Organometallic Chemistry of Pentaruthenium-Gold Carbonyl Cluster Complexes

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Introduction

Over the years, there has been considerable interest in the synthesis and structures of transition metal carbonyl cluster complexes containing gold [1]. Recent studies of the organometallic chemistry of gold [2 - 3] have revealed a range of new catalytic transformations of organic compounds by gold clusters [4] and nanoparticles [5] and have provided a renewed interest in the organometallic chemistry of metal cluster complexes containing gold. A number of bimetallic catalysts containing gold have been shown to exhibit catalytic activity that is superior to that of pure gold catalysts [6].

In recent studies, it has been shown that alkyl- and arylgold phosphine compounds, such as $(PPh_3)AuR$, $R = Me, Ph, Np, Py$ etc. can be readily, oxidatively added to activated 3rd row polynuclear metal carbonyl cluster complexes to yield bimetallic cluster complexes containing alkyl and aryl ligands with bridging gold phosphine groupings, e.g. Eqs. (1) – (3) [7-9]. In some cases, the aryl ligands have adopted unusual bridging coordination modes that can result in interesting physical and chemical properties, such as hindered rotation about the metal-metal bond [10].

We have also shown that $\text{Ru}_5(\text{C})(\text{CO})_{15}$, **1** reacts with $\text{PhAu}(\text{NHC})$, $\text{NHC} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl-imidazol-2-ylidene})$ to yield the Ru_5AuC complexes: $\text{Ru}_5(\text{C})(\text{CO})_{14}(\text{Ph})[\mu\text{-Au}(\text{NHC})]$, **2** and $\text{Ru}_5(\text{C})(\text{CO})_{13}(\mu\text{-}\eta^2\text{-Ph})[\mu\text{-Au}(\text{NHC})]$, **3** by oxidative-addition of the Au – C phenyl bond at the ruthenium atoms. Compounds **2** and **3** were found to add CO at 1 atm to yield

the CO insertion product $\text{Ru}_5(\text{C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CPh})[\mu\text{-Au(NHC)}]$, **4** that contains a bridging benzoyl ligand in an opened Ru_5 cluster complex, Scheme 1 [11].

Scheme 1

Osmium-gold complexes containing methyl groups were obtained from reactions by using $\text{MeAu(PPh}_3\text{)}$ with osmium carbonyl cluster complexes [12].

We have now investigated the reactions of **1** with $\text{MeAu(PPh}_3\text{)}$. A series of methyl-containing Ru_5AuC complexes: $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CMe})[\mu\text{-Au(PPh}_3\text{)}]$, **5**; $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{13}(\mu\text{-}\eta^2\text{-O=CMe})(\text{Me})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **6**; $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CMe})(\eta^1\text{-O=CMe})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **7**, $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{13}(\text{PPh}_3)(\mu\text{-}\eta^2\text{-O=CMe})[\mu\text{-Au(PPh}_3\text{)}]$, **8**, and nonmethyl complexes $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{11}(\mu\text{-CO})_2[\mu\text{-Au(PPh}_3\text{)}]_2$, **9** [13], and $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{11}(\mu\text{-CO})_2[\mu\text{-Au(PPh}_3\text{)}]_4$, **10** have been obtained. The synthesis, structures and interrelationships of these new complexes are described in this report.

Experimental Section

General Data. All reactions were performed under an atmosphere of nitrogen unless indicated otherwise. Reagent grade solvents were dried by the standard procedures and were freshly distilled just prior to use. Infrared spectra were recorded on a Nicolet IS10 Mid-infrared FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 300

spectrometer operating at 300.1 MHz. Variable temperature ^{31}P NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 400 MHz for compounds **9** and **10**. Mass spectrometric (MS) measurements were performed by a direct-exposure probe by using electron impact ionization (EI) or electrospray ionization (ESI). $\text{Ru}_3(\text{CO})_{12}$ and $\text{MeAu}(\text{PPh}_3)$ were purchased from STREM and were used without further purification. $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$, **1**, was prepared according to a previously reported procedure [14]. Product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F_{254} glass plates. Elemental analyses were performed by Galbraith Labs., Knoxville, TN.

Reaction of $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$, **1 with MeAuPPh_3 .** 39.0 mg (0.042 mmol) of **1** was added to a 50 mL three-neck flask with a solution of 22.7 mg (0.048 mmol) of $\text{MeAu}(\text{PPh}_3)$ in 20 mL of hexane. After heating to reflux for 1 h, the solvent was removed *in vacuo*, and the products were then isolated by using TLC by using a hexane/methylene chloride solvent mixture to yield in order of elution: 17.7 mg of the known compound $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CMe})[\mu\text{-Au}(\text{PPh}_3)]$, **5** (30% yield) [15]; 24.0 mg of $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{13}(\mu\text{-}\eta^2\text{-O=CMe})(\text{Me})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **6** (31% yield); and 1.6 mg of $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CMe})(\eta^1\text{-O=CMe})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **7** (2% yield). Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane): 2095(m), 2057(m), 2050(vs), 2033(m), 2018(w), 2001(m), 1989(m), 1947(w). ^1H NMR (CD_2Cl_2 , in ppm) δ = 7.56-7.45 (m, 15H, $\text{P}(\text{C}_6\text{H}_5)_3$), 2.14 (s, 3H, $\mu\text{-}\eta^2\text{-O=CCH}_3$). ^{31}P NMR (CD_2Cl_2 , in ppm) δ = 68.4 (s, 1P, $\text{P}(\text{C}_6\text{H}_5)_3$). Mass spectrum (EI^+): 1385 ($\text{M}^+ - \text{CO}$). Spectral data for **6**: IR ν_{CO} (cm^{-1} in hexane): 2067(m), 2041(m), 2019(m), 2009(vs), 1991(vw), 1974(w). ^1H NMR (CD_2Cl_2 , in ppm) δ = 7.42-7.20 (m, 15H, $(\text{P}(\text{C}_6\text{H}_5)_3)_2$), 2.39 (s, 3H, $\mu\text{-}\eta^2\text{-O=CCH}_3$), 1.68 (s, 3H, CH_3). ^{31}P NMR (CD_2Cl_2 , in ppm) δ = 62.0 (s, 2P, $\text{P}(\text{C}_6\text{H}_5)_3$). Mass spectrum (ESI^+): 1859 (M^+). Spectral data for **7**: IR ν_{CO} (cm^{-1} in dichloromethane): 2071(s), 2040(vs), 2025(s), 1990(w), 1973(m), 1926(vw). ^1H NMR (CD_2Cl_2 ,

in ppm) δ = 7.42-7.21 (m, 15H, $(P(C_6H_5)_3)_2$), 2.66 (s, 3H, $O=CCH_3$), 2.46 (s, 3H, $\mu-\eta^2-O=CCH_3$). ^{31}P NMR (CD_2Cl_2 , in ppm) δ = 61.9 (s, 2P, $(P(C_6H_5)_3)_2$).

Transformation of 5 to 6. 20.6 mg (0.015 mmol) of **5** was added to a 50 mL three-neck flask containing a solution of 20 mg (0.042 mmol) of $MeAu(PPh_3)$ in 20 mL of hexane. After heating to reflux for 1.5 h, the solvent was removed *in vacuo*, and the products were then isolated by TLC by using a hexane/methylene chloride mixture to yield in order of elution 0.2 mg unreacted **5**, 1.4 mg $Ru_5(\mu_5-C)(CO)_{13}(PPh_3)(\mu-\eta^2-O=CMe)[\mu-Au(PPh_3)]$, **8** (6% yield) and 10.6 mg (39% yield) **6**. Spectral data for **8**: IR ν_{CO} (cm^{-1} in hexane): 2067(m), 2040(vs), 2024(s), 1994(m), 1985(w), 1975(m), 1968(w), 1959(vw), 1939(vw). 1H NMR (CD_2Cl_2 , in ppm) δ = 7.70-7.63 (m, 15H, $Ru-P(C_6H_5)_3$), 7.55-7.42 (m, 15, $Au-(PC_6H_5)_3$), 1.86 (s, 3H, CH_3). ^{31}P NMR (CD_2Cl_2 , in ppm) δ = 67.7 (s, 1P), 31.4 (s, 1P). Elemental Anal. % Calc (% Found): C = 37.94 (38.15) and H = 2.02 (2.14).

Pyrolysis of 6. 29.6 mg (0.016 mmol) of **6** was added to a 50 mL three-neck flask containing a solution benzene. The solution was heated to reflux for 1 h. The solvent was removed *in vacuo*, and the products were then isolated by TLC by using a hexane/methylene chloride mixture to yield in order of elution: 3.7 mg (16% yield) **5**, 10.4 mg of orange $Ru_5(\mu_5-C)(CO)_{11}(\mu-CO)_3[\mu-Au(PPh_3)]_2$, **9** (35% yield) [13] and 2.2 mg of grey-green $Ru_5(\mu_5-C)(CO)_{11}(\mu-CO)_2[\mu-Au(PPh_3)]_4$, **10**, (5% yield). Spectral data for **10**: IR ν_{CO} (cm^{-1} in methylene chloride): 2027(2), 1984(s), 1936(w). ^{31}P NMR (CD_2Cl_2 , -55 °C, in ppm) δ = 62.8 (s, 1P), 60.4 (s, 1P), 57.4 (s, 1P), 34.0 (s, 1P).

Synthesis of 7 by Addition of CO to 6. 13.7 mg (0.0070 mmol) of **2** of **6** was added to an NMR tube as a solution in CD_2Cl_2 solvent. The NMR tube was evacuated and then filled with CO to 1 atm. Solution was then stored under CO for 3 days at room temperature. The solvent

was removed by a steady flow of nitrogen and the products were then isolated by TLC to provide 8.8 mg **7** (63% yield) and 2.1 mg of unreacted **6**.

Formation of Acetone by Addition of CO to 6. 11 mg (0.006 mmol) of **6** was dissolved in C₆D₆ and placed in a NMR tube. The solution was purged with CO and the mixture was placed in an oil bath at 80°C for 23 h. A ¹H NMR spectrum taken at this time confirmed the formation of acetone. After removal of the solvent, the products were isolated by TLC to provide 1.2 mg (14% yield) of **5**, 4.2 mg (43% yield) of **6**, 1.7 mg (16% yield) of the previously reported compound Ru₅(μ₅-C)(CO)₁₁(μ-CO)₂[μ-Au(PPh₃)₂]₂, **9**, [13]. 0.4 mg (4% yield) of **6**, and 0.7 mg (6% yield) of **7**.

Thermal Decarbonylation of 7. 10.4 mg (0.006 mmol) of **7** was dissolved in toluene-d₈ and then placed to a NMR tube. The solution was heated at 60 °C for 23.5 h. The solvent was removed by a steady flow of N₂ and the products were then isolated by TLC to yield in order of elution: 1.0 mg (13% yield) of **5**, 0.3 mg (3% yield) of **8**, 2.8 mg (27% yield) of **6**, 0.1 mg (1% yield) of **9**, 0.4 mg (3% yield) of **7** and 0.6 mg (6% yield) of starting material **7**.

Synthesis of 8 by addition of PPh₃ to 5. 19.4 mg (0.014 mmol) of **5** was added to a 50 mL three-neck flask with a solution of 7.2 mg (0.027 mmol) PPh₃ in 20 mL of hexane. After heating to reflux for 1.5 h, the solvent was removed *in vacuo*, and the products were then isolated by TLC to yield 17.1 mg (76% yield) of **8**.

Synthesis of 10 from 9 and CH₃Au(PPh₃). 10 mg (0.0050 mmol) of **9** was added to a 50 mL three-neck flask in 15 mL of heptane. 13 mg (0.029 mmol) of CH₃Au(PPh₃) was added and the solution was heated at reflux for 3 h. The solvent was then removed *in vacuo* and the products were isolated by TLC to provide 1.3 mg of **10** (9% yield).

Crystallographic Analyses: Red single crystals of **6** suitable for x-ray diffraction analysis were obtained by slow evaporation from a solution in hexane solvent at room temperature. Dark red crystals of **7** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution in a hexane/methylene chloride solvent mixture at room temperature. Orange crystals of **8** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution in hexane solvent at room temperature. Orange crystals of **9** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution in hexane solvent at room temperature. Dark brown crystals of **10** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution in a hexane/methylene chloride solvent mixture at room temperature. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity measurements were made by using a Bruker SMART APEX CCD-based diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm [16]. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied by using the program SADABS [16]. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least squares on F^2 by using the SHELXTL software package [17]. All non-hydrogen atoms were placed in geometrically idealized positions included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Compounds **6**, **7**, and **8** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Compound **9** crystallized with two independent molecules in the asymmetric crystal unit. Compound **10**

crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established by the systematic absences in the data and then confirmed by the successful solution and refinement of the structure. Crystal data, data collection parameters and results for the analyses are listed in Table 1.

Results

The reaction of **1** with $\text{MeAu(PPh}_3\text{)}$ provided two products: $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CMe})[\mu\text{-Au(PPh}_3\text{)}]$, **5** (30% yield) and $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{13}(\mu\text{-}\eta^2\text{-O=CMe})(\text{Me})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **6** (31% yield) in significant amounts, and one minor product $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CMe})(\eta^1\text{-O=CMe})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **7** (2% yield). All three products were characterized by a combination of IR, mass spectrum, ^1H NMR spectroscopy and a single-crystal X-ray diffraction analyses. Compound **6** can be obtained from **5** by reaction with $\text{MeAu(PPh}_3\text{)}$, see below. We have not tried to optimize the yields of **5** and **6** by changing the ratios of the reagents in the initial reaction, although one should certainly be able to increase the yield of **6** at the expense of **5** by increasing the amount of $\text{CH}_3\text{Au(PPh}_3\text{)}$ relative to the amount of **1**.

Compound **5** was obtained previously by Cowie et al. from the reaction of **1** with LiMe , followed by the addition of $[\text{Ph}_3\text{PAu}][\text{Cl}]$ [15]. The metrical parameters for **5** determined in our study are similar to those reported previously [15], see Supplementary Material. Compound **5** consists of an open Ru_5C cluster consisting of a carbide-bridged Ru_4 butterfly cluster with an $\text{Au(PPh}_3\text{)}$ group bridging the hinge metal atoms of the cluster and an acetyl ligand bridging the nonbonded pair of ruthenium atoms.

An ORTEP diagram of the molecular structure of **6** as found in the solid state is shown in Figure 1. Compound **6** also consists of an opened Ru₅ cluster with an acetyl ligand, Me-C(14)-O(14), bridging the nonbonded pair of ruthenium atoms Ru(1) and Ru(4). Atom C(1) is bonded to Ru(1), Ru1-C14 = 2.046(8) Å and the oxygen atom O(1) is bonded to Ru(4), Ru(4)-O(14) = 2.106(6) Å. The C = O bond distance is 1.250(10) Å. Unlike **5**, compound **6** contains a single σ -coordinated methyl group to the bridging ruthenium atom Ru(4), Ru4-C1 = 2.309(15) Å. The resonance of the acetyl methyl group observed at $\delta = 2.39$ in the ¹H NMR spectrum of **6** and the resonance of the σ -coordinated methyl group was found at 1.68 ppm. Most importantly, compound **6** contains two Au(PPh₃) groups which are mutually bonded, Au1-Au2 = 2.8145(4) Å and are bonded to the Ru₄ portion of the cluster. Atom Au(1) is bonded to three Ru atoms, Ru1-Au1 = 2.7954(7) Å, Ru2-Au1 = 2.9153(7) Å, Ru5-Au1 = 3.0948(7) Å but the Ru(5) – Au(1) bond is significantly longer than the other two. Atom Au(2) is bonded to only two Ru atoms, Ru1-Au2 = 2.8349(7) Å, Ru2-Au2 = 2.8761(7) Å. The Ru3-Au2 distance of 3.798(1) Å is too long for a significant direct bonding interaction. The metal atoms of the cluster of **6** contain a total of 76 valence electrons which is consistent with that of an “open” square pyramidal cluster of five metal atoms [18].

Figure 1. An ORTEP diagram of the molecular structure of $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{13}(\mu\text{-}\eta^2\text{-O=CMe})(\text{Me})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **6**, showing 15% thermal ellipsoid probability. The hydrogen atoms on the PPh_3 ligands are omitted for clarity. Selected interatomic bond distances (Å) are as follow: $\text{Ru1-Ru3} = 2.8447(9)$, $\text{Ru1-Ru5} = 2.9089(5)$, $\text{Ru1-Ru2} = 2.9913(9)$, $\text{Ru2-Ru5} = 2.8464(9)$, $\text{Ru2-Ru3} = 2.8651(10)$, $\text{Ru3-Ru4} = 2.9480(10)$, $\text{Ru4-Ru5} = 2.9342(10)$, $\text{Ru1-Au1} = 2.7954(7)$, $\text{Ru2-Au1} = 2.9153(7)$, $\text{Ru5-Au1} = 3.0948(7)$, $\text{Ru1-Au2} = 2.8349(7)$, $\text{Ru2-Au2} = 2.8761(7)$, $\text{Au1-Au2} = 2.8145(4)$, $\text{Ru4-O14} = 2.106(6)$, $\text{Ru4-C1} = 2.309(15)$, $\text{Ru1-C14} = 2.046(8)$, $\text{O14-C14} = 1.250(10)$, $\text{Ru1-C0} = 2.057(8)$, $\text{Ru2-C0} = 2.128(8)$, $\text{Ru3-C0} = 1.976(8)$, $\text{Ru4-C0} = 2.126(8)$, $\text{Ru5-C0} = 1.989(8)$.

When **5** was allowed to react with MeAuPPh_3 in hexane solvent at reflux for 1.5 h, compound **6** was obtained in 39% yield together with a side product $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{13}(\text{PPh}_3)(\mu\text{-}\eta^2\text{-O=CMe})[\mu\text{-Au}(\text{PPh}_3)]$, **8** in 6% yield obtained by substitution of a CO ligand of **5** by PPh_3 . The PPh_3 was evidently derived from the added MeAuPPh_3 . Compound **8** was synthesized independently and was fully characterized, see below.

An ORTEP diagram of the molecular structure of **7** as found in the solid state is shown in Figure 2. Compound **7** is very similar to **6** except that it contains a second acetyl ligand, Me-C(42)-O(42), that is coordinated to Ru(4) in terminal η^1 -coordination site in the location of the σ -methyl group in **6**, Ru4-C42 = 2.029(9) Å, C42-O42 = 1.171(12) Å. Other bond distances and angles are similar to those found in **6**. As expected, the methyl groups of the two acetyl groups in **7** exhibit separate resonances in the ^1H NMR spectrum, δ = 2.66 (s) and 2.46 (s).

Compound **7** was obtained in a low yield (2% yield) because its formation requires an addition of a molecule of CO. As expected, it was found that **7** can be obtained from **6** in a better yield (63%) by reaction of **6** with CO (1 atm) at room temperature, and so we believe it was formed in this way in the original reaction of **1** with MeAu(PPh₃). When heated to 60 °C for 23.5 h in a toluene solution, compound **7** eliminated CO, presumably from the terminally coordinated acetyl group, to regenerate **6** in 27% yield.

Figure 2. An ORTEP diagram of the molecular structure of $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CMe})(\eta^1\text{-O=CMe})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **7**, showing 15% thermal ellipsoid probability. The hydrogen atoms on the PPh_3 ligands are omitted for clarity. Selected interatomic bond distances ($\text{\AA}$) are as follow: $\text{Ru1-Ru3} = 2.8240(8)$, $\text{Ru1-Ru5} = 2.9066(8)$, $\text{Ru1-Ru2} = 2.9891(8)$, $\text{Ru2-Ru5} = 2.8440(8)$, $\text{Ru2-Ru3} = 2.8600(9)$, $\text{Ru3-Ru4} = 2.9781(9)$, $\text{Ru4-Ru5} = 2.9502(9)$, $\text{Ru1-Au1} = 2.8011(7)$, $\text{Ru2-Au1} = 2.9258(6)$, $\text{Ru5-Au1} = 3.1476(6)$, $\text{Ru1-Au2} = 2.8241(6)$, $\text{Ru2-Au2} = 2.8505(6)$, $\text{Au1-Au2} = 2.8029(4)$, $\text{Ru4-O14} = 2.107(5)$, $\text{Ru4-C42} = 2.029(9)$, $\text{Ru1-C14} = 2.033(8)$, $\text{O14-C14} = 1.239(9)$, $\text{C42-C1} = 1.426(18)$, $\text{C42-O42} = 1.171(12)$, $\text{Ru1-C0} = 2.068(7)$, $\text{Ru2-C0} = 2.131(7)$, $\text{Ru3-C0} = 1.971(7)$, $\text{Ru4-C0} = 2.143(7)$, $\text{Ru5-C0} = 1.987(7)$.

When **5** was allowed to react with PPh_3 in a hexane solution at reflux for 1.5 h, compound **8** was obtained in 76% yield. Compound **8** was characterized by a single-crystal X-ray diffraction analysis and an ORTEP diagram of its molecular structure as found in the solid state is shown in Figure 3. The structure of **8** is very similar to that of compound **5** except that it contains a PPh_3 ligand coordinated to the bridging Ru atom Ru(4), $\text{Ru4 - P2} = 2.417(2) \text{ \AA}$ in the place of one of the CO ligands in **5**. The acetyl ligand bridges the atoms Ru(1) and Ru(4) which are not mutually bonded, $\text{Ru1-C14} = 2.020(9) \text{ \AA}$, $\text{Ru4-O14} = 2.124(6) \text{ \AA}$ and $\text{C14-O14} = 1.279(10) \text{ \AA}$. The methyl resonance of the bridging acetyl ligand occurs at $\delta = 1.86$ in the ^1H NMR spectrum and there are two phosphorus resonances, $\delta = 67.7$ (s), 31.4 (s) in the ^{31}P NMR spectrum.

Figure 3. An ORTEP diagram of the molecular structure of **8** showing 15% thermal ellipsoid probability. The hydrogen atoms of the PPh₃ ligands are omitted for clarity. Selected interatomic bond distances (Å) are as follows: Ru1-Ru3 = 2.8248(10), Ru1-Ru5 = 2.8119(11), Ru1-Ru2 = 2.9451(10), Ru2-Ru5 = 2.8668(11) Ru2-Ru3 = 2.8545(10), Ru3-Ru4 = 2.9494(10), Ru4-Ru5 = 2.8901(10), Ru1-Au1 = 2.7686(8), Ru2-Au1 = 2.7636(8), Ru4-P2 = 2.417(2), Ru1-C14 = 2.020(9), Ru4-O14 = 2.124(6), O14-C14 = 1.279(10), Ru1-C1 = 2.061(8), Ru2-C1 = 2.086(8), Ru3-C1 = 1.976(8), Ru4-C1 = 2.092(8), Ru5-C1 = 2.001(8).

When a solution of **6** in benzene solvent was heated to reflux for 1 h, two products that do not contain methyl groups $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{11}(\mu\text{-CO})_3[\mu\text{-Au}(\text{PPh}_3)]_2$, **9** and $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{11}(\mu\text{-CO})_2[\mu\text{-Au}(\text{PPh}_3)]_4$, **10** were obtained in 35% and 5% yields, respectively, were obtained. Compound **9** was reported a number of years ago as a product of the reaction of the anion $[\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}]^{2-}$ with $[\text{AuPPh}_3][\text{ClO}_4]$ [13]. Compound **9** has not yet been structurally characterized crystallographically, so we have done that together with an X-ray diffraction structural analysis of compound **10** and both of these analyses are reported here.

An ORTEP diagram of the molecular structure of **9** as found in the solid state is shown in Figure 4. Compound **9** contains a square pyramidal Ru₅ cluster with two mutually bonded Au(PPh₃) groups bridging one triangular Ru₃ face Ru1-Ru2-Ru3 and an edge Ru2-Ru3 of the square pyramid, Au1-Au2 = 2.8817(5) Å. The compound contains fourteen carbonyl ligands; three of them are bridging ligands about the base of the Ru₅ square pyramid. The five ruthenium atoms in **9** contain a total of 74 valence electrons which is consistent with a square-pyramidal cluster, as observed [17]. The structure of **9** is very similar to that of the compound Ru₅(μ₅-C)(CO)₁₄[μ-Au₂(Ph₂PCH₂CH₂PPh₂)] which contains a bridging Ph₂PCH₂CH₂PPh₂ ligand across the two gold atoms [19].

Figure 4. An ORTEP diagram of the molecular structure of **9** showing 15% thermal ellipsoid probability. The hydrogen atoms on the PPh₃ ligands are omitted for clarity. Selected interatomic bond distances (Å) are as follow: Ru1-Ru3 = 2.8892(9), Ru1-Ru5 = 2.8335(10), Ru1-Ru2 = 2.8632(10), Ru1-Ru4 = 2.8103(10), Ru2-Ru5 = 2.7361(10) Ru2-Ru3 = 3.0919(9), Ru3-Ru4 = 2.7819(9), Ru4-Ru5 = 2.7781(11), Ru1-Au1 = 2.7994(7), Ru2-Au1 = 2.9697(8), Ru3-Au1 = 2.8934(8), Ru2-Au2 = 2.7989(7), Ru3-Au2 = 2.7855(7), Au1-Au2 = 2.8817(5),

Ru1-C0 = 2.179(8), Ru2-C0 = 1.996(8), Ru3-C0 = 2.007(8), Ru4-C0 = 2.055(8), Ru5-C0 = 2.036(8).

An ORTEP diagram of the molecular structure of **10** is shown in Figure 5. Compound **10** contains a square pyramidal cluster of five ruthenium atom with four Au(PPh₃) groups. Two of the Au(PPh₃) groups form a mutually bonded pair on the Ru1-Ru2-Ru3 face and Ru2-Ru3 edge of the square pyramid, Au1-Au2 = 2.8277(6) Å, similar to that found in **9**. An additional Au(PPh₃) group, Au4, is found along the Ru4 – Ru5 edge of the Ru₅ square base and for the fourth Au(PPh₃) group, atom Au3, is asymmetrically bonded across the square base and includes bonding to the interstitial carbido ligand C0, Ru2-Au3 = 3.1831(9) Å, Ru4-Au3 = 2.8963(8) Å, Ru5-Au3 = 2.8532(9) Å, Au3-C0 = 2.126(8) Å. The Ru3-Au3 distance, 3.387(8) Å, seems to be too long for a significant bonding interaction. The ³¹P NMR spectrum of **10** exhibits four resonances, δ = 62.8 (s), 60.4 (s), 57.4 (s), and 34.0 (s) which is consistent with the structure found in the solid state. The five ruthenium atoms in **10** contain a total of 74 valence electrons which is consistent with the observed square-pyramidal cluster [17]. Compound **10** was also obtained directly from compound **9** in a low yield (9%) by reaction with MeAu(PPh₃) in a heptane solution at reflux for 3 h.

Figure 5. An ORTEP diagram of the molecular structure of **10** showing 15% thermal ellipsoid probability. For clarity only *ipso*-carbon atoms of the PPh₃ phenyl rings are shown. Selected interatomic bond distances (Å) are as follow: Ru1-Ru3 = 2.8495(10), Ru1-Ru5 = 2.8306(10), Ru1-Ru2 = 2.9243(11), Ru1-Ru4 = 2.8498(10), Ru2-Ru5 = 2.8148(11) Ru2-Ru3 = 3.0316(10), Ru3-Ru4 = 2.7968(10), Ru4-Ru5 = 3.0933(10), Ru1-Au1 = 2.8728(9), Ru2-Au1 = 2.8609(9), Ru3-Au1 = 2.9559(8), Ru2-Au2 = 2.7868(9), Ru3-Au2 = 2.8185(8), Ru2-Au3 = 3.1831(9), Ru4-Au3 = 2.8963(8), Ru5-Au3 = 2.8532(9), Ru4-Au4 = 2.7589(8), Ru5-Au4 = 2.7603(9), Au1-Au2 = 2.8277(6), Ru1-C0 = 2.136(8), Ru2-C0 = 2.047(8), Ru3-C0 = 2.097(8), Ru4-C0 = 2.081(8), Ru5-C0 = 2.104(8), Au3-C0 = 2.126(8).

Discussion

A summary of the reactions described in this report is given in Scheme 2.

Scheme 2. A schematic for the reactions of **1** with MeAu(PPh₃) reported in this study.

In this work we have shown that the reaction of **1** with MeAu(PPh₃) yields two products, **5** and **6**, by the loss of CO from **1** and the oxidative addition of one and two equivalents MeAu(PPh₃), respectively, to **1** in a cluster opening process. Both products contain a bridging acetyl ligand formed presumably by a CO insertion process involving in an unobserved precursor complex containing a σ -methyl ligand. A similar transformation was observed in the addition of CO to compound **2** to form **4**, the Ph homolog of **5** [11]. Compound **5** reacts with MeAu(PPh₃) to form **6** which contains σ -methyl ligand and **6** adds CO accompanied by an insertion reaction to yield **7** which contains a terminally coordinated acetyl ligand. The formation of **7** is reversible and heating **7** leads to regeneration of **6** by CO elimination. Most interestingly, compound **6** also

eliminates the acetyl ligand and the σ -methyl ligand in the form of acetone with addition of CO to yield the digold compound **9**. Compound **9** can add two more Au(PPh₃) groups and eliminate CO to yield the interesting tetragold complex **10**.

Conclusions

Methyl groups can be added to compound **1** by cluster opening reactions that oxidatively add the Au-C bond of the MeAu(PPh₃) to the ruthenium atoms under mild conditions. The Au(PPh₃) group(s) are added as bridges across the ruthenium atoms. The methyl groups engage in facile CO insertion reactions leading to stable complexes containing bridging acetyl ligands and in one case, compound **6**, the acetyl ligand was combined with a methyl ligand to form acetone by reductive elimination.

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Supplementary Material. Crystallographic data (cif files) for all of the structural analyses have been uploaded with this report and have also been deposited with the Cambridge Crystallographic Data Centre, CCDC 1497552-1497557 for compounds **5** - **10**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [Fax. (int code) +44(1223)336-033, or Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

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Table 1. Crystallographic Data for Compounds 6 - 10.

Compound	6	7	8	σ^a R1 = $\frac{\sum_{hkl} (F_{obs} - F_{calc})}{\sum_{hkl} F_{obs}}$
Empirical formula	Ru ₅ Au ₂ P ₂ O ₁₄ C ₅₃ H ₃₆	Ru ₅ Au ₂ P ₂ O ₁₅ C ₅₄ H ₃₆	Ru ₅ AuP ₂ O ₁₄ C ₅₂ H ₃₃	
Formula weight	1858.04	1886.05	1646.04	
Crystal system	Triclinic	Triclinic	Triclinic	
Lattice parameters				
<i>a</i> (Å)	10.0683(3)	10.0366(7)	10.5517(9)	
<i>b</i> (Å)	14.5070(4)	14.8042(10)	15.1516(12)	
<i>c</i> (Å)	21.3998(6)	21.6258(14)	17.1661(14)	
α (deg)	108.3630(10)	71.2160(10)	92.095(2)	
β (deg)	91.2510(10)	79.5360(10)	93.142(2)	
γ (deg)	107.4400(10)	71.7660(10)	97.190(2)	
<i>V</i> (Å ³)	2806.72(14)	2877.6(3)	2716.1(4)	
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	
Z value	2	2	2	
ρ_{calc} (g / cm ³)	2.199	2.177	2.013	
μ (Mo K α) (mm ⁻¹)	6.635	6.474	4.167	
Temperature (K)	294(2)	294(2)	294(2)	
2 Θ_{max} (°)	50.06	50.06	50.06	
No. Obs. (<i>I</i> > 2 σ (<i>I</i>))	9890	10150	9592	
No. Parameters	687	705	668	
Goodness of fit (GOF)	1.033	1.014	1.029	
Max. shift in cycle	0.000	0.002	0.098	
Residuals*: R1; wR2	0.0375; 0.0837	0.0360; 0.0903	0.0494; 0.1149	
Absorption Correction, Max/min	Multi-scan 1.000 / 0.626	Multi-scan 1.000/0.693	Multi-scan 1.000 / 0.678	
Largest peak in Final Diff. Map (e ⁻ / Å ³)	1.049	1.251	1.901	

Table 1. (continued)

Compound	9	10
Empirical formula	$\text{Ru}_5\text{Au}_2\text{P}_2\text{O}_{14}\text{C}_{51}\text{H}_{30}$	$\text{Ru}_5\text{Au}_4\text{P}_4\text{O}_{13}\text{C}_{86}\text{H}_{60}$
Formula weight	1847.50	2718.44
Crystal system	Monoclinic	Monoclinic
Lattice parameters		
a (Å)	51.2765(13)	24.2834(9)
b (Å)	14.5935(4)	12.9674(5)
c (Å)	35.3322(9)	27.0725(6)
α (deg)	90.00	90.00
β (deg)	122.533(10)	91.631(1)
γ (deg)	90.00	90.00
V (Å ³)	22290.4(10)	8521.5(6)
Space group	$C2/c$	$P2_1/c$
Z value	16	4
ρ_{calc} (g / cm ³)	2.202	2.199
μ (Mo K α) (mm ⁻¹)	6.683	7.853
Temperature (K)	294(2)	294(2)
$2\Theta_{\text{max}}$ (°)	50.06	50.06
No. Obs. ($I > 2\sigma(I)$)	19677	15072
No. Parameters	1345	979
Goodness of fit (GOF)	1.134	1.021
Max. shift in cycle	0.002	0.000
Residuals*: R1; wR2	0.0445; 0.0674	0.0430; 0.1039
Absorption Correction, Max/min	Multi-scan 0.4908 / 0.3488	Multi-scan 1.000 / 0.653
Largest peak in Final Diff. Map (e ⁻ / Å ³)	1.084	1.429

^a $R = \sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|$; $R_w = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$;
 $\text{GOF} = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$.

Graphic for Table of Contents

Description for Graphic for TOC

$\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$ adds two equivalents of MeAuPPh_3 to yield the complex $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{13}(\mu\text{-}\eta^2\text{-O=CMe})(\text{Me})[\mu\text{-Au}_2(\text{PPh}_3)_2]$, **6** which contains a bridging acetyl ligand and a σ -methyl ligand. When heated, **6** eliminates acetone to yield the digold complex $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{11}(\mu\text{-CO})_3[\mu\text{-Au}(\text{PPh}_3)]_2$, **9**.