The Heteronuclear Cluster Chemistry of the Group 1B Metals. Part 12.[1] Variable Temperature Nuclear Magnetic Resonance Spectroscopic Studies of the Dynamic Behaviour of the Mixed-metal Cluster Compounds $[M_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}L)(CO)_{12}]$ [M = Cu or Ag, L = $Ph_2P(CH_2)_nPPh_2$ (*n* = 1—6) or *cis*-$Ph_2PCH{=}CHPPh_2$; M = Cu, L = $Ph_2As(CH_2)_nPPh_2$ (*n* = 1 or 2)] in Solution

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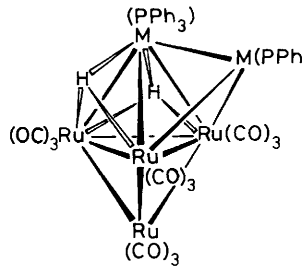
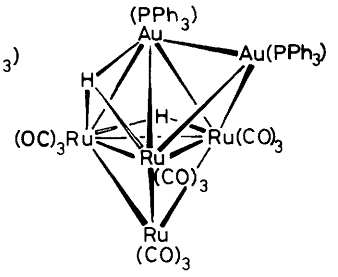
The free energies of activation ($\Delta G^\ddagger$) for the intramolecular metal core rearrangements which the clusters $[M_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}L)(CO)_{12}]$ [M = Cu or Ag, L = $Ph_2P(CH_2)_nPPh_2$ (*n* = 1—6); M = Cu, L = $Ph_2As(CH_2)_nPPh_2$ (*n* = 1 or 2)] undergo in solution have been calculated by band-shape analysis of variable temperature $^{31}P\text{-}\{^1H\}$ or ^1H n.m.r. spectra or estimated from the coalescence temperature in $^{31}P\text{-}\{^1H\}$ n.m.r. spectra. Changes in the nature of the bidentate ligands attached to the coinage metals cause relatively large alterations of up to *ca.* 13 and *ca.* 10 kJ mol^{-1} in the values of $\Delta G^\ddagger$ for the copper- and silver-containing species, respectively. The formal replacement of two PPh_3 groups in $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ by a $Ph_2PCH_2PPh_2$ or $Ph_2P(CH_2)_2PPh_2$ ligand reduces the value of $\Delta G^\ddagger$ by *ca.* 8 and *ca.* 4 kJ mol^{-1}, respectively. These decreases, together with the previously reported distortions in metal framework geometry from capped trigonal bipyramidal to or towards capped square-based pyramidal, which occur for the same formal change of ligands in the analogous gold-containing species, provide some indirect evidence to support a restricted Berry pseudo-rotation mechanism for the Group 1B metal site-exchange process in the clusters studied. The new heteronuclear cluster compounds $[M_2Ru_4H_2(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$ [M = Cu (**20**), Ag (**21**), or Au (**22**)] have been synthesized and the effect of the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand on the value of $\Delta G^\ddagger$ for the metal core rearrangement of (**21**) and on the skeletal geometry adopted by (**22**) is also consistent with the restricted Berry pseudo-rotation mechanism. The magnitude of $\Delta G^\ddagger$ for the silver-containing species (**21**) is *ca.* 7 kJ mol^{-1} lower than that for the analogous PPh_3-ligated cluster and the metal framework geometry of the gold-containing compound (**22**) is altered from capped trigonal bipyramidal to capped square-based pyramidal when two PPh_3 groups are formally replaced by the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand. In addition, variable temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopic studies show that the hydrido ligands in the copper and silver clusters containing $Ph_2E(CH_2)_nPPh_2$ (E = P, *n* = 1—6; E = As, *n* = 1 or 2) are rendered equivalent by dynamic behaviour which involves conformational changes in the methylene backbones of the bidentate ligands and that the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand in (**21**) undergoes a novel fluxional process involving intramolecular site exchange of the two phosphorus atoms between the two silver atoms.

In marked contrast to the vast majority of transition-metal cluster compounds, which have polyhedral frameworks that do not undergo dynamic behaviour in solution, the metal cores of heteronuclear clusters containing two or more $M(PR_3)$ (M = Cu, Ag, or Au; R = alkyl or aryl) units often exhibit novel stereochemical non-rigidity.[2,3] Dynamic behaviour, which is thought to involve coinage metal site exchange, is frequently observed when $M(PR_3)$ fragments adopt structurally inequivalent positions in the ground-state geometries of such clusters. For example, single-crystal *X*-ray diffraction studies reveal that, in the solid state, the clusters $[M_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ [M = Cu (**1**), Ag (**2**), or Au (**3**)] exhibit capped trigonal bipyramidal metal frameworks, with two geometrically distinct $M(PPh_3)$ sites.[4] However, for each cluster, only a single resonance was observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum at ambient temperature and the high-field hydrido ligand signal in the ^1H n.m.r. spectrum showed couplings to two equivalent phosphorus atoms, although spectra consistent with the ground-state structures were obtained at low temperatures for (**1**) and (**2**). An intramolecular rearrangement of the metal skeletons of clusters (**1**)—(**3**) in solution was proposed to explain the n.m.r. results.[4] The analogous clusters $[M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ [M = Cu, *n* = 1 (**4**), 2 (**5**), 3 (**6**), 4 (**7**), 5 (**8**), or 6 (**9**); M = Ag, *n* = 1 (**10**), 2 (**11**), 3 (**12**), 4 (**13**), 5 (**14**), or 6 (**15**)] all adopt similar metal core structures to those exhibited by (**1**)—(**3**) and n.m.r. spectroscopic studies also show equivalent phosophorus atoms at ambient temperature for each of (**4**)—(**15**).[5,6] In addition, only a single silver resonance was observed in the ambient temperature $^{109}Ag\text{-}\{^1H\}$ INEPT n.m.r. spectra of compounds (**10**), (**11**), and (**13**).[6] Thus, the Group 1B metals in (**4**)—(**15**) undergo site exchange, even when they are linked together by the bidentate diphosphine ligands.

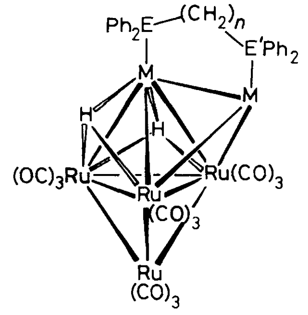
We have postulated a restricted Berry pseudo-rotation mechanism for the intramolecular metal core rearrangements exhibited by clusters (**1**)—(**3**) (Figure 1)[4] and by other clusters containing trigonal bipyramidal M_2Ru_3 (M = Cu, Ag, or Au) fragments in their metal skeletons.[7-9] This proposal is consistent with the theoretical work of Mingos,[10] which shows that the interchange between face-capping and edge-bridging $Au(PR_3)$ units should be a facile process, and with the suggestion of Johnson[11] that polyhedral rearrangements in cluster compounds occur *via* mechanisms which involve the



M
(**1**) Cu
(**2**) Ag



(**3**)



	M	n			M	n
(**4**)	Cu	1	E=E'=P	(**10**)	Ag	1
(**5**)	Cu	2		(**11**)	Ag	2
(**6**)	Cu	3		(**12**)	Ag	3
(**7**)	Cu	4		(**13**)	Ag	4
(**8**)	Cu	5		(**14**)	Ag	5
(**9**)	Cu	6		(**15**)	Ag	6

