Reactivity of $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\{M(PPh_3)\}]$ (M = Cu, Ag or Au) and $[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PPh_3)\}]$ with PPh_3

John Evans and Philip M. Stroud
Department of Chemistry, The University, Southampton SO9 5NH, UK

Addition of PPh_3 to $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\{Cu(PPh_3)\}]$ **1** results in rapid heteronuclear decapping to form the anion $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^-$. A similar reaction occurs for the silver analogue **2** with excess of PPh_3. However a 1:1 reaction mixture affords $[Ag(PPh_3)_4][\{Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\}_2Ag]$ **5**, which is stable in solution at low temperatures. NMR evidence is consistent with the anion having C_2 symmetry in which an approximately tetrahedrally co-ordinated silver centre links the two triruthenium clusters by edge bridging to each cluster. Reaction of $[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PPh_3)\}]$ **4** with PPh_3 (1:1) affords an equilibrium mixture (at 173 K) of $[Ru_3H(CO)_9(\mu_3\text{-}PPh)]^-$, **4**, $[Ag(PPh_3)_n]^+$ ($n = 3$ and 4) and $[\{Ru_3H(CO)_9(\mu_3\text{-}PPh)\}_2Ag]^-$. All these reactions are faster than the carbonyl substitution reactions which occur at room temperature.

Although many examples of heterometallic clusters containing $M(PR_3)$ moieties (M = Cu, Ag or Au; R = aryl or alkyl) have been characterised, few studies on the reactivity of these species have been made, especially in relation to the $M(PR_3)$ unit itself. One such study[1] shows the reaction of $[Ru_4H_3(CO)_{12}\{M(PPh_3)\}]$ (M = Cu or Au) with PPh_3 to result in fluxional heterometal decapping with formation of the parent cluster anion *i.e.* $[Ru_4H_3(CO)_{12}]^-$ and the species $[Cu(PPh_3)_3]^+$ and $[Au(PPh_3)_2]^+$ as in equations (1) and (2). The

$$[Ru_4H_3(CO)_{12}\{Au(PPh_3)\}] + PPh_3 \rightleftharpoons [Au(PPh_3)_2]^+[Ru_4H_3(CO)_{12}]^- \quad (1)$$

$$[Ru_4H_3(CO)_{12}\{Cu(PPh_3)\}] + 2PPh_3 \rightleftharpoons [Cu(PPh_3)_3]^+[Ru_4H_3(CO)_{12}]^- \quad (2)$$

compound $[RuCo_3(CO)_{12}\{\mu_3\text{-}M(PPh_3)\}]$ (M = Cu or Au) reacts with 1 equivalent of PPh_3 in similar fashion,[2] *i.e.* as in equations (3) and (4). Neither of the two studies mentioned

$$[RuCo_3(CO)_{12}\{\mu_3\text{-}Au(PPh_3)\}] + PPh_3 \longrightarrow [Au(PPh_3)_2]^+[RuCo_3(CO)_{12}]^- \quad (3)$$

$$[RuCo_3(CO)_{12}\{\mu_3\text{-}Cu(PPh_3)\}] + PPh_3 \longrightarrow \tfrac{2}{3}[Cu(PPh_3)_3]^+[RuCo_3(CO)_{12}]^- + \ldots \quad (4)$$

above report behaviour for the silver analogues.

The aim of this work was to study the reactivity of (*a*) the clusters $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\{M(PPh_3)\}]$ (M = Cu, **1**; Ag, **2**; or Au, **3**, and (*b*) the cluster $[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PPh_3)\}]$ **4**, with PPh_3, particularly in relation to reactions at the heterometallic $M(PPh_3)$ moiety.

