3) Å falls into the range of Pd–P distances compiled for compounds containing Pd–P bonds trans to another Pd–P unit.[5] For a group of compounds with bridging bis(diphenylphosphino)methane ligands (which includes $Pd_2(\mu\text{-dpm})_2Cl(SnCl_3)$,[26] $Pd_2(\mu\text{-dpm})_2(\mu\text{-SO}_2)Cl_2$,[17] $Pd_2(\mu\text{-dpm})_2(\mu\text{-S})Cl_2$,[17] $Pd_2(\mu\text{-dpm})_2(\mu\text{-}C_2(CF_3)_2)Cl_2$,[25] and $[Pd_2(\mu\text{-dpm})_2(\mu\text{-I})(CH_3)I]^+$),[15] the average Pd–P distance is 2.327 Å with these distances ranging from 2.295 to 2.372 Å. In the chelated complexes $(dpm)PdCl_2$ and $(dpm)Pd(SCN)_2$, the Pd–P distances are 2.234 (1) and 2.250 (1) (trans to Cl)[6] and 2.282 (2) and 2.264 (2) Å (trans to S).[5] While these distances are shorter than those found for bridging and monodentate bis(diphenylphosphino)methane complexes, the principal factor affecting the bond shortening probably is the change in the trans ligand and not the alteration in mode of coordination of the diphosphine. Two phenyl rings effectively block the axial coordination sides of the palladium ion. The Pd–ring center distance is 4.38 Å, so these rings are not actually bonded to the metal ions.

Turning our attention to the diphosphine ligand, it is apparent from several features that P(2) is uncoordinated. Not only is it 3.729 (3) Å from the palladium to which the diphosphine is attached but it is 11.41 Å from the nearest palladium of a neighboring complex cation. Additionally the lone pair on P(2) is not directed toward the palladium ion within the complex cation. This is best visualized by reference to the stereoscopic view in Figure 2. Comparison of the disposition of the carbon atoms about P(1) and P(2) shows the effect of coordination upon the phosphorus environment. All of the P–C distances are slightly larger at P(2) than at P(1). More significantly, all of the C–P–C angles at P(2) (98.7 (5), 101.5 (5), 103.4 (5)°) are smaller than the corresponding angles at P(1) (106.3 (5), 105.1 (5), 107.3 (5)°). This occurs even though P(1) has the more crowded environment since it is attached to the palladium ion. The larger C–P–C bond angles about P(1) must be due to an increase in s character in the orbitals which phosphorus uses to bond to carbon.

The P(1)–C(6)–P(2) angle of 111.7 (6)° is close to the anticipated value of 109.5°. In complexes where bis(diphenylphosphino)methane is a bridging ligand, this angle can vary from 102.4 to 119.7°.[4] This bending is, to a considerable extent, responsible for the variation in metal–metal separations spanned by this diphosphine when it acts as a bridging ligand. In the chelated complexes $(dpm)PdCl_2$ and $(dpm)Pd(SCN)_2$ the P–C–P angles of 94.7 (3) and 93.0 (1)° respectively indicate that a significant degree of distortion occurs in order to obtain chelating ring formation. Similar compression of the P–C–P angles occurs in the six-coordinate chelated complex $Ir(O_2)(dpm)_2^+$ where the P–C–P angles are 92.6 (7) and 93.2 (7)° in the hexafluorophosphate salt and 93.1 (6) and 95.5 (6)° in the perchlorate salt.[8] In $Mo(dpm)_2(CO)_2Cl_2$, the P–C–P angles are 90.0° for the chelated diphosphine and 116.0° for the monodentate diphosphine.[11] In $Ru(dpm)_2TPP$, the P–C–P angle is 118.7 (6)°.[12]

The isocyanide ligands in **1** are linearly coordinated as expected. The methyl carbons of the *tert*-butyl groups are poorly

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(21) Goldberg, S. Z.; Eisenberg, R.; Miller, J. S.; Epstein, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5173.

