Journal of Organometallic Chemistry, 400 (1990) 321–340
Elsevier Sequoia S.A., Lausanne
JOM 21149

A quarter-century of organometallics—most of it down-under

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(Received June 8th, 1990)

I thank the Editors for the invitation to describe some of the events that have given me pleasure and satisfaction during my career. I shall only briefly describe my early studies, many of which have been summarised in other places. However, I think that the paths by which I have become involved in my present activities may be of interest, and I shall describe some recent results. My interest in organometallic chemistry had been first aroused by a lecture I heard from Gordon Stone when I was in my Honours Year at Oxford. In it he described the work that he had been carrying out at Harvard during the late fifties, and my supervisor, Luigi Venanzi, had also been active in the area with Chatt. However, my studies at the time were confined to syntheses and reactions of polyarsine ligands such as TAs and QAs.

An opportunity to study in this area for myself did not arise until after my return to the U.K. from my first stint in Canberra, Australia, where I had been working in CSIRO's Division of Plant Industry on plant cell-division initiators (cytokinins). As well as working on these hormones from a natural source [1], I discovered a new class of synthetic cytokinins, the 1,3-diarylureas [2]. During my time in Canberra, however, I had read widely about organometallics, and I determined to enter this field. Consequently, I was pleased when I was accepted for a Ph.D. at Bristol.

Bristol days

There I started work alongside Peter Jolly on nucleophilic substitution of various fluorocarbons with metal carbonyl anions [3]; I concentrated on the newly available polyfluoroaromatic compounds which were produced by Imperial Smelting just up the road at Avonmouth [4]. I became interested in extending the scope of the carbonyl anions as reagents, and proposed that we begin a study of the ruthenium analogue of the very reactive $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ anion. An attractive route to $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2$ appeared to be the reaction of $[C_5H_5]^-$ with $\{RuCl_2(CO)_2\}_n$, for which the literature preparation involved passing CO over $RuCl_3$ heated in a glass tube. While this worked, it also gave a ruthenium-plated tube! Fortunately I happened to read the paper by Collman and Roper [5] about the synthesis of

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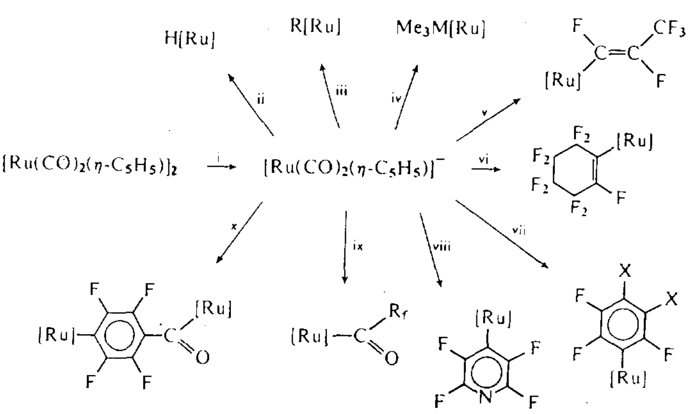
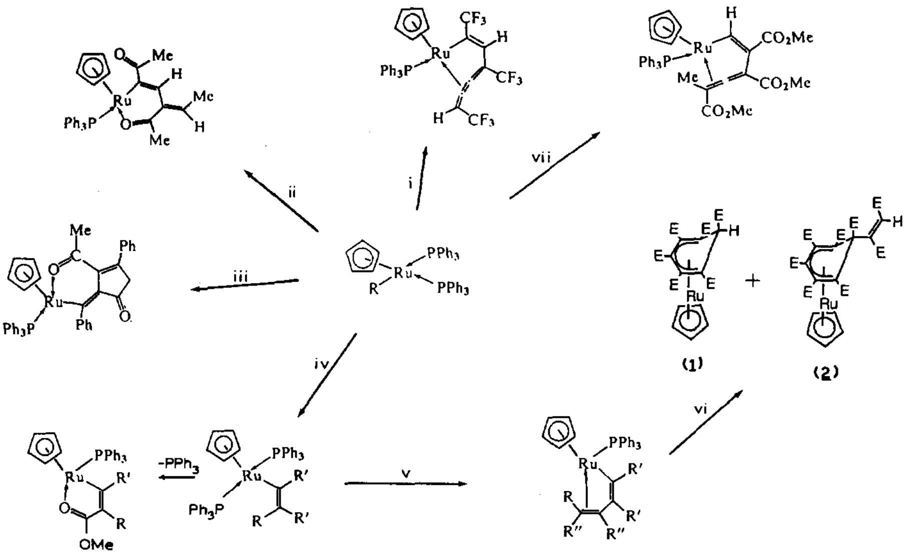


Scheme 1. [Ru] = $Ru(CO)_2(\eta\text{-}C_5H_5)$. Reagents: (i) Na/Hg, THF; (ii) H_3PO_4; (iii) RX; (iv) Me_3MX (M = Si, Ge); (v) $CF_3CF{=}CF_2$; (vi) perfluorocyclohexene; (vii) $C_6F_4X_2$ (X = F, CN); (viii) C_5F_5N; (ix) R_fCOCl ($R_f = CF_3$, C_3F_7); (x) C_6F_5COCl.

$Ru(CO)_3(PPh_3)_2$, where they described the carbonylation of $RuCl_3$ in methanol solution. Further examination of this reaction showed that not only was $\{RuCl_2(CO)_3\}_2$ formed in high yield, but that part of the ruthenium was always present as well-formed orange crystals. The original work with $Ru(CO)_2(\eta\text{-}C_5H_5)$ derivatives was carried out with Tim Blackmore, but proved rather uninteresting, largely duplicating the results obtained with the iron analogue (Scheme 1) [6].

Contemporary chemistry suggested that an increase in reactivity should be obtained if the CO groups were replaced by PPh_3. Attempts to carry this out with a variety of $Ru(CO)_2(\eta\text{-}C_5H_5)$ precursors gave only complexes containing one CO

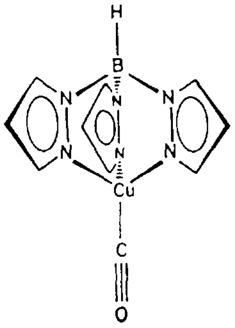


Scheme 2. E = CO_2Me. Reagents: (i) HC_2CF_3 (R = Me); (ii) HC_2CO_2Me (R = Me); (iii) PhC_2CO_2Me (R = Me); (iv) $C_2R'_2$ (R = H, Me; R' = CF_3, CO_2Me); (v) $C_2R''_2$ (R = H, Me; R', R'' = CF_3, CO_2Me); (vi) $C_2(CO_2Me)_2$ (R = H, R' = R'' = CO_2Me); (vii) HC_2CO_2Me (R = H).