	M	E	E'	n
(**16**)	Cu	As or P	P or As	1
(**17**)	Cu	As or P	P or A	2

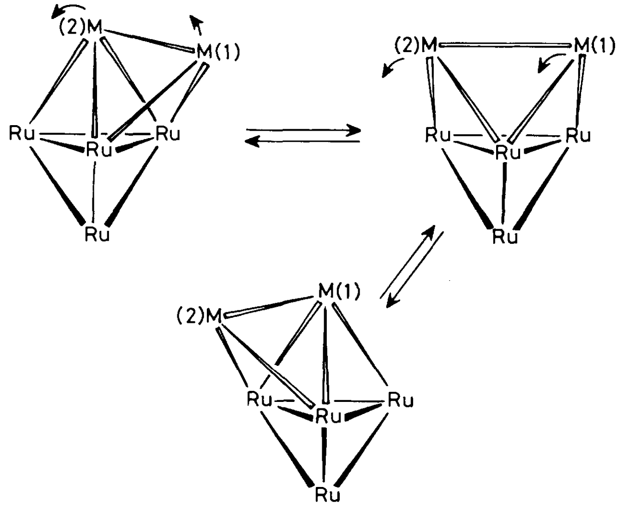


Figure 1. The restricted Berry pseudo-rotation mechanism previously proposed[4] for the coinage metal site-exchange process in [$M_2Ru_4H_2(CO)_{12}(PPh_3)_2$] [M = Cu (**1**), Ag (**2**), or Au (**3**)]. The two Group 1B metals, which occupy sites M(1) and M(2) in the trigonal bipyramidal M_2Ru_3 units of these species, are exchanged *via* an intermediate which contains a square-based pyramidal M_2Ru_3 fragment. All of the ligands have been omitted for clarity, but the mechanism must also involve a concomitant site-exchange process for the two hydrido ligands

cleavage of only one metal–metal contact at a time. Experimental evidence for the restricted Berry pseudo-rotation is provided by the structures of a number of clusters containing Au_2Ru_3 units which are distorted in the same manner as that required in the mechanism. In some species,[1,7,12] the Au_2Ru_3 fragments adopt square-based pyramidal structures similar to those of the M_2Ru_3 units in the intermediates for the proposed mechanism and, in others,[1,8,9] the Au_2Ru_3 moieties are distorted to geometries which are in between trigonal bipyramidal and square-based pyramidal. For the latter type of cluster, the gold atoms are still observed to undergo site exchange at ambient temperature in solution.[1,8,9] In addition, a recent analysis[13] of the crystal structures of sixteen clusters containing the Au_2Ru_3 fragment has allowed a detailed pathway of a Berry pseudo-rotation mechanism for a metal core rearrangement to be defined.

We wished to investigate the novel dynamic behaviour of clusters (**4**)—(**15**) and that of the closely related species [$Cu_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2As(CH_2)_nPPh_2\}(CO)_{12}$] [*n* = 1 (**16**) or 2 (**17**)][14] further by determining the effect of the nature of the bidentate ligand attached to the coinage metals on the magnitudes of the free energy of activation ($\Delta G^‡$) for the metal core rearrangement process in these clusters. In addition, we wanted to extend the study by synthesizing clusters analogous to (**1**)—(**17**), in which the Group 1B metals are ligated by the bidentate diphosphine ligand *cis*-$Ph_2PCH{=}CHPPh_2$, and investigating their dynamic behaviour. A preliminary account describing some of our results has already been published.[15]

Results and Discussion

Studies of the Stereochemical Non-rigidity of the Metal Skeletons of the Clusters [$M_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}L)(CO)_{12}$] [M = Cu *or* Ag, L = $Ph_2P(CH_2)_nPPh_2$ (*n* = 1—6); M = Cu, L = $Ph_2As(CH_2)_nPPh_2$ (*n* = 1 *or* 2)].—As n.m.r. spectra consistent with the ground-state structures can be obtained for the clusters (**4**)—(**9**) and (**11**)—(**17**),[5,14,*] band-shape analysis of variable temperature spectra can be used to calculate the energy parameters for the metal core rearrangements which these species undergo in solution. It is well established that energies quoted in terms of $\Delta G^‡$ values are less prone to systematic errors than the other parameters calculated by band-shape analysis,[16,17] so the discussions of the relative ease of the dynamic process in each cluster (see below) are based on the magnitudes of $\Delta G^‡$ obtained. Band-shape analysis of variable temperature ^1H or $^{31}P\text{-}\{^1H\}$ n.m.r. spectra can be used to calculate $\Delta G^‡$, but values measured from the $^{31}P\text{-}\{^1H\}$ spectra are intrinsically more accurate, because the changes in band shape occur over a much wider temperature range.[16] Therefore, the magnitudes of $\Delta G^‡$ at 25 °C for clusters (**4**)—(**9**) and (**11**)—(**17**) were all determined from $^{31}P\text{-}\{^1H\}$ spectra (Table 1) and Figures 2 and 3 show examples. In the case of (**4**)—(**9**), $\Delta G^‡$ parameters were also calculated at 25 °C from the high-field hydrido ligand signal in the variable temperature ^1H n.m.r. spectra (Table 1) and the two values of $\Delta G^‡$ obtained for the skeletal rearrangement in each cluster are identical within the error limits. No spectra consistent with the ground-state structure could be obtained for (**10**), even at −100 °C, although the $^{31}P\text{-}\{^1H\}$ n.m.r. signal is very severely broadened at this temperature.[5] The free energy of activation for the metal core

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[*] In the case of compounds (**16**) and (**17**), which contain the asymmetrical bidentate ligands $Ph_2As(CH_2)_nPPh_2$ (*n* = 1 or 2), signals due to two different structural isomers are observed in solution at low temperatures, as either an arsenic atom or a phosphorus atom can be attached to each of the two distinct coinage metal sites in the cluster skeletons. The intramolecular metal core rearrangement interconverts the pair of isomers for each cluster at ambient temperature.[14]

Table 1. Free energies of activation ($\Delta G^{\ddagger}$) (kJ mol^{-1}) for the intramolecular metal core rearrangements in the copper- and silver-ruthenium clusters $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ [M = Cu or Ag, L = PPh_3 or L_2 = $\mu\text{-}Ph_2P(CH_2)_nPPh_2$ (*n* = 1—6) or μ-*cis*-$Ph_2PCH{=}CHPPh_2$; M = Cu, L_2 = $\mu\text{-}Ph_2As(CH_2)_nPPh_2$ (*n* = 1 or 2)]

L_2	M = Cu[a]	M = Cu[b]	M = Ag[a]
2 × PPh_3	43.0 ± 0.1[c]	42 ± 1	40 ± 1[d]
$\mu\text{-}Ph_2PCH_2PPh_2$	40.8 ± 0.2	41 ± 1	*ca.* 32[e]
$\mu\text{-}Ph_2P(CH_2)_2PPh_2$	48.1 ± 0.1	48 ± 1	36.0 ± 0.2
$\mu\text{-}Ph_2P(CH_2)_3PPh_2$	52.8 ± 0.1	52 ± 1	40.4 ± 0.1
$\mu\text{-}Ph_2P(CH_2)_4PPh_2$	52.1 ± 0.1	52 ± 1	41.5 ± 0.1
$\mu\text{-}Ph_2P(CH_2)_5PPh_2$	42.9 ± 0.1	43 ± 1	38.4 ± 0.1
$\mu\text{-}Ph_2P(CH_2)_6PPh_2$	43.1 ± 0.1	43 ± 1	42.2 ± 0.1
$\mu\text{-}Ph_2AsCH_2PPh_2$	40.2 ± 0.2	—	—
$\mu\text{-}Ph_2As(CH_2)_2PPh_2$	45.0 ± 0.1	—	—
μ-*cis*-$Ph_2PCH{=}CHPPh_2$	44.8 ± 0.1	—	33 ± 1[f]

