

Some new concepts in the chemistry of the p-block elements

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Abstract

Of all elements in the Periodic Table, the chemistry of the First Row Elements of the p-block (i.e. boron to fluorine) is known to follow classical rules of bonding most closely, and it was for these elements that e. g. the Octet Rule (Lewis) and standard coordination numbers and geometries (Van't Hoff, Le Bel) have first been proposed. Only in extreme electron-deficient situations the traditional electron count had to be reconsidered to account for special types of molecular or solid state structures. Recent work has shown, however, that hypercoordination of small First Row Elements can also be detected in simple compounds with the very heavy Late Transition Elements. Though being isobal analogues of transient species like CH_5^+ , CH_6^{2+} , NH_5^{2+} , (PH_5^{2+} , PH_6^{3+}), or OH_4^{2+} , these complexes show stunning stability. The results of detailed spectroscopic investigations and structural work, together with a thorough theoretical treatment including relativistic effects, not only allow a consistent account of the data accumulated to date, but lead also to predictions regarding other novel species.

INTRODUCTION

Heteroatoms in molecules may serve as centers for derivatization in many ways. In standard reactions using nucleophiles and electrophiles the heteroelements are thereby transformed into new functionalities or eliminated to leave a molecule with a new structure. Generally, these transformations follow classical rules of stoichiometry, valency, and structure. This is particularly true for the light atoms of the early rows in the Periodic Table, with the Octet Rule as a prominent example.

In the course of studies of the chemistry of the very heavy Post-Lanthanide metals it has recently been found, that reactions with compounds of these elements lead to products of unexpected composition, as functional groups become excessively metallated beyond the standard valency and coordination numbers. The effect is most pronounced with univalent gold Au^+ as a ligand to First and Second Row Elements, for which a complete "gilding" of atoms can be observed, with coordination numbers e.g. equal to, but also in excess of four for carbon and nitrogen (1).

These species can be referred to as 'metallo-complexes' (2), in which metal-functional ligands cluster at a metalloid center. As introductory representative examples the novel hypercoordinate species $C(AuL)_5^+$ and $N(AuL)_5^{2+}$ should be mentioned, or their derivatives $HC(AuL)_4^+$ and $RC(AuL)_4^+$, where L is a donor ligand.

The present account is meant to be a summary of the state of the art in this area, for clarity totally devoted to gold as the metallo-ligand. There are a number of parallels appearing now for other, neighbouring metals, but the chemistry is less advanced for these elements and not yet matured to a state where a coverage is equally meaningful.

THE QUEST FOR TETRA(AURIO)METHANE $C(AuL)_4$

Tetra(mercurio)methanes $C(HgX)_4$ have been described very early on in the development of organometallic chemistry (3), and the complexity of the system of mercurated ammonia has been with us for well over a century. It was therefore surprising that all attempts to prepare the analogous tetra(aurio)methanes $C(AuL)_4$ with carbon as well as gold in their most common states of valency and coordination were unsuccessful until very recently. It was only in 1992 that experimental work in the Munich laboratories has finally lead to the isolation and full characterization of such a species, which turned out to be perfectly stable if ligands L of sufficient bulk were employed (4). Tetrakis[(tricyclohexylphosphine)gold(I)]methane has been obtained as a colourless crystalline solid with the expected tetrahedral array of gold atoms around the central carbon atom. The resonance of the central atom could be detected upon enrichment with ^{13}C as a quintet signal (1.4.6.4.1) at $\delta = 99.3$ ppm ($J = 61$ Hz). This result (4) was proof that there is nothing fundamentally wrong with tetracoordination of gold(I) at carbon. Why then had previous experiments (with other, smaller ligands L) not yielded analogous products?

Careful examination of the products obtained in pertinent experiments showed that cationic (aurio)methane species were present, which could be identified as monocations $RC(AuL)_4^+$ and $C(AuL)_5^+$ as well as dications $C(AuL)_6^{2+}$, associated with innocent (non-basic and non-nucleophilic) counterions like BF_4^- (5-7). Based on these results the chemistry of hypercoordinate heteroatoms has been developed and extended rapidly to other elements than carbon (1).

