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High-resolution ^{31}P-{^{1}H} nuclear magnetic resonance studies of Group IB metal heteronuclear cluster compounds in the solid state

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Abstract

High-resolution ^{31}P-{^{1}H} NMR spectra of a series of crystalline mixed-metal cluster compounds containing $M(PR_3)$ ($M = Cu$, Ag, or Au; $R =$ alkyl or aryl) fragments have been recorded using magic angle sample spinning. The solid-state spectra are compared with those measured for the same compounds in solution and the values of the chemical shifts and, for the silver-containing species, the magnitudes of $J(^{107,109}AgP)_{av}$, are generally very similar. The solid-state NMR spectra suggest that the dynamic processes involving hydrido ligand site-exchange or intermolecular exchange of PR_3 ligands between clusters, which have been previously observed at ambient temperature in solution for some of the clusters studied, do not occur or are not sufficiently rapid to be detected when the same compounds are in the crystalline state. In addition, the intramolecular metal core rearrangements, which all of the bimetallic clusters containing inequivalent $M(PR_3)$ fragments undergo at ambient temperature in solution, are also not observed by solid-state NMR spectroscopy in the crystalline compounds. For some of the clusters of this latter class, the solid-state spectra can provide useful structural information about the ground-state metal framework geometries which it is impossible to obtain from solution studies, even at low temperatures.

Introduction

Considerable interest has recently been shown in high-resolution solid-state NMR spectroscopy as a technique for providing structural information about a wide variety of chemical systems [1]. The chemistry of mixed-metal cluster compounds containing one or more $M(PR_3)$ ($M = Cu$, Ag, or Au; $R =$ alkyl or aryl)

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fragments is also currently attracting much attention [2] and we anticipated that high-resolution solid-state $^{31}P-\{^1H\}$ NMR spectroscopy would be a valuable tool to facilitate the study of such species. Although a number of gold-containing homonuclear clusters have been studied using high-resolution solid-state $^{31}P-\{^1H\}$ NMR spectroscopy [3,4], no spectra of Group IB metal heteronuclear clusters have been previously reported to the best of our knowledge.

Techniques which have the potential to provide information about the ground state structures are particularly important for Group IB metal heteronuclear clusters, since the metal skeletons of bimetallic species, in which the $M(PR_3)$ units adopt structurally inequivalent positions, often undergo dynamic behaviour involving coinage metal site-exchange at ambient temperature in solution [2]. Thus, the $^{31}P-\{^1H\}$ NMR spectra of such clusters, which are measured in solution at ambient temperature, show fewer resonances than would be anticipated from the ground state structures. In some cases, spectra consistent with the solid-state metal framework geometries can be obtained at low temperatures, but this is often not possible, even at −90 or −100 °C. A recent $^{31}P-\{^1H\}$ NMR spectroscopic study on homonuclear gold-containing clusters has shown that, with the possible exception of the cluster $[Au_{11}(PMe_2Ph)_{10}][BPh_4]_3$, the metal frameworks of these species do not undergo any dynamic process in the solid state, even though most are stereochemically non-rigid in solution [3]. The solid-state $^{31}P-\{^1H\}$ NMR spectrum of $[Au_{11}(PMe_2Ph)_{10}][BPh_4]_3$ was found to consist of a single resonance. The structure of the cluster has not been determined by single-crystal X-ray diffraction because of crystallographic disorder [3], but the closely related species $[Au_{11}I_3\{P(C_6H_4F\text{-}4)_3\}_7]$ has been structurally characterized and shown to have four chemically distinct phosphorus environments [5]. Thus, the metal skeleton of $[Au_{11}(PMe_2Ph)_{10}][BPh_4]_3$ is either still stereochemically non-rigid in the solid state or it adopts a different structure to that established for $[Au_{11}I_3\{P(C_6H_4F\text{-}4)_3\}_7]$. In view of these results, we wished to conduct a systematic high-resolution solid-state $^{31}P-\{^1H\}$ NMR spectroscopic study of a series of Group IB metal heteronuclear clusters with stereochemically rigid metal frameworks in order to determine the factors that affect the solid-state spectra and then to investigate the spectra of some species which are known to have metal cores that are stereochemically non-rigid in solution. The results are reported herein.