[a] The free energies of activation have been calculated at 25 °C by band-shape analysis of variable temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra, unless otherwise stated. [b] The free energies of activation have been calculated at 25 °C by band-shape analysis of the high-field hydrido ligand signal in variable temperature ^1H n.m.r. spectra. [c] Ref. 18. [d] The free energy of activation was estimated at the coalescence temperature from the $^{31}P\text{-}\{^1H\}$ n.m.r. coalescence temperature.[4] [e] N.m.r. spectra consistent with the ground-state structure could not be observed at −100 °C for the cluster, but the $^{31}P\text{-}\{^1H\}$ n.m.r. signal is very broad at this temperature.[5] The free energy of activation has been estimated at the coalescence temperature by assuming that the coalescence temperature is −100 °C and that the frequency difference between the two phosphorus environments in the ground state is 400 Hz, which is a similar value to the differences in frequency observed for the analogous silver-containing clusters (**11**) and (**12**).[5] [f] The two phosphorus signals in the $^{31}P\text{-}\{^1H\}$ spectrum of the cluster at −100 °C are still very broad, so the free energy of activation was estimated at the coalescence temperature from the observed $^{31}P\text{-}\{^1H\}$ n.m.r. coalescence temperature of between −85 and −90 °C.

rearrangement in (**10**) has been estimated at the coalescence temperature by assuming that the coalescence temperature for the dynamic process is −100 °C and that the frequency difference between the two phosphorus environments in the ground state is of a similar magnitude to those observed for the analogous silver-containing clusters (**11**) and (**12**) (Table 1).

Table 1 shows that, within the series of clusters (**4**)—(**15**), the magnitude of $\Delta G^{\ddagger}$ for the intramolecular metal core rearrangement in the copper-containing compound is always larger than that for the analogous silver-containing species, as has been previously observed for the closely related PPh_3-containing species (**1**) and (**2**).[4,18] The magnitudes of $\Delta G^{\ddagger}$ for the dynamic behaviour of (**4**)—(**17**) are also controlled by the nature of the ligands attached to the Group 1B metals. The formal replacement of two PPh_3 groups attached to the silver atoms in (**2**) by a $Ph_2PCH_2PPh_2$ ligand in (**10**) causes a substantial decrease of *ca.* 8 kJ mol^{-1} in $\Delta G^{\ddagger}$, but a similar change of ligands in the case of the copper-containing clusters (**1**) and (**4**) has the very much smaller effect of lowering $\Delta G^{\ddagger}$ by *ca.* 2 kJ mol^{-1}. The formal addition of more methylene groups to the backbones of the bidentate diphosphine ligands causes the value of $\Delta G^{\ddagger}$ for the copper clusters to increase steadily until a maximum is reached at *n* = 3. Further lengthening of the backbone by one more methylene group decreases $\Delta G^{\ddagger}$ by less than 1 kJ mol^{-1}, but then $\Delta G^{\ddagger}$ drops substantially by *ca.* 9 kJ mol^{-1} for the longer chain diphosphines, in which *n* = 5 and 6. Interestingly, the values of $\Delta G^{\ddagger}$ for (**8**) and (**9**) are identical to that for the PPh_3-ligated species (**1**), within the error limits. For the silver-containing clusters, $\Delta G^{\ddagger}$ also increases steadily as the methylene backbone of the ligand lengthens, although the maximum value is at *n* = 4, instead of *n* = 3. However, the drop in the magnitude of $\Delta G^{\ddagger}$ for *n* = 5 (*ca.* 3 kJ mol^{-1}) is much smaller than that for the copper-containing species (**7**) and (**8**) and then, in contrast to the analogous copper cluster, $\Delta G^{\ddagger}$ increases at *n* = 6 to a value which is slightly larger than that for *n* = 4. It is interesting that the changes in the number of methylene groups in the backbones of the bidentate diphosphine ligands attached to the Group 1B metals in the copper-containing species (**4**)—(**9**) and the silver-containing clusters (**10**)—(**15**) cause relatively large differences of up to *ca.* 12 and *ca.* 10 kJ mol^{-1}, respectively, in the values of $\Delta G^{\ddagger}$ for the skeletal rearrangements. In contrast, alterations in the cone angles of the monodentate phosphine and phosphite ligands bonded to the copper atoms in $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ [L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PMe_3, $P(OPh)_3$, $P(OEt)_3$, or $P(OMe)_3$] cause much smaller changes of up to *ca.* 3 kJ mol^{-1} in the magnitude of $\Delta G^{\ddagger}$.[18]

The formal replacement of phosphorus by arsenic in the bidentate ligands $Ph_2ECH_2PPh_2$ (E = As or P) attached to the copper atoms in (**4**) and (**16**) has relatively little effect on the value of $\Delta G^{\ddagger}$. However, a similar change for the $Ph_2E(CH_2)_2PPh_2$-containing clusters (**5**) and (**17**) causes a decrease in $\Delta G^{\ddagger}$ of *ca.* 3 kJ mol^{-1}.

The alterations in $\Delta G^{\ddagger}$ values for (**1**), (**2**), (**4**), (**10**), and (**11**) can be related to the structural changes previously reported[1,4] for the analogous gold-containing clusters (**3**) and $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ [*n* = 1 (**18**) or 2 (**19**)] by the restricted Berry pseudo-rotation mechanism discussed in the Introduction. The formal replacement of two PPh_3 groups attached to the gold atoms in (**3**) by a $Ph_2PCH_2PPh_2$ ligand in (**18**) causes a change in the metal framework structure from capped trigonal bipyramidal to a capped square-based pyramidal geometry, which is very similar to that of the intermediate in the proposed mechanism (Figure 1). The stereochemical demands of the $Ph_2PCH_2PPh_2$ ligand would also be expected to cause some stabilization of the capped square-based pyramidal metal framework structure with respect to the capped trigonal bipyramidal core geometry for the silver-containing cluster (**10**). In this case, the effect is not sufficient to change the ground-state metal framework structure of (**10**), although the $Ph_2PCH_2PPh_2$ ligand causes a substantial reduction of *ca.* 0.1 Å in the Ag–Ag separation of (**2**) and it also produces a considerable distortion of the Ag–P vectors from their orientations in (**2**).[4,6] However, if the proposed mechanism is correct, the change in ligands should lead to the value of $\Delta G^{\ddagger}$ for the metal core rearrangement in cluster (**10**) being lower than that of (**2**). A substantial reduction of *ca.* 8 kJ mol^{-1} in $\Delta G^{\ddagger}$ is actually observed when two PPh_3 groups in (**2**) are formally replaced by a $Ph_2PCH_2PPh_2$ ligand in (**10**). In the case of copper, which is much smaller than silver or gold, the steric strain imposed by the same formal change of ligands would be expected to be much less and this is reflected by a difference of only *ca.* 2 kJ mol^{-1} between the $\Delta G^{\ddagger}$ values for (**4**) and (**1**). When the two PPh_3 groups attached to the gold atoms in cluster (**3**) are formally replaced by a $Ph_2P(CH_2)_2PPh_2$ ligand in (**19**), the metal framework structure is distorted from capped trigonal bipyramidal towards a capped square-based pyramidal geometry, but the extent of the structural change is very much smaller than that caused by the $Ph_2PCH_2PPh_2$ ligand in (**18**). Therefore, if the postulated Berry pseudo-rotation mechanism is correct, the stereochemical demands of the $Ph_2P(CH_2)_2PPh_2$ ligand in the analogous silver-containing cluster (**11**) would be expected to cause a decrease in the value of $\Delta G^{\ddagger}$ for the metal core rearrangement relative to that of (**2**), but the magnitude of the reduction should be significantly less than that which occurs for (**10**). When the two PPh_3 groups attached to the silver atoms in (**2**) are formally changed to a $Ph_2P(CH_2)_2PPh_2$ ligand in (**11**), a decrease in the magnitude of $\Delta G^{\ddagger}$ of *ca.* 4 kJ mol^{-1} is actually observed, which is much smaller than the *ca.* 8 kJ mol^{-1} reduction that occurs for the $Ph_2PCH_2PPh_2$-containing species (**10**).

