atoms of the π-allyl grouping, C_6, C_7, and C_8, are, respectively, 2.115, 2.103, and 2.120 A distant from the palladium ion. These values are in excellent agreement with those obtained by Smith[14] in his accurate low-temperature analysis of dimeric π-allylpalladium chloride (2.123, 2.108, 2.121 A; $\sigma = 0.008$ A). It is interesting to note that, in each case, the central carbon atom is slightly closer to the metal than are the terminal carbon atoms. The differences are, however, too small to be considered statistically significant. The apical angle of 119.0° for the allyl group and a mean carbon–carbon bond length of 1.405 A for the allyl system in the present complex may be compared to Smith's values of 119.8° and 1.376 A.

The coordination plane of the palladium ion, as defined by the atoms Pd, O_1, and O_2, fits the equation $1.924X + 3.616Y + 0.590Z = 1$. Atoms C_6 and C_8 are 0.22 and 0.40 A above, and C_7 is 0.30 A below, this plane. The π-allyl group (C_6–C_7–C_8) makes a dihedral angle of 121.5° with the coordination plane of the palladium ion. This is not an isolated example of this phenomenon. Other π-allyl complexes show the same effect to varying degrees (see Table V). This rather surprising result has been explained by Kettle and Mason,[15] who are able to predict a value of approximately 110°, by considering the various π-allylpalladium overlap integrals.

TABLE V

THE DIHEDRAL ANGLE BETWEEN THE METAL COORIDNATION PLANE AND THE π-ALLYL SYSTEM IN A NUMBER OF π-ALLYLPALLADIUM COMPLEXES

Complex	Dihedral angle, deg	Ref
$[exo\text{-}C_2H_5O[C_4(C_6H_5)_4]PdCl]_2$	95[a]	*b*
$[endo\text{-}C_2H_5O[C_4(C_6H_5)_4]PdCl]_2$	95[a]	*b*
$[C_3H_5PdCl]_2$	111.5	13
$CH_3C_3H_4Pd[P(C_6H_5)_3]Cl$	116	*c*
$[C_3H_4PdCH_3CO_2]_2$	117 (av)	11
$C_8H_{11}Pd(CH_3COCHCOCH_3)$	121	

[a] This angle would probably be greater but for the effect of the nonbonding interaction between the fourth carbon of the cyclobutenyl system and the palladium atom. [b] L. F. Dahl and W. E. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965). [c] R. Mason and D. R. Russell, *Chem. Commun.*, 26 (1966).

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Notes

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Behavior of Bis(hexamethylphosphoramide)cobalt(II) Complexes in Solutions Containing Excess Hexamethylphosphoramide

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The complexes $Co(HMPA)_2X_2$, in which HMPA is hexamethylphosphoramide, $O{=}P[N(CH_3)_2]_3$, and X is chloride, bromide, iodide, or thiocyanate, have been characterized[2] as pseudo-tetrahedral complexes. Some of these complexes have been found to undergo interesting reactions with excess HMPA. Since no changes in the absorption spectrum of the thiocyanato or chloro complexes, $Co(HMPA)_2X_2$, were observed when the complex was dissolved in a solution containing an excess of HMPA, it was concluded that no reaction occurred. Extensive displacement of iodide occurred for the iodo complex. The spectrophotometric data in chloroform solution fit an equilibrium constant expression for dissociation of one iodide per molecule, but in nitromethane, containing excess ligand, dissociation of both iodides occurs, producing the species $Co(HMPA)_4^{2+}$.

In contrast to this behavior, the $CHCl_3$ solutions of a similar series of complexes of general formula CoL_2X_2—in which L is pyridine or isoquinoline and which contain excess ligand L—exhibit an equilibrium[3,4] between the four-coordinate species and a six-coordinate species, CoL_4X_2.

These reactions can be rationalized by employing steric considerations and the principles outlined in the coordination model for nonaqueous solvent behavior.[5,6]

Experimental Section

The compounds were prepared by a method previously reported.[2] Reagent grade nitromethane was used after 2-weeks storage over Linde 4A Molecular Sieves. Chloroform was shaken over calcium chloride, stored overnight, and distilled. Hexamethylphosphoramide was distilled under reduced pressure from barium oxide. The portion boiling at 127° (20 mm) was used. Electronic spectra were obtained with a Cary Model 14 M recording spectrometer, using matched quartz cells. When excess ligand was added to a solution, the same amount of ligand was added to the reference solution. Equilibrium constant measurements were performed with a Beckman DU spectrometer using matched quartz cells and a sample compartment

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thermostated at 28 ± 0.5°. The method of calculation has been previously reported.[7,8]