Results and discussion

1. Clusters exhibiting metal skeletons that are stereochemically rigid in solution

High-resolution solid-state $^{31}P-\{^1H\}$ NMR spectroscopic studies were performed at ambient temperature on the previously reported clusters $[MRu_3(CO)_9(C_2{}^tBu)(PPh_3)]$ [6,7] [M = Cu (**1**) or Ag (**2**)], $[CuRu_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_8(PPh_3)_2]$ [8] (**3**), $[MRu_4(\mu_3\text{-}H)_3(CO)_{12}L]$ [6] [M = Cu, L = PPh_3 (**4**) or $PMePh_2$ (**5**); M = Ag, L = PPh_3 (**6**)], $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ [9] [M = Cu, M′ = Ag (**7**) or Au (**8**); M = Ag, M′ = Au (**9**)] and $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ [10] (**10**). The results are summarized in Table 1 and details of the spectra measured for the same compounds in solution have been included for comparison. The solid-state $^{31}P-\{^1H\}$ NMR spectra of some of the clusters which were initially crystallized from dichloromethane–light petroleum mixtures showed more resonances than would be expected from their known structures. These extra signals were not, however,

Table 1

High-resolution solid-state ^{31}P-{^{1}H} NMR data for the Group IB metal heteronuclear clusters which have metal frameworks that are stereochemically rigid in solution. Details of the spectra measured for the same compounds in solution are included for comparison

Cluster	Solid-state ^{31}P-{^{1}H} NMR data [a,b]	Solution ^{31}P-{^{1}H} NMR data [a,c]
(1) $[CuRu_3(CO)_9(C_2{}^tBu)(PPh_3)]$	−0.5 (asymmetrical q)	[d] −1.4(s)
(2) $[AgRu_3(CO)_9(C_2{}^tBu)(PPh_3)]$	13.9 [d, $J(^{107,109}AgP)_{av}$ 445]	[d] 12.2 [2×d, $J(^{109}AgP)$ 482, $J(^{107}AgP)$ 417, mean value of $J(AgP)$ 449.5]
(3) $[CuRu_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_8(PPh_3)_2]$	36.8 [s, $Ru(PPh_3)$], 3.7 [asymmetrical q, $Cu(PPh_3)$]	[e,f] 32.2 [d, $Ru(PPh_3)$, $J(PP)$ 13], 4.1 [d, $Cu(PPh_3)$, $J(PP)$ 13]
(4) $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}(PPh_3)]$	13.6 (asymmetrical q)	[d] 10.9(s)
(5) $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}(PMePh_2)]$	−7.0 (asymmetrical q)	[d] −5.5(s)
(6) $[AgRu_4(\mu_3\text{-}H)_3(CO)_{12}(PPh_3)]$	18.5 [d, $J(^{107,109}AgP)_{av}$ 651]	[d] 22.0 [2×d, $J(^{109}AgP)$ 693, $J(^{107}AgP)$ 601, mean value of $J(AgP)$ 647]
(7) $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$	14.3 [d, $Ag(PPh_3)$, $J(^{107,109}AgP)_{av}$ 458], 7.7 [asymmetrical q, $Cu(PPh_3)$]	[g] 14.7 [2×d, $Ag(PPh_3)$, $^{1}J(^{109}AgP)$ 481, $^{1}J(^{107}AgP)$ 417, mean value of $^{1}J(AgP)$ 449], 6.4 [d, $Cu(PPh_3)$, $^{2}J(^{107,109}AgP)_{av}$ 2]
(8) $[AuCuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$	67.2 [s, $Au(PPh_3)$], 10.0 [asymmetrical q, $Cu(PPh_3)$]	[g] 66.9 [s, $Au(PPh_3)$], 4.8 [s, $Cu(PPh_3)$]
(9) $[AgAuRu_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$	61.6 [s, $Au(PPh_3)$], 15.7 [d, $Ag(PPh_3)$, $J(^{107,109}AgP)_{av}$ 529]	[g] 64.6 [s, $Au(PPh_3)$], 17.4 [2×d, $Ag(PPh_3)$, $J(^{109}AgP)$ 596, $J(^{107}AgP)$ 515, mean value of $J(AgP)$ 555.5]
(10) $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$	59.5 (s), 56.5 (s)	[e,h] 52.3 (s)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Chemical shifts are positive to high frequency of 85% H_3PO_4 (ext.). [b] Measured at 20 °C. [c] Measured at −90 °C, unless otherwise stated. [d] Ref. 6. [e] Measured at ambient temperature. [f] Ref. 8. [g] Ref. 9. [h] Ref. 10.

present in the spectra of samples of the same clusters which were recrystallized from diethyl ether–light petroleum mixtures. We propose, therefore, that they arise from the presence of dichloromethane of crystallization in the original samples.