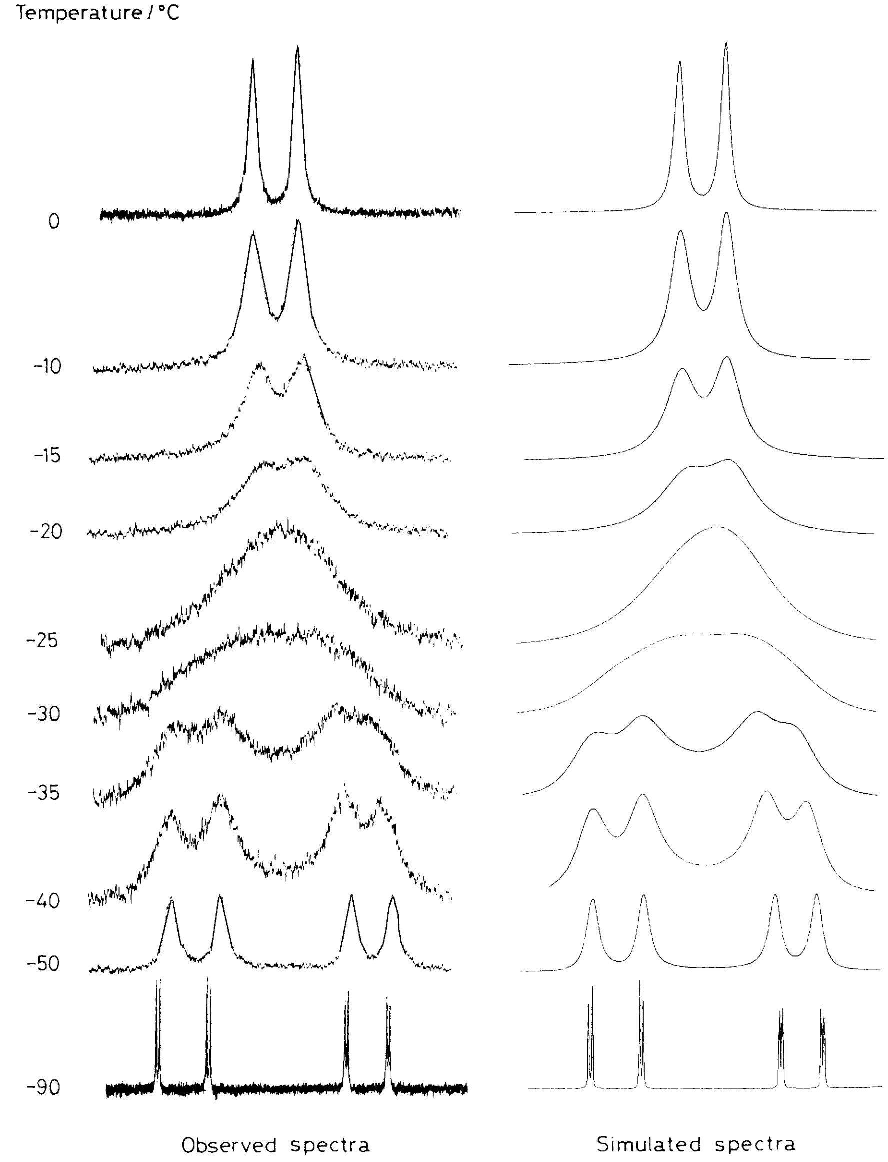
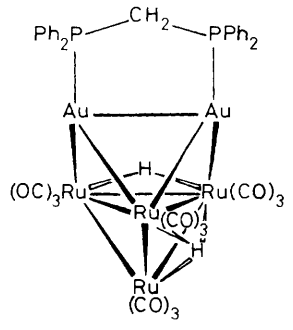


Figure 2. Variable temperature $^{31}P-\{^{1}H\}$ n.m.r. spectra of the cluster $[Ag_2Ru_4(\mu_3-H)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}(CO)_{12}]$ (**13**), together with their computer simulations, showing the effect of the silver atom site-exchange process. The spectra are complicated by $^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ couplings through one and two bonds



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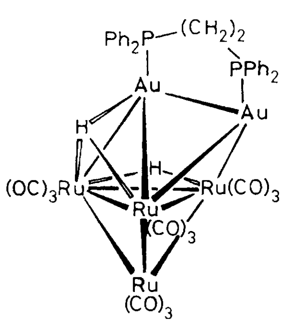

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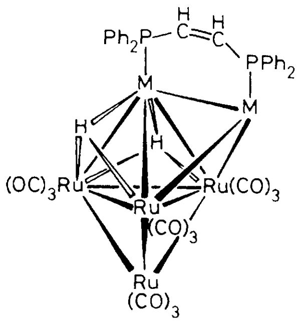
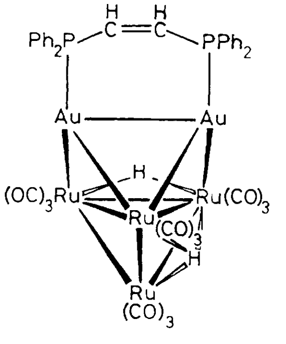


M

(**20**) Cu ,(**21**) Ag



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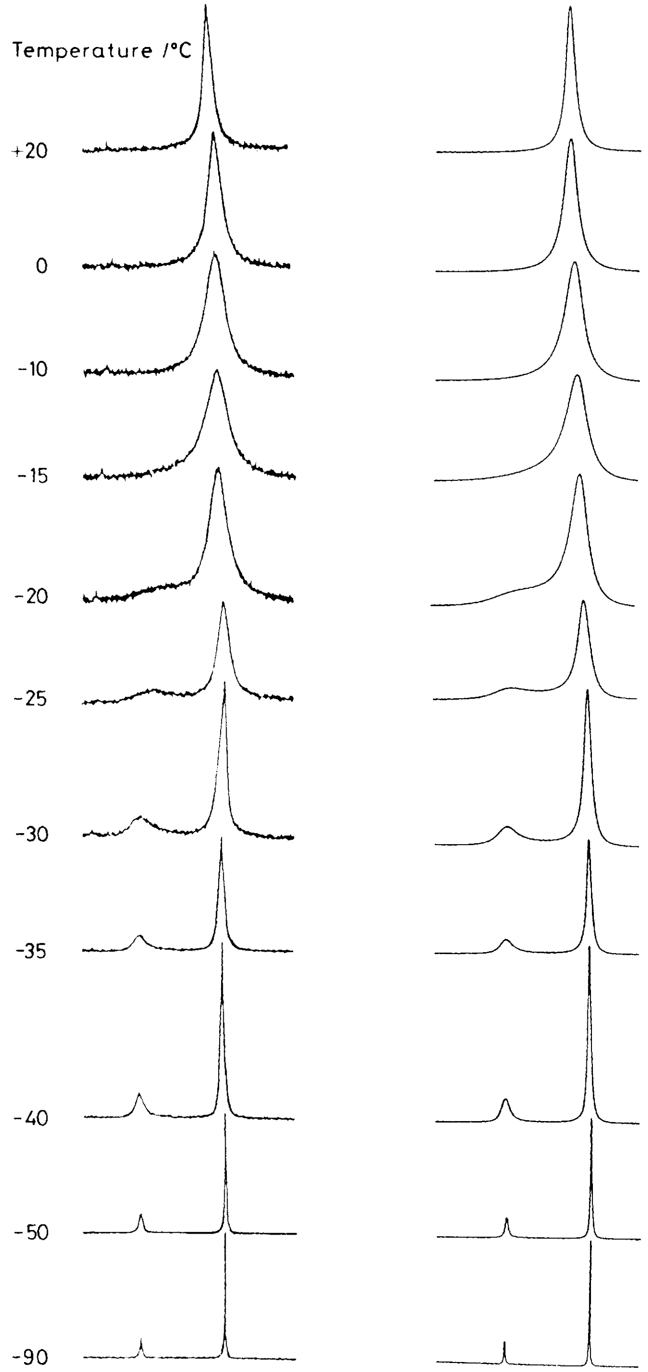

