Inorg. Chem. **2003**, *42*, 1334–1342

Inorganic Chemistry

Article

Stability of the Gold(I)–Phosphine Bond. A Comparison with Other Group 11 Elements

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Received October 9, 2002

The stability of gold phosphine complexes of the form $[Au(PH_3)_n]^+$ (n = 1–4) and $[AuCl(PH_3)_n]$ (n = 1–3) is analyzed in detail by applying quantum theoretical methods and compared to the coordination behavior of the lighter group 11 elements copper and silver. It is shown that, once $[M(PH_3)_2]^+$ or $[MClPH_3]$ (M = Cu, Ag, and Au) is formed, further coordination by PH_3 ligands is relatively weak; i.e., the energy gain to form $[M(PH_3)_3]^+$ from $[M(PH_3)_2]^+$ is less than 60 kJ mol^{-1}, and less than 100 kJ mol^{-1} to form $[MCl(PH_3)_2]$ from $[MClPH_3]$. Relativistic effects in gold significantly influence these factors and reduce the tendency for phosphine coordination beyond two-coordination. This implies that the most favored coordination number for gold is two with either a linear P–Au–P or P–Au–X arrangement (X = a strongly coordinating ligand like Cl^-). Instead, X–Au–PH_3 units prefer to interact via close Au–Au contacts (aurophilic interactions) keeping the linear structure approximately intact, while the corresponding copper and silver compounds prefer PH_3 coordination to strongly bound M_2Cl_2 units (M = Cu or Ag) where two chlorine atoms bridge the two metal atoms thus having the formal coordination number of three for copper or silver.

Introduction

Gold(I) phosphine complexes have been studied extensively in the past.[1,2] These compounds have interesting chemical and physical properties.[3−5] For instance, phosphine ligands stabilize gold−gold bonding[6] thus inducing the formation of a large variety of gold clusters[7−11] like $[(Ph_3PAu)_6C]^{2+}$ or $[Au_{55}(PPh_3)_{12}]Cl_6$.[12,13] Gold phosphine cluster compounds can also show interesting photophysical properties such as the luminescence behavior[14] observed in [Au(dppn)$_2$]Cl derivatives (dppn = diphenylphosphinonaphthaline)[15] or related compounds.[16] Phosphine coordination is also used to stabilize otherwise unstable gold compounds such as $AuCH_3$.[17−18,19]

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10.1021/ic026098v CCC: $25.00

Despite the fact that the coordination chemistry of gold phosphine compounds has been investigated intensively,[2,3,7,20] the factors influencing the coordination number (N_c) of gold are not so well understood. In general, coordination numbers in mononuclear gold compounds range from two to six with two (linear arrangement) being the most common coordination number for Au(I), and four (square planar arrangement) for Au(III) and six (octahedral) for Au(V).[3] The most notable new structure with coordination number four is the Au(II) compound $AuXe_4^{2+}$, which has recently been synthesized by Seppelt's group in Berlin.[21]

The structures of group 11 phosphine complexes of the type $[M(PR_3)_n]^+X^-$ (M = Cu, Ag, or Au; $n = 1-4$; R any organic ligand; X any counterion more or less tightly bound to the gold center) are well known and characterized for PR_3 coordination numbers up to four, e.g., $[M(PPh_3)_4]^+$.[3,22−26] However, there are some marked differences in phosphine coordination within the group 11 series of compounds. In a recent study by Zank et al., the bis[2-(diphenylphosphino)-phenyl]phenyl-phosphine (TP) gold complex [Au(TP)Cl] (**1**) has two phosphine ligands coordinated to gold at distances of 2.32 and 2.37 Å, respectively, the third one less well bound to gold at a distance of 2.46 Å.[27] In contrast, the corresponding silver complex has all three phosphine atoms bound to the metal center at distances between 2.49 and 2.55 Å. This indicates a preference for coordination number two over three for gold in contrast to silver. The shorter Au−P bond distance in gold compared to silver reflects the importance of relativistic effects which is at a maximum at gold in the 6th period of the periodic table.[6,28−30] We mention that in the gas phase the formation of $[Au(PR_3)_2]^+$ and $[Au(PR_3)_3]^+$ (R = PPh$_3$, etc.) has been observed by electrospray mass spectroscopy, the latter complex being relatively unstable and decomposing into $[Au(PR_3)_2]^+$ and PR_3.[31] Interestingly, the tetrakis(phosphine) complex of gold, $[Au(PR_3)_4]^+$, which exists in solution as well as in the solid state,[32] has not been found in the gas phase. We also mention that at temperatures $T > 213$ K PR_3 ligand exchange in gold phosphine complexes is rapid on the NMR time scale.[32]

(1)

Since Au(I) has a complete d-shell, the geometry of Au(I) complexes is easily predicted. Ligands formally donating two electrons, like PR_3 (R any substituent), usually obey the VSEPR rules ranging from linear ($N_C = 2$) to trigonal planar ($N_C = 3$) to tetrahedral ($N_C = 4$) geometries. Small deviations from these ideal arrangement are only due to steric repulsion of the substituents R or due to solid state effects.[3,33] There are a few exceptions to the simple VSEPR arrangement. For example, we recently showed that the T-shaped $AuGe_3$ arrangement in $[Au(GeCl_3)_3]^{2-}$ (which is isoelectronic to $[Au(PR_3)_3]^+$) is due to the influence of the counterions in the solid state.[34] AuX_3 compounds with X being ligands formally donating only one electron to the gold center, e.g., ligands like F, Cl, CN, or CR_3, lead to half filled e′-orbitals for the trigonal planar arrangement and therefore cause a first-order Jahn−Teller distortion toward a planar T-shaped AuX_3 structure.[35]

At long range, the interaction between the ligand and a positively charged gold atom Au^+ can be explained by charge induced dipole and simple Coulomb interactions with a ligand L which is polarizable or has a permanent dipole moment. If little charge transfer or overlap effects between Au^+ and L take place, the coordination sphere will fill up to the point where ligand−ligand repulsion sets in. For example,