The ^{31}P-{^{1}H} NMR spectrum of each cluster compound in the solid state consists of a number of peaks with chemical shifts between δ −7.0 and 67.2 ppm, each of which has a series of sidebands spaced at the spinning frequency. For the spinning speeds used in this work, the sideband intensities are small. Although the spectra are generally well-resolved, the linewidths of the signals are invariably in excess of 100 Hz and they are dependent on the identity of the Group IB metal bonded to the phosphorus atom. The narrowest linewidths were observed for the silver-containing species and the resonances of the gold-containing clusters were generally much broader. The solid-state linewidths for clusters containing either coinage metal are, therefore, all very much larger than those observed in solution (normally < 5 Hz). At least part of the broadening of the signals due to the $Au(PR_3)$ moieties in the solid state may be attributable to dipolar coupling between the phosphorus atoms and the ^{197}Au nuclei, which is averaged in solution. This effect is not removed by magic angle spinning, because the quadrupole interaction with gold is comparable in magnitude with the nuclear Zeeman interaction [3,11]. In the case of the copper-containing clusters, a large variation of linewidths was observed, with some values being as small as 200 Hz, whereas considerable broadenings in excess of 1 kHz occur for other species. The origin of the broadening of the signals due to the $Cu(PR_3)$ moieties is quadrupolar and it is discussed in more detail below.

(a) Spectra of clusters containing a $Cu(PR_3)$ fragment. Comparison of the chemical shifts observed in the ^{31}P-{^{1}H} NMR spectra of the copper-containing clusters in the solid state and in solution shows that these values are generally very similar. Although the chemical shift of the $Cu(PPh_3)$ unit in **8** varies by 5.2 ppm between the solid and solution state, the differences for **1**, **3**, **4**, **5** and **7** all lie in the narrow range of 0.4–2.7 ppm. For most of the clusters studied, the value of the chemical shift measured in the solid state is slightly more positive than that obtained in solution, but the opposite is true for **3** and **5**. Similar observations have been made previously for a series of homonuclear gold–phosphine cluster compounds [3].

The patterns of the signals due to the $Cu(PR_3)$ units in the solid-state spectra are, however, in marked contrast to those observed in solution. An asymmetric "quartet" occurs for each $Cu(PR_3)$ moiety in the solid-state spectra (e.g. Fig. 1a), but a broadened singlet is always observed at ambient temperature in solution. The broadening of the solution signals is thought to be due to quadrupolar effects [6,8] and singlets with much narrower line-widths can be observed in solution spectra measured at low temperatures, where relaxation rates are even faster. The splittings that occur in the solid-state spectra are closely similar to those seen previously in some other copper–phosphine complexes [4,12,13] and are attributable to the interplay of dipolar and scalar coupling between the quadrupolar Cu nucleus and the phosphorus atom bonded to it. The effect of the large nuclear quadrupole coupling constant of 30 MHz is to tip the axis of quantization of the Cu nucleus away from the magnetic field. Magic angle spinning will no longer fully remove the dipolar coupling between the copper and the phosphorus and the appearance of the scalar coupling multiplet will, therefore, be distorted [12]. The solid-state resonance splittings, which will arise from incomplete averaging of the dipolar coupling, have

