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Short review

Synthesis of cluster compounds by photolysis of azido complexes [☆]

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Abstract

Photolysis of R_3PAuN_3 results in a reductive elimination of the azide group to yield R_3PAu^0 moieties which then combine to form Au clusters. The composition of the clusters mainly depends on the steric demand of the ligands bound to the gold atoms. When the photolysis of R_3PAuN_3 is carried out in the presence of metal carbonyl complexes, heterometallic clusters $[M(CO)_x(AuPR_3)_y]^{z+}$ may be formed. The composition of these clusters is determined by the electronic demand of the transition metal M with the electronic configuration d^n, which requires a closed shell configuration, i.e. $2x + y + n - z = 18$. The MAu_y skeleton forms a structure in which the transition metal M is within bonding distance of all the gold atoms, and the Au_y part of the skeleton consists of an icosahedron fragment. Reactions that can be used to degrade and to build up the clusters are presented, and the bonding in the clusters is discussed. Photolysis of R_3PAuN_3 and $L_2M(N_3)_2$ (L_2 = dppe, $(PPh_3)_2$; M = Pd, Pt) yields heteronuclear Pd–Au and Pt–Au clusters, including the $PdAu_{12}$ cluster, which involves a complete Au_{12} icosahedron with the Pd atom at its center.

Keywords: Gold; Transition metals; Clusters; Azido complexes; Photochemistry; Crystal structure

1. Introduction

In recent decades controlled thermal decomposition of azido complexes [1], which presumably proceeds through the cleavage of the N_α–N_β bond of the azido group, has proved to be as an excellent method for the synthesis of nitrogen compounds such as nitrido [2,3], *N*-halogenoimido [4] or phosphorane iminato complexes [5]. Our attempts to decompose the gold(I) complexes R_3PAuN_3 to give gold nitrogen compounds failed however, only gold metal being obtained by the thermal treatment of the azido complexes. We therefore tried to activate the azido ligand at low temperatures by irradiation with UV light, and in this case reductive elimination of the complete azido group, in the form of molecular nitrogen, and formation of homonuclear gold cluster compounds were observed.

The reactive intermediates of this cluster synthesis can also be used to build up heteronuclear gold cluster compounds when, for instance, a metal carbonyl complex is added to the reaction mixture, and a wide variety of heteronuclear cluster compounds $[M(CO)_x(AuPPh_3)_y]^{z+}$ (with $n + 2x + y - z = 18$; n the number of valence electrons of the transition metal M) were obtained in this way. The synthesis, structure, and reactivity of these cluster compounds are discussed below.

The initial studies of the photolysis of azido complexes of palladium(II) and platinum(II) show that in this case also, metal(0) fragments are formed and can be used as building units for heteronuclear cluster compounds. On the other hand, attempts to carry out analogous reactions with azido complexes of copper(I) and silver(I) have so far been unsuccessful.

It should be mentioned that heteronuclear clusters analogous to those obtained by the photolysis reaction have been synthesized by other methods, as described in a recent review [6].

2. Synthesis by photolysis of R_3PAuN_3

2.1. Synthesis of homonuclear gold cluster compounds

The type of homonuclear gold cluster compound formed by the photolysis of R_3PAuN_3 depends mainly

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[☆] Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday.

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on the steric demand of the ligand bound to the gold atom. If Ph_3PAuN_3 is used for the photolytic reaction in THF then $[(Ph_3PAu)_8]^{2+}$ is obtained as main product [7] (Eq. (1)).

$$6Ph_3PAuN_3 + 2Ph_3PAu^+ \xrightarrow{h\nu} [(Ph_3PAu)_8]^{2+} + 9N_2 \qquad (1)$$

In contrast, in the presence of smaller ligands like Cl^-, which can come from a chlorinated solvent like CH_2Cl_2 or can be added as Ph_3PAuCl to the reaction mixture, the larger cluster $[Au_{11}(PPh_3)_8Cl_2]^+$ is usually formed [8] (Eq. (2)).

$$8Ph_3PAuN_3 + 3Ph_3PAu^+ + 2Cl^- \xrightarrow{h\nu} [Au_{11}(PPh_3)_8Cl_2]^+ + 3PPh_3 + 12N_2 \qquad (2)$$

Moreover, reduction in the bulk of the phosphine ligand by using $Me_2PhPAuN_3$ as the starting material results in the formation of the gold-centered Au_{13} cluster $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ [9].

The structures of the inner skeletons of the cluster compounds, whose identities were proved by crystal structure determinations, are shown in Fig. 1. These clusters had previously been synthesized by other methods [10,11].

These homonuclear clusters are also commonly obtained as by-products in the photolytic synthesis of the heteronuclear cluster compounds (Section 2.2).

2.2. *Synthesis of heteronuclear gold cluster compounds*

Photolysis of Ph_3PAuN_3 in the presence of a metal carbonyl complex yields the heteronuclear cluster compounds $[M(CO)_x(AuPPh_3)_y]^{z+}$, whose composition is determined by the electronic demand of the transition metal M, which requires a stable 18 electron configuration. Therefore each CO ligand will be replaced by two $Ph_3PAu(0)$ fragments, and usually a series of cluster compounds with different degrees of substitution of the CO ligands at the metal atom M are produced by the photolysis. The photolytically induced substitution stops, however, when the stable $M(CO)_3$ step is reached.

The photolysis of $Mo(CO)_6$ and Ph_3PAuN_3 in THF, for example, yields the cluster compounds $[Mo(CO)_5(AuPPh_3)_3]^+$, $[Mo(CO)_4(AuPPh_3)_5]^+$, and $[Mo(CO)_3(AuPPh_3)_7]^+$ [12-14] (Eq. (3), Fig. 2).

$$Mo(CO)_6 + 2nPh_3PAuN_3 + Ph_3PAu^+ \xrightarrow{h\nu} [Mo(CO)_{6-n}(AuPPh_3)_{2n+1}]^+ + nCO + 3nN_2 \qquad (3)$$

An excess of the metal carbonyl is necessary since otherwise the homonuclear gold cluster compounds are formed as the main product. The yields of the various heteronuclear cluster compounds can be influenced by the irradiation time, longer times favoring formation of the larger clusters. The influence of the wavelength used has not been studied in detail, but activation of the gold(I) azide, which has a maximum absorption at 231 nm, is best brought about by use of a high pressure mercury lamp in a quartz tube. UV radiation filtered through Duran glass primarily activates the metal carbonyls and thus the yields of the larger clusters are