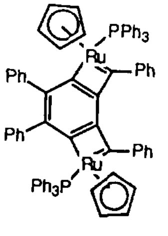
and one PPh_3 ligand. We considered replacing one of the chlorines in $RuCl_2(PPh_3)_3$ by a cyclopentadienyl group, and used TlC_5H_5; meanwhile Wilkinson had published the synthesis of the desired compound by direct reaction between $RuCl_2(PPh_3)_3$ and C_5H_6 [7]. Our initial studies led to a description of the basic chemistry of the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ system, including the ready loss of a PPh_3 ligand [8]. Of most interest, perhaps, were the unusual alkyne dimerisation and oligomerisation reactions which occurred in reactions with the hydride or alkyls; complexes containing vinyl, butadienyl and cumulenyl ligands were discovered during the studies carried out by Blackmore and Richard Gardner [9]. More recently, we have shown that the mononuclear ruthenium system acts as a centre for unusual tri- and tetra-merisation of $C_2(CO_2Me)_2$ to give the η^5-cyclohexadienyl complexes **1** and **2** (Scheme 2) [10].

The orange crystals, mentioned above, turned out to be $Ru_3(CO)_{12}$. In the usual carbonylation of $RuCl_3$, they were obtained in up to 18% yield, which became nearly quantitative in the presence of zinc as a halogen acceptor, with very moderate pressures of CO (reported as 10 atm, but in reality just enough to move the needle off the rest in the pressure dial). After this synthesis was first reported [11], several workers reported having difficulties with it. For a time we kept Alfa supplied with the carbonyl, but after the patent was issued [12], they found an alternative route. Subsequently, a detailed investigation of the reaction conditions showed that the zinc was unnecessary if the CO pressure was increased to about 50 atmospheres [13]. Some preliminary investigations of its chemistry were carried out, together with that of $Os_3(CO)_{12}$, which had been made by Nyholm's group at about the same time [14].

While at Bristol, my other interests centred around cyclometallation reactions (Zafar Iqbal and Brian Goodall) [15] and mass spectrometry of organometallics, which were carried out with the then newly installed MS9 spectrometer [16]. But perhaps the most satisfying chemistry was that centred around the reactions of the Group 11 metals. Following a visit by Jerry Trofimenko, we considered the possibility of stabilising a copper carbonyl by having a polypyrazolylborate ligand on the copper. In one of the simplest experiments I have ever done, I bubbled CO into a solution containing $K[HB(pz)_3]$ and CuCl; evaporation and hexane extraction gave a colourless solution which showed a single $\nu(CO)$ band at 2083 cm^{-1}, from



(**3**)



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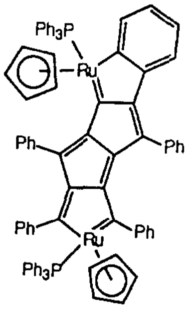
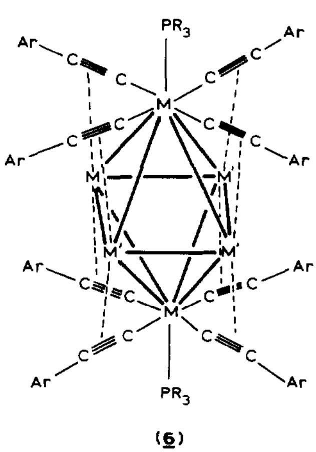


(5)

which could be isolated the stable, white crystalline $Cu(CO)\{(pz)_3BH\}$ (3) [17]. Extension to tetrapyrazolylborates gave a series of fluxional derivatives which occupied Omar Abu Salah for the first part of his thesis work [18].

At the same time I became interested in the reactions of transition metal acetylide complexes. Looking for a route to these compounds, the reactions of copper and silver acetylides with metal halide complexes were studied. These investigations gave the first η^2-alkyne complex of copper(I) in the reaction between CuC_2Ph and $FeCl(CO)_2(\eta\text{-}C_5H_5)$: the product, containing an η^2-bonded $PhC_2Fe(CO)_2(\eta\text{-}C_5H_5)$ ligand, opened the way to the synthesis of many more such derivatives [19]. The preparation of silver analogues was sometimes thwarted by oxidation, as occurred in the reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and AgC_2Ph, which afforded the remarkable dimetallapolycyclic complexes **4** and **5** by tetra- and penta-merisation of the C_2Ph residues. Abu Salah also looked at the reactions with Vaska's complex and the rhodium analogue, which afforded unusual cluster complexes (6) containing octahedral $M_2M'_4$ cores ($M = Rh$, Ir; $M' = Cu$, Ag) [20]. Analogous complexes containing platinum were described earlier this year [21].



(6)

A move to Australia

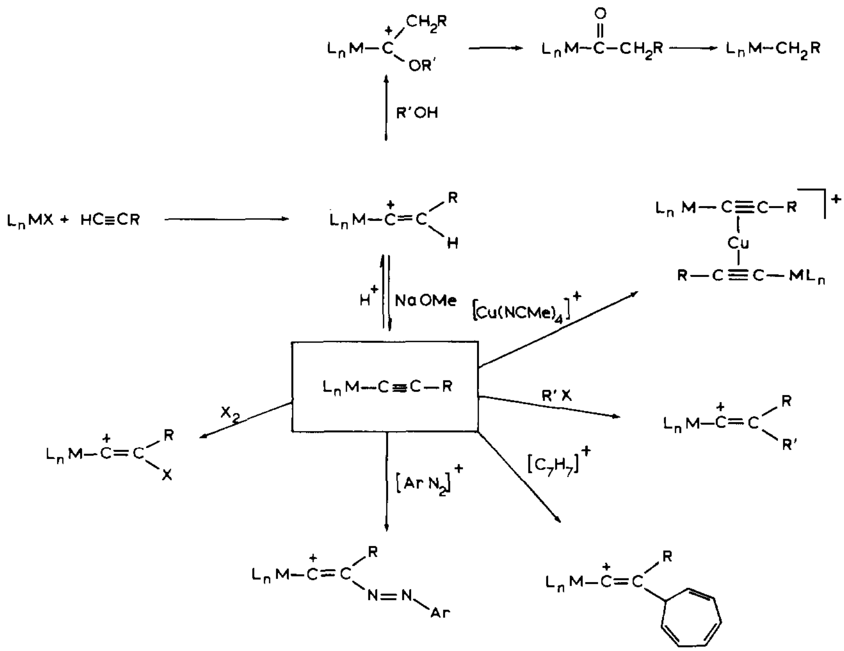
My appetite for Australia had been whetted by my first stay in Canberra, and when the Chair at Adelaide was vacated by the late Don Stranks's move to Melbourne, Gordon Stone enthusiastically supported my decision to apply for it. In December 1973, I packed my belongings and moved with my family to Adelaide, perhaps the most English of Australian cities—it also boasts of being the Athens of the South, has a very successful biennial festival, and enjoys a Mediterranean climate. Another attraction was the conveniently close location to four areas in which over half Australia's wine production is centred.