HYPERCOORDINATE TETRA- AND PENTA(AURATED) CARBON

Carbanionic carbon centers, like in phosphonium ylides, are readily aurated by (phosphine)gold(I) reagents to give species of classical carbon tetracoordination: $R_3P-C(AuL)_3^+ BF_4^-$ (8). Hypercoordination is not possible probably only owing to steric reasons. Less bulky carbon-acidic methyl-oxazolines, however, are tetra-aurated under similar reaction conditions to give polynuclear products containing cations $RC(AuL)_4^+$ with $L = PPh_3$ and $R =$ oxazolinyll (5). Following this initial observation, simple compounds with ($R = Me$ or even H) could be generated from the corresponding borylated precursors: $HC(AuL)_4^+$ and $MeC(AuL)_4^+$ from $HC[B(OMe)_2]_3$ or $MeC[B(OMe)_2]_3$, respectively (9). The cations were shown to have a square of gold atoms capped by a HC or MeC unit

to give a pentacoordinate carbon atom in a square-pyramidal environment. The species are colourless and diamagnetic solids, stable at ambient temperature, and their structures are fully confirmed by X-ray, NMR spectroscopic, and mass spectrometric data.

Homoleptic penta(aurated) cations could be generated from tri- and tetraborylated methanes with aurating agents (7). The products have been identified as colourless, diamagnetic salts $C(AuL)_5^+ BF_4^-$, where the cations have a trigonal-bipyramidal structure of gold atoms centered by a pentacoordinate interstitial carbon atom. In addition to the methods already mentioned, ^{197}Au Mössbauer spectroscopy was a useful tool to further confirm the unusual structures identified both for $L = PPh_3$, $PTol_3$, and $P(Cy)_3$ (9).

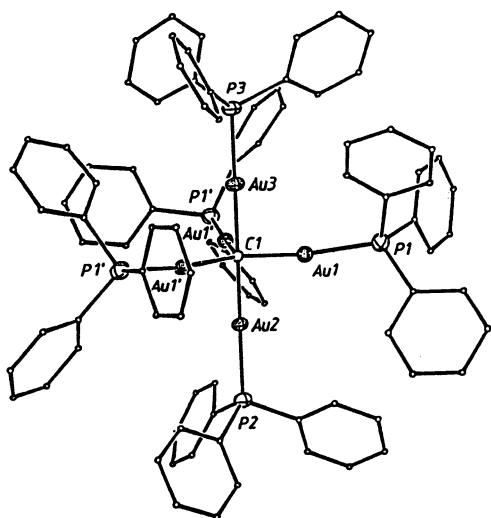


Fig. 1: Structure of the cation $C[AuP(C_6H_5)_3]_5^+$ (ref. 7)

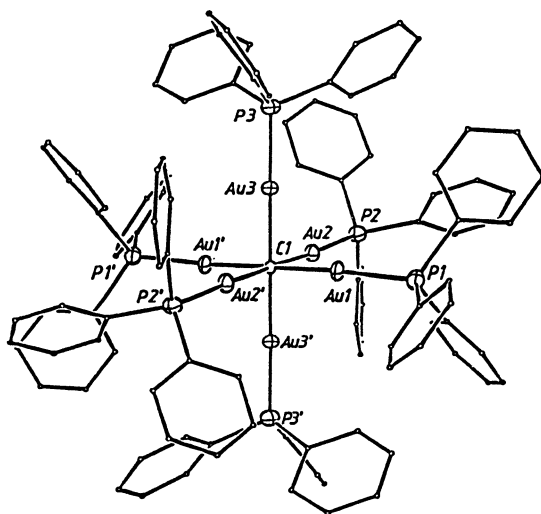


Fig. 2: Structure of the dication $C[AuP(C_6H_5)_3]_6^{2+}$ (ref. 6)

HEXA(AURATED) CARBON: $C(AuL)_6^{2+}$

Treatment of $C[B(OMe)_2]_4$ with aurating agents in excess affords the hypercoordinate species $C(AuL)_6^{2+}$ with carbon in the center of an octahedron of gold atoms (5). Dications with a large variety of ligands L have been isolated and characterized ($R = Et, iPr, Ph, C_6H_4Me, C_6H_4X$ with $X = Cl, Br, NMe_2, OMe$ etc.), including tailor-made chelating ligands (10,11). The interstitial carbon can be monitored by NMR spectroscopy of ^{13}C enriched material, with a septet as the diagnostic feature (12), (while for $C(AuL)_5^+$ cations, above, sextets are registered) (13). Single crystal X-ray structure analyses were performed for four different compounds with fully complementary results (5,11,13,14).