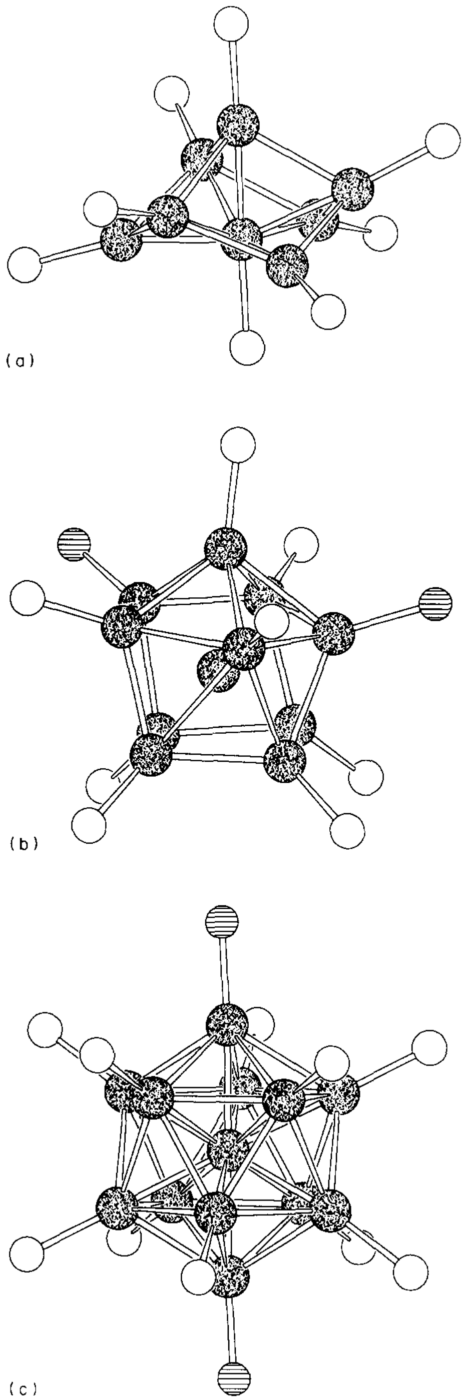

Fig. 1. Structure of the homonuclear gold clusters (a) $[(AuPPh_3)_8]^{2+}$, (b) $[Au(AuPPh_3)_8(AuCl)_2]^+$, and (c) $[Au(AuPMe_2Ph)_{10}(AuCl)_2]^{3+}$ obtained by the photolysis of R_3PAuN_3. Only the P atoms of the phosphane ligands are shown [38].

increased. The various products of photolysis can be isolated by chromatographic separation on an Al_2O_3 column of the readily soluble PF_6^- salts.

The analogous tungsten gold clusters $[W(CO)_4(AuPPh_3)_5]^+$ and $[W(CO)_3(AuPPh_3)_7]^+$, as well as $[W(CO)_4(AuPPh_3)_6]^{2+}$, were synthesized by Steggerda et al. from the homonuclear gold cluster $[(AuPPh_3)_8]^{2+}$ and $W(CO)_3(EtCN)_3$ or $W(CO)_6$ [15].

The iron carbonyl $Fe(CO)_5$ behaves like $Mo(CO)_6$. Co-photolysis with Ph_3PAuN_3 gave $[Fe(CO)_3(AuPPh_3)_5]^+$ [16], the $FeAu_5$ skeleton of which resembles that of $[Mo(CO)_4(AuPPh_3)_5]^+$ (Fig. 2). The same product is obtained when $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ is used as starting material. When the carbonyl cluster compound $Ru_3(CO)_{12}$ is used however, oxidative addition of Ph_3PAuN_3 takes place at one Ru–Ru bond and simultaneously the azido group is transformed by CO into a cyanato ligand, so that $Ru_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}NCO)$ is obtained [16]. Presumably in this case the greater strength of the metal–metal bonds prevent cleavage of the Ru_3 cluster to form a heteronuclear ruthenium gold cluster analogous to $[Fe(CO)_3(AuPPh_3)_5]^+$.

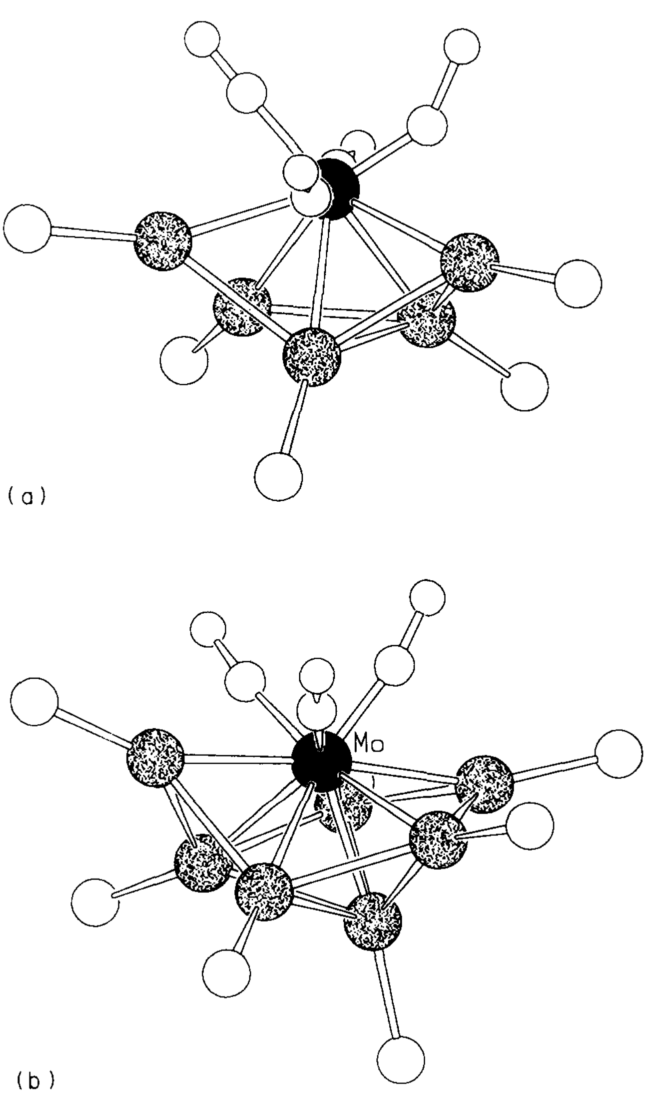

Fig. 2. Structure of the inner core of the heteronuclear gold molybdenum clusters (a) $[Mo(CO)_4(AuPPh_3)_5]^+$ and (b) $[Mo(CO)_3(AuPPh_3)_7]^+$.

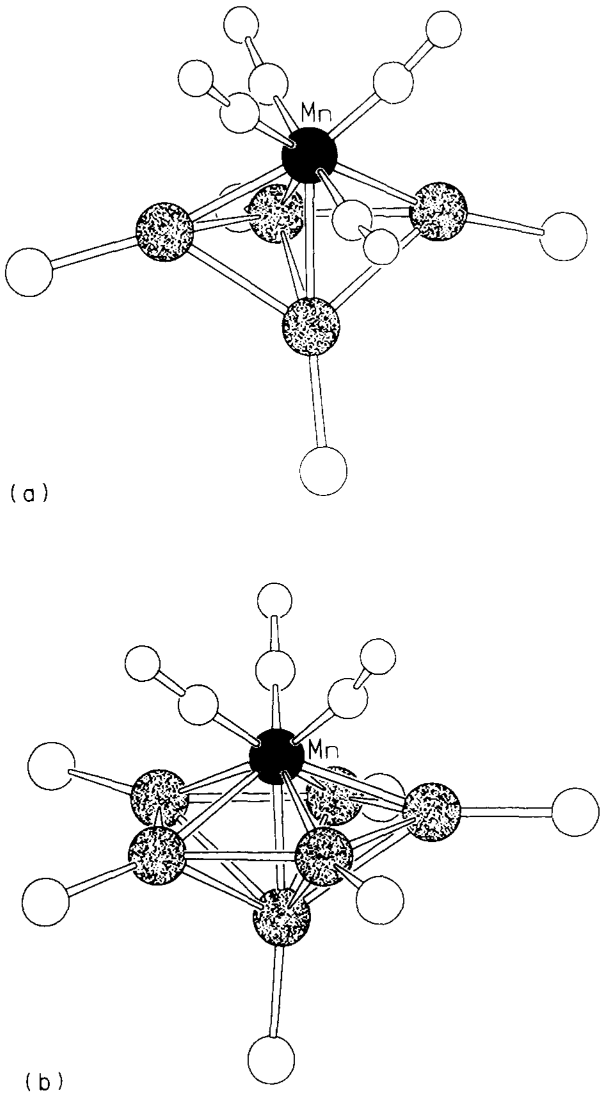

Fig. 3. Structure of the inner core of the heteronuclear gold manganese clusters (a) $[Mn(CO)_4(AuPPh_3)_4]^+$ and (b) $[Mn(CO)_3(AuPPh_3)_6]^+$.

