3660 *Inorg. Chem.* **1993**, *32*, 3660–3669

Ruthenium Tri- and Digold Hydride Clusters

Alberto Albinati,[1a] Luigi M. Venanzi,*,[1b] and Guozhi Wang[1b]

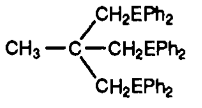
Laboratorium für Anorganische Chemie, ETH-Z, CH-8092 Zürich, Switzerland, and Istituto di Chimica Farmaceutica, Università di Milano, I-20131 Milano, Italy

Received February 3, 1993

The synthesis and characterization of ruthenium–gold clusters, of composition [(triars)RuH$_3${Au(L)}$_3$][PF$_6$]$_2$ (triars = CH$_3$C(CH$_2$AsPh$_2$)$_3$; L = PPh$_3$, PEt$_3$ P-*i*-Pr$_3$) and [(triphos)RuH$_3${Au(L)}$_3$][PF$_6$]$_2$ (triphos = CH$_3$C(CH$_2$PPh$_2$)$_3$; L = PPh$_3$, P-*i*-Pr$_3$, AsPh$_3$, As-*i*-Pr$_3$), type C, is reported. They were obtained by reacting the gold cations {Au(L)}$^+$ (3 equiv) with either [RuH$_4$(triars)] or [RuH(BH$_4$)(triphos)] (1 equiv). The X-ray crystal structure of [(triphos)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$ shows the presence of a RuAu$_3$ tetrahedron with the ruthenium atom capped by triphos, while each gold atom is coordinated to one PPh$_3$. The hydride ligands, which could be located, occupy bridging positions above each of the Ru–Au$_2$ faces but are displaced toward one RuAu edge. Crystal data: space group *R*3*c*, a = 20.150(3) Å, c = 45.229(9) Å, Z = 6, V = 15904(9) Å^3, ρ(calcd) = 1.501 g cm^{-3}, and R = 0.051. The addition of the gold cations {Au(L)}$^+$ (2 equiv) to either [RuH$_4$(triars)] or [RuH(BH$_4$)(triphos)] (1 equiv), in the presence of a base, gave the trinuclear species [(triars)RuH$_3${Au(L)}$_2$][PF$_6$] (L = PPh$_3$, P-*o*-Tol$_3$, P-*i*-Pr$_3$, AsPh$_3$) and [(triphos)RuH$_3${Au(L)}$_2$][PF$_6$] (L = PPh$_3$, P-*o*-Tol$_3$, P-*i*-Pr$_3$, AsPh$_3$), respectively, type **B**. These complexes are highly fluxional in solution and have been assigned static structures based on a RuHAu$_2$ tetrahedron, the ruthenium atom being capped by the *tripod* ligand and each gold being coordinated to a ligand L, while the other two H-atoms are assumed to bridge the Ru–Au edges. Some highly fluxional binuclear compounds of composition [(triars)RuH$_3${Au(L)}] (L = PPh$_3$, P-*o*-Tol$_3$) and [(triphos)RuH$_3${Au(P-*o*-Tol$_3$)}], type A, could also be characterized in solution.

Introduction

In recent years several groups have reported the formation of hydrido-bridged heterometallic compounds by the addition of gold–phosphine cations to transition metal hydrides.[2] Of particular interest are the tetrahedral heterometallic clusters of the type "MAu$_3$", where M = Rh,[3] Ir,[3] and Re,[4] as in these complexes the number of the hydride ligands associated with the MAu$_3$ unit can vary from 1 to 3 and appears to be related to the positive ionic charge of the cluster, the maximum acceptable value being 2. Compounds which form MAu clusters particularly easily are the trihydrides [MH$_3$(*tripod*)] (M= Rh, Ir; *tripod* = triphos, triars).[3]



tripod
E = P = triphos
E = As = triars

These can add successively up to three gold phosphine or arsine cations, "{Au(L)}$^+$", although stable trigold clusters are formed only after proton dissociation (eqs 1a–c). The compounds of

$$[\text{MH}_3(\textit{tripod})] + [\text{Au(S)L}]^+ \rightarrow [(\textit{tripod})\text{MH}_3\{\text{Au(L)}\}]^+ + \text{S} \quad \text{(1a)}$$

type A

$$[(\textit{tripod})\text{MH}_3\{\text{Au(L)}\}]^+ + [\text{Au(S)L}]^+ \rightarrow [(\textit{tripod})\text{MH}_3\{\text{Au(L)}\}_2]^{2+} + \text{S} \quad \text{(1b)}$$

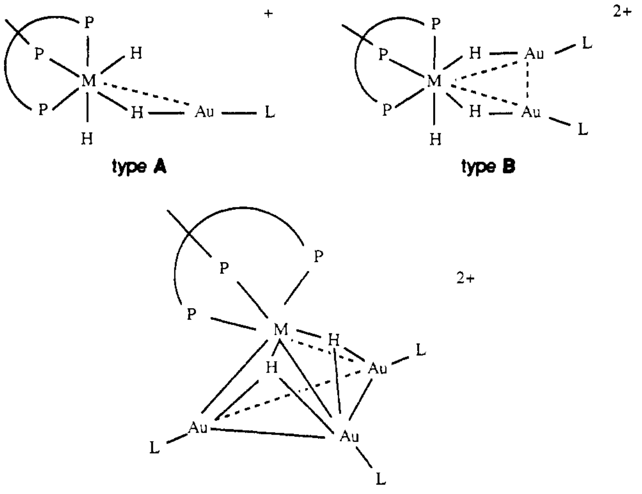
type **B**

$$[(\textit{tripod})\text{MH}_3\{\text{Au(L)}\}_2]^{2+} + [\text{Au(S)L}]^+ \rightarrow [(\textit{tripod})\text{MH}_2\{\text{Au(L)}\}_3]^{2+} + \text{SH}^+ \quad \text{(1c)}$$

type C

types **A** and **B** were assigned the structures shown in Chart I on the basis of their NMR spectra, while the structure of one of the compounds of type C was established also by X-ray diffraction.[3]

Chart I



type A

type B

type C

As the ruthenium trihydrides [RuH$_3$(L′)$_3$]$^-$ are anionic, it seemed probable that clusters containing the RuAu$_3$ moiety and *three* bridging hydride ligands could be prepared. However, it was thought desirable to carry out the study of heterometallic cluster formation using complexes of the type *fac*-[RuH$_3$(*tripod*)]$^-$, as it was expected that they would form more stable clusters than those given by the corresponding hydrides with monodentate ligands.

This paper reports the synthesis and characterization of complexes of the types [(*tripod*)RuH$_3${Au(L)}], type A, [(*tripod*)-RuH$_3${Au(L)}$_2$]$^+$, type **B**, and [(*tripod*)RuH$_3${Au(L)}$_3$]$^{2+}$, type C (*tripod* = triphos, triars; L = monodentate phosphine, arsine).

---

(1) (a) Università di Milano. (b) ETH Zürich.

(2) Boyle, P. D.; Johnson, B. J.; Buheler, A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 7.

(3) Albinati, A.; Demartin, F.; Janser, P.; Rhodes, L. F.; Venanzi, L. M. *J. Am. Chem. Soc.* **1989**, *111*, 2115.

(4) Sutherland, B. R.; Folting, K.; Streib, W. E.; Ho, D. M.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1987**, *109*, 3489.

0020-1669/93/1332-3660$04.00/0

Table I. Relevant ^{1}H and ^{31}P{^{1}H} NMR Data (Recorded at Room Temperature; Chemical Shifts in ppm, *J* in Hz) for Compounds [(tripod)RuH$_3${Au(L)}$_3$][PF$_6$]$_2$, [(tripod)RuH$_3${Au(L)}$_2$][PF$_6$], and [(tripod)RuH$_3${Au(L)}]

no.	compd	^{H} NMR (hydride^{a})	^{31}P NMR
C1	[(triars)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$^{b}	−4.69 (q); ^2J(P^{Au}, H) = 24.3	P^{Au} 44.0 (s)
C2	[(triars)RuH$_3${Au(PEt$_3$)}$_3$][PF$_6$]$_2$^{b}	−5.04 (q); ^2J(P^{Au}, H) = 24.2	P^{Au} 45.2 (s)
C3	[(triars)RuH$_3${Au(P-*i*-Pr$_3$)}$_3$][PF$_6$]$_2$^{b}	−5.21 (q); ^2J(P^{Au}, H) = 23.1	P^{Au} 75.7 (s)
C4	[(triars)RuH$_3${Au(AsPh$_3$)}$_3$][PF$_6$]$_2$^{b}	−5.64 (s)	
C5	[(triphos)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$^{b}	−2.82 (qxm); ^2J(P^{Au}, H) = 23.1, $\|N\|$ = 2.2	P^{Au} 42.6 (q); P^{tr} 38.5 (q); ^4J(P^{Au}, P^{tr}) = 15.0
C6	[(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_3$][PF$_6$]$_2$^{b}	−3.48 (qxm); ^2J(P^{Au}, H) = 24.7, $\|N\|$ = 1.6	P^{Au} 73.6 (q); P^{tr} 36.7 (q); ^4J(P^{Au}, P^{tr}) = 15.0
C7	[(triphos)RuH$_3${Au(AsPh$_3$)}$_3$][PF$_6$]$_2$^{b}	−4.03 (m); $\|N\|$ = 4.5	P^{tr} 37.0 (s)
C8	[(triphos)RuH$_3${Au(As-*iso*-Pr$_3$)}$_3$][PF$_6$]$_2$^{b}	−4.05 (m); $\|N\|$ = 4.0	P^{tr} 36.1 (s)
B1	[(triars)RuH$_3${Au(PPh$_3$)}$_2$][PF$_6$]^{c}	−6.12 (t); ^2J(P^{Au}, H) = 31.5	P^{Au} 46.5 (s)
B2	[(triars)RuH$_3${Au(P-*o*-Tol$_3$)}$_2$][PF$_6$]^{c}	−6.83 (t); ^2J(P^{Au}, H) = 31.0	P^{Au} 34.6 (s)
B3	[(triars)RuH$_3${Au(P-*i*-Pr$_3$)}$_2$][PF$_6$]^{c,d}	−6.07 (t); ^2J(P^{Au}, H) = 29.4	P^{Au} 75.2 (s)
B4	[(triars)RuH$_3${Au(AsPh$_3$)}$_2$][PF$_6$]^{c,d}	−6.73 (s)	
B5	[(triphos)RuH$_3${Au(PPh$_3$)}$_2$][PF$_6$]^{c,d}	−3.99 (txm); ^2J(P^{Au}, H) = 32.4, $\|N\|$ = 11.6	P^{Au} 44.8 (q); P^{tr} 46.2 (t); ^4J(P^{Au}, P^{tr}) = 14.8
B6	[(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_2$][PF$_6$]^{c,d}	−3.90 (txm); ^2J(P^{Au}, H) = 31.6; $\|N\|$ = 11.1	P^{Au} 74.2 (q); P^{tr} 45.1 (t); ^4J(P^{Au}, P^{tr}) = 15.1
B7	[(triphos)RuH$_3${Au(P-*o*-Tol$_3$)}$_2$][PF$_6$]^{c,d}	−4.67 (txm); ^2J(P^{Au}, H) = 33.5; $\|N\|$ = 9.6	P^{Au} 36.2 (q); P^{tr} 42.0 (t); ^4J(P^{Au}, P^{tr}) = 17.8
B8	[(triphos)RuH$_3${Au(AsPh$_3$)}$_2$][PF$_6$]^{c,d}	−4.70 (m); $\|N\|$ = 8.0	P^{tr} 45.6 (s)
A1	[(triars)RuH$_3${Au(PPh$_3$)}]^{d,e}	−8.15 (d); ^2J(P^{Au}, H) = 39.3	P^{Au} 48.5 (s)
A2	[(triars)RuH$_3${Au(P-*o*-Tol$_3$)}]^{d,e}	−8.43 (d); ^2J(P^{Au}, H) = 40.5	P^{Au} 34.0 (s)
A3	[(triphos)RuH$_3${Au(P-*o*-Tol$_3$)}]^{d,f}	−6.33 (dxm); ^2J(P^{Au}, H) = 35.3; $\|N\|$ = 14.2	P^{Au} 31.4 (q); P^{tr} 43.3 (d); ^4J(P^{Au}, P^{tr}) = 16.0

[a] $|N|$ Denotes the separation between the two intense sharp peaks of the AA′A″XX′X″ system, which corresponds to the sum of *J*(b,X) + 2*J*(b,X′), according to the notation by: Jones, R. G.; Hirst, R. C.; Bernstein, H. J. *Can. J. Chem.* **1965**, *43*, 683. [b] In CD$_2$Cl$_2$. [c] In CDCl$_3$. [d] Obtained in solution. [e] In THF, using a d^6-acetone capillary as a lock. [f] In d^6-benzene.