Experimental

The general experimental procedures were as described in ref. 1, with the additional feature of fast atom bombardment mass spectrometry (FAB-MS) using a VG 70-250SE mass spectrometer and *m*-nitrobenzyl alcohol as the matrix. The following compounds were prepared by established methods: $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\{M(PPh_3)\}]$ (M = Cu, **1**; Ag, **2**; or Au, **3**,[3] $[Ru_3H_2(CO)_9(\mu_3\text{-}PPh)]$[4] and $[Ag(PPh_3)Cl]$.[5]

Preparation of $[Ag(PPh_3)_4][\{Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\}_2Ag]$ **5**.—A CH_2Cl_2 solution (5 cm^3) of compound **2** (45 mg, 0.046 mmol) and PPh_3 (12 mg, 0.046 mmol) was cooled to −90 °C. Addition of hexane (also at −90 °C) led to precipitation of compound **5** as a yellow solid which was collected by filtration and washed with MeOH (3 × 10 cm^3 portions), yield 37 mg (65%). The compound is very soluble in CH_2Cl_2 and insoluble in MeOH (Found: C, 45.7; H, 3.0. Calc. for $C_{94}H_{70}Ag_2O_{20}P_4Ru_6$: C, 45.8; H, 2.9%). NMR (183 K): ^1H (CD_2Cl_2), δ 6.5–7.6 (m, Ph, 60 H), 3.72 (s, OMe, 6 H), −17.90 (s, μ-H, 2 H) and −18.02 (s, μ-H, 2 H); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ 5.4 [2d, $J(^{109}AgP)$ 258, $J(^{107}AgP)$ 223 Hz]; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 265.0 (s, *C*OMe), 207.9 (s, 1C), 207.1 (s, 1C), 197.4 (s, 1C), 197.2 (s, 1C), 195.8 (s, 1C), 195.1 (s, 1C), 194.0 (s, 1C), 190.6 (s, 2C), 138–126 (Ph resonances) and 68.3 (s, CO*Me*); ^{109}Ag (CH_2Cl_2), δ 1580.5 (s) (relative to $AgNO_3$).

Preparation of $[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PPh_3)\}]$ **4**.—The compound $[Ru_3H_2(CO)_9(\mu_3\text{-}PPh)]$ was prepared by the method described in ref. 4 which led to isolation of a mixture of $[Ru_3H_2(CO)_9(\mu_3\text{-}PPh)]$ and $[Ru_3H(CO)_{10}(\mu\text{-}PHPh)]$ (in the ratio 3:1 by NMR spectroscopy). A solution of this mixture {*ca.* 0.75 mmol $[Ru_3H_2(CO)_9(\mu_3\text{-}PPh)]$ and KOH (0.066 g, 1.18 mmol)} in MeOH (150 cm^3) was stirred at room temperature for 60 min and solid $[Ag(PPh_3)Cl]$ (278 mg, 0.75 mmol) added. The resultant solution was stirred for 60 min and then evaporated to dryness. The solid residue was chromatographed on a silica column and the required product isolated as an orange solid (272 mg, *ca.* 25%) from the third band (orange) using CH_2Cl_2–light petroleum (b.p. 40–60°C) (1:3 v/v) as the eluent. Compound **4** was purified by recrystallisation from CH_2Cl_2 and MeOH and washed with MeOH (3 × 10 cm^3 portions). It is very soluble in CH_2Cl_2, moderately soluble in non-polar organic solvents and insoluble in MeOH (Found: C, 38.1; H, 2.1. Calc. for $C_{33}H_{21}AgO_9P_2Ru_3$: C, 38.3; H, 2.0%). FAB-MS showed M^+ and loss of *n* CO ($n = 1$–9). IR (cyclohexane): 2071m, 2047s, 2020vs, 2003s, 1996s, 1984m, 1976m, 1963m and 1943m cm^{-1}. NMR: ^1H (CD_2Cl_2), δ 7.2–8.1 (m, Ph, 20 H) and −20.30 [d, *J*(Ph–PH) 16, μ-H, 1 H]; $^{31}P\text{-}\{^1H\}$ [$(CD_3)_2CO$ at 173 K], δ 12.6 [2d, J (^{109}AgP) 461, J (^{107}AgP) 400] and 324.0 [d, *J*(AgP) 7]; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 197.2 [d, *J*(PC) 13 Hz] and 135–129 (Ph).