The main product of the photolysis of $Mn_2(CO)_{10}$ with Ph_3PAuN_3 is $[Mn(CO)_4(AuPPh_3)_4]^+$ (Fig. 3), which is specifically obtained when a quartz apparatus is used [17]. With a glass tube around the UV source $[Mn(CO)_3(AuPPh_3)_6]^+$ (Fig. 3) can also be obtained, in small yield. Somewhat better yields of $[Mn(CO)_3(AuPPh_3)_6]^+$ are achieved by using $[Ph_3PAuMn(CO)_5]$ [18], Ph_3PAuN_3 and $Ph_3PAuNCO$ as the starting materials for the photolysis (Eq. (4)) [19]. In this case, the neutral cluster $[Mn(CO)_4(AuPPh_4)_3]$ (Fig. 4) is the main by-product [20].

$$[Ph_3PAuMn(CO)_5] + Ph_3PAu^+ + 4Ph_3PAuN_3 \xrightarrow{h\nu} [Mn(CO)_3(AuPPh_3)_6]^+ + 2CO + 6N_2 \qquad (4)$$

Dicobalt octacarbonyl is the only metal carbonyl that reacts with Ph_3PAuN_3 without irradiation, $Ph_3PAuCo(CO)_4$ being formed (Eq. (5)) [21].

$$Co_2(CO)_8 + 2Ph_3PAuN_3 \longrightarrow 2Ph_3PAuCo(CO)_4 + 3N_2 \qquad (5)$$

The complex $Ph_3PAuCo(CO)_4$ was therefore used for the synthesis of heteronuclear gold cobalt clusters. Photolysis of this complex yields the cluster cation $[Co_2(CO)_6Au(AuPPh_3)_6]^+$, whose inner skeleton consists of two $CoAu_4$ trigonal bypiramids sharing one axial Au atom (Fig. 5) [13,14]. A possible equation for this reaction is as follows:

$$\begin{aligned} &7Ph_3PAuCo(CO)_4 \\ &\xrightarrow{h\nu} [Co_2(CO)_6Au(AuPPh_3)_6]^+ \\ &\qquad + [Co(CO)_4]^- + 2Co_2(CO)_8 \\ &\qquad + PPh_3 + 2CO \qquad (6) \end{aligned}$$

When Ph_3PAu^+ as PF_6^- salt is added without further irradiation to the product of photolysis, the $[Co_2(CO)_6Au(AuPPh_3)_6]^+$ is converted into $[Co(CO)_3(AuPPh_3)_4]^+$ (Eq. (7)) [14,21]. This has the same trigonal-bipyramidal structure as $[Mn(CO)_4(AuPPh_3)_4]^+$ (Fig. 3).

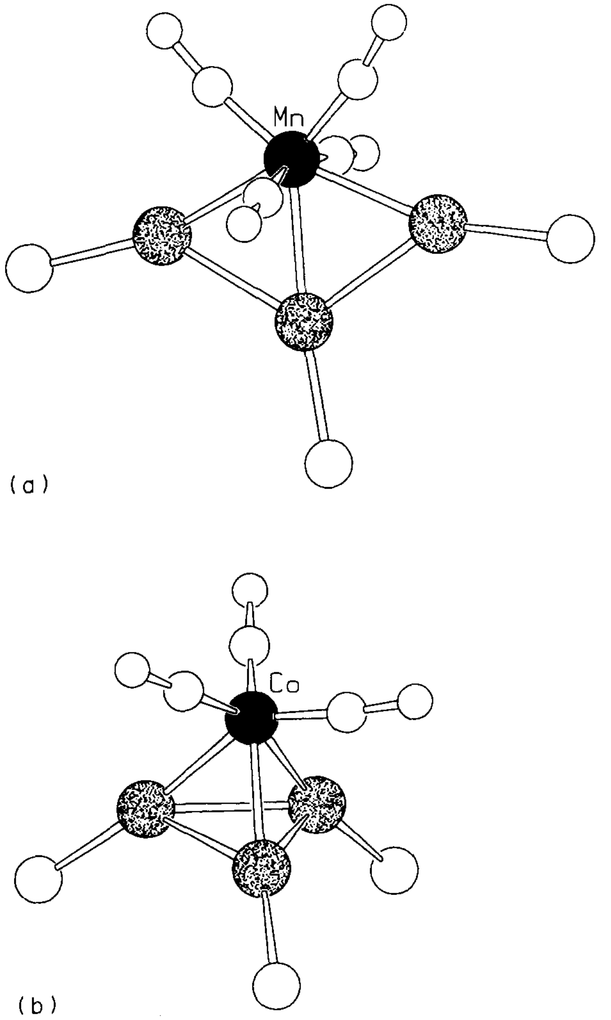

Fig. 4. Structure of the inner core of the neutral clusters (a) $[Mn(CO)_4(AuPPh_3)_3]$ and (b) $[Co(CO)_3(AuPPh_3)_3]$.

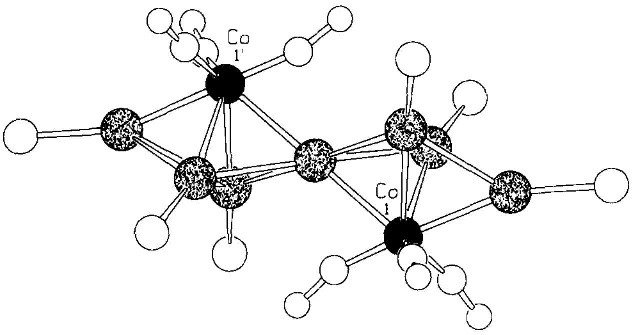

Fig. 5. Structure of the inner core of the condensed cluster $[Co_2(CO)_6Au(AuPPh_3)_6]^+$.

$$[Co_2(CO)_6Au(AuPPh_3)_6]^+ + Ph_3PAu^+ + PPh_3 \longrightarrow 2[Co(CO)_3(AuPPh_3)_4]^+ \qquad (7)$$

The initial attempts to synthesize $[V(CO)_4(AuPPh_3)_6]^+$ from $Ph_3PAuV(CO)_6$ [22] and Ph_3PAuN_3 were unsuccessful, only homonuclear gold cluster cations with $V(CO)_6^-$ as counterion being obtained [23]. After treatment of the reaction mixture with CH_2Cl_2 and chromatographic separation, the main product was $[(Ph_3PAu)_8(AuCl)_2Au][V(CO)_6]$. Presumably the presence of an excess of azide groups resulted in reduction of $Ph_3PAuV(CO)_6$ to the stable carbonyl vanadate $[V(CO)_6]^-$. The synthesis of $[V(CO)_4(AuPPh_3)_6]^+$ was therefore carried out with some of the Ph_3PAuN_3 replaced by $Ph_3PAuNCO$ in order to avoid an excess of azide groups, and to provide an appropriate counter-ion to stabilize the heteronuclear cluster cation. The best results were obtained with a 3:2 molar mixture of $Ph_3PAuNCO/Ph_3PAuN_3$, $[V(CO)_4(AuPPh_3)_6]^+$ (Fig. 6) then being obtained in 35% yield in addition to 30% of homonuclear gold clusters and 30% of $[V(CO)_5(AuPPh_3)_3]$ [23].

