Inorg. Chem. **1994,** *33,* 3261–3268 **3261**

Are Strong Gold–Gold Interactions Possible in Main Group $X_nA(AuPR_3)_m$ Molecules?

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Received August 5, 1993[⊗]

The isolobal analogy between a proton and gold phosphine unit ($AuPR_3$) and the existence of molecules such as CH_5^+, suggests the possibility of stabilization of Au–Au linkages by coordination to a main group fragment. Calculations of the extended Hückel type on $AX_n(AuPR_3)_m$ molecules show that since the energies of the orbitals associated with Au–Au bonding in the neutral $(AuPR_3)_m$ fragments lie above empty levels of the neutral AX_n fragments to which they are coordinated, there is invariably formal electron transfer between the two on coordination. The result is a large diminution of Au–Au bonding. This electronic situation for the main group case is quite different to that for transition metal $ML_n(AuPR_3)_m$ molecules which such formal charge transfer does not occur and stronger AuAu interactions are possible. Really strong Au–Au interactions are found only to occur in systems isoelectronic with $H_n^{(n-2)+}$ such as in the known molecule $(AuPR_3)_4I_2$, and may be expected in the as yet unknown species $(AuPR_3)_3I$. The case of $As(AuPR_3)_4^+$ is a particularly interesting one. Here the C_{4v} geometry is one where close Au–Au contacts are possible. It is suggested however that such enhanced Au–Au interactions are only one of the reasons behind the adoption of this geometry. Comparisons are made with the nontetrahedral geometry of $SiLi_4$.

Introduction

The isolobal analogy (**1**) between a gold phosphine unit, $AuPR_3$, and a hydrogen atom is one which is well used in organometallic

$$\cdot Au-PR_3 \xleftrightarrow[o]{} \cdot H$$

1

chemistry.[1] Gold phosphines and hydrogen are common ligands in transition metal chemistry.[2] The $(AuPR_3)_2$ unit is isolobal to H_2, and indeed complexes containing both are known. Less well-developed is the idea that $(AuPR_3)_n$ oligomers may behave similarly to their H_n analogs. Although H_3 and H_4 fragments have been suggested[3] as ligands for transition metals, currently, experimental data only exists[4] for coordinated H_2, although the triangular H_3^+ molecule has been spectroscopically well-characterized in the gas phase.[5] For the main groups, however, the chemistry appears to be even more limited. Molecular H_2 exists coordinated to carbon only in theory in studies[6] of CH_5^+ ($CH_3^+(H_2)$) and CH_6^{2+} ($CH_2^{2+}(H_2)_2$), and in studies[7] of the "small angle" states of CH_2 and related systems. There is some evidence that formation of Au–Au bonds is in general easier than formation of H–H bonds, a phenomenon often described as "aurophilicity",[8] an observation in accord with the valence bond ideas of Hiberty and co-workers.[9] Theoretical comparisons,[10] however, of the isoelectronic main group systems such as (CH_2)-H_2 i.e., CH_4) and its transition metal analog, $(Fe(CO)_4)H_2$, suggest that there is an attractive interaction between the hydrogen atoms in the transition metal case (and indeed the dihydrogen complex may lie very close in energy to the electronic ground state) which is absent in the main group case. On these grounds then stronger Au-Au interactions are probably more likely for transition metals. However, there has been dramatic progress[8] in the last few years in the synthesis and characterization of a wide range of main group complexes containing the $AuPR_3$ unit which contain close Au-Au contacts and present interesting challenges to the way we view such species.

This article presents a study of $R_3PAu\cdots AuPR_3$ interactions in such molecules containing main group atoms. Extended Hückel calculations are used to support our orbital arguments. It has been argued (see the references cites in ref 8a) that the electronic origin of aurophilicity lies beyond the Hartree–Fock limit, but we will find that one-electron models are very revealing, since the effect shows up quite clearly here. Although, as we mentioned the isolobal analogy between H and $AuPR_3$ is a useful one, it is

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1994.

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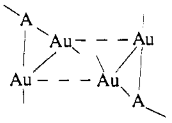
quite clear that the electronic situation is somewhat richer.[1] The presence of low-lying p orbitals on gold can lead to important qualifications to this analogy, as we recently showed[11] for the case of $[(C_5H_4(SiMe_3))_2NbAuH_2]_3$. However we will find electronic evidence that argues against making compounds with strong Au···Au interactions.

The Au–Au separation in the solid element is 2.878 Å. The Au–Au distances in the molecule[12] $(AuPR_3)_4I_2$ and ion $(AuPR_3)_4{}^{2+}$, which each contain a gold tetrahedron, are around 2.7 Å, which suggests a strong interaction between the metals, although the iodine atoms may not be weakly bound (Au–I = 2.954 Å). In molecules such as $C(AuPR_3)_6{}^{2+}$,[13] $C(AuPR_3)_5{}^{+}$,[13] and $N(AuPR_3)_5{}^{2+}$,[14] the closest Au–Au distances are between 2.88 and 3.05 Å. In the four-coordinate species $N(AuPR_3)_4{}^{+}$,[15] the ideal tetrahedron of gold atoms is distorted in the crystal toward a pyramidal arrangement, leading to three close distances (3.012–3.160 Å) and three longer ones (3.321–3.504 Å). In $AX(AuPR_3)_3{}^{n+}$ (A = C, N) the Au–Au distances are 3.1–3.2 Å, although in the cases of A = N and X = Ph[16] and cyclohexyl,[17] where there is a steric unevenness around the nitrogen atom, the Au–Au distances are found to be ~2.9, ~3.0, and ~3.3 Å. In $C(CN)_2(AuPR_3)_2$[18] and in $CQ(AuPR_3)_2$[19] (where CQ represents a 1,3-diboretane) distances of 2.91 and 2.98 Å are found, respectively. Shorter Au–Au distances (as low as 2.80 Å) are found in the interesting series of molecules $AX(AuPR_3)_4{}^{n+}$ (A = B, C, P, AS; X may be one- or two-electron donor ligand but is sometimes absent)[20–22] where there are not enough electrons for describe the species in classical terms. For example the molecule $(o\text{-Tol})P(AuPR_3)_4{}^{2+}$[20] is isoelectronic with $PH_5{}^{2+}$. Longer Au–Au distances (over 3.0 Å) are the rule in $AX(AuPR_3)_2{}^{+}$ complexes, where A = O,[23] S,[24] and Se[25] and X = R or $AuPR_3$.[26] Here though these systems always form dimers of the type shown in **2**, where the intermolecular Au–Au distances are frequently shorter than the intramolecule ones. In these molecules we certainly need to go beyond the analogy between $AuPR_3$ and H; there are just not enough electrons to form these extra linkages on the simplest orbital scheme.



