ONIOM Study of the Coordination Chemistry of Ag^+ with the Nitrogen-Bridged Ligands $Ph_2P-NH-PPh_2$ and $Ph_2P-NCH_3-PPh_2$: Ligand Chelation versus Bridging

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The coordination chemistry of Ag^+ with the nitrogen-bridged ligands $H_2P-NR-PH_2$ and $Ph_2P-NR-PPh_2$ ($R = H, CH_3$) has been studied at the B3LYP/6-31G(d)/ECP level where an effective core potential (ECP) replaces the core electrons of silver. The ONIOM method (B3LYP/ECP:STO-3G*) is used to model the effect of replacing hydrogens on phosphorus with phenyl groups ($Ph_2P-NR-PPh_2$, R = H (dppa) and R = CH_3 (dppma). Free energy calculations predict that $[Ag_2(dppa)_2]^{2+}$ is favored over $[Ag(dppa)]^+$ (R = H, less replusion), while formation of $[Ag(dppma)]^+$ is favored over $[Ag_2(dppma)_2]^{2+}$ ($R = CH_3$, more repulsion), which is in agreement with experimental observations. The complexes of Ag^+ with $H_2P-NR-PH_2$, $R = H, CH_3$, do not show differential behavior, indicating that the presence of phenyl groups is important in determining the balance between chelation and bridging. The relationship of the present results to the Thorpe−Ingold effect is discussed. Calculations on $[Ag_2(dppa)_3]^{2+}$ indicated that there is a significant barrier to racemization ($D_3 \rightarrow D_{3h}$), which is due to steric repulsion between phenyl groups in the transition state.

Introduction

Bis(diphenylphosphine)s, $Ph_2P-X-PPh_2$, where X=CH_2, CHR, CR_2, O, N^-, NH, NR, form coordination compounds with a variety of metals.[1−23] Depending on the metal and the nature of the linking unit "X", the bisphosphine ligands can either chelate a single metal atom or can bridge two metal atoms. In addition, some bisphosphines ligands such as, $Ph_2P-CH_2-PPh_2$ (dppm), can bridge several metal centers in the μ-bonding mode, forming polynuclear complexes in the presence of a suitable capping ligand.[24−26]

The nature of the linking unit X may be a deciding factor in the balance between chelation and bridging. A bulky group at X will experience less steric repulsion in the complex compared to the repulsion within the free ligand if the ligand is chelated since the exocyclic substituents are attached to the corners of the four-membered ring, which allows more space between substitutents. Offsetting this decreased steric repulsion, however, is the increased ring strain within the four-membered ring. On the other hand, if the bisphosphine ligand bridges two metal centers, atoms in the X linkage may experience more steric repulsion with the phenyl groups on phosphorus in the complex compared to the repulsion within the free ligand.

The rates of cyclization reactions are known to increase when the two hydrogens of a methylene are replaced with alkyl groups. This is known as the Thorpe−Ingold and *gem*-dialkyl effects, which refer to an accelerated rate of cyclization due to "angle compression" caused by alkyl substitution.[27] In bisphosphine−metal coordination chemistry, substitution of methyl groups for hydrogen at the methylene carbon of dppm to give 2,2-bis(diphenylphosphino)propane (i.e., $Ph_2P-CMe_2-PPh_2$) results in the ligand having a significantly greater propensity to form stable four-membered chelate rings than dppm.[11]

The coordination chemistry of the nitrogen-containing bisphosphine ligand, bis(diphenylphosphino)amine, $Ph_2P-NH-PPh_2$, dppa (isoelectronic with dppm), and its alkylated analogues, primarily bis(diphenylphosphino)methylamine, $Ph_2P-NMe-PPh_2$, dppma, is well-known.[13] While both dppm and dppa display chelating versus bridging behavior, there are differing opinions as to which ligand is better for the different bonding modes.[14] However, dppa has the advantage of having an acidic proton (NH hydrogen) that can be functionalized.[15] Analogous to dppm, it has been found that methylating the NH group of dppa to give dppma gives superior chelation (over dppa) in square-planar platinum(II) complexes.[16]

We report a computational investigation of the effect of methylation at the nitrogen bridge on the coordination chemistry of dppa and dppma with Ag^+. We also report calculations on the dinuclear silver, triple bisphosphine bridged cation $[Ag_2(dppa)_3]^{2+}$. Theoretical calculations were undertaken to seek a thermodynamic basis for chelating versus bridging behavior of these nitrogen-bridged ligands.