3. Synthesis by photolysis of Ph_3PAuN_3 and $L_2M(N_3)_2$ (M = Pd, Pt; L_2 = dppe, $(PPh_3)_2$)

Platinum and palladium atoms do not show the same tendency as gold atoms to cluster together, and so photolysis of palladium(II) and platinum(II) azido complexes in the presence of metal carbonyls does not give the comparable heteronuclear clusters. Most of the metal carbonyls do not form heteronuclear clusters with Pd or Pt at all, and the only one that has given a heteronuclear cluster is $Co_2(CO)_8$. This reacts with $(dppe)Pt(N_3)_2$ under photolytic conditions to yield $[(dppe)PtCo_2(CO)_7]$ (Eq. (8)) [24]. In this case, one of

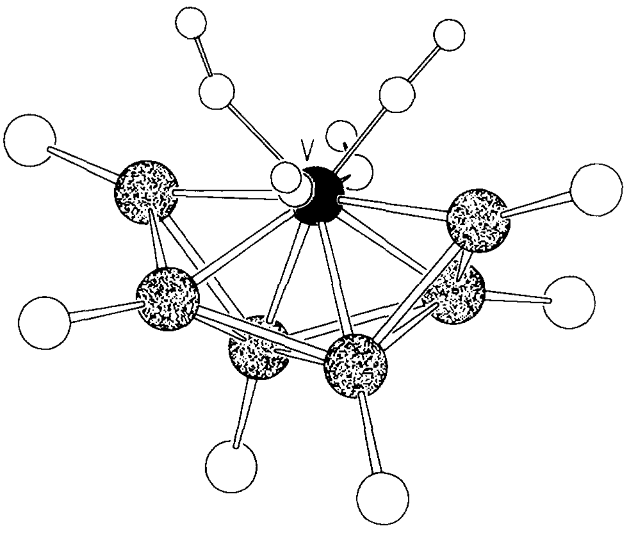

Fig. 6. Structure of the inner core of the heteronuclear gold vanadium cluster $[V(CO)_4(AuPPh_3)_6]^+$.

the bridging CO ligands is replaced by a (dppe)Pt(0) group with formation of a triangular Co_2Pt cluster (Fig. 7).

$$(dppe)Pt(N_3)_2 + Co_2(CO)_8 \xrightarrow{h\nu} [(dppe)PtCo_2(CO)_7] + 3N_2 + CO \qquad (8)$$

When $[(dppe)PtCo_2(CO)_7]$ is used as the starting material for a photolysis reaction with Ph_3PAuN_3, the triangular Co_2Pt cluster is cleaved and the heteronuclear cluster cations $[Pt(dppe)(AuPPh_3)_4]^{2+}$ (Fig. 8) and $[Co_2(CO)_6Au(AuPPh_3)_6^+]$ (Fig. 5) are formed (Eq. (9)) [24].

$$\begin{aligned}&[(dppe)PtCo_2(CO)_7] + 8Ph_3PAuN_3 + 3Ph_3PAu^+\\&\xrightarrow{h\nu} [Pt(dppe)(AuPPh_3)_4]^{2+}\\&\quad + [Co_2(CO)_6Au(AuPPh_3)_6]^+\\&\quad + PPh_3 + CO + 12N_2 \qquad (9)\end{aligned}$$

The photolysis of a mixture of $(Ph_3P)_2Pt(N_3)_2$, Ph_3PAuN_3 and Ph_3PAuCl in THF affords a mixture of products, which after chromatographic separation yields the neutral clusters $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]$ and $[Pt(CO)(AuPPh_3)_6(AuCl)_3]$ [24]. The skeleton of the clusters consists of an icosahedral fragment of nine Au atoms with the Pt atom in its center (Fig. 9). Surprisingly, in one of the clusters the Pt atom is coordinated to a CO ligand. In accordance with a previous report [25], we assume that it was formed from the ethanol used as an eluant during the chromatographic separation. The cluster $[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]$ was previously synthesized by the reaction of $[Pt(AuPPh_3)_8]^{2+}$ with Cl^- [27]. Additional gold platinum clusters obtained by other methods have been reviewed by Steggerda [26].

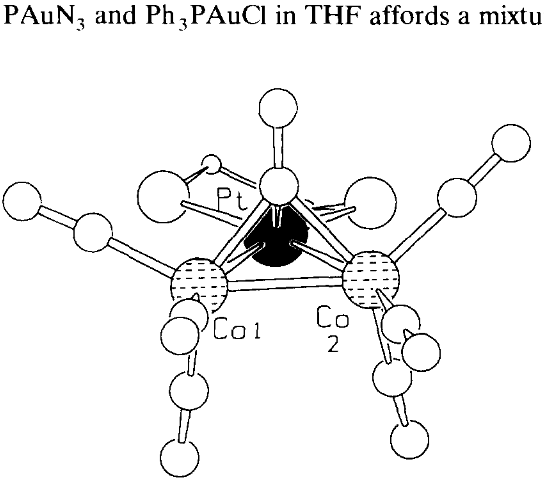

Fig. 7. Structure of the inner core of the cluster $[(dppe)PtCo_2(CO)_7]$.

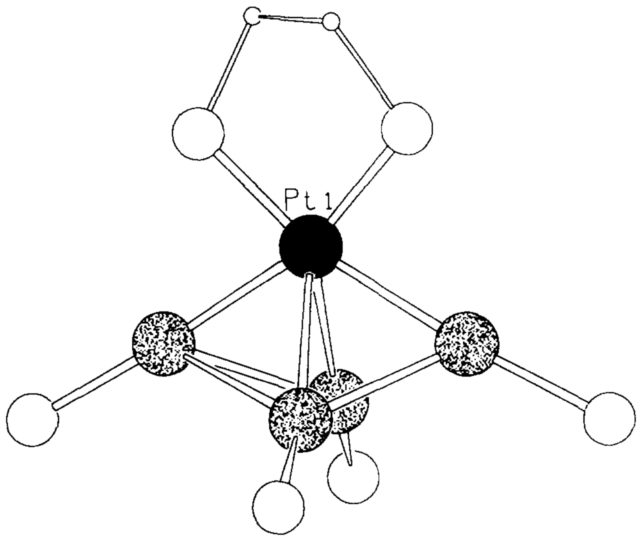

Fig. 8. Structure of the inner core of the cluster $[(dppe)Pt(AuPPh_3)_4]^{2+}$.