After my arrival, the first area that I concentrated on was an extension of the $Ru(PR_3)_2(\eta\text{-}C_5H_5)$ work, for which a new synthesis was required. After a little time, Neville Windsor found that $RuCl_3$ could be converted quantitatively to $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ by adding a methanol solution containing the chloride and cyclopentadiene to one of PPh_3; after two hours, orange crystals of the chloride separated on cooling. This reaction could be run on a large scale (25 g) and gave a product that could be used directly [22]. Furthermore, exchange of PPh_3 for other phosphines could be achieved very simply.

Acetylides and vinylidenes

Our earlier studies on the reactivity of transition metal acetylides had convinced us that these were useful substrates for building up new cluster complexes. Bob Wallis was given the task of making $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ to extend this chemistry. In the course of this work he found that direct reaction with the chloride and 1-alkynes gave a cationic cherry-red (or claret!) complex containing an unusual isomer of the alkyne [23]. After some difficulties persuading our NMR colleagues that organometallic carbon resonances could be found as low as δ 350 ppm, and that these compounds required rather longer collection times than conventional organic molecules, observation of the characteristically low-field signal at δ 350 for the metal-bonded carbon enabled us to establish that our complexes contained the new vinylidene ligand. This is a tautomer of the alkyne which has a very short lifetime in the free state. Independently, both Russian and American groups had also discovered similar reactions [24]; the former were able to characterise manganese and rhenium complexes crystallographically. It was to be several years before we were able to obtain a crystalline sample of one of our complexes suitable for an X-ray study [25]. During attempts to purify these complexes, we also discovered that passage down a column of basic alumina caused an immediate colour change to bright yellow, deprotonation occurring to give the sought-after acetylide complexes, also in quantitative yield.

The chemistry of the vinylidene complexes was investigated by Geoff Swincer, who found their conversion to alkoxy(alkyl)carbene complexes when treated with alcohols and to the corresponding alkyls when water was added, a spontaneous elimination of PPh_3 occurring as the acyl carbonyl was eliminated to the metal centre (Scheme 3) [26]. The reprotonation of the acetylide to the vinylidene was accompanied by the finding that the acetylide group could also be alkylated, firstly by trialkyloxonium salts, and later by alkyl halides, by Mark Humphrey. This unusual chemical behaviour demonstrated the nucleophilicity of C_β of the acetylide, as shown theoretically by Kostic and Fenske [27].

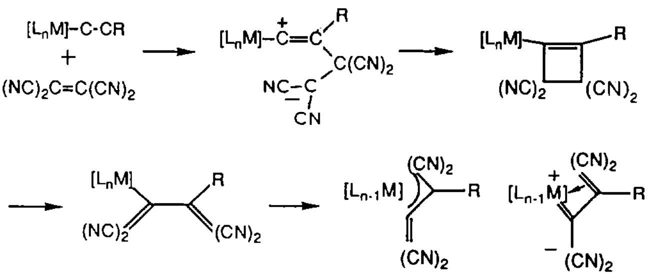


Scheme 3. L_nM typically (Fe, Ru, Os)$(PR_3)_2(\eta\text{-}C_5H_5)$.

More recently, Humphrey and George Koutsantonis have shown the reactivity of the acetylides towards electrophilic reagents could be extended to the tropylium cation, which afforded cycloheptatrienyl-vinylidene complexes, aryldiazo cations, giving aryldiazovinylidenes, and to halogens, which afforded halovinylidene complexes [28]. The latter reaction is surprising, since one might expect that the metal–carbon bond would be cleaved in this reaction.

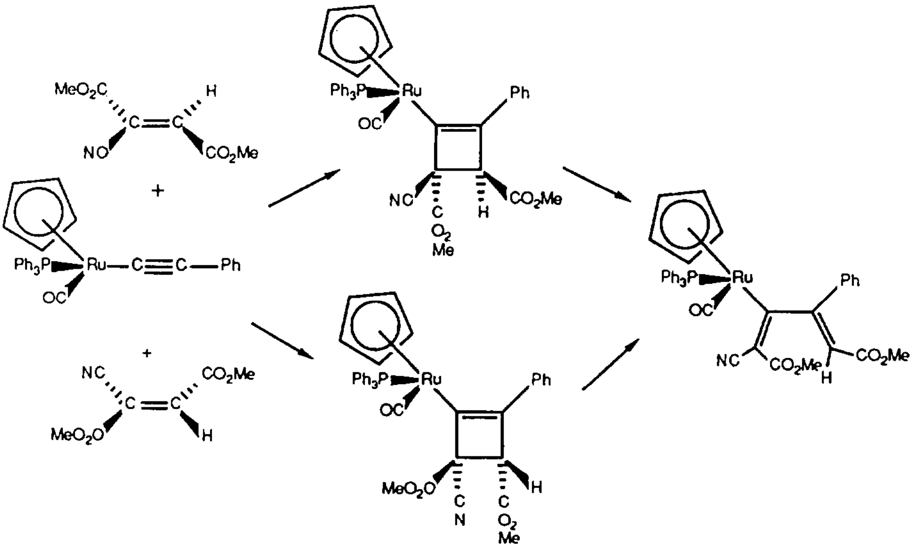
These reactions involved the addition of cationic substrates to the acetylides. The next step was extension to neutral electrophiles, particularly electron-deficient olefins and acetylenes. Consequently, Swincer examined the reaction of $C_2(CN)_4$ (tcne) with $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ and found the immediate formation of a dark-green solution, which faded over several hours with concomitant deposition of orange crystals. A structural determination showed the unusual allylic structure (**7**) (Scheme 4), in which the C=C double bond of the olefin has apparently been cleaved to form the new allylic ligand. Painstaking work over the next couple of years, involving a variety of transition metal acetylides, demonstrated that several steps were involved in this reaction [29]. The formation of the dark-coloured intermediate, which is paramagnetic and whose identity is still not completely clear, is followed by formal cycloaddition of the olefin to the acetylide to give a cyclobutenyl complex. More or less rapid ring-opening of this complex to a butadienyl derivative follows, and this can then chelate, with loss of CO or PPh_3, to form the allylic ligand. The structural and NMR parameters of the latter suggest that an appropriate formulation of this ligand is as a dipolar chelating vinylcarbene (**8**).

The ring-opening reaction is another example of the well-known cyclobutene → butadiene conversion studied by Woodward and Hoffmann. Michael Liddell con-



(7) (8)

Scheme 4. $[L_nM] = W(CO)_3(\eta\text{-}C_5H_5)$, $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$, $Ni(PPh_3)(\eta\text{-}C_5H_5)$.



Scheme 5

structed an appropriately substituted cyclobutenyl complex to determine the direction of ring-opening. The olefin $CH(CO_2Me){=}C(CN)(CO_2Me)$, available from the work of Roy Jackson and Patrick Perlmutter at Monash, added to the ruthenium acetylide to give two isomers of the trisubstituted cyclobutenyl (Scheme 5). These were crystallographically characterised as being the products of approach of the acetylide above and below the plane of the olefin. The butadienyl, which is formed by heating either of these complexes, was also studied crystallographically, and shown to be the product that would be expected from conrotatory ring-opening [30].