The X-ray crystal structure of [(triphos)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$ is also reported.

Results and Discussion

RuAu$_3$ Clusters [(triphos)RuH$_3${Au(L)}$_3$]X$_2$, Type C. These will be discussed first as they are most easily produced. The most direct way of obtaining complexes of this type would be by reacting 3 equiv of a gold cation of the type "AuL$^+$" with 1 equiv of an anion of the type [RuH$_3$(*tripod*)]$^-$. The latter, however, do not appear to have been reported in the literature, although [RuH$_3$(PPh$_3$)$_3$]$^-$ has been much studied.[5,6] A solution to this problem was provided by the observation that, as mentioned earlier, the trihydrides [MH$_3$(*tripod*)] (M = Rh, Ir) deprotonate spontaneously, in the presence of protic solvents, on addition of 3 equiv of the gold cations AuL$^+$ giving the clusters containing the "MH$_2$Au$_3$" moiety.[3] Thus it seemed probable that complexes of type **C** could be obtained starting from the tetrahydrides [RuH$_4$(*tripod*)]. The limitation here was that [RuH$_4$(triars)] (**1**), but not its triphos analogue,[7] had been obtained, and thus only the preparation of the clusters derived from **1** could be attempted by this method.

Complex **1** reacted within minutes with 3 equiv of [Au(THF)(L)]$^+$ (prepared *in situ* from [AuCl(L)] and Tl[PF$_6$] in THF) giving [(triars)RuH$_3${Au(L)}$_3$][PF$_6$]$_2$ (eq 2).

$$\underset{\mathbf{1}}{[\mathrm{RuH_4(triars)}]} + 3[\mathrm{Au(THF)L}][\mathrm{PF_6}] \rightarrow \underset{\mathbf{C1\text{–}4}}{[\mathrm{(triars)RuH_3\{Au(L)\}_3}][\mathrm{PF_6}]_2} + [\mathrm{H(THF)}][\mathrm{PF_6}] + 2\mathrm{THF} \qquad (2)$$

$$\mathrm{L = PPh_3,\ PEt_3,\ P\text{-}\mathit{i}\text{-}Pr_3,\ AsPh_3}$$

When the above reaction was carried out without removing chloride, i.e., in the absence of Tl[PF$_6$], instead of obtaining complexes of type **C** the solution contained digold complex cations of composition [(triars)RuH$_3${Au(L)}$_2$]$^+$, type **B** (see later), and unreacted [AuCl(L)]. However, it was not necessary to neutralize the released protons prior to the isolation of the type **C** clusters as they are stable in acidic solution. The compounds prepared are listed in Table I.

It is noteworthy that while the formation of complexes of type [(*tripod*)MH$_2${Au(L)}$_3$][PF$_6$]$_2$ (M = Rh, Ir) from [MH$_3$(*tripod*)] and 3 equiv of [Au(THF)L]$^+$ required the presence of a protic solvent,[3] in the case of [RuH$_4$(triars)] proton liberation occurred even in THF or CH$_2$Cl$_2$, indicating that the ruthenium tetrahydride is "more acidic" than either [RhH$_3$(triars)] or its iridium analogue.

As mentioned earlier, it has not been possible to prepare [RuH$_4$(triphos)],[7] and thus a different starting material had to be used to prepare RuAu$_3$ clusters containing triphos. The formal analogy between "H$^+$" and "BH$_2$$^+$" and the ability of {Au(L)}$^+$ cations to displace a proton from [RuH$_4$(triars)] indicated that the gold cations might also displace a BH$_2$$^+$ moiety from the complex [RuH(BH$_4$)(triphos)],[8] in a reaction of the type shown in eq 3. Reactions 2 and 4 are equivalent, at least in a formal sense, as the loss of a proton from [RuH$_4$(triars)] produces the ruthenium(II) anion [RuH$_3$(triars)]$^-$ while loss of BH$_2$$^+$ from [RuH(BH$_4$)(triphos)], which contains ruthenium(II), leaves the oxidation state of the metal unchanged.

$$\underset{\mathbf{2}}{[\mathrm{RuH(BH_4)(triphos)}]} + 3[\mathrm{Au(THF)(L)}][\mathrm{PF_6}] \rightarrow \underset{\mathbf{C5,6,8}}{[\mathrm{(triphos)RuH_3\{Au(L)\}_3}][\mathrm{PF_6}]_2} + \text{“}[\mathrm{BH_2(THF)_2}][\mathrm{PF_6}]\text{”} + \mathrm{THF} \qquad (3)$$

$$\mathrm{L = PPh_3,\ P\text{-}\mathit{i}\text{-}Pr_3,\ As\text{-}\mathit{i}\text{-}Pr_3}$$

This was indeed the case, and the complexes thus obtained are also listed in Table I. As found for the triars clusters, the corresponding triphos compounds cannot be obtained in the absence of Tl[PF$_6$] when [AuCl(L)] is used.

It is likely that the fragment BH$_2$$^+$, which is liberated during the reaction shown in eq 3, is probably present in the form "BH$_2$(THF)$_2$$^+$" as THF was used as the solvent. This boron-containing species did not interfere with the isolation of the products.

It was found that the compound [(triphos)RuH$_3${Au(AsPh$_3$)}$_3$][PF$_6$]$_2$ (**C7**) could not be prepared by this method, as the hydridoborohydride **2** reacted with [AuCl(AsPh$_3$)] with formation of metallic gold. However, the cluster **C7** was obtained starting

---

(5) Shieh, H. S.; Chan, A. S. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1379.

(6) (a) Wilczynski, R.; Fordyce, W. A. Halpern, J. *J. Am. Chem. Soc.* **1983**, *105*, 2066. (b) Linn, D. E.; Halpern, J. *J. Organomet. Chem.* **1987**, *333*, 155. (c) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969. (d) Halpern, J. *Pure Appl. Chem.* **1987**, *59*, 173.

(7) (a) Sorato, C. Dissertation, ETH Zürich, No. 8775, Zürich, 1989. (b) Wang, G. Dissertation, ETH Zürich, No. 9398, 1991.

(8) Rhodes, L. F.; Venanzi, L. M. *Inorg. Chem.* **1987**, *26*, 2692.

from the complex $[RuH_2(AsPh_3)(triphos)]$ (**3**) by the reaction shown in eq 4. This method was suggested by the observation[7] that $AsPh_3$ in complex **3** is readily exchanged when its solution is heated up to 60 °C.

$$\underset{\mathbf{3}}{[RuH_2(AsPh_3)(triphos)]} + 3[Au(THF)(AsPh_3)][PF_6] + H_2 \xrightarrow[THF]{60\,°C} \underset{\mathbf{C7}}{[(triphos)RuH_3\{Au(AsPh_3)\}_3][PF_6]_2} + [H(THF)][PF_6] + AsPh_3 + 2THF \quad (4)$$

As found for the corresponding rhodium and iridium clusters, the ruthenium compounds of type **C** with very bulky phosphines, e.g., tris(*o*-tolyl)phosphine (cone angle 194°),[9] coordinated to gold could not be prepared, presumably because of steric hindrance.

The type **C** clusters were characterized by elemental analyses and IR and NMR spectroscopy. It is noteworthy that the highest energy absorptions in infrared spectra assignable to RuH_3-stretching modes of these compounds are broad bands at ca. 1600 cm^{-1}. Confirmation of these assignments was obtained by comparing the IR and incoherent inelastic neutron spectroscopy of $[(triphos)RuH_3\{Au(PPh_3)\}_3][PF_6]_2$ and of the corresponding trideuteride.[10a] Thus the hydride ligands are strongly bridging.

The ^1H, in the hydride region, and ^{31}P NMR spectra of the compounds of type **C** were most informative, particularly when selective decoupling techniques were used. Some relevant parameters are listed in Table I. As the spectra of the clusters containing triars are simpler, they will be discussed first.

(a) Clusters Containing Triars. The $^{31}P\{^1H\}$ NMR spectra of the $[(triars)RuH_3\{Au(PR_3)\}_3]^{2+}$ cations gave singlets, which became quartets when the spectra were recorded under conditions of selective decoupling, i.e., where the hydride ligands remained coupled. This observation confirmed the presence of three hydride ligands in these clusters.

The ^1H NMR spectra in the hydride region of these cations appeared as quartets consistent with first-order spin systems. The spectra were temperature-independent in the range 183–300 K. The coupling of the three phosphorus atoms on gold (P^{Au}) with the hydrides was further confirmed by decoupling at the frequency of the P^{Au} atoms, whereby each quartet reduced to a singlet.

As expected, the ^1H NMR spectra of the clusters with tertiary arsines on gold, $[(triars)RuH_3\{Au(AsR_3)\}_3]^{2+}$, showed only singlets in the hydride region.

(b) Clusters Containing Triphos. The $^{31}P\{^1H\}$ NMR spectra of the complexes $[(triphos)RuH_3\{Au(AsR_3)\}_3]^{2+}$ consisted of singlets, while those of the complexes $[(triphos)RuH_3\{Au(PR_3)\}_3]^{2+}$ showed two quartets. In the latter cases allowing the hydrides to couple with the phosphorus atoms did not significantly change the appearence of the signals due to triphos, P^{tr}, while those due to P^{Au} became pseudoseptets (resulting from q × q with $^4J(P^{tr}, P^{Au}) \approx {}^2J(P^{Au}, H)$). These spectra showed, once again, that three hydride ligands were present in the clusters.

The ^1H NMR spectra, in the hydride region, of the *clusters containing arsine ligands on gold* of the type $[(triphos)RuH_3\{Au(AsR_3)\}_3][PF_6]_2$ (**C7,8**) showed multiplets consistent with the spin system $AA'A''XX'X''$.[11] This pattern of resonances is similar to those of complexes of the type $[(triphos)MH_2\{Au(AsPh_3)\}_3][CF_3SO_3]_2$ (M = Rh, Ir).[3] However, in the former cases the separation between the two stronger lines is quite small, e.g., ca. 4.5 Hz for the $AsPh_3$ complex **C7**. These multiplets reduced to singlets, when the spectra were recorded with simultaneous decoupling at the frequency of the phosphorus atoms of triphos, P^{tr}.

