



Bimetallic cluster complexes: synthesis, structures and applications to catalysis

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Abstract

A brief history of the seminal discoveries in the field of bimetallic cluster complexes with discussion of their structures is presented. A review of some recent studies of palladium and platinum–ruthenium cluster complexes is included with a discussion of applications of these complexes in the area of homogeneous hydrogenation catalysis of alkynes.

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1. Introduction

Much of the motivation for the study of bimetallic cluster complexes today stems from the discoveries in the late 1960s that platinum catalysts alloyed with iridium, rhenium or tin exhibited properties that were far superior to those of their components in the important industrial process known as petroleum reforming [1]. Later, platinum–rhodium catalysts were shown to be the most effective catalysts for the oxidation of hydrocarbons, CO and simultaneous reduction of nitrogen oxides, NO_x. Today, supported platinum–rhodium catalysts are the active component of the three-way automotive catalytic converter [2]. Recent studies have shown that platinum–ruthenium mixtures are the most effective catalysts for the oxidation of methanol, and are the catalyst of choice at the anode of the Direct Methanol Fuel Cell [3].

The structures of these heterogeneous catalysts are of considerable interest. Studies have shown that many are not uniform homogeneous solid solutions (i.e., true alloys), but on the contrary there is considerable evidence to show that they exhibit segregation of the metals by type within the catalyst particle themselves [4].

It is widely believed that bimetallic cluster complexes can be valuable precursors for supported bimetallic catalysts, because they contain intimately associated combinations of the metal components, their stoichiometries can be accurately controlled and may also provide better control of the size of the metal particles formed from them on supports [5]. In fact, recent studies have shown that when cluster complexes are used to generate nanoparticle catalysts on mesoporous supports unusually active hydrogenation catalysts are indeed formed [6]. These new catalysts represent one of the most promising frontiers for heterogeneous catalysis research today. In this review, we will present highlights of the development of *organo*-bimetallic cluster complexes. Inorganic bimetallic complexes and polynuclear metal complexes that do not contain metal–metal bonds will not be considered here. This review is not intended to be comprehensive.

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1.1. Bimetallic carbonyl complexes

Metal carbonyl anions were the first reagents used to prepare complexes containing heteronuclear metal–metal bonds. One of the first bimetallic transition metal carbonyl complexes was prepared by Hieber when he was studying the chemistry of $[\text{Co}(\text{CO})_4]^-$ in the 1930s. From the reaction of AgNO_3 with $\text{NaCo}(\text{CO})_4$, the air and light sensitive compound $\text{Ag}_4[\text{Co}(\text{CO})_4]_4$ was obtained [7]. The compound contains a planar Ag_4 core with a $\text{Co}(\text{CO})_4$ group bridging each of the four Ag–Ag atom pairs [8], see Fig. 1. The first compounds containing transition metal–gold and –copper bonds were obtained by Nyholm from reactions of metal carbonyl anions with gold and copper halides in 1964, the same year that Journal of Organometallic Chemistry was founded, e.g. $\text{PPh}_3\text{AuCo}(\text{CO})_4$, $\text{PPh}_3\text{AuMn}(\text{CO})_5$, $(\text{PPh}_3\text{Au})_2\text{Fe}(\text{CO})_4$, $\text{PPh}_3\text{AuV}(\text{CO})_6$, $(\text{triars})\text{CuV}(\text{CO})_6$ [9]. The first heteronuclear transition metal–transition metal carbonyl complexes appeared in the early 1960s. These included $\text{Cp}(\text{CO})_3\text{Mo–W}(\text{CO})_3\text{Cp}$ [10], $\text{Cp}(\text{CO})_3\text{Mo–Fe}(\text{CO})_2\text{Cp}$ [11], $(\text{CO})_5\text{Mn–Fe}(\text{CO})_2\text{Cp}$ [11] and $\text{Cp}(\text{CO})\text{Ni–Fe}(\text{CO})_2\text{Cp}$ [12]. These were also made by the metal carbonyl anion/halide displacement reactions. Vahrenkamp [13] showed some years later that these heterodinuclear compounds and many others can be made more conveniently by irradiation of mixtures of the appropriate homodinuclear compounds, e.g. UV irradiation of solutions containing $\text{Mn}_2(\text{CO})_{10}$ and $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ gives $(\text{CO})_5\text{Mn–Fe}(\text{CO})_2\text{Cp}$ in a good yield. The metal–metal bonds in these compounds can be viewed as covalent heteronuclear bonds derived from two 17 electron metal-containing fragments. Recently, Pomeroy et al. have prepared the first examples of mixed metal compounds containing heteropolar dative bonds, e.g. $(\text{CO})_5\text{W} \leftarrow \text{Os}(\text{CO})_4\text{PMe}_3$ [14] and $(\text{CO})_5\text{W} \leftarrow \text{Ir}(\text{CO})_2\text{Cp}$ [15], containing 16 electron and 18 electron metal-containing groups linked solely by the metal–metal bond.

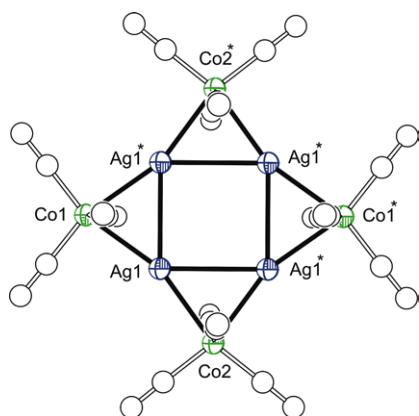


Fig. 1. The molecular structure of $\text{Ag}_4[\text{Co}(\text{CO})_4]_4$.