Computational Method

All calculations were made with the Gaussian 98 program system.[28] The ONIOM hybrid method[29] was used where different levels of theory were used for different layers of the complex. In this study, the model system for the bisphosphine was chosen to be the $H_2P-NR-PH_2$ backbone, where R = H, CH_3, and was calculated at the B3LYP/6-31G(d) level, while the real system, $Ph_2P-NR-PPh_2$, R = H, CH_3 (i.e., phenyl groups replace hydrogens) was calculated at the STO-3G* level. The designation for this method is ONIOM(B3LYP/6-31G(d): STO-3G*). The two-tier hybrid model where phenyl groups in the real system replace hydrogens in the model system on phosphorus has been used in previous ONIOM studies of transition metal systems.[30] In the coordination complexes with silver, a pseudo-relativistic effective core potential was used[31] where the valence electrons of Ag were described with a (8s,7p,6d) basis set contracted to (6s,5p,3d).

The computational data using the ONIOM methodology and energies of the truncated model system optimized at the higher QM level (B3LYP/6-31G(d)) are given in Table 1, while the optimized geometries are given in Figure 1.

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TABLE 1: Absolute Energies (hartrees) and Zero-Point Corrections (kcal/mol) for Various Species Optimized at the STO-3G*, B3LYP/6-31G(d), and ONIOM(B3LYP/6-31G(d)/ECP:STO-3G*) Levels[a]

	$L = H_2P-NR-PH_2$						$L = Ph_2P-NR-PPh_2$	
	$R = H$			$R = CH_3$			$R = H$	$R = CH_3$
	B3LYP/6-31G(d)	ZPE(NIF)[b]	entropy[c]	B3LYP/6-31G(d)	ZPE(NIF)[b]	entropy[c]	ONIOM	ONIOM
Ag^+	−146.70062	0.0(0)		−146.70062	0.0(0)		−146.70062	−146.70062
L (C_2/C_1)[d]							−1647.50438	−1686.80561
L (C_{2v}/C_s)[d]	−740.43339	32.82(0)		−779.74118	50.65(0)		−1647.50048	
AgL^+ (C_s/C_1)[d]	−887.23575	34.37(0)	82.95	−926.54496	52.00(0)	93.17	−1794.32542	−1833.63053
$Ag_2L_2^{2+}$ C_{2h}	−1774.45896	71.13(0)	128.65	−1853.08077	106.45(1)	136.88	−3588.67293	−3667.27788
$Ag_2L_3^{2+}$ D_3	−2514.95041	105.37(0)	161.93				−5236.20387	
$Ag_2L_3^{2+}$ D_{3h}	−2514.95032	105.38(1)	157.08				−5236.15872	

[a] An effective core potential is used for silver. The valence electrons are described with a (8s,7p,6d) basis set contracted to (6s,5p,3d). [b] Zero-point energy calculated at the B3LYP/6-31G(d) level (with ECP on silver). The number in parentheses is the number of imaginary frequencies. [c] Entropy [cal/(mol·K)] calculated from unscaled vibrational frequencies. [d] The first point group refers to R = H, while the second point group refers to R=CH_3.