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for a system like $Au^+ + He$, we simply predict an almost additive charge induced dipole interaction with no clear preference for any coordination number unless the coordination sphere is full. However, in a recent paper, Frenking and co-workers showed that for group 11 and 12 carbonyl compounds $[M(CO)_n]^{m+}$ charge transfer and covalent contributions are important in the metal−CO interaction.[36] The situation is probably similar for the phosphine ligand, although phosphine ligands have stronger σ-donor capabilities than CO ligands (and basically no π-acceptor properties). In these carbonyl compounds, the coordination number $N_C = 2$ is clearly preferred as for most other ligands.[36] Higher coordination numbers become less favorable. Nevertheless, salts with the cation $[Cu(CO)_4]^+$ have been isolated very recently[37] and the cations identified by spectroscopic methods in the gas phase.[38] Most of the other polycarbonyl compounds require, however, high pressure of CO to prevent loss of the CO ligand.[39]

In order to understand the phosphine coordination chemistry of gold in more detail, we studied the structure and stability of all group 11 $[M(PH_3)_n]^+$ complexes (M = Cu, Ag, and Au) for coordination numbers up to CN = 4 at the ab initio level of theory, thus extending the previous work by Rösch and co-workers.[20] We also investigated the influence of the counterion on phosphine complexation by choosing a more strongly coordinating ligand, chloride, i.e., $[MCl(PH_3)_n]$. For the monophosphine complex $[MClPH_3]$, we also studied the possible structural arrangement for the dimerization reaction to form $[MClPH_3]_2$. Finally, we modeled compound **1** by substituting the phenyl ligands by hydrogen atoms in order to discuss differences in PR_3 coordination between the corresponding gold and silver compounds.

Computational Details

All $[M(PH_3)_n]^+$ and $[MCl(PH_3)_n]$ (M = Cu, Ag, and Au) compounds were preoptimized at the pseudopotential (PP) Hartree−Fock level using Hay−Wadt relativistic PPs and basis sets (LANL2DZ)[40,41] and then further refined using energy consistent scalar relativistic small-core pseudopotentials for Au and Ag[42] including electron correlation at the second-order Møller−Plesset (MP2) level.[43] The accuracy of the pseudopotential approximation for gold has been demonstrated recently.[44] For lower oxidation states of gold, the MP2 approximation gives reasonably accurate results.[45] All minima were confirmed by subsequent frequency analyses at the LANL2DZ level. Minimization of the model compound $[MP_3H_5(C_2H_4)_2]Cl$ (M = Au, Ag) for simulating **1** took several month of computer time on our 32-processor SGI Origin 2000. We also investigated possible structures for the dimerization reaction of two $[MClPH_3]$ units.

Table 1. Optimized Bond Distances *r*, Angles α, and Dissociation Energies Δ*E* for the Dissociation $[M(PH_3)_n]^+ \rightarrow [M(PH_3)_{n-1}]^+ + PH_3$ (M = Cu, Ag, Au)[a]

cmpd	*r*(M−P)	*r*(P−H)	α(M−P−H)	Δ*E*
$AuPH_3^+$	2.291	1.396	114.3	267.4
	2.696	*1.400*	*117.4*	*120.9*
$Au(PH_3)_2^+$	2.349	1.398	115.8	244.1
	2.646	*1.400*	*117.7*	*121.3*
$Au(PH_3)_3^+$	2.420	1.400	120.0/118.6	60.6
	2.731	*1.402*	*119.6/118.4*	*66.5*
$Au(PH_3)_4^+$	2.446	1.402	118.6	70.1
	2.780	*1.404*	*119.4*	*58.2*
$AgPH_3^+$	2.475	1.398	116.4	159.0
$Ag(PH_3)_2^+$	2.447	1.399	117.1	160.4
$Ag(PH_3)_3^+$	2.518	1.401	119.8/117.7	74.6
$Ag(PH_3)_4^+$	2.555	1.404	119.2	68.3
$CuPH_3^+$	2.206	1.398	115.7	227.6
$Cu(PH_3)_2^+$	2.224	1.399	116.7	210.1
$Cu(PH_3)_3^+$	2.256	1.402	120.0/115.6	106.5
$Cu(PH_3)_4^+$	2.261	1.404	119.0	96.6
PH_3		1.412	122.6	

[a] Units: *r*, Å; α, deg; Δ*E*, kJ mol^{-1}. In the case of PH_3, the angle between H, P, and the C_3 axis is taken. Values calculated with a nonrelativistic pseudopotential for Au are given in italics. For geometries, see Figure 1.

All calculations were performed with a parallel version of Gaussian98.[40] The following contracted basis sets were used: for H, a [6s1p]/(4s1p) set; for C, a [9s4p1d/3s2p1d] set; for P, a [10s7p1d/4s3p1d] set; for Cl, a [10s7p1d/4s5p1d] set; and for Cu, a [18s12p7d/7s5p4d] set.[46] For the heavier group 11 metals, we used a [9s8p7d/8s6p5d] set for Ag and a [8s6p5d/7s5p4d] set for Au. For Au, we also used a nonrelativistic valence [9s7p6d/8s5p5d] set. f-Functions were omitted due to the fact that calculations for compounds such as $[Au(PH_3)_4]^+$ required a large excess of computer time. The bonding situation has been examined using the natural bond orbital (NBO) partitioning of Weinhold and Reed.[47]

Results and Discussion

All structural data obtained from geometry optimizations are listed in Tables 1 and 2, and for the gold compounds shown in Figure 1. The corresponding population analyses are given in Tables 3 and 4. The geometric parameters for the $[M(PR_3)_n]X$ (M = Cu, Ag, Au; R = Ph, etc.; X = ClO_4, Cl, etc.) compounds obtained from X-ray crystallography[3] are all in reasonable agreement with our calculated results.

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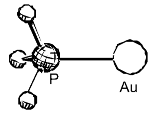
Table 2. Optimized Bond Distances *r*, Angles α, and Dissociation Energies Δ*E* for the Dissociation $[MCl(PH_3)_n] \rightarrow [MCl(PH_3)_{n-1}] + PH_3$ (M = Cu, Ag, Au)[a]

cmpd	*r*(M−P)	*r*(M-Cl)	*r*(P−H)	α(Cl−M−P)	α(M−P−H)	Δ*E*
$ClAuPH_3$	2.249	2.300	1.400	180	117.9	222.4
	2.589	*2.453*	*1.402*	*180*	*119.0*	*92.8*
$ClAu(PH_3)_2$	2.253/3.569	2.302	1.398−1.412	103.7/178.2	80.7−173.8	22.5
	2.948/2.632	*2.512*	*1.403−1.411*	*152.8/86.4*	*107.1−143.7*	*31.7*
$ClAu(PH_3)_3$	2.400	2.566	1.403	95.0	119.3/115.6	12.4
	2.762	*2.611*	*1.405*	*95.3*	*119.2/111.1*	*37.8*
ClAu		2.285				
		2.471				
$ClAgPH_3$	2.372	2.306	1.401	180	118.6	128.7
$ClAg(PH_3)_2$	2.412/2.693	2.381	1.403−1.410	146.6/90.4	109.3−139.0	29.1
$ClAg(PH_3)_3$	2.522	2.501	1.404/1.409	97.3	113.5/131.5	45.8
ClAg		2.321				
$ClCuPH_3$	2.159	2.097	1.402	180	118.6	171.6
$ClCu(PH_3)_2$	2.244	2.184	1.404/1.406	115.2	116.0/126.1	44.9
$ClCu(PH_3)_3$	2.268	2.251	1.404/1.409	104.6	114.6/122.6	58.5
ClCu		2.104				