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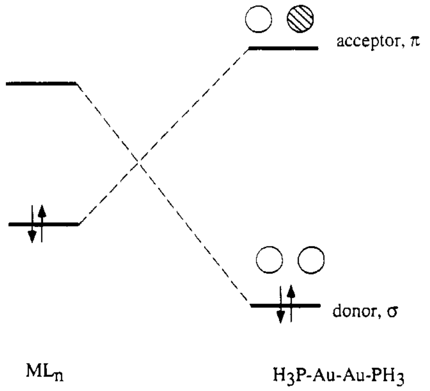
Stabilization of Z_n Molecules Coordinated to a Main Group Atom

The characterization of a $Z_2 = H_2$ unit coordinated in an η^2 fashion to a transition metal atom has led to new insights into the way hydrogen is coordinated to metal atoms and has encouraged the search for coordinated polyhydrides. The basic tenets of the Dewar–Chatt–Duncanson picture for ethylene (**3**) lead to a useful orbital picture to view[3] the attachment of not only H_2 but H_n units in both main group and transition metal systems. (**4** shows the analogy between $H_3{}^+$ and H_2 complexes such as $Cr(CO)_5(H_2)$ and CH_5 ($CH_3{}^+(H_2)$).) The interaction is in two parts: the donor contribution arising through σ interaction of an empty fragment orbital with the deepest lying orbital of the H_n fragment, and the acceptor via the higher energy, π type, orbitals of the unit. This is σ* in the case of H_2 but the degenerate e pair in the case of $H_3{}^+$. The key features of the attachment of $(AuPR_3)_2$ to a main group containing fragment are shown in **5**. A major difference between the main group and transition metal cases is associated with the energetic ordering of the σ and π functionalities on the main group fragment. For the transition metal systems the π-type orbital on the metal fragment is filled and lies deeper in energy. On this simple model, in both cases, coordination of



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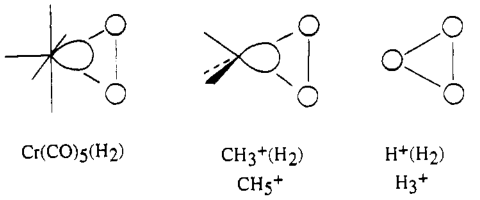

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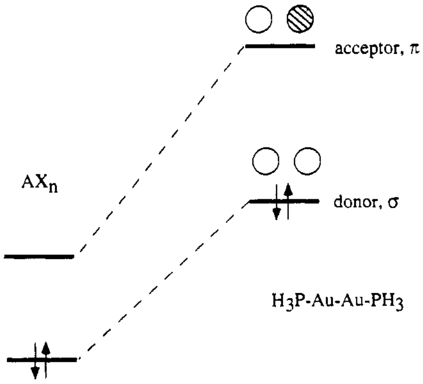

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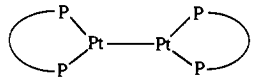
the Z_2 unit (Z = H, $AuPR_3$) in the η^2 mode is encouraged by decreasing the importance of the π-type interaction, which if strong enough will lead to fission of the Z_2 unit.

For the $Z = AuPR_3$ case there is another important interaction however. It is clear that, ostensibly closed shell, d^{10} centers may form quite strong bonds. This is evidenced most clearly by the structure of the dimeric Pt(0) compound $[Pt(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2]_2$ (**6**) where the platinum atoms are not bridged but have



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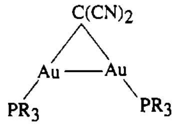
a remarkably short bond length of 2.765 Å.[27] The generation of d^{10} bonding interactions in dimers and clusters has been shown to occur by the mixing of higher energy s and p functions into predominantly d-type molecular orbitals. The result is the replacement of closed shell d^{10}–d^{10} repulsive interactions by weakly bonding interactions.[28–31] Strong hybridization of these unoccupied levels with the filled d block leads overall to a positive overlap population. A similar effect is to be expected here associated with the 6s and 6p orbitals on gold. Their importance has been stressed before,[1,11] although[32] ab initio calculations place the source of this beyond the Hartree–Fock limit. Our calculations on a $H_3PAuAuPH_3$ fragment with the same geometry as that in a typical $X_nA(H_3PAuAuPH_3)$ complex (we chose a Au–Au distance of 2.82 Å, a little shorter than that in $AX_n = C(CN)_2$ of 2.91 Å[18] and in AX_n = boretane of 2.98 Å[19]) lead to a bond overlap population of 0.505 for the neutral species (simply understood in terms of the analogy with H_2) and a small but positive overlap population of 0.073 for the dication with a d^{10}–d^{10} configuration.