Results and Discussion

It is observed that when excess HMPA is added to either chloroform or nitromethane solutions of either the thiocyanate complex or the chloride complex, no changes in λ_{max} occur. Some minor changes in the values of the molar absorptivities are observed, which may be due to changes in the solvating media. When, however, excess HMPA is added to the iodide complex in these solvents, pronounced spectral changes occur, indicating that a new species is being formed (Table I). In nitromethane solution the change is so great that the resulting spectrum is identical with that of $Co(HMPA)_4(ClO_4)_2$. Since the spectral changes in chloroform solution for the iodide complex indicate that the species being formed is tetrahedral, a calculation was performed assuming the equilibrium

$$Co(HMPA)_2I_2 + HMPA \rightleftharpoons Co(HMPA)_3I^+ + I^- \quad (1)$$

The data (Table II) were found to fit an equilibrium constant expression for this reaction very well. The equilibrium constant was calculated as 1.8. Excellent crossings in the K *vs.* ϵ plot were obtained. This is not a true thermodynamic equilibrium constant because extensive ion pairing is expected in chloroform. The only reason a constant value was obtained for K is that the concentration of ions was not varied much in this experiment so activity coefficients did not change much. This constant would not be expected to hold over a large variation in the concentrations of the ions. Over the limited concentration range employed in this study, the data fit eq 2 involving the ion pair almost as well as eq 1. Therefore, the only significance that can

$$Co(HMPA)_2I_2 + HMPA \rightleftharpoons [Co(HMPA)_3I^+][I^-] \quad (2)$$

be attached to the reported K is that of supporting the qualitative interpretation of the spectral changes (Tables I and II) by the formation of a tetrahedral species in which one iodide has been displaced from the coordination sphere of the cobalt.

TABLE I
ELECTRONIC SPECTRA OF $Co(HMPA)_2I_2$ WITH AND WITHOUT EXCESS HMPA

Solvent	Concn, $M \times 10^4$	λ_{max}, mμ[a]
$CHCl_3$	5.75	610 (410), 626 (403), 653 (435), 670 sh, 720 (379)
CH_3NO_2	5.01	610 (359), 620 (363), 655 (423), 675 (395), 720 (351)
$CHCl_3$ + HMPA[b]	3.46	580 sh, 600 sh, 612 (249), 638 (289), 676 (237), 718 (121)
CH_3NO_2 + HMPA[b]	4.05	550 sh, 565 (123), 583 (153), 605 (175), 635 (202), 685 sh

[a] Values in parentheses designate molar absorptivity at λ_{max} (ϵ_{max}). [b] Ratios of molar concentration of HMPA added to molar concentration of HMPA complexes are 578 for the $CHCl_3$ solution and 1062 for the CH_3NO_2 solution.

When excess HMPA is added to solutions of the bromide complex in these solvents, spectral changes indicate some new species are present. In chloroform solution, the changes are slight, but in nitromethane solution the changes are more striking. Attempts to calculate an equilibrium constant for a reaction analogous to eq 1 were unsuccessful. At 680 mμ, the wavelength most sensitive to spectral change for the bromide complex, the changes in absorbance were too small to allow calculation of an accurate equilibrium constant. Crude calculations indicate that it is no larger than 5×10^{-4}.

TABLE II
DATA FOR $Co(HMPA)_2I_2$ EQUILIBRIUM CONSTANT CALCULATION

$M_{Co^{2+}}$	$M_{HMPA\ added}$	$A_{630m\mu}$[a]	A^0_{cor}[b]
0.01103	. . .	0.522	0.522
0.01076	0.3225	0.462	0.509
0.01079	0.3887	0.459	0.511
0.01082	0.5511	0.449	0.512
0.01079	0.7751	0.436	0.511
0.01088	1.1010	0.429	0.515

[a] Absorbance reading for the complex with excess HMPA at 630 mμ. [b] Absorbance for the complex with no excess HMPA, corrected to account for the slightly differing Co^{2+} concentration. $A - A^0$ must be multiplied by 10 to give ϵ in the right units, because 0.1-cm cells were used.

There are several interesting aspects of this behavior worthy of comment. The fact that no tetrahedral–octahedral equilibria exist, as are present in the analogous pyridine and isoquinoline systems, is probably due to steric hindrance from the large HMPA molecules. For example, no solid complexes of HMPA have been reported in which four HMPA molecules and two halide ions surround a divalent metal ion in a six-coordinate complex. Both $Fe(HMPA)_6(ClO_4)_3$ and $Cr(HMPA)_6(ClO_4)_3$ have, however, been prepared.[9]

The equilibrium described in eq 1 is easily encompassed by the general equation discussed in the formulation of the coordination model[6]

$$MS_pX(solv) + S(solv) \rightleftharpoons MS_{p+1}(solv)^+ + X^-(solv)$$

Nitromethane solvates the charged species to a greater extent than chloroform, and, consequently, when excess HMPA is added to nitromethane solutions, more extensive anion dissociation occurs, leading to $Co(HMPA)_4^{2+}$. The greater ease with which iodide ion is displaced is attributed to either a greater chloride, bromide, or thiocyanate ion donor strength (*i.e.*, a stronger cobalt–chlorine bond than cobalt–iodine) and/or a greater solvation of iodide ion.

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