Multicenter Transformations of the Methyl Ligand in $\text{CH}_3\text{Os}_3\text{Au}$ Carbonyl Cluster Complexes: Synthesis, Characterization and DFT Analyses[†]

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[†]Dedicated to the memory of Professor Jack Lewis, the Lord Lewis of Newnham, a pioneer in the chemistry of polynuclear metal carbonyl cluster complexes.

Introduction

With the boom of shale oil and gas in U. S. [1], there is a renewed interest in finding direct routes for the transformation of methane and other low boiling hydrocarbons into higher value chemicals and fuels.² Today, the industrial conversion of methane is performed in two steps: 1) steam reforming of methane to produce syngas (CO and H_2); and 2) catalytic hydrogenation of the CO (e.g. Fischer-Tropsch Synthesis, FTS) to make higher boiling hydrocarbons for fuels or for the synthesis of methanol and other commodities [2,3]. Because of

the high capital cost and energy inefficiencies in the FTS, there is considerable interest in developing new routes for the utilization of methane [2,4,5]. The greatest challenge to the chemistry of methane is the activation of the C-H bonds. The C-H bond strength in methane is the highest of the saturated hydrocarbons, 434 kJ/mol [6]. Understanding C-H bond activation and the transformations of the CH₃, CH₂ and CH fragments on metal surfaces is essential for optimizing methane utilization by heterogeneous catalysts. The relative stability and reactivity of CH₃, CH₂, CH and C ligands on a particular transition metal surface is important to subsequent chain growth, propagation and termination steps during FTS [7]. The activation and transformation of methane on metal surfaces has been investigated by a variety of computational methods [2e,2f,2h,8]. In a recent study, Campen, et al. reported that absorbed hydrogen atoms on Ru(0001) inhibit the CH₂ → CH + H transformation at an activation barrier of 65 kJ/mol [8b].

Organometallic clusters having the empirical formula M₃(CO)₉{CH₄} are of great interest because of their potential to be obtained from M₃(CO)₁₂ compounds via activation of a C-H bond in methane. A number of years ago, Shapley studied the transformations of CH₃, CH₂ and CH ligands in Os₃(CO)₉{CH₄} complexes that he obtained from the reaction of Os₃(CO)₁₀(μ-H)₂ with CH₂N₂ [9]. He showed that the methyl complex Os₃(CO)₁₀(μ-CH₃)(μ-H) was readily isomerized to the methylene complex, Os₃(CO)₁₀(μ-CH₂)(μ-H)₂, by a CH bond cleavage and was in turn transformed to the methylidyne complex, Os₃(CO)₉(μ₃-CH)(μ-H)₃, by elimination of a CO ligand. The interconversions of the “Os₃(CO)₁₀{CH₄}” tautomers was studied by ¹H NMR spectroscopy. Fehlner and coworkers studied the chemistry of the hydrocarbyl ligands in solution for a series of iron complexes having the empirical formula “Fe₃(CO)₉{CH₄}” [10]. Norton and coworkers studied the chemistry of Os(CO)₄(CH₃)₂ obtained by reaction of Na₂Os(CO)₄ with excess methyl tosylate [11]. Thermolysis of HOs(CO)₄(CH₃) yielded HOs₂(CO)₈(CH₃) and

methane [12]. Treatment of $\text{HOs}_2(\text{CO})_8(\text{CH}_3)$ with $\text{HOs}(\text{CO})_4(\text{CH}_3)$ yielded the triosmium complex $\text{Os}_3(\text{CO})_{12}(\text{CH}_3)_2$ and molecular hydrogen [13]. The formation of the dinuclear and polynuclear complexes was proposed to occur by homolysis of metal-carbon bonds and formation of metal-metal bonds.

In our recent studies, it has been shown that aryl-Au(PPh_3) compounds can be readily added to reactive polynuclear metal carbonyl complexes by cleavage of the Au – C bond to yield complexes containing coordinated aryl ligands that can undergo subsequent transformations at multi metal centers, e.g. eq. (1) [14-16].

In this work, we have investigated the reactions of $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ with the triosmium carbonyl complexes $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ and $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$. Because of the strong isolobal similarities between $\cdot\text{H}$ and $\cdot\text{Au}(\text{PPh}_3)$ [17], we believe that $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ will serve as a viable mimic for CH_4 for studies of its activation and transformations. The new complexes $\text{Os}_3(\text{CO})_{10}(\mu\text{-O=CCH}_3)(\mu\text{-AuPPh}_3)$, **1**, $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_2(\mu\text{-AuPPh}_3)$, **2** and $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})(\mu\text{-AuPPh}_3)_2$, **3** have been obtained. Interestingly, it was found that the hydrido ligands in **2** can be shifted back to methyldiyne ligand by reaction with CO to yield two new complexes: $(\text{CH}_3)\text{Os}_3(\text{CO})_{12}\text{AuPPh}_3$, **4** and $(\text{CH}_3)\text{Os}_2(\text{CO})_8\text{AuPPh}_3$, **5** containing terminally coordinated methyl groups. Complex **4** loses CO spontaneously and goes back to **1** and **2** when

heated or irradiated with visible light. The nature of CO dissociation and the transformations of the hydrocarbyl ligands in these triosmium complexes was studied by single-crystal X-ray diffraction analysis, mass-spec and ^1H NMR analyses and by density functional theory (DFT) molecular orbital calculations. These results are reported herein.