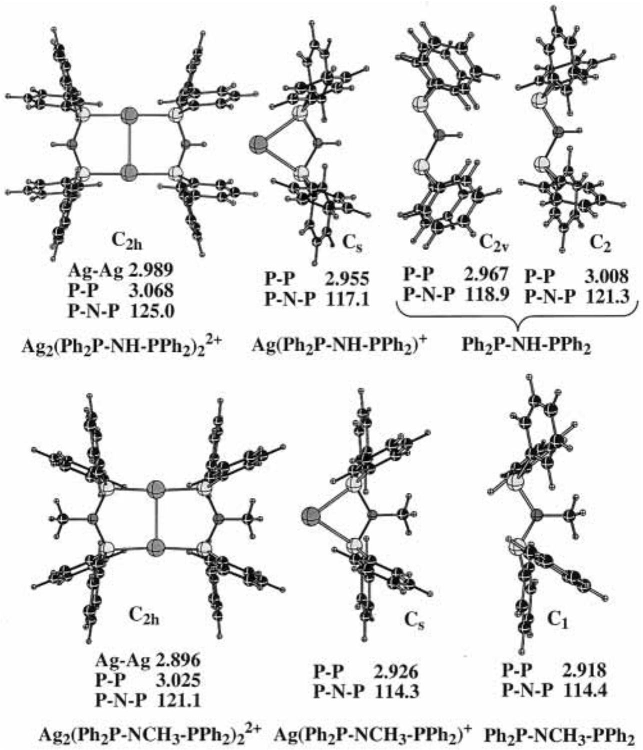

Figure 1. Plot of geometries at the ONIOM(B3LYP/6-31G(d)/ECP: STO-3G*) level of theory and selected geometric parameters. Bond distances are in Ångstroms, and bond angles are in degrees.

Results and Discussion

Several theoretical studies have included the $H_2P-NH-PH_2$ or $H_2P-CH_2-PH_2$ ligand.[32−35] Previous experimental work has shown[36] that the lowest-energy conformation of the free $Ph_2P-NR-PPh_2$ ligand, R = H or CH_3, has phosphorus lone pairs pointing away from the R group. However, when the substituent on nitrogen is larger (such as R = *i*Pr), the increased steric repulsion causes one of the phosphine groups to rotate by 180°. In the present study, only the experimentally established conformer was optimized for $H_2P-NR-PH_2$ and $Ph_2P-NR-PPh_2$. This conformation is also the one suitable for chelation/bridging with one or more metal atoms.

The X-ray structure[37] of $Ph_2P-NH-PPh_2$ has C_2 symmetry rather than the more symmetrical C_{2v} symmetry as a result of steric interaction among the phenyl groups. The calculated C_{2v} structure of $H_2P-NH-PH_2$ is a minimum at B3LPY/6-31G(d), but it is a transition state for $Ph_2P-NH-PPh_2$ to a C_2 minimum (Figure 1), which is 2.4 kcal/mol (Table 2) lower in energy at the ONIOM(B3LPY/6-31G(d):STO-3G*) level of theory. The nitrogen center is planar by symmetry in both the C_{2v} and C_2 structures. The P−N and average P−C distances of $Ph_2P-NH-PPh_2$ are calculated to be longer than the X-ray value[37] (calc/X-ray: 1.725/1.692 and 1.862/1.830 Å, respectively). In addition, the calculated PNP angle is somewhat large than the X-ray value[37] (calc/X-ray: 121.3°/118.9°). Overall, the agreement between theory and X-ray is reasonably good.

The binding energy of Ag^+ for $H_2P-NR-PH_2$ is less than that calculated for $Ph_2P-NR-PPh_2$ which agrees with the observation that the use of bulkier substituents, R′ in $R'_2P-X-PR'_2$, leads to increased chelating power of the ligand.[11a] The substitution of R = CH_3 for R = H in $H_2P-NR-PH_2$ and $Ph_2P-NR-PPh_2$ has a much smaller effect on the binding energy ($Ag^+ + L \rightarrow AgL^+$). For both ligands, substituting R = CH_3 for R = H increases the binding energy by about 1−2 kcal/mol (Table 2).

The dimerization energies of $2AgL^+ \rightarrow Ag_2L_2^{2+}$ for L = $Ph_2P-NH-PPh_2$ and L = $Ph_2P-NCH_3-PPh_2$ are quite similar, with the former being favored by 3.3 kcal/mol (Table 2). This effect can be thought of as arising from the shorter P−P distance (i.e., the smaller P−N−P angle in R = CH_3) shown in Figure 1. The effect of phenyl groups on dimerization is substantial. Thus, dimerization of AgL^+ is more exothermic for L = $Ph_2P-NR-PPh_2$ than L = $H_2P-NR-PH_2$ by 21.8 kcal/mol for R = H and 19.7 kcal/mol for R = CH_3 (Table 2).