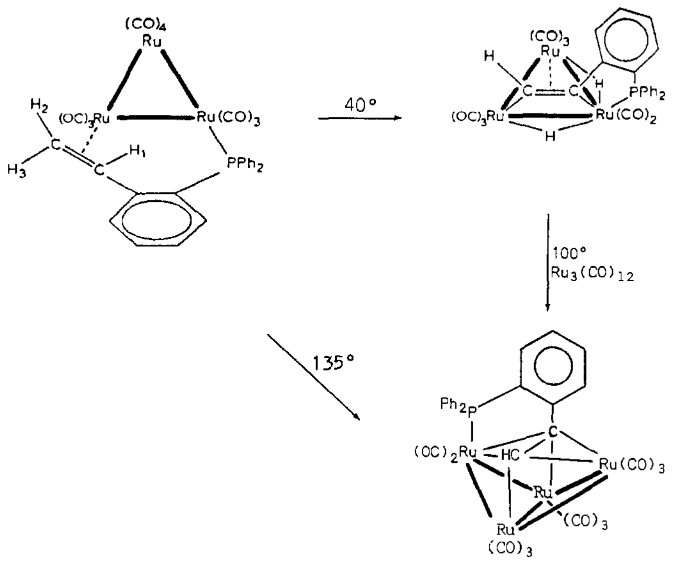
Cluster carbonyl substitution reactions

Another area of continuing interest has been that of cluster chemistry. One of the characteristics of the chemistry of ruthenium and osmium cluster carbonyls is that reactions occur at elevated temperatures, often sufficient to cause further reaction of the initial products. One of the most celebrated examples was the reaction of

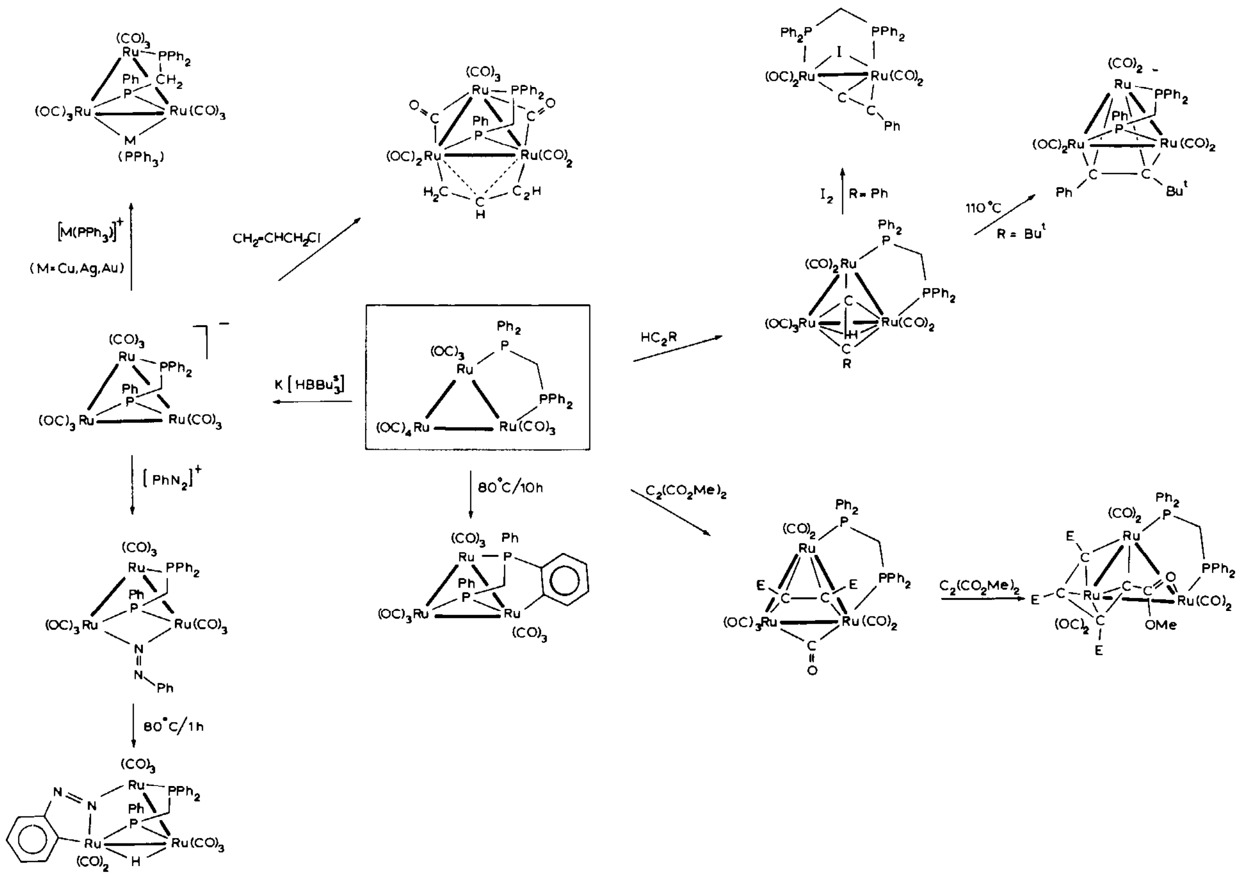
$Os_3(CO)_{12}$ with PPh_3, which afforded nine products, including not only the expected substitution products $Os_3(CO)_{12-n}(PPh_3)_n$ ($n = 1$–3) but also other clusters formed by various C–H, C–C and C–P bond breaking and forming reactions [31]. We were anxious to develop further the chemistry of $Ru_3(CO)_{12}$, and in the course of studying its reactions with isocyanides, Wallis found that $Ru_3(CO)_{11}(CNBu^t)$ could be obtained under mild conditions [13,32]. Subsequent reactions of this complex with tertiary phosphines, for example, afforded a readily separable mixture of $Ru_3(CO)_{11}(PR_3)$ and $Ru_3(CO)_{10}(CNBu^t)(PR_3)$ [33]. The way seemed open for us to develop this chemistry further.

At this time, however, we were fortunate to have Brian Nicholson, from the University of Waikato, staying with us for what turned out to be a very productive study leave. When he learnt of our desire to activate $Ru_3(CO)_{12}$ towards substitution under mild conditions, he reminded us of the results that other workers had achieved with electrochemical activation of substitution in binuclear complexes [34]. We decided to attempt the same type of reaction using chemical means, and accordingly tried these reactions using sodium diphenylketyl as a catalyst. We were overjoyed to find that the reactions went exceedingly well, in a minimum time, and apparently quantitatively at room temperature or below [35]. John Matisons then developed this reaction, making nearly seventy known and new tertiary phosphine and phosphite, and isocyanide substituted complexes of ruthenium, osmium, Co_3C and rhodium carbonyls [36]. A detailed study of the structures of more than 25 tertiary phosphine derivatives of $Ru_3(CO)_{12}$ was also carried out [37]. Particularly, the expansion of the cluster as larger and more PR_3 molecules coordinate has been established; the net electronic effects seem to be overshadowed by the steric influences of the ligands.

