
Electrospray Mass Spectrometric Characterization of Bimetallic Group 8 - Gold Clusters

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Bimetallic clusters containing gold in conjunction with Group 8 metals have been intensively studied as it is proposed that these compounds may find uses as catalysts or materials (or as precursors to catalysts/materials). These types of compounds are very difficult to characterize by the mass spectrometric techniques traditionally used to analyse transition metal clusters. In this paper we report a derivatization method employing electrospray ionization mass spectrometry that is reliable and informative for these types of compounds.

Transition metal carbonyl clusters are essentially small metal aggregates containing typically between three and 50 metal atoms. Smaller than colloids, they are soluble in common organic solvents, and in addition possess well defined structures (thousands of examples having been characterized by X-ray crystallography) (1). Many clusters are active catalysts and operate under homogeneous conditions, or by heterogenizing the cluster, by attachment to supports such as silica and alumina surfaces and intrazeolite anchoring (2). Catalysis by clusters differs from that of mononuclear homogeneous catalysts in that multicentre bond activation may take place that can give rise to different products unavailable by other homogeneous methods (3).

A large number of bimetallic clusters have been prepared and characterized in the laboratory and some prominent review articles have been published (4), including one on those containing gold (5). There are also some impressive catalytic applications, too many to be listed here, but some examples include the use of Ru-Pt clusters for alkyne hydrogenation (6), Rh-Co clusters for hydrosilylation (7), Fe-Ru clusters for isomerization of alkenes (8), and Pt-Au clusters for H₂-D₂ equilibration (9). It is not unreasonable to assume that many bimetallic compounds may have better

homogeneous catalytic properties than homonuclear species since many alloys are superior to single component heterogeneous catalysts.

Despite the intense research activity in this area, characterization of the clusters relies extensively on single crystal X-ray diffraction methods, as spectroscopic techniques such as IR and NMR are of little help, and mass spectrometry tends to be quite unreliable. Good mass spectra of bimetallic clusters are difficult to obtain as they have, typically, low volatilities, high molecular weights, complicated isotopic distributions and competing fragmentation pathways.

SYNTHETIC METHODOLOGY

The synthesis of bimetallic gold/Group 8 metal clusters involves a metathesis reaction (usually referred to as an ionic coupling reaction by cluster chemists) between a gold(I) phosphine fragment, [Au(PR₃)]⁺, and a cluster anion (10). The gold cation is generated *in situ* from the reaction of the corresponding chloride with a suitable chloride abstractor such as a silver or thallium salt. These reactions typically proceed in yields exceeding 80%.

The [Au(PR₃)]⁺ fragment is isolobal to the hydride

and, in principle, it is possible to replace any hydride in a cluster with the gold-phosphine fragment (although direct substitution of a hydride by a gold-phosphine fragment is usually not possible) (11). Clearly, steric effects play a part as the gold-phosphine unit is considerably more bulky than a hydride, and the nature of the phosphine ligand attached to the Au(I) ion also has a marked influence on the structure of the product. For example, dianionic clusters that react with two equivalents of the gold reagent can give rise to skeletal isomers. In certain cases the gold ions will cap opposite faces of the cluster whereas chelating phosphine-gold fragments such as $[\text{AuPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Au}]^{2-}$ force the gold centres to cap the same face (10).

MASS SPECTROMETRY

Mass spectrometric characterization of clusters has improved dramatically over the last few years (12). The main developments have come from applying techniques such as laser desorption ionization (LDI) and electrospray ionization (ESI), which were developed with polymers and biomolecules in mind, to cluster molecules. Both LDI and ESI work very well for charged clusters (13) but both are less straightforward for the characterization of neutral clusters. With neutral clusters, LDI gives rise to extensive clustering, leading to extremely complicated spectra (14), and ESI requires the use of reagents to chemically induce charge onto the cluster (15). The use of ESI mass spectrometry in organometallic chemistry (including that of clusters) continues to expand, and we have now found that it is the only technique that gives reliable spectra of heteronuclear gold/Group 8 metal clusters.