The oft-quoted isolobal relationship between H and Au–PR_3 is usually based on the idea that the HOMO of the unit is largely made up of gold 6s. Our calculations show however, that using the parameters given in the Appendix, although gold 6s and phosphine lone pair dominate the Au–P bonding orbital, this HOMO shows as much 6p character as 6s. This is understandable from simple perturbation theory arguments. The bonding orbital is well-separated from gold 6p, but this HOMO lies much closer. What might be the experimental evidence for such mixing? One piece of support comes from the observation that in all of the $X_nA(H_3PAuAuPH_3)$ complexes known where A is a main group element and n = 1, 2, the A–Au–P angle is close to 180°. Our calculations on the known[18] molecule $(CN)_2C(H_3PAuAuPH_3)$, **7**, reveal a strong energetic destabilization on moving away from this linear structure. Such a theoretical result, in keeping with the experimental one, may be interpreted in terms of directional (hence p involvement) character of the A–Au bond. We shall see more evidence of such a viewpoint in the next section.



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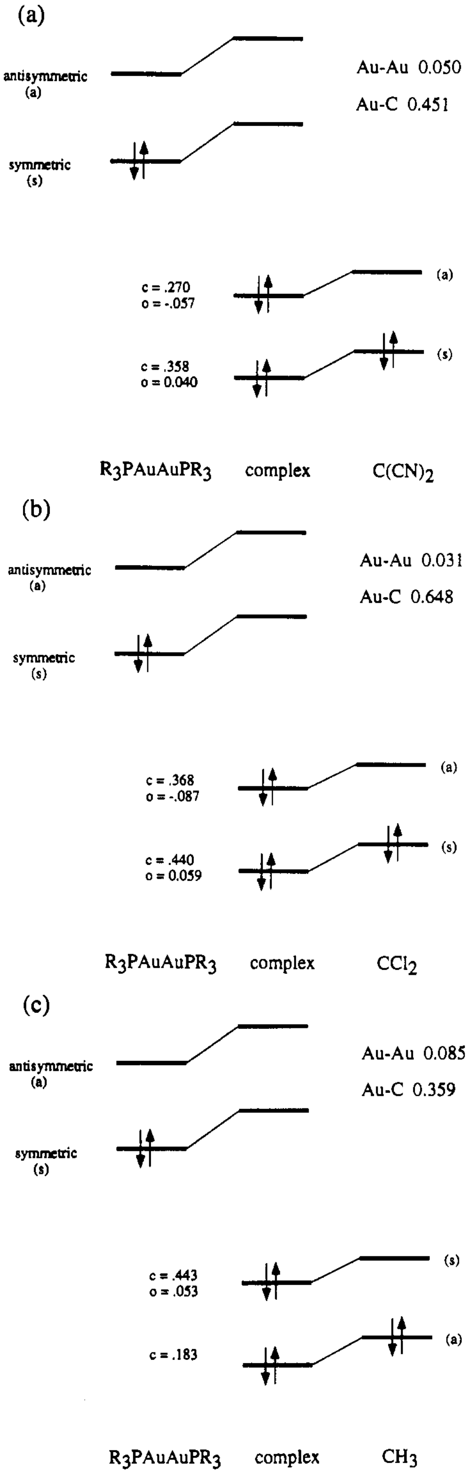

Figure 1. Results of three sets of calculations on $AX_n(AuPR_3)_2$ molecules which show how the gold phosphine unit is coordinated to the main group fragments (a) $AX_n = C(CN)_2$; (b) $AX_n = CCl_2$; (c) $AX_n = CH_3^+$. Only the vital part of the orbital interaction diagrams are shown. Shown are the coefficients (c) describing the admixture of the symmetric and antisymmetric, largely Au 6s/6p, $H_3PAuAuPH_3$ fragment orbitals in the calculated orbitals of the product. Also indicated is the contribution (o) to the Au–Au overlap population from double occupation of the filled orbitals shown.

Figure 1 shows a typical orbital interaction diagram between the $H_3PAuAuPH_3$ unit and CR_2 or CH_3 fragments. (In all of the calculations reported below we chose a Au–Au distance of 2.82 Å so that comparisons of overlap populations from compound to compound will be meaningful.) One very important point to note is that, in contrast to the situation for transition metal–dihydrogen interaction, electrons are formally transferred from the $H_3PAuAuPH_3$ unit to the main group fragment as suggested in **5**. For transition metals with dihydrogen[3] it is the dihydrogen

