A Density Functional Study of Metal−Ligand Bonding in [(PR₃)₂M]⁺ and [PR₃MCl] (M = Ag, Au; R = H, Me) Complexes

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Relativistic and nonrelativistic electronic structure calculations were carried out on [(PR₃)₂M]⁺ and [PR₃MCl] (M = Ag, Au; R = H, Me) complexes using the all-electron linear combination of Gaussian-type orbitals density functional (LCGTO-DF) method. The calculated relativistic metal−ligand bond lengths show good agreement with experimental values. The relativistic contraction of the M−P bonds in [(PR₃)₂M]⁺ is about 8 and 22 pm for M = Ag and Au, respectively, resulting in Au−P bonds that are about 10 pm shorter than the Ag−P bonds in these species, in good agreement with recent crystallographic results for the cations [(PMes₃)₂M]⁺ (M = Ag, Au). The relativistic contraction of the Au−Cl bond in [PR₃AuCl] is significantly less than that of the Au−P bond, and this explains the experimentally observed differential Au−X and Au−P bond length contractions from [PR₃AgX] to [PR₃AuX]. The calculated relativistic bond lengths for corresponding PH₃ and PMe₃ complexes are very similar, confirming a previous conclusion that PH₃ is a good model for structural properties of larger tertiary phosphine ligands. However, the bond lengths for the PMe₃ complexes are all slightly longer than those for the corresponding PH₃ complexes, whereas the M−P dissociation energies are 20−40% higher for the PMe₃ complexes. These findings provide computational support for the concept of "longer but stronger bonds", which was recently proposed on the basis of experimental studies of transition metal complexes involving various substituted phosphine ligands.

Introduction

Relativistic effects play an important role in gold chemistry, and one such effect is the contraction of bond lengths involving gold atoms.[1−3] We recently showed that the Au−P bond in [(PMes₃)₂Au]⁺ (Mes = mesityl, 2,4,6-C₆H₂(CH₃)₃) is nearly 10 pm shorter than that in the corresponding silver(I) complex [(PMes₃)₂Ag]⁺,[4] and this is in line with theoretical considerations, since relativistic effects are predicted to be more important for gold than for silver.[1] A direct comparison, such as the one described above, of the structure of a gold(I) complex with that of the corresponding silver(I) (or copper(I)) species is normally not possible because the univalent group 11 metal ions have different preferred coordination geometries: linear two-coordination for gold(I) and tetrahedral four-coordination for copper(I) and silver(I).[5] However, by utilizing the strongly sterically hindered phosphine ligand TMPP [tris(2,4,6-tri-methoxyphenyl)phosphine], it has been possible to prepare the isostructural series [(TMPP)MX] (M = Cu, Ag, Au; X = Cl, Br, I), which, with the exception of the AgI complex to date, form isomorphous solids in which the metals all display the linear P−M−X structure which is normally characteristic only of gold(I) complexes.[6−8] Comparison of the corresponding M = Ag, Au species shows that these compounds also display bond length contractions from Ag to Au, but the magnitude of this effect seems to be rather larger for the Au−P than for the Au−X bonds. We have therefore carried out electronic structure calculations on the species [(PR₃)₂M]⁺ and [PR₃MCl] (M = Ag, Au; R = H, Me) in order to investigate the relativistic bond length contractions and the reason for the differential effects observed between Au−P and Au−Cl bonds.

A second reason for carrying out this study was to investigate the relative M−P bond lengths and bond strengths in complexes of gold(I) with PH₃ and PMe₃ ligands. Phosphine ligands PR₃ are components of many different types of gold complexes, including several classes which have interesting and unusual properties, such as low-valent gold clusters[9] and gold (I) clusters which display "aurophilic" gold-gold interactions.[10] Several quantum mechanical calculations on gold complexes containing

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.
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phosphine ligands have been reported,[11-15] and in most cases the PR_3 groups (R = alkyl, aryl) which are present in the experimentally observed compounds of this type were replaced by PH_3 in order to simplify the calculations involved.[11-13] In one recent study it was shown that, at least as far as structural properties are concerned, PH_3 is a good model for the larger PMe_3 and PPh_3 ligands.[15] This is a somewhat surprising result, given that PH_3 is expected to be a significantly weaker base than PR_3 ligands. However, it was also claimed recently, on the basis of some experimental studies, that metal-phosphorus bond lengths are not always good indicators of the strengths of the bonds concerned, when complexes involving different phosphines are compared.[16] In agreement with this, calculations of the Au−P bond dissociation energies in the species [MeAu-PR_3] (R = H, Me, Ph) showed that the Au−P bond strengths increase along this series, despite the near equality of the Au−P bond lengths calculated for these compounds.[15] In order to determine whether this behavior is more general, we have now carried out similar calculations on cations and molecules of the types [$(PR_3)_2M]^+$ and [PR_3MCl] (M = Ag, Au; R = H, Me).