Experimental Section

General Data. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. All reactions were performed under a nitrogen atmosphere. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ^1H NMR and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe using electron impact ionization (EI) were made on a VG 70S instrument, Positive/negative ion mass spectra were recorded on a Micromass Q-TOF instrument by using electrospray (ES) ionization. $(\text{CH}_3)\text{AuPPh}_3$ and $\text{Os}_3(\text{CO})_{12}$ were obtained from STREM and were used without further purification. $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ and $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ were prepared according to the previously reported procedures [18, 19]. Product isolations were performed by TLC in air on Analtech 0.50mm silica gel 60 Å F254 glass plates and Analtech 0.25 mm aluminum oxide UV_{254} glass plates.

Synthesis of $\text{Os}_3(\text{CO})_{10}(\mu\text{-O}=\text{CCH}_3)(\text{AuPPh}_3)$, **1** and $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\text{H})_2(\text{AuPPh}_3)$, **2**.

(a) *Reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$:* $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ (19 mg, 0.021 mmol) were added to a 50 mL three neck flask containing a solution of $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ (9.7 mg, 0.021 mmol) in 30 mL methylene chloride. The reaction mixture was allowed to stir for 5 h with intermittent monitoring by IR spectroscopy. The solvent was then removed *in vacuo*, and the

product was isolated by TLC by using pure hexane solvent to yield three bands. In order of elution they gave 7.0 mg of yellow $\text{Os}_3(\text{CO})_{10}(\mu\text{-O=CCH}_3)(\mu\text{-AuPPh}_3)$, **1** (37 % yield), 1.9 mg of the known reddish compound $\text{Os}_3(\text{CO})_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)$ [20], (10% yield) and 6.2 mg of colorless $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_2(\mu\text{-AuPPh}_3)$, **2** (33% yield). Spectral data for **1**: IR ν_{CO} (cm^{-1} in hexane): 2091(m), 2039(s), 2032(m), 2013(m), 2005(s), 1989(w), 1972(w), 1959(m). ^1H NMR (CD_2Cl_2 , 25°C , TMS, in ppm) δ = 2.19 (s, 3H, OCCH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C , 85% ortho- H_3PO_4) δ = 85.71 (s, 1P, P-Au). Mass Spec. Pos. Ion ES/MS m/z 1354. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2093 (m), 2063(s), 2048(s), 2007(s), 1996(m), 1972(m), 1964(sh). ^1H NMR (CD_2Cl_2 , 25°C , TMS, in ppm) δ = 10.59 (dd, 1H, CH, $^3J_{\text{H-H}} = 1.1$ Hz, $^4J_{\text{P-H}} = 1.1$ Hz), -21.12 (dd, 2H, Hydride, $^3J_{\text{P-H}} = 1.1$ Hz, $^3J_{\text{H-H}} = 1.1$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C , ref. 85% ortho- H_3PO_4) δ = 80.57 (s, 1P, P-Au). Mass Spec. EI+/MS m/z = 1298 (M^+).

NMR Analysis of the Reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$: 5.0 mg (0.005 mmol) of $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ were dissolved in an NMR tube in CD_2Cl_2 . 4.0 mg (0.007 mmol) of $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ were added. The spectra were recorded as a function of time and are shown in a series of overlays in Figure 1. In the first spectrum (5 min), two resonances had appeared at 0.86 and 0.95 ppm. This is attributed to an intermediate formulated as $\text{Os}_3(\text{CO})_{11}(\text{CH}_3)(\mu\text{-AuPPh}_3)$, **I1** which was formed by the elimination the NCCH_3 ligand of the $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ and the addition of one equivalent of $(\text{CH}_3)\text{Au}(\text{PPh}_3)$. The presence of two resonances indicates that **I1** exists as a mixture of two isomers **I1-a** and **I1-b**, see below. There was also a minor, but important, resonance at -3.62 ppm. This is attributed to an intermediate formulated as $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_3)(\mu\text{-AuPPh}_3)$, **I2** having an agostically coordinated methyl group that was formed by the loss of one CO ligand from **I1** [9,21]. Finally, **I2** converts to compound **2** via

decarbonylation and subsequent C-H bond cleavage at the methyl group while **11** transforms to compound **1** through methyl migration/CO insertion steps.