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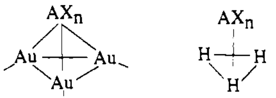
σ bonding level which lies deeper in energy, but here it is the more electronegative main group fragment orbitals which are predominantly occupied. Shown in Figure 1 are the calculated Au–Au and Au–C overlap populations when linked of $C(CN)_2$, and CH_3^+ units. Also shown are the coefficients (c) describing the admixture of the symmetric and antisymmetric, largely Au 6s/6p, $H_3PAuAuPH_3$ fragment orbitals in the calculated orbitals of the product. Shown too is the contribution (o) to the Au–Au overlap population from double occupation of the filled orbitals derived from these starting orbitals. The results are exactly in accord with the expectation from study of transition metal–dihydrogen complexes noted above. The largest admixture of the antisymmetric combination is for the CCl_2 fragment since here the antisymmetric (pπ) orbital on this unit is strongly localized on the carbon atom but has been pushed up in energy by antiboding interactions with chlorine pπ orbitals. In the case of the $C(CN)_2$ fragment the carbon pπ orbital is well mixed with the CN π orbitals, and thus the admixture of $H_3PAuAuPH_3$ is smaller. For the case of CH_3^+, the relevant orbital lies deeper in energy and is strongly involved in σ interactions with the hydrogen atoms. The interaction with the gold unit in this case is of the hyperconjugative type. (The orbital picture is actually a little more complex than we have shown. There is admixture of the pπ orbitals of the $H_3PAuAuPH_3$ fragment into the picture too which stabilize both the occupied symmetric and antisymmetric orbitals in the same broad way a for the σ orbitals of the unit.) It is then straightforward to understand why the calculated Au–Au bond strengths increase in the order $CCl_2 < C(CN)_2 < CH_3^+$. Note the strong negative overlap population contribution from the HOMO in the case of CCl_2 and $C(CN)_2$. It means that if the dication were made, the Au–Au bond overlap population would dramatically increase. Of the three molecules only the $C(CN)_2$ complex is known. (We can ask whether the 1,3 diboretane complex[19] noted above is stabilized by the same electronic mechanism.) It is difficult to comment from these results in general on the stability of the other two examples. Notice that the increase in Au–Au population is accompanied by a decrease in Au–C population. Thus the stability of the complexes in general will reflect the balance between Au–Au bonding and Au–C bonding. The last example of the trio is an interesting one in that using the isolobal analogy between $AuPH_3$ and H, this species is isoelectronic with CH_5^+. A "classical" description of this molecule in terms of two-center–two electron bonds is not possible. It is thus interesting that it has the highest Au–Au bond overlap population of the series, similar to those calculated below for other $XA(AuPR_3)_4$ molecules which may not be described classically.

In the case of transition metal–dihydrogen complexes,[3] increasing the electronegativity of the metal atom strengthens the metal–donor interaction since it brings the two interacting levels closer together, and weakens the metal–acceptor interaction since it moves the two interaction levels further apart. This favors formation of $M(H_2)$. For the cases treated here the situation is a little different since an increase in electronegativity increases the energy gaps associated with both types of interaction (see Figure 1). However from calculation, replacement of C by N^+ leads to an increase in the Au–Au overlap population, indicating perhaps the greater importance of the interaction with the antisymmetric $H_3PAuAuPH_3$ combination.

There are several complexes known[16,17,33] of the form $X_nA(AuPR_3)_3$ where $n = 1$, A = C, X = $P(CH_3)^+$, A = N^+, and X = Ph, Cy, and ^{t}Bu. Note that these complexes are the gold analogs of cyclopropenium-like cyclic trihydrogen complexes (**8**) which are at present unknown for either transition metal or main group cases. A calculation on a triangular $(AuPR_3)_3^+$ moiety shows a strong Au–Au bond (with a bond overlap population of 0.247 at a Au–Au distance of 3.0 Å) just as expected from its analogy with H_3^+. The electronic picture for coordination to a main group fragment is, though, very similar to that of **5** for the digold systems. In this picture σ is replaced by the a_1 orbital of the triangle and σ^* with the digenerate e′ pair. There is formal transfer of electrons from the gold-containing unit to the main group fragment in the trigold species too. There is also population of the σ^* orbital (e symmetry) of the $(AuPR_3)_3$ unit in just the same fashion as population of σ^* in Figure 1. Thus the calculated Au–Au overlap populations in these $XA(AuPR_3)_3$ molecules are rather small too. Of course they depend on the Au–Au distance, but are of similar magnitude to those reported in Figure 1. The effect of increasing the electronegativity of the central atom, A, in $XA(AuPR_3)_3$ complexes is calculated to be similar to that found for the $X_2A(AuPR_3)_2$ series. For $XA(AuPR_3)_3$ we find that by comparing the total energy as a function of geometry, the system wishes to distort away from tetrahedral as the central atom becomes more electronegative in the direction associated with shorter Au–Au distances. A similar electronic picture holds too for the "ligand-free" $A(AuPR_3)_n$ species such as $N(AuPR_3)_4^+$.[15] Here the a_1 bonding orbital of the $(AuPR_3)_4$ tetramer mixes with the central atom 2s and the t_2 antibonding orbital with central atom 2p (**9**).



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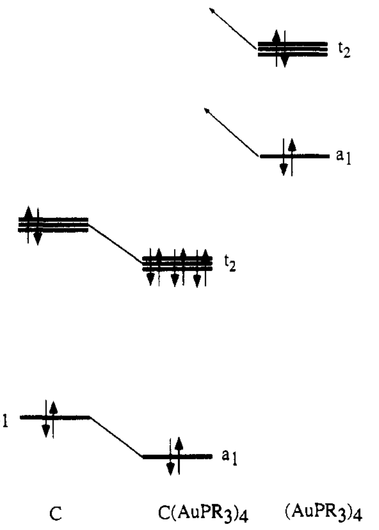

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That the Au–Au overlap population calculated for all of these systems is rather small is due to two factors. (i) The first is population of the antibonding orbital of the Au_n units by strong mixing with an occupied orbital of the same symmetry located on the main group fragment. (Recall the results of Figure 1 concerning the contribution to the overlap population by occupation of this antisymmetric orbital.) (ii) The second is formal charge transfer of the pair of electrons initially located in the σ bonding orbital of the $(AuPR_3)_n$ unit to the main group fragment. (Parenthetically we note that this electronic state-of-affairs is reminiscent of the orbital explanation[34] behind the failure to see strong hydrogen–hydrogen interactions in the *nido* cluster $B_{11}H_{14}^-$.)