Results and Discussion

The Reactivity of $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\{M(PPh_3)\}]$ (M = Cu, **1**; Ag, **2**; *or* Au, **3**) *with* PPh_3.—*Compound* **2**. If a

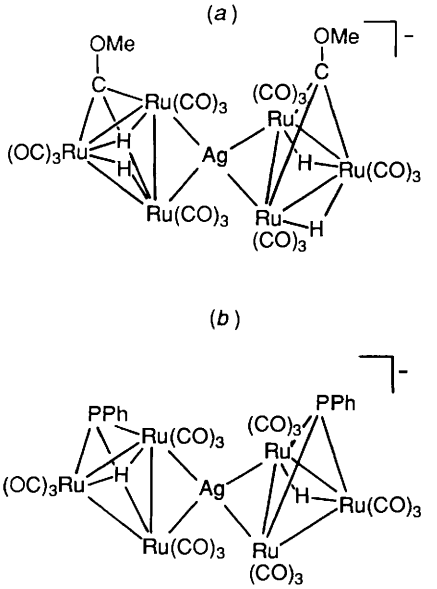

Fig. 1 The proposed structure for the anions (*a*) $[\{Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\}_2Ag]^-$ of **5** and (*b*) $[\{Ru_3H(CO)_9(\mu_3\text{-}PPh)\}_2Ag]^-$ **7**

solution of compound **2** and PPh_3 (1 equivalent) is left at room temperature, substitution of CO by PPh_3 occurs to give $[Ru_3H_2(CO)_8(PPh_3)(\mu_3\text{-}COMe)\{Ag(PPh_3)\}]$[3] **6**, a reaction which at temperatures lower than 273 K is so slow it can be disregarded. However, if a similar solution is cooled to 183 K, $[Ag(PPh_3)_4]^+[\{Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\}_2Ag]^-$ **5** is formed in yields greater than 90% (as estimated by ^1H NMR spectroscopy). This reaction is reversible and on warming the solution back to room temperature the starting materials are regenerated along with a small proportion of **6**.

Evidence for compound **5** comes mainly from NMR studies of the aforementioned solution as follows:

(*a*) ^1H NMR (CD_2Cl_2, 183 K). In addition to the phenyl signals of the phosphines a singlet is observed at δ 3.72 due to the methyl group of the COMe ligands and two μ-H signals of equal intensity are seen at δ −17.90 and −18.02.

(*b*) $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2, 183 K). One signal is observed at δ 5.4 which consists of two doublets arising from coupling to the two isotopes of Ag with $J(^{109}AgP) = 258$ and $J(^{107}AgP) = 223$ Hz. This unambiguously indicates the presence of the $[Ag(PPh_3)_4]^+$ ion when compared with the $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[Ag(PPh_3)_4][BF_4]$ under the same conditions, *i.e.* δ 5.5 [2d, $J(^{109}AgP) = 258$ Hz].

(*c*) $^{13}C\text{-}\{^1H\}$ NMR (CD_2Cl_2, 183 K). Eight signals (seven of relative intensity 1 and one of relative intensity 2) consistent with terminal carbonyl groups are observed suggesting that all the carbonyls are inequivalent. The signal of relative intensity 2 is attributed to coincidental chemical shifts. Other signals at δ 265.0 and 68.3 are consistent with the carbyne carbon and methyl carbon of the μ_3-COMe ligand respectively.

(*d*) ^{109}Ag NMR (CH_2Cl_2, 183 K). Only a singlet is observed which is assigned to the anion of **5**. The expected quintet for the cation $[Ag(PPh_3)_4]^+$ could not be detected, perhaps due to a relatively long T_1.

Compound **5** has been precipitated from solution at 183 K by the addition of hexane also at 183 K. The yellow solid obtained gave satisfactory elemental analysis (C:H). The $[\{Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\}_2Ag]^-$ anion was also identified (^1H NMR spectroscopy, 183 K) as one of the major products from the reaction of $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^-$ with $AgBF_4$.