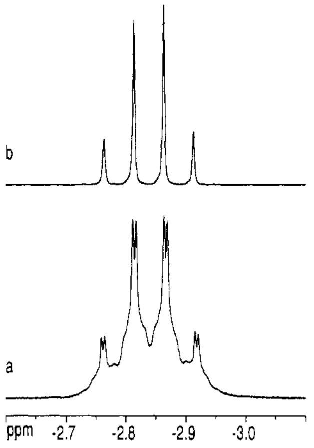


Figure 1. ^1H NMR (500.13 MHz, CD_2Cl_2) spectra (in the hydride region) of $[(triphos)RuH_3\{Au(PPh_3)\}_3][PF_6]_2$, **C5**, at room temperature: (a) normal; (b) P^{tr}-decoupled.

The ^1H NMR spectra, in the hydride region, of the corresponding *clusters containing phosphine ligands on gold*, i.e., **C5,6**, showed quartets of multiplets assignable to the spin system $AA'A''M_3XX'X''$. The spectrum of $[(triphos)RuH_3\{Au(PPh_3)\}_3][PF_6]_2$ (**C5**) is shown in Figure 1a. On decoupling at the frequency of P^{tr}, the hydride signals reduced to a quartet (Figure 1b) of appearance similar to that of the corresponding clusters containing triars, while on decoupling at P^{Au} one obtained a multiplet of appearance similar to that of the corresponding clusters containing arsine ligand on gold.

It should be noted that, in the temperature range 183–300 K, the phosphorus atoms on gold in these clusters appear as magnetically equivalent with respect to the three hydride ligands. As the phosphorus atoms of triphos in the "$(triphos)RuH_3$" unit are not magnetically equivalent, this moiety and the "Au_3L_3" unit must be dynamic relative to each other on the NMR time scale.

According to Hall et al.[12] the energy barrier for the intramolecular exchange process in gold–phosphine clusters is very small. Therefore, one can describe the fluxional behavior as being caused by rapid mutual rotation of the Au_3L_3 framework and the $(triphos)RuH_3$ unit around the cluster C_3 symmetry axis. This type of relative motion has now been demonstrated in complexes of the type $[(triphos^*)RhH_2\{Au(PPh_3)\}_3]^{2+}$ (triphos* = (*RRS*/*SSR*)-$CH_3C(CH_2P^*MePh)_3$).[13]

It is now well-established that many polyhydride compounds often contain coordinated molecular hydrogen; i.e., they are "nonclassical" hydrides. These are generally highly dynamic. Hamilton and Crabtree[14] have shown that nonclassical hydrides have very short longitudinal relaxation times, T_1, (generally less than 150 ms), while those of "classical" hydrides are much longer. In order to establish whether the dynamic properties mentioned above are caused by the presence of coordinated molecular hydrogen, the relaxation time T_1 of the hydrides in one of the type **C** clusters was measured by means of the inversion–recovery method.[15] The compound $[(triphos)RuH_3\{Au(PPh_3)\}_3][PF_6]_2$ was chosen for this study. The T_1 temperature-dependence of the values between 233 and 333 K gave a minimum of 476 ms at 293 K indicating that, at least in this compound, the hydride

---

(9) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(10) (a) Albinati, A.; Eckert, H. J.; Hofmann, P.; Rüegger, H.; Venanzi, L. M. *Inorg. Chem.* **1993**, *32*, 2377. (b) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1973**, *10*, 265. (c) Moore, D. S.; Robison, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415. (d) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145. (e) Cooper, G. B.; Shriver, D. F.; Onaka, S. *Adv. Chem. Ser.* **1978**, *No. 167*, 232. (f) Gates, B. C., Guczi, L., Knözinger, H., Eds. *Metal Clusters in Catalysis;* Elsevier: Amsterdam, 1986; p 137.

(11) Jones, R. G.; Hirst, R. C.; Bernstein, H. J. *Can. J. Chem.* **1965**, *43*, 683

(12) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 327.

(13) Imhof, D.; Rüegger, H.; Venanzi, L. M.; Ward, T. R. *Magn. Reson. Chem.* **1991**, *29*, S73.

(14) (a) Hamilton, D. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Hamilton, D. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3124.

(15) Martin, L. M., Martin, G. J., Eds. *Practical NMR Spectroscopy;* Heyden: London, 1980.

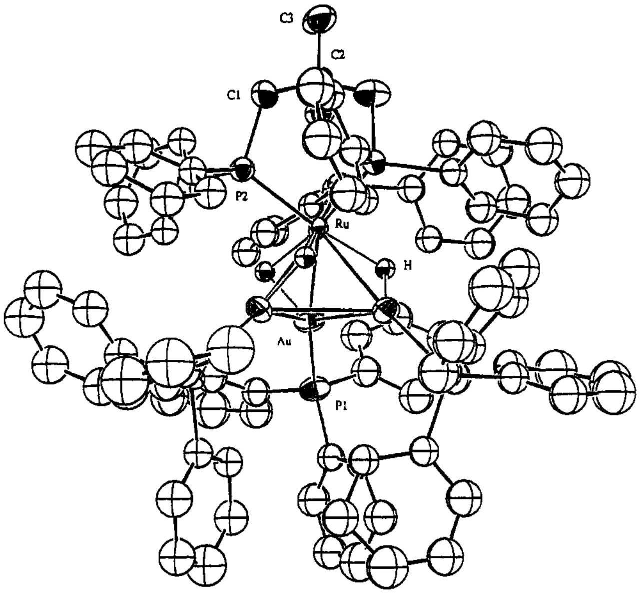


Figure 2. ORTEP view of the $[(\text{triphos})\text{RuH}_3\{\text{Au}(\text{PPh}_3)\}_3]^{2+}$ cation in $[(\text{triphos})\text{Ru}(\mu\text{-H})_3\{\text{Au}(\text{PPh}_3)\}_3][\text{PF}_6]_2$, **C5**.

Table II. Relevant Bond Lengths (Å) and Bond and Torsion Angles (deg) for the Cations of $[(\text{triphos})\text{RuH}_3\{\text{Au}(\text{PPh}_3)\}_3][\text{PF}_6]_2$, **C5**, and of $[(\text{triphos})\text{RhH}_2\{\text{Au}(\text{PPh}_3)\}_3](\text{CF}_3\text{SO}_3)_2$, **C′1**

params	**C5** (M = Ru)	**C′1** (M = Rh)	diff
M–Au	2.679(2)	2.695(2)	–0.017
Au–Au′	3.003(1)	2.887(1)	+0.116
Au–P1	2.326(5)	2.260(5)	+0.065
M–P2	2.330(5)	2.313(5)	+0.017
M–Au–P1	169.4(1)	167.9(1)	+1.5
Au–M–P2	87.9(1)	87.7(1)	+0.2
Au′–M–P2	150.2(1)	144.0(1)	+6.2
Au–M–Au	68.20(5)	64.78(6)	+3.42
M–Au–Au′	55.90(3)	57.61(3)	–1.73
P2–M–P′2	89.3(1)	90.5(2)	–1.2
Ru–H	1.9(2)		
Au–H	1.7(2)		
Au′–H	2.6(2)		
Ru–H–Au	92(3)		
P2–Ru–H	168(5)		
P1–Au–H	137(6)		
P1–Au–Ru–P2	34.9	15.1	
P2–Ru–H–Au1′	177		
P2–Ru–H–Au1	92		

ligands remain classical and molecular hydrogen coordination is not responsible for the dynamic behavior observed.

In conclusion, on the basis of the above data, it is proposed that compounds of type **C**, in solution, can be assigned a static structure similar to that of crystalline $[(\text{triphos})\text{RuH}_3\{\text{Au}(\text{PPh}_3)\}_3][\text{PF}_6]_2$ (**C5**), found by X-ray diffraction and described below.

X-ray Crystal Structure of $[(\text{triphos})\text{Ru}(\mu\text{-H})_3\{\text{Au}(\text{PPh}_3)\}_3][\text{PF}_6]_2$ (C5). The crystals contain discrete $[(\text{triphos})\text{Ru}(\mu\text{-H})_3\{\text{Au}(\text{PPh}_3)\}_3]^{2+}$ cations and disordered $[\text{PF}_6]^-$ anions. An ORTEP view of the molecular structure of the cation is shown in Figure 2. A selection of bond lengths and angles is given in Table II, where the corresponding parameters for the closely related compound $[(\text{triphos})\text{Rh}(\mu\text{-H})_2\{\text{Au}(\text{PPh}_3)\}_3](\text{CF}_3\text{SO}_3)_2$ [3] (**C′1**) are also given. A full listing of bond lengths and angles is given in supplementary material Tables S1 and S2. The full atomic numbering scheme is given in supplementary material Figure S1.

The molecular structure of **C5** is best described as a triangle of gold atoms capped by a ruthenium atom, forming a tetrahedral cluster. The triphos ligand is placed above the ruthenium atom, and each gold atom is bonded to one molecule of PPh_3. As found for the analogous rhodium complex, **C′1**, the cation lies on a crystallographic 3-fold axis which goes through the CH_3–C bond of triphos, the ruthenium atom, and the center of the Au_3 triangle. As a consequence, all the Ru–Au, Au–Au, Au–P, and Ru–P distance are equal within each set. The cluster hydrogen atoms were located on the Fourier difference map and could be refined. Although the distances and angles concerned are not very accurate, they allow their unambigous positional assignment as having *quasi*-μ_3-coordination, taking an intermediate position between μ_2 and μ_3. Furthermore, if one ignores the direct Ru–Au interactions, the P- and H-atoms define an acceptable octahedral coordination around the ruthenium atom as would be expected for the anion $[\text{RuH}_3(\text{triphos})]^-$, which should be isostructural with $[\text{RuH}_3(\text{PPh}_3)_3]^-$.[5,6]

In view of the structural similarity between **C5** and **C′1** (hydride ligands excepted) and of the fact that the two compounds are isoelectronic, the bonding parameters of **C5** are best discussed by comparing them with the corresponding parameters obtained for **C′1**.

The first feature requiring comment concerns the Ru–Au distances (2.679(1) Å in **C5**, which are very similar to the Rh–Au distances (2.695(2) Å) in **C′1**. This can be taken as a indication that the M–Au direct interaction is comparable in the two cases.

A major difference between the two clusters, however, is found in the Au–Au′ distances which increase from 2.887(1) Å in the rhodium complex **C′1** to 3.003(1) Å in the ruthenium complex **C5**. Clearly, in the latter case, the Au–Au′ interactions have been considerably weakened. Indeed, the Au–Au distances in the ruthenium complex are the longest reported for this type of cluster, i.e., 2.931(2) Å in $[(\text{PPhMe}_2)_3)\text{Re}(\mu\text{-H})_3\{\text{Au}(\text{PPh}_3)\}_3]^+$, **4**,[4] and 2.87(5) Å (average) in $[(\text{PPh}_3)_2(\text{CO})\text{Rh}(\mu\text{-H})\{\text{Au}(\text{PPh}_3)\}_3]^+$, **5**,[2] the longest Au–Au distance there being 2.914(1) Å. It is likely that the weakening of the Au–Au interactions in the ruthenium complex is associated with the presence of three cluster hydrogen atoms, as opposed to the two in the rhodium complex. In a general sense, one can expect that the removal of a proton from **C5** would strenghen cluster bonding at the expense of more localized M–H and Au–H interactions. These differences have been discussed elsewhere, together with the corresponding data for the rhodium complexes.[10a]

The weaker cluster bonding in the ruthenium complex is also consistent with the longer Au–P distance in **C5** (2.326(5) Å) vs the Au–P distance in **C′1** (2.260(5) Å).