The basic principle of electrospray ionization (ESI) involves spraying a solution of a substance through a capillary into a chamber, through which a stream of dry gas passes in the opposite direction to the spray (16). A potential of several kV is applied between the capillary and the chamber wall. Charged droplets are produced that become smaller as the solvent is evaporated, and eventually bare ions are formed which pass through a glass capillary into the pre-analyser region, where the remaining bath gas and residual solvent is pumped away. The ions are then focused through the lensing system into the analyser of the mass spectrometer.

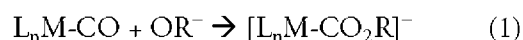
A number of methods have been developed for the analysis of neutral metal carbonyl clusters using ESI-MS (15). Because the oxygen of the carbonyl ligand is not appreciably basic, it will not protonate and hence

species of the type $[\text{M} + \text{H}]^+$ are not observed. Various other charged species have, however, been shown to derivatize neutral carbonyl clusters.

Silver (I) ions also behave as ionization agents with a limited number of neutral metal carbonyl clusters providing $[\text{M} + \text{Ag}]^+$ and/or $[\text{M} + \text{Ag} + \text{solvent}]^+$ type ions (depending on the solvent and the cone voltage) (17). It seems likely that the interaction is between an electron-rich metal-metal bond of a cluster and the silver ion to form a M_2Ag triangle. Clusters of this type are known which are sufficiently stable to be characterised structurally, though all the examples have strongly electron donating ligands.

The alkali metal ions Li^+ , Na^+ and K^+ will also associate with very electron-rich clusters such as $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ to give species of the type $[\text{M} + \text{cation}]^+$. It is believed that the attachment of the ion is likely to be via an iso-carbonyl link of the type $\text{L}_n\text{M}-\text{C}\equiv\text{O}\dots\text{Na}^+$.

The most effective and general method to date is the use of alkoxide ion as an ionization agent (15). The sample is dissolved in the corresponding alcohol, and a small quantity of sodium alkoxide solution is added. Nucleophilic attack by the alkoxide ion on a coordinated carbonyl ligand provides a charged species:



The reaction represented by Equation (1) is quite general for metal carbonyl compounds, and is rapid and large equilibrium constants favour the product, all of which are ideal characteristics for a derivatization process. It is this alkoxide ion derivatization method that affords reliable and reproducible spectra of bimetallic gold/Group 8 metal clusters. Figure 1 shows the ESI-MS of the new cluster $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{AuPPh}_2(\text{C}_{16}\text{H}_{15})\}_2^*$ obtained from a methanolic solution containing sodium methoxide. Two peaks are observed, one of high intensity centred at m/z 2276.67 and one of lower intensity centred at m/z 1655.57. Expansions of these two peaks are shown in Figure 2 together with calculated models for

* Preparation of $\text{Ru}_6\text{C}(\text{CO})_{16}\{\text{AuPPh}_2(\text{C}_{16}\text{H}_{15})\}_2$: The cluster $[\text{Ru}_6\text{C}(\text{CO})_{16}][\text{PPN}]_2$ (100 mg, 0.047 mmol) (PPN = the bis(triphenylphosphoranylidene)ammonium cation, $\text{ClAuPPh}_2(\text{C}_{16}\text{H}_{15})$) (58 mg, 0.093 mmol) ($\text{PPh}_2(\text{C}_{16}\text{H}_{15}) = \text{diphenyl}[2.2]$ paracyclophanylphosphine) and AgBF_4 (27 mg, 0.0141 mmol) were dissolved in CH_2Cl_2 and stirred for 18 h at room temperature. The reaction mixture was filtered and the solvent removed *in vacuo*. The product was then recrystallized from CH_2Cl_2 -hexane mixture (yield 36 mg).