Fig. 1 shows the proposed structure of the anion of **5** with the Ag tetrahedrally co-ordinated, two pairs of hydride ligands and each CO ligand in a Ru_3 unit terminal and inequivalent. A structure with the Ag atom face-bridging each Ru_3 unit is considered unlikely as it would be inhibited by the hydride ligands. Some similar silver environments are reported for a series of Rh/Ag clusters,[6] one of which, $[\{Rh_6(CO)_{15}C\}_2Ag]^{3-}$, has had its crystal structure determined and shows a silver atom sandwiched between trigonal faces of two trigonal-prismatic Rh_6 units. Bismuth and mercury environments analogous to that of the Ag atom in **5** have also been reported for ruthenium clusters.[7,8]

NMR studies of a solution of PPh_3 and compound **2** in the ratio 5:1 at 183 K show a single μ-H signal (δ −17.15) and a single methyl signal (δ 3.70) in the ^1H NMR spectrum {due to $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^-$, ref. 3} and signals due to $[Ag(PPh_3)_4]^+$ and free PPh_3 in the $^{31}P\text{-}\{^1H\}$ NMR spectrum. These observations are consistent with heterometal decapping of **2** *via* reaction (5). Warming this solution to room temperature results in regeneration of **2** but *via* a third species for which the ^1H NMR data are not inconsistent with those observed for **5** in the 1:1 (PPh_3:**2**) NMR study.

$$[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)\{Ag(PPh_3)\}] + 3PPh_3 \longrightarrow [Ag(PPh_3)_4]^+[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^- \quad (5)$$

With 3 equivalents of PPh_3 the ^1H NMR spectrum (CD_2Cl_2, 183 K) shows that both **5** and $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^-$ are present and hence indicates that heterometal decapping to form $[Ag(PPh_3)_4]^+[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^-$ is an equilibrium process that, as described above, can be driven to completion by excess of phosphine.

The additon of less than an equivalent of PPh_3, *e.g.* 0.5 or 0.33 equivalent, results in a mixture of compounds **5** and **2** at 183 K with the proportion of **5** increasing with the amount of PPh_3 added.

As reported previously[3] the μ-H signal in the ^1H NMR spectrum of compound **2** is a singlet at room temperature and a doublet ($J = 2$ Hz) at 183 K with the loss of coupling at room temperature attributed to an intermolecular exchange of $Ag(PPh_3)$ moieties. However, the addition of an equivalent or more of PPh_3 to **2** appears to affect this exchange process as indicated by the ^1H NMR spectra of 1:1 and 5:1 mixtures of PPh_3 and **2** at room temperature. These show methyl and μ-H signals consistent with **2** (although slightly shifted) with a coupling of 2 Hz for the hydride signal. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of a 1:1 mixture at room temperature shows a broad signal with no Ag–P coupling and a chemical shift consistent with the average of those for **2** and free PPh_3. This points to the coupling observed in the corresponding ^1H NMR spectrum as arising from a $^2J(AgH)$ interaction as opposed to $^3J(PH)$. The magnitude of these two possible couplings would be expected to be similar as shown by the ^1H NMR spectrum of $[Ru_3H_2(CO)_8(PPh_3)(\mu_3\text{-}COMe)\{Ag(PPh_3)\}]$ **6** where small couplings to the hydrides of 3 and 1 Hz are observed for the silver and phosphorus nuclei of the $Ag(PPh_3)$ unit. These observations indicate that the addition of the PPh_3 results in exchange of the free PPh_3 with the cluster-bound PPh_3 and suppression of the intermolecular $Ag(PPh_3)$ exchange. A possible explanation for the loss of this exchange process is the presence of an interaction of the silver centre with one (or more) of the phenyl rings of the added phosphine. Such an interaction is not unreasonable as virtually all alkenes and many aromatic compounds form complexes when shaken with aqueous solutions of soluble silver salts.[9] With 0.5 equivalent of PPh_3 the μ-H signal remains a singlet, presumably because there is insufficient phosphine for complete co-ordination.

Compound **1**. Proton NMR studies (CD_2Cl_2, 183 K) of compound **1** and amounts of PPh_3 ranging from a 1:1 to a 4:1 ratio (PPh_3:**1**) show the existence of an equilibrium mixture of **1** and the anion $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^-$ with the proportion of anion increasing with greater quantities of phosphine.