Chini [16] was one of the pioneers of the redox “condensation” reaction of metal carbonyl anions with uncharged metal carbonyl complexes for preparing higher nuclearity heteronuclear metal clusters. Working initially with Chini, Dahl and Longoni have developed this technique to a high level. Longoni’s nickel–platinum compounds: $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{44}]^{6-}$ (1) [17] and $[\text{Ni}_{37}\text{Pt}_4(\text{CO})_{46}]^{6-}$ (2) [18] are classic examples of metal segregated clusters that contain Pt_6 octahedral and Pt_4 tetrahedral cores inside octahedral and tetrahedral nickel shells, respectively, see Fig. 2. The Dahl group has recently reported the novel nickel–silver cluster anion $[\text{Ag}_{16}\text{Ni}_{24}(\text{CO})_{40}]^{4-}$ (3) that contains a metallic core of 16 silver atoms [19], see Fig. 3. Lewis and Raithby have created some remarkable high nuclearity metal-segregated ruthenium–copper complexes from reactions of ruthenium carbonyl cluster anions with $[\text{Cu}(\text{NCMe})_4]^+$, e.g. $[\text{Ru}_{12}\text{Cu}_6\text{Cl}_2(\text{CO})_{34}\text{H}_2]^{2-}$ (4) [20] and $[\text{Ru}_{20}\text{Cu}_6\text{Cl}_2(\text{CO})_{48}\text{H}_4]^{4-}$ (5) [21]. In these large anions a hexacopper cluster is situated between two ruthenium clusters, see Fig. 4.

1.2. Interstitial carbido ligands

Bridging carbon ligands have been used to assemble a variety of interesting heteronuclear metal cluster complexes. Metal carbonyl anions containing carbido ligands such as $[\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$ have been used to prepare hexanuclear metal clusters having octahedral arrangements of the six metal atoms with an interstitial carbido ligand in the center of the octahedron. Muettterties [22] and Shriver [23] were pioneers of this area in the 1970s, Eqs. (1) and (2). Mixed metal carbide cluster complexes with incomplete octahedra have been prepared by metal atom substitution, Eq. (3) [24].

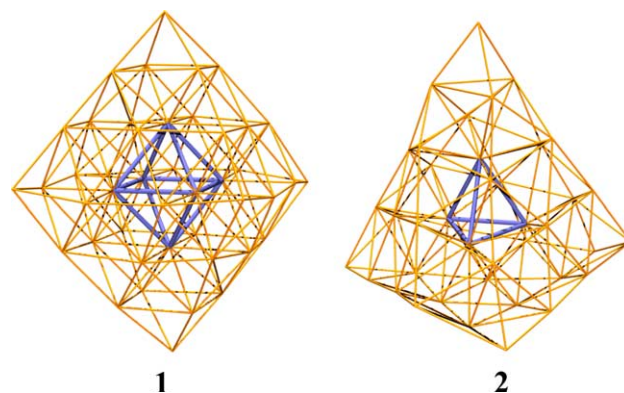


Fig. 2. Representations of the metal framework in $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{44}]^{6-}$ (1) and $[\text{Ni}_{37}\text{Pt}_4(\text{CO})_{46}]^{6-}$ (2). The octahedral Pt_6 and tetrahedral Pt_4 groups are shown in blue, and the frameworks of the Ni atoms are shown in orange. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

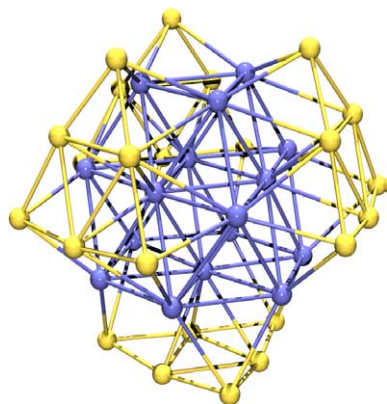
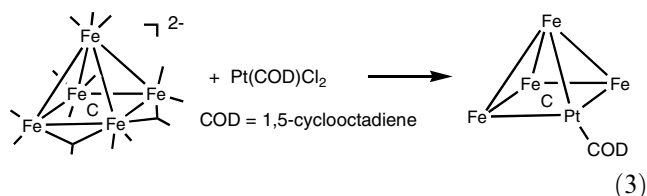
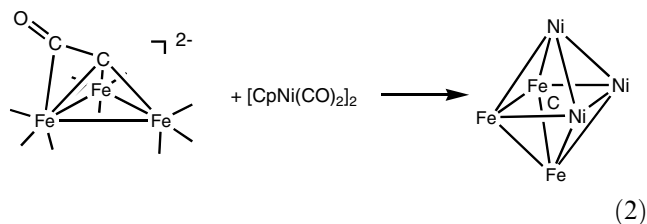


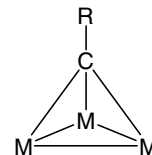
Fig. 3. The structure of $[\text{Ag}_{16}\text{Ni}_{24}(\text{CO})_{40}]^{4-}$ (3). Ag atoms are shown in blue and Ni atoms are shown in green. The CO ligands have been omitted for clarity.



Wakatsuki in Japan has synthesized some remarkable segregated high nuclearity ruthenium–palladium carbonyl complexes from carbido-ruthenium complexes. For example, the reaction of $[\text{Ru}_5\text{C}(\text{CO})_{14}]^{2-}$ with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ yielded the octadecanuclear cluster $\text{Pd}_8\text{Ru}_{10}\text{C}_2(\text{CO})_{27}(\text{C}_3\text{H}_5)_4$ (6), containing a Pd_8 cluster between two Ru_5C clusters, see Fig. 5 [25].