Computational Method

The electronic structure calculations have been performed by using the all-electron linear combination of Gaussian-type orbitals density functional (LCGTO-DF) method.[17] For the relativistic calculations, scalar relativistic effects including the mass-velocity correction and the Darwin term, were treated in a self-consistent fashion.[18-20] For the exchange-correlation potential, the generalized gradient approximation (GGA), according to the parametrization suggested by Becke and Perdew (BP),[21] was applied in a self-consistent fashion.

For Au, P, C, and H, the orbital basis sets used were the same as those employed in previous studies of $MeAuPR_3$.[15] The basis set for P was extended, and two, instead of one, d exponents were included (0.34, 1.00). For Cl, a (12s,9p) basis set[22] was used, enlarged by one p exponent (0.049 994 4) and two d exponents (0.45, 1.70). Also, the Ag basis set[23] was extended by a diffuse d exponent (0.110 795). The basis sets were contracted in a general fashion by using local density atomic eigenvectors of nonrelativistic (NR) and relativistic (R) atomic calculations for the corresponding molecular calculations. The resulting atomic orbital basis sets and their contractions are (21s,17p,11d,7f) → (11s,10p,7d,3f) for Au, (18s,13p,9d) → (9s,8p,5d) for Ag, (12s,10p,-2d) → (8s,6p,2d) for Cl, (12s,9p,2d) → (8s,6p,2d) for P, (9s,5p,1d) → (7s,4p,1d) for C, and (6s,1p) → (4s,1p) for H. The fitting basis sets employed in the LCGTO-DF approach to represent the electronic charge density were constructed in a standard fashion by scaling orbital exponents to generate s- and r^2-type functions.[15,17] In addition, five p-type and five d-type polarization fitting functions were employed.[15] The structural parameters for the PH_3 and PMe_3 ligands were the same

Table 1. Bond Lengths d (pm) and Au−P Dissociation Energies ΔE (kJ mol^{-1}) for [$(PR_3)_2M]^+$

species	method	d(Au−P)	ΔE	ref
[$(PH_3)_2Ag]^+$	NR R	249.3 240.9	302 371	*a*
[$(PMe_3)_2Ag]^+$	NR R	248.7 241.1	421 502	*a*
[$(PMes_3)_2Ag]^+$	exp	244.09(9)		4
[$(TMPP)_2Ag]^+$	exp	238^b		25
[$(TCEP)_2Ag]^+$	exp	238.32(9)		26
[$(PH_3)_2Au]^+$	NR R	253.8 231.6	302 595	*a*
[$(PMe_3)_2Au]^+$	NR R	253.3 233.2	424 754	*a*
[$(PMe_3)_2Au]^+$	exp	230.4(1)		27
[$(PMes_3)_2Au]^+$	exp	235.25(10)		4
[$(PEt_3)_2Au]^+$	exp	229.7(4)		28
[$(PBu^t_3)_2Au]^+$	exp	230.2(6)		29
[$(PCy_3)_2Au]^+$	exp	232.5(6)		30
[$(PPh_3)_2Au]^+$	exp	228.6(3)		31
[$(PPh_2Me)_2Au]^+$	exp	231.6(4)		32
[$(PTol^o_3)_2Au]^+$	exp	230.4(6)		33
[$(TCEP)_2Au]^+$	exp	231.4(2)		34

^{a} This work: NR = nonrelativistic calculation and R = relativistic calculation. ^{b} Average for two inequivalent Ag−P bonds.

Table 2. Bond Lengths d (pm) and Au−P Dissociation Energies ΔE (kJ mol^{-1}) for [PR_3MCl]

molecule	method	d(M−P)	d(M−Cl)	ΔE	ref
[PH_3AgCl]	NR	242.0	234.8	105	*a*
	R	233.3	229.9	134	
[PMe_3AgCl]	NR	242.9	235.5	142	*a*
	R	234.4	230.8	174	
[$(TMPP)AgCl$]	exp	237.9(1)	234.2(1)		7
[PH_3AuCl]	NR	244.8	240.9	109	*a*
	R	222.2	227.0	220	
[PMe_3AuCl]	NR	245.2	241.0	144	*a*
	R	223.5	228.3	269	
[PMe_3AuCl]	exp	223.4(4)^b	230.9(4)^b		27
[PEt_3AuCl]	exp	223.2(9)	230.5(8)		35
[PPh_3AuCl]	exp	223.5(3)	227.9(3)		36
[PCy_3AuCl]	exp	224.2(4)	227.9(5)		37
[$(TMPP)AuCl$]	exp	225.3(5)	230.3(6)		8