Bowmaker et al.[38] used relativistic DFT calculations with the Becke−Perdew (BP) exchange-correlation functional and a contracted (8s,6p,2d) basis set for silver to compute bond dissociation energies for AgL_2^+, L = PH_3 and PMe_3. The bond dissociation energy (BDE) of two PMe_3 groups from $Ag(PMe_3)_2^+$ is 31.3 kcal/mol greater than the BDE of two PH_3 groups from $Ag(PH_3)_2^+$ (120.0 versus 88.7 kcal/mol), which can be attributed to the greater ability of methyl groups to stabilize the positive charge on silver. The BDEs of $H_2P-NR-PH_2$ and $Ph_2P-NR-PPh_2$, R = H and CH_3, in the complexes $[Ag(H_2P-NR-PH_2)]^+$ and $[Ag(Ph_2P-NR-PPh_2)]^+$ are smaller than those of AgL_2^+, L = PH_3 and PMe_3 (Table 3), because the optimum P−Ag−P angle cannot be realized in the bidentate ligands. However, the phenyl groups do increase the binding over hydrogens by 12−13 kcal/mol due to their ability to stabilize the positive charge.

The Ag−P distance in Ag^+−bisphosphine complexes is longer than the Ag−P distance in Ag^+ complexes with similar unlinked phosphines. Thus, the calculated Ag−P distance in $[Ag(Ph_2P-NR-PPh_2)]^+$ is 2.578 and 2.564 Å for R = H and

TABLE 2: Relative Energies (kcal/mol) for Various Species Optimized at B3LYP/6-31G(d) and ONIOM(B3LYP/6-31G(d):STO-3G*) Levels

	$L = H_2P-NR-PH_2$		$L = Ph_2P-NR-PPh_2$	
	R = H B3LYP/6-31G(d)	R = CH_3 B3LYP/6-31G(d)	R = H ONIOM	R = CH_3 ONIOM
$Ag^+ + L \rightarrow AgL^+$	−63.8	−64.7	−75.6	−78.0
$2AgL^+ \rightarrow Ag_2L_2^{2+}$	7.9	5.7	−13.9	−10.6
$Ag_2L_2^{2+} + L \rightarrow Ag_2L_3^{2+}$	−36.4		−16.7	
$Ag_2L_3^{2+}$ ($D_3 \rightarrow D_{3h}$)	0.1		28.3	
L ($C_{2v} \rightarrow C_2$)			−2.4	

[a] Zero-point corrections have been included.

TABLE 3: Comparison of Ag−P Bond Dissociation Energies (kcal/mol) in AgL^+, $L = 2PX_3$, $X_2P-NH-PX_2$, and $X_2P-NCH_3-PX_2$

AgL^+	X = H	X = Me	X = Ph
$L = 2PX_3$	88.7[a]	120.0[a]	
$L = X_2P-NH-PX_2$	63.8		75.6
$L = X_2P-NCH_3-PX_2$	64.7		78.0

[a] The P−Ag−P angle in $Ag(PX_3)_2^+$ is 180°.[38]

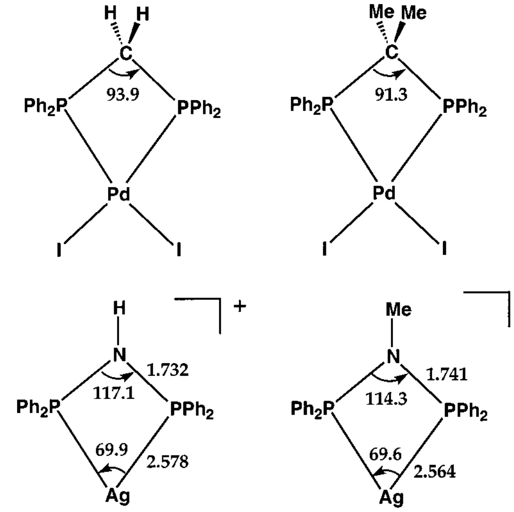

Figure 2. Comparison of the X-ray structures[11a] of $[PdI_2(\mu\text{-}Ph_2P-CR_2-PPh_2)]$ with $[Ag(\mu\text{-}Ph_2P-NR-PPh_2)]^+$, R = H and CH_3. The greater repulsion caused by the substitution of CH_3 for H at the linking atom causes the P−X−P angle (X = C or N) to become smaller.