Figure 3. Variable temperature $^{31}P-\{^1H\}$ n.m.r. spectra of the cluster $[Cu_2Ru_4(\mu_3-H)_2\{\mu-Ph_2As(CH_2)_2PPh_2\}(CO)_{12}]$ (**17**), together with their computer simulations, showing the effect of the interconversion of the two distinct structural isomers

We anticipated that the bidentate diphosphine *cis*-$Ph_2PCH=CHPPh_2$, which has a relatively rigid backbone, might also stabilize the capped square-based pyramidal metal framework structure relative to the capped trigonal bipyramidal skeletal geometry for silver- and gold-containing clusters analogous to those discussed previously, because the ligand should tend to favour an approximatey parallel orientation of the two M–P (M = Ag or Au) vectors. Therefore, we wished to synthesize the series of clusters $[M_2Ru_4H_2(\mu$-*cis*-$Ph_2PCH=CHPPh_2)(CO)_{12}]$ (M = Cu, Ag, or Au) and to study their metal core structures and dynamic behaviour.

Synthesis and Structures of the Clusters $[M_2Ru_4H_2(\mu$-*cis*-$Ph_2PCH=CHPPh_2)(CO)_{12}]$ *(M = Cu, Ag, or Au)*.—Treatment of a dichloromethane solution of the salt $[N(PPh_3)_2]_2[Ru_4(\mu-H)_2(CO)_{12}]$[19] with 2 equivalents of the complex $[M(NCMe)_4]PF_6$ (M = Cu or Ag) at −30 °C, followed by the addition of 1 equivalent of *cis*-$Ph_2PCH=CHPPh_2$, affords the dark red cluster compounds $[M_2Ru_4(\mu_3-H)_2(\mu$-*cis*-$Ph_2PCH=CHPPh_2)(CO)_{12}]$ [M = Cu (**20**) or Ag (**21**)] in *ca.* 70—75% yield. The analogous gold-containing species $[Au_2Ru_4(\mu_3-H)(\mu-H)(\mu$-*cis*-$Ph_2PCH=CHPPh_2)(CO)_{12}]$ (**22**) was prepared in *ca.* 60% yield by adding an acetone solution of $[N(PPh_3)_2]_2[Ru_4(\mu-H)_2(CO)_{12}]$, together with solid $TlPF_6$, to a dichloromethane solution of $[Au_2(\mu$-*cis*-$Ph_2PCH=CHPPh_2)Cl_2]$. The new clusters (**20**)—(**22**) were characterized by microanalyses and by spectroscopic measurements (Tables 2 and 3). Two phosphorus environments are visible in the low-temperature $^{31}P-\{^1H\}$ n.m.r. spectra of (**20**) and (**21**), although the signals for (**21**) are still very broad at −100 °C. The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**20**) at ambient temperature shows a singlet, broadened by quadrupolar effects,[4,5] whereas that of (**21**) at −10 °C is a complex multiplet. Analysis of the latter signal, in a similar manner to that previously described,[6] shows that it consists of a single phosphorus resonance which is split by $^{107,109}Ag-^{31}P$ couplings through one and two bonds and also by $^{107,109}Ag-^{107,109}Ag$ and $^{31}P-^{31}P$ couplings and is further complicated by second-order effects. The i.r. spectra and the high-field hydrido ligand signals in the ^1H n.m.r. spectra of (**20**) and (**21**) are very similar to those reported[4,5] for the analogous species containing PPh_3 and $Ph_2P(CH_2)_nPPh_2$ (n = 1—6), although a ^1H n.m.r. spectrum consistent with the ground state structure could not be obtained for (**21**), even at −90 °C. Thus, the clusters (**20**) and (**21**) adopt similar capped trigonal bipyramidal metal core structures to those of (**1**), (**2**), and (**4**)—(**15**) and undergo similar skeletal rearrangements in solution.[4,5] The spectroscopic data for (**22**) are significantly different to those reported[4] for the analogous PPh_3-containing species (**3**), but they are closely similar to those of the cluster (**18**),[1] in which the gold atoms are ligated by $Ph_2PCH_2PPh_2$. Thus, it seems likely that (**22**) adopts a similar structure to that of (**18**). A single-crystal *X*-ray diffraction study[20] on (**22**) has confirmed this hypothesis and showed that the cluster exhibits a capped square-based pyramidal skeletal geometry with the *cis*-$Ph_2PCH=CHPPh_2$ ligand bridging the Au–Au vector, one hydrido ligand occupying a site bridging a Ru–Ru edge, and the other capping a Ru_3 face, and each Ru atom ligated by three CO groups, which are essentially linear. Figure 4 compares the metal–metal separations within the capped square-based pyramidal metal skeletons of (**22**), the monoclinic and orthorhombic crystalline forms of (**18**),[1] and $[Au_2Ru_4(\mu_3-H)(\mu-H)(\mu-Ph_2AsCH_2PPh_2)(CO)_{12}]$.[12] As expected, the Au–Au separation in (**22**) is between *ca.* 0.03 and *ca.* 0.04 Å longer than those for the other clusters and there is little variation in the equivalent Ru–Ru separations for the capping $Ru(CO)_3$ fragment. However, there are differences of between 0.025 and 0.136 Å for the equivalent Au–Ru and Ru–Ru distances in the square-based pyramidal Au_2Ru_3 units of the four clusters. This observation is not surprising, as the relative 'softness' of the metal–metal bonds in (**18**) has already been demonstrated by the fact that the modest forces of crystal packing cause differences of up to 0.091 Å in the lengths of the equivalent metal–metal separations within the Au_2Ru_3 fragments in the two crystalline forms of the cluster.[1]

Studies of the Stereochemical Non-rigidity of the Metal Skeletons of the Clusters $[M_2Ru_4(\mu_3-H)_2(\mu$-*cis*-$Ph_2PCH=$

Table 2. Analytical[a] and physical data for the new Group 1B metal heteronuclear cluster compounds

Compound	M.p. (θ_C/°C)	$\nu_{max.}$(CO)[b]/cm^{-1}	Yield (%)[c]	Analysis	
				C	H
(20) $[Cu_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$	256—260	2 072s, 2 036vs, 2 022vs, 2 008s, 1 978m(br), 1 939w(br)	76	35.9 (36.0)	2.0 (1.9)
(21) $[Ag_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$	146—150	2 069s, 2 034vs, 2 018vs, 2 004s, 1 973m(br), 1 937w(br)	70	33.7 (33.7)	1.8 (1.8)
(22) $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$	140—146	2 073s, 2 044s, 2 021vs, 1 977m(br), 1 933w(br)	60	29.8 (29.8)	1.7 (1.6)

[a] Calculated values given in parentheses. [b] Measured in dichloromethane solution. [c] Based on ruthenium reactant.