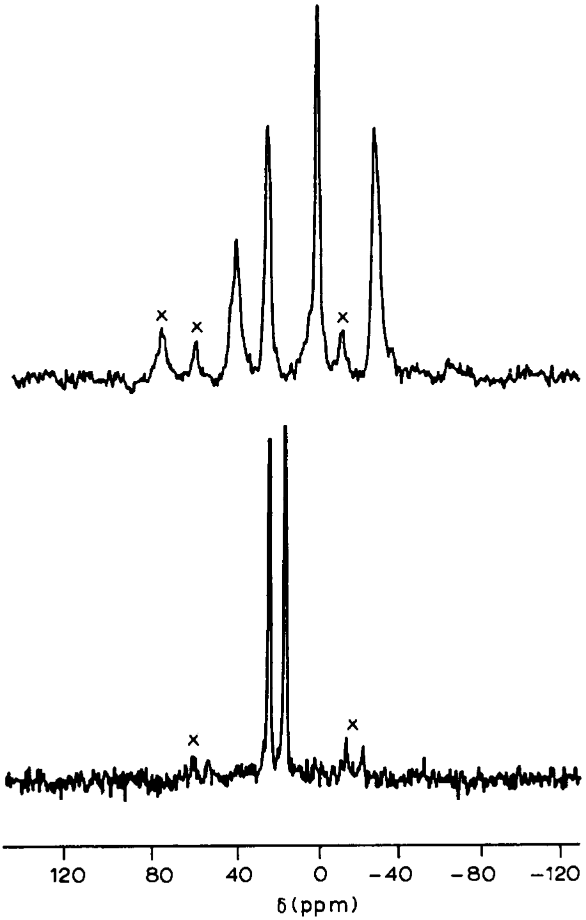

Fig. 1. Solid-state ^{31}P-{^{1}H} NMR spectra of (a) $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}(PPh_3)]$ (4) and (b) $[AgRu_4(\mu_3\text{-}H)_3(CO)_{12}(PPh_3)]$ (6). Groups of peaks marked by × are spinning sidebands.

been calculated [12]. Initially, the cases of dipolar and scalar coupling were considered separately, but this was found to be incompatible with the experimental results and a combination of the two gave the best fit with the experimental data. The magnetogyric ratios for the copper isotopes are too similar to allow the separate splittings due to ^{63}Cu and ^{65}Cu to be resolved in any of the solid-state spectra of the copper-containing clusters studied. On the basis of these calculations, the magnitude of the observed splittings are indicative of Cu–P distances of 2.2–2.5 Å. These values are in accord with Cu–P distances of ca. 2.2 Å obtained from single-crystal X-ray diffraction studies on the clusters **1**, **5** and **7** [6,9]. Given the assumptions and approximations required for such calculations, a more detailed comparison has not been attempted.

At ambient temperature in solution, the $PMePh_2$ ligands in $[CuRu_4(\mu_3\text{-}H)_3(CO)_{12}(PMePh_2)]$ (**5**) undergo dynamic behaviour involving intermolecular exchange between clusters [6]. However, the ^{63}Cu–^{31}P coupling observed in the ambient temperature solid-state ^{31}P-{^{1}H} NMR spectrum of **5** shows that this dynamic process does not occur or is not sufficiently rapid to be detected in the crystalline state.

(b) Spectra of clusters containing a $Ag(PR_3)$ fragment. In the solid state, the ^{31}P-$\{^1H\}$ NMR signals due to the $Ag(PR_3)$ units all appear as doublets (e.g. Fig. 1b). The splitting is due to $^{107,109}Ag-^{31}P$ coupling, but the separate contributions from the two different silver isotopes cannot be resolved in the solid-state spectra, although two doublets can always be observed in the spectra of the same cluster measured in solution. As can be seen from Table 1, the chemical shifts and the values of $J(^{107,109}AgP)_{av}$ measured in the solid state and in solution are generally very similar. The differences lie in the ranges 0.4–3.5 ppm and 4–9 Hz for the chemical shifts and the coupling constants, respectively, apart from $J(^{107,109}AgP)_{av}$ for **9**, which varies by 26.5 Hz. The chemical shifts measured in solution are all more positive than those observed in the solid state, except that of **2**. Solid-state ^{31}P-$\{^1H\}$ NMR spectroscopic studies on some silver-containing complexes have been previously reported and the values of $J(^{107,109}AgP)_{av}$ observed in the solid state and in solution were found to be very similar for most of the compounds investigated [14]. This similarity was attributed to similar solution and solid-state characteristics for the silver-containing complexes [14].

At ambient temperature in solution, the PPh_3 ligands in **2** and **6** undergo dynamic behaviour involving intermolecular exchange between clusters, which severely broadens the ^{31}P-$\{^1H\}$ NMR spectra of these compounds [6]. However, the relatively narrow line-widths and the $^{107,109}Ag-^{31}P$ couplings observed in the ambient temperature solid-state spectra of **2** and **6** indicate that this dynamic process does not occur or is not sufficiently rapid to be detected in the crystalline state.

(c) Spectra of clusters containing a $Au(PR_3)$ fragment. The ^{31}P-$\{^1H\}$ NMR signals of the $Au(PR_3)$ units show no splittings due to couplings in the solid state, unlike those due to the $M(PR_3)$ ($M = Cu$ or Ag) moieties. The chemical shifts for the trimetallic clusters **8** and **9** show differences of 0.3 and 3.0 ppm, respectively, between the solid-state and solution spectra, but the mean shift of the two signals in the solid-state spectrum of the $Ph_2PCH_2PPh_2$-containing cluster **10** is 5.7 ppm more positive than that of the singlet observed in solution. An average increase in chemical shift of 4.2 ppm with respect to that observed in solution has been previously reported for a solid-state ^{31}P-$\{^1H\}$ NMR spectroscopic study of a series of homonuclear gold-containing clusters [3].