$R = CH_3$, respectively, which is longer than the Ag−P distance in $Ag(PMes_3)_2^+$ (X-ray distance,[39] 2.441 Å).

The effect of the changing the X linkage in complexes with $Ph_2P-X-PPh_2$ can be seen by comparing the X-ray structure of two closely related complexes,[11a] one with $Ph_2P-CH_2-PPh_2$ (dppm) and the other with $Ph_2P-CMe_2-PPh_2$ (2,2-bis(diphenylphosphino)propane, 2,2-dppp). The internal P−C−P angle in $[PtI_2(dppm)]$ decreases from 93.9° to 91.3° in $[PtI_2(2,2\text{-dppp})]$ when two methyl groups replace the CH hydrogens on the central carbon. The present calculations reveal a similar trend in AgL^+ for $L = Ph_2P-NH-PPh_2$ and $Ph_2P-NCH_3-PPh_2$ where the P−N−P angle decreases from 117.1° to 114.3° when a methyl group replaces the NH hydrogen (Figure 2).

For the $Ag_2L_2^{2+} + L \rightarrow Ag_2L_3^{2+}$ reaction, the binding energy for $L = Ph_2P-NH-PPh_2$ (16.7 kcal/mol) is much smaller than the binding energy of $L = H_2P-NH-PH_2$ (36.4 kcal/mol, Table 2) due to the steric effect of the phenyl groups. Furthermore, the isomerization for $Ag_2L_3^{2+}$ ($D_3 \rightarrow D_{3h}$) is almost zero for $L = H_2P-NH-PH_2$ (0.1 kcal/mol), while it is significant (28.3 kcal/mol, Table 2) for $L = Ph_2P-NH-PPh_2$. The D_3 and D_{3h} geometries are shown in Figure 3 along with the calculated dihedral angle for the D_3 case. The calculated P−Ag−Ag−P angle (Figure 3) was 20.7° in close agreement to the 22° found in the X-ray crystallographic study;[1] the calculated and observed Ag−Ag distances were 2.933 and 2.812 Å, respectively. A triple-bridged complex has been reported,[40] which is related to $[Ag_2(Ph_2P-NH-PPh_2)_3]^{2+}$ by the removal of two NH protons to give neutral $[Ag_2(Ph_2P-N-PPh_2)_2(Ph_2P-NH-PPh_2)]$. The structure is very similar, with the Ag−Ag distance determined by X-ray[40] to be 2.816 Å.

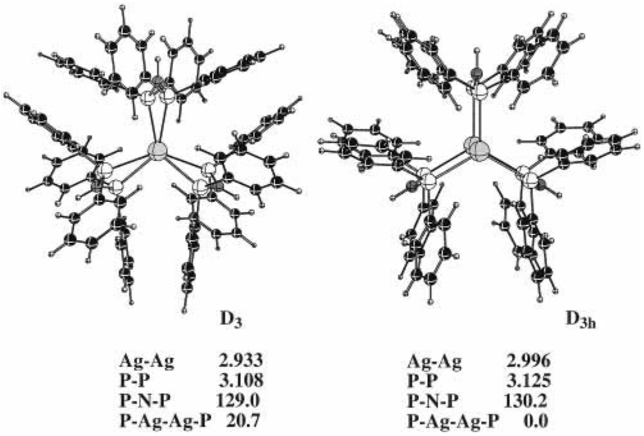

Figure 3. Plot of $[Ag_2(Ph_2P-NH-PPh_2)_3]^{2+}$ in D_3 and D_{3h} point groups optimized at the ONIOM level of theory. The view is down the Ag−Ag axis. The computed barrier of isomerization (without zero-point correction) is 28.3 kcal/mol.

As pointed out above, calculations on the geometry of the $Ph_2P-NH-PPh_2$ ligand show a preference for a C_2-symmetry geometry over the C_{2v}-symmetry geometry by about 2.4 kcal/mol. This contributes to the stabilization of the D_3-symmetry structure for $Ag_2L_3^{2+}$ (over D_{3h}-symmetry) by about 7 kcal/mol (3 × 2.4 kcal/mol). The balance of the activation (28.3 kcal/mol, $D_3 \rightarrow D_{3h}$) must come from steric repulsion between the ligands in the complex.