Having these derivatives to hand, we then decided to investigate their reactivity. One of the first to be studied was the complex $Ru_3\{\mu_3\text{-}PPh_2(C_6H_4CH{=}CH_2\text{-}2)\}$-



Scheme 6



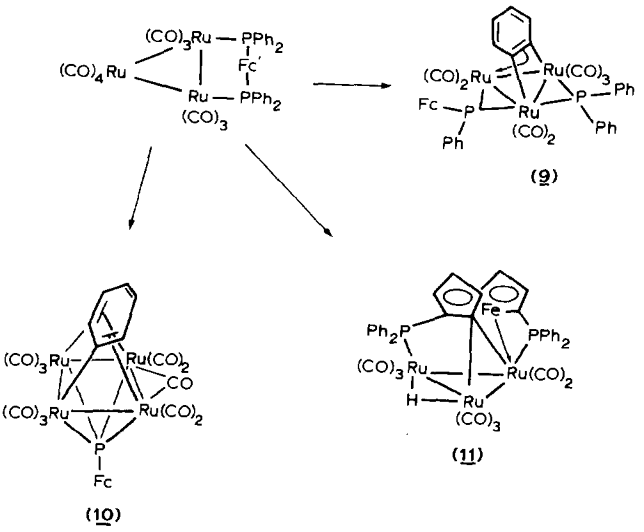
Scheme 7. E = CO$_2$Me.

$(CO)_{10}$, which incidentally was the first simple olefin complex of the ruthenium cluster to be isolated. Michael Williams found that this compound transformed very readily on warming to 40 °C (summer in Adelaide!) to the intramolecular oxidative adduct, $Ru_3(\mu\text{-}H)(\mu_3\text{-}HC{=}CHC_6H_4PPh_2)(CO)_9$, and on heating further, to the μ_4-alkyne derivative, $Ru_4(\mu_4\text{-}HC_2C_6H_4PPh_2)(CO)_{11}$ (Scheme 6) [38]. Thus the individual steps in the dehydrogenation of an olefin to an alkyne on a cluster were defined.

Much more chemistry was obtained in studies of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (Scheme 7). Attempts to deprotonate the coordinated dppm led instead to dephenylation: treatment with K-Selectride for 2–3 h afforded the anion $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$. Williams proceeded to derivatise this anion using a variety of electrophiles. Acidification afforded $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$, and not surprisingly, addition of sources of $M(PPh_3)$ (M = Cu, Ag, Au) gave the corresponding MRu_3 clusters. A crystallographic study of these showed for the first time the alternation of M–Ru distances in the clusters (Cu, 2.635; Ag, 2.787; Au, 2.769 Å) [39]. The anion was also sufficiently reactive to give the μ-allyl derivative with $CH_2{=}CHCH_2Cl$ and the aryldiazo complex with $[ArN_2]^+$ [40]. Some of these reactions were paralleled by the analogous dppe derivative, but these were much slower and gave lower yields.

Studies of the substitution reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$ have also provided an entry to some interesting chemistry. A feature of the reactions seems to be the isolation of products which, while having the same structures as those obtained from similar reactions of $Ru_3(CO)_{12}$, are obtained in much higher yield and more cleanly. Thus Paul Humphrey has found that reactions of alkynes give complexes also shown in Scheme 7; most of these have been crystallographically characterised [41]. Particularly interesting are the variety of C–C bond forming reactions that are found in these species, including an unprecedented transfer of a phenyl group from the phosphine to the cluster-bonded alkynyl group.

A period in Vancouver with Bill Cullen directed our attention to cluster com-

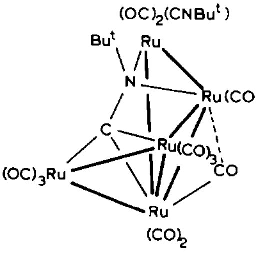


Scheme 8. Fc = $Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)$; Fc′ = $Fe(\eta\text{-}C_5H_4)_2$.

plexes of the ferrocene derivative dppf. In an attempt to stabilise the still elusive ferrocyne on a cluster, we studied the pyrolysis of $Ru_3(\mu\text{-dppf})(CO)_{10}$ (Scheme 8). As is often the case, a plethora of complexes was obtained, but painstaking work by Omar bin Shawkataly enabled most of the products to be isolated and crystallographically characterised. Products of C–H and C–P bond cleavage predominated, such as the purple μ_3-benzyne derivative (**9**), which was the end-product of several competitive degradations. The related tetranuclear derivative (**10**) was also found. The major product is an olive-green complex (**11**) which contains an unusual Fe–Ru interaction [3.098 Å] which appears to be forced by the conformation adopted when one of the C_5 rings is metallated [42].