The two equal intensity signals observed for **10** in the solid-state spectrum are in marked contrast to the single resonance which occurs in the solution spectrum. The metal framework of **10** adopts a capped square-based pyramidal structure and the two phosphorus atoms are only rendered inequivalent by the face-capping hydrido ligand [10]. In solution, dynamic behaviour involving hydrido ligand site-exchange causes the two phosphorus atoms in **10** to become equivalent [10]. The dynamic process clearly has a very low free energy of activation, because the solution ^{31}P-$\{^1H\}$ NMR spectrum of **10** still consists of a singlet with a narrow linewidth at −90 °C. The solid-state spectrum suggests, however, that hydrido ligand site-exchange does not occur at ambient temperature when the cluster is crystalline. This observation is interesting in view of the fact that carbonyl ligand site-exchange is thought to occur in the solid-state, as well as in solution, for $[Co_2(CO)_8]$ [15,16], $[Fe_3(CO)_{12}]$ [16,17] and $[Co_4(CO)_{12}]$ [18,19] and that the magnitude of the free energy of activation for the dynamic process in crystalline $[Co_4(CO)_{12}]$ is only slightly higher than that observed for the cluster in solution [18]. Although it is possible to explain the site-exchange processes in solid $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$ by mechanisms involving the trigonal planar Fe_3 unit and the Co_4 tetrahedron, respectively, changing their orientations within an icosahedron of carbonyl ligands, which remains fixed in the lattice [16–19], movements of ca. 3 Å for the carbonyl ligands have been postulated to explain the variable-temperature solid-state ^{13}C NMR spectra for $[Co_2(CO)_8]$ [15].

2. *Clusters exhibiting metal skeletons that are stereochemically non-rigid in solution*

High-resolution solid-state $^{31}P\text{-}\{^1H\}$ NMR spectroscopic studies were performed at ambient temperature on the previously reported clusters $[M_2Ru_3(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_9]$ [8] [M = Cu (**11**) or Au (**12**)], $[M_2Ru_4H_2(CO)_{12}(PPh)_2]$ [20] [M = Cu (**13**), Ag (**14**) or Au (**15**)], $[M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2E(CH_2)_nPPh_2\}(CO)_{12}]$ [21–23] [M = Cu, E = P, $n = 1$ (**16**) or E = As, $n = 2$ (**17**); M = Ag, E = P, $n = 3$ (**18**)], and $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$ [24] (**19**). The results are summarized in Table 2 and details of the spectra measured for the same compounds in solution have been included for comparison. As was observed for the clusters with metal frameworks that are stereochemically rigid in solution, the solid-state $^{31}P\text{-}\{^1H\}$ NMR spectra of some of **11**–**19** showed more resonances than would be expected from their known structures when these compounds were crystallized from dichloromethane–light petroleum mixtures. However, these extra signals were again not present in the spectra of samples of the same clusters which were recrystallized from diethyl ether–light petroleum mixtures, so again it seems likely that they arise from the presence of dichloromethane of crystallization in the original samples. The general features of the solid-state $^{31}P\text{-}\{^1H\}$ NMR spectra of **11**–**19** and the variations in the line-widths of the signals with the nature of the Group IB metal bonded to the phosphorus atom are very similar to those described for the clusters in the preceding section.

(a) Spectra of clusters containing $Cu(PR_3)$ *fragments.* The resonances due to the $Cu(PR_3)$ units in the solid-state spectra of **11**, **13**, **16**, and **17** are all split into asymmetric "quartets" by coupling to the quadrupolar ^{63}Cu nuclei as discussed in detail in the preceding section.

The metal skeletons of the clusters **11**, **13**, and **16** all contain trigonal bipyramidal Cu_2Ru_3 units with two distinct $Cu(PR_3)$ sites. However, at ambient temperature, only one phosphorus resonance was observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of each of these clusters, measured in solution [8,20,22], although spectra consistent with the ground state structures of **13** and **16** could be obtained at low temperatures [20,22]. In contrast, the solid-state spectra of **11**, **13** and **16** all show two phosphorus resonances (e.g. Fig. 2a). Thus, although the metal skeletons of **11**, **13**, and **16** are all stereochemically non-rigid at ambient temperature in solution, this dynamic behaviour is not observed by solid-state NMR spectroscopy when these species are crystalline. Interestingly, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **11** in the solid state provides information about the metal framework structure of the cluster which cannot be obtained from studies performed in solution, where the dynamic process cannot be "frozen out", even at low temperatures [8].