The photolysis of the palladium(II) azido complexes $(Ph_3P)_2Pd(N_3)_2$ and $(dppe)Pd(N_3)_2$ in the presence of

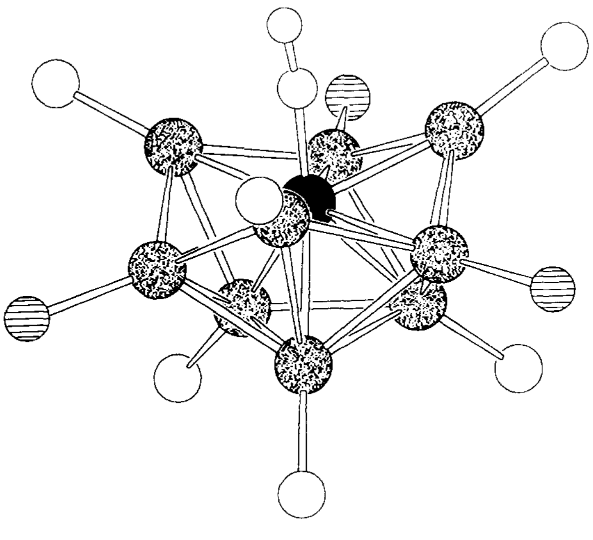

Fig. 9. Structure of the inner core of the heteronuclear gold platinum cluster $[Pt(CO)(AuPPh_3)_6(AuCl)_3]$.

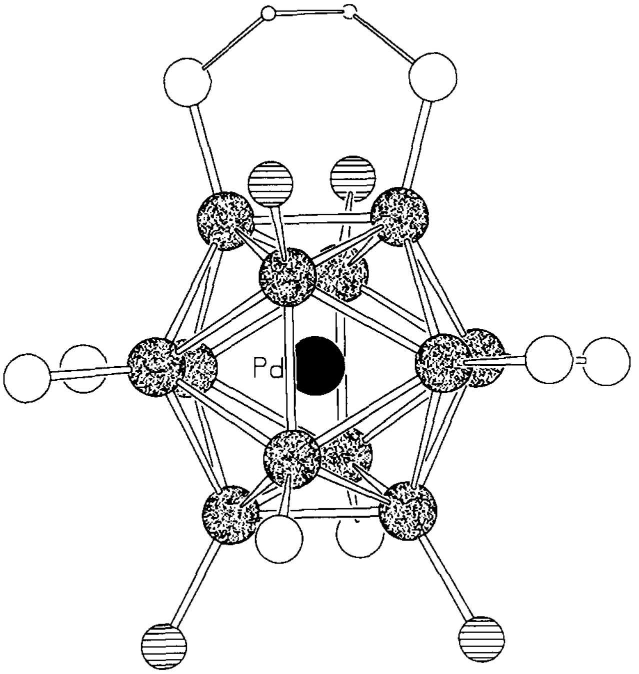

Fig. 10. Structure of the inner core of the icosahedral gold palladium cluster $[Pd(AuPPh_3)_6(Au_2dppe)(AuCl)_4]$.

Ph_3PAuN_3 and Ph_3PAuCl yields products of a different type than those formed from the analogous Pt complexes, the $PdAu_{12}$ clusters $[Pd(AuPPh_3)_8(AuCl)_4]$ and $[Pd(AuPPh_3)_6(Au_2dppe)(AuCl)_4]$ (Fig. 10) being obtained (Eq. (10)) [28]. They are analogous to the homonuclear Au_{13} cluster $[Au(AuPMe_2Ph)_{10}(AuCl)_2]^{3+}$ [9,29], and represent the first examples of heteronuclear clusters involving a complete icosahedron of 12 Au atoms with the heteroatom in its center.

$$(dppe)Pd(N_3)_2 + 8Ph_3PAuN_3 + 4Ph_3PAuCl \xrightarrow{h\nu} [Pd(AuPPh_3)_6(Au_2dppe)(AuCl)_4] + 15N_2 + 6PPh_3 \quad (10)$$

4. Reactions of heteronuclear gold cluster compounds

The heteronuclear cluster compounds are air-stable at ambient temperatures. When the $M(CO)_3$ step is reached, no further substitution of CO ligands is possible under photolytic conditions. Nevertheless, it is possible to build up and to degrade the clusters.

The high stability of Ph_3PAuCl and the high tendency for it to be formed can be used to degrade the cluster cations with Cl^- to produce the neutral clusters containing one less Ph_3PAu^+ group. Cluster ions undergoing this type of degradation are $[Co(CO)_3(AuPPh_3)_4]^+$ and $[Mn(CO)_4(AuPPh_3)_4]^+$, which yield $[Co(CO)_3(AuPPh_3)_3]$ (Eq. (11)) [14] and $[Mn(CO)_4(AuPPh_3)_3]$ [20] upon treatment with Ph_4PCl in CH_2Cl_2 (Fig 4).

$$[Co(CO)_3(AuPPh_3)_4]^+ + Cl^- \rightleftharpoons [Co(CO)_3(AuPPh_3)_3] + Ph_3PAuCl \quad (11)$$

On the other hand, the reverse reaction can be brought about by reaction of the neutral clusters with Ph_3PAu^+. Thus it seems that there is an equilibrium between the neutral cluster and the corresponding cluster cations containing one or two additional Au atoms. This equilibrium is mediated by Cl^- or Ph_3PAu^+.

The problem presented by the fact that once the $M(CO)_3$ stage is reached further substitution of CO ligands by Ph_3PAu groups does not occur under photolytic conditions, was overcome by using the well known nucleophilic attack of OH^- on the CO group. (Hieber and Leutert showed as long ago as 1932 [30]

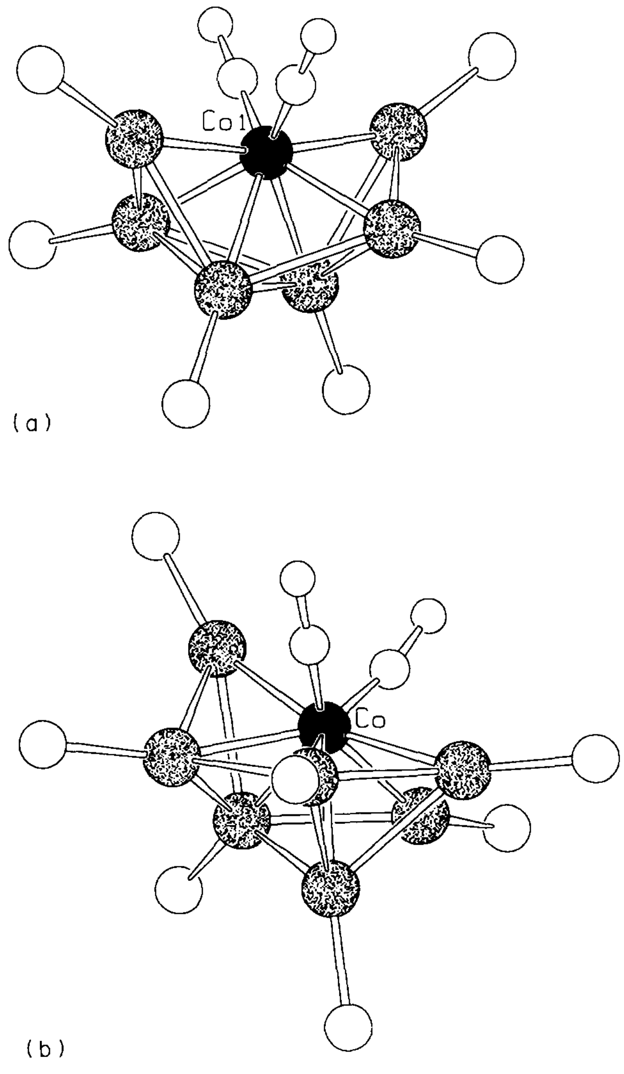

Fig. 11. Structure of the inner core of the heteronuclear gold cobalt clusters (a) $[Co(CO)_2(AuPPh_3)_6]^+$ and (b) $[Co(CO)_2(AuPPh_3)_7]^{2+}$.