1.3. Bridging alkylidyne ligands

The alkylidyne ligand can conveniently bond to three metal atoms simultaneously.



Needless to say, this structure provides great opportunities to create mixed metal clusters. It has been fairly easy to add metal atoms to mononuclear metal reagents containing terminal alkylidyne ligands, such as $\text{CpW}(\text{CO})_2\text{CR}$, $\text{R} = \text{Me}, \text{Et}, \text{tolyl}$, as in the following equation [26].

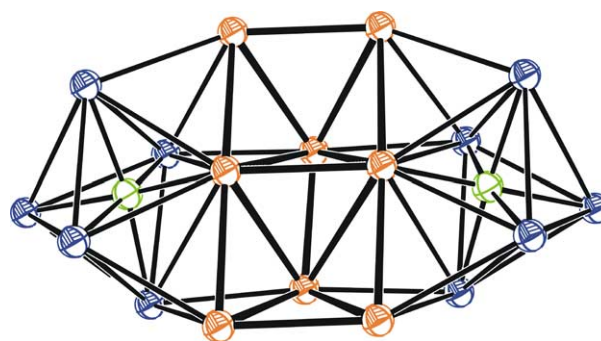


Fig. 5. The structure of the $\text{Pd}_8\text{Ru}_{10}\text{C}_2$ core of $\text{Pd}_8\text{Ru}_{10}\text{C}_2(\text{CO})_{27}(\text{C}_3\text{H}_5)_4$ (6). Pd (orange), Ru (blue), carbido C (green).

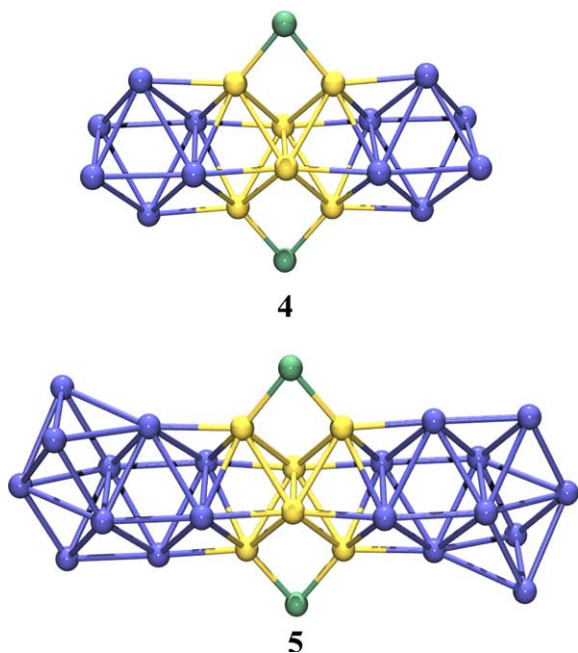
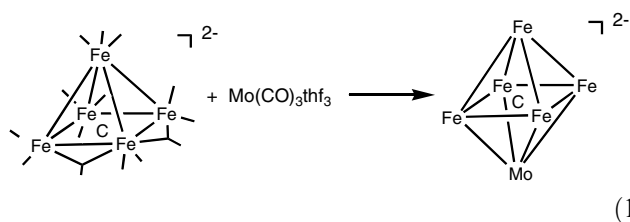
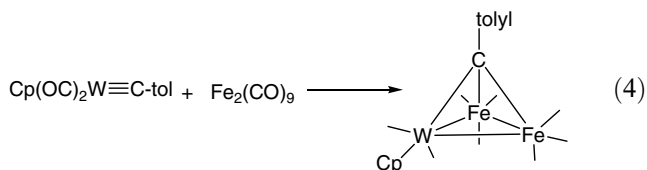
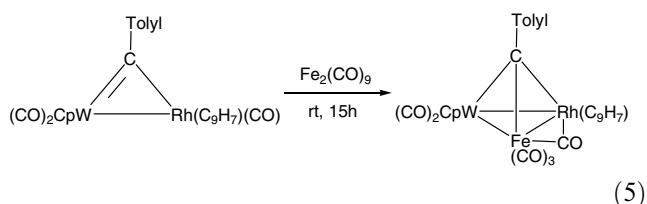


Fig. 4. The structures of $[\text{Ru}_{12}\text{Cu}_6\text{Cl}_2(\text{CO})_{34}\text{H}_2]^{2-}$ (4) and $[\text{Ru}_{20}\text{Cu}_6\text{Cl}_2(\text{CO})_{48}\text{H}_4]^{4-}$ (5). Ru (blue), Cu (yellow), and Cl (green). The CO and hydride ligands have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

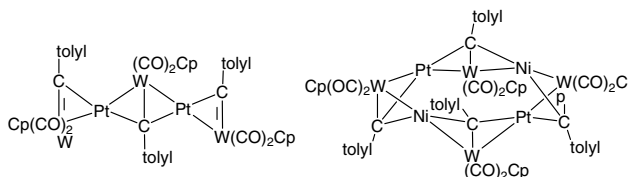




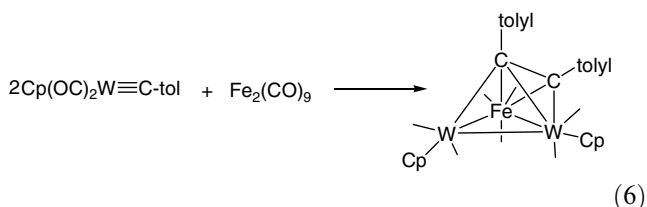
By using three different metal atoms, it is possible to prepare chiral molecules where the chirality is derived from the structure of the MM'M'C core, as in the following equation [27].



Stone was the pioneer of this field in the early 1980s and developed it into an art form by combining the “ligand-free” platinum [28] and nickel reagents with CpW(CO)₂CR to prepare novel oligomers and his famous “star” clusters [29,30].



When two alkylidyne ligands are introduced into the same molecule they will often couple to form a bridging alkyne ligand, as shown below [26].



Alkynes are effective ligands in metal cluster complexes because they can donate electrons to the metal atoms from both of their π -bonds and can simultaneously bond to several metal atoms through bridging coordination modes [31]. Because of this and their high unsaturation, alkynes have been the subject of a number of hydrogenation catalysis studies with metal cluster complexes, see below.

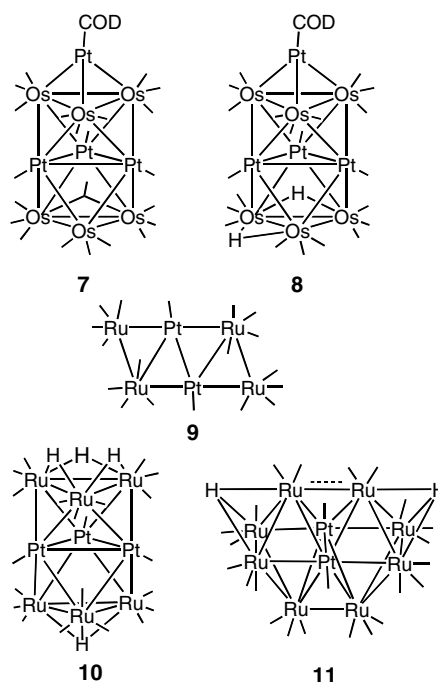
1.4. High nuclearity bimetallic clusters containing platinum or palladium combined with ruthenium or osmium.

A variety of new methods have been developed over the years for synthesizing mixed metal cluster complexes

[32]. Adams et al. have used the “ligand-free” platinum compounds championed by Stone to prepare a number of novel high nuclearity “layer-segregated” platinum–osmium and –ruthenium cluster complexes. For example, the reaction of Os₃(CO)₁₀(NCMe)₂ with Pt(COD)₂ yielded the pentanuclear bimetallic complex Pt₂Os₃(CO)₁₀(COD)₂ that condenses to the decanuclear bimetallic complex Pt₄Os₆(CO)₂₂(COD) (7) when heated. Compound 7 consists of three stacked triangular layers of metal atoms that alternate as Os₃Pt₃Os₃ with an additional PtCOD group capping one of the Os₃ triangles [33]. Treatment of Os₃(CO)₁₀(μ -H)₂ with Pt(COD)₂ yielded the pentanuclear bimetallic complex Pt₂Os₃(CO)₉(COD)₂(μ -H)₂ that condenses to the layer-segregated decanuclear dihydrido cluster complex Pt₄Os₆(CO)₂₁(COD)(μ -H)₂ (8) [34]. Compound 7 can be converted to 8 by treatment with hydrogen.

From the reaction of Ru(CO)₅ with Pt(COD)₂, the compound Pt₂Ru₄(CO)₁₈ (9) that has a two dimensional structure with two platinum atoms sandwiched between two Ru₂(CO)₈ groups, was obtained [35]. Compound 9 reacts with hydrogen to produce the layer-segregated cluster Pt₃Ru₆(CO)₂₁(μ_3 -H)(μ -H)₃ (10) that contains a triangular group of three platinum atoms sandwiched between to ruthenium triangles [36]. Compound 10 exhibits very interesting reactivity toward alkynes [37] and was shown to be a good catalyst of the hydrogenation of PhC₂Ph to *Z*-stilbene, see below.

Compound 9 condenses with the ruthenium cluster complex Ru₄(CO)₁₃(μ -H)₂ to yield the novel decanuclear bimetallic complex Pt₂Ru₈(CO)₂₃(μ -H)₂ (11) that contains two platinum atoms sharing a common edge of two fused metal octahedra [37].



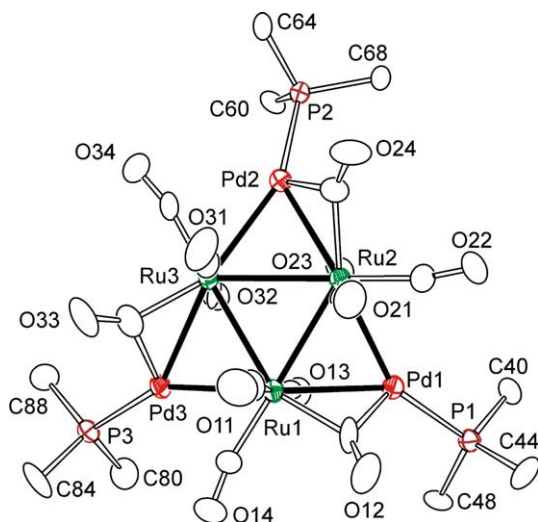


Fig. 6. An ORTEP diagram of $\text{Ru}_3(\text{CO})_{12}[\text{Pd}(\text{PBu}_3)_3]$ (**12**). The methyl groups have been omitted for clarity.

Recently, we have found that the platinum and palladium compounds, $\text{Pt}(\text{PBu}_3)_2$ and $\text{Pd}(\text{PBu}_3)_2$ that contain only two bulky PBu_3 ligands are excellent reagents for the addition of $\text{M}(\text{PBu}_3)$ groups to the metal–metal bonds of metal carbonyl complexes. For example, the reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{Pd}(\text{PBu}_3)_2$ yielded the tripalladated complex $\text{Ru}_3(\text{CO})_{12}[\text{Pd}(\text{PBu}_3)_3]$ (**12**), see Fig. 6 [38]. Reaction of $\text{Ru}_6(\text{CO})_{17}(\text{C})$ with $\text{Pd}(\text{PBu}_3)_2$ yielded the dipalladated hexaruthenium complex $\text{Ru}_6(\text{CO})_{17}(\text{C})[\text{Pd}(\text{PBu}_3)_2]$ (**13**), see Fig. 7 [38]. The reaction of $\text{Ru}_5(\text{CO})_{15}(\text{C})$ with $\text{Pd}(\text{PBu}_3)_2$ yielded both mono- and di-palladated pentaruthenium complexes $\text{Ru}_5\text{CO}_{15}(\text{C})[\text{Pd}(\text{PBu}_3)]$ (**14**) and $\text{Ru}_5\text{CO}_{15}(\text{C})[\text{Pd}(\text{PBu}_3)_2]$ (**15**) [39]. Several of the platinum homologues were obtained from the corresponding reactions with $\text{Pt}(\text{PBu}_3)_2$. All of these products are the result

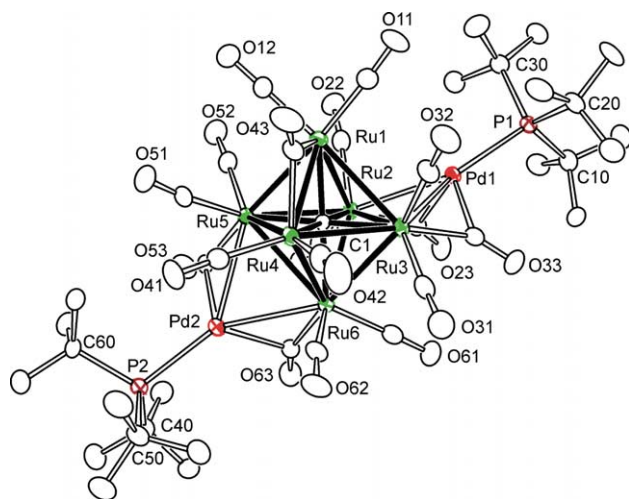
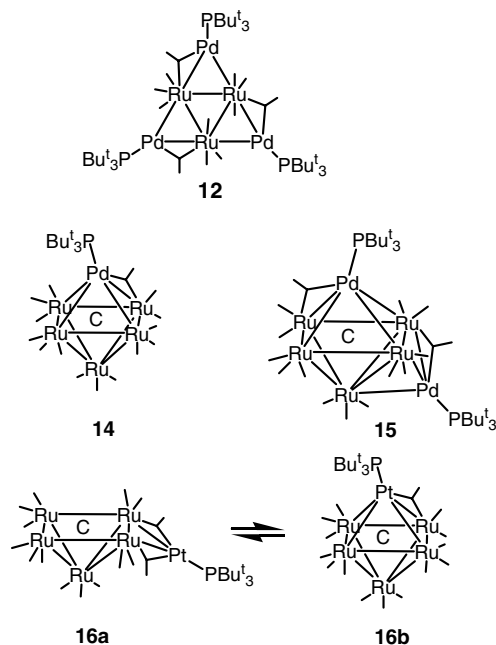


Fig. 7. An ORTEP diagram of the molecular structure of $\text{Ru}_6(\text{CO})_{17}(\mu_6\text{-C})[\text{Pd}(\text{PBu}_3)_2]$ (**13**).

of the addition of $\text{M}(\text{PBu}_3)$ groups to the ruthenium complexes. No ligands were eliminated from the ruthenium carbonyl complexes. The electron deficient $\text{M}(\text{PBu}_3)$ group is added to a ruthenium–ruthenium bond, and delocalized three center–two electron bonds are formed [40]. In all of these complexes, some of the carbonyl ligands adopt bridging coordinations to help to stabilize some of the heterometallic bonds.



Compounds **14**, **15** and the platinum homologue of **14**, $\text{Ru}_5(\text{CO})_{15}(\text{C})[\text{Pt}(\text{PBu}_3)]$ (**16**) exhibit interesting dynamical activity. Compounds **14** and **16** exist as two structural isomers, **16a** and **16b**. One contains an open cluster in which the $\text{M}(\text{PBu}_3)$ group bridges an edge of the square pyramidal Ru_5 cluster and the second has a closed structure in which the $\text{M}(\text{PBu}_3)$ group is positioned across the square base of the Ru_5 cluster. Interestingly, these two isomers interconvert rapidly on the NMR time scale. The rate of interconversion is 24,000 times/s at room temperature for **16** [39]. Compound **15** exhibits a similar dynamical activity in which the two $\text{Pd}(\text{PBu}_3)$ groups are interchanged.

1.5. Catalytic activity of bimetallic clusters containing ruthenium

Muetterties was one of the early advocates of homogeneous catalysis by metal cluster complexes [41]. There has been progress in research in this area [42], but in general the activity of the complexes is low compared to heterogeneous catalysts and mononuclear metal homogeneous catalysts. However, low activity can lead to improvement in reaction selectivities. There were some early reports that some bimetallic complexes

exhibited some enhanced activity as homogeneous hydrogenation catalysts relative to that of the individual components [43]. The term *synergism* is applied often without implying mechanistic details whenever such enhancements were identified. Ugo and Braunstein were among the first to study the catalytic hydrogenation of carbon–carbon multiple bonds by bimetallic complexes containing platinum, but the activities were low [44].

We found that the layer-segregated nine metal cluster **10** readily reacts with PhC_2Ph to yield the alkyne complex $\text{Pt}_3\text{Ru}_6(\text{CO})_{20}(\mu\text{-PhC}_2\text{Ph})(\mu\text{-H})_2$ (**17**) by displacement of one CO ligand and elimination of two of the four hydride ligands [36]. The PhC_2Ph ligand assumed a triply bridging position on one of the ruthenium triangles, see Fig. 8. The two hydride ligands that were eliminated were transferred to a second molecule of PhC_2Ph to yield *Z*-stilbene. When **17** was treated with CO, its two hydride ligands were transferred to the PhC_2Ph ligand and to form a second equivalent of *Z*-stilbene. Interestingly, it was possible to isolate an intermediate from this reaction in which only one of the two hydride ligands was transferred to the PhC_2Ph ligand. This compound $\text{Pt}_3\text{Ru}_6(\text{CO})_{21}(\mu\text{-PhCC(H)Ph})(\mu\text{-H})$ (**18**) contained a 1,2-diphenylvinyl ligand coordinated to an edge of the ruthenium triangle and the two phenyl rings had the *cis*-stereochemistry, see Fig. 9. Accordingly, compound **17** was tested for catalytic hydrogenation activity.

When **17** was treated with 100 equivalents of PhC_2Ph under hydrogen (at 1 atm) at 50 °C, *Z*-stilbene was formed catalytically at a rate of 47 turnovers/h [45]. Considerable efforts were made to characterize the

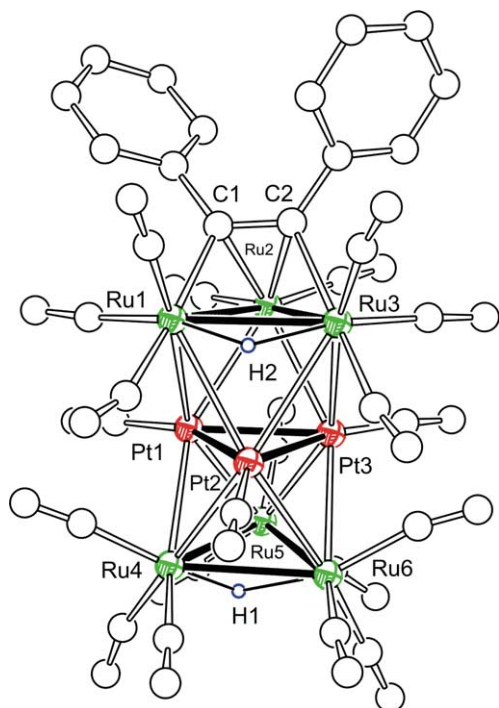


Fig. 8. An ORTEP diagram of $\text{Pt}_3\text{Ru}_6(\text{CO})_{20}(\mu\text{-PhC}_2\text{Ph})(\mu\text{-H})_2$ (**17**).

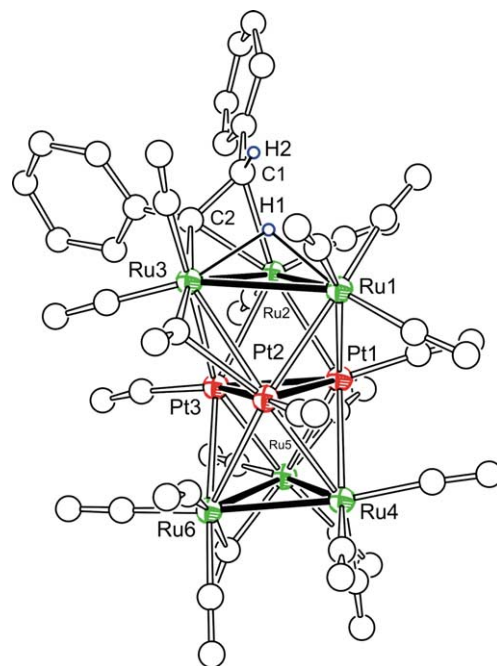


Fig. 9. An ORTEP diagram of $\text{Pt}_3\text{Ru}_6(\text{CO})_{21}(\mu\text{-PhCC(H)Ph})(\mu\text{-H})$ (**18**).

mechanism of the catalysis by this complex. The rate of the reaction was determined to be: first order in the concentration of cluster complex, first order in the concentration of alkyne and first order in the concentration of hydrogen. The catalysis was inhibited by CO. Labeling studies using D_2 and ToIc_2ToI further confirmed that the cluster complex was the true catalyst.

The catalytic cycle that was developed is shown in Fig. 10. The first step is believed to involve the dissociation of a CO ligand from the electronically saturated complex **17** to provide a “vacant” site for the activation of hydrogen in the next step. This step would explain the inhibition by CO. The site of hydrogen activation could not be established. Ligand substitution studies on **17** showed a preference for CO ligand replacement on the ruthenium atoms containing the bridging PhC_2Ph ligand [46]. Thus, it seems reasonable to assume that hydrogen activation also occurs at one of these ruthenium sites. The next step is addition of another molecule of PhC_2Ph . This probably occurs at the ruthenium triangle containing the originally coordinated PhC_2Ph ligand. As with the CO addition, see above, this induces the sequential shift of two hydride ligands to the initially coordinated PhC_2Ph ligand which is subsequently expelled as *Z*-stilbene and replaced by the added PhC_2Ph molecule that was added. This completes and closes the catalytic cycle so that the reaction can proceed a second time. Although compound **17** is one of the most active cluster based alkyne hydrogenation catalysts reported to date, it is, unfortunately, not long lived. After only a few hundred turnovers, it is nearly completely degraded to other complexes. Several of these

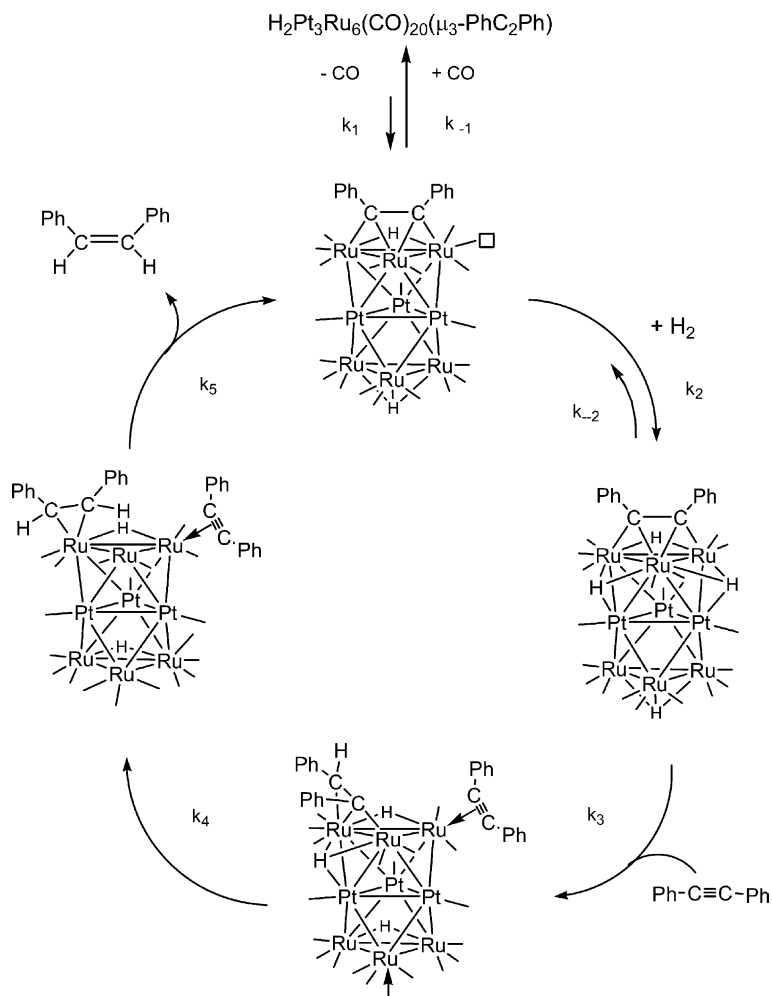


Fig. 10. A proposed catalytic cycle for the hydrogenation of PhC₂Ph by the bimetallic cluster complex **17**.

degradation products were isolated and characterized. These products also exhibited some activity for catalytic hydrogenation of PhC₂Ph, but the activity was much lower than that of **17**.

For comparison, the triruthenium complex Ru₃(CO)₉(μ₃-PhC₂Ph)(μ-H)₂ (**19**) was also tested for PhC₂Ph hydrogenation catalysis. It is indeed active, but its activity is far less than that of **17**. It appears that the platinum in **17** does enhance the catalytic activity relative to **19** although there is no evidence for direct participation of the platinum in the actual mechanism [46]. Compound **17** is also an effective catalyst for the hydrosilylation of PhC₂Ph by HSiEt₃ to *E*-[(1,2-diphenyl)ethenyl]triethylsilane [47].

Süss-Fink and co-workers [48] prepared the iridium–triruthenium complex IrRu₃(CO)₁₃(μ-H) (**20**) that also exhibited high activity for the catalytic hydrogenation of PhC₂Ph, but the main product was *E*-stilbene. Alkyne complexes of **20** were isolated, but these were reported to have slightly lower activity than **20** itself. Catalytic cycles involving the “intact” cluster were proposed.

Recently, we have undertaken an investigation of the catalytic activity of compound **16** toward a combination of PhC₂H and hydrogen [49]. Compound **16** reacts with PhC₂H to yield the product Ru₅(CO)₁₃(μ₅-C)(PhC₂H)[Pt(PBu₃)₃] (**21**), see Fig. 11, that consists of a platinum capped square-pyramidal carbido-pentarruthenium cluster. A PhC₂H ligand bridges one of the PtRu₂ triangles and a PBu₃ ligand is coordinated to the platinum atom. When **21** was treated with hydrogen (30 psi) in the presence of a 50-fold excess PhC₂H at 80 °C, the hydrogenated product, styrene, was obtained catalytically at a rate of 20(2) turnovers/h. From the reaction solutions, the bimetallic cluster complex, Ru₅(CO)₁₂(μ₅-C)[Pt(PBu₃)₃](PhC₂H)(μ-H)₂ (**22**) was isolated. Compound **22** was characterized crystallographically and an ORTEP diagram of its structure is shown in Fig. 12. Compound **22** contains a platinum-capped Ru₅ cluster, but the Ru₅ cluster is not a square-pyramidal cluster as in **16** or **21**, but instead, one of the Ru–Ru bonds in the Ru₅ cluster was cleaved. The reason for this cleavage is not clear. Compound **22** contains a PhC₂H ligand that bridges a PtRu₂ triangle