The metal core of **17** also contains a trigonal bipyramidal Cu_2Ru_3 unit, but two different structural isomers are possible, as an arsenic or a phosphorus atom can be attached to each of the distinct copper sites [23]. Interestingly, a signal due to each

Table 2

High-resolution solid-state $^{31}P\text{-}\{^1H\}$ NMR data for the Group IB metal heteronuclear clusters which have metal cores that are stereochemically non-rigid in solution. Details of the spectra measured for the same compounds in solution are included for comparison

Cluster	Solid-state $^{31}P\text{-}\{^1H\}$ NMR data [a,b]	Solution $^{31}P\text{-}\{^1H\}$ NMR data at ambient temperature [a]	Solution $^{31}P\text{-}\{^1H\}$ NMR data at low temperature [a,c]
(11) $[Cu_2Ru_3(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_9]$	−9.0 (asymmetrical q) −16.0 (asymmetrical q)	–	[d] −7.5 (s)
(12) $[Au_2Ru_3(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_9]$	48.8 (s), 46.5 (s)	[d] 52.4 (s)	[d] 50.8 (s)
(13) $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$	9.0 (asymmetrical q), 2.5 (asymmetrical q)	[e] 4.3 (s, br)	[e] 6.8 (s), −0.4 (s)
(14) $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$	15.1 [d, $J(^{107,109}AgP)_{av}$ 509], 12.9 [d, $J(^{107,109}AgP)_{av}$ 448]	[e] ca. 23 (s, vbr), ca. 10 (s, vbr)	[e] 18.4 [2 × d of d, $^1J(^{107}AgP)$ 490, $^1J(^{109}AgP)$ 565, $^2J(^{107,109}AgP)_{av}$ 8, mean value of $^1J(AgP)$ 528], 13.4 [2 × d of d, $^1J(^{107}AgP)$ 410, $^1J(^{109}AgP)$ 473, $^2J(^{107,109}AgP)_{av}$ 12, mean value of $^1J(^{107,109}AgP)$ 442]
(15) $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$	56.0 (s), 49.9 (s)	[e] 58.7 (s)	[e] ca. 51 (s, vbr)
(16) $[Cu_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$	0 (asymmetrical q), −7 (asymmetrical q)	[f] −3.8 (s, br)	[f] 2.5 [d, $J(PP)$ 91], −9.5 [d, $J(PP)$ 91]
(17) $[Cu_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2As(CH_2)_2PPh_2\}(CO)_{12}]$	2 (asymmetrical q)	[g] −2.6 (s, br)	[g] 3.6 (s, 0.37 P), −5.1 (s, 1.0 P)
(18) $[Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(CO)_{12}]$	17.3 [d, $J(^{107,109}AgP)_{av}$ 549], 14.6 [d, $J(^{107,109}AgP)_{av}$ 448]	[h] 15.8 [m, $^1J(^{107}AgP)$ 450.2, $^1J(^{109}AgP)$ 520.5, $^2J(^{107}AgP)$ 6.8, $^2J(^{109}AgP)$ 7.8, $J(PP)$ 2.9, $J(^{107}Ag^{107}Ag)$ 33.2, $J(^{107}Ag^{109}Ag)$ 38.2, $J(^{109}Ag^{109}Ag)$ 44.1, mean value of $^1J(AgP)$ 485]	[f,i] 18.7 [2 × d of d, $^1J(^{107}AgP)$ 509, $^1J(^{109}AgP)$ 590, $^2J(^{107,109}AgP)_{av}$ 7, mean value of $^1J(AgP)$ 550], 14.3 [2 × d of d, $^1J(^{107}AgP)$ 405, $^1J(^{109}AgP)$ 471 $^2J(^{107,109}AgP)_{av}$ 6, mean value of $^1J(AgP)$ 438]
(19) $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$	62.2 (s,2 P), 55.3 (s,1 P)	[j] 61.3 (s)	[j,k] 62.3 (s,2 P), 53.5 (s,1 P)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Chemical shifts are positive to high frequency of 85% H_3PO_4 (ext.). [b] Measured at 20 °C. [c] Measured at −90 °C, unless otherwise stated. [d] Ref. 8. [e] Ref. 20. [f] Ref. 22. [g] Ref. 23. [h] Ref. 21. [i] Measured at −95 °C. [j] Ref. 24. [k] Measured at −60 °C.