that $Fe(CO)_5$ reacts with OH^- to form the metallate $[Fe(CO)_4]^-$ (Hiebers Basenreaktion).) Thus $[Co(CO)_3(AuPPh_3)_4]^+$ reacts with ethanolic NaOH in the presence of Ph_3PAuCl to afford the larger cluster $[Co(CO)_2(AuPPh_3)_6]^+$ in approximately 83% yield, in addition to small quantities of the di-cation $[Co(CO)_2(AuPPh_3)_7]^{2+}$ [31] (Fig. 11). In accordance with Hieber and Leutert's results it can be assumed that the reaction proceeds through $[Co(CO)_2(AuPPh_3)_4]^-$, which then undergoes addition of two or three Ph_3PAu^+ cations (Eqs. (12), (13)).

$$[Co(CO)_3(AuPPh_3)_4]^+ + 4OH^- \longrightarrow [Co(CO)_2(AuPPh_3)_4]^- + CO_3^{2-} + 2H_2O \qquad (12)$$

$$[Co(CO)_2(AuPPh_3)_4]^- + 2Ph_3PAu^+ \longrightarrow [Co(CO)_2(AuPPh_3)_6]^+ \qquad (13)$$

The rhodium clusters $[Rh(CO)_2(AuPPh_3)_6]^+$ and $[Rh(CO)_2(AuPPh_3)_7]^{2+}$, which have the same compositions as their cobalt analogues, have been obtained by the reduction of Ph_3PAu^+ with BH_4^- in the presence of $[Rh(CO)_2(MeCN)_2]^+$ [32].

Another interesting reaction is the condensation of two heteronuclear clusters, which so far has been observed only in the case of the cobalt gold clusters; thus $[Co(CO)_3(AuPPh_3)_4]^+$ reacts with $[Co(CO)_3(AuPPh_3)_3]$ to form $[Co_2(CO)_6Au(AuPPh_3)_6]^+$ (Fig. 5) in high yield (Eq. (14)) [14].

$$[Co(CO)_3(AuPPh_3)_4]^+ + [Co(CO)_3(AuPPh_3)_3] \longrightarrow [Co_2(CO)_6Au(AuPPh_3)_6]^+ + PPh_3 \qquad (14)$$

The condensed cluster $[Co_2(CO)_6Au(AuPPh_3)_6]^+$, on the other hand, can be converted by treatment with Ph_3PAu^+ and PPh_3 into two cluster cations $[Co(CO)_3(AuPPh_3)_4]^+$ (Eq. (7)).

5. Structure of the heteronuclear gold cluster compounds

All the heteronuclear gold transition metal clusters described in the above chapters consist of one central heteroatom M and three to twelve gold atoms connected at approximately equal distances to the heteroatom. The heteroatom occupies the position of highest connectivity within the clusters. The peripheral gold atoms form a close-packed surface which is built up by triangular faces. The structure of the larger heteronuclear clusters can be regarded as a close-packing of MAu_3 tetrahedra sharing MAu_2 faces having the central heteroatom M as a common corner. An example of a single tetrahedron is the $CoAu_3$ cluster $[Co(CO)_3(AuPPh_3)_3]$ (Fig. 4) [14], and the MAu_4 clusters with a trigonal bipyramidal structure can be regarded as involving a double tetrahedron (Figs. 3, 8). For the larger clusters, the arrangement of the peripheral Au atoms is best described as a fragment of an icosahedron, which is complete in the case of the $PdAu_{12}$ cluster $[Pd(AuPPh_3)_6(Au_2dppe)(AuCl)_4]$ (Fig. 10) [28]. The structure of the inner skeletons of the different heteronuclear clusters is shown in Fig. 12.

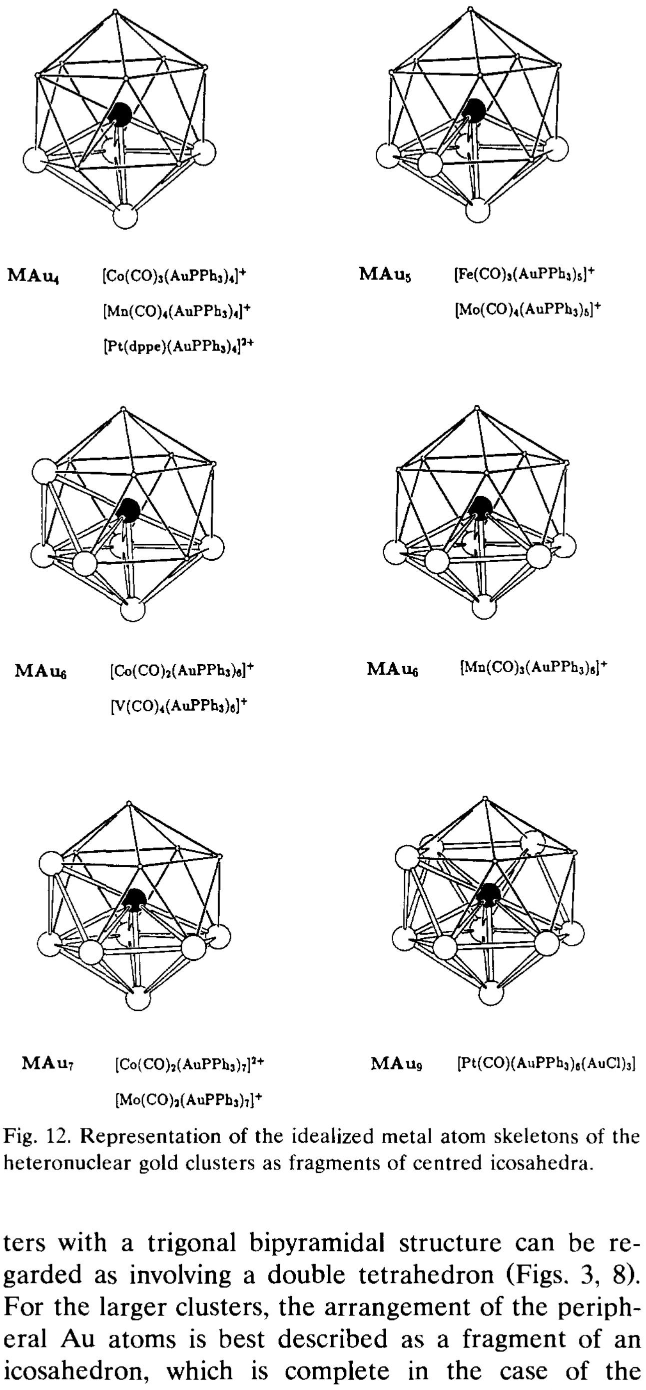

Fig. 12. Representation of the idealized metal atom skeletons of the heteronuclear gold clusters as fragments of centred icosahedra.

An exception to these rules is the $MnAu_3$ cluster $[Mn(CO)_4(AuPPh_3)_3]$ [20]. Its skeleton forms a planar $MnAu_3$ rhombus with the Mn atom in an equatorial position (Fig. 4).

It is noteworthy that the MAu_6 clusters, despite all having the same total number of electrons, exist as two different isomers. The MAu_6 skeleton in $[Mn(CO)_3(AuPPh_3)_6]^+$ [19] takes the form of a pentagonal bipyramid with the Mn atom occupying one apex, while in $[V(CO)_4(AuPPh_3)_6]^+$ [23] and $[Co(CO)_2(Au-$

$PPh_3)_6]^+$ [31] the skeleton can be described as a double-capped trigonal bipyramid with the heteroatom M in an equatorial position (Figs. 6, 11). We account for the occurrence of the two different structures in terms of the stereochemistry and bonding [19]. Model studies show that the elliptical form of VAu_6 results in a lower repulsion between the four CO ligands and the $(AuPPh_3)_6$ part of the framework than would exist with a more spherical structure such as that observed for the $MnAu_6$ framework. On the other hand, the individual structures for the clusters $[Mn(CO)_3(AuPPh_3)_6]^+$, $[V(CO)_4(AuPPh_3)_6]^+$, and $[Co(CO)_2(AuPPh_3)_6]^+$ obviously lead to a more effective orbital overlap in each case (see Section 6).

The need for the most effective overlap is presumably also responsible for the formation of the different structures found in the case of the MAu_3 clusters $[Co(CO)_3(AuPPh_3)_3]$ [14] and $[Mn(CO)_4(AuPPh_3)_3]$ [20] (Section 6).

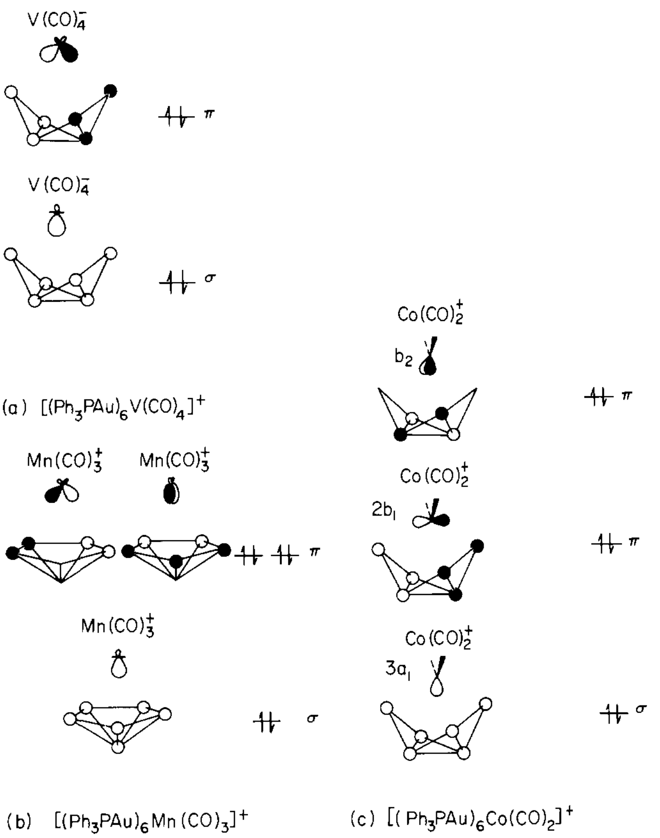

Fig. 13. Representation of the orbital interaction in the cluster skeletons of (a) $[V(CO)_4(AuPPh_3)_6]^+$, (b) $[Mn(CO)_3(AuPPh_3)_6]^+$ and (c) $[Co(CO)_2(AuPPh_3)_6]^+$. The radial sp hybrid orbitals of the Ph_3PAu groups are represented as filled and open circles.

6. Bonding in the heteronuclear gold clusters

The structure and bonding of homonuclear and heteronuclear gold cluster compounds have been discussed by Mingos [6,10,33]. We also described some aspects of the bonding in heteronuclear gold transition metal clusters [21], and specifically discussed the origin of the isomerism observed for the MAu_6 [19] and MAu_3 [20] clusters.

For a discussion of the bonding in the heteronuclear gold transition metal clusters $[M(CO)_x(AuPPh_3)_y]^{z+}$, the clusters are best dismantled into the $(AuPPh_3)_y$ and the $M(CO)_x$ fragments. Each Au atom in the $(AuPPh_3)_y$ fragment can be assumed to adopt sp hybridization, with one of the hybrid orbitals binding the phosphane ligand, while the other one points radially to the center of the cluster and is available for the metal-metal bonding. The remaining degenerate pair of energetically high-lying p_x and p_y orbitals have only a minor role in the bonding and can therefore be neglected [6].

The number and type of frontier orbitals of the $M(CO)_x$ groups ($x = 2, 3, 4$) depends on the value of x [34]. Thus, for the heteronuclear clusters $[M(CO)_x(AuPPh_3)_y]^{z+}$ different MOs must be expected. The $M(CO)_3$ group has three frontier orbitals; they can be classified into one radial orbital pointing to the center of the cluster and one set of two degenerate tangential orbitals. They combine with the radial orbitals of the y Ph_3PAu groups to form three bonding MOs. One of them can be characterized as being of the σ-type, while the other two contain one nodal plane each, and therefore, are of the π-type. This situation is illustrated for the case of $[Mn(CO)_3(AuPPh_3)_6]^+$ [19] in Fig. 13(b). It is interesting to note that in this case, the bonding is similar to that in the cyclopentadienyl complex $CpMn(CO)_3$, since the hemispherical, pentagonal pyramidal $(AuPPh_3)_6$ unit behaves like a cyclopentadienyl ring.

Of the frontier orbitals of a $M(CO)_2^+$ group, as present in $[Co(CO)_2(AuPPh_3)_6]^+$ [31], three are unoccupied and suitable for a combination with the orbitals of the $(AuPPh_3)_6$ fragment, to form once three bonding cluster MOs (Fig. 13(c)).

A $M(CO)_4$ group, on the other hand, has only two frontier orbitals, one of them radially oriented and the other arranged tangentially. In this case, therefore, only two bonding cluster MOs can be formed of σ and π types. In Fig. 13(a) $[V(CO)_4(AuPPh_3)_6]^+$ is shown as an example of this.

The different structures of the isomeric MAu_6 clusters are probably influenced by the different number of π MOs. Since the two tangential orbitals of the $[Mn(CO)_3]^+$ group in $[Mn(CO)_3(AuPPh_3)_6]^+$ are arranged perpendicular to one another, a hemispherical $(AuPPh_3)_6$ fragment is preferred. When there is only one tangential orbital, as in the $[V(CO)_4]^-$ group of $[V(CO)_4(AuPPh_3)_6]^+$, the elliptical cluster structure obviously leads to a more effective overlap. A similar argument seems to be valid for the bonding in $[Co(CO)_2(AuPPh_3)_6]^+$ in this case the tangential orbital $2b_1$ (Fig. 13(c)) would not achieve an effective overlap with a hemispherical $(AuPPh_3)_6$ group. In the comparable complex $CpCo(CO)_2$ this orbital is also assumed to overlap weakly with the orbitals of the cp-ring [35]. The elliptical form of the $(AuPPh_3)_6$ fragment in $[Co(CO)_2(AuPPh_3)_6]^+$, however, allows a more effective overlap [31].

In the case of the MAu_3 clusters $[Co(CO)_3(AuPPh_3)_3]$ [14] and $[Mn(CO)_4(AuPPh_3)_3]$ [20,36], two isomeric structures are observed (Fig. 4). They can be accounted for in the same way in terms of the different orbital interactions. The tetrahedral structure of the $CoAu_3$ core is well-suited for the formation of the two perpendicular π-MOs, while the core structure of a planar rhombus in $[Mn(CO)_4(AuPPh_3)_3]$ is more appropriate since only one π-MO is present.

It can be assumed that the bonding discussed for the MAu_6 clusters can also be applied to the other heteronuclear clusters having the same group $M(CO)_x$. Therefore, the clusters $[M(CO)_4(AuPPh_3)_y)]^{z+}$ have two occupied bonding core MOs, and the clusters $[M(CO)_3(AuPPh_3)_y)]^{z+}$ and $[M(CO)_2(AuPPh_3)_y)]^{z+}$ have three of them. The small number of bonding electrons in the relatively large clusters seems to be out of keeping with their stability, and an additional stabilization by gold–gold interactions must be considered. This phenomenon was termed aurophilicity by Schmidbaur [37]. The Au–Au interactions can also be recognized from the short Au–Au distances of between ca. 272 and 310 pm observed in all the heteronuclear clusters (Table 1). They are in the same range as the distances between peripheral gold atoms in the homonuclear clusters [10]. On the other hand, stronger interactions and shorter distances are found between the central and the peripheral Au atoms in these clusters [10]. In the heteronuclear clusters also the strongest bonds are those between the central heteroatom M and the peripheral Au atoms (Table 1).

As mentioned earlier, the composition of the heteronuclear clusters is determined by the need for the central heteroatom M to acquire a stable 18-electron configuration. This is achieved by adding to the number of d-electrons of the metal M, the electrons donated by the x CO ligands and by the $(AuPPh_3)_y^{z+}$ fragment. Only one exception from this rule has been observed so far, this is provided by the cluster cation $[Pt(dppe)(AuPPh_3)_4]^{2+}$ [24] in which the central Pt atom only achieves 16 electrons, which is not unusual for platinum.

The bonding described above for the heteronuclear clusters cannot be applied to the clusters $[Pt(CO)(AuPPh_3)_6(AuCl)_3]$ [24], $[Pd(AuPPh_3)_8(AuCl)_4]$ [28], and $[Pd(AuPPh_3)_6(Au_2dppe)(AuCl)_4]$ [28]. Instead, these are to be compared with the homonuclear gold clusters of the spherical type [33]. In this case, four occupied bonding core MOs are present [33].

The relatively low values of the wave numbers of the CO stretching vibration confirm the good donor ability of the $(AuPPh_3)_y$ fragments. The donor ability in-

Table 1
Metal–metal bond lengths in heteronuclear clusters MAu_n obtained by the photolysis of azido complexes, and with data for some clusters synthesized by other methods [a]

Cluster compound	M–Au distances in pm	Au–Au distances in pm	Ref.
$[Co(CO)_3(AuPPh_3)_3]$	250.4(1)–254.0(2)	279.5(1)–285.1(1)	[14]
$[Mn(CO)_4(AuPPh_3)_3]$	258.4(4)–262.0(4)	276.6(2)–281.3(2)	[20]
$[Co(CO)_3(AuPPh_3)_4]^+$	258.0(2)–264.7(1)	278.4(1)–293.4(1)	[21]
$[Mn(CO)_4(AuPPh_3)_4]^+$	263.3(3)–273.3(3)	277.3(1)–292.2(1)	[17]
$[Pt(dppe)(AuPPh_3)_4]^{2+}$	266.1(1)–268.9(1)	276.0(1)–283.9(2)	[24]
$[Fe(CO)_3(AuPPh_3)_5]^+$	259.0(1)–265.1(1)	277.6(1)–308.8(1)	[16]
$[Mo(CO)_4(AuPPh_3)_5]^+$	279.9(5)–284.6(7)	272.2(4)–301.3(4)	[14]
$[W(CO)_4(AuPPh_3)_5]^+$	275.2(3)–284.9(3)	276.3(5)–293.2(3)	[15]
$[Rh(CNC_8H_9)_3(AuPPh_3)_5]^{2+}$	266.9(4)–273.1(4)	279.5(3)–300.5(3)	[32]
$[Co(CO)_2(AuPPh_3)_6]^+$	254.9(1)–257.1(2)	280.4(1)–288.4(1)	[31]
$[Mn(CO)_3(AuPPh_3)_6]^+$	261.8(1)–272.3(2)	279.2(1)–295.1(1)	[19]
$[V(CO)_4(AuPPh_3)_6]^+$	273(1)–284(1)	275.3(5)–296.2(4)	[23]
$[Co(CO)_2(AuPPh_3)_7]^{2+}$	256.8(6)–264.7(5)	274.8(3)–332.6(3)	[31]
$[Rh(CO)_2(AuPPh_3)_7]^{2+}$	264(1)–276.5(8)	278.8(4)–311.8(5)	[32]
$[Mo(CO)_3(AuPPh_3)_7]^+$	277.1(1)–286.0(1)	283.8(1)–303.1(1)	[12,13]
$[W(CO)_3(AuPPh_3)_7]^+$	276.0(4)–285.6(3)	285.7(3)–303.5(4)	[15]
$[Rh(CNC_8H_9)_2(AuPPh_3)_6(AuCl)_2]^+$	265.4(3)–281.9(3)	278.1(2)–300.9(2)	[32]
$[Pt(CO)(AuPPh_3)_6(AuCl)_3]$	267.5(2)–273.8(2)	279.6(2)–300.4(2)	[24]
$[Pt(PPh_3)(AuPPh_3)_6(AuCl)_3]$	268(2)–278.9(4)	280(3)–300(3)	[27]
$[Pd(AuPPh_3)_6(Au_2dppe)(AuCl)_4]$	272.2(2)–276.7(1)	285.4(2)–293.5(2)	[28]
$[Co_2(CO)_6Au(AuPPh_3)_6]^+$	257.6(1)–265.6(1)	278.2(1)–291.9(1)	[13]

[a] Further examples have been described by Mingos [6].

creases with the increasing number of $AuPPh_3$ groups as can be seen from the frequencies shown by $[Co(CO)_3(AuPPh_3)_4]^+$, at 1915, 1925 and 1980 cm^{-1} [21], $[Co(CO)_2(AuPPh_3)_6]^+$, 1873 and 1904 cm^{-1} [31], or $[Mo(CO)_4(AuPPh_3)_5]^+$ 1890, 1915, 1975 cm^{-1} [14] and $[Mo(CO)_3(AuPPh_3)_7]^+$, 1835, 1895 cm^{-1} [13].

7. Conclusions

The photolysis of azido complexes of gold, palladium and platinum has been shown to provide an effective and versatile method for making a large variety of homonuclear and heteronuclear clusters. One advantage of this method is that the azido group used as a reducing agent is oxidized to molecular nitrogen, so causing no contamination. It is to be expected that the photolysis of azido complexes can be extended to other metals, and the synthesis of heteronuclear clusters containing Main Group metals seems probable. The synthesis of mononuclear metal complexes is another possible application of the photolysis reaction.

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