Is it possible to generate a strong Au–Au interaction by shortening the Au–Au separation such that the σ-bonding orbital of this unit drops below that of the σ functionality of the AX_n

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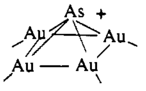
fragment? The answer is no. Our calculations show that the energy of this gold orbital drops rather slowly in energy as the distance shortens. A 2.68 Å the HOMO has only dropped to −10.02 eV, still above the relevant orbital on each of the fragments studied so far. Thus this particular approach is not a possibility. Another strategy for strengthening Au–Au bonding is to decrease the electronegativity of the AX_n unit such that the Au–Au σ bonding orbital is not formally emptied. The obvious way to do this is to use a transition metal fragment (**3**), with its "symmetric" orbital lying to higher energy, and indeed we note the large number of such species known with strong metal–gold and gold–gold interactions. Another route may be to choose a different geometry for the main group fragment, one where there is no "antisymmetric" orbital at all in the AX_n fragment. One such case is the arsonium species $As(AuPR_3)_4^+$ and the series of molecules $AX(AuPR_3)_4^{n+}$.

In contrast to the tetrahedral $N(AuPR_3)_4^+$ molecule, the $As(AuPR_3)_4^+$ species has[35] the C_{4v} arrangement show in **10**. The Au–Au distances are 2.90 Å, to be compared with 3.28 Å found in tetrahedral $N(AuPR_3)_4^+$, and a predicted distance of over 4 Å if the gold atoms were tetrahedrally arranged aound the arsenic atom. Is the stability of this structure driven by strong gold–gold interactions? We believe not, but first report the results of calculations at such a geometry. The electronic picture is interesting in that the antibonding (a_2) orbital of the $(AuPR_3)_4$ square finds no symmetry match with a central atom orbital (Figure 2). In addition the orbitals of e symmetry are σ nonbonding between adjacent gold atoms. Thus the picture is quite different from that shown in Figure 1 for the case of a C_{2v} AX_n fragment. There is no formal mixing of antibonding Au–Au orbitals into the occupied orbitals, but the "σ nonbonding" e pair acquire bonding character from mixing with the higher energy gold 6p orbitals and some antibonding character from interaction with the deeper energy gold 5d orbitals. (The balance between the two interactions and therefore whether this e set are Au–Au bonding or antibonding will be important in our discussion below.) The contribution of the symmetric Au(a_1) to the $2a_1$ orbital is smaller than before, an understandable result since this is a lone pair orbital which points away from the square. A comparison of the Au–Au overlap populations in $C(CN)_2(AuPR_3)_2$ and $As(AuPR_3)_4^+$ with the same Au–Au distance is shown also in Figure 2 and shows that it is indeed the absence of mixing of these antibonding orbitals which leads to the enhanced Au–Au overlap population in the latter. (However, the computed Au–Au overlap population for a $(AuPR_3)_4^{2+}$ molecule with the same geometry is 0.228, evidence for important interactions between Au and As.) Is this enhanced Au–Au bonding responsible for the unusual structure of this molecule? Au–Au interactions at the tetrahedral structure (with a Au–Au distance of over 4 Å) are surely close to zero. High-quality calculations[32c] show indeed that this structure is more stable numerically but offer no insights into the reasons why. We believe that, in addition to the obvious stabilization via the aurophilic interaction, there are other forces at work here.



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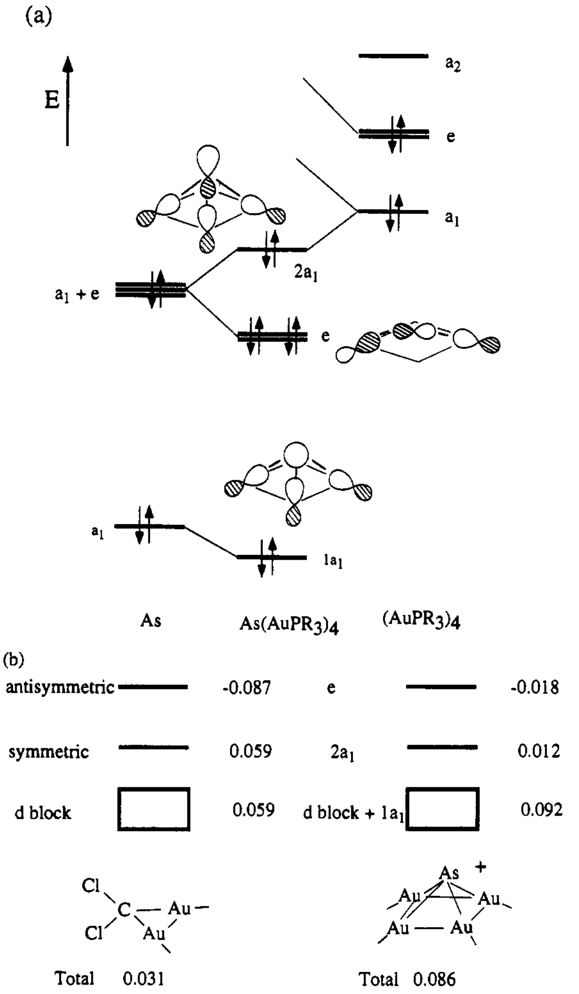
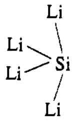


Figure 2. (a) Results of calculations on the $As(AuPR_3)_4^+$ molecule which show how the gold phosphine unit is coordinated to the arsenic atom. (b) Comparison of the contribution to the Au–Au overlap population in the two molecues, $CCl_2(AuPR_3)_2$ and $As(AuPR_3)_2$ and $As(AuPR_3)_4^+$.

The structures of most eight electron AX_4 molecules are tetrahedral, an observation understandable from several different theoretical viewpoints. However, whereas the lowest energy structure of $CuLi_4$ is calculated to be tetrahedral, the lowest energy geometry of $SiLi_4$ is calculated.[36] to be considerably distorted away from this arrangement and is the C_{2v} structure shown in **11**.