The addition of an equivalent of PPh_3 to compound **1** shows methyl and μ-H signals in the ^1H NMR spectrum at room temperature consistent with **1** but with no coupling for the

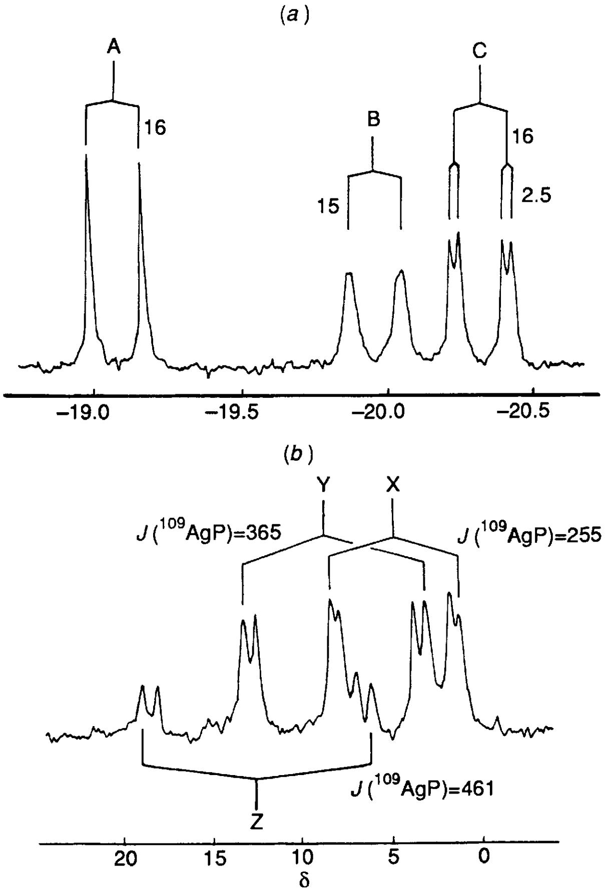

Fig. 2 NMR spectra [173 K, $(CD_3)_2CO$] of a 1:1 mixture of $[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PPh_3)\}]$ **4** and PPh_3: (*a*) ^1H at 89.55 MHz and (*b*) $^{31}P\text{-}\{^1H\}$ at 36.23 MHz

hydride signal (a coupling of 1.5 Hz is observed for the hydride signal of **1** at 183 K). This is the expected result considering the behaviour of the silver analogue **2** whether the $Cu(PPh_3)$ exchange (observed for **1** alone[3]) is suppressed or not.

If solutions of compound **1** and PPh_3 are left at room temperature, substitution of CO by PPh_3 occurs to give $[Ru_3H_2(CO)_8(PPh_3)(\mu_3\text{-}COMe)\{Cu(PPh_3)\}]$[3] (this reaction can be disregarded at temperatures below 273 K).

Compound **3**. The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra of a 1:1 mixture of compound **3** and PPh_3 at 183 K (CD_2Cl_2) show signals due only to **3** and free PPh_3 and hence no reaction occurs. However, the ^1H NMR spectrum of this mixture shows loss of the $^3J(PH)$ coupling (2 Hz) seen for **3** with no PPh_3, an observation best explained by an exchange of the gold-bound PPh_3 ligand with the free PPh_3. In support of this explanation the $^{31}P\text{-}\{^1H\}$ NMR signals for the cluster-bound phosphine and the free phosphine are both broad ($\Delta\nu_{\frac{1}{2}} \approx 15$ Hz). As expected, loss of PH coupling is also observed in the ^1H NMR spectrum at room temperature.

In similar fashion to compounds **1** and **2**, solutions of **3** and PPh_3 left at room temperature result in substitution of CO by PPh_3 to give $[Ru_3H_2(CO)_8(PPh_3)(\mu_3\text{-}COMe)\{Au(PPh_3)\}]$[3] (again this reaction can be disregarded at temperatures below 273 K).

The Heterometallic Cluster $[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PPh_3)\}]$ **4**.—The cluster **4** was prepared so that its reactivity with PPh_3 could be compared with that shown by **2** and was synthesised from the reaction of $[Ru_3H(CO)_9(\mu_3\text{-}PPh)]^-$ with $[Ag(PPh_3)Cl]$ in *ca.* 25% yield. The analogous compound $[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PEt_3)\}]$ has been previously synthesised by a similar route[10] and it is not unreasonable to suggest that these two clusters have analogous structures.

The ^1H NMR spectrum of compound **4** at 223 K [$(CD_3)_2CO$] shows, in addition to the phenyl signals of the PPh_3 and PPh ligands, a doublet of doublets for the hydride (δ −20.20) with coupling constants of 16 and 2.5 Hz. The larger of these couplings is consistent with $^2J(PH)$ coupling involving the μ_3-PPh phosphorus and the smaller coupling is assigned to interaction with either the silver or phosphorus nucleus of the $Ag(PPh_3)$ moiety. The $^{31}P\text{-}\{^1H\}$ NMR spectrum [$(CD_3)_2CO$, 173 K] shows a doublet signal for the capping phosphorus (δ 324.0, J = 7 Hz) and a signal at δ 12.6 due to the phosphorus of the PPh_3 ligand [two doublets, $^1J(^{109}AgP)$ = 461 Hz]. As only $^1J(AgP)$ coupling is observed for the phosphorus signal of PPh_3 the coupling of 7 Hz for the capping phosphorus signal must be due to $^2J(AgP)$ coupling.

At room temperature the $^{31}P\text{-}\{^1H\}$ NMR spectrum ($CDCl_3$) is somewhat dependent on the sample. The observed signal of the PPh_3 phosphorus consisted of two clearly resolved doublets, with $^1J(AgP)$ coupling, for one sample and a broad doublet, with $^1J(AgP)$ coupling, for another sample. This is presumably due to small amounts of PPh_3 impurities initiating exchange of PPh_3. The rate of this process is increased in acetone. The ^1H NMR spectrum at room temperature shows loss of the 2.5 Hz coupling to the hydride signal observed at lower temperatures. As Ag–P coupling is observed this loss of coupling is best explained by an intermolecular exchange of $Ag(PPh_3)$ units as observed for complex **2**.

The $^{13}C\text{-}\{^1H\}$ NMR spectrum at room temperature shows that the carbonyl signals undergo rapid averaging (only one signal is seen) with an average coupling of 13 Hz, presumably due mainly to coupling with the μ_3-PPh phosphorus site.

The Reactivity of Compound **4** *with* PPh_3.—The ^1H NMR spectrum [$(CD_3)_2CO$, 173 K] of a 3:1 mixture of PPh_3 and **4** shows just one hydride signal *i.e.* a doublet (J = 16 Hz) at δ −19.07 with the corresponding $^{31}P\text{-}\{^1H\}$ NMR spectrum showing two signals, a singlet at δ 294.8 and two doublets [δ 4.9, $J(^{109}AgP)$ = 257 Hz]. The ^{31}P NMR signal at δ 4.9 is indicative of $[Ag(PPh_3)_4]^+$ while the other phosphorus signal and hydride signal correspond to the anion $[Ru_3H(CO)_9(\mu_3\text{-}PPh)]^-$. The salt $[N(PPh_3)_2][Ru_3H(CO)_9(\mu_3\text{-}PPh)]$ gives a hydride signal in the ^1H NMR spectrum [$(CD_3)_2CO$, 173 K] at δ −19.06 [$J(PH)$ = 16 Hz] and a μ_3-PPh singlet in the $^{31}P\text{-}\{^1H\}$ NMR spectrum [$(CD_3)_2CO$, 173 K] at δ 294.4. These observations are consistent with heterometal decapping of **4** *via* reaction (6).

$$[Ru_3H(CO)_9(\mu_3\text{-}PPh)\{Ag(PPh_3)\}] + 3PPh_3 \longrightarrow [Ag(PPh_3)_4]^+[Ru_3H(CO)_9(\mu_3\text{-}PPh)]^- \quad (6)$$

With just 1 equivalent of PPh_3 a much more complicated system is observed. At 173 K [$(CD_3)_2CO$] the ^1H NMR spectrum [Fig. 2(*a*)] shows three hydride signals, A at δ −19.08 (d, J = 16), B at δ −19.96 (d, J = 15) and C at δ −20.32 (d of d, J = 16, 2.5 Hz). Signals A and C correspond to the anion $[Ru_3H(CO)_9(\mu_3\text{-}PPh)]^-$ and **4** respectively. The $^{31}P\text{-}\{^1H\}$ NMR spectrum [$(CD_3)_2CO$], 173 K] of the PPh_3 phosphorus nuclei is shown in Fig. 2(*b*) and contains three signals, X at δ 4.7 [2 × d, $J(^{109}AgP)$ = 255], Y at δ 8.1 [2 × d, $J(^{109}AgP)$ = 365] and Z at δ 12.5 [2 × d, $J(^{109}AgP)$ = 461 Hz]. Signals X and Z correspond to $[Ag(PPh_3)_4]^+$ and **4** respectively while Y is believed to be due to $[Ag(PPh_3)_3]^+$. Evidence for the presence of $[Ag(PPh_3)_3]^+$ comes from consideration of the magnitude of the observed $J(AgP)$ coupling which is consistent with other $[AgL_3]^+$ species where L = phosphine, *e.g.* $^1J(^{109}AgP)$ = 350 Hz for L = PEt_3, 350 Hz for $PBu^n{}_3$ and 370 Hz for $P(C_6H_4Me\text{-}p)_3$.[11] Three capping phosphorus signals are also observed, (i) δ 324.0 (d, J = 6 Hz), (ii) δ 314.0 (s) and (iii) δ 294.8 (s), of which (i) and (iii) are consistent with **4** and $[Ru_3H(CO)_9(\mu_3\text{-}PPh)]^-$ respectively.

Signal (ii) is assigned to the same compound giving rise to the hydride signal B in Fig. 2(*a*).

With 4/3 equivalents of PPh_3 the same signals are observed in the ^1H and $^{31}P-\{^1H\}$ NMR spectra [$(CD_3)_2CO$, 173 K] but with a relatively greater proportion of the anion $[Ru_3H(CO)_9(\mu_3-PPh)]^-$ and less **4**. A ^1H NMR spectrum of compound **4** with just a trace of PPh_3 shows essentially only signals for **4** and a weak signal corresponding to the unidentified signal B [Fig. 2(*a*)]. The ^1H NMR spectrum at room temperature [$(CD_3)_2CO$] of a 1:1 mixture shows a broadened doublet hydride signal (J = 16 Hz) at δ -19.69.

The NMR spectra described above indicate that the reaction of compound **4** with PPh_3 results in an equilibrium mixture of three cluster species {two of which are identified as **4** and $[Ru_3H(CO)_9(\mu_3-PPh)]^-$} which, with 3 equivalents of PPh_3, is driven to complete heterometal decapping to give $[Ag(PPh_3)_4]^+$ $[Ru_3H(CO)_9(\mu_3-PPh)]^-$. The third cluster species has a doublet hydride signal in the ^1H NMR spectrum (J = 15 Hz) and just one signal (singlet) corresponding to a capping PPh group in the $^{31}P-\{^1H\}$ NMR spectrum. By analogy with **5**, formed from the reaction of **2** with PPh_3, this third cluster is believed to be $[\{Ru_3H(CO)_9(\mu_3-PPh)\}_2Ag]^-$ **7** which is consistent with the NMR data. The structure for this anion would be expected to be very similar to that for the anion of **4** and is shown in Fig. 1(*b*).

Consideration of the fact that compound **4** has just one hydride suggests the possibility of forming larger clusters *i.e.* $[\{Ru_3H(CO)_9(\mu_3-PPh)\}_nAg_{n-1}]^-$ (n = 1, 2, *etc.*) as there is an extra Ru–Ru bond available that is not hydride-bridged. No such reactivity, however, was observed.

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