It is noteworthy that $C(AuL)_6^{2+}$ had previously been predicted from theoretical work (15), and experimental confirmation of these elegant molecular orbital studies of the 1970's was highly gratifying indeed. The high stability of the materials, their optical and magnetic properties are in full agreement with the theoretical models. Recent more sophisticated treatment including relativistic effects has led to further improvement (16,17).

TRI- AND TETRA(AURIO)AMMONIUM CATIONS $RN(AuL)_3^+$ AND $N(AuL)_4^+$

The auration of ammonia or its derivatives to give tetra(aurio)-ammonium cations was first accomplished in the late 1970's by Russian scientists (18). This work did not make the impact it deserved because of the obvious analogy with the related mercury compounds (above). Therefore it was observed only much later that ammonia (19,20) (Fig. 3) and virtually any primary amine could be aurated equally readily (21-25). Salts of the formula $RN(AuL)_3^+ X^-$ have recently been studied in great detail, including poly-aurated diamines etc. (24). The results have indicated that amino nitrogen is quite generally a nucleation center for gold cluster formation with relevance for bio-diagnostics and -analyses.

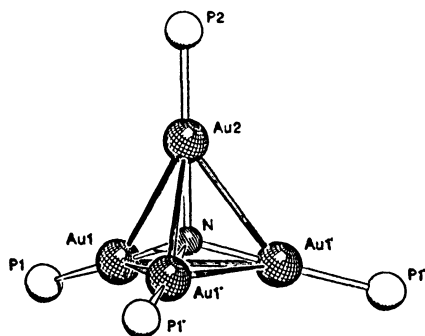


Fig. 3: Core of the structure of the cation $N[AuP(C_6H_5)_3]_4^+$ (ref. 20)

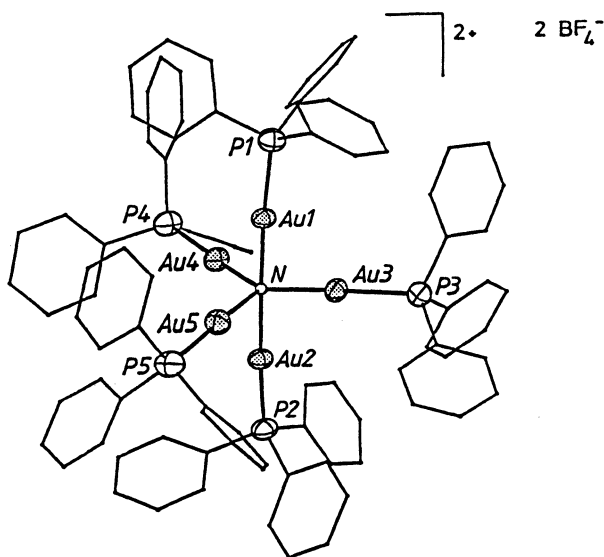


Fig. 4: Structure of the dication $N[AuP(C_6H_5)_3]_5^{2+}$ (ref. 21)

PENTA(AURIO)AMMONIUM DICATIONS $N(AuL)_5^{2+}$

Work with carbon-centered gold(I) clusters suggested an initiative to generate analogous hypercoordinate nitrogen species. Surprisingly, the experiments turned out to be extremely easy. Auration with $LAu^+ BF_4^-$ of the ammonium salt precursors give quantitative yields of stable ammon-di-onium salts, whose dications have a trigonal-bipyramidal array of gold atoms with pentacoordinate nitrogen in the center (22). The novel structure with electron-deficient bonding in the NAu_5^{2+} core has been confirmed by a series of careful analytical studies of single crystalline material (Fig. 4). The dications could not be aurated further, however, and no hexa(aurio)ammon-tri-onium species could be confirmed.