[a] Units: *r*, Å; α, deg; Δ*E*, kJ mol^{-1}. Values calculated with a nonrelativistic Au pseudopotential are given in italics.



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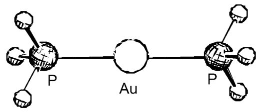

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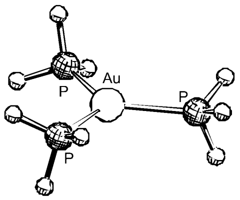

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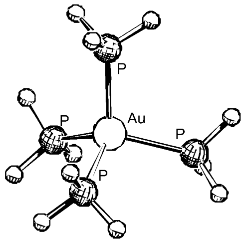

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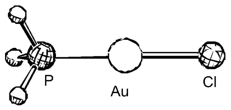

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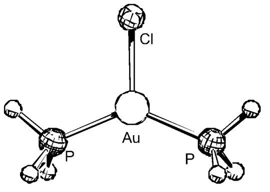

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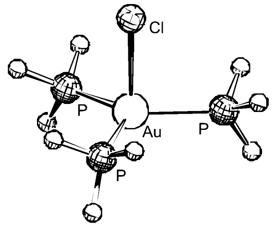

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Figure 1. Optimized structures for (**2**) $[AuPH_3]^+$, (**3**) $[Au(PH_3)_2]^+$, (**4**) $[Au(PH_3)_3]^+$, (**5**) $[Au(PH_3)_4]^+$, (**6**) $[AuClPH_3]$, (**7**) $[AuCl(PH_3)_2]$ (first-order transition state), and (**8**) $[AuCl(PH_3)_3]$.

Small deviations are due to solid state effects and the computational method chosen in our calculations. We mention that the nature of the ligand R (R = H chosen in our computations) for the PR_3 ligand has a significant influence on the bonding and stability of these phosphine complexes, as was clearly demonstrated by Rösch and coworkers for a number of gold phosphine compounds.[10,48]

Table 3. NBO Population Analysis for $[M(PH_3)_n]^+$ (M = Cu, Ag, Au)[a]

cmpd	*q*(M)	*q*(P)	*n*(d)	*n*(s)	*n*(p)
$AuPH_3^+$	0.66	0.25	9.890	0.438	0.011
	0.85	*0.07*	*9.945*	*0.202*	*0.001*
$Au(PH_3)_2^+$	0.36	0.27	9.825	0.796	0.011
	0.58	*0.16*	*9.888*	*0.519*	*0.003*
$Au(PH_3)_3^+$	0.47	0.18	9.858	0.627	0.030
	0.65	*0.11*	*9.901*	*0.423*	*0.010*
$Au(PH_3)_4^+$	0.50	0.16	9.854	0.584	0.051
	0.64	*0.11*	*9.893*	*0.417*	*0.024*
$AgPH_3^+$	0.86	0.07	9.973	0.156	0.005
$Ag(PH_3)_2^+$	0.61	0.15	9.923	0.449	0.006
$Ag(PH_3)_3^+$	0.63	0.12	9.938	0.405	0.014
$Ag(PH_3)_4^+$	0.60	0.12	9.939	0.417	0.025
$CuPH_3^+$	0.85	0.07	9.971	0.168	0.007
$Cu(PH_3)_2^+$	0.61	0.15	9.936	0.444	0.009
$Cu(PH_3)_3^+$	0.60	0.13	9.940	0.430	0.020
$Cu(PH_3)_4^+$	0.56	0.15	9.931	0.456	0.033

[a] Nonrelativistic values are set in italics. Charges *q* and metal orbital populations *n*.

Table 4. NBO Population Analysis for $[MCl(PH_3)_n]$ (M = Cu, Ag, Au)[a]

cmpd	*q*(M)	*q*(P)	*q*(Cl)	*n*(d)	*n*(s)	*n*(p)
$ClAuPH_3$	0.40	0.30	−0.64	9.763	0.772	0.046
	0.59	*0.18*	*−0.73*	*9.849*	*0.500*	*0.042*
$ClAu(PH_3)_2$	0.40	0.31/0.12	−0.65	9.766	0.774	0.043
	0.59	*0.19/0.11*	*−0.74*	*9.851*	*0.501*	*0.029*
$ClAu(PH_3)_3$	0.51	0.21	−0.82	9.845	0.548	0.059
	0.64	*0.16*	*−0.84*	*9.886*	*0.390*	*0.041*
$ClAgPH_3$	0.60	0.17	−0.73	9.892	0.447	0.041
$ClAg(PH_3)_2$	0.64	0.17/0.13	−0.78	9.921	0.379	0.023
$ClAg(PH_3)_3$	0.61	0.16	−0.83	9.932	0.371	0.039
$ClCuPH_3$	0.61	0.18	−0.74	9.905	0.421	0.050
$ClCu(PH_3)_2$	0.63	0.17	−0.80	9.931	0.376	0.040
$ClCu(PH_3)_3$	0.60	0.19	−0.82	9.929	0.398	0.031

[a] Nonrelativistic values are set in italics. Charges *q* and metal orbital populations *n*.