The calculated entropy change and heat capacity correction to 298 K were computed for eq 1 and combined with the energy change for eq 2 to compute enthalpy and free energy changes at 298 K for eq 2 (Table 4). Since the reactants and product in eqs 1 and 2 have very similar structures and the number of phenyl groups in eq 2 remains constant between reactant and product, the entropy change in eq 2 should be very close to the entropy change calculated in eq 1. Guthrie[41] has found that entropies can be calculated with an accuracy of about 1 cal/

$$2[AgL]^+ \rightarrow [Ag_2L_2]^{2+} \qquad L = H_2P-NR-PH_2,\ R = H, CH_3 \quad (1)$$

$$2[AgL]^+ \rightarrow [Ag_2L_2]^{2+} \qquad L = Ph_2P-NR-PPh_2,\ R = H, CH_3 \quad (2)$$

TABLE 4: Calculated Thermodynamic Parameters for the Dimerization of AgL^+

	$2[Ag(Ph_2P-NR-PPh_2)]^+ \rightarrow [Ag_2(Ph_2P-NR-PPh_2)_2]^{2+}$	
property	R = H	$R = CH_3$
$\Delta H_{rxn}{}^a$	−11.5	−8.2
$\Delta S_{rxn}{}^b$	−37.25	−49.46
$\Delta G(298K)_{rxn}{}^c$	−0.4	6.5

[a] In kcal/mol, calculated at the ONIOM(B3LYP/6-31G(d):STO-3G*) level with zero-point corrections and heat capacity corrections to 298 K obtained from B3LYP/6-31G(d) calculations for the $2[Ag(H_2P-NR-PH_2)]^+ \rightarrow [Ag_2(H_2P-NR-PH_2)_2]^{2+}$ dimerization. [b] In cal/(mol·K), calculated for the reaction $2[Ag(H_2P-NR-PH_2)]^+ \rightarrow [Ag_2(H_2P-NR-PH_2)_2]^{2+}$ using vibrational frequencies at the B3LYP/6-31G(d) level. [c] In kcal/mol, calculated at 298 K from the equation $\Delta G = \Delta H - T\Delta S$.

(K·mol) at the B3LYP/6-31G(d,p) level. Presumably, the calculated error in entropy differences between similar compounds might be smaller.

Values obtained were $\Delta G = -0.4$ and 6.5 kcal/mol for L = dppa and dppma, respectively (Table 4), and show that the dimer is more favored for $Ph_2P-NH-PPh_2$ than for $Ph_2P-NCH_3-PPh_2$. This result shows that dppma has a greater thermodynamic preference for the closed four-membered ring complex than does dppa. This preference arises from the Thorpe−Ingold effect,[27e] where the shorter P−P separation in the $Ph_2P-NCH_3-PPh_2$ ligand compared to the P−P separation in the $Ph_2P-NH-PPh_2$ ligand (Figure 1) favors chelation.

The thermodynamic preference of the dppma ligand for chelation versus the dppa ligand for bridging, which is caused by the presence (dppma) or absence (dppa) of a methyl group on nitrogen, is not large. Thus, under appropriate conditions the dppma ligand ($Ph_2P-NCH_3-PPh_2$) can bridge despite the thermodynamic preference for chelation. In a recent study by Browning et al.[42] an X-ray structure was reported for $[Ag_2(dppma)_2(THF)_2]^{2+}$ where the bridging structure was found with dppma with two THF molecules weakly coordinated to the silver atoms.

Conclusions

The Thorpe−Ingold effect on the nitrogen, i.e., the smaller P−N−P bond angle obtained by alkylation of nitrogen, results in favored formation of a four-membered ring, a ring size well documented to be highly strained. Calculations on the bridging versus chelation behavior for dppa ($Ph_2P-NH-PPh_2$) and dppma ($Ph_2P-NCH_3-PPh_2$) thermodynamically confirm the fact that dppa prefers bridging while dppma prefers chelation.

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