Figure 1. ^1H NMR spectra of the reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ at room temperature in CD_2Cl_2 solvent as a function of time.

b) Reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$: 77.0 mg (0.0825 mmol) of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ were added to a 50 mL three neck flask containing a solution of $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ 44.3 mg (0.093 mmol) in 30 mL methylene chloride. The reaction mixture was stirred for 6 h at 25 °C. The solvent was then removed *in vacuo*, and the product was isolated by TLC by using pure hexane solvent to yield in order of elution: 49 mg of **2** (64% yield), 5.0 mg of $\text{Os}_3(\text{CO})_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)$, (6.5% yield) and 3.8 mg of **1** (5% yield).

NMR Analysis of the Reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$: 5.0 mg (0.005 mmol) of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ were dissolved in an NMR tube in CD_2Cl_2 . $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ of 4.0 mg (0.007 mmol) were added. The spectra were recorded as a function of time and are shown in a series of overlays in Figure 2.

Figure 2. ^1H NMR spectra of the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ at room temperature as a function of time.

In the first spectrum (6 min) a major resonance had appeared at -3.62 ppm. This is attributed to an intermediate formulated as $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_3)(\mu\text{-AuPPh}_3)$, **I2** having an agostic coordinated methyl group that was formed by the elimination the two NCCH_3 ligands of the $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ and the addition of one equivalent of $(\text{CH}_3)\text{Au}(\text{PPh}_3)$, see also Figure 1. This resonance decreases in intensity with time. Two small resonances at 4.55 ppm (dt, $^2J_{\text{H-H}} =$

12 Hz, $^3J_{\text{H-H}} = 2$ Hz, $^4J_{\text{P-H}} = 2$ Hz) and 5.62 ppm (dd, $^2J_{\text{H-H}} = 12$ Hz, $^3J_{\text{H-H}} = 3$ Hz) and a hydride resonance at -21.19 ppm (t, $^2J_{\text{H-H}} = 3$ Hz, $^3J_{\text{P-H}} = 3$ Hz) had also appeared at 6 min and grow with time. These are attributed to a second intermediate formulated as $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-H})(\mu\text{-AuPPh}_3)$, **I3**. Additional resonances appear at 20 min at 4.61 ppm ($^2J_{\text{H-H}} = 8$ Hz) and 6.32 ($^2J_{\text{H-H}} = 8$ Hz) and grow with time. This compound is formulated as $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-AuPPh}_3)_2$, **I4** and it can be isolated by TLC in a low yield. Additional spectra for **I4**: IR ν_{CO} (cm⁻¹ in hexane): 2077(w), 2032(m), 2016(s), 2004(s), 1996(sh), 1961(m), 1937(w). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C, 85% ortho- H_3PO_4) $\delta = 82.94$ (s, 2P, P-Au); Mass Spec. Pos. Ion ES/MS m/z . 1785(M^+). **I4** is believed to be formed by a reaction of **I3** with an additional quantity of $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ that also results in the formation of CH_4 which is also observed in the spectrum at 0.21 ppm at this time. Finally, small resonances are observed to form at $\delta = 11.94$ (s, 1H, CH) and -22.50 (s, hydride) (not shown in Figure 2) which are attributed to a final product formulated as $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})(\text{AuPPh}_3)_2$, **3**. Compound **3** can also be obtained from the thermal transformation of **2** and was fully characterized including a single-crystal X-ray diffraction analysis, see below. During the entire reaction period, the resonances of compound **2**, 10.59 ppm and -21.12 ppm, (the major product, see above) are forming and growing in intensity.

Synthesis of $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})(\mu\text{-AuPPh}_3)_2$, **3** from **2**.

A solution of **2** was heated to reflux in octane solvent. 22.9 mg of **2** is dissolved in 30 mL hot octane at a 50 mL three neck flask. The solution was heated to reflux for 4 h (125 °C). The solvent was removed in *vacuo*, and the product was then isolated by TLC using a 5:1 hexane/methylene chloride solvent mixture. 9.0 mg of **2** is recovered after the reaction, while 7.6 mg (55% yield) of $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})(\text{AuPPh}_3)_2$, **3** and 2.4 mg (17% yield) of $\text{Os}_3(\text{CO})_9(\mu_3\text{-$

CH)(μ -H)₃ were isolated. Spectral data for **3**: IR ν_{CO} (cm⁻¹ in hexane): 2070(s), 2045(s), 2031(s), 1987(m), 1965(m), 1922(w). ¹H NMR (CD₂Cl₂, 25°C, TMS, in ppm) δ = -22.50 (s, 1H, hydride), δ = 11.94 (s, 1H, CH); ³¹P{¹H} NMR (CD₂Cl₂, 25 °C, 85% ortho-H₃PO₄) δ = 82.93 (s, 2P, P-Au); Mass Spec. EI+/MS *m/z*. 1756.