In more detail, for the two-coordinate species (with $N_C = 2$), an X-ray analysis[49] yields the following values: for $[AuClPPh_3]$ (calculated values for $[AuClPH_3]$ are set in parentheses), *r*(Au−P) = 2.235 Å (2.249 Å), *r*(Au−Cl) = 2.279 Å (2.300 Å), α(P−Au−Cl) = 179.6° (180°); and for $[Au(PMePh_2)_2]^+(PF_6^-)]$ (calculated values for $[Au(PH_3)_2]^+$ are set in parentheses), *r*(Au−P) = 2.316 Å (2.349 Å) and α(P−Au−P) = 180° (180°).[50] Our calculated bond distances are also in good agreement with previous results by Bowmaker et al.[20] who obtained *r*(Au−P) = 2.316 Å for $[Au(PH_3)_2]^+$, and *r*(Au−P) = 2.222 Å and *r*(Au−Cl) = 2.227 Å for $[AuClPH_3]$ using scalar relativistic density functional theory. We can also compare with results by Pyykkö et al.[51] who obtained *r*(Au−P) = 2.333 Å for $[Au(PH_3)_2]^+$, and *r*(Au−P) = 2.243 Å and *r*(Au−Cl)= 2.263 Å for $[AuClPH_3]$ using the same theoretical approach as in this work, or with Kickelbein and Schubert who obtained *r*(Au−P) = 2.283 Å and *r*(Au−Cl)= 2.325 Å for $[AuClPH_3]$ using density functional theory (B3LYP) within a scalar relativistic pseudopotential approach.[52]

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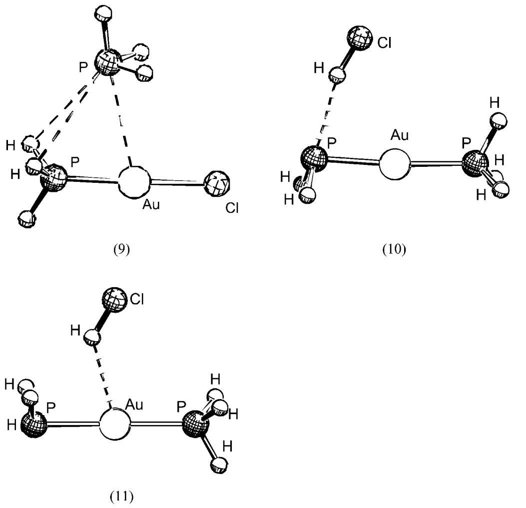

(9) (10)

(11)

Figure 2. Optimized structures for [AuCl(PH_3)$_2$] showing (a) one strong and one weak PH_3 coordination to gold (**9**), (b) HCl interacting with the PH_2 unit (**10**), and (c) HCl interacting with the Au-center (**11**).

For $N_C = 3$, Jones found for $[Au(PPh_3)_3]^+(BPh_4^-)$ distances of r(Au$-$P) between 2.365 and 2.403 Å[53] (2.420 Å) and α(P$-$Au$-$P) between 115.2° and 125.4° (120°) (calculated values for $[Au(PH_3)_3]^+$ are set in parentheses). Fackler and co-workers obtained bond distances between 2.374 and 2.417 Å for $[Au(TPPTS)_3]^{8-}$ (TPPTS = trisulfonated triphenylphosphine).[54] It is obvious that solid state effects, steric repulsion between the phenyl ligands, and the influence of the counterion explain most of the differences with our values. The comparison between the X-ray structure of [AuCl(PPh_3)$_2$] and the calculated structure of [AuCl(PH_3)$_2$] is even more interesting. The X-ray analysis[55] reveals larger differences between the Au$-$P bond distances, i.e., r(Au$-$P) = 2.230 and 2.313 Å, r(Au$-$Cl) = 2.526 Å, and α(P$-$Au$-$Cl) = 108.1° and 115.1°. The calculation of [AuCl(PH_3)$_2$] favors an almost linear P$-$Au$-$Cl unit (r(Au$-$P) = 2.253 and r(Au$-$Cl) = 2.300 Å) with an additional loosely bound PH_3 unit at a distance of 3.569 Å. The calculation of [AuCl(PH_3)$_2$] with two identical Au$-$P bond lengths (2.360 Å) is a first-order saddle point and $\Delta E = 26.6$ kJ mol^{-1} above the minimum structure with one strong and one weak bonding PH_3 ligand to the Au center, Figure 2. In fact, Figure 2 shows that the lone pair of the PH_3 ligand is directed toward the hydrogen atoms and the linear Cl$-$Au$-$P unit is almost unperturbed with an angle of 178.2°. The energy difference between both structures **7** and **9** is very small, and in the solid state, the chlorine ligand becomes more detached from the gold center allowing for stronger phosphine coordination. Moreover, PPh_3 is a more strongly coordinating ligand compared to PH_3,[48] which also explains the different binding situation in the solid state. The distances listed in Table 2 show that the same bonding situation is obtained for the nonrelativistic case, although the two Au$-$P bond distances do not differ so dramatically anymore. The results clearly indicate that for strongly coordinating ligands such as PH_3, causing substantial charge transfer from the P lone pair to the metal center, the coordination number $N_C = 2$ is preferred. We mention, however, the structure of [Au(PCy_3)$_2$]Cl (Cy= cyclohexyl) obtained by Bowmaker et al.[56] which consists of $[Au(PCy_3)_2]^+$ with a linear P$-$Au$-$P unit and the Cl^- ion interacting with hydrogen atoms of the cyclohexyl ligand. Indeed, we find two more structures, **10** and **11**, with an almost linear P$-$Au$-$P unit as also shown in Figure 2. In **10**, we have Cl^- interacting with a hydrogen atom of one of the PH_3 ligands forming HCl (r(H$-$Cl) = 1.284 Å) with the hydrogen atom detached from the P-center (r(P$-$H)= 2.531 Å). The P$-$Au$-$P angle is 176.2°. In **11**, we have r(H$-$Cl) = 1.288 Å and a weak Au$-$H bond with r(Au$-$H)= 2.554 Å. Here, the P$-$Au$-$P angle is 177.0°. Both structures are minima on the potential energy surface and only slightly above structure **9** in energy ($\Delta E = 10.5$ kJ mol^{-1} for **10** and 13.3 kJ mol^{-1} for **11**).