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(23) Bailey, N. A.; Walter, N. W.; Williams, J. A. W. *J. Organomet. Chem.* **1972**, *37*, C49.

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(25) Balch, A. L.; Lee, C.-L; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979**, *177*, C22.

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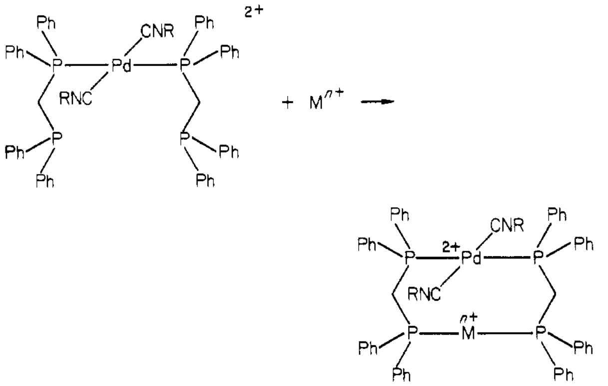
defined in the structural analysis as a result of either rotation or disorder. This results in one abnormally long C–C(methyl) distance.

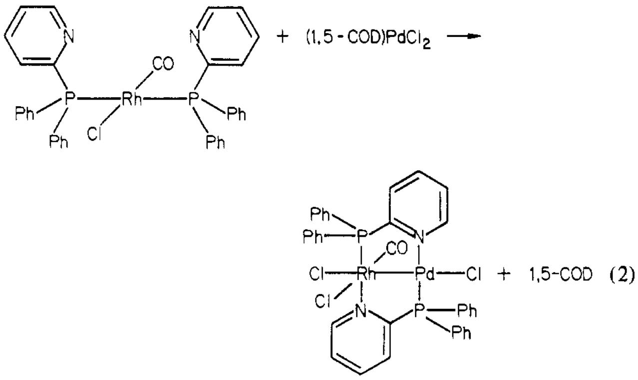
While the solid-state structural results show that **1** has two chemically inequivalent phosphorus atoms, the ^{31}P NMR spectra taken in solution show only one phosphorus resonance. From the breadth of this resonance it is clear that an exchange process is probably occurring. Unfortunately we have not been able to slow this process down sufficiently to characterize it more thoroughly. The presence of four-coordinate Pd(II) in this cation makes an associative pathway for exchange likely. This could involve either an intraionic process or an exchange of phosphine ligands between complex cations. Although P(2) is not coordinated in the solid state, it could easily move into a coordinating site once set free in solution. The observation of a concentration dependence of the ^{31}P NMR chemical shift suggests that an interionic process may be involved. Most probably both are involved.

With its two uncoordinated phosphorus atoms, **1** should be capable of binding another metal ion or ions. We may anticipate the occurrence of reactions like that shown in eq 1.



(1)

In this respect this compound should resemble the complexes of 2-(diphenylphosphino)pyridine which are also capable of assemblage into binuclear complexes in a stepwise fashion.[26-29] For example, the formation of a rhodium–palladium bond results from reaction 2.[27] To date most complexes involving



(2)

bridging bis(diphenylphosphino)methane have been symmetrical in that the coordination about both metal ions is identical. The cation **1** offers a route to the creation of complexes with different ligands at each of the two metals and also the possibility of introducing two different metals into the complex. The potential for utilizing **1** in this capacity is under investigation.

Acknowledgment. We thank the National Science Foundation (Grant CHE79 245750) for support and Mr. J. P. Farr for obtaining the NMR spectra.

Registry No. 1, 81476-80-4; **2**, 78274-93-8; $(C_6H_5CN)_2PdCl_2$, 14220-64-5; (dpm)$PdCl_2$, 38425-01-3.

Supplementary Material Available: Listings of thermal parameters and structure factors (24 pages). Ordering information is given on any current masthead page.

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