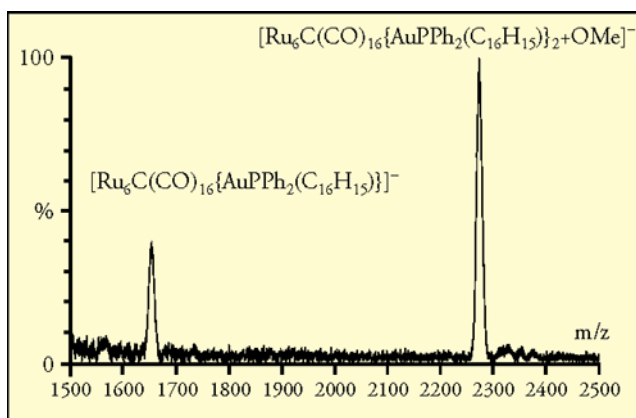


Figure 1 The ESI-MS of the new cluster $[Ru_6C(CO)_{16}\{AuPPh_2(C_{16}H_{15})\}_2]$ obtained from a methanolic solution containing sodium methoxide, showing the $[Ru_6C(CO)_{16}AuPPh_2(C_{16}H_{15})]^-$ impurity.

comparison. The peak centred at m/z 2276.67 corresponds extremely well to intact cluster with a methoxide ion and the peak centred at m/z 1655.6 corresponds to the cluster anion $Ru_6(CO)_{16}\{AuPPh_2(C_{16}H_{15})\}^-$ which has not been methoxylated (see Figure 3). $Ru_6(CO)_{16}\{AuPPh_2(C_{16}H_{15})\}^-$ could not be identified by other spectroscopic methods or other mass spectrometric techniques as these give complicated fragmentation patterns that obscure the presence of the anion. The great advantage of derivatization ESI-MS is the fact that intact cluster species are detected due to the softness of the method.

We have investigated a range of related clusters using the same method and in each case found the results to be consistent with the compound reported above (some also containing the anion impurity).

CONCLUSIONS AND OUTLOOK

The potential role of bimetallic clusters containing gold with Group 8 metals in catalysis and materials is enormous. Reliable characterization of these compounds is not trivial and we have demonstrated a new method that gives reproducible molecular weight data.

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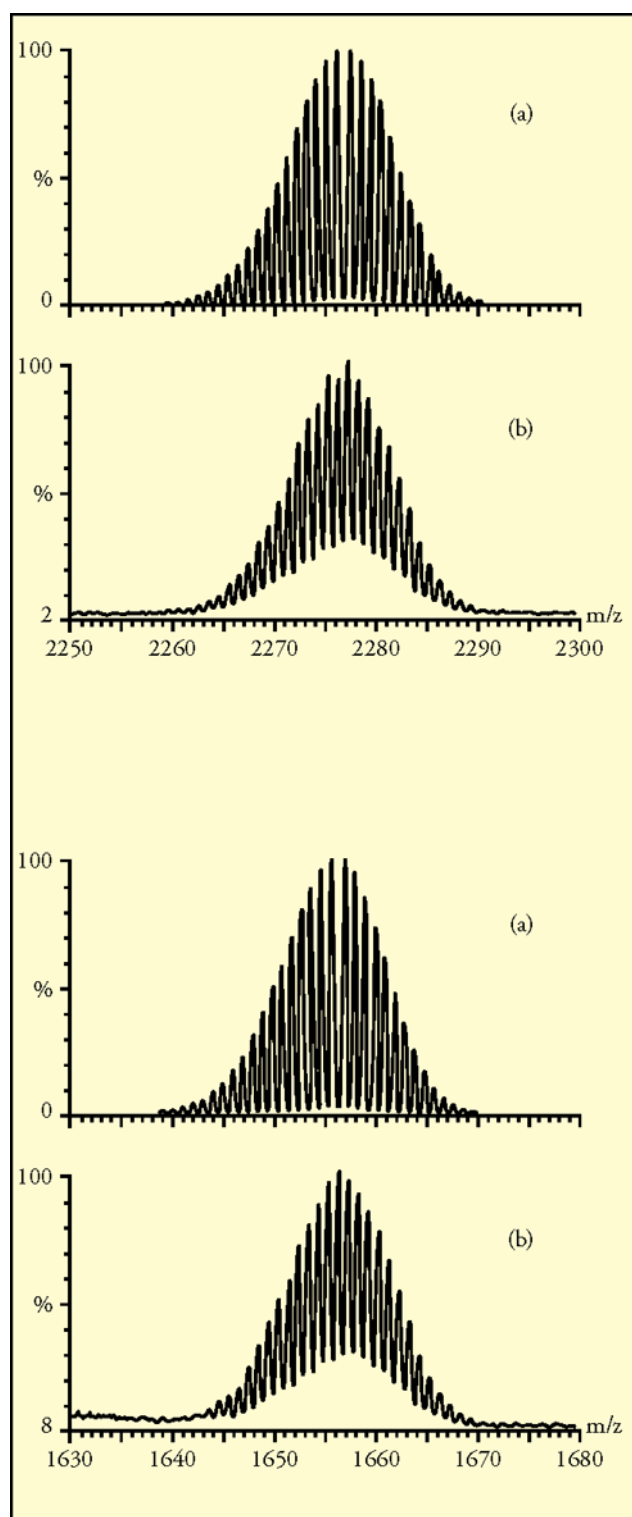