11

There is still debate as to the origin of this distortion (see the discussion in ref 37), the role of Li–Li interactions not being completely clear. One approach which has considerable appeal uses second order Jahn–Teller arguments of the type used to understand[38,39] in a broad way the goemetries of small molecules. If there is a low-lying electronic state at some reference geometry of a molecule, then it may mix into the ground state along some suitable distortion coordinate. If such mixing is large enough, then the reference geometry may be destabilized with respect to this distortion. Strong mixing in of such a low-lying state was used to understand[40] the structure of XeF_6, distorted away from the octahedral structure. In this case the orbital description of the process is of an empty low-lying t_2 set mixing into an occupied a_1 orbital.

12 shows how the orbitals of the molecule behave during the distortion of a square AZ_4 molecule to the pyramidal C_{4v} structure.

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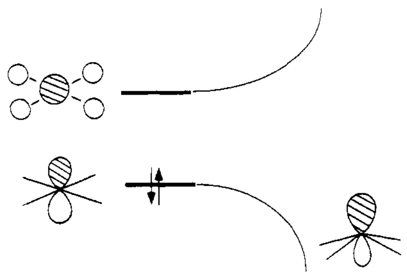
Table 1. Some Calculated Au-Au Overlap Populations

molecule[a]	Au-Au distance (Å)[b]	overlap population
$C(CN)_2(AuPR_3)_2$	3.1	0.059
$(o\text{-Tol})P(AuPR_3)_4^{2+}$	2.9-3.0	0.062
$As(AuPR_3)_4^+$	2.90	0.086
$(PH_3)B(AuPR_3)_4$	2.80, 2.82, 2.83, 2.84 (2.82)	0.106
$RC(AuPR_3)_4^+$	2.65, 2.77, 2.77, 2.83 (2.76)	0.210

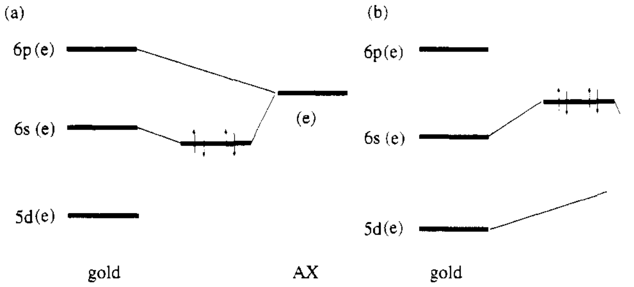
[a] All calculations were performed using an Au-Au distance of 2.82 Å. [b] Many of these structures are distorted. The averaged Au-Au distance is given in parentheses.



12

The electronic requirements of Z are for the present that it has a single "s" type orbital (e.g., H, Li, $AuPR_3$). The distortion is driven by the mixing of the HOMO (pure p_z on A) and LUMO ($2a_1'$, the out-of-phase interaction between a_1' Z_4 and central atom s orbitals). If the driving force is large then the molecule will distort away from the square geometry; if very large the energy of the new structure may lie below that of the tetrahedron and a nonsymmetric arrangement may be found. The argument of course is very similar to that used[41] to understand the greater pyramidalization of PH_3 over NH_3. The electronic requirements for strong mixing are clear to see. The energy gap from perturbation theory between the two orbitals should be as small as possible. The energetic location and orbital character of the $2a_1'$ orbital is thus crucial. Clearly for a small gap the interaction of the Z_4 a_1 orbital combination with the s orbital on A should be small, a result typical of the heavier main group elements. (It leads eventually to an inert s^2 pair of electrons for compounds of elements at the very bottom of the table.) The energy of the unperturbed a_1 Z_4 orbital combination should lie close to that of the p orbital on A, requirements which are met for Z = Li, $AuPR_3$, and especially so for A = heavy element. Our own calculations show a very soft potential surface linking C_{4v}, D_{4h}, and C_{2v} structures for heavier central atoms but an extremely stiff one for central nitrogen and carbon. Thus we see a much stronger stabilization of the tetrahedral structure for CLi_4 compared to SiL_4 and for NH_4^+ compared to AsH_4^+. The combination of both this effect and that of aurophilicity (or Li-Li interactions in the case of $SiLi_4$) favor these distorted structures.

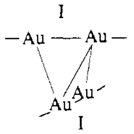
The molecules $(o\text{-Tol})P(AuPR_3)_4^{2+}$,[20] $(PCy_3)B(AuPR_3)_4^+$,[21] and a compound which could be viewed as containing two $RC(AuPR_3)_4^+$ units[22] have recently been characterized. They present orbital pictures similar to that of Figure 2. The orbitals of the (*o*-Tol)P, $(PCy_3)B$, and RC fragments replace those of As. As noted earlier these $XA(AuPR_3)_4^+$ molecules may not be described in "classical" terms; there are not enough electrons to form the two-center-two-electron A-Au bonds needed. The calculated Au-Au overlap populations for these species (for a fixed Au-Au distance of 2.82 Å) are given in Table 1. Notice the correlation between calculated overlap population and Au-Au distance. There is no entry for the case of XA = RC since here the experimentally determined structure[22] is a dimer. It is in fact easy to understand why the computed overlap populations show the variation they do. It centers around the electronic description of the occupied e pair of orbitals of Figure 2. For XA = As, they are antibonding between adjacent Au atoms but for XA = $(PH_3)B$ they are found to be bonding. **13** shows the behavior of this orbital as a function of the electronegativity of atom A. In **13a** where the A atom orbitals lie energetically much higher than the gold 5d (as in $PPCy_3)B(AuPR_3)_4^+$,[21] for example), the mixing into the e set is predominantly via the gold 6p levels, to a situation which is Au-Au bonding. In **13b** where the A atom orbitals lie energetically much closer to gold 5d and thus further away from 6p (as in $(o\text{-Tol})P(AuPR_3)_4^{2+}$ [20] or $As(AuPR_3)_4^+$,[35] for example), the mixing into the e set is predominantly a destabilizing one with the gold 5d levels and leads to Au-Au antibonding. Such simple arguments allow an understanding of the differences in this series. For strong Au-Au interactions an electropositive atom is needed here. Note though, that even in the best case, the overlap population is about half the size of that calculated in the $(AuPR_3)_4^{2+}$ unit.