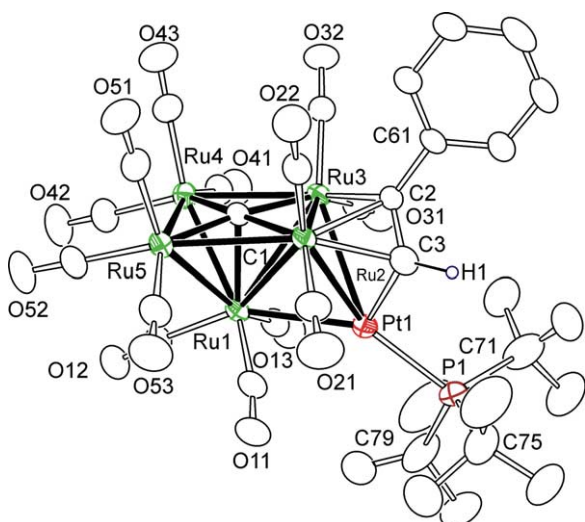


Fig. 11. An ORTEP diagram of $\text{Ru}_5(\text{CO})_{13}(\mu_5\text{-C})(\text{PhC}_2\text{H})[\text{Pt}(\text{PBu}_3)]$ (**21**).

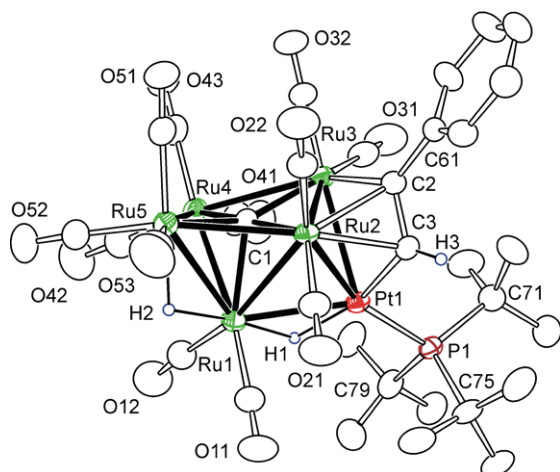
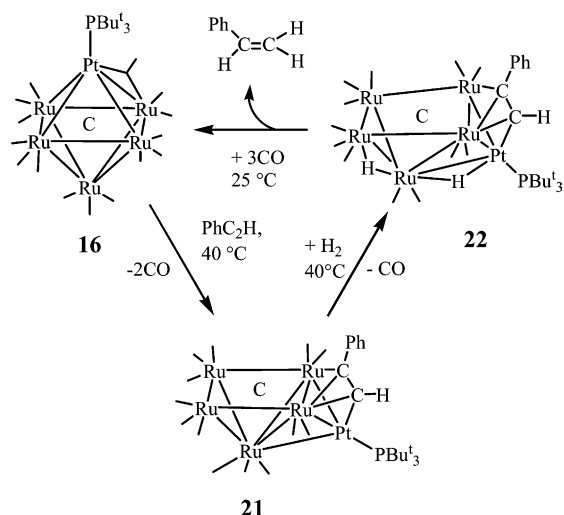


Fig. 12. An ORTEP diagram of $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-C})[\text{Pt}(\text{PBu}_3)](\mu_3\text{-PhC}_2\text{H})(\mu\text{-H})_2$ (**22**).

similar to that in **21**. Surprisingly, compound **22** was found to contain two hydride ligands. One bridges the Pt(1)–Ru(1) bond and the other bridges the Ru(1)–Ru(5) bond. These hydride ligands must have been derived from the addition of one equivalent of H_2 to the compound **21**. In the process one CO ligand was eliminated. When **22** was treated with CO at 25 °C, both hydrides and the PhC_2H ligand were eliminated in the form of styrene and compound **16** was formed, see Scheme 1. When solutions of **22** were treated with hydrogen and an excess of PhC_2H , styrene was formed catalytically, 21(2) turnovers/h, a rate comparable to that of **20**. Compound **22** appears to be an intermediate in the catalytic cycle. Interestingly, $\text{Ru}_6(\text{CO})_{17}(\mu_6\text{-C})$ does not produce styrene when treated with hydrogen and PhC_2H under similar conditions, so it appears that the platinum atom does play a key role in activating the cluster for catalysis. This is apparent from the observa-



Scheme 1.

tion that both the alkyne, PhC_2H , and one of the hydride ligands in **22** are bonded directly to the platinum atom. Further studies to establish the mechanism of the catalytic process are in progress.

Recent studies have shown that compound **9** produces metal segregated nanoclusters on supports when the ligands are removed [4c–4e]. The greatest potential for applications of the bimetallic complexes seems to be in the area of heterogeneous catalysts. By preparing the bimetallic complex before deposition on a support, one has a greater degree of control over composition than by mixing measured amounts of solutions or solid samples of the components. With the advent of nanoporous supports, it may now be possible to put these clusters on supports that will minimize their redistribution and sintering when the ligands are removed. This will, in turn, provide greater degree of tuning and control of the catalytic activity. Thomas has already shown that a variety of bimetallic cluster complexes containing ruthenium including carbide containing platinum–ruthenium complexes similar to **16** are precursors to highly active hydrogenation catalysts when placed on nanoporous supports [6,50].

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