Figure 2 Comparison of (top) the peak envelope corresponding to $[Ru_6C(CO)_{16}\{AuPPh_2(C_{16}H_{15})\}_2]$ and (bottom) the peak envelope corresponding to $[Ru_6C(CO)_{16}AuPPh_2(C_{16}H_{15})]^-$. (a) is the calculated model and (b) is the observed spectrum.

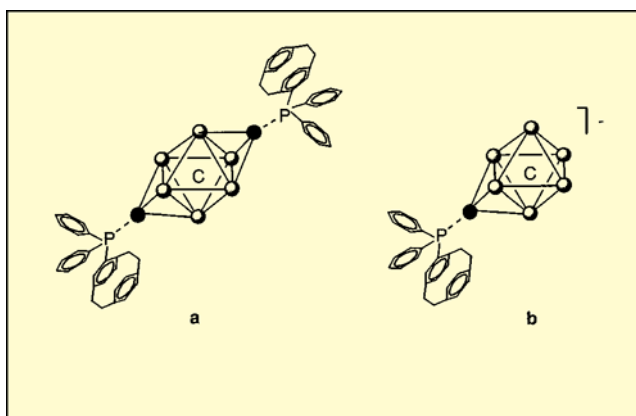


Figure 3 The proposed structures of
 (a) $[Ru_6C(CO)_{16}\{AuPPh_2(C_{16}H_{15})\}_2]$ and
 (b) $[Ru_6C(CO)_{16}AuPPh_2(C_{16}H_{15})]^-$: CO ligands
 have been omitted for clarity.

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ABOUT THE AUTHORS

Dr Dyson commenced his research career under the supervision of Professor Brian Johnson at The University of Cambridge working on the synthesis and characterization of ruthenium clusters. He moved with his supervisor to The University of Edinburgh where he completed his PhD. He then spent four years as a lecturer and Royal Society University Research Fellow at Imperial College, moving to The University of York in 1998. He also runs his own company, DMD Chiral Ltd, that is actively involved in the design and manufacture of chiral phosphine co-catalysts. Dr Bhalla obtained his PhD from the University of Manchester, moving to the University of East Anglia for a brief spell before moving to the University of York in 1997. Mr Lauterwasser is a student at Aachen University and spent a three month period in Dr Dyson's research group at the University of York. Dr McIndoe obtained his PhD at The University of

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