Pentanuclear ruthenium clusters

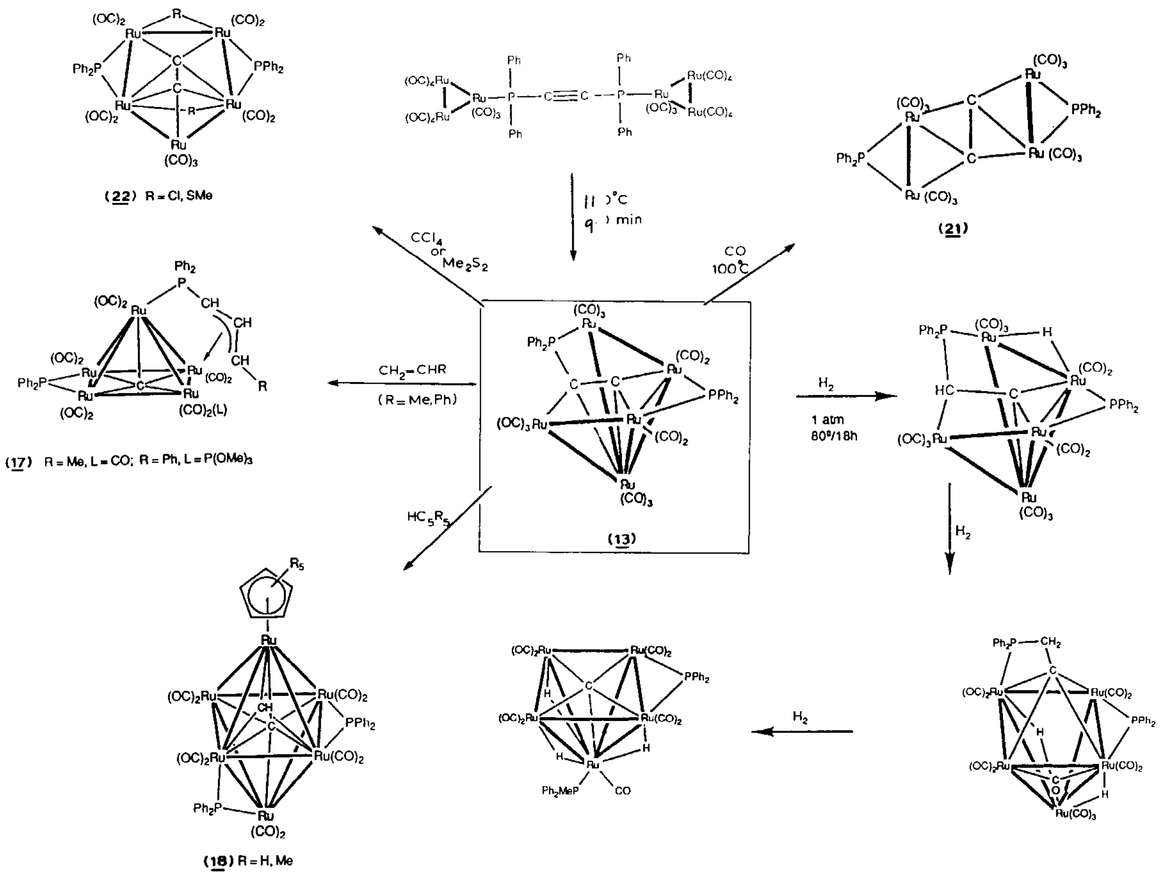
An early finding was the ready thermal condensation of $Ru_3(CO)_{11}(CNBu^t)$ to the pentanuclear cluster, $Ru_5(\mu_5\text{-CNBu}^t)(CO)_{14}(CNBu^t)$ (**12**), containing a new arrangement of metal atoms which we christened the 'swallow'—others have used the term 'edge-bridged butterfly' [43]. The metal skeleton can be obtained by formal cleavage of two metal–metal bonds of a *closo*-trigonal bipyramidal core. Unfortunately, yields of this interesting complex are not sufficient to allow a detailed examination of its chemistry, although further pyrolysis is known to afford the hexanuclear $Ru_6C(CO)_{16}(CNBu^t)$ [44].



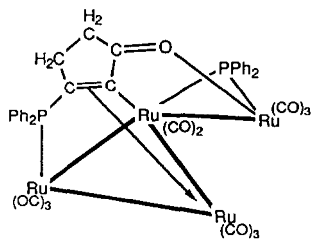
(**12**)

A desire to prepare higher nuclearity clusters of ruthenium suggested that thermal condensation of $\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})$ (dppa = $C_2(PPh_2)_2$) might achieve such an objective. Williams found that heating this 'binuclear' cluster in cyclohexane resulted in the formation of black $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**13**) in over 80% isolated yield (Scheme 9) [45]. We have been involved in a detailed investigation of the reactivity of this cluster, which also contains a swallow cluster; the carbon atoms of the C_2PPh_2 ligand occupy a cavity formed by the five metal atoms, and the multi-site attachment results in a high reactivity of this fragment. Thus, hydrogenation of **13** proceeds stepwise to give sequential addition of three molecules of hydrogen, which add one atom each to the cluster and to C_α, to give vinylidene and methylidyne complexes, and finally cleavage of the C≡C bond to methyl and carbon [46]. I have recently summarised much of this chemistry [47], so I will confine my attention to some more recent results.

Addition of unsaturated molecules to the C_2 fragment often proceeds with concomitant incorporation of CO in three-component assemblies facilitated by the metal cluster. For example, ethene gave **15** and 1,3-butadiene afforded the open Ru_4 complex (**16**). In these examples, the PCC unit present in **13** is preserved. However,


(22) R = Cl, SMe
11)°C
q) min
CCl4 or Me2S2
CO 100°C
(21)
CH2=CHR
(R = Me, Ph)
(17) R = Me, L = CO; R = Ph, L = P(OMe)3
(13)
H2
1 atm
80°/18h
H2
HC5R5
H2
(18) R = H, Me

Scheme 9



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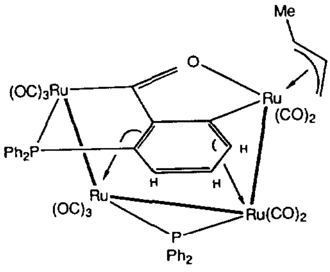

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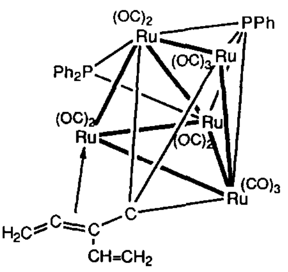

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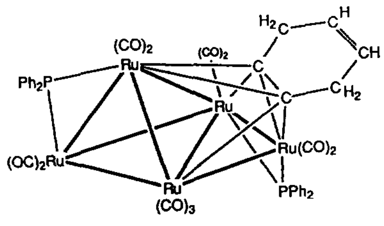
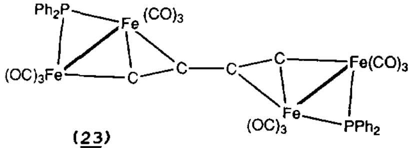


(20)

instances of C–C bond cleavage have also been found, such as in the formation of the well-known Ru_5C and Ru_6C clusters found in **17** and **18**, which were obtained from reactions between **13** and mono-olefins or cyclopentadienes, respectively. In the former, the hydrocarbon has added to C_β to give bridging allyl or diene systems. Finally, **13** appears to be a source of the C_2 fragment, which can be identified in several derivatives; cleavage of the P–C_β bond occurs at some stage in these complex reactions. Examples of this type of reaction include the formation of the $C_2(C_2H_2)(C_2H_3)$ ligand found in **19** (from **13** and ethene) and the cyclohexenyne derivative (**20**) obtained from butadiene.

These observations, together with the facile cleavage of P–C(*sp*) bonds known to occur on cluster complexes, as shown, indeed, by the synthesis of **13**, prompted us to search for clusters containing C_n ligands. This was first achieved in the present case by heating **13** under CO, when $Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$ (**21**) was obtained [48]. The C_2 fragment in this complex behaves as a bridging ethynyl dianion, being σ-bonded to one of the Ru atoms in each Ru_2 unit, and π-bonded to the other Ru atoms. Of interest is the RuC_2 dihedral angle of ca 168°, compared with ca 90° in the well-known $Co_2(\mu\text{-}C_2R_2)(CO)_6$ complexes [49].