Synthesis of (CH₃)Os₃(CO)₁₂(AuPPh₃) **4**, (CH₃)Os₂(CO)₈(AuPPh₃) **5** and Os(CO)₄PPh₃ **6**.

35 mg (0.027mmol) of **2** was dissolved in warm octane, transferred to a Parr high pressure reactor and then filled with CO to 600 psi. The reactor was heated in an oil bath to 100 °C for 4 h and then allowed to cool to room temperature. The solvent was removed in vacuo, and the product was isolated by TLC by using a hexane/methylene chloride solvent mixture (6/1, v/v) to yield in order of elution: 0.7 mg, of Os(CO)₄(PPh₃) **6**, (2% yield); 2.5 mg (CH₃)Os₂(CO)₈(AuPPh₃) **5**, (7% yield); 18.4 mg (CH₃)Os₃(CO)₁₂(AuPPh₃) **4** (53% yield); and 1.6 mg compound **1** (5% yield) and Os₃(CO)₁₂ (2.5% yield). Spectral data for **4**: IR ν_{CO} (cm⁻¹ in hexane): 2115(w), 2071(m), 2045(w), 2023(s), 2004(s), 1990(m), 1983(w), 1973(w), 1963(w). ¹H NMR (CD₂Cl₂, 25°C, TMS, in ppm) δ = 0.23 (s, 3H, CH₃), ³¹P{¹H} NMR (CD₂Cl₂, 25 °C, 85% ortho-H₃PO₄) δ = 55.31 (s, 1P, P-Au); Mass Spec. EI+/MS *m/z*. 1382(M⁺), 1354 (M⁺-CO), 1326 (M⁺-2CO), 1298 (M⁺-3 CO). Spectral data for **5**: IR ν_{CO} (cm⁻¹ in hexane): 2103(w), 2050(s), 2019(s), 2007(w), 2000(m), 1992(w), 1988(w), 1977(m), 1972(sh). ¹H NMR (CD₂Cl₂, 25°C, TMS, in ppm) δ = 0.26 (s, 3H, CH₃), ³¹P{¹H} NMR (CD₂Cl₂, 25 °C, 85% ortho-H₃PO₄) δ = 55.04 (s, 1P, P-Au); Mass Spec. EI+/MS *m/z*. 1080 (M⁺). Spectral data for **6**: IR ν_{CO} (cm⁻¹ in hexane): 2062(s), 1983(m), 1945(s), ³¹P{¹H} NMR (CD₂Cl₂, 25 °C, 85% ortho-H₃PO₄) δ = 7.88 (s, 1P, PPh₃).

Conversions of compound **4** to **1** and **2**.

- a) **Thermal Treatment:** 16.3 mg (0.012mmol) of $(\text{CH}_3\text{Os}_3(\text{CO})_{12}\text{AuPPh}_3)$, **4** was dissolved in 30 mL heptane solvent in a 50 mL three neck flask. The solution was then heated to reflux (97 °C) for 2.5 h. The solvent was then removed in *vacuo* and the products were then isolated by TLC by using a pure hexane solvent to yield: 8.2 mg of yellow $\text{Os}_3(\text{CO})_{10}(\mu\text{-O}=\text{CCH}_3)(\text{AuPPh}_3)$, **1**, (50% yield), 1.6 mg of colorless **2**, (10% yield), and 0.34 mg of light yellow $\text{Os}_3(\text{CO})_{12}$, (2% yield).
- b) **Irradiation with Room Light:** 5.0 mg of **4** was dissolved in an NMR tube in CD_2Cl_2 . The sample was exposed to room light for 9 days at room temperature. A control experiment was performed by dissolving same amount of **4** in an NMR tube in CD_2Cl_2 , but the tube was fully covered by aluminum foil to prevent exposure room light. Based on the ^1H NMR analyses, the sample exposed to room light showed over 90% conversion of **4** to compounds **1** and **2** in a 10/1 ratio, respectively, after 9 days. The sample maintained in the dark showed less than 2% loss of **4** and only traces of compound **1** were detected after the 9 day period.

Crystallographic Analyses: X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer by using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm [22]. Corrections for Lorentz and polarization effects were also applied by using SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS. 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 [23]. Crystallographic data for compounds **1** – **6** are listed in Table 1.

Computational Analyses:

All calculations were performed with ADF2014 program by using the PBEsol functional with

scalar relativistic correction and valence triple- ζ +polarization, relativistically optimized TZP basis sets, with small frozen cores. All computations were done in gas phase and the triphenylphosphine ligand geometry was constrained throughout the calculations. This choice of computational model was based on prior testing of various functionals and basis sets [16]. The PBEsol functional, which was originally developed primarily for solids, