Products Obtained from Reactions between 1 and *t*-BuLi. **1-(Trimethylgermyl)-2-((trimethylstannyl)methyl)benzene (13)**: colorless liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ –0.03 (s, $^2J_{Sn-H}$ = 50.6, 52.9 Hz, 9 H, $SnCH_3$), 0.33 (s, 9 H, $GeCH_3$), 2.37 (s, $^2J_{Sn-H}$ = 62.5 Hz, 2 H, CH_2), 6.90 (t, ^3J = 7.4 Hz, 2 H, aryl H), 7.09 (td, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H, aryl H), 7.23 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1 H, aryl H), 7.32 (m, 1 H, aryl H); ^{13}C NMR (63 MHz, $CDCl_3$) δ –9.3 (q, ^1J = 128 Hz, $SnCH_3$), –0.1 (q, ^1J = 126 Hz, $GeCH_3$), 21.8 (t, ^1J = 125 Hz, CH_2), 122.8 (dd, ^1J = 160 Hz, ^3J = 8 Hz, C_5), 127.3 (d, ^1J = 156 Hz, C_3), 128.8 (dd, ^1J = 159 Hz, ^3J = 8 Hz, C_4), 133.7 (d, ^1J = 170 Hz, C_6), 137.6 (s, C_1), 148.3 (s, C_2); HRMS ($C_{13}H_{24}{}^{74}Ge^{120}Sn$) calcd 374.0127, found 374.0110; mass spectrum *m/z* (relative intensity) 374 (6 $M^{\bullet+}$), 359 (6, $M^{\bullet+} - CH_3$), 240 (3, $C_9H_{12}Sn^+$), 225 (3, $C_8H_9Sn^+$), 209 (3, $C_{10}H_{15}Ge^+$), 194 (15, $C_9H_{12}Ge^+$), 179 (17, $C_8H_9Ge^+$), 165 (100, $C_7H_7Ge^+$), 150 (8, $C_2H_6Sn^+$), 135 (15, CH_3Sn^+), 120 (4, Sn^+), 119 (16, $C_3H_9Ge^+$), 90 (8, CH_3Ge^+). Anal. Calcd for $C_{13}H_{24}GeSn$: C, 42.02; H, 6.51. Found: C, 42.45; H. 6.39.

1-(Trimethylgermyl)-2-((trimethylgermyl)methyl)benzene (14): colorless liquid; properties identical with those reported.[9,10]

1-(Trimethylgermyl)-2-((*tert*-butyldimethylstannyl)methyl)benzene (15): colorless liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 9 H, $GeCH_3$), 0.17 (s, $^2J_{Sn-H}$ = 46.7, 48.9 Hz, 6 H, $SnCH_3$), 1.02 (s, $^3J_{Sn-H}$ = 65.6, 68.2 Hz, 9 H, CCH_3), 2.20 (s, $^4J_{Sn-H}$ = 5.8 Hz, 2 H, CH_2), 6.93–6.96 (m, 2 H, aryl H), 7.09 (td, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 1 H, aryl H), 7.21 (dd, ^3J = 7.8 Hz, ^4J = 2.1 Hz, 1 H, aryl H); mass spectrum *m/z* (relative intensity) 359 (3, $M^{\bullet+} - C_4H_9$), 225 (5, $C_8H_9Sn^+$), 209 (8, $C_{10}H_{15}Ge^+$), 165 (100, $C_7H_7Ge^+$), 149 (10, $C_2H_5Sn^+$), 135 (23, CH_3Sn^+), 121 (12, SnH^+), 120 (10 Sn^+), 91 (10, $C_7H_7^+$), 89 (12, CH_3Ge^+), 57 (22, $C_4H_9^+$).

***tert*-Butyltrimethylstannane (19)**: colorless liquid; ^{1}H NMR (90 MHz, $CDCl_3$) δ –0.05 (s, $^2J_{Sn-H}$ = 48 Hz, 9 H, $SnCH_3$), 1.05 (s, $^3J_{Sn-H}$ = 64 Hz, 9 H, CH_3);[23] mass specrum *m/z* (relative intensity) 222 (2, $M^{\bullet+}$), 207 (7, $M^{\bullet+} - CH_3$), 165 (100, $C_3H_9Sn^+$), 150 (24), 135 (24), 121 (11), 120 (19), 57 (51).[19b]

Di-*tert*-butyldimethylstannane (20): colorless liquid; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.17 (s, $^2J_{Sn-H}$ = 43.5 Hz, 6 H, $SnCH_3$), 1.04 (s, $^3J_{Sn-H}$ = 59.6 Hz, 18 H, CH_3);[24] mass spectrum *m/z* (relative intensity) 264 (1, $M^{\bullet+}$), 249 (2, $M^{\bullet+} - CH_3$), 207 (45, $M^{\bullet+} - C_4H_9$), 193 (3, $C_5H_{12}Sn^+$), 165 (6, $C_3H_9Sn^+$), 151 (88), 135 (47), 121 (12), 120 (15), 57 (100).[25]

Tri-*tert*-butylmethylstannane (21): mass spectrum *m/z* (relative intensity) 235 (17, $M^{\bullet+} - C_5H_{11}$), 207 (8), 151 (100), 135 (31), 121 (9), 120 (9), 57 (35).[26]

^{119}Sn NMR Experiments. A high vacuum dried (10^{-6} mbar) and sealed glass apparatus was equipped with a small reaction flask, two ampules (containing 0.7 mL of a 1.42 M solution of *n*-BuLi in *n*-hexane and a solution of 336 mg of 1 (1.0 mmol) in 2.0 mL of diethyl ether, respectively) and a 10-mm NMR tube. The flask was charged with the solution of *n*-BuLi and cooled to –100 °C. The solution of 1 was cooled to –100 °C, whereafter it was added to the flask. The mixture was transferred to the NMR tube at –100 °C, and the NMR tube was sealed off. The ^{119}Sn NMR spectrum of this mixture, recorded at –80 °C, showed the presence of 1 (7.10 ppm), 6 (0.89 ppm[27]), and 8 (0.35 ppm[25]) in a ratio of 1:9.3:1.3. With THF a similar result was obtained; when 0.5 mL of TMEDA was added before the addition of 1, only 1 and two unidentified products (22.4 and 67.7 ppm) were observed in a ratio of 3.8:1:7.8.

Registry No. 1, 54031-00-4; 2, 129521-10-4; 3, 129521-11-5; 4, 129521-12-6; 5, 129521-13-7; 6, 1527-99-7; 7, 129521-14-8; 8, 1528-00-3; 9, 1528-01-4; 10, 13397-96-1; 11, 129521-15-9; 12, 129521-16-0; 13, 114198-52-6; 14, 113419-98-0; 15, 129521-17-1; 19, 3531-47-3; 20, 35569-11-0; 21, 35569-12-1; ^{119}Sn, 14314-35-3.

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Cluster Chemistry. 62.[1] Preparation of the Heptanuclear Clusters $Ru_5M_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (M = Ag, Au): X-ray Structure of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$

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The heptanuclear title complex was obtained from reactions between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and a mixture of $[O\{Au(PPh_3)\}_3][BF_4]$ and $[ppn][M(CO)_n]$ (M = Co, $n = 4$; M = Mn, $n = 5$) or by reduction (Na/Hg or $K[HBBu^s{}_3]$) of the Ru_5 complex and treatment with $AuCl(PPh_3)$; the silver analogue was made by the latter route. The structure of a $P(OEt)_3$ derivative of the Au_2Ru_5 cluster was determined. The metal core consists of an Ru/AuRu$_2$/Au trigonal bipyramid, two edges of which are bridged by Ru atoms. Addition of the $Au_2(PPh_3)_2$ unit has resulted in cleavage of one of the Ru–Ru bonds present in the original Ru_5 cluster. $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ is triclinic, space group $P\bar{1}$, with a = 14.031 (15) Å, b = 16.741 (4) Å, c = 18.721 (6) Å, α = 98.64 (2)°, β = 97.61 (6)°, γ = 98.04 (6)°, and Z = 4; 6848 data were refined to R = 0.0595 and R_w = 0.0617.

Introduction

The reactions of the open pentaruthenium cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1; Scheme I) with H_2 have been discussed in detail previously.[2] There is a stepwise addition of 3 equiv of H_2, so that the first adds to C_β of the μ_5-acetylide–phosphine unit of 1, converting it into a μ_5-vinylidene–phosphine species with the other H bridging a Ru–Ru bond as in 2. The second mole of H_2 adds sim-

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(1) Part 61: Bruce, M. I.; Liddell, M. J., Nicholson, B. K. *Appl. Organomet. Chem.*, in press.

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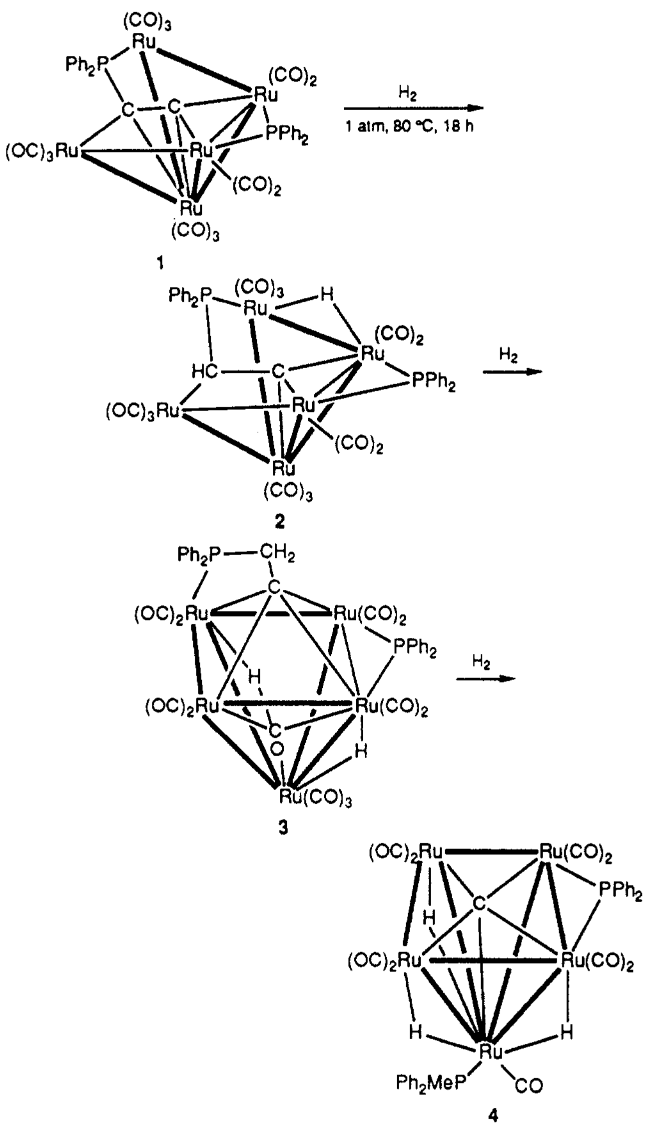
Scheme I



ilarly to give a μ_4-CCH_2PPh_2 group and two hydrogen-bridged Ru–Ru bonds (**3**), and finally the third H_2 cleaves the C–C bond to give a pentanuclear Ru_5C cluster with a CH_3PPh_2 ligand and three hydrogen-bridged Ru–Ru bonds (**4**).

In terms of the isolobal analogy[3] H_2 is equivalent to $Au_2(PPh_3)_2$. This species has been briefly described[4] but cannot be regarded as being generally available for use in synthesis. However, we have recently developed a method for simultaneously adding two $Au(PPh_3)$ groups to a cluster,[5] which is formally equivalent to adding $Au_2(PPh_3)_2$.

In this paper we discuss the cluster obtained on addition of two $Au(PPh_3)$ groups to **1**, together with some related species, and compare the observed reactions with those found earlier for the addition of H_2 to **1**.

Experimental Section

Reactions were performed under a nitrogen atmosphere with use of standard Schlenk techniques, as described earlier.[2] Instrumentation used included a Perkin-Elmer Model 683 spectrometer (IR) and Bruker WP-80DS or CXP300 spectrometers (NMR). FAB mass spectra were obtained on a VG ZAB 2HF instrument fitted with a FAB source. Argon was used as the excitation gas with the samples dispersed in a 3-nitrobenzyl alcohol matrix. Starting materials were $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**),[6] $[O\{Au(PPh_3)\}_3][BF_4]$,[7] $[ppn][Co(CO)_4]$ and $[ppn][Mn(CO)_5]$ ($[ppn]^+ = [N(PPh_3)_2]^+$),[8] and $Ag[C_5(CO_2Me)_5](PPh_3)$.[9]

Syntheses of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (5). (a) With Use of $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][Co(CO)_4]$. A mixture of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; 51 mg, 0.040 mmol), $[O\{Au(PPh_3)\}_3][BF_4]$ (62 mg, 0.041 mmol), and $[ppn][Co(CO)_4]$ (30 mg, 0.042 mmol) in THF (20 mL) was stirred at room temperature for 24 h, giving a green solution. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2 (minimum volume). Diethyl ether (20 mL) was then added and the volume reduced; after the solution was cooled (−15 °C), the resulting white precipitate was filtered off and identified (IR, FAB MS) as $[ppn][BF_4]$ (7 mg, 0.01 mmol, 26%). The filtrate was evaporated to dryness under reduced pressure and purified by TLC (silica gel, 2/1 petroleum ether/CH_2Cl_2). A minor white band (R_f 0.60) was identified as $AuCo(CO)_4(PPh_3)$. IR (cyclohexane): ν(CO) 2055 s, 1988 m, 1958 vs cm^{-1}. FAB MS (m/z): 630, $[M]^+$; loss of 4 CO groups. (Lit.[10] IR (CS_2): 2054 s, 1988 s, 1957 s cm^{-1}.) The major band (R_f 0.24) was crystallized (CH_2Cl_2/petroleum ether) as dark green-black crystals of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (**5**; 66 mg, 0.031 mmol, 77%), mp >330 °C dec. Anal. Calcd for $C_{74}H_{50}Au_2O_{12}P_4Ru_5$: C, 41.26; H, 2.34; M_r, 2154. Found: C, 41.61; H, 2.62; M_r 2154 (mass spectrometry, 2155 = $[M + H]^+$). IR (CH_2Cl_2): ν(CO) 2057 w, 2036 s, 1984 vs, 1957 (sh), 1917 m cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.5–6.6 (m, Ph). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, δ): 215.3, 214.7, 212.8 (3 s, CO); 206.2, 202.1, 198.0, 194.6 (4 m, CO); 144.1 (dd, J_{P-C} = 27, 11 Hz, C_α); 141.2–126.0 (m, Ph); C_β not observed. FAB MS (m/z): 2155, $[M + H]^+$; loss of 12 CO groups.

A larger scale reaction (**1**, 100 mg; $[O\{Au(PPh_3)\}_3][BF_4]$, 124 mg; $[ppn][Co(CO)_4]$, 60 mg; THF, 35 mL) was worked up after 24 h by removing the solvent under vacuum and purifying the residue by column chromatography (Florisil). $AuCo(CO)_4(PPh_3)$ (41 mg, 0.065 mmol, 83%) was removed first (8/1 petroleum ether/CH_2Cl_2, colorless band), followed by **5** (140 mg, 0.065 mmol, 83%; 3/1 petroleum ether/CH_2Cl_2, green band).

(b) With Use of $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][Mn(CO)_5]$. Similarly **1** (50 mg, 0.040 mmol), $[O\{Au(PPh_3)\}_3][BF_4]$ (60 mg, 0.041 mol), and $[ppn][Mn(CO)_5]$ (29 mg, 0.041 mmol) in THF (25 mL) were stirred at room temperature for 20 h. Following removal of the solvent under vacuum, TLC (2/1 petroleum ether/CH_2Cl_2) of the residue gave two bands: white (R_f 0.65) $AuMn(CO)_5(PPh_3)$ (7 mg, 0.01 mmol, 27%) identified spectroscopically (IR (cyclohexane): ν(CO) 2067 m, 1962 vs cm^{-1}. FAB MS (m/z): 654, $[M]^+$; loss of 2 CO groups. Lit.[11] IR (hexane): 2063 m, 1964 vs cm^{-1}) and green (R_f 0.24) **5** (63 mg, 0.029 mmol, 73%), identified by IR spectroscopy.

(c) With Use of $[O\{Au(PPh_3)\}_3][BF_4]/Na[Co(CO)_4]$. $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; 100 mg, 0.079 mmol) was added to a filtered (Celite) solution of $Na[Co(CO)_4]$ (0.12 mmol), prepared from $Co_2(CO)_8$ (20 mg, 0.058 mmol) and 1% Na amalgam in THF (15 mL). No reaction was apparent after 20 h, and spot TLC indicated that both starting materials were still present. Addition of $[O\{Au(PPh_3)\}_3][BF_4]$ (118 mg, 0.080 mmol) gave a green solution after 4 h. The solvent was removed under vacuum and the residue purified by TLC (8/5 petroleum ether/acetone). A major green band (R_f 0.35) was collected and identified (IR, FAB MS) as **5** (59 mg, 0.027 mmol, 35%).

(d) With Use of Only $[O\{Au(PPh_3)\}_3][BF_4]$. A solution of **1** (50 mg, 0.040 mmol) and $[O\{Au(PPh_3)\}_3][BF_4]$ (59 mg, 0.041

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mmol) in THF (20 mL) was stirred at room temperature for 20 h. The solvent was then removed under vacuum. Preparative TLC (8/5 petroleum ether/acetone) of the residue eluted six bands, three of which were collected and identified (IR, spot TLC) as (1) a brown band (R_f 0.53) of unreacted **1** (5 mg, 0.004 mmol, 10%), (2) a green band (R_f 0.35) of **5** (19 mg, 0.009 mmol, 22%), and (3) a major brown base line (extracted CH_2Cl_2/MeOH) containing $Au_3Ru_5(CO)_{10}(dppa^*)(PPh_3)_3$.[23] IR (cyclohexane): ν(CO) 2047 w, 2024 w, 2014 (sh), 2006 (sh), 1978 vs, 1916 (sh) cm^{-1}. FAB MS (m/z): 2556, $[M]^+$.

(e) With Use of Sodium Amalgam and $AuCl(PPh_3)$. Reduction of a solution of **1** (50 mg, 0.040 mmol) in THF (24 mL) with 1% sodium amalgam (4 mL) for 40 min gave a black solution (IR (THF): ν(CO) 2021 (sh), 2005 (sh), 1968 vs (overlaps with THF), 1948 (sh) cm^{-1}). This was then syringed into a flask containing $AuCl(PPh_3)$ (40 mg, 0.081 mmol). The solution immediately turned green, and after it was stirred for 15 min, the reaction mixture was filtered (Celite) and evaporated to dryness under reduced pressure. The residue was purified by TLC (2/1 petroleum ether/CH_2Cl_2), and a major green band (R_f 0.27) was collected and precipitated (CH_2Cl_2/petroleum ether) as **5** (73 mg, 0.034 mmol, 85%; identified by IR and FAB mass spectroscopy).

N.B. The reduced solution produced from **1** (50 mg, 0.040 mmol) and sodium amalgam in THF (24 mL) (as above) was added to [ppn]Cl (50 mg, 0.087 mmol) in MeCN (10 mL) and stirred for 20 min. A color change to brown was observed. The solution was filtered (Celite) and evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2, and EtOH was added; volume reduction of this solution gave a red-brown precipitate. This product is thought to be $[ppn]_2[Ru_5(CO)_{12}(dppa^*)]$ (65 mg, 0.028 mmol, 70%). IR (CH_2Cl_2): ν(CO) 2025 m, 1987 vs, 1970 (sh) cm^{-1}. IR (THF): ν(CO) 2020 m, 1983 vs cm^{-1}. FAB MS (negative ion, m/z): 1236, $[M]^-$; ions formed by stepwise loss of 8 CO groups. MS (positive ion, m/z): 538, $[ppn]^+$; no Ru-containing peaks. ^1H NMR (3/1 C_6D_6/acetone-d_6): δ 7.4–7.2 (m, Ph). No reaction occurred when this product was treated with $AuCl(PPh_3)$.

(f) With Use of $K[HBBu^s_3]/AuCl(PPh_3)$. A solution of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; 50 mg, 0.04 mmol) in THF (10 mL) was treated with $K[HBBu^s_3]$ (0.5 mol L^{-1} in THF) until all starting material was consumed (by IR spectroscopy). Solid $AuCl(PPh_3)$ (20 mg, 0.04 mmol) was added to the black solution, giving an immediate color change to olive green. After a further 30 min the solution was evaporated to dryness and the residue chromatographed, with petroleum ether/acetone (4/1) as eluent, to give four bands. Band 1 (R_f 0.67) was a red compound in trace amount and was uncharacterized; Band 2 (R_f 0.61) was blue-gray and was recrystallized from CH_2Cl_2/MeOH to give black crystals of $AuRu_5(C_2HPPh_2)(PPh_2)(CO)_{13}(PPh_3)$ (**10**; 13 mg, 19%), mp >300 °C dec. Anal. Calcd for $C_{57}H_{36}AuO_{13}P_3Ru_5$: C, 39.71; H, 2.10. Found: C, 38.96; H, 2.10. IR (cyclohexane): ν(CO) 2081 w, 2066 w, 2048 vs, 2013 s, 2000 s, 1979 w, 1966 w, 1947 w, 1920 w, cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.35 (m, 35 H, Ph), 3.87 (dd, $J_{P\text{-}H}$ = 12 and 21 Hz, 1 H, C_2HPPh_2). Band 3 (R_f 0.52) was olive green and was recrystallized from CH_2Cl_2/heptane to give dark green needles of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (**5**; 22 mg, 26% based on Ru_5 cluster, 52% based on $AuCl(PPh_3)$). Band 4 (R_f 0.40) was a red compound in trace amount and was uncharacterized.

The reaction was repeated with use of excess $K[HBBu^s_3]$ and a 1/2 ratio of Ru_5 cluster/$AuCl(PPh_3)$, giving 45% of the Au_2Ru_5 cluster and 5% of the $AuRu_5$ species.

Preparation of $Ag_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (6). A solution of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (260 mg, 0.206 mmol) in THF (10 mL) rapidly darkened after the addition of an excess of $K[HBBu^s_3]$ (0.5 mol L^{-1} in THF); after 5 min solid $Ag[C_5(CO_2Me)_5](PPh_3)$ (152 mg, 0.21 mmol) was added. The solution immediately turned dark green, and after 5 min the solvent was removed in vacuo and the residue chromatographed, with petroleum ether/acetone (4/1) as eluent, to give one major green band (R_f 0.35). Recrystallization from CH_2Cl_2/MeOH gave olive green needles of $Ag_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (**6**; 110 mg, 27% based on Ru_5 cluster, 54% based on silver compound), mp >300 °C dec. Anal. Calcd for $C_{74}H_{50}Ag_2O_{12}P_4Ru_5$: C, 44.98; H, 2.56; M_r 1975. Found: C, 44.64; H, 2.56; M_r 1975. FAB MS (m/z): 1976, $[M + H]^+$; loss of 12 CO groups. IR (CH_2Cl_2): ν(CO) 2052 w, 2032 s, 1982 s, 1949 w, 1912 m, 1893 w cm^{-1}. ^1H NMR ($CDCl_3$, δ): 7.25 (m, Ph).

N.B. Solutions of **6** are slightly light-sensitive and after 12 h deposit silver metal.

Synthesis of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)\{P(OEt)_3\}$ (7), $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)\{P(OEt)_3\}_2$ (8), and $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ (9). Complex **5** (70 mg, 0.033 mmol) and $P(OEt)_3$ (9 mg, 0.054 mmol) were heated in refluxing CH_2Cl_2 (15 mL) for 1 h. A further portion of $P(OEt)_3$ (6 mg, 0.037 mmol) was added, and heating was continued for 15 min. At this stage the reaction appeared to be complete (by spot TLC). The volume was then reduced to 1 mL and petroleum ether (10 mL) was added to precipitate a green solid, which was washed with further petroleum ether. Preparative TLC (8/2/1 petroleum ether/CH_2Cl_2/acetone) of this product gave three green bands. The first band (R_f 0.53) was crystallized (CH_2Cl_2/cyclohexane) as microcrystalline $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)\{P(OEt)_3\}$ (**7**; 8 mg, 0.004 mmol, 12%), mp 230 °C dec. Anal. Calcd for $C_{62}H_{50}Au_2O_{15}P_4Ru_5$: C, 36.18; H, 2.45; M_r, 2058. Found: C, 35.82; H, 2.44; M_r, 2058 (mass spectrometry, m/z 2059, $[M + H]^+$). IR ($CHCl_2$): ν(CO) 2058 w, 2036 s, 1998 (sh), 1988 vs, 1962 (sh), 1921 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.9–6.9 (m, 35 H, Ph); 3.62 (m, 6 H, CH_2); 0.85 (t, $J_{H\text{-}H}$ = 7.0 Hz, 9 H, CH_3). FAB MS (m/z): 2059, $[M + H]^+$; loss of 2 CO groups. The second band (R_f 0.40) crystallized (CH_2Cl_2/petroleum ether) as green microcrystalline $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)\{P(OEt)_3\}_2$ (**8**; 26 mg, 0.012 mmol, 36%), mp 174–178 °C. Anal. Calcd for $C_{67}H_{65}Au_2O_{17}P_5Ru_5$: C, 36.63; H, 2.98; M_r 2196. Found: C, 37.15; H, 2.82; M_r 2196 (mass spectrometry, m/z 2197 = $[M + H]^+$). IR (CH_2Cl_2): ν(CO) 2035 m, 2002 m, 1976 vs, 1965 (sh), 1912 m cm^{-1}. ^1H NMR ($CDCl_3$, δ): 8.2–6.9 (m, 35 H, Ph); 4.18 (m, 6 H, CH_2); 3.58 (m, 6 H, CH_2); 1.30 (t, $J_{H\text{-}H}$ = 7.0 Hz, 9 H, CH_3); 0.83 (t, $J_{H\text{-}H}$ = 7.0 Hz, 9 H, CH_3). FAB MS (m/z): 2197, $[M + H]^+$; loss of 10 CO groups. The last band (R_f 0.33) crystallized (CH_2Cl_2/petroleum ether) as large green-black crystals of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ (**9**; 11 mg, 0.0048 mmol, 15%), mp 275 °C dec. Anal. Calcd for $C_{79}H_{65}Au_2O_{14}P_5Ru_5$: C, 41.39; H, 2.86; M_r, 2292. Found: C, 41.46; H, 2.95; M_r 2292 (mass spectrometry). IR (CH_2Cl_2): ν(CO) 2036 m, 2005 m, 1977 vs, 1964 (sh), 1911 m cm^{-1}. ^1H NMR ($CDCl_3$, δ): 8.2–6.6 (m, 50 H, Ph); 4.18 (m, 6 H, CH_2); 1.29 (t, $J_{H\text{-}H}$ = 7.0 Hz, 9 H, CH_3). FAB MS (m/z): 2292, $[M]^+$; loss of 10 CO groups.

X-ray Crystal Structure of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ (9). Suitable green-black crystals were obtained from CH_2Cl_2/petroleum ether. The space group was defined by precession photography, and a regular block-shaped crystal of dimensions 0.44 × 0.25 × 0.20 mm was used to obtain accurate cell dimensions and intensity data on a Nicolet P3 diffractometer, using monochromated Mo Kα X-radiation (λ = 0.71069 Å).

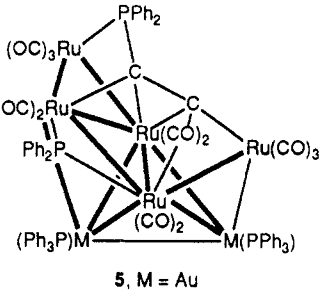
Crystal data: $C_{79}H_{65}Au_2O_{14}P_5Ru_5$, M_r 2292.5, triclinic, space group $P\bar{1}$, a = 14.031 (15) Å, b = 16.741 (4) Å, c = 18.721 (6) Å, α = 98.64 (2)°, β = 97.61 (6)°, γ = 98.04 (6)°, V = 4251 (5) Å^3, D_c = 1.75 g cm^{-3} for Z = 2, $F(000)$ = 2208, μ(Mo Kα) = 44 cm^{-1}, T = 138 K.

Intensity data were collected in two stages, because of the size of the problem. A small data set was collected that allowed an initial solution of the structure. This approximate model was used to calculate F_o for the full data set. These were converted to E values, which were then used as a basis to predict which reflections were likely to give measurable intensity. These were then collected with use of ω scans in the range $4° < 2\theta < 60°$ ($0 < h < 20$, $-24 < k < 24$, $-27 < l < 27$), to give a total of 7556 reflections, of which 7302 were unique (R(merg) = 0.013). Monitoring of three standards at regular intervals showed no crystal decay. The data were corrected for absorption with use of the ϕ-scan technique (transmission factors were 0.899 (max) and 0.719 (min)). The 6848 data with $I > 2\sigma(I)$ were used in all calculations.

The structure was solved by direct methods and the full structure routinely developed. In the final cycles of full-matrix least-squares refinement Au, Ru, and P atoms were assigned anisotropic temperature factors while other atoms were treated as isotropic. The phenyl rings were included as rigid hexagons ($D_{C\text{-}C}$ = 1.395 Å), and H atoms were included in calculated positions with common temperature factors for each type. Refinement converged at $R = 0.0595$ and $R_w = 0.0617$ where $w = [\sigma^2(F) + 0.004212F^2]^{-1}$. The largest parameter shift (0.3σ) in the final cycle related to the orientation of the CH_3 groups. A final difference map showed several peaks of ca. 1.0 e Å^{-3} adjacent to the Au atoms, but no other significant features. All calculations were performed using SHELXS-86 or SHELX-76,[12] with scattering factors, $\Delta f'$, and $\Delta f''$ values from ref 24. Positional parameters are listed in Table I.

Results and Discussion

Formal addition of the digold unit $Au_2(PPh_3)_2$ to **1** resulted in the formation of the heptanuclear cluster $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (**5**). Various routes to **5** have been investigated. The most convenient for preparative purposes was found to be the addition of $[O\{Au(PPh_3)\}_3][BF_4]$, followed by $[ppn][Co(CO)_4]$, to **1** in THF at room temperature; this gave **5** in 83% yield. The binuclear compound $AuCo(CO)_4(PPh_3)$ was also isolated in 83% yield. In directly analogous procedures treatment of **1** with $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][Mn(CO)_5]$ or $[O\{Au(PPh_3)\}_3][BF_4]/Na[Co(CO)_4]$ gave **5** in 73% and 35% yields, respectively. For these reactions the order of addition is important, since the addition of $[ppn][Co(CO)_4]$ to the oxonium salt in THF gave an orange solution, which did not subsequently react with **1** to form **2**. As discussed elsewhere,[5] this suggests that the cluster may be reacting with the unstable intermediate "$O[Au(PPh_3)]_2$", formed by removal of a "$[Au(PPh_3)]^+$" unit from $[O\{Au(PPh_3)\}_3]^+$ by $[Co(CO)_4]^-$. The fate of the oxygen atom was not determined, but it presumably ends up as CO_2 by combination with the eliminated CO.



5, M = Au
6, M = Ag

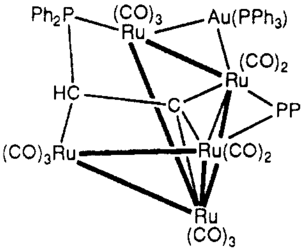
These reactions confirm that this reagent is useful in introducing "$Au_2(PR_3)_2$" units into clusters under mild conditions, without the requirement that the cluster be a dianion or multihydride complex. At this stage, it seems that the cluster must be capable of facile CO loss for the above reaction to work successfully.

The green cluster $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (**5**) was characterized by microanalysis and spectroscopic data. The FAB mass spectrum had a molecular ion at m/z 2155, corresponding to $[M + H]^+$, which fragmented by stepwise loss of twelve CO groups. In the ^1H NMR spectrum, resonances were found between δ 7.5 and 6.6 for the phenyl protons. In the ^{13}C NMR spectrum, resonances were found for the carbonyl ligands (δ 215.3, 214.7, 212.8, 206.2, 202.1, 198.0, 194.6) and the phenyl groups (δ 141.2–126.0); a signal at δ 144.1 showing coupling to two phosphorus ligands was assigned to the α-carbon of the acetylide. The complex $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$, unlike most other Ru_5 clusters, is virtually insoluble in hydrocarbon solvents, and although it crystallized readily, the crystals were not suitable for an X-ray study. The structure was therefore deduced as that indicated in **5** by comparison with a $P(OEt)_3$ derivative (see below).

The reaction of **1** with $[O\{Au(PPh_3)\}_3][BF_4]$ alone also gave **5**, but the yield was considerably lower (22%) and the reaction did not go to completion. A side product from this reaction, $Au_3Ru_5(CO)_{10}(dppa^*)(PPh_3)_3$ (identified by FAB MS), was apparently formed by addition of a third "$Au(PPh_3)$" fragment to **5**, but this could not be characterized further. This reaction parallels those of $[O\{Au(PPh_3)\}_3][BF_4]$ with anionic clusters, which commonly add three $Au(PPh_3)$ groups.[13]

Another route to **5** was the reaction between $AuCl(PPh_3)$ and the reduced solution formed by reacting **1** with sodium amalgam; complex **5** was obtained in 85% yield. From this result, it seems likely that the reduced species is $[Ru_5(CO)_{12}(dppa^*)]^{2-}$, since dianions generally react with two $[Au(PR_3)]^+$ units to give neutral species, whereas monoanions react with only one $Au(PR_3)$ moiety. The reduced form of **5** could be precipitated as the $[ppn]^+$ salt, assumed to be $[ppn]_2[Ru_5(CO)_{12}(dppa^*)]$, but this was not fully characterized. Addition of $AuCl(PPh_3)$ to the $[ppn]^+$ salt did not give **5**, but this is not unexpected since $[ppn]^+$ salts are less reactive in salt-elimination reactions than the corresponding Na^+ salts.[14]

A variation on this synthesis involves the reduction of **1** with excess $K[HBBu^s{}_3]$ and subsequent coupling with $AuCl(PPh_3)$; however, yields of **5** are lower than with sodium amalgam as the reducing agent. If **1** was reacted with 1 equiv of $K[HBBu^s{}_3]$, followed by addition of $AuCl(PPh_3)$, then, in addition to **5**, a cluster of formula $AuRu_5(C_2HPPh_2)(PPh_2)(CO)_{13}(PPh_3)$ (**10**) could be isolated in moderate yield. It was characterized as a vinylidene species by microanalysis and spectroscopy. In particular a ^1H NMR signal at δ 3.87 was assigned to the vinylidene proton, although it is shifted to higher field compared[2] with the corresponding signal in the analogue $Ru_5(\mu\text{-}H)\{\mu_5\text{-}C_2H(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{13}$ (**2**).



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The silver analogue of **5**, namely $Ag_2Ru_5(\mu^5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (**6**), could be prepared in moderate yields by reducing **1** with $K[HBBu^s{}_3]$ and then coupling the resulting anionic species with $Ag[C_5(CO_2Me)_5](PPh_3)$. A comparison of the infrared spectra of **5** and **6** in the ν(CO) region strongly indicate the same structure is adopted by both.

X-ray-quality crystals of **5** could not be obtained, so a triethyl phosphite substituted derivative was synthesized. The reaction of **5** with $P(OEt)_3$ was not entirely straightforward: three products (Scheme II) were obtained when a 2/1 ratio of phosphite to **5** was used, while at a lower

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[12] G. M. Sheldrick, SHELXS86-Program for Solving Crystal Structures; University of Göttingen: Göttingen, FRG, 1986; SHELX76-Program for Crystal Structure Determination, University of Cambridge: Cambridge, England, 1976. A version of the latter modified by D. Rabinovich and K. Reich, Weizmann Institute of Science, Rehovot, Israel, to accept up to 400 atoms was used.

[13] Bruce, M. I.; bin Shawkataly, O.; Nicholson, B. K. *J. Organomet. Chem.* **1984**, *275*, 223. Bruce, M. I.; Nicholson, B. K. *Organometallics* **1984**, *3*, 101.

[14] Duffy, D. N.; Nicholson, B. K. *J. Organomet. Chem.* **1979**, *164*, 227.

Table I. Final Positional Parameters for $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ (9)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Au(1)	0.2157 (1)	0.3055 (1)	0.1648 (1)	C(122)	0.228 (1)	0.5200 (7)	−0.0475 (6)
Au(2)	0.4186 (1)	0.3884 (1)	0.2476 (1)	C(123)	0.308 (1)	0.5733 (7)	−0.0056 (6)
Ru(1)	0.5331 (1)	0.2622 (1)	0.2639 (1)	C(124)	0.333 (1)	0.5698 (7)	0.0684 (6)
Ru(2)	0.3834 (1)	0.2369 (1)	0.1480 (1)	C(125)	0.278 (1)	0.5132 (7)	0.1005 (6)
Ru(3)	0.3089 (1)	0.2585 (1)	0.2895 (1)	C(126)	0.198 (1)	0.4600 (7)	0.0586 (6)
Ru(4)	0.2121 (1)	0.1282 (1)	0.1801 (1)	C(131)	0.0656 (8)	0.2677 (7)	−0.0201 (7)
Ru(5)	0.1570 (1)	0.1458 (1)	0.3207 (1)	C(132)	0.0006 (8)	0.2231 (7)	−0.0804 (7)
P(1)	0.1264 (5)	0.3879 (3)	0.1030 (3)	C(133)	−0.0944 (8)	0.2394 (7)	−0.0934 (7)
P(2)	0.4701 (5)	0.5269 (2)	0.2929 (3)	C(134)	−0.1244 (8)	0.3003 (7)	−0.0462 (7)
P(3)	0.6477 (5)	0.1824 (3)	0.2563 (3)	C(135)	−0.0595 (8)	0.3449 (7)	0.0141 (7)
P(4)	0.2984 (5)	0.0843 (3)	0.3325 (3)	C(136)	0.0355 (8)	0.3286 (7)	0.0271 (7)
P(5)	0.3035 (4)	0.1110 (2)	0.0874 (3)	C(211)	0.556 (1)	0.5550 (6)	0.1718 (7)
C(1)	0.336 (2)	0.127 (1)	0.2566 (9)	C(212)	0.593 (1)	0.6015 (6)	0.1227 (7)
C(2)	0.416 (2)	0.180 (1)	0.246 (1)	C(213)	0.587 (1)	0.6848 (6)	0.1305 (7)
C(11)	0.626 (2)	0.355 (1)	0.245 (1)	C(214)	0.544 (1)	0.7215 (6)	0.1874 (7)
O(11)	0.679 (2)	0.406 (1)	0.233 (1)	C(215)	0.508 (1)	0.6749 (6)	0.2365 (7)
C(12)	0.573 (2)	0.279 (1)	0.364 (1)	C(216)	0.514 (1)	0.5917 (6)	0.2287 (7)
O(12)	0.596 (2)	0.291 (1)	0.427 (1)	C(221)	0.280 (1)	0.5401 (6)	0.3084 (6)
C(21)	0.343 (2)	0.299 (1)	0.074 (1)	C(222)	0.205 (1)	0.5747 (6)	0.3364 (6)
O(21)	0.335 (1)	0.3352 (8)	0.0254 (8)	C(223)	0.227 (1)	0.6457 (6)	0.3891 (6)
C(22)	0.501 (2)	0.249 (1)	0.112 (1)	C(224)	0.324 (1)	0.6821 (6)	0.4138 (6)
O(22)	0.563 (1)	0.2590 (9)	0.0775 (8)	C(225)	0.399 (1)	0.6475 (6)	0.3858 (6)
C(31)	0.221 (2)	0.332 (1)	0.313 (1)	C(226)	0.377 (1)	0.5764 (6)	0.3332 (6)
O(31)	0.171 (1)	0.3743 (9)	0.3357 (8)	C(231)	0.664 (1)	0.5926 (9)	0.3663 (8)
C(32)	0.364 (2)	0.289 (1)	0.387 (1)	C(232)	0.743 (1)	0.5960 (9)	0.4211 (8)
O(32)	0.393 (2)	0.311 (1)	0.4498 (9)	C(233)	0.734 (1)	0.5478 (9)	0.4753 (8)
C(41)	0.160 (2)	0.017 (1)	0.175 (1)	C(234)	0.647 (1)	0.4962 (9)	0.4747 (8)
O(41)	0.124 (1)	−0.0498 (8)	0.1665 (7)	C(235)	0.568 (1)	0.4928 (9)	0.4199 (8)
C(42)	0.095 (2)	0.147 (1)	0.120 (1)	C(236)	0.576 (1)	0.5410 (9)	0.3656 (8)
O(42)	0.025 (2)	0.149 (1)	0.0852 (9)	C(411)	0.233 (1)	−0.0776 (8)	0.3410 (8)
C(51)	0.149 (2)	0.198 (1)	0.416 (1)	C(412)	0.227 (1)	−0.1624 (8)	0.3246 (8)
O(51)	0.140 (2)	0.232 (1)	0.473 (1)	C(413)	0.281 (1)	−0.1963 (8)	0.2739 (8)
C(52)	0.059 (2)	0.196 (1)	0.272 (1)	C(414)	0.341 (1)	−0.1454 (8)	0.2396 (8)
O(52)	−0.007 (2)	0.222 (1)	0.244 (1)	C(415)	0.347 (1)	−0.0606 (8)	0.2560 (8)
C(53)	0.065 (2)	0.051 (1)	0.319 (1)	C(416)	0.293 (1)	−0.0267 (8)	0.3067 (8)
O(53)	0.011 (2)	−0.005 (1)	0.315 (1)	C(421)	0.361 (1)	0.1277 (9)	0.4826 (8)
O(311)	0.749 (3)	0.214 (2)	0.304 (2)	C(422)	0.428 (1)	0.1369 (9)	0.5464 (8)
C(311)	0.789 (6)	0.271 (5)	0.348 (4)	C(423)	0.523 (1)	0.1226 (9)	0.5424 (8)
C(312)	0.883 (4)	0.280 (3)	0.396 (3)	C(424)	0.551 (1)	0.0989 (9)	0.4746 (8)
O(321)	0.677 (2)	0.170 (1)	0.177 (1)	C(425)	0.484 (1)	0.0897 (9)	0.4107 (8)
C(321)	0.766 (2)	0.153 (1)	0.155 (1)	C(426)	0.389 (1)	0.1040 (9)	0.4147 (8)
C(322)	0.807 (3)	0.220 (2)	0.118 (2)	C(511)	0.2853 (9)	0.1386 (7)	−0.0588 (6)
O(331)	0.617 (2)	0.095 (1)	0.275 (1)	C(512)	0.2414 (9)	0.1257 (7)	−0.1319 (6)
C(331)	0.682 (2)	0.035 (2)	0.275 (1)	C(513)	0.1542 (9)	0.0712 (7)	−0.1552 (6)
C(332)	0.631 (4)	−0.041 (2)	0.294 (2)	C(514)	0.1109 (9)	0.0296 (7)	−0.1055 (6)
C(111)	0.005 (1)	0.4156 (6)	0.2049 (7)	C(515)	0.1548 (9)	0.0425 (7)	−0.0325 (6)
C(112)	−0.054 (1)	0.4597 (6)	0.2446 (7)	C(516)	0.2420 (9)	0.0970 (7)	−0.0091 (6)
C(113)	−0.060 (1)	0.5404 (6)	0.2364 (7)	C(521)	0.3144 (8)	−0.0563 (7)	0.0610 (8)
C(114)	−0.007 (1)	0.5771 (6)	0.1886 (7)	C(522)	0.3616 (8)	−0.1244 (7)	0.0564 (8)
C(115)	0.052 (1)	0.5330 (6)	0.1490 (7)	C(523)	0.4631 (8)	−0.1140 (7)	0.0719 (8)
C(116)	0.058 (1)	0.4523 (6)	0.1572 (7)	C(524)	0.5173 (8)	−0.0354 (7)	0.0919 (8)
C(121)	0.173 (1)	0.4634 (7)	−0.0153 (6)	C(525)	0.4700 (8)	0.0327 (7)	0.0965 (8)
				C(526)	0.3686 (8)	0.0223 (7)	0.0811 (8)

phosphite/cluster ratio the reaction did not go to completion. The three green phosphite-substituted compounds $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)\{P(OEt)_3\}$ (**7**), $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)\{P(OEt)_3\}_2$ (**8**), and $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ (**9**) were characterized by analytical and spectroscopic data. The IR spectrum of **7** was very similar to that of **5**, while **8** and **9** showed shifts to lower wavenumber and band patterns different from that of **5**. Molecular ions were observed in the FAB mass spectra of these complexes at *m/z* 2059 (**7**), 2197 (**8**), and 2292 (**9**). The number of phosphite ligands was easily ascertained by ^1H NMR spectroscopy. The CH_2 environments in all complexes demonstrated the long-range coupling patterns discussed previously.[15]

X-ray-quality crystals of **9** were obtained, and a full structural analysis was performed; the structures of **5**, **6**, **7**, and **8** discussed herein were assigned by comparison with that found for **9**. We assume no major core change has occurred on derivatization of **5** to give **9**, since the $P(OEt)_3$ ligand has attached to a wingtip site, as found earlier for the parent Ru_5 cluster.[15] The full molecular structure of **9** is shown in Figure 1, while Figure 2 shows the details of the core geometry; Table II collects significant bond distances and angles. The structure of **9** is quite closely related to that of **1**.[5] The Ru(1)–Ru(3) bond of **1** has been cleaved, and the Ru(3)Ru(4)Ru(5) triangle has bent back to become essentially coplanar with the Ru(2)Ru(3)Ru(4) triangle: deviations from the least-squares plane through the unit defined by Ru(2)Ru(3)Ru(4)Ru(5) are less than 0.06 Å; Ru(1) is 1.909 Å below this plane. The Ru_5 core can be described as a spiked-distorted-square structure. This is the second example of a Ru_5 core with this geometry, Carty et al.[16] having described a rather distorted form

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(15) Bruce, M. I.; Liddell, M. J.; Nicholson, B. K.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H. Manuscript in preparation.

(16) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1986**, 5, 2565.

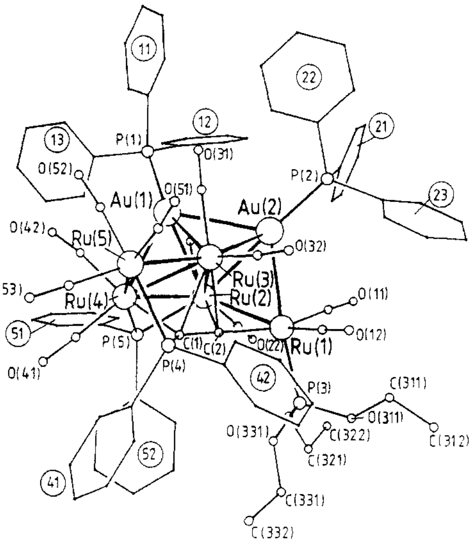


Figure 1. PLUTO diagram of the full structure of $Au_2Ru_5(\mu_5\text{-}\eta^2,P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ (**9**) showing the atom-labeling scheme. The carbon atoms of the phenyl rings are not individually labeled, but for ring *xy* the atoms are C(*xy*1)–C(*xy*6), with C(*xy*6) bonded to P in each case.

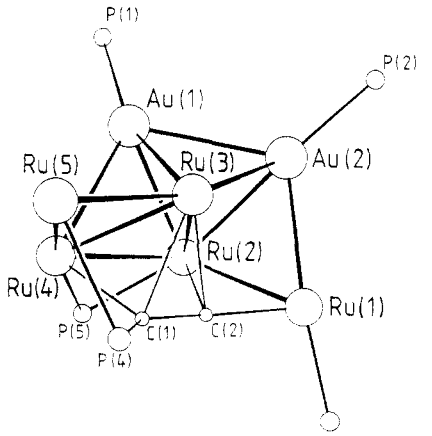
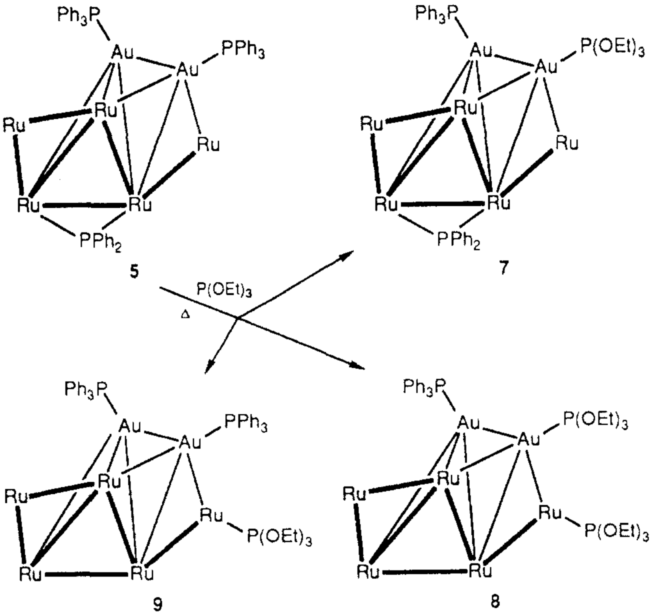


Figure 2. Diagram of the core of **9**.

Scheme II



of the arrangement in the cluster $Ru_5(\mu_4\text{-}C_2Pr^i)\{\mu_4\text{-}NC(O)NCPh_2\}(\mu\text{-}PPh_2)(CO)_{13}$.

Table II. Selected Bond Distances (Å) and Angles (deg) in $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ (9)

Bond Lengths			
Au(1)–Au(2)	3.085 (1)	Ru(2)–Ru(3)	2.965 (2)
Au(1)–Ru(2)	2.792 (2)	Ru(2)–Ru(4)	2.990 (2)
Au(1)–Ru(3)	2.794 (2)	Ru(2)–P(5)	2.296 (4)
Au(1)–Ru(4)	3.020 (1)	Ru(2)–C(2)	2.21 (2)
Au(1)–P(1)	2.321 (5)	Ru(3)–Ru(4)	2.809 (2)
Au(2)–Ru(1)	2.855 (2)	Ru(3)–Ru(5)	2.825 (2)
Au(2)–Ru(2)	2.854 (1)	Ru(3)–C(1)	2.30 (2)
Au(2)–Ru(3)	2.758 (2)	Ru(3)–C(2)	2.29 (2)
Au(2)–P(2)	2.323 (4)	Ru(4)–Ru(5)	2.825 (2)
Ru(1)–Ru(2)	2.751 (2)	Ru(4)–P(5)	2.299 (6)
Ru(1)–Ru(3)	3.238 (3)	Ru(4)–C(1)	2.11 (2)
Ru(1)–P(3)	2.235 (6)	Ru(5)–P(4)	2.360 (6)
Ru(1)–C(2)	1.94 (2)	P(4)–C(1)	1.79 (2)
		C(1)–C(2)	1.39 (3)

Bond Angles			
Au(2)–Au(1)–Ru(2)	57.8 (1)	Au(2)–Ru(3)–Ru(1)	56.2 (1)
Au(2)–Au(1)–Ru(3)	55.7 (1)	Au(2)–Ru(3)–Ru(2)	59.7 (1)
Au(2)–Au(1)–Ru(4)	103.0 (1)	Au(2)–Ru(3)–Ru(4)	118.2 (1)
Ru(2)–Au(1)–Ru(3)	64.1 (1)	Au(2)–Ru(3)–Ru(5)	165.5 (1)
Ru(2)–Au(1)–Ru(4)	61.8 (1)	Au(2)–Ru(3)–C(1)	120.9 (5)
Ru(3)–Au(1)–Ru(4)	57.6 (1)	Au(2)–Ru(3)–C(2)	86.6 (5)
Au(1)–A(2)–Ru(1)	107.3 (1)	Ru(1)–Ru(3)–Ru(2)	52.4 (1)
Au(1)–Au(2)–Ru(2)	55.9 (1)	Ru(1)–Ru(3)–Ru(4)	101.6 (1)
Au(1)–Au(2)–Ru(3)	56.8 (1)	Ru(1)–Ru(3)–Ru(5)	137.7 (1)
Ru(1)–Au(2)–Ru(2)	57.6 (1)	Ru(1)–Ru(3)–C(1)	70.6 (6)
Ru(1)–Au(2)–Ru(3)	70.4 (1)	Ru(1)–Ru(3)–C(2)	36.2 (5)
Ru(2)–Au(2)–Ru(3)	63.8 (1)	Ru(2)–Ru(3)–Ru(4)	62.3 (1)
Au(2)–Ru(1)–Ru(2)	61.2 (1)	Ru(2)–Ru(3)–Ru(5)	122.3 (1)
Au(2)–Ru(1)–Ru(3)	53.4 (1)	Ru(2)–Ru(3)–C(1)	68.6 (5)
Au(2)–Ru(1)–C(2)	90.8 (6)	Ru(2)–Ru(3)–C(2)	47.5 (4)
Ru(2)–Ru(1)–Ru(3)	58.7 (1)	Ru(4)–Ru(3)–Ru(5)	60.2 (1)
Ru(2)–Ru(1)–C(2)	52.7 (5)	Ru(4)–Ru(3)–C(1)	47.5 (5)
Ru(3)–Ru(1)–C(2)	44.1 (6)	Ru(4)–Ru(3)–C(2)	69.0 (5)
P(3)–Ru(1)–C(2)	100.8 (6)	Ru(5)–Ru(3)–C(1)	69.8 (5)
Au(1)–Ru(2)–Au(2)	66.2 (1)	Ru(5)–Ru(3)–C(2)	105.0 (5)
Au(1)–Ru(2)–Ru(1)	119.4 (1)	C(1)–Ru(3)–C(2)	35.3 (7)
Au(1)–Ru(2)–Ru(3)	58.0 (1)	Au(1)–Ru(4)–Ru(2)	55.4 (1)
Au(1)–Ru(2)–Ru(4)	62.9 (1)	Au(1)–Ru(4)–Ru(3)	57.1 (1)
Au(1)–Ru(2)–C(2)	106.1 (6)	Au(1)–Ru(4)–Ru(5)	95.4 (1)
Au(2)–Ru(2)–Ru(1)	61.2 (1)	Au(1)–Ru(4)–P(5)	90.0 (1)
Au(2)–Ru(2)–Ru(3)	56.6 (1)	Au(1)–Ru(4)–C(1)	105.4 (5)
Au(2)–Ru(2)–Ru(4)	109.7 (1)	Ru(2)–Ru(4)–Ru(3)	61.4 (1)
Au(2)–Ru(2)–C(2)	85.8 (4)	Ru(2)–Ru(4)–Ru(5)	121.4 (1)
Ru(1)–Ru(2)–Ru(3)	68.9 (1)	Ru(2)–Ru(4)–C(1)	70.1 (5)
Ru(1)–Ru(2)–Ru(4)	109.6 (1)	Ru(3)–Ru(4)–Ru(5)	60.2 (1)
Ru(1)–Ru(2)–C(2)	44.5 (5)	Ru(3)–Ru(4)–C(1)	53.4 (5)
Ru(3)–Ru(2)–Ru(4)	56.3 (1)	Ru(5)–Ru(4)–C(1)	72.2 (5)
Ru(3)–Ru(2)–C(2)	49.9 (5)	P(5)–Ru(4)–C(1)	89.5 (6)
Ru(4)–Ru(2)–C(2)	66.3 (6)	Ru(3)–Ru(5)–Ru(4)	59.6 (1)
P(5)–Ru(2)–C(2)	88.3 (5)	Ru(3)–C(1)–Ru(4)	79.2 (6)
Au(1)–Ru(3)–Au(2)	67.5 (1)	Ru(3)–C(1)–P(4)	99.2 (8)
Au(1)–Ru(3)–Ru(1)	104.8 (1)	Ru(3)–C(1)–C(2)	71 (1)
Au(1)–Ru(3)–Ru(2)	57.9 (1)	Ru(4)–C(1)–C(2)	111 (1)
Au(1)–Ru(3)–Ru(4)	65.2 (1)	P(4)–C(1)–C(2)	135 (2)
Au(1)–Ru(3)–Ru(5)	100.7 (1)	Ru(1)–C(2)–C(1)	161 (1)
Au(1)–Ru(3)–C(1)	107.5 (5)	Ru(2)–C(2)–Ru(3)	82.6 (7)
Au(1)–Ru(3)–C(2)	103.8 (5)	Ru(2)–C(2)–C(1)	112 (1)
		Ru(3)–C(2)–C(1)	72 (1)

The structure of **9** can also be envisaged as a trigonal bipyramid (formed by Ru(4)/Au(1)Ru(2)Ru(3)/Au(2)), edge-bridged by Ru(1), Ru(5), and P(5). The trigonal-bipyramidal structure formally results from the addition of one gold to a triangular Ru(2)Ru(3)Ru(4) face of **1**, the Au(1)Ru(2)Ru(3) face then being capped by the second gold fragment. This polyhedron has been noted previously[17] in clusters such as $Au_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ and $Au_2Ru_4(\mu\text{-}H)_2(CO)_{12}(PPh_3)_2$. With use of accepted electron-counting rules for clusters containing multigold units, **9** is a 100-electron, 8-SEP cluster.

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[17] Bruce, M. I.; bin Shawkataly, O.; Nicholson, B. K. *J. Organomet. Chem.* **1985**, *286*, 427. Freeman, M. J.; Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 1332.

In **9**, the 11 CO ligands are distributed two to each ruthenium, except for Ru(5), which has three. Semibridging carbonyl interactions are found for C(21) and C(22) on Ru(2), the angles and nonbonded distances for Ru(2)C(21)O(21), Au(1)–C(21) and Ru(2)C(22)O(22), Ru(1)–C(22) being 166 (2)°, 2.64 Å and 168 (2)°, 2.79 Å, respectively. Gold–carbonyl interactions have been noted previously in the complex $[AuOs_{10}C(CO)_{24}(PPh_3)]^-$, where Au–C contacts of 2.661 and 2.668 Å were found.[18] The phosphino–acetylide ligand is bonded in the μ_5-η^2,*P* mode found in **1**. The C(1)–C(2) separation (1.39 (3) Å) is similar to that in **1** (1.383 (6) Å), and the Ru–C separations are all normal, except for R1(1)–C(2), which is rather short at 1.94 (2) Å.

The metal–metal separations are of three types: six Ru–Ru (2.751 (2)–2.990 (2) Å), six Au–Ru (2.758 (2)–3.020 (1) Å), and one Au–Au (3.085 (1) Å). All values fall within the ranges already reported for complexes containing ruthenium–gold cores.[19] The major changes from the structure of **1** are the breaking of Ru(1)–Ru(3) and the elongation of Ru(2)–Ru(3): this was the shortest Ru–Ru bond (2.731 (2) Å) in **1**, whereas in **9** it is the longest (2.990 (2) Å). The difference in length appears to be due to the presence of the $Au_2(PPh_3)_2$ fragment bridging this bond.

The reaction of "$Au_2(PPh_3)_2$" with **1** is somewhat different from that between H_2 and **1** (although the digold fragment can be regarded as the isolobal equivalent of H_2). In the hydrogenation, the complex $Ru_5(\mu_5\text{-}CCHPPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_{13}$ (**2**) was the first product formed. This complex has been shown to possess a μ_5-vinylidene ligand ($CCH(PPh_2)$) and a μ-hydrido ligand that bridges the Ru(4)–Ru(5) edge (in terms of the Au_2Ru_5 structure). We[13] and Mingos[20] have emphasized that the isolobal relationship between $Au(PR_3)$ and H is of limited use in predicting structures when more than one gold atom is present. This is due to the strong propensity of gold to form Au–Au bonds. Examination of the structure of **1** with use of molecular modeling suggests that there is insufficient room to introduce a $Au(PPh_3)$ unit at the β-carbon, because of interactions with the phosphido group.

For compound **10**, where $AuH(PPh_3)$ (the intermediate species between H_2 and $Au_2(PPh_3)_2$) has formally added to **1**, it appears there is a direct parallel with the H_2 reaction since the H atom adds to the β-carbon to generate a vinylidene ligand and it seems probable the $Au(PPh_3)$ fragment bridges the Ru(4)–Ru(5) edge, although crystallographic evidence is not available.

The formal addition of H_2 to **1** has also been demonstrated previously[2] with H^-/H^+. When a solution of **1** is reduced with sodium amalgam and treated with H^+, no evidence for formation of a vinylidene cluster was found. Neither was any reaction found when **1** was treated with $HBF_4{\cdot}Et_2O$. These results confirm that the H^-/H^+ reaction actually proceeds by addition of H^- to the β-carbon of the acetylide, followed by addition of H^+ to the cluster.

The substitution of the phosphite on the wingtip ruthenium atom to convert **2** into **9** follows the pattern observed[15] for the parent cluster **1** and presumably arises from the formal electron deficiency at this ruthenium (17e) and the steric constraints that are present. The other products formed in the substitution, **7** and **8**, demonstrate the lability of the tertiary phosphine ligands on the gold atoms. It seems likely that interphenyl interactions encourage replacement of the bulky phosphine by a phosphite ligand (cone angles 145 and 109°, respectively). Relief of steric interactions is seen in the torsion angle P(1)Au(1)Au(2)P(2), which is 25.18°. Previous work has demonstrated phosphine exchange between the clusters $Au_2Ru_6C(CO)_{16}(PEt_3)_2$ and $Au_2Ru_6C(CO)_{16}(PPh_3)_2$, where equilibrium was attained in 8 h.[21] Another equilibrium situation was found for the complex $Au_2Fe_4(BH)(CO)_{12}(PEt_3)_2$, which underwent phosphine exchange in the presence of [ppn]Cl to form complexes containing $Au_2(PPh_3)_2$ and $Au_2(PEt_3)(PPh_3)$ moieties.[22]

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Registry No. **1**, 97349-41-2; **2**, 99921-24-1; **5**, 129570-19-0; **6**, 129570-20-3; **7**, 129570-21-4; **8**, 129570-22-5; **9**, 129570-23-6; **10**, 129540-73-4; $[ppn][Co(CO)_4]$, 53433-12-8; $[O\{Au(PPh_3)\}_3][BF_4]$, 53317-87-6; $[ppn][Mn(CO)_5]$, 52542-59-3; $Na[Co(CO)_4]$, 14878-28-5; $AuCo(CO)_4(PPh_3)$, 15154-50-4; $AuMn(CO)_5(PPh_3)$, 14692-78-5; $Ag[C_5(CO_2Me)_5](PPh_3)$, 79151-50-1; $P(OEt)_3$, 122-52-1.

Supplementary Material Available: Listings of all bond lengths and angles, thermal parameters for non-hydrogen atoms, and final positional and thermal parameters for hydrogen atoms of **9** (7 pages); a table of observed and calculated structure factors for **9** (37 pages). Ordering information is given on any current masthead page.

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[23] dppa* is used to indicate the presence of the elements of dppa (bis(diphenylphosphino)acetylene) in the cluster when the bonding is uncertain; it does not imply the dppa ligand is intact.

[24] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.