Reactions of **13** with sources of 3e donor ligands result in further opening of the Ru_5 cluster to the previously unknown pentagonal arrangement carrying a μ_5-C_2 ligand (**22**) [50]. The preparation of these systems will allow a study of the reactions of complexed C_2, which will be of interest in relation to its behaviour on metal surfaces. We have long believed that open clusters containing more than three metal atoms might allow a better consideration of the behaviour of small molecules on



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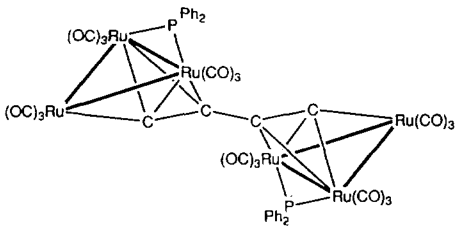
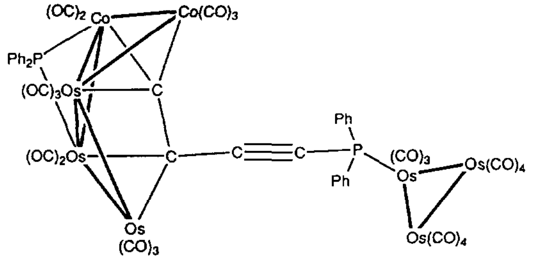


(24)

surfaces. In addition, these clusters demonstrate remarkable flexibility of the metal core geometry to accommodate the variety of unusual organic ligands that are formed.

We have extended this concept to clusters containing the C_4 ligand, the first of which, $\{Co_3(CO)_9(\mu_3\text{-}C)\}_2C_2$, was obtained many years ago [51]. The ligand $Ph_2PC_2C_2PPh_2$ (p_2c_4), first described in 1966 [52], readily forms complexes with transition metals bonding to the P donor atoms. Chris Adams has found that pyrolysis of some of these compounds results in ready cleavage of both C(*sp*)–P bonds to give derivatives containing C_4. For example, the reaction of $\{Fe(CO)_4\}_2(\mu\text{-}p_2c_4)$ with $Fe_2(CO)_9$ (toluene, 90 °C) gave **23**, in which the C_4 unit behaves as a $\mu,\mu\text{-}C_4^{\,2-}$ dianion linking two $Fe_2(\mu\text{-}PPh_2)(CO)_6$ moieties. Pyrolysis of $\{Ru_3(CO)_{11}\}_2(\mu\text{-}p_2c_4)$ (refluxing CH_2Cl_2, 20 h) similarly gave **24**, in which the buta-1,3-dien-1,4-diyl fragment is μ_3-bonded to each $Ru_3(\mu\text{-}PPh_2)(CO)_9$ unit.

The 'binuclear' complexes derived from dppa are sterically too congested about the C≡C triple bond to allow further coordination of fragments such as $Pt(PR_3)_2$, $Ni_2(\eta\text{-}C_5H_5)_2$, $Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$ or $Co_2(CO)_6$, for example, so that mixed metal clusters cannot be assembled by this route. This is not the case with similar derivatives of p_2c_4, from which multinuclear complexes containing these fragments may readily be obtained. Subsequent condensation occurs under mild conditions, an example being the Co_2Os_3 cluster **25** obtained from the $Co_2(CO)_6$ derivative of $\{Os_3(CO)_{11}\}_2(\mu\text{-}p_2c_4)$ [53]. Obviously the permutations of possible substrates are many: our present studies are directed to finding the most profitable combinations for further development of this chemistry.



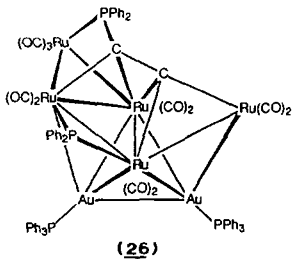
(25)

At the same time, we have succeeded in making mixed 'binuclear' derivatives of dppa and p_2c_4, and Adams has amused himself with elaborating some of the permutations now possible. Of interest is the mixed Ru_3/Os_3 derivative, which on pyrolysis afforded the Ru_2Os_3 analogue of **13**. Interestingly, four of the metal atoms in the core are disordered. This feature, together with the knowledge that one Ru atom is lost, allows us to make some guesses at the method by which this cluster is assembled. The method has also been applied to the synthesis of mixed trimetallic systems, such as $\{Ru_3(CO)_{11}\}\{\mu\text{-}PPh_2C{\equiv}C[(\mu\text{-}C{\equiv}C)Co_2(CO)_6]PPh_2\}\{Re_3(\mu\text{-}H)_3(CO)_{11}\}$, which undergoes ready condensation on heating.

Clusters with gilt edges

The last ten years have seen much interest in gold-containing clusters, both homo- and hetero-metallic [54]. In seeking a route to heterometallic clusters containing more than one gold atom, we examined the reactions of the trigold-oxonium salt $[O\{Au(PPh_3)\}_3][BF_4]$, first described by Russian workers [55], with several metal cluster carbonyls. It was known that this reagent reacts readily with activated hydrogens, with the introduction of up to three gold atoms into organic substrates, e.g. malononitrile gave $[C(CN)_2\{Au(PPh_3)\}_3]^+$ [56]. Direct replacement of the hydrogen atoms in $Ru_4(\mu\text{-}H)_4(CO)_{12}$ was studied by Nicholson in 1984; up to three could be replaced by $Au(PPh_3)$ groups, but in contrast to the expectations occasioned by Lauher and Wald [57], we found that the $Au(PPh_3)$ groups did not take up the positions of the μ-H atoms [58]. Instead, there was a tendency for the formation of Au–Au bonds, which is characteristic of polygold clusters and often results in the failure of the isolobal analogy. More recently, the trigold-oxonium route has been used to form osmium clusters containing four or five gold atoms [59].

In contrast, we have found that similar reactions carried out in the presence of $[ppn]^+$ salts are good routes to clusters containing two $Au(PR_3)$ units. While many of these have been made by the other available routes, the latest method appears to offer advantages in yield and selectivity. The method was first applied to the Ru_5 cluster **13** described above, to see if analogues of the H_2 addition products could be prepared; instead the heptanuclear cluster **26** was obtained [60]. This reagent has also been used to synthesise the unusual complex **27** in which one of the $Au(PPh_3)$ groups is interacting with a carbon of the bridging phenylacetylide ligand [61]. Paul Humphrey has examined the scope of this reaction, finding that complexes containing two $Au(PR_3)$ groups are formed in good yield: they may contain Au–Au bonds, as in $Ru_3Au_2(\mu_3\text{-}E)(CO)_9(PPh_3)_2$ (E = NPh, S), or be close but too far for there to be any significant metal–metal interaction, as in $Os_3Au_2(CO)_{10}(PPh_3)_2$, or be as far apart as possible, as in $Ru_6Au_2C(CO)_{16}(PPh_3)_2$ [61]. However, in solution many of these complexes are fluxional by rapid site exchange of the $Au(PR_3)$ groups; the Ru_6Au_2 complex, for example, is in equilibrium with an isomer apparently containing an Au–Au bond [62].