TRI-, TETRA-, PENTA- AND HEXA(AURIO)PHOSPHONIUM CATIONS

Auration of primary phosphines RPH_2 leads to cations $RP(AuL)_3^+$ in quantitative yield (26). These species have the expected tetrahedral structures at the phosphonium centers. With PH_3 , $P(SiMe_3)_3$, or tri(acyl)phosphines, the homoleptic tetra(aurio)phosphonium

cations can be generated, but none of these has been fully characterized to date in an uncomplexed form (27,28). Adducts observed have formulae like $L_2AuP(AuL)_4^{2+}$ or $(LAu)_4PAuP(AuL)_4^{3+}$ with pentacoordinate phosphorus. It appears from these studies, that $P(AuL)_4^+$ cations are strong nucleophiles or donors, which reach stability only with suitable acceptors (27,28). This phenomenon may have its origin in a non-classical square-pyramidal structure as detected also for the arsenic analogue (below). Cations $RP(AuL)_3^+$, on the other hand, are easily aurated to give dications $RP(AuL)_4^{2+}$ with a square pyramidal structure (29). A similar structure is found for 8-quinolinyl-assisted nitrogen compounds (30).

Contrary to tetra(aurio)ammonium salts, the phosphorus analogues can be aurated further to give di- and finally even tri-cations $P(AuL)_5^{2+}$ and $P(AuL)_6^{3+}$. The hapticity of the central P-atom is easily monitored by ^{31}P NMR spectroscopy in these cases (27,28). This is just one of the parallels with the poly(aurated) carbon cations (above).

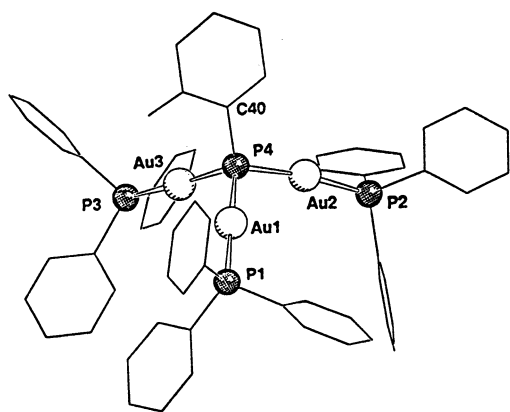


Fig. 5: Structure of the cation $(o\text{-Tol})P[AuP(C_6H_5)_3]_3^+$ (ref. 26,29)

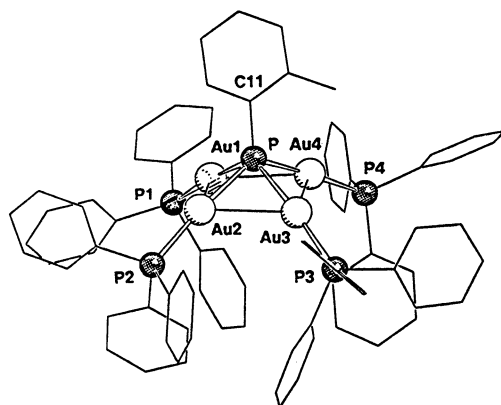


Fig. 6: Structure of the dication (ref. 29) $(o\text{-Tol})P[AuP(C_6H_5)_3]_4^{2+}$

TETRA(AURIO)ARSONIUM SALTS $As(AuL)_4^+ X^-$

Auration of AsH_3 or $As(SiMe_3)_3$ gives high yields of the title compounds, which appear as very stable diamagnetic materials, sometimes in different crystalline forms, which were found to contain the same type of cation: square-pyramidal structures with arsenic capping a square of gold atoms (20)!

This structure is of course at variance with standard rules for valency and structure, which would predict arsonium cations to adopt a tetrahedral configuration. The unexpected finding has been rationalized in terms of the influence of relatively strong metal-metal interactions, which induce a reorganisation of the polyhedron to bring the gold atoms as close together as possible. This force - termed "auriophilicity" - appears to be the origin of most of the new clustering phenomena of gold(I) atoms even at "saturated" molecules like $C(AuL)_4$ or $N(AuL)_4^+$. Relativistic effects have been shown to be responsible to a large

extent for the bonding interaction between seemingly closed-shell metal centers ($\text{Au}^+ : 5d^{10} !$). On this basis a series of new compounds and structures can be envisaged and predicted to be stable, including e.g. boron-centered clusters (16,17).