13

Gold Clusters

The term aurophilicity was coined to describe the interesting tendency of $AuPR_3$ units to cluster around a main group atom. The molecules described above clearly have positive but small Au-Au overlap populations which can be thought of an arising from d-block effects within the one-electron model. In addition to these systems which contain AX_n units, there is a series of gold clusters centered by single main group atoms including $A(AuPR_3)_6^{n+}$, $A(AuPR_3)_5^{n+}$, and $A(AuPR_3)_6^{n+}$. Mingos showed[42] many years ago that the simplest electron description of these compounds was of an octet of electrons round the central atom counting each $(AuPR_3)$ as contributing one electron just as in **9**. The molecule[12] $I_2(AuPR_3)_4$ (**14**) and the ion $(AuPR_3)_4{}^21+$



14

however, are of a very different electronic type. Here the Au-Au distances are quite short (2.65, 2.77 (2×), 2.83 Å in the iodide and between 2.70 and 2.73 Å in the ion) and suggest stronger Au-Au bonds than in the molecules described earlier. The reason is simple to see. Using the analogy between $(AuPR_3)$ and H, the core of this species is isoelectronic with the molecule H_4^{2+}, an unknown species, but one which has been discussed theoretically.[3] The orbital pattern is shown in **15** (only one component of the degenerate orbitals is shown) and shows that with this electron cound, the single bonding orbital is formally filled by a pair of electrons which hold the cluster together. There is no charge transfer of electrons out of this Au-Au bonding orbital which characterized the $X_nA(AuPR_3)_m$ species above, and was one contributor to weak Au-Au linkages.

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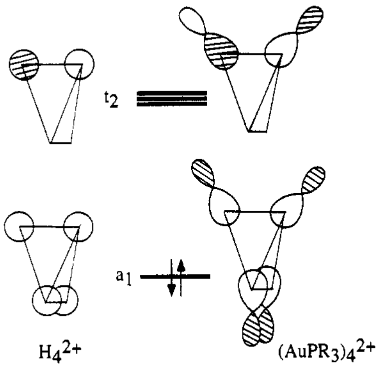
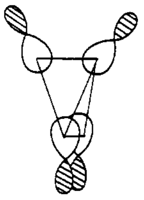


15

We noted above the calculated stability (significant and positive Au-Au bond overlap population) of the related $(AuPR_3)_3^+$ fragment. In view of the stability of **14**, the related molecule $I(AuPR_3)_3$ could be a synthetic target. The orbital patterns for all of these cluster species $Z_n^{(n-2)+}$ show double occupancy[3] of the single bonding "a_1" orbital. The stabilization of a particular Au-Au linkage drops off therefore rather rapidly with *n*, since, for example there are three Au-Au contacts for $n = 3$ (and hence a formal bond order of $^1/_3$), six for $n = 4$ (and hence a formal bond order of $^1/_6$) and 12 for the octahedron (and hence a formal bond order of $^1/_2$). The smaller clusters will thus have the larger stabilization per gold atom from this source.

Although in the ion $(AuPR_3)_4^{2+}$ the Au-P vectors point toward the centroid of the gold tetrahedron, a particular feature of the analogous gold iodide complex in **14** is that the phosphine ligands do not and are bent, as shown, to give an approximately D_{2d} structure. The Au-Au-P angles are 174 and 176° from experiment. Our calculations show that this geometrical preference is not found in the isolated $(AuPR_3)_4^{2+}$ unit. Given the description of the HOMO of the $AuPR_3$ unit introduced above, the best Au-Au HOMO overlap results when the set of s/p hybrid orbitals points towards the centroid of the Au_4 tetrahedron as in **16**. Indeed our calculations on the naked cluster show that the energies are dominated by the behavior of this a_1 orbital on bending and that the T_d structure is of lowest energy in accord with the structure of the ion.[12b] Inclusion of the I^- ions into the calculations leads to a change in the calculated lowest energy geometry. Now it is the linear structure which is found to be of lowest energy. The minimum is found for an Au-Au-P angle of 174°, in excellent agreement with experiment. The orbital explanation of this electronic effect confirms the role played by the gold 6p orbitals. Figure 3 shows the essentials of the orbital interaction diagram between the $(AuPR_3)_4^{2+}$ cluster and the two iodine atoms. There is a four-electron-two-orbital (1,4) destabilization associated with the interaction of the HOMO of the gold unit with an iodine 6p orbital combination. The maximum interaction is at the linear Au-Au-P geometry. Thus the HOMO (1) of the $I_2(AuPR_3)_4$ cluster is maximally destabilized from both Au-Au and Au-I interactions at this structure. There are however two, two-orbital-two-electron stabilizing interactions (2,3) with iodine p orbitals antisymmetric with respect to an Au-Au bond. These are maximally stabilized at the linear Au-Au-P structure. The equilibrium geometry is set by the balance of all four occupied orbitals and is calculated to be close to the linear arrangement. The result highlights the importance of the gold 6p orbitals. If the $(AuPR_3)_4$ HOMO were composed of gold 4s alone then there would be no variation of the interaction of (1)-(4) with angle. Thus these p orbitals control the geometry of the structure in an interesting way. These interactions weaken the Au-Au interactions along the top and bottom edges of the Au_4 tetrahedron (but strengthen Au-I interactions of course). The result is that the four Au-Au overlap populations, calculated at the experimental geometry, are quite similar in $I_2(AuPR_3)_4$ but quite different in $(AuPR_3)_4$.