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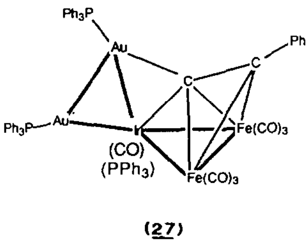
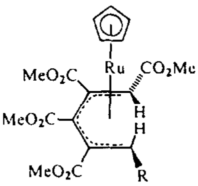


(27)

These new complexes may model the first steps in the addition of molecular hydrogen to clusters. At the time of writing, no cluster complexes containing H_2 as a ligand have been reported. In the same way, clusters containing trigold fragments may be analogous to the as yet unknown complexes of H_3^+, which is calculated to have either open or closed geometry when complexed. The known $Au_3(PR_3)_3$ derivatives contain open (as in $Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3$) or closed arrangements (as in $Au_3Ru_3(\mu_3\text{-}C_2Ph)(CO)_8(PPh_3)_3$) of the Au_3 unit; in the latter the centre of the Au_3 triangle is above one of the ruthenium atoms [63].

Highly substituted cyclopentadienes

The presence of the tetrasubstituted η^5-pentadienyl ligand in **28**, formed by pyrolysis of the butadienyl $Ru\{C(CO_2Me)C(CO_2Me){=}C(CO_2Me){=}CMe(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$, led us to speculate about the existence of metallocenes containing the $C_5(CO_2Me)_5$ ligand. Williams and Jenny Walton commenced a survey of the transition metal chemistry of the parent diene, which is one of the strongest organic acids known. Most of the first-row transition elements form water-soluble complexes, which in the solid state contain the $C_5(CO_2Me)_5$ ligand chelating the metal atom with the ester oxygens of two adjacent CO_2Me groups. This type of bonding is also found in the diene itself, the acidic proton hydrogen bonding to these oxygens. However, the second and third row elements form complexes containing η^5-$C_5(CO_2Me)_5$ ligands. The first to be made was $Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}$ (**29**), in which the substituted C_5 ring, although closer to the ruthenium than the C_5H_5 ring, is the more readily displaced, for example, by tertiary phosphine ligands [64]. Also of interest are the rhodium(I) and rhodium(III) complexes: in $Rh(\eta^4\text{-}C_8H_{12})\{\eta\text{-}C_5(CO_2Me)_5\}$ the metal is attached to the carbons of the C_5 ring, whereas in $Rh(azb)_2\{C_5(CO_2Me)_5\}$ (azb = (2-phenylazo)phenyl), it is chelated by the two ester oxygen atoms. These differences can be rationalised using the hard–soft acid–base principle.



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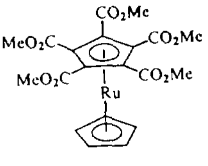

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The Group 11 metals form a series of unusual complexes. Orange $Cu\{C_5(CO_2Me)_5\}_2$ is the first cyclopentadienyl derivative of copper(II), and contains the C_5 ligand bound by the ester oxygens, as do the complexes $Cu(EPh_3)_2\{C_5(CO_2Me)_5\}$ (E = P, As). With silver(I), a series of complexes is formed, containing the C_5 ligand bonded by ring carbon and ester oxygen interactions: as PPh_3 is added, the ring carbons are displaced. With gold(I), the complex $Au(PPh_3)\{C_5(CO_2Me)_5\}$ contains a slipped cyclopentadienyl interaction, with one strong and two weak Au–C bonds; addition of PPh_3 gave $[Au(PPh_3)_2][C_5(CO_2Me)_5]$. The anion is very stable, and can be used as a counterion for large cations; unfortunately, there is often severe disorder in the resulting crystals, which preclude its use for crystallographic characterisation. This chemistry has recently been reviewed [65].

Ion aggregation studies

The acquisition of a VG ZAB 2HF mass spectrometer with a fast-atom bombardment (FAB) source made the characterisation of ionic and high molecular weight organometallics much easier. In the course of these studies, we often observed the formation of ions of higher mass than the molecular ion. These were similar to those found in earlier studies of electron impact mass spectra of cyclopentadienyl-metal complexes [66], for example, but much more intense. We have found that ionic compounds often associate to give aggregates such as $[M_{n+1}L_n]^+$ or $[M_nL_{n+1}]^-$, together with their fragment ions; these were a feature of the FAB mass spectra of many $C_5(CO_2Me)_5$ derivatives. Alternatively, compounds containing $Au(PR_3)$ groups often gave spectra in which an $Au(PR_3)$ fragment had added to the molecular ion. The resulting $[M + Au(PR_3)]^+$ ions are isolobal with the protonated molecular ions that are frequently found in the spectra of organic compounds. Perhaps the extreme example of this found so far is in the spectrum of $C_2\{Au(PR_3)\}_2$ (R = *m*-tolyl), where there are series of ions corresponding to $[M_n + Au(PR_3)]^+$ for $n = 1$–4 [67]. In the crystal structure of this compound, although there is not the common Au ··· Au interaction found in organogold complexes, an association of three of the molecules forms a cavity which can be occupied by a benzene solvate molecule (Fig. 1).

Conclusion

I have derived much pleasure from the studies which are mentioned above. When I was at Oxford, I was equally attracted to organic and inorganic chemistry;

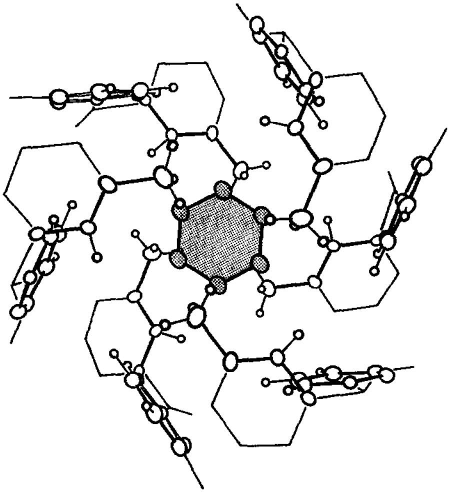

Fig. 1. Octahedral cavity in $C_2\{Au[P(C_6H_4Me\text{-}m)_3]\}_2$ containing a benzene molecule (stippled), viewed perpendicular to the C_6H_6 plane (ref. 67).

organometallic chemistry has provided a challenging synthesis of these interests. Later developments in which the reactivity of molecules on trinuclear clusters has commanded attention has provided as much in the way of novel reactions as did the initial studies of molecules on single metal centres. Expansion to larger aggregates is now the next synthetic challenge and promises to give more aesthetic satisfaction as previously unknown molecular arrangements are found.

Acknowledgements

My able students and coworkers have been mentioned by name in the text and I acknowledge their intellectual and experimental input. The crystallographic studies necessary to define properly this chemistry, particularly that of cluster complexes, have been carried out by several groups. I are indebted to the time spent on these by Michael Snow, and latterly, Edward Tiekink, at Adelaide, by Brian Nicholson at Waikato, and especially by Allan White and Brian Skelton in Perth. I also wish to take this opportunity to thank Gordon Stone and Eddie Abel for all their help and encouragement over the years. The work in Australia has been supported by the Australian Research Council (under its various guises) and by research grants from the University of Adelaide.

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