Changes consequential upon the lengthening of the Au–Au distance are the wider Au–Ru–Au′ angle (68.20(5)°) relative to Au–Rh–Au′ (64.78(6)°) and the smaller Ru–Au–Au′ angle (55.90(3)°) relative to Rh–Au–Au′ (57.61(3)°).

The gold triangle and that defined by the three triphos P-atoms take a conformation which is intermediate between staggered and eclipsed, the torsion angle P2–Ru–Au–P1 being 35°. It is noteworthy that the corresponding angle in the RhAu_3 cluster, **C′1**, is 15°, while in the ReAu_3 cluster, $[(\text{PMe}_2\text{Ph})_3\text{ReH}_3\{\text{Au}(\text{PPh}_3)\}_3]^+$, **4**, it is 2°.[4]

Finally, the Ru–H and Au–H distances (1.9(1) and 1.7(1) Å, respectively) are reasonable, given the accuracy of the method, while the Ru–H–Au angle of 92(5)° is indicative of a "closed" Ru–H–Au interaction.

RuAu_2 Compounds, Type B. The clusters of this type containing triars were prepared by treating $[\text{RuH}_4(\text{triars})]$ (**1**) with 2 equiv of the gold-containing compounds in the presence of K_2CO_3 as shown in eq 5.

$$\underset{\mathbf{1}}{[\text{RuH}_4(\text{triars})]} + 2[\text{AuCl(L)}] + 2\text{Tl}[\text{PF}_6] + \text{K}_2\text{CO}_3 \rightarrow \underset{\mathbf{B1\text{–}4}}{[(\text{triars})\text{RuH}_3\{\text{Au(L)}\}_2][\text{PF}_6]} + \text{KHCO}_3 + \text{K}[\text{PF}_6] + 2\text{TlCl} \quad (5)$$

$$\text{L} = \text{PPh}_3,\ \text{P-}o\text{-Tol}_3,\ \text{P-}i\text{-Pr}_3,\ \text{AsPh}_3$$

It is noteworthy that the interaction between **1** and $\{\text{Au(L)}\}^+$ cations is so strong that the formation of these compounds does not require chloride abstraction with $\text{Tl}[\text{PF}_6]$. However, the isolation of compounds giving satisfactory elemental analyses required replacement of the ionic chloride by $[PF_6]^-$.

When the above reaction was carried out in the absence of K_2CO_3, one observed the formation of mixtures of the type **B** and type **C** clusters. As will be shown later, the formation of compounds of the latter type is caused by the presence of the protons liberated during reaction 5.

The simultaneous formation of complexes of the types **B** and **C** was also observed when $[RuH(BH_4)(triphos)]$ (**2**) was reacted with the appropriate amounts of $[AuCl(L)]$ and $Tl[PF_6]$ without addition of a reagent capable of taking up the liberated BH_2^+ fragment. However, the formation of the clusters of type **C** could be suppressed by addition of PPh_3 to the reaction mixture (eq 6).

$$\underset{\mathbf{2}}{[RuH(BH_4)(triphos)]} + 2[AuCl(L)] + Tl[PF_6] + PPh_3 \rightarrow \underset{\mathbf{B5,6}}{[(triphos)RuH_3(AuL)_2][PF_6]} + [BH_2Cl(PPh_3)] + TlCl \qquad (6)$$

$$L = PPh_3,\ P\text{-}i\text{-}Pr_3$$

The boron-containing species $[BH_2Cl(PPh_3)]$ is analogous to the complexes $[BH_2Cl(PMe_3)]$ and $[BH_2Br(PMe_3)]$.[16] This formulation is based on (1) the $^{31}P\{^1H\}$ NMR spectrum, which consisted of a broad singlet centered at 45.6 ppm, (2) the $^{11}B\{^1H\}$ NMR spectrum, which showed a dublet centered at −38.1 ppm with coupling constant equal to 55 Hz, and (3) its ^{11}B NMR spectrum, which gave a doublet of triplets with $J(^{11}B, ^1H) = 95$ Hz when only the protons of triphenyl phosphine were selectively decoupled.

Complexes of type **B**, in which very bulky phosphines, e.g., tris(*o*-tolyl)phosphine, were coordinated to gold, could not be prepared by the reaction shown in eq 6, as significant phosphine exchange occurred. Thus the reaction of $[RuH(BH_4)(triphos)]$ (**2**) with 2 equiv of $[AuCl(P\text{-}o\text{-}Tol_3)]$ and PPh_3, according to eq 6, gave a mixture of $[(triphos)RuH_3\{Au(PPh_3)\}_2][PF_6]$ (**B5**) and $[(triphos)RuH_3\{Au(P\text{-}o\text{-}Tol_3)\}_2][PF_6]$ (**B7**), in the ratio of 4:1. Furthermore, tris(*o*-tolyl)phosphine could not be used to remove the boron fragment, because the reaction occurred as if the bulky phosphine were not present. This is likely to be due to a steric effect, the size of the phosphine preventing its coordination to the boron species, as a ^{31}P NMR study of the above solution revealed the presence of free tris(*o*-tolyl)phosphine in solution.

This problem was solved using an amine to "remove" the released BH_2^+, as amines are generally good ligands for boron[17] but poor ligands for gold, at least when compared with phosphines. For this purpose *N,N,N',N'*-tetramethyl-1,8-naphthalenediamine, TMND, was chosen, as (1) the released BH_2^+ could be stablized through formation of a boron complex containing a six-membered ring and (2) the distance between the two nitrogen atoms would be too short for effective chelation to the gold atom. Thus the cluster with tris(*o*-tolyl)phosphine on gold, **B7**, was obtained in high yield as shown in eq 7.

$$\underset{\mathbf{2}}{[RuH(BH_4)(triphos)]} + 2[AuCl(P\text{-}o\text{-}Tol_3)] + Tl[PF_6] + TMND \rightarrow \underset{\mathbf{B7}}{[(triphos)RuH_3\{Au(P\text{-}o\text{-}Tol_3)\}_2][PF_6]} + TlCl + \text{“}[BH_2(TMND)]\text{”}Cl \qquad (7)$$

Finally, mention should be made that compounds of type **B** could also be prepared by abstraction of an AuL^+ fragment from the corresponding type **C** clusters, as described in a later section.

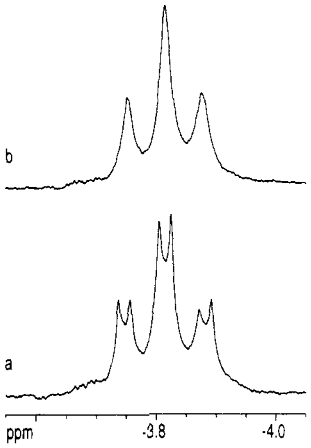


Figure 3. ^1H NMR (500.13 MHz, THF/d_6-acetone) spectra (in the hydride region) of $[(triphos)RuH_3\{Au(PPh_3)\}_2][PF_6]$, **B5**, at room temperature: (a) normal; (b) P^{tr}-decoupled.

Indeed, the compound $[(triphos)RuH_3\{Au(AsPh_3)\}_2][PF_6]$ (**B8**) could only be obtained this way.

Only two compounds of type **B** were isolated, and their elemental analyses are given in the Experimental Section. The other compounds were prepared *in situ* and characterized by multinuclear NMR spectroscopy. Some relevant NMR data are given in Table I.

The main features of the spectra of compounds of this type will be illustrated using $[(triphos)RuH_3\{Au(PPh_3)\}_2][PF_6]$ (**B5**). Its $^{31}P\{^1H\}$ NMR spectrum showed a triplet assigned to the P^{tr} atoms and a quartet assigned to the P^{Au} atoms. Its ^1H NMR spectrum, in the hydride region, is best discussed by considering Figure 3. As can been seen there, the normal spectrum (a) has the appearance of a triplet of doublets overlapping a broad region of absorption. This spectrum reduced to a triplet (b) on selective decouplig at the frequency of P^{tr}. On the other hand, selective decoupling at the frequency of P^{Au} left a spectrum similar to that of $[(triphos)RuH_3\{Au(AsPh_3)\}_3][PF_6]_2$ (**C7**) when recorded under conditions of selective P^{Au} decoupling. Thus the broad region of absorption in the normal spectrum (a) of **B5** is due to the overlap of the "wings" associated with the sharp signals.

The $^{31}P\{^1H\}$ NMR spectra of the other compounds containing triars gave singlets, which became triplets when the spectra were recorded under conditions of selective decoupling of the aromatic and aliphatic protons, confirming the presence of three hydride ligands in these complexes. These spectra showed no significant temperature dependence down to 183 K.

The ^1H NMR spectra, in the hydride region, of the above compounds appeared as triplets. The coupling of the (P^{Au}) atoms with the hydrides was further confirmed by decoupling at the frequency of the former atoms, whereby the triplets reduced to singlets. As expected, the ^1H NMR spectra of the clusters with tertiary arsines on gold showed only singlets in the hydride region.

As mentioned earlier, the room-temperature ^1H NMR spectra showed only one type of hydride ligand, although the molecular stoichiometry leads one to expect two types of hydrides, at least in a static structure. Therefore, the ^1H NMR spectrum of $[(triars)RuH_3(AuPPh_3)_2][PF_6]$ (**B1**) was recorded at lower temperatures. However, even at 143 K (in a 1:3 mixure of CD_2Cl_2 and $CClF_3$) only line broadening was observed. Once again, the fluxional properties of the complexes formed by the the (tripod)RuH_3 unit and the $\{Au(L)\}$ moieties are evident.

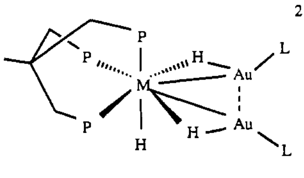
A comparison of the ^1H NMR spectra of the corresponding clusters of types **B** and **C** containing triphos shows that in the former compounds the separation between the sharp doublets is a factor of 2–5 larger (ca. 11 Hz). This may reflect the fact that in the compounds of type **B** the three hydride ligands are associated only with two gold–phosphine fragments, while in compounds of type **C** there are three hydride ligands and three gold atoms.

---

(16) (a) Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302. (b) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288.

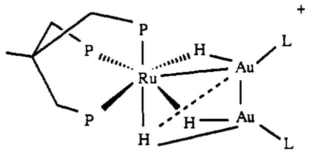
(17) Muetterties, E. L., Ed. *The Chemistry of Boron and its Compounds*; Wiley: New York, 1967; Chapter 9.

Surprisingly, also the IR spectra of compounds of type **B** showed no bands obviously attributable to Ru–H or Ru–H–Au streching vibrations in the region 800–2200 cm^{-1}.[10] As the IR spectra of the corresponding $RhAu_2$ and $IrAu_2$ clusters show terminal metal–hydrides vibrations,[3] it is suggested that, even in the solid state, all three hydrides in the compounds of type **B** are strongly bridging to the Ru and Au atoms. Thus while the rhodium and iridium compounds were formulated as having the static structure **6**, that of the ruthenium digold compounds is probably best formulated as shown schematically in **7**.