For $[Au(PPh_3)_4]^+(BPh_4^-)\cdot CH_3CN$ with $N_C = 4$, an X-ray analysis[57] gives rather long bond distances between r(Au$-$P) = 2.504 and 2.561 Å (2.446 Å for $[Au(PH_3)_4]^+$) in a tetrahedral coordination environment. For $[Au(PPh_3)_4]^+(BPh_4^-)\cdot CHCl_3$, there is also a second modification observed with one PPh_3 ligand detached from the central gold atom with r(Au$-$P) = 3.946 Å.[57] This indicates rather weak bonding of the fourth PR_3 ligand. Even more interesting, for [AuCl(PPh_3)$_3$] we have three phosphine ligands bound equally well to the Au center[58] with r(Au$-$P) between 2.395 and 2.431 Å (2.400 Å), but with a very large Au$-$Cl bond length of 2.710 Å which is nicely confirmed by our calculated result (2.566 Å). Schmidbaur and co-workers found similar results for $[AuCl(PPh_3)_3]\cdot(CH_2Cl_2)_2$ with r(Au$-$Cl) of 2.796 Å.[59] The long Au$-$Cl bond can be interpreted as a weak ionic Au^+-Cl^- interaction, as the P$-$Au$-$Cl angles with values of 92.0°, 98.3°, and 116.6° (95.0° for [AuCl(PH_3)$_3$]) are found to be close to 90°. This is further supported by the population analysis (Table 4) showing a charge for Cl of almost -1.

Copper and silver phosphine compounds of the form [MX(PH_3)] (M = Cu, Ag; X= Cl, Br, etc.) tend to oligomerize, and therefore, only few X-ray data for monomeric structures are available for comparison.[60,61] For example, for [AgCl(PPh_3)$_3$], we have r(Ag$-$P) between 2.520 and 2.556 Å, and r(Ag$-$Cl) = 2.552 Å[59,62] in reasonable agreement with our values for [AgCl(PH_3)$_3$], r(Ag$-$P) = 2.552 Å, and r(Ag$-$Cl) = 2.501 Å. [CuCl(PPh_3)$_3$] is also known,[63] r(Cu$-$P) varies between 2.348 and 2.355 Å (2.268 Å for [CuCl-

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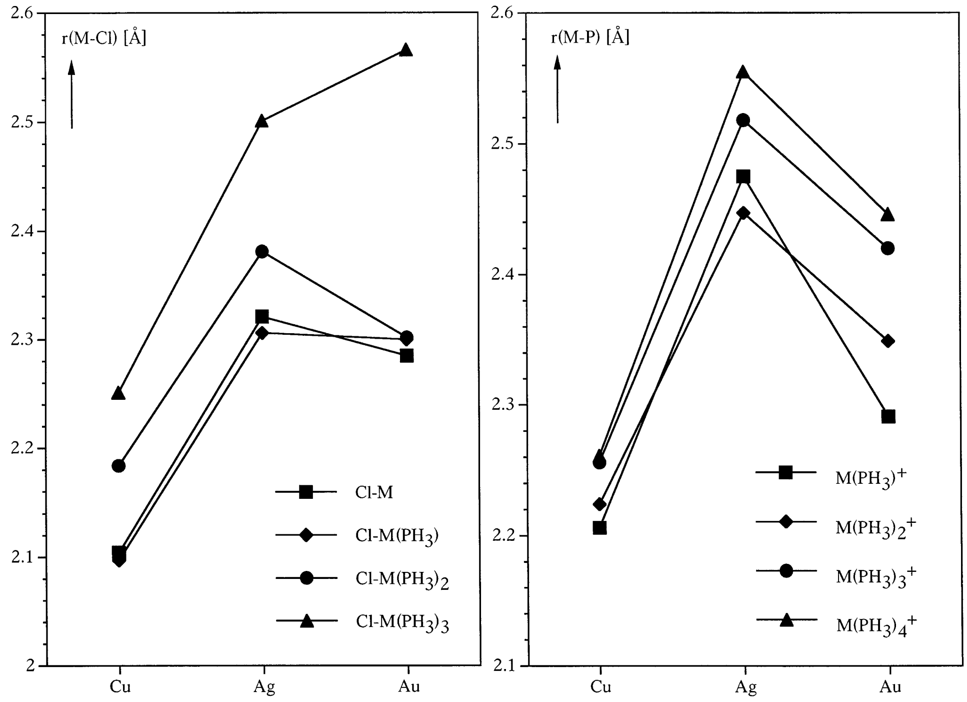

Figure 3. Comparison between M−P and M−Cl bond distances for $[M(PH_3)_n]^+$ and $[MCl(PH_3)_n]$ (M = Cu, Ag, and Au).

$(PH_3)_3]$), r(Cu−Cl) = 2.336 Å (2.251 Å), and the Cl−Cu−P angle varies between 108.4° and 109.8° (104.6°). $[Cu(PPh_3)_4]^+$ and $[Ag(PPh_3)_4]^+$ have also been known since 1960 when Cotton and Goodgame synthesized these compounds.[23] Engelhardt et al.[24] were able to obtain crystal structures: r(Ag−P)= 2.650 and 2.668 Å (2.555 Å for $[Ag(PH_3)_4]^+$), and r(Cu−P)= 2.524 and 2.605 Å (2.261 Å for $[Cu(PH_3)_4]^+$). Interestingly, the difference between the calculated and measured bond distances for the copper compound is rather large which is not explained so easily and is probably due to solid state influences including the field of the counterion. We mention that a similar coordination compound, $[Cu(dppe)_2]^+$, shows much smaller Cu−P bond distances of 2.305 Å.[64] Although some of these compounds can be crystallized, they are rather unstable in solution; for example, $[Ag(PR_3)_4]X$ cannot be detected in solution by NMR.[65]

It is interesting to compare the calculated distances within the group 11 series of coordination compounds, Figure 3. They reveal what is now well documented and expected.[20,28,42,66] The M−P and M−Cl bond distances within a specific series of isostructural compounds increase from copper to silver and (with a few exceptions) decrease from silver to gold. This is due to rather large relativistic effects at gold (relativistic 6s contraction) as the nonrelativistic calculations listed in Tables 1 and 2 show. A more detailed discussion can be found in refs 20 and 66. One notable exception is the series of group 11 elements with high coordination number four, $[MCl(PH_3)_3]$, where the Au−Cl bond distance is significantly larger compared to the Ag−Cl distance, indicating a rather weak and ionic Au−Cl bond. A recent comparison between crystal structures obtained for group 11 $[MCl(PPh_3)_3]$ (M = Cu, Ag, and Au) came to the same conclusion.[59] As mentioned before, this points toward a saturation in the coordination number at $N_C = 2$, especially for gold. Table 2 shows that relativistic bond contractions are much smaller for the Au−Cl bond than for the Au−P bond. As pointed out before,[20,42] relativistic bond contractions are sensitive to the electronegativitiy of the ligand attached to gold.

The NBO analyses shown in Tables 3 and 4 indicate only little 6p participation in Au−P or AuCl bonding as mentioned before by DeKock et al.[67] However, relativistic effects increase both 5d and 6p participation as the orbital populations show. Interestingly, increasing the number of PH$_3$ ligands does not change the 5d population significantly.

It is worth discussing the group 11 metal−phosphine bond stability by considering the following reactions:

$$[M(PH_3)_{n-1}]^+ + PH_3 \rightarrow [M(PH_3)_n]^+ + \Delta E \text{ (M = Cu, Ag, and Au)} \quad (1)$$

$$[MCl(PH_3)_{n-1}] + PH_3 \rightarrow [MCl(PH_3)_n] + \Delta E \text{ (M = Cu, Ag, and Au)} \quad (2)$$

The calculated energy differences ΔE for reactions 1 and 2 are listed in Tables 1 and 2 and are also depicted in Figure 4. We mention that PH$_3$ is a weaker base compared to, for example, $P(CH_3)_3$ and the ΔE values listed in Tables 1 and 2 may therefore be at the lower end for typical Au−P bond stabilities.[20] For the group 11 series of $[MClPH_3]$, we can compare with results obtained from pseudopotential B3LYP calculations of Kickelbein and Schubert[52] who obtained for

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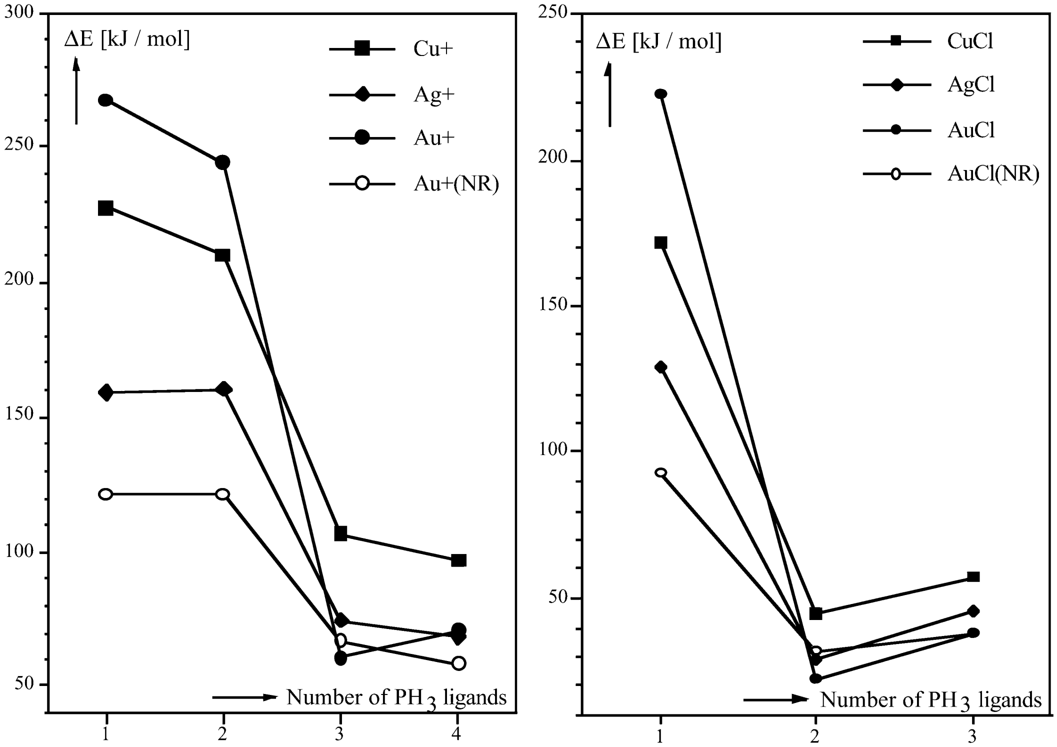

Figure 4. Au−P bond energies for $[M(PH_3)_n]^+$ and $[MCl(PH_3)_n]$ with increasing number of PH_3 ligands. See eqs 1 and 2 for details.

reaction 2 with $n = 1$ $\Delta E = 143$ (M = Cu), 96 (M = Ag), and 174 (M = Au) kJ mol^{-1} in qualitative agreement with our values, Table 2.

Figure 4 clearly shows that all group 11 compounds prefer coordination number $N_C = 2$; that is, after formation of either $[M(PH_3)_2]^+$ or $[MClPH_3]$, subsequent coordination by a PH_3 ligand gives a binding energy that is much smaller compared to that of the initial phosphine coordination. For the nonrelativistic case, the stability of the M−P bond up to $N_C = 2$ is M = Cu > Ag > Au, but this changes when relativistic effects are introduced, and we finally obtain the order in stability for the M−P bond M = Au > Cu > Ag. This is easily explained by the relativistically increased electronegativity of gold (from ca. 1.9 to 2.4)[68] which enhances substantially the possibility for σ-charge donation from the PH_3 lone pair. However, this trend reverses again when adding another PH_3 ligand to form either $[M(PH_3)_3]^+$ or $[M(PH_3)_2]Cl$. Due to relativistic effects, gold is now the least accepting for further phosphine coordination. This becomes also clear from the population analyses shown in Tables 3 and 4. The initial addition of a PH_3 ligand to either M^+ or MCl diminishes substantially the charge on the metal center, but even more so for relativistic gold. Hence, relativistic effects do influence the coordination behavior of gold substantially. The less favorable coordination numbers $N_C = 3$ and 4 in $[Au(PH_3)_n]^+$ also explain why $[Au(PR_3)_4]^+$ has not been found in electrospray mass spectrometry experiments by Colton et al. and why $[Au(PR_3)_3]^+$ decomposes easily in the gas phase.[31] In solution, these complexes are relatively labile on the NMR time scale,[32,65] although a relatively stable tetrahedral four-coordinate Au(I) complex of 1,3,5-triaza-7-phosphaadamentane has been isolated by Fackler and co-workers.[69]

Using our results for the model compounds, we are now able to discuss the difference in the coordination behavior found for the bis[2-(diphenylphosphino)phenyl]phenyl-phosphine (TP) gold and silver complexes [M(TP)Cl], M = Au, Ag. As mentioned before, two phosphine ligands are coordinated to gold at distances of 2.32 and 2.37 Å, respectively; the third one is further removed at a distance of 2.46 Å. In the corresponding silver complex, all three phosphine atoms are bound to the metal center at distances between 2.49 and 2.55 Å. A number of geometry optimizations with different starting geometries for the model compound $[Au(P_3C_4H_9)]Cl$ revealed the final structures shown in Figure 5. There are other possible local minima of higher energy, but the structures shown are sufficient to discuss the main bonding features.

Structure **13** (Figure 5) is the only one found with three PR_3 ligands relatively close to the gold center. However, two PR_3 ligands coordinate relatively strongly to gold with r(Au−P) = 2.357 Å, and the third PR_3 ligand coordinates relatively weakly to gold with a much larger distance of r(Au−P) = 2.861 Å. The same structure is found for the silver complex but with all three PH_3 ligands close to the metal center (r(Ag−P) between 2.567 and 2.647 Å). This simply reflects what has been found in the X-ray structure of **1**. However, structure **13** does not represent the global minimum for the Au compound and is in fact 19.0 kJ mol^{-1} above the global minimum structure, **14**. Compound **14** has the shortest Au−P bond length of 2.258 Å, very close to the one calculated for

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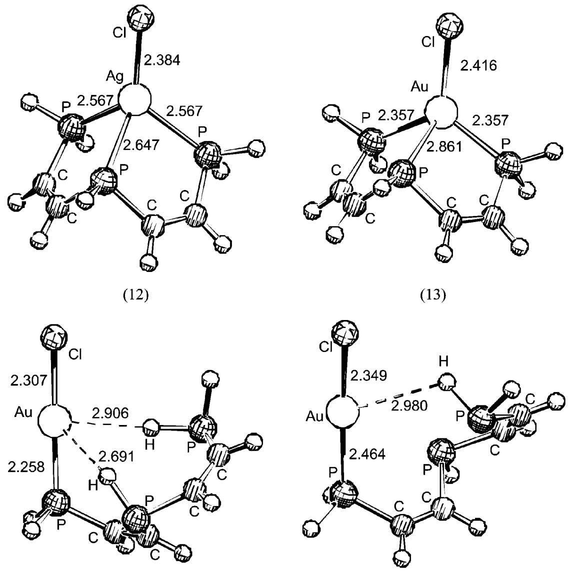


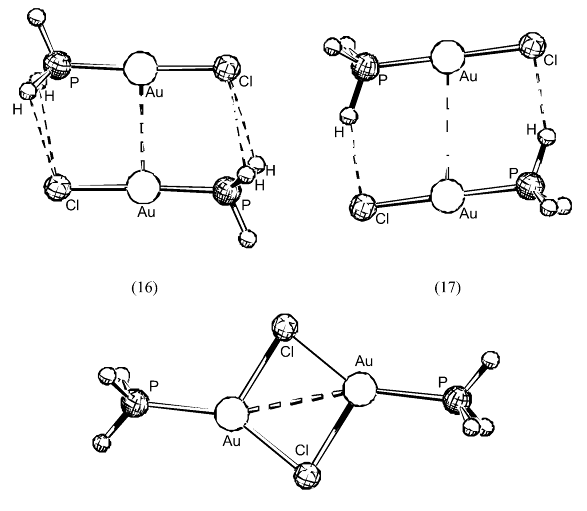
(12) (13)

(14) (15)

Figure 5. Selected optimized structures for [PH$_2$−C$_2$H$_2$−PH−C$_2$H$_2$−PH$_2$]-AgCl **12** and [PH$_2$−C$_2$H$_2$−PH−C$_2$H$_2$−PH$_2$]AuCl **13**−**15**. Au−P and AuCl bond distances are also shown (in Å).

the [AuPH$_3$]Cl unit with r(Au−P) = 2.249 Å. The Cl−Au−P angle is, with 179.0°, close to the linear arrangement. Other conformations like, e.g., structure **15** are possible but higher in energy; **15** is +34.9 kJ mol^{-1} above the global minimum **14**, Figure 5.

It is known that all group 11 Cl−M−PR$_3$ compounds oligomerize. The structures formed depend on the nature of the ligand R. We mention some structures such as [AgCl(PPh$_3$)]$_2$,[70] [AgX(PR$_3$)]$_4$ (X = Cl, Br; R = Ph, Et, C$_6$H$_{11}$),[71,72] [CuBr(PR$_3$)]$_4$ (R = Ph, Et),[73] or [CuClP-{cyclohexyl}$_3$]$_2$.[74,75] These structures contain dipole bound M−X units (M = Cu, Ag; X = Cl, Br, etc.) as a basic structure, e.g., M$_2$X$_2$ with X bridging the two metal atoms, and one PR$_3$ ligand bound to each metal atom. That results in a formal coordination number of three for the metal. In contrast, Cl−Au−PR$_3$ oligomerizes in the solid state by keeping the linear P−Au−Cl structure intact and forming short Au−Au bonds.[76] Such aurophilic interactions have been studied intensively in the past.[77] The different possible intermolecular contacts between L−Au−X units (L = neutral donor ligand, X= anionic ligand) were also discussed in detail by Pyykkö and Zhao,[79] and by Bauer and Schmidbaur.[80] We mention that similar metallophilic interactions are also known for the other group 11 elements M = Cu, Ag, but they are much weaker and therefore influence the coordination behavior less significantly. This is in agreement with recent work by Molina and co-workers who found no metal−metal interactions in either [CuCl(PH$_3$)]$_2$ or [Ag$_2$Br$_2$(PH$_3$)$_3$].[81]



(16) (17)

(18)

Figure 6. Optimized dimeric structures for [ClAuPH$_3$]$_2$ for the relativistic cases **16** and **17** and the nonrelativistic case **18**.