^{a} This work: NR = nonrelativistic calculation and R = relativistic calculation. ^{b} Average for three crystallographically inequivalent molecules.

as those used in the previous study of [$MeAuPR_3$] (R = H, Me),[15] and these were held constant during the geometry determination in which Au−P and Au−Cl distances were optimized by means of analytical forces.[20,24] The geometry optimizations were carried out under D_{3d} and C_{3v} symmetry contraints for [$(PR_3)_2M]^+$ and [PR_3MCl], respectively.

Results and Discussion

The results of the bond length calculations for [$(PR_3)_2M]^+$ and [PR_3MCl] are given in Tables 1 and 2, respectively, where they are compared with experimental data for a number of complexes of these types. The trends in the results for the PH_3 complexes are shown graphically in Figure 1.

Previously reported Hartree−Fock (HF) calculations on [$(PH_3)_2Au]^+$ yielded Au−P bond distances of 279.3 (NR) and 245.3 (R) pm.[3] These are 25 (NR) and 14 (R) pm longer than the present LCGTO-DF results, and it is clear from the data in Table 1 that the relativistic Au−P bond length obtained in the present study (231.6 pm) is in good agreement with the experimental bond lengths for a range of [$(PR_3)_2Au]^+$ species for which structural data have been reported (mean value d(Au−P) = 231 ± 2 pm for the nine [$(PR_3)_2Au]^+$ species in Table 1), whereas the HF value is about 15 pm too high. In the case of

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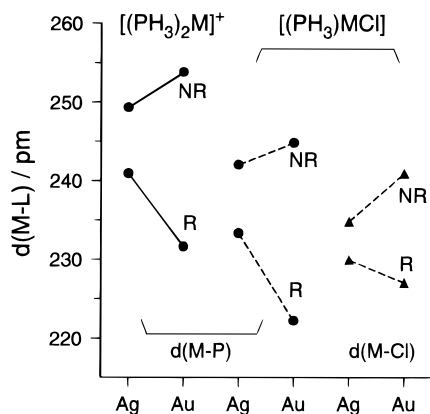
Figure 1. Trends in the calculated metal–ligand bond lengths in $[(PH_3)_2M]^+$ and $[(PH_3)MCl]$ for M = Ag, Au.

$[(PMe_3)_2Au]^+$, a more direct comparison of theory with experiment is possible, since the structure of this species has been determined in a single-crystal structure study of $[(PMe_3)_2Au]^+Cl^-$ [27] and the present calculated Au–P is only 3 pm longer than the experimental value.

The relativistic contractions of the Au–P bond lengths in $[(PH_3)_2Au]^+$ and $[(PMe_3)_2Au]^+$ are 22 and 20 pm, respectively. The relativistic effect on the bond lengths is thus considerable, although not as large as the value of 34 pm obtained in the HF study of $[(PH_3)_2Au]^+$.[3] However, the latter value is, at least in part, a consequence of the fact that the Au–P bond is described as quite significantly weaker (longer) at the HF level of theory than by the present density functional method. Thus, relativistic effects provide a stronger "perturbation" of the nonrelativistic Au–P bond in the HF description.

The relativistic Ag–P bond length in $[(PH_3)_2Ag]^+$ (240.9 pm) is in good agreement with the experimental bond lengths that have been determined in the relatively small number of compounds for which structural data have been obtained to date. The mean value of the three $[(PR_3)_2Ag]^+$ species is $d(Ag-P)$ = 240 ± 3 pm (Table 1). As expected, the relativistic contraction in the Ag–P bond lengths, about 8 pm, is significantly less than that in the Au–P bonds, about 20 pm. The reduction in the M–P bond length in going from $[(PH_3)_2Ag]^+$ to $[(PH_3)_2Au]^+$ is 9.3 pm. This is in very good agreement with the value 8.8 pm found experimentally for the corresponding PMes$_3$ complexes,[4] confirming that this decrease is indeed due to a decrease in the size of the metal atom from Ag to Au and not to differences in crystal packing or other solid state effects.