(M = Rh and Ir)

6



7

RuAu Compounds, Type A. Very few compounds of this type could be prepared, as they are quite unstable. Initially attempts were made to prepare them from [RuH_4(triars)] (**1**) by adding 1 equiv of the gold phosphine cation, as it was expected that it would have been easier to remove a proton from **1** than a BH_2^+ fragment from **2**. Furthermore, the presence of triars would have facilitated the NMR monitoring of the reaction in complexes where a phosphine was coordinated to gold.

When [RuH_4(triars)] (**1**) was reacted with the gold-containing compounds, using the bases as shown in eq 8, the simultaneous formation of the complexes of types **A** and **B** was observed, even when an excess of base was used.

$$\underset{\mathbf{1}}{[RuH_4(triars)]} + [AuCl(L)] + base \rightarrow$$
$$x\underset{\mathbf{A1,2}}{[(triars)RuH_3\{Au(L)\}]} + y\underset{\mathbf{B1,2}}{[(triars)RuH_3\{Au(L)\}_2]Cl} + \quad \ldots (8)$$

base = K_2CO_3, EtN-*i*-Pr_2, NaOMe, *t*-BuOK; L = PPh_3, P-*o*-Tol_3

Although the yield of the type **A** compounds increased from *ca.* 5 to 50%, as stronger bases were used, i.e., on going from K_2CO_3 and EtN-*i*-Pr_2 to NaOMe and *t*-BuOK, attempts to isolate type **A** compounds containg triars in the pure state were not successful.

This behavior was investigated by monitoring the temperature dependence of reaction 8 by NMR spectroscopy. On mixing of [RuH_4(triars)] and [Au(d_6-acetone)(P-*i*-Pr_3)][PF_6], in a 1:1 ratio, in d^6-acetone at –50 °C, a single compound was produced. Its $^{31}P\{^1H\}$ NMR spectrum consisted of a singlet at 75.6 ppm, while its ^1H NMR spectrum, in the hydride region, showed a broad doublet centered at –7.3 ppm. While this is consistent with the formation of the desired compound, [(triars)RuH_3{Au(P-*i*-Pr_3)}], the number of hydride ligands present in this cation could not be established by observing the ^{31}P NMR spectrum under conditions of selective proton decoupling, as the signals were too broad. Lowering of the temperature to –90 °C gave even broader signals. On raising of the temperature above –50 °C, slow formation of **B2** was observed. Finally, only the signal of compound **B2** could be observed in the hydride region after the solution had been allowed to warm up to room temperature. When the reaction was carried out using [Au(d_6-acetone)(PPh_3)][PF_6], in the presence of NaOMe, one observed the formation of the compound which is also obtained in the absence of base, i.e., **A1**, and the appearance of the hydride signal did not significantly change if the temperature was kept below –50 °C. When the temperature was raised above –50 °C, one observed the simultaneous formation of **B1** and **A1**. These were present in a ratio of ca 1:1 after the solution had been allowed to warm to room temperature.

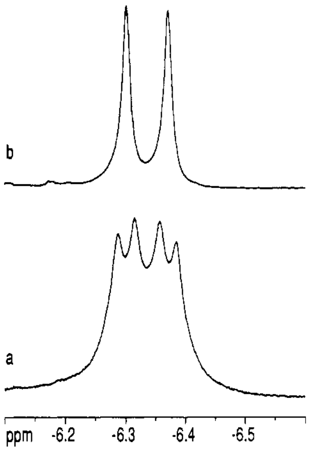


Figure 4. ^1H NMR (500.13 MHz, C_6D_6) spectra (in the hydride region) of [(triphos)RuH_3{Au(P-*o*-Tol_3)}], **A3**, at room temperature: (a) normal; (b) P^{tr}-decoupled. I.

The preparation of a compound of type **A** was more satisfactory when [RuH(BH_4)(triphos)] (**2**) and [AuCl(P-*o*-Tol_3)] were used as starting materials and TMND was added to remove the liberated boron fragment (eq 9). However, even in this case, a mixture of complexes was obtained.

$$\underset{\mathbf{2}}{[RuH(BH_4)(triphos)]} + [AuCl(P\text{-}o\text{-}Tol_3)] + TMND \rightarrow$$
$$\underset{\mathbf{A3}}{[(triphos)RuH_3\{Au(P\text{-}o\text{-}Tol_3)\}]} + [BH_2(TMND)]Cl \quad (9)$$

The desired product **A3**, however, could only be characterized by means of NMR spectroscopy, as attempts to isolate it led to its slow decomposition.

The relevant NMR data for this compound are listed in Table I. Its $^{31}P\{^1H\}$ NMR spectrum consisted of a quartet assigned to the phosphorus atom on gold, P^{Au}, and a doublet assigned to the phosphorus atoms of triphos, P^{tr}. Its room-temperature ^1H NMR spectrum in the hydride region (a) is shown in Figure 4, where only the resonances due to **A3** have been reproduced. As can be seen there, on decoupling at the frequency of the P^{tr} atoms, the original "doublet of doublets" (a) reduces to a doublet due to the coupling of P^{Au} (b), while decoupling at the frequency of the P^{Au} atom give rise to a multiplet of similar appearance to that of the compound **C7**, i.e., that typical of a complex containing the (triphos)RuH_3 unit. The separation between the two strongest signals (14 Hz) is comparable with that found in compounds of type **B** (11 Hz).

The $^{31}P\{^1H\}$ NMR spectra of [(triars)RuH_3{Au(L)}] (L = PPh_3, P-*o*-Tol_3; **A1** and **A2**, respectively) gave singlets, which became quartets when the spectra were recorded under conditions of selective decoupling of the aromatic and aliphatic protons. This observation confirmed the presence of three hydride ligands in these complexes.

Their ^1H NMR spectra in the hydride region appeared as doublets consistent with a first-order spin system. The coupling of the phosphorus atom on gold (P^{Au}) with the hydrides was further confirmed by decoupling at the frequency of the P^{Au} atom, the doublets reducing to singlets.

Reactivities of the Compounds of Types A–C. These were studied (a) toward acids and (b) toward nucleophiles.

(a) Reactivity toward Acids. As shown in eqs 2–7, the formation of the three types of compounds is accompanied by the liberation of either a proton or a BH_2^+, i.e., of a Lewis acid. Generally all the type **C** compounds are stable toward protons or BH_2^+, so that, as mentioned earlier, their removal is not necessary before cluster isolation. The corresponding compounds of type **B**, however, are sensitive to the above "acids", as, in their presence, they slowly decompose with formation of the corresponding compounds of type **C**. This was confirmed by treating $[(\mathrm{triars})\mathrm{RuH_3\{Au(PPh_3)\}_2}][\mathrm{PF_6}]$, **B1**, in $\mathrm{CDCl_3}$, with an excess of $\mathrm{CF_3SO_3H}$: the slow formation of **C1** was observed and ^{1}H NMR spectroscopic studies showed that within 2 h this compound was the only hydrido complex present in solution. This explains the observation that when $[\mathrm{RuH(BH_4)(triphos)}]$ (**2**), or $[\mathrm{RuH_4(triars)}]$ (**1**), was reacted with 2 equiv of gold cations, in the absence of base, mixtures of types **B** and **C** compounds were invariably obtained. Type **A** compounds are even more acid-sensitive, as slight traces of moisture can cause their decomposition.

(b) Reactivity toward Nucleophiles. In order to obtain a qualitative estimate of the strengths of the RuAu_n interactions, these compounds were reacted with several nucleophiles and with $[\mathrm{IrH_3(triphos)}]$ to establish the extent of the reaction:

$$[(\textit{tripod})\mathrm{RuH_3\{Au(L)\}}_n]^{(n-1)+} + \mathrm{Nu} \rightleftharpoons [(\textit{tripod})\mathrm{RuH_3\{Au(L)\}}_{n-1}]^{(n-2)+} + [\mathrm{Au(L)(Nu)}]^+ \tag{10}$$

$$\mathrm{Nu} = \mathrm{MeOH},\ \mathrm{AsPh_3},\ \mathrm{PPh_3},\ \mathrm{Cl^-},\ \mathrm{I^-},\ [\mathrm{IrH_3(triphos)}]$$

The compounds of type **C** containing triars were partially degraded to the corresponding compounds of type **B** (*ca.* 10%) by addition of 1 equiv of $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, or an excess of MeOH, while those containing triphos were inert to these reagents. These observations indicate that the gold fragments are more strongly held in triphos-containing compounds. A similar effect was previously observed[3] in complexes of the type $[(\textit{tripod})\mathrm{MH_2\{Au(L)\}_3}]^{(n-1)+}$ (*tripod* = triphos, triars; M = Ir, Rh; L = $\mathrm{PR_3}$, $\mathrm{AsR_3}$) and was attributed to the lower electron donor capacity of arsenic relative to phosphorus when there is parity of the R group.

A much higher reactivity was shown by $\mathrm{Cl^-}$ and $\mathrm{I^-}$, as they quantitatively degraded all of the type **C** to the corresponding type **B** compounds (eq 11).

$$[(\textit{tripod})\mathrm{RuH_3\{Au(L)\}_3}][\mathrm{PF_6}]_2 + \mathrm{M'X} \rightarrow [(\textit{tripod})\mathrm{RuH_3\{Au(L)\}_2}][\mathrm{PF_6}] + \mathrm{M'[PF_6]} + [\mathrm{AuX(L)}] \tag{11}$$

$$\mathrm{M'X} = [\mathrm{PPN}]\mathrm{Cl},\ [\mathrm{NEt_4}]\mathrm{I};\ [\mathrm{PPN}] = [\mathrm{Ph_3P{=}N{=}PPh_3}]$$

This behavior accounts for the observation that, in the absence of $\mathrm{Tl[PF_6]}$, one could only get type **B** compounds even when 3 equiv of gold cations/ruthenium atom was used.

Another interesting comparison is that between the ruthenium clusters described here and the related iridium compounds $[(\textit{tripod})\mathrm{IrH}_m\mathrm{\{Au(L)\}}_n]^{(n-1)+}$ (*tripod* = triphos, triars; L = $\mathrm{PR_3}$, $\mathrm{AsR_3}$; $m = 3$ for $n = 1$ and 2; $m = 2$ for $n = 3$; **A′**, **B′**, and **C′**, respectively) or their precursor $[(\textit{tripod})\mathrm{IrH_3}]$.

In a first experiment $[\mathrm{IrH_3(triphos)}]$, **4**, was reacted with $[\mathrm{(triphos)RuH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}_3}][\mathrm{PF_6}]_2$, **C6** (eq 12).

$$\underset{\mathbf{C6}}{[\mathrm{(triphos)RuH_3\{Au(P\text{-}\mathit{i}\text{-}Pr_3)\}_3}][\mathrm{PF_6}]_2} + \underset{\mathbf{4}}{[\mathrm{IrH_3(triphos)}]} \rightarrow \underset{\mathbf{B6}}{[\mathrm{(triphos)RuH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}_2}][\mathrm{PF_6}]} + \underset{\mathbf{A'6}}{[\mathrm{(triphos)IrH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}}][\mathrm{PF_6}]} \tag{12}$$

As can be seen there, the iridium hydride quantitatively abstracted one gold fragment from the tetrametallic cluster. It is, however, noteworthy that, even in the presence of an excess of iridium trihydride, **B6** does not transfer a gold fragment to iridium. In this respect **B6** does not behave like $[\mathrm{(triphos)IrH_3\{Au(P\text{-}\mathit{i}\text{-}Pr_3)\}_2}][\mathrm{PF_6}]_2$, **B′6**, which does give up an $\{\mathrm{Au(PPh_3)}\}^+$ fragment to $[\mathrm{IrH_3(triphos)}]$. Thus, it can be deduced that the gold fragments in the ruthenium compound **B6** are more tightly held than in the corresponding iridium compound **B′6**.