Only arrangements where the linear Cl−Au−PR$_3$ unit is preserved were considered in the past by theoretical calculations. Indeed, geometry optimizations for Cl−Au−PH$_3$ gave the expected structures **16** and **17** (Figure 6 and Table 5), thus maximizing dipole−dipole interactions between the two units, as pointed out earlier by Pyykkö and co-workers.[77] In **17**, aurophilic interactions are small, and the corresponding Au−Au distance is relatively large with r(Au−Au) = 3.749 Å. The Cl−Au−PH$_3$ units are close to linear with α(Cl−Au−P) = 179.2°, and there are also close contacts between the neighboring nonbonding H- and Cl-atoms, i.e., r(Cl−H) = 2.497 Å. This structure has also been considered by Pyykkö and Zhao who obtained a Au−Au distance of 3.70 Å.[79] However, compared to **17**, structure **16** which has not been considered before is lower in energy by 13 kJ mol^{-1}. In **17**, we have r(Au−Au) = 3.202 Å and α(Cl−Au−P) = 177.2°. The larger deviation from the ideal linear P−Au−Cl arrangement points toward aurophilic interactions in this compound. It is clear that large bulky ligands such as R =

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Table 5. Structural Data for the Dimeric Compounds of Group 11, MCl and [$MClPH_3$] (Compound **16** or **18**, Figure 6)[a]

	r				α		
cmpd	(M−M)	(M-Cl)	(M−P)	(P−H)	(P−M−Cl)	(M−P−H)	ΔE
[$ClAuPH_3$]$_2$	3.202	2.327	2.263	1.394/1.402	177.2	117.4/115.3	81.8
	3.560	*2.639*	*2.660*	*1.404*	*147.3*	*117.4/124.0*	*137.0*
Au_2Cl_2	2.636	2.464					152.0
	3.044	*2.587*					*196.8*
[$ClAgPH_3$]$_2$	3.439	2.507	2.412	1.403	140.6	118.2/121.8	114.8
Ag_2Cl_2	2.755	2.450					199.9
[$ClCuPH_3$]$_2$	3.014	2.300	2.181	1.405	133.8	118.5/121.5	119.3
Cu_2Cl_2	2.386	2.224					245.3

[a] Bond distances r (in Å), angles α (in deg), and dissociation energies ΔE (in kJ mol^{-1}) for the dissociation $M_2Cl_2 \rightarrow 2$ MCl and [$ClMPH_3$]$_2 \rightarrow 2$ [$ClMPH_3$] (M = Cu, Ag, Au). Nonrelativistic values are set in italics. Two values listed implies different P−H bond distances or M−P−H angles were obtained in the geometry optimization, and the first values listed stand for two hydrogen atoms on the PH_3 ligand.

Ph in Cl−Au−PR_3 will cause additional repulsive effects and will cause the two units to dimerize at a P−Au−Au−P torsion angle close to 90° which optimizes aurophilic interactions but reduces dipole interactions between the two units. This has been discussed intensively in the past,[77,79] and we will not repeat the results in this work. Instead, we focus on the nonrelativistic case.

Starting with the geometry **16** or **17**, nonrelativistic [$ClAuPH_3$]$_2$ optimizes into structure **18** also shown in Figure 6. Here, we have two PH_3 ligands coordinated to a Au_2Cl_2 unit consisting of Au_2 bridged by two chlorine atoms. The same structures were obtained for the corresponding silver and copper compound. In fact, the P−M−Cl angle increases from Cu to Ag to Au showing an increasing trend toward linearity for the P−M−Cl unit with increasing nuclear charge of the metal atom. Relativistic effects increase this trend even more. The dimerization energy of all compounds is between 119 (for Cu) and 137 (for nonrelativistic Au) kJ mol^{-1}, with relativistic effects lowering the tendency for dimerization by 55 kJ mol^{-1}. Hence, this explains nicely the different coordination chemistry within the group 11 [$MXPR_3$] compounds; the gold compounds seem to polymerize with linear [$XAuPR_3$] chains at a P−Au−Au−P torsion angle of 90° thus maximizing the aurophilic interaction, while the corresponding copper and silver compounds oligomerize with PR_3 ligands attached to M_2X_2 units with bridging ligands X such as Cl or Br.

Another possible explanation for the different behavior of these [$XAuPR_3$] units comes from considering the stability of M_2Cl_2 units toward fragmentation into two MCl molecules. The dissociation energies for the reaction $M_2Cl_2 \rightarrow 2MCl$ are listed in Table 5.[82] The stability of M_2Cl_2 decreases from Cu to Ag and further to Au, even more so due to relativistic effects. As a result, it takes less energy to break up the M_2Cl_2 unit for gold and form aurophilic interactions. Moreover, the dimerization energies for MCl are roughly twice as high as for the corresponding phosphine complexes $ClMPH_3$. It is also interesting that PH_3 coordination to M_2Cl_2 substantially increases the metal−metal distance. Finally, while the four M−Cl bond distances are the same for a specific group 11 element M (see Table 5), in the [$ClMPH_3$]$_2$ compounds one chlorine is more strongly bound to the metal center with a shorter M−Cl distance, as this is also found in the crystal structures of the corresponding copper and silver compounds.[70,74] Subsequently, the angles P−Au−Cl_a and P−Au−Cl_b differ where Cl_a and Cl_b are the two bridging chlorine ligands as can be seen in compound **18**, Figure 6. The structure obtained for [$CuCl(PH_3)$]$_2$ by Molina and coworkers[81] was obtained from a geometry optimization restricted to C_{2h} symmetry and does not represent a minimum on the potential energy surface.

We draw the following main conclusions from our calculations: (1) The preferred coordination number is two for all group 11 phosphine complexes with gold being the least likely element to increase the coordination number beyond 2. (2) For [$MXPR_3$] compounds (M = Cu or Ag), oligomerization is favored via M_nX_n units (X= Cl, Br, etc.) with X bridging the two metal atoms and PR_3 coordinating to each metal atom thus reaching coordination number three. For gold, the stability of the M_nX_n cluster is weak enough to prefer oligomerization between linear [$AuXPR_3$] with close Au−Au contacts (aurophilic interactions). (3) Relativistic effects in gold substantially influence the trends discussed in points 1 and 2. (4) The weak coordination of additional PR_3 ligands to the [$AuXPR_3$] unit explains the structure observed for the Au(I) complex of bis[2-(diphenylphosphino)phenyl]phenyl-phosphine[27] and the difference in coordination to the corresponding silver compound.

Acknowledgment. We are grateful to the Alexander von Humboldt Foundation (Bonn/Germany), to the Marsden fund (Wellington), and to the Auckland University Research Committee for financial support. We thank Prof. G. A. Bowmaker for valuable discussions.

IC026098V

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(82) We mention that MP2 may overestimate such dimerization energies and basis set effects should also be considered. For example, for Au_2Cl_2 we used rather large basis sets (for Au and for Cl) which give ΔE = 145.2 kJ mol^{-1} at the MP2 level and 95.8 at the B3LYP level of theory.