The results of the present relativistic calculations on $[PH_3-AuCl]$ are in good agreement with previously published MP2 calculations on this molecule.[38] The LCGTO-DF method thus

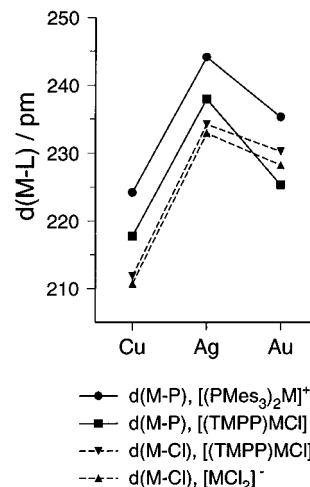(27) Angermaier, K.; Zeller, E.; Schmidbaur, H. *J. Organomet. Chem.* **1994**, *472*, 371.
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Figure 2. Dependence of the metal–ligand bond length d(M-L) on M: $d(M-P)$ (●) in $[(PMes_3)_2M]^+$ (data from ref 4); $d(M-P)$ (■) and $d(M-Cl)$ (▼) in $[(TMPP)MCl]$ (data from refs 6–8); $d(M-Cl)$ (▲) in $[MCl_2]^-$ (data from refs 40–42).

gives results comparable in quality to those of the MP2 method, as expected, but is much less expensive, so that similar-quality calculations on larger systems such as $[PMe_3AuCl]$ may be carried out using the LCGTO-DF method.

The agreement between the calculated (relativistic) and experimental bond lengths in $[PMe_3AuCl]$ is very good, although the Au–P bond lengths are in slightly better agreement than the Au–Cl distances. The theoretical values are in fact closer to the experimental values for $[PPh_3AuCl]$. A significant difference between the solid state structures of $[PMe_3AuCl]$ and $[PPh_3AuCl]$ is that the former consists of infinite chains of molecules weakly bound by aurophilic Au---Au interactions at an average distance of 334 pm, whereas the latter consists of well-isolated molecules with an Au---Au separation of 699 pm. The question of whether the shorter Au---Au distance in the PMe$_3$ compound has any effect on the Au–P and Au–Cl bond lengths must therefore be considered. However, model calculations on the $[PH_3AuCl]_2$ dimer, which has a still shorter equilibrium Au---Au distance of 325 pm, show that the Au–P and Au–Cl bond lengths increase by less than 0.5 pm upon dimerization,[39] so it is unlikely that the differences between the solid state structures of $[PMe_3AuCl]$ and $[PPh_3AuCl]$ which are evident in Table 2 are due to the presence of significant Au---Au interactions in the former.

The crystal structures of all complexes $[(TMPP)MX]$ (M = Cu, Ag, Au; X = Cl, Br, I) have been determined (except for the AgI complex) and were found to be all isomorphous, the metal atoms displaying a linear P–M–X coordination.[6–8] In contrast to the situation of the $[(PMes_3)_2M]^+$ compounds,[4] the $[(TMPP)MX]$ series involve two different kinds of bond (M–P and M–X) at the metal atom. The variation of the M–P bond length with M in $[(PMes_3)_2M]^+$ and of the M–P and M–Cl bond lengths in the $[(TMPP)MCl]$ compounds is shown in Figure 2. The change in the M–P bond length with M follows a similar pattern for both types of compounds. The behavior of the M–X bond length is significantly different, however, the decrease from M = Ag to Au being less pronounced than that for the M–P bond. In order to investigate this question further, corresponding data for the M–X bond length in $[MCl_2]^-$ were plotted in Figure 2. The bond lengths were obtained from the crystal structures of $[NBu^n_4][CuCl_2]$,[40] $[K(crypt-2,2,2)]$-$[AgCl_2]$,[41] and $[NEt_4][AuCl_2]$,[42] and the comparison is restricted

(39) Krüger, S.; Rösch, N.; Bowmaker, G. A.; Schmidbaur, H. Unpublished results.

to the chloro complexes because this silver complex is the only one known to possess a linear two-coordinate $[AgX_2]^-$ species. Figure 2 shows that the variation of the M−Cl bond length with M in $[MCl_2]^-$ is very similar to that in [(TMPP)MCl]. The calculated M−P and M−Cl bond lengths for the [PR$_3$MCl] compounds (Table 2, Figure 1) show exactly the same trends as those illustrated in Figure 2 for [(TMPP)MCl]; the decrease in the M−P bond length from M = Ag to Au is about 11 pm, whereas that in the M−Cl bond is only about 3 pm.