A surprising result was obtained when equimolar amounts of $[\mathrm{(triphos)RuH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}_2}][\mathrm{PF_6}]$, **B6**, and $[\mathrm{(triphos)IrH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}}][\mathrm{PF_6}]$,[3] **A′6**, were treated with 1 equiv of $[\mathrm{Au}(d_6\text{-acetone})(\mathrm{P\text{-}\mathit{i}\text{-}Pr_3})][\mathrm{PF_6}]$. Only the reaction shown in eq 13 took place. The same type of reaction occurred with the set of complexes in which $\mathrm{PPh_3}$ or $\mathrm{AsPh_3}$ was bonded to the gold fragment.

$$\underset{\mathbf{B6}}{[\mathrm{(triphos)RuH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}_2}][\mathrm{PF_6}]} + \underset{\mathbf{A'6}}{[\mathrm{(triphos)IrH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}}][\mathrm{PF_6}]} + [\mathrm{Au}(d_6\text{-acetone})(\mathrm{P\text{-}\mathit{i}\text{-}Pr_3})][\mathrm{PF_6}] \rightarrow \underset{\mathbf{C6}}{[\mathrm{(triphos)RuH_3\{Au(P\text{-}\mathit{i}\text{-}Pr_3)\}_3}][\mathrm{PF_6}]_2} + \underset{\mathbf{A'6}}{[\mathrm{(triphos)IrH_3\{Au\{P\text{-}\mathit{i}\text{-}Pr_3\}\}}][\mathrm{PF_6}]} + d_6\text{-acetone} \tag{13}$$

These results clearly indicate that the affinity for $\{\mathrm{Au(L)}\}^+$ fragments is greater in the ruthenium system in general and that, if one compares the Lewis basicity of $[\mathrm{IrH_3(triphos)}]$ with that of $[\mathrm{RuH_3(triphos)}]^-$, the latter is a better base as it is able to form an $\mathrm{RuAu_3}$ cluster in preference to the $\mathrm{IrAu_2}$ species, $[\mathrm{(triphos)IrH_3\{Au\{L\}\}_2}]^{2+}$.

A comparison of the ruthenium–gold compounds with their rhodium (or iridium) analogues allows one to write the two sets of isoelectronic complexes listed as follows:

Type **A**(or **A'**)	$[(\textit{tripod})\mathrm{RuH_3\{Au(L)\}}]$	$[(\textit{tripod})\mathrm{MH_3\{Au(L)\}}]^+$
Type **B**(or **B'**)	$[(\textit{tripod})\mathrm{RuH_3\{Au(L)\}_2}]^+$	$[(\textit{tripod})\mathrm{MH_3\{Au(L)\}_2}]^{2+}$
Type **C**(or **C'**)	$[(\textit{tripod})\mathrm{RuH_3\{Au(L)\}_3}]^{2+}$	$[(\textit{tripod})\mathrm{MH_2\{Au(L)\}_3}]^{2+}$

(M = Rh or Ir)

While the sets of compounds of the first two types contain the same number of cluster hydrogen atoms, the sets **C** and **C′** contain three and two hydrogen atoms, respectively. This raises the question whether compounds of the type $[(\textit{tripod})\mathrm{RuH_2\{Au(L)\}_3}]\mathrm{X}$, **C″**, could also be obtained. This is the case, and a compound of this type will be described in a later publication.

In conclusion, trihydrides of the type $[\mathrm{MH_3(L)_3}]$ (or $[\mathrm{MH_3}(\textit{tripod})]$) (M = Re, Ru, Rh, Ir) appear to have the general property of forming heterometallic clusters containing the tetrahedral $\mathrm{MAu_3}$ unit associated with 1, 2, or 3 hydrogen atoms, the latter number depending on the ionic charge of the cluster.

X-ray diffraction, IR, and incoherent inelastic neutron scattering spectroscopic studies indicate that the position and bonding mode of the hydrogen on the cluster surface varies with the type of cluster.[10] However, neutron diffraction studies will be required to define more precisely the mode of bonding of the hydride ligands in cluster compounds of this type.

Experimental Section

Physical Measurements and Reagents. The ^{1}H NMR spectra were recorded at 250.13 and 500.13 MHz, the ^{11}B NMR spectra at 80.24 MHz, and the ^{31}P NMR spectra at 101.25 and 202.5 MHz on Bruker WM-250 and AMX-500 instruments. The NMR specta are referenced as follows: ^{1}H, external $\mathrm{Me_4Si}$, ^{31}P, external 85% $\mathrm{H_3PO_4}$, and ^{11}B, external $\mathrm{BF_3{\cdot}Et_2O}$, with a positive sign indicating a chemical shift downfield of the reference. The T_1 measurements were carried out at 500 MHz by means of the inversion–recovery method,[15] where the sample was degassed using a freeze–pump–thaw cycle.[15] The following values were obtained [T (K), T_1 (ms)]: 233, 794; 253, 577; 273, 490; 293, 476; 303, 480; 313, 493; 333, 520. The IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer, the compounds being in KBr pellets, Nujol suspensions, or in $\mathrm{CH_2Cl_2}$ solutions.

All the manipulations of the ruthenium and Ru–Au compounds were carried out in a inert atomosphere (nitrogen or argon) using standard

Schlenk techniques. The solvents, unless otherwise stated, were used as received from Fluka AG but deoxygenated by bubbling inert gas through the solvents for a period of 10 min before use.

The gold complexes [AuCl(As-*i*-Pr$_3$)], [AuCl(AsPh$_3$)], [AuCl(P-*i*-Pr$_3$)], [AuCl(P-*o*-tol$_3$)], [AuCl(PPh$_3$)], and [AuCl(PEt$_3$)] were prepared as described by McAuliffe et al.[18] Also the ruthenium complexes [RuCl$_2$(DMSO)$_4$], [RuCl$_2$(DMSO)(triars)], [Ru(CH$_3$CN)$_3$(triars)]X$_2$, [Ru(PhCN)$_3$(triars)]X$_2$ (X = [BF$_4$], (CF$_3$SO$_3$)), [Ru$_2$Cl$_3$(triphos)$_2$]Cl, and [Ru(CH$_3$CN)$_3$(triphos)](CF$_3$SO$_3$)$_2$, were prepared by the methods described in the literature.[7,8] For the preparation of [RuH$_4$(triars)], [RuH(BH$_4$)(triphos)], and [RuH$_2$(AsPh$_3$)(triphos)] the literature methods[7,8] were modified as described below.

[RuH$_4$(triars)] (1). A suspension of [Ru(CH$_3$CN)$_3$(triars)]X$_2$ (0.40 mmol; 426.6 mg, for X = [BF$_4$], and 416.7 mg, for X = (CF$_3$SO$_3$)) in 15 mL of degassed ethanol was treated with solid Na[BH$_4$] (154.8 mg, 4 mmol). The slurry was then warmed to 50 °C for 1.5 h. During this time both [Ru(CH$_3$CN)$_3$(triars)][X]$_2$ and Na[BH$_4$] went into solution, while white [RuH$_4$(triars)] precipitated out. After cooling of the suspension to room temperature, [RuH$_4$(triars)] was collected by filtration. The crude product was recrystallized from CH$_2$Cl$_2$/MeOH, washed with ether and pentane, and dried over an H$_2$ stream. Yields ranged from 60 to 72%. Its NMR parameters corresponded to those reported elsewhere.[7]

[RuH(BH$_4$)(triphos)] (2). Solid [NaBH$_4$] (110 mg, 2.91 mmol) was slowly added to a solution of [Ru(CH$_3$CN)$_3$(triphos)](CF$_3$SO$_3$)$_2$ (424 mg, 0.370 mmol) in methanol and diethyl ether (5:1). The slurry evolved gas and deposited a yellow precipitate over a 5-min period. This solid was filtered out, washed with water, MeOH, and ether, and dried under high vacuum. Yield: 191 mg, 69%. Its NMR parameters corresponded to those reported elsewhere.[8]

[RuH$_2$(AsPh$_3$)(triphos)] (3). Solid [Ru$_2$Cl$_3$(triphos)$_2$]Cl[19] (159.3 mg, 0.10 mmol) and AsPh$_3$ (61.2 mg, 0.2 mmol) were suspended in a well-degassed mixture of 2-propanol and toluene (1:2). Solid KOH (40 mg, 0.71 mmol) was then added, and the slurry was refluxed for 14 h. The reaction mixture was cooled to room temperature and degassed water (10 mL) added. After separation of the organic phase the aqueous phase was extracted twice with ether (ca. 10 mL each time). The combined organic phases were then evaporated to dryness, and the residue was washed with methanol. The crude product was recrysallized from ether/methanol. The white solid was filtered off and washed with pentane and dried over H$_2$ stream. Yield: 144.7 mg, 70%. Its NMR parameters corresponded to those reported elsewhere.[7]

Preparation of Type C Compounds. Compounds of this type were prepared by the following general method: Three equivalents of [AuCl(L)] (L = tertiary phosphine or arsine) and of Tl[PF$_6$] were successively added to a THF solution containing 1 equiv of [RuH$_4$(triars)] or of [RuH(BH$_4$)(triphos)]. The solution became immediately turbid. The mixture was stirred at ambient temperature for a period of 30 min, and the precipitate was then filtered off through Celite. The column was washed with acetone, and the resulting solution was then evaporated under reduced pressure to ca. $^1/_3$ of the original volume. The product was precipitated by addition of either ether or pentane. The crude product was recrystallized from acetone/THF or CH$_2$Cl$_2$/ether by dissolving the crude product in the first solvent and then slowly adding the second solvent. The recrystallization was repeated, until satisfactory ^{1}H NMR spectra and microanalytical data were obtained. The solvents used for the preparation and recrystallization are given below.

[(triars)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$ (C1). It was prepared as described above from [RuH$_4$(triars)] (17.2 mg, 0.02 mmol), [AuCl(PPh$_3$)] (29.7 mg, 0.06 mmol), and Tl[PF$_6$] (21.0 mg, 0.06 mmol) in THF (5 mL). The crude product was precipitated with pentane and recrystallized from acetone/THF/ether. Yield: 41.3 mg (80%). Anal. Calcd for C$_{97}$H$_{87}$F$_{12}$Au$_3$As$_3$P$_5$Ru: C, 45.13; H, 3.47. Found: C, 45.14; H, 3.43.

[(triars)RuH$_3${Au(PEt$_3$)}$_3$][PF$_6$]$_2$ (C2). It was prepared as described above from [RuH$_4$(triars)] (17.2 mg, 0.02 mmol), [AuCl(PEt$_3$)] (21.0 mg, 0.06 mmol), and Tl[PF$_6$] (21.0 mg, 0.06 mmol) in THF (5 mL). The crude product was precipitated with pentane and recrystallized from acetone/THF/ether. Yield: 40.4 mg (80%). Anal. Calcd for C$_{59}$H$_{87}$F$_{12}$Au$_3$As$_3$P$_5$Ru: C, 33.81; H, 4.18. Found: C, 33.46; H, 4.28.

[(triars)RuH$_3${Au(P-*i*-Pr$_3$)}$_3$][PF$_6$]$_2$ (C3). It was prepared as described above from [RuH$_4$(triars)] (17.2 mg, 0.02 mmol), [AuCl(P-*i*-Pr$_3$)] (23.6 mg, 0.06 mmol), and Tl[PF$_6$] (21.0 mg, 0.06 mmol) in THF (5 mL). The crude product was precipitated with pentane and recrystallized from acetone/THF/ether. Yield: 33.5 mg (82%). Anal. Calcd for C$_{68}$H$_{105}$F$_{12}$Au$_3$As$_3$P$_5$Ru: C, 36.75; H, 4.76. Found: C, 37.69; H, 4.78.

[(triars)RuH$_3${Au(AsPh$_3$)}$_3$][PF$_6$]$_2$ (C4). It was prepared as described above from [RuH$_4$(triars)] (17.2 mg, 0.02 mmol), [AuCl(AsPh$_3$)] (32.3 mg, 0.06 mmol), and [TlPF$_6$] (21.0 mg, 0.06 mmol) in THF (5 mL). The crude product was precipitated with pentane and recrystallized from acetone/THF/ether. Yield: 44.4 mg (89%). Anal. Calcd for C$_{97}$H$_{87}$F$_{12}$Au$_3$As$_6$P$_2$Ru: C, 42.89; H, 3.30. Found: C, 42.13; H, 3.36.

[(triphos)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$ (C5). It was prepared as described above from [RuH(BH$_4$)(triphos)] (14.8 mg, 0.02 mmol), [AuCl(PPh$_3$)] (29.7 mg, 0.06 mmol), and [TlPF$_6$] (21.0 mg, 0.06 mmol) in THF (5 mL). The crude product was precipitated with pentane and recrystallized from acetone/THF/ether. Yield: 48.3 mg (83%). Anal. Calcd for C$_{97}$H$_{87}$F$_{12}$Au$_3$P$_8$Ru: C, 47.61; H, 3.66. Found: C, 47.29; H, 3.71.

[(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_3$][PF$_6$]$_2$·CH$_2$Cl$_2$ (C6). It was prepared as described above from [RuH(BH$_4$)(triphos)] (14.8 mg, 0.02 mmol), [AuCl(P-*i*-Pr$_3$)] (23.6 mg, 0.06 mmol), and [TlPF$_6$] (21.0 mg, 0.06 mmol) in THF (5 mL). The crude product was precipitated with pentane and recrystallized from acetone/THF/ether. Yield: 35.2 mg (81%). Anal. Calcd for C$_{69}$H$_{107}$Cl$_2$F$_{12}$Au$_3$P$_8$Ru: C, 38.09; H, 4.96. Found: C, 37.65; H, 4.88.

[(triphos)RuH$_3${Au(AsPh$_3$)}$_3$][PF$_6$]$_2$ (C7). A well-degassed solution of [RuH$_2$(AsPh$_3$)(triphos)] (31.0 mg, 0.03 mmol) in 8 mL of THF was saturated with H$_2$ (the gas was bubbled through the solution for 5 min) and, under H$_2$ atmosphere, heated up to 60 °C for 15 min. Then [AuCl(AsPh$_3$)] (48.5 mg, 0.09 mmol) and Tl[PF$_6$] (31.5 mg, 0.09 mmol) were successively added. Immediate precipitation of TlCl occurred. The slurry was kept at this temperature for ca. 30 min and then cooled to ambient temperature. The precipitate was filtered off through Celite and washed twice with 2 mL of acetone. The filtrate and the acetone solution were combined and evaporated under reduced pressure to $^1/_3$ of the oringinal volume, and the crude product was precipitated with 10 mL of pentane. A white product was obtained after recrystallization from acetone/THF/ether. Yield: 55.9 mg (74%). Anal. Calcd for C$_{97}$H$_{87}$F$_{12}$Au$_3$As$_3$P$_5$Ru: C, 45.13; H, 3.47. Found: C, 45.10; H, 3.54.

[(triphos)RuH$_3${Au(As^{i}Pr$_3$)}$_3$][PF$_6$]$_2$ (C8). It was prepared by the following modification of general method: [AuCl(AsP-*i*-Pr$_3$)] (26.2 mg, 0.06 mmol) and Tl[PF$_6$] (21.0 mg, 0.06 mmol) were successively added to a solution of 14.8 mg (0.02 mmol) of [RuH(BH$_4$)(triphos)] in 5 mL of THF which had been cooled to −20°°C. The mixture was stirred at this temperature for 1 h, and then the precipitates of TlCl and black metallic gold were filtered off through Celite. The resulting solution was evaporated to dryness under reduced pressure. The residue was redissolved in 0.4 mL of CDCl$_3$, and the NMR spectra were recorded. A 65% yield was estimated by using CH$_2$Cl$_2$ as an internal standard reference.

[(triars)RuH$_3${Au(PPh$_3$)}$_2$][PF$_6$] (B1). To dry THF (5 mL), containing K$_2$CO$_3$ (13.8 mg, 0.10 mmol) and [RuH$_4$(triars)] (17.2 mg, 0.02 mmol), were added [AuCl(PPh$_3$)] (19.8 mg, 0.04 mmol) and Tl[PF$_6$] (14.0 mg, 0.04 mmol) successively. The mixture was stirred at room temperature for 30 min, and then the precipitate was filtered off through Celite. The resulting solution was evaporated to ca. $^1/_3$ of the original volume, and the crude product was precipitated with ether. The crude product was recrystallized from CH$_2$Cl$_2$/ether. Yield: 29.2 mg (76%) Anal. Calcd for C$_{77}$H$_{72}$F$_6$Au$_2$As$_3$P$_3$Ru: C, 48.07; H, 3.77. Found: C, 47.50; H, 3.76.

[(triars)RuH$_3${Au(P-*o*-Tol$_3$)}$_2$][PF$_6$] (B2). It was prepared analogously to **B1** using K$_2$CO$_3$ (13.8 mg, 0.10 mmol) and [RuH$_4$(triars)] (17.2 mg, 0.02 mmol), [AuCl(P-*o*-Tol$_3$)] (21.5 mg, 0.04 mmol), and Tl[PF$_6$] (14.0 mg, 0.04 mmol) in 5 mL of THF. The crude product was precipitated with pentane and recrystallized from CH$_2$Cl$_2$/ether. Yield: 14.1 mg (70%). Anal. Calcd for C$_{83}$H$_{84}$F$_6$Au$_2$As$_3$P$_3$Ru: C, 49.69; H, 4.22. Found: C, 49.04; H, 4.17.

Solutions of Compounds B3–7. These were prepared by the following general procedure: Two equivalents of [AuCl(L)] (L = tertiary phosphine or arsine) were added to a THF solution containing 1 equiv of [RuH$_4$(triars)] and an excess of K$_2$CO$_3$ (or [RuH(BH$_4$)(triphos)] and 1 equiv of PPh$_3$). The slurry was stirred at ambient temperature for 1 h; 2 equiv of Tl[PF$_6$] (only 1 equiv of Tl[PF$_6$] for the triphos compounds) was then added, and the solution became immediately turbid. After 10 min the precipitate was filtered off through Celite and the residue washed with THF. The solution was evaporated under reduced pressure to ca. $^1/_3$ of the original volume, and pentane was added to precipitate the crude product. The ^{31}P{^{1}H} NMR and ^{1}H NMR spectra of solutions obtained by dissolving these solids showed that the expected product was the only hydride- and/or phosphine-containing species present in solution. The ^{1}H NMR spectra of the complexes were used to estimate the yields, CH$_2$Cl$_2$ being used as an internal standard. The compounds prepared by

---

(18) McAuliffe, C. A.; Parish, R. V. D.; Randall, P. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1730.

(19) Rhodes, L. F.; Sorato, C.; Venanzi, L. M.; Bachechi, F. *Inorg. Chem.* **1988**, *27*, 604.

this method and their chemical yields are listed in the following paragraph. In the case of compound **B7** PPh$_3$ was replaced by TMND.

Compound, yield: [(triars)RuH$_3${Au(P-*i*-Pr$_3$)}$_2$][PF$_6$] (**B3**), 70%; [(triars)RuH$_3${Au(AsPh$_3$)}$_2$][PF$_6$] (**B4**), 76%; [(triphos)RuH$_3${Au(PPh$_3$)}$_2$][PF$_6$] (**B5**), 85%; [(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_2$][PF$_6$] (**B6**), 90%; [(triphos)RuH$_3${Au(P-*o*-Tol$_3$)}$_2$][PF$_6$] (**B7**), 70%.

[(triphos)RuH$_3${Au(AsPh$_3$)}$_2$][PF$_6$] (B8). A solution of this compound was prepared by adding 1 equiv of solid [PPN]Cl (PPN = Ph$_3$PdNdPPh$_3$) to a solution of [(triphos)RuH$_3${Au(AsPh$_3$)}$_3$][PF$_6$]$_2$ (**C8**), in degassed *d*^{6}-acetone. Examination of this sample by ^{1}H and ^{31}P NMR 1 h after the chloride had dissolved showed the presence of **B8** in 56% yield.

[(triars)RuH$_3${Au(PPh$_3$)}] and [(triars)RuH$_3${Au(P-*o*-Tol$_3$)}] (A1, A2). These complexes were prepared and studied *in situ* in a 5-mm NMR tube. Solid [(AuCl(PPh$_3$)] (or [AuCl(P-*o*-Tol$_3$)]) and an excess of NaOMe (*ca.* 5 equiv) were added to a degassed solution of THF which had been dried over Li[AlH$_4$]. Solid [RuH$_4$(triars)] was then added. After thorough shaking, the NMR tube was sealed under argon atmosphere. One hour later ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were taken using a *d*^{6}-acetone capillary lock. The THF peaks were partially saturated during the time required for recording of the ^{1}H NMR spectra.

[(triphos)RuH$_3${Au(P-*o*-Tol$_3$)}] (A3). A solution of this compound was prepared by dissolving [RuH(BH$_4$)(triphos)] (7.4 mg, 0.01 mmol) in degassed THF, in a Schlenk tube wrapped with black paper. To the stirred solution were added NTMN (2.2 mg, 0.01 mmol) and [AuCl(P-*o*-Tol$_3$)] (5.4 mg, 0.01 mmol) successively. Stirring was continued for 30 min, and then the solvent was evaporated under reduced pressure. The residue was then dissolved in dry *d*^{6}-benzene and examined by ^{1}H NMR and ^{31}P{^{1}H} NMR. A yield of ca. 80% yield could be estimated by integration of the hydride signal against CH$_2$Cl$_2$ used as internal standard.

Attempts to isolate the compounds of type **A** were unsuccessful as they decomposed during workup.