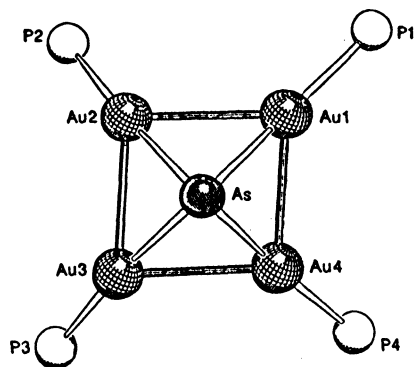


Fig. 7: Core of the structure of the cation $\text{As}[\text{AuP}(\text{C}_6\text{H}_5)_3]_4^+$ (ref. 20)

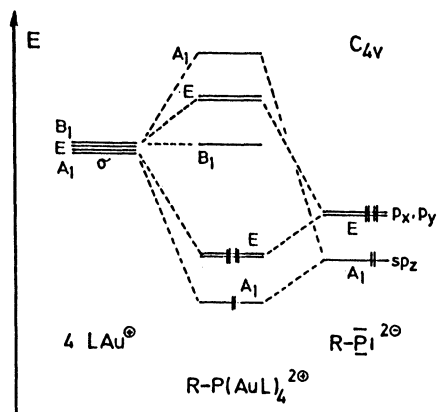


Fig. 8: Molecular orbital diagram for a description of bonding in the structure of Figure 6 (ref. 29)

POLY(AURIO)OXONIUM CATIONS

Early work in Russian laboratories (31) has proven the existence of tri(aurio)oxonium salts $\text{O}(\text{AuL})_3^+ \text{X}^-$. The cations of these compounds have a pyramidal structure at oxygen and are aggregated in pairs in the two crystalline forms known with $\text{X} = \text{BF}_4^-$ (31, 25). Recent studies have shown that these salts can be aurated further with $\text{LAu}^+ \text{BF}_4^-$ to give tetra(aurio)ox-d \bar{u} -onium salts $\text{O}(\text{AuL})_4^{2+} 2 \text{BF}_4^-$. Though no crystal structure could be determined, the results of all other physical methods indicate a diamagnetic, highly symmetrical dication, probably tetrahedral like the ammonium analogue (above) (32).

Like primary amines, alcohols and particularly phenols can be aurated to afford compounds $\text{RO}(\text{AuL})_2^+ \text{X}^-$ with a pyramidal oxonium structure, but no higher degree of auration has been observed to-date (32).

POLY(AURIO)SULFONIUM AND -SELENIUM COMPOUNDS

Hydrogen sulfide, silyl sulfides, and also mercaptanes as well as their selenium analogues are all easily aurated to give sulfonium and selenonium salts with pyramidal cations $\text{S}/\text{Se}(\text{AuL})_3^+$ and $\text{RS}/\text{Se}(\text{AuL})_2^+$ (33-38). The cations form steep pyramids indicative of significant intramolecular $\text{Au} \cdots \text{Au}$ attraction. In many cases the cations are also aggregated in the crystal via additional intermolecular $\text{Au} \cdots \text{Au}$ contacts. Polynuclear species are well documented and the diversity of stoichiometries and structures shows that there is still a rich field lying unexploited in $\text{S}/\text{Se}-\text{Au}$ chemistry.

DI(AURIO)CHLORONIUM SALTS

(Phosphine)gold(I) chlorides can be aurated at the chloride ligand to give di(aurio)chloronium salts $(\text{LAu})_2\text{Cl}^+ \text{Cl}^-$. The cations are strongly bent at the chlorine atom to allow short $\text{Au} \cdots \text{Au}$ contacts (39). This result can be taken as an early

example of gold nucleation at a strongly electronegative (non-metal) atom. Higher degrees of auration at chlorine have not been observed, and there are no data on aurio complexes of other halogens.

CONCLUSIONS

The message for heteroatom chemistry from recent work in the area of auated molecules is that the phenomenon of 'auriophilicity' (1,6) leads to many completely unexpected reactions and products. Their new features of stoichiometry and structure can only be understood in terms of strong metal-metal interactions even for seemingly closed-shell centers. Highly sophisticated theoretical calculations including relativistic effects provide a basis for concepts which can be used for discovery and identification of new systems with clusters of gold and its congeners in the Periodic Table as ligands to functional groups and for carbon itself. Since most of the novel species are by no means just unstable intermediates, or products which do not survive in a standard environment, but rather very robust materials, this field will probably grow and produce many more interesting species with a bearing on a number of other areas of chemistry.

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