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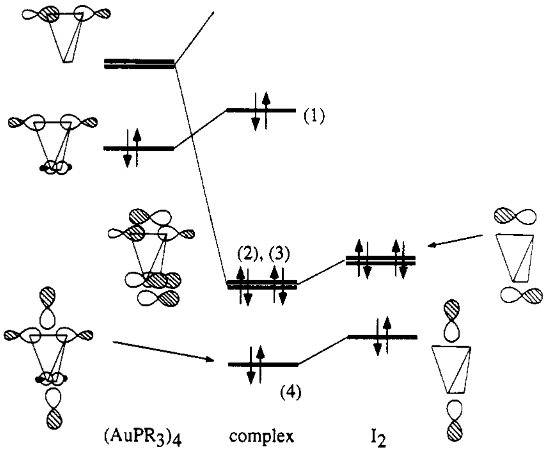

Figure 3. Part of the orbital interaction diagram between I_2 and $(AuPR_3)_4$ fragments to generate the level diagram for the $I_2(AuPR_3)_4$ cluster. The important interaction may be divided into two. There is a four electron-two orbital destabilization labeled (1,4) and associated with the interaction of the HOMO of the gold unit with iodine 6p. There are two, two-orbital-two-electron stabilizing interactions labeled (2,3) with iodine p orbitals. Only the component of the degenerate orbitals is shown.

One of the striking features of the $AX(AuPR_3)_2$ complexes is their tendency to form dimers (**2**) in the solid state, for E = O, S, and Se[23-26]. If the tetrahedral $(AuPR_3)_4^{2+}$ structure is isoelectronic with H_4^{2+}, then these dimers are isoelectronic with H_4^{4+}, a system with no bonding electrons at all. The electronic situation is thus similar to that in $[Pt(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2]_2$ (**6**). As a result, the Au-Au distances are considerably longer than those found in the tetrahedral system just described.

Discussion

It is interesting to compare here the differences between main group $AX_n(Z)_m$ and transition metal $ML_n(Z)_m$ molecules for the cases of Z = H and $AuPR_3$. Two effects were identified earlier as being important, namely formal electron transfer between the two fragments and orbital mixing between the two. Since the energy of the orbitals associated with Au-Au bonding lie above relevant levels of the AX_n fragments to which they are coordinated, there is invariably formal electron transfer out of these levels on coordination with a large diminution of Au-Au bonding as a result. Thus the electronic situation for the main group $AX_n(AuPR_3)_m$ case is quite different to that for $ML_n(AuPR_3)_m$ molecules, and for coordination of H_2. The calculated Au-Au bond overlap population of a neutral free $(AuPR_3)_2$ species is 0.505 and this is drastically reduced to around 0.05 in the $AX_2(AuPR_3)_2$ complexes of Figure 1. (The same Au-Au distance is used of course.) For the transition metal case the calculated Au-Au overlap population in free PH_3-Au-Au-PH_3 of 0.45 is reduced to 0.24 when coordinated to a typical d^6 ML_5 fragment $(W(CO)_5)$. Here the reduction in overlap population comes from the mixing between the metal and gold orbitals. (The difference between the overlap populations on the two "free" gold phosphine units arises from the two different P-Au-Au angles appropriate for the complexes and underscores the importance of gold 6p contribution to the HOMO.) This figure of 0.24 is not reached in any of our calculations on $AX_n(AuPR_3)_m$ molecules. Even in the case of $(PCy_3)B(AuPR_3)_4^+$, where the electronic state of affairs of the main group unit appears most benign, the overlap population is not large. By way of comparison, the calculated overlap populations for a free H_2 molecule and one coordinated to $(W(CO)_5)$ at the same internuclear separation are 0.82 and 0.78, respectively.

It appears from our calculations, that strong, Au–Au interaction are really only to be found in systems, isoelectronic with $H_n^{(n-2)+}$. We note the important role played by the gold 6p orbitals, especially in the HOMO of the $AuPR_3$ fragment and in the $(PCy_3)B(AuPR_3)_4^+$ species but clear too in the orbital diagram of Figure 3. "Aurophilicity" appears in quite natural way in calculations here and elsewhere which employ the extended Hückel model. Its origin is clear to see in terms of spd mixing[29,29] and as a result of mixing with orbitals of the AX_n unit. Although this view has been impugned by results of *ab initio* studies[32] which place its origin beyond the Hartree–Fock limit, it is clear that the one-electron model provides a very useful tool with which to construct a broad orbital picture.

Acknowledgment. The Laboratoire de Chimie Théorique is associated with the CNRS (UA506) and is a member of ICMO and IPCM. The stay of J.K.B. at Orsay was supported by a grant (No. 910553) from NATO.

Table 2. Atomic Parameters

orbital	ζ_1	c_1	ζ_2	c_2	H_{ii}
Au 6s	2.602				−10.92
Au 6p	2.584				−5.55
Au 5d	6.163	0.6851	2.794	0.5696	−15.07
As 4s	2.23				−16.22
As 4p	1.89				−12.16

Appendix

The H_{ii} and Slater parameters were taken from standard sources except those from Au[43] and As[44] (listed in Table 2). The extended Hückel[45] calculations were performed using the program ICON8.

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