Table 3. Hydrogen-1 and phosphorus-31 n.m.r. spectroscopic data[a] for the new Group 1B metal heteronuclear cluster compounds

Cluster	θ_c/°C	^1H[b]	$^{31}P\text{-}\{^1H\}$[c]
(20)	Ambient	−17.96 [t, 2 H, μ_3-H, *J*(PH) 6], 7.08—7.53 (m, 22 H, Ph and CH=CH)	−8.2(br s)
	−90	−18.04 [d, 2 H, *J*(PH) 13]	−1.3 [d, *J*(PP) 28], −15.5 [d, *J*(PP) 28]
(21)	+70		0.5 [apparent t of t, *J*(^{109}AgP) 230, *J*(^{107}AgP) 200][d]
	Ambient	−17.76 [apparent t of t of t, 2 H, μ_3-H, *J*(^{109}AgH) 19, *J*(^{107}AgH) 17, *J*(PH) 4], 7.03—7.68 (m, 22 H, Ph and CH=CH)	
	−10		0.3 [m, ^{1}*J*(^{109}AgP) 474, ^{1}*J*(^{107}AgP) 411, ^{2}*J*(^{109}AgP) − 2, ^{2}*J*(^{107}AgP) − 2, *J*(PP) 31, *J*(^{109}Ag^{109}Ag) 43, *J*(^{107}Ag^{109}Ag) 38, *J*(^{107}Ag^{107}Ag) 33][e]
	−90	−17.85 [br t, μ_3-H, 2 H, *J*(^{107,109}AgH)$_{av.}$ 18]	
	−100		*ca.* 4.5 [vbr d, *J*(^{107,109}AgP)$_{av.}$ *ca.* 500], *ca.* −5 [vbr d, *J*(^{107,109}AgP)$_{av.}$ *ca.* 400]
(22)	Ambient	−16.92 (s, 2 H, hydrido H), 7.27—7.51 (m, 20 H, Ph), 7.82 [AA′X pattern, 2 H, CH=CH, *N*(PH) 45][f]	45.6(s)
	−90	*ca.* −17 (vbr s)	45.7(s)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in [$^2H_2$]dichloromethane solution. At −90 °C, only the data for the high-field hydrido ligand signal are presented. [c] Hydrogen-1 decoupled, measured in [$^2H_2$]dichloromethane–CH_2Cl_2 solution, unless otherwise stated, chemical shifts positive to high frequency of 85% H_3PO_4 (external). [d] Measured in [$^2H_8$]toluene solution. [e] The multiplet consists of the superimposed subspectra due to the $^{107}Ag^{107}Ag$, $^{107}Ag^{109}Ag$, and $^{109}Ag^{109}Ag$ isotopomers of the cluster and it is complicated by second-order effects and by a wide variety of couplings. The values of the coupling constants listed in the Table were obtained by an analysis similar to that previously described for some closely related species.[6] Only the relative signs of the coupling constants could be determined. [f] *N*(PH) = |*J*(PH) + *J*(P′H)|.

$CHPPh_2)(CO)_{12}]$ (M = Cu *or* Ag).—The value of $\Delta G^\ddagger$ for the metal core rearrangement in the copper-containing cluster (**20**) has been calculated by band-shape analysis of variable temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra, but $\Delta G^\ddagger$ for the silver-containing species (**21**) had to be estimated at the coalescence temperature from the coalescence temperature, as the spectrum at −100 °C is still very broad. For both (**20**) and (**21**), the effect of the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand on the magnitude of $\Delta G^\ddagger$ seems to be intermediate between that caused by $Ph_2PCH_2PPh_2$ and that caused by $Ph_2P(CH_2)_2PPh_2$ on the analogous clusters (**4**), (**5**), (**10**), and (**11**). The formal replacement of two PPh_3 groups in the silver-containing species (**2**) by the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand in (**21**) reduces the value of $\Delta G^\ddagger$ by *ca.* 7 kJ mol^{-1}, which is similar to the magnitude of the decrease caused by the $Ph_2PCH_2PPh_2$ ligand, but significantly larger than the effect of the $Ph_2P(CH_2)_2PPh_2$ ligand. This observation is consistent with the proposed Berry pseudo-rotation mechanism for the coinage metal site-exchange process (Figure 1), because when the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand formally replaces the two PPh_3 groups in the gold-containing cluster (**3**) it actually alters the skeletal geometry from capped trigonal bipyramidal to capped square-based pyramidal in a similar manner to the $Ph_2PCH_2PPh_2$ ligand in (**18**), whereas the $Ph_2P(CH_2)_2PPh_2$ ligand only causes a distortion towards the latter structure, as in (**19**).[1]

Dynamic Behaviour involving the Ligands attached to the Group 1B Metals in the Clusters $[M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2E(CH_2)_nPPh_2\}(CO)_{12}]$ (M = Cu *or* Ag, E = P, *n* = 1—6; M = Cu, E = As, *n* = 1 *or* 2) *and* $[Ag_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$.—The spectroscopic data for the clusters (**4**)—(**9**), (**11**)—(**17**), and (**21**) show that these species undergo dynamic processes, which involve the ligands attached to the Group 1B metals, in addition to the intramolecular metal core rearrangements. Although there is a plane of symmetry through the metal skeleton of each of (**4**)—(**17**) [*e.g.* through Cu(1), Cu(2), Ru(1), and Ru(3) in Figure 5], the conformations adopted by the methylene backbones of the $Ph_2E(CH_2)_nPPh_2$ (E = P, *n* = 1—6; E = As, *n* = 1 or 2) ligands in the ground-state structures of these clusters render the two hydrido ligands inequivalent (*e.g.* Figure 5).[5] However, only one high-field hydrido ligand resonance is observed in the ^1H n.m.r. spectrum of each of (**4**)—(**9**) and (**11**)—(**15**) at temperatures low enough to prevent the metal framework rearrangement process operating.[5,*] In the case of clusters (**16**) and (**17**), one ^1H n.m.r. hydrido ligand resonance is observed for each of the structural isomers at temperatures low enough to stop them interconverting.[14] Thus the clusters (**4**)—(**9**) and (**11**)—(**17**) all undergo some dynamic process which renders the hydrido ligands equivalent. At −100 °C, the high-field ^1H n.m.r. hydrido ligand signals of (**5**) and (**7**) consist of two doublets of equal intensity

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[*] The $\Delta G^\ddagger$ value for the metal core rearrangement in cluster (**10**) is low enough for the process still to occur at −100 °C.