A possible reason for this difference could be that M−P bonds involve a greater degree of metal valence s character than M−X bonds, as predicted by Bent's rule.[43,44] Mössbauer studies of [PR$_3$AuX] complexes provide some experimental support for this proposal.[45] This rule suggests a greater bond length contraction in the M−P than in the M−Cl bond, since the M−P bond has greater valence s character, and the relativistic contraction of the Au 6s should be greater than that of the Ag 5s orbital.[1−3] Differential relativistic bond contractions were noted previously in calculations on diatomic AuX molecules, and it was found that the magnitude of the contraction decreases with increasing electronegativity of the ligand X.[2] The explanation given for this result is that no contraction would be expected for a purely ionic bond Au$^+$X$^-$, since this does not involve occupation of the Au 6s orbital, and that the contraction would progressively increase through covalent Au−X to ionic Au$^-$X$^+$ (e.g., where X is an alkali metal) with increasing occupation of the Au 6s orbital. In [PH$_3$AuCl], the atomic charges obtained from a population analysis of the molecular orbitals from the relativistic calculation are +0.07 (H), −0.14 (P), +0.31 (Au), and −0.39 (Cl). Thus, the Au−Cl bond is more polar in the Au$^+$X$^-$ sense than is the Au−P bond. In accordance with the above-mentioned results for diatomic systems, the contraction of the Au−Cl bond should be less than that of the Au−P bond, and this agrees well with the results of the present calculations (Table 2). It should be noted, however, that there is no causal relationship between the relativistic contraction of the Au 6s orbital and the Au−P and Au−Cl bond length contractions. It has been well established that, while the relativistic contraction of orbitals and the relativistic contraction of bond lengths are parallel effects, the orbital contraction is not the direct cause of the bond length contraction.[1] Another possible explanation for the greater contraction of the Au−P bond relative to the Au−Cl bond involves changes in Au−P back-bonding. Relativistic effects destabilize d orbitals,[1−3] and this would enhance back-donation from the Au 5d orbitals to the PR$_3$ molecule, thus strengthening the Au−P bond. There is some evidence to support this view in the Au $5d_\pi$ populations. These are approximately 2.0 in the nonrelativistic calculations (indicating

that there is no π back-donation), but they decrease by about 0.05 in the relativistic case (indicating a small degree of π back-donation). The present methods do not permit a determination of the relative importance of the two mechanisms described above to explain the greater relativistic contraction of the Au−P bond. In addition to the differences in the M−P and M−Cl bond length contractions from M = Ag to Au discussed above, the following experimentally observed trends (Figure 2) are well repoduced by the LCGTO-DF calculations (Figure 1): (a) the M−P bond distances in $[(PR_3)_2M]^+$ are longer than those in [PR$_3$MCl]; (b) the decrease in the M−P bond length from M = Ag to Au is greater in [PR$_3$MCl] than in $[(PR_3)_2M]^+$.

The calculated bond lengths for the corresponding PH$_3$ and PMe$_3$ complexes in Tables 1 and 2 are almost identical, confirming the conclusion reached previously on the basis of similar calculations[15] on [PR$_3$AuMe] that PH$_3$ is a good model for the larger PMe$_3$ ligand, at least for the calculation of structural properties. In fact, the agreement for the present complexes is within 2 pm and is significantly closer than for the corresponding [PR$_3$AuMe] molecules, where differences of 3−4 pm were reported.[15] However, in the previous study of the [PR$_3$AuMe] complexes, substantial differences were found in the Au−P bond dissociation energies when the PR$_3$ ligand was varied,[15] and the same was found in the present study. The dissociation energies ΔE for the processes

$$[(PR_3)_2M]^+ \rightarrow 2PR_3 + M^+ \qquad (1)$$

$$[PR_3MCl] \rightarrow PR_3 + MCl \qquad (2)$$
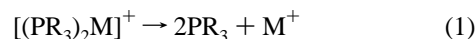
are given in Tables 1 and 2. In all cases, the ΔE values for the PMe$_3$ complexes are higher (by 20−40%) than to those for the corresponding PH$_3$ complexes. This contrasts with the situation regarding the M−P bond lengths, where the values for the PMe$_3$ complexes are always slightly longer than those for the corresponding PH$_3$ complexes. This provides computational support for the concept of "longer but stronger bonds", which was proposed on the basis of experimental studies of M−P bonds in transition metal complexes involving various substituted phosphine ligands.[16] It should be emphasized that this concept only applies when complexes involving different phosphine ligands are compared. The expected, more common correlation of shorter bond lengths with stronger bonds is observed in the comparison of the relativistic with the nonrelativistic results for particular $[(PR_3)_2M]^+$ or [PR$_3$MCl] species; for the M = Au complexes, the relativistic bond lengths are about 20 pm shorter than the nonrelativistic ones, and the dissociation energies are nearly a factor of 2 higher for the relativistic compared with the nonrelativistic calculation, further emphasizing the importance of relativistic effects in gold chemistry.[1−3]

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