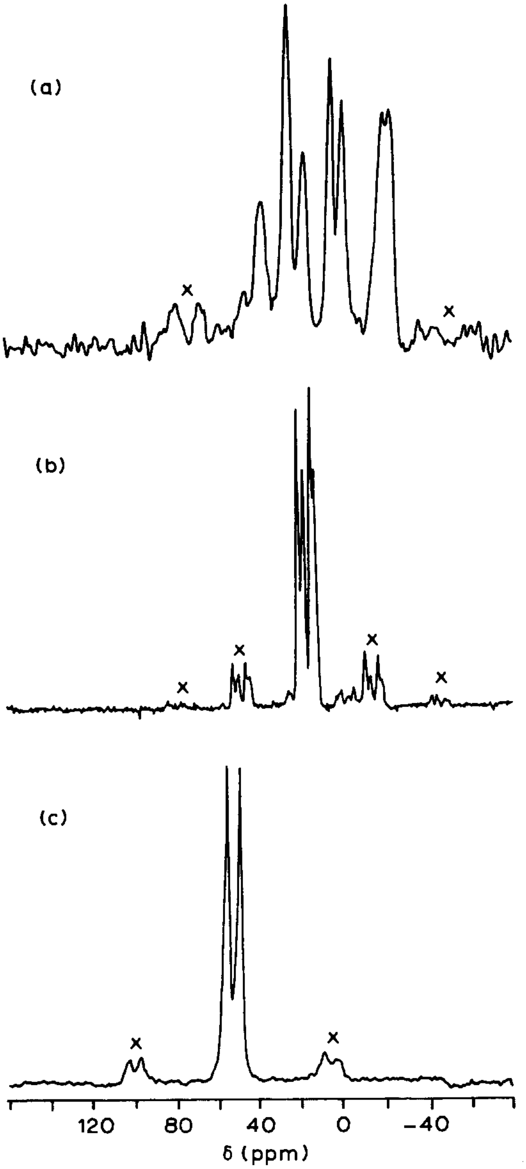

Fig. 2. Solid-state ^{31}P-{^{1}H} NMR spectra of (a) [$Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2$] (**13**), (b) [$Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2$] (**14**), (c) [$Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2$] (**15**). Groups of peaks marked by × are spinning sidebands.

isomer of **17** is visible in the ^{31}P-{^{1}H} NMR spectrum of the cluster measured in solution at $-90\,^\circ$C and the disorder observed between the arsenic and phosphorus atoms in the X-ray crystal structure suggests that both isomers are also present in the solid state. However, at ambient temperature in solution, the two isomers are interconverted by an intramolecular metal core rearrangement [23]. The solid-state ^{31}P-{^{1}H} NMR spectrum of **17** shows a single phosphorus resonance, despite the fact that the X-ray diffraction study suggests that both isomers exist in the crystalline cluster. However, although it is not possible to obtain a quantitative result for the relative proportions of the two isomers in the solid state from X-ray diffraction, the mixing of the arsenic and phosphorus atoms is qualitatively consistent with the ratio of 0.37 : 1.0 observed in solution at −90 °C, so it is likely that the signal due to the minor isomer is obscured by that of the predominant isomer in the solid-state spectrum. The possibility that **17** still undergoes an intramolecular metal core rearrangement in the solid state cannot be ruled out on the evidence available, but it seems unlikely in view of the fact that the metal skeleton of the closely related species **16** is stereochemically rigid when the cluster is crystalline.

In the preceding section, we described how the magnitudes of the splittings in the asymmetric "quartet" signals observed for the $Cu(PR_3)$ fragments in the solid-state $^{31}P\text{-}\{^1H\}$ NMR spectra can provide information about the approximate distances between the copper and phosphorus atoms. A range of Cu–P distances of 2.2–2.5 Å was calculated from the spectra of **11**, **13**, and **17** and these values are in accord with the range of bond lengths of ca. 2.2–2.3 Å, which was obtained from X-ray diffraction studies on the clusters [8,20,22,23].

(b) Spectra of clusters containing $Ag(PR_3)$ fragments. The resonances due to the $Ag(PR_3)$ units in the solid-state spectra of **14** and **18** are all split into doublets by $^{107,109}Ag\text{–}^{31}P$ couplings, as discussed in detail in the preceding section.