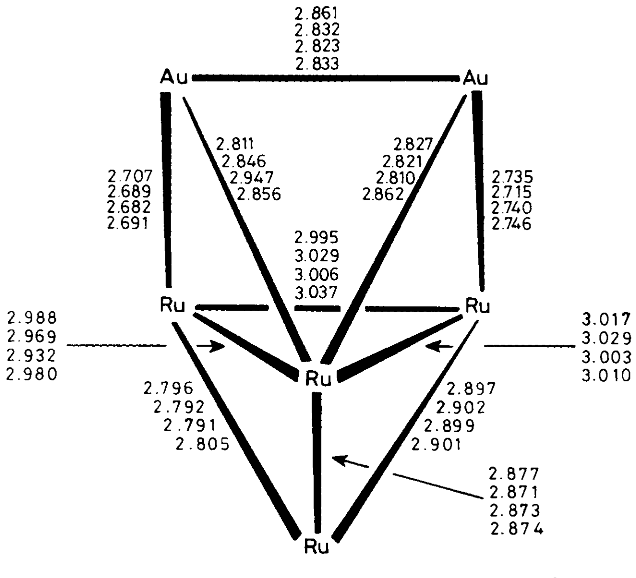

Figure 4. A comparison of the metal–metal separations (Å) in the capped square-based pyramidal metal cores of the clusters $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}L)(CO)_{12}]$ [L = *cis*-$Ph_2PCH{=}CHPPh_2$ (**22**), $Ph_2AsCH_2PPh_2$, or $Ph_2PCH_2PPh_2$ (**18**)]. Distances are given in the following descending order: (**22**),[20] $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2AsCH_2PPh_2)(CO)_{12}]$,[12] the monoclinic crystalline form of (**18**),[1] and the orthorhombic form of (**18**)[1]

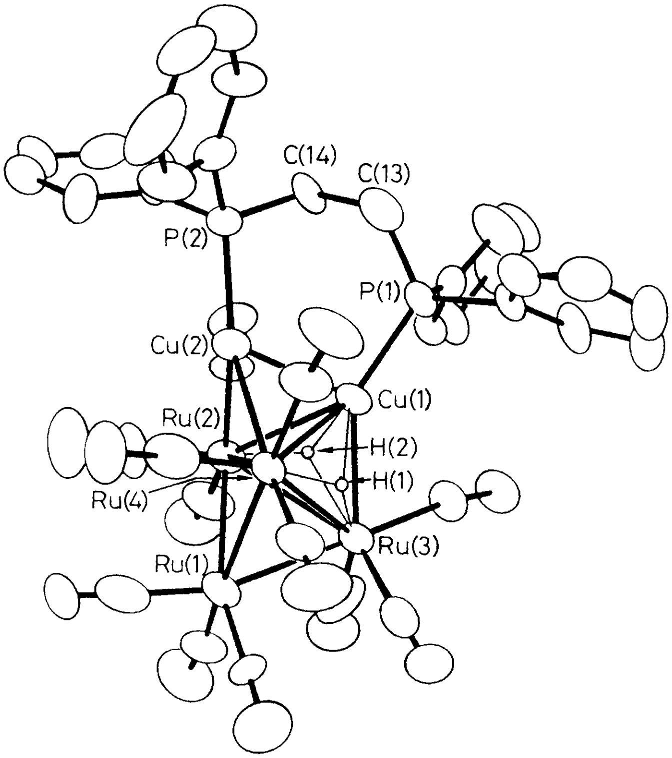

Figure 5. The molecular structure of $[Cu_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ (**5**), showing how the ground state conformation adopted by the methylene backbone of the $Ph_2P(CH_2)_2PPh_2$ ligand renders the hydrido ligands H(1) and H(2) inequivalent by removing the mirror plane through Cu(1), Cu(2), Ru(1), and Ru(3)[5]

and a very broad singlet, respectively (Table 4). A broadened signal, consisting of two singlets of equal intensity and two doublets of equal intensity, was observed at −108 °C for the two isomers of (**17**) (Table 4). Free energies of activation have been calculated for the dynamic process in these three clusters (Table 4). However, the ^1H n.m.r. spectra of (**4**), (**6**), (**8**), (**9**), and (**11**)—(**16**) all show equivalent hydrido ligands, even at −90 or −100 °C, so the energy barriers for the dynamic process in these species must be considerably lower than the values measured for (**5**), (**7**), and (**17**).

When no metal core rearrangements are occurring, there are two possible explanations for the observed equivalence of the hydrido ligands in (**4**)—(**9**) and (**11**)—(**17**). The hydrido ligands themselves may actually be undergoing dynamic behaviour involving site exchange or the methylene backbones of the bidentate ligands may be stereochemically non-rigid in solution. Rapid exchange of the methylene groups in the ligand backbones between the various possible conformations will render the hydrido ligands equivalent. Although dynamic behaviour involving hydrido ligand site exchange is well established for transition metal clusters,[1,4,12,21] it seems unlikely that the free energy of activation for such a process in (**4**)—(**9**) and (**11**)—(**17**) would be altered so significantly by the number of methylene groups in the backbones of the bidentate ligands or by the formal replacement of one phosphorus atom in (**5**) by an arsenic atom in (**17**). In addition, a hydrido ligand site-exchange process cannot explain the band-shape changes and/or broadening which occur for the methylene group signals in the ^1H n.m.r. spectra of some of the above clusters on cooling. Therefore, we propose that the n.m.r. results observed for (**4**)—(**9**) and (**11**)—(**17**) arise from the stereochemical non-rigidity of the bidentate ligands attached to the copper and silver atoms. Similar dynamic behaviour, which involves conformational changes in the methylene backbones of $Ph_2P(CH_2)_nPPh_2$ (n = 1—4) ligands producing time-averaged planes of symmetry, has been recently reported[22] for the clusters $[Os_3\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{10}]$ and $[Os_3(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{10}][PF_6]$. Interestingly, the free energy of activation for the dynamic process in $[Os_3\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{10}]$ is considerably higher than that for the analogous species in which n = 1, 3, or 4, as observed for (**4**)—(**7**).

The high-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the silver-containing cluster (**21**) show that this species undergoes another fluxional process, involving the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand, in addition to the intramolecular metal core rearrangement. As the temperature is raised from −10 °C, some of the peaks in the complex multiplet observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**21**), measured using $[^2H_2]$dichloromethane–CH_2Cl_2 or $[^2H_1]$chloroform as the solvent, broaden and undergo changes in band shape. The relatively low boiling points of the above solvents do not allow spectra to be obtained at the high temperature limit. The free energy of activation for the dynamic process seems to be lower when cluster (**21**) is dissolved in $[^2H_8]$toluene. Although the energy barriers for the silver atom site exchange and the second fluxional process are such that it is not possible to obtain a well resolved $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum for the situation where only the skeletal rearrangement is in progress when (**21**) is dissolved in $[^2H_8]$toluene, the pattern of peaks in the spectrum at 20 °C is very similar to that observed for the cluster at 60 °C in $[^2H_1]$chloroform solution. At 70 °C, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**21**) in $[^2H_8]$toluene solution is a well resolved apparent triplet of triplets, which is due to superimposed subspectra from three different isotopomers. The subspectrum of the $^{107}Ag^{109}Ag$ isotopomer (49.9% abundance) consists of a doublet of doublets, split by $^{107}Ag\text{–}^{31}P$ and $^{109}Ag\text{–}^{31}P$ couplings, whereas the subspectra due to the $^{107}Ag^{107}Ag$ (26.9% abundance) and $^{109}Ag^{109}Ag$ (23.2% abundance) isotopomers are both triplets, although the magnitudes of the coupling constants are obviously different in each case. A similar analysis has been previously reported in detail for the high-field hydrido ligand signals in the ambient-

Table 4. Low-temperature ^{1}H n.m.r. data for the high-field hydrido ligand signals and free energies of activation for the conformational changes in the bidentate ligand backbones of [$Cu_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2E(CH_2)_nPPh_2\}(CO)_{12}$] [E = P, n = 2 (**5**) or 4 (**7**); E = As, n = 2 (**17**)]

Cluster	Low-temperature ^{1}H n.mr. hydrido ligand signal[a]	Free energy of activation, $\Delta G^{\ddagger}$ (kJ mol^{-1})
(**5**)	−17.84 [d, 1 H, J(PH) 13], −17.63 [d, 1 H, J(PH) 12][c]	37 ± 1[b]
(**7**)	*ca.* −17.5 (vbr s)	*ca.* 33[d]
(**17**)	−17.72 (br s, 1.0 H, isomer B), −17.76 [br d, 0.4 H, isomer A, J(PH) 14], −17.94 (br s, 1.0 H, isomer B), −17.99 [br d, 0.4 H, isomer A, J(PH) 14][f]	34 ± 1[e]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Spectra measured at −100 °C, using [$^{2}H_2$]dichloromethane as the solvent, unless otherwise stated. [b] Calculated at 25 °C by band-shape analysis of the high-field hydrido ligand signal in the variable temperature ^{1}H n.m.r. spectra. [c] Ref. 5. [d] A spectrum consistent with the ground-state structure could not be observed at −100 °C, although the hydrido ligand signal is very broad at this temperature. The free energy of activation has been estimated at the coalescence temperature by assuming that the coalescence temperature is between −100 and −105 °C and that the frequency difference between the two hydrido ligand environments in the ground state is 85 Hz, which is a similar value to the differences in frequency observed for the analogous clusters (**5**) and (**17**). [e] The hydrido ligand signals are still broad at −108 °C, so the free energy of activation was estimated at the coalescence temperature from the observed ^{1}H n.m.r. coalescence temperature of between −95 and −100 °C. [f] Measured at −108 °C. See ref. 14 for diagrams of structural isomers A and B.

temperature ^{1}H n.m.r. spectra of (**10**)—(**15**).[5] Thus, at the high-temperature limit, the two silver atoms in the ^{107}Ag^{107}Ag and ^{109}Ag^{109}Ag isotopomers and the two phosphorus atoms in all three isotopomers are actually *magnetically* equivalent and the subspectra are not complicated by second-order effects (*cf.* ref. 6). The dynamic process causing the magnetic equivalence must be intramolecular, as ^{107,109}Ag–^{31}P couplings are still observed, and the only explanation for the n.m.r. results is an intramolecular site exchange of the two phosphorus atoms of the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand between the two silver atoms, which are themselves rendered equivalent by the skeletal rearrangement of the cluster. Similar dynamic behaviour has been recently reported[14] for the $Ph_2As(CH_2)_nPPh_2$ (n = 1 or 2) ligands in [$Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2As(CH_2)_nPPh_2\}(CO)_{12}$]. The bidentate ligands in these clusters also undergo intermolecular exchange at high temperatures, but no evidence for a similar process for the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand in (**21**) was obtained between 70 °C and the decomposition temperature of the compound, 90 °C. Although intermolecular exchange of monodentate phosphine ligands at room temperature in solution is well established[2,4,8,23] for silver-containing heteronuclear clusters, low-energy processes involving intramolecular phosphine ligand site exchange are extremely rare for cluster compounds in general. The only other example that has been reported[24] is the migration of the ligands L around the triangular Pt_3 faces of the co-ordinatively unsaturated clusters [$Pt_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3L$][$PF_6$]$_2$ (L = PMe_2Ph, $PMePh_2$, PPh_3, or PH_2Ph). Interestingly, however, intramolecular site exchange of the phosphorus atoms of the bridging $R_2PCH_2PR_2$ (R = Me or Ph) ligands between the silver atoms in the complexes [$Ag_2(\mu\text{-}R_2PCH_2PR_2)_3$]$X_2$ (X_2 = O_3SCF_3 or X = AsF_6) has been observed[25] very recently.

The novel dynamic behaviour of (**21**) prompted us to perform a high-temperature ^{31}P-{^{1}H} n.m.r. spectroscopic study on one of the silver clusters which contain a bidentate diphosphine ligand with a saturated backbone. However, the ^{31}P-{^{1}H} n.m.r. spectrum of (**13**) at 100 °C, measured using [$^{2}H_8$]toluene as the solvent, consists of a similar complex multiplet with narrow linewidths to that observed at ambient temperature.[5,6] Thus, the $Ph_2P(CH_2)_4PPh_2$ ligand in (**13**) does not undergo intra- or inter-molecular site exchange, even at 100 °C.

Conclusions

It has been shown that changes in the nature of the bidentate ligands attached to the coinage metals in the copper clusters (**4**)—(**9**), (**16**), (**17**), and (**20**) and the silver-containing species (**10**)—(**15**) and (**21**) cause relatively large alterations of up to *ca.* 13 and *ca.* 10 kJ mol^{-1}, respectively, in the values of $\Delta G^{\ddagger}$ for the skeletal rearrangements that these compounds undergo in solution. The changes in the magnitude of $\Delta G^{\ddagger}$ observed for some of the silver-containing clusters, together with the distortions in metal framework geometry from capped trigonal bipyramidal to or towards capped square-based pyramidal, which occur for the same formal change in ligands in the analogous gold-containing species, provide some indirect evidence to support a restricted Berry pseudo-rotation mechanism for the Group 1B metal site-exchange process in (**1**)—(**17**). In addition to the intramolecular metal core rearrangements, dynamic behaviour involving the ligands attached to the Group 1B metals was observed in solution for many of the clusters studied. The methylene backbones of the $Ph_2E(CH_2)_nPPh_2$ (E = P, n = 1—6; E = As, n = 1 or 2) ligands in (**4**)—(**9**) and (**11**)—(**17**) undergo conformational changes which render the two hydrido ligands in each cluster equivalent and the *cis*-$Ph_2PCH{=}CHPPh_2$ ligand in the silver-containing species (**21**) undergoes a very novel fluxional process which involves an intramolecular site exchange of the two phosphorus atoms between the two silver atoms.

Experimental

The clusters [$M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}$] (M = Cu or Ag, n = 1—6)[5] and [$Cu_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2As(CH_2)_nPPh_2\}(CO)_{12}$] ($n$ = 1 or 2)[14] were prepared as previously described. Adaptations of published routes were utilized to synthesize [$M_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}$][5,26] and [$Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}$].[12,27] The ligand *cis*-$Ph_2PCH{=}CHPPh_2$ was purchased from Strem Chemicals Inc. and used without further purification. The instrumentation employed for the spectroscopic characterization of the new cluster compounds has been described elsewhere.[12] Analytical and other physical data for these species are presented in Table 2, together with their i.r. spectra. Table 3 summarizes the results of n.m.r. spectroscopic measurements.

Variable Temperature N.M.R. Spectroscopic Studies.—Variable temperature ^{31}P-{^{1}H} and ^{1}H n.m.r. spectra were recorded using a Bruker AM250 spectrometer operating at 101.26 and 250.13 MHz, respectively. Samples were prepared under an atmosphere of dry, oxygen-free nitrogen in standard 10-mm n.m.r. tubes, using [$^{2}H_2$]dichloromethane–CH_2Cl_2 as a solvent, for the ^{31}P-{^{1}H} n.m.r. studies and in standard 5-mm n.m.r. tubes, using [$^{2}H_2$]dichloromethane as a solvent, for the ^{1}H n.m.r. measurements. The n.m.r. band-shape analyses were performed with a modified version[28] of the DNMR program of Kleier and Binsch.[29]

Acknowledgements

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spectrum of $[Ag_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}cis\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$, the S.E.R.C. for a studentship (to S. S. D. B.), the Nuffield Foundation for support, Johnson Matthey Ltd. for a generous loan of gold, silver, and ruthenium salts, and Mrs. L. J. Salter for drawing the diagrams.

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