Reactivity Studies of the Compounds of Types A–C. (a) Toward Acids. The compound to be studied was added to 0.4 mL of degassed CD$_2$Cl$_2$ which had been placed in a 5-mm NMR tube. After the compound had dissolved, CF$_3$SO$_3$H was added. The solution was then examined by NMR spectroscopy. The reactions carried out and the results obtained are tabulated as follows:

starting material/acid/time	products
[(triphos)RuH$_3${Au{PPh$_3$)}$_3$][PF$_6$]$_2$/ excess of CF$_3$SO$_3$H/48 h	no reaction
[(triars)RuH$_3${Au{PPh$_3$)}$_2$][PF$_6$]/ excess of CF$_3$SO$_3$H/2 h	[(triars)RuH$_3${Au{PPh$_3$)}$_3$][PF$_6$]$_2$ slowly formed and was the only hydride compound present in solution
[(triars)RuH$_3${Au{PPh$_3$)}$_2$][PF$_6$]/ 1 equiv of CF$_3$SO$_3$H/2 h	as above

(b) Toward Nucleophiles. The compound to be studied was added to degassed CD$_2$Cl$_2$, CDCl$_3$, or *d*^{6}-acetone (0.4 mL) which had been placed in a 5-mm NMR tube. After the compound had dissolved, 1 equiv of the nucleophile was added. The solution was allowed to stand at room temperature for 1 h after the nucleophile had completely dissolved, and then the solution was examined by NMR spectroscopy. The reactions carried out and the results obtained are tabulated as follows:

starting material/reagent	main products/yield
[(triphos)IrH$_3${Au(P-*i*-Pr$_3$)}][PF$_6$]/ MeOH, AsPh$_3$, PPh$_3$	no reaction
[(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_3$][PF$_6$]$_2$/ [PPN]Cl or NEt$_4$I	[(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_2$]-[PF$_6$] + [AuX(P-*iso*-Pr$_3$)] (X = Cl, I), 1:1; *ca.* 100%
[(triphos)RuH$_3${Au(AsPh$_3$)}$_3$][PF$_6$]$_2$/ [PPN]Cl	[(triphos)RuH$_3${Au(AsPh$_3$)}$_2$]-[PF$_6$] + [AuCl(AsPh$_3$)], 1:1; *ca.* 56% (+starting material)
[(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_3$][PF$_6$]$_2$/ [IrH$_3$(triphos]	[(triphos)RuH$_3${Au(P-*i*-Pr$_3$)}$_2$]-[PF$_6$] + [(triphos)IrH$_3$-{Au{P-*i*-Pr$_3$)}][PF$_6$], 1:1; *ca.* 100%
[(triars)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$/ MeOH, AsPh$_3$, or PPh$_3$	[(triars)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$, *ca.* 10% (+starting material)
[(triars)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$/ [PPN]Cl or NEt$_4$I	[(triars)RuH$_3${Au(PPh$_3$)}$_2$]-[PF$_6$] + [AuX(PPh$_3$)] (X = Cl, I), 1:1; *ca.* 100%
[(triars)RuH$_3${Au(EPh$_3$)}$_3$][PF$_6$]$_2$ (E = P, As)/[IrH$_3$(triphos]	[(triars)RuH$_3${Au(EPh$_3$)}$_2$]-[PF$_6$] + [(triphos)IrH$_3$-{Au(EPh$_3$)}][PF$_6$], 1:1; ca. 100%

Table III. Experimental Data for the X-ray Diffraction Study of [(triphos)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$, **C5**

chem formula	C$_{95}$H$_{87}$Au$_3$F$_{12}$P$_8$Ru
mol wt	2396.48
space group	*R*3*c* (No. 161)
a, Å	20.150(3)
c, Å	45.229(9)
Z	6
V, Å^3	15 904(9)
r(calcd), g cm^{-3}	1.501
μ, cm^{-1}	44.397
T, °C	22
λ, Å	0.710 69 (graphite monochrom, Mo Kα)
transm coeff	0.691–1.000
R^a	0.051
$R_w{}^a$	0.062

^{a} $R = \sum||F_o| - 1/k|F_c||/\sum|F_o|$. $R_w = [\sum(|F_o| - 1/k|F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o{}^2) + f^2(F_o{}^2)^2]^{1/2}/2F_o$ with $f = 0.045$.

Table IV. Final Atomic Positional Parameters and Equivalent Isotropic Displacement Coefficients (Å^2) for the Cation in [(triphos)RuH$_3${Au(PPh$_3$)}$_3$][PF$_6$]$_2$, **C5**

atom	*x*	*y*	*z*	B^a
Au	0.09421(7)	0.07443(7)	0.24514(7)	3.42(3)
Ru	0.000	0.000	0.200	2.24(5)
P1	0.1788(5)	0.1594(5)	0.2800(2)	3.6(2)
P2	0.0805(4)	0.1031(4)	0.1699(2)	2.7(2)
C1	0.076(2)	0.071(2)	0.1312(8)	4.1(9)
C2	0.000	0.000	0.121(1)	4.3(9)
C3	0.000	0.000	0.088(1)	6(1)
C11	0.060(2)	0.183(2)	0.1710(7)	3.7(7)*
C12	0.186(2)	0.159(2)	0.1761(7)	3.2(6)*
C21	0.073(2)	0.221(2)	0.1977(7)	3.5(7)*
C22	0.223(2)	0.127(2)	0.1912(8)	4.2(8)*
C31	0.059(2)	0.280(2)	0.1994(9)	4.8(8)*
C32	0.304(2)	0.172(2)	0.1948(9)	4.5(8)*
C41	0.030(2)	0.301(2)	0.176(1)	5.6(9)*
C42	0.342(2)	0.246(2)	0.1826(9)	5.1(9)*
C51	0.019(2)	0.265(2)	0.1485(9)	5.4(9)*
C52	0.303(2)	0.279(2)	0.1684(9)	5.4(9)*
C61	0.030(2)	0.204(2)	0.1461(8)	3.8(7)*
C62	0.227(2)	0.234(2)	0.1633(9)	4.8(8)*
C111	0.264(2)	0.153(2)	0.2805(8)	4.1(8)*
C121	0.146(2)	0.152(2)	0.3184(8)	3.5(7)*
C131	0.205(2)	0.256(2)	0.2688(9)	4.7(8)*
C211	0.261(2)	0.088(2)	0.2728(9)	4.8(8)*
C221	0.198(2)	0.176(2)	0.3416(9)	5.3(9)*
C231	0.168(2)	0.294(2)	0.283(1)	6(1)*
C311	0.325(3)	0.080(3)	0.274(1)	8(1)*
C321	0.173(2)	0.176(2)	0.3701(9)	5.4(9)*
C331	0.188(3)	0.370(2)	0.271(1)	6(1)*
C411	0.398(3)	0.146(3)	0.281(1)	8(1)*
C421	0.099(2)	0.147(2)	0.375(1)	7(1)*
C431	0.233(2)	0.400(2)	0.247(1)	7(1)*
C511	0.398(3)	0.206(3)	0.288(1)	8(1)*
C521	0.039(2)	0.120(2)	0.351(1)	5.2(9)*
C531	0.268(2)	0.361(2)	0.235(1)	6(1)*
C611	0.335(2)	0.216(2)	0.290(1)	6(1)*
C621	0.068(2)	0.121(2)	0.3226(8)	3.7(7)*
C631	0.257(2)	0.291(2)	0.2464(9)	5.3(9)*
H	0.09(2)	0.01(2)	0.22(1)	4(2)*

^{a} Starred *B* values are for atoms that were refined anisotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement coefficients defined as one-third of the trace of the orthogonalized **B** tensor.

Determination and Refinement of the structure of [(triphos)RuH$_3${Au{PPh$_3$)}$_3$][PF$_6$]$_2$ (C5). Moderately air-stable, pale violet crystals of **C5** were obtained as described above. A small prismatic crystal was mounted at a random orientation on a glass fiber and covered with acrylic resin for protection.

Space group and cell constants were determined on a Nonius CAD4 diffractometer which was subsequently used for data collection. As expected, this complex is isomorphous with [(triphos)RhH$_2${Au{PPh$_3$)}$_3$](CF$_3$SO$_3$)$_2$, **C'1**, as can be seen both from the symmetry (trigonal, with systematic absences consistent with space groups *R*3*c* and $R\bar{3}c$) and the cell constants, obtained by least-squares fit of 25 high-angle reflections (9.4° < θ < 16.5°) using the CAD4 centering routines.[20] The small variation in lattice parameters may be due to the different counterions presents in the two compounds, i.e., [PF$_6$]$^-$and CF$_3$SO$_3$$^-$, respectively.

Crystallographic and experimental data are listed in Table III and in supplementary material Table S3. The three reflections chosen as standards to check the decay of the crystal and the stability of the experimental conditions were measured every 1 h; the crystal orientation was checked by measuring three standards every 300 reflections.

Data were collected at variable scan speed to ensure constant statistical precision of the measured intensities. A total of 8658 reflections ($\pm h,+k,+l$) were measured and corrected for Lorentz and polarization factors and for decay (corrections factors in the range 1.000–1.225). An absorption correction was then calculated using the ψ scans of 5 reflections at high χ angles ($\chi > 87.9°$). The corrected data were averaged to give a set of 3065 unique reflections of which 2165, having $|F_o^2| > 2.0\sigma(F_o^2)$, were considered as observed while $F_o^2 = 0.0$ was given to those reflections having negative net intensities. The standard deviations on intensities were calculated in terms of statistics alone. The structure was refined by starting from the coordinates of the heavy atoms of **C′1** by full-matrix least squares minimizing the function $\sum w[|F_o| - 1/k|F_c|]^2$, with $w = [\sigma_2(F_o)]^{-1}$. No extinction correction was applied. The scattering functions used, corrected for the anomalous dispersion,[21] were taken from tabulated values.[20]

Anisotropic temperature parameters were used for the Ru, Au, P, and aliphatic carbon atoms, while isotropic parameters were used for the other atoms. The contribution of the hydrogen atoms, held fixed at their calculated positions (C–H = 0.95 Å, B_{iso} = 5.0 Å^2) was also taken into account but not refined.

The $[PF_6]^-$ moiety was found to be disordered and could not be adequately modeled. Thus, only the strongest peaks in the difference Fourier maps were retained and refined with the appropriate occupancy factor. As expected, this gave only an approximate geometry for this anion.

Upon covergence a difference Fourier map showed a peak (approximately 0.85 e/Å^3) in an acceptable position for a hydride bridging the Ru–Au bond. The hydride location was confirmed by calculating a difference Fourier map with limited data set[22] ((sin θ)/λ cutoff = 0.33 Å^{-1}). Thus this peak was retained and included in the refinement leading to acceptable convergence even with the expected high esd's for the H atom.

All calculations were carried out using the NONIUS-SDP package. The handedness of the crystal was tested by refining the two possible sets of coordinates and comparing the R_w factors.[23] The positional parameters corresponding to the lowest R_w are listed in Table IV.

Acknowledgment. G.W. carried out the work during the tenure of a research fellowship of the Swiss National Science Foundation. A.A. acknowledges the support of the Italian National Research Council. The authors are greatly indebted to Prof. P. S. Pregosin and Dr. H. Rüegger for much valuable discussion, particularly to the latter for recording the NMR spectra shown in the figures, using samples prepared by Mr. S. Chaloupka, and for taking the T_1 measurements.

Supplementary Material Available: Tables giving an extended listing of bond lengths and angles (Tables S1 and S2), full crystallographic and experimental data (Table S3), anisotropic displacement coefficients (Table S4), and calculated hydrogen positions (Table S5); and a figure giving the full atomic numbering scheme (Figure S1) (11 pages). Ordering information is given on any current masthead page. A table of final observed and calculated structure factors (22 pages) is available from A.A. upon request.

---

(20) Enraf Nonius: *Enraf-Nonius Structure Determination Package, SDP;* Delft: The Netherlands, 1980.

(21) *International Tables for X-ray Crystallography;* Kynoch Press: Birmingham, England, 1974; Vol. 4.

(22) La Placa, S. J.; Ibers J. A. *Acta Crystallogr.* **1965**, *18*, 511.

(23) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.