The solid-state $^{31}P\text{-}\{^1H\}$ NMR spectra of **14** and **18** are in marked contrast to those obtained at ambient temperature in solution, but they are similar to the solution spectra measured at low temperatures for these clusters. In each case, two phosphorus resonances are observed in the solid state (e.g. Fig. 2b), which is consistent with the capped trigonal bipyramidal metal core geometries of these species [20–22]. However, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **18**, measured at ambient temperature in solution, consists of a complex multiplet. Analysis of this signal revealed that the two phosphorus atoms were chemically equivalent and dynamic behaviour involving silver atom site-exchange was proposed to explain the result [21,22]. This dynamic process was subsequently directly observed for some very closely related clusters by $^{109}Ag\text{-}\{^1H\}$ INEPT NMR spectroscopy [21]. Two chemically equivalent phosphorus atoms are observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **14** measured at −50 °C in solution, so the metal skeleton of **14** is also stereochemically non-rigid in solution [20]. Thus, the solid-state $^{31}P\text{-}\{^1H\}$ NMR spectra of **14** and **18** suggest that the intramolecular metal core rearrangements that these species undergo at ambient temperature in solution do not occur or are not sufficiently rapid to be observed when the compounds are crystalline.

At ambient temperature, the solution $^{31}P\text{-}\{^1H\}$ NMR spectrum of **14** is severely broadened by a second dynamic process which is thought to involve intermolecular exchange of PPh_3 ligands between clusters [20]. However, the relatively narrow line-widths and the $^{107,109}Ag\text{–}^{31}P$ couplings observed in the ambient temperature solid-state spectrum of **14** implies that this dynamic process also only occurs in solution.

(c) Spectra of clusters containing $Au(PR_3)$ fragments. The solid-state $^{31}P\text{-}\{^1H\}$ NMR spectra of **12**, **15**, and **19** are again in marked contrast to those observed at ambient temperature in solution. For each cluster, the solid-state spectra show two phosphorus resonances (e.g. Fig. 2c), which is consistent with the ground state structures of these species [8,20,24]. However, at ambient temperature, the solution spectra of **12**, **15**, and **19** all show a single phosphorus environment and stereochem-

ically non-rigidity of the metal skeletons of the clusters has been proposed as an explanation [8,20,24]. Although the spectrum of **19** measured in solution at $-60\,^\circ$C [24] is very similar to that observed in the solid state, it is interesting that it is not possible to obtain solution-state NMR spectra consistent with the ground state metal framework structures of **12** and **15**, even at $-90\,^\circ$C [8,20]. Thus, in the latter two cases, the solid-state ^{31}P-$\{^1$H$\}$ NMR spectra provide useful structural information that cannot be obtained from studies performed in solution.

Conclusions

The values of the chemical shifts and, for the silver-containing species, the magnitudes of $J(^{107,109}\mathrm{AgP})_{\mathrm{av}}$ observed in the solid-state ^{31}P-$\{^1$H$\}$ NMR spectra of a series of mixed-metal clusters containing $M(PR_3)$ (M = Cu, Ag or Au; R = alkyl or aryl) units are generally very similar to those obtained from the spectra measured in solution. For the copper-containing clusters, the solid-state NMR signals show splittings due to couplings between the quadrupolar ^{63}Cu nucleus and the phosphorus atoms, which are not visible in solutions, and the magnitudes of these splittings are consistent with the Cu–P separations. The solid-state NMR spectra, however, in many cases are observed to give a larger number of distinct resonances than are seen in the solution spectra. The possibility cannot be completely eliminated that in individual cases multiple crystal forms are present and give rise to multiple resonances from single atomic sites [25]. The results imply, however, that the dynamic processes involving hydrido ligand site-exchange or intermolecular exchange of PR_3 ligands between clusters, which have been previously observed at ambient temperature in solution for some of the clusters studied, frequently do not occur or are not sufficiently rapid to be detected when the compounds are in the crystalline state. In addition, the intramolecular metal core rearrangements, which some of the clusters undergo at ambient temperature in solution, were not detectable in the solid state.

Experimental

The clusters **1–19** were prepared as previously described [6,8–10,20,22–24]. A diethyl ether–light petroleum mixture (b.p. 40–60 °C) was used for the crystallization of those clusters for which the literature procedure specified crystallization from a dichloromethane–light petroleum mixture.

Solid-state NMR spectra were recorded on a Bruker CXP 200 spectrometer operating at 80.96 MHz for ^{31}P and 200.13 MHz for ^{1}H. Magic angle sample spinning was carried out using a Delrin Andrew-type rotor and spinning speeds of up to 4 kHz were employed. Cross-polarization was used for most experiments in order to enhance the sensitivity; the Hartman–Hahn condition was met with a B_1 field of 10 G for ^{1}H and 24.7 G for ^{31}P. A contact time of 1.5 ms was found to be optimal for compounds of the type studied here [3]. Several thousand transients were accumulated with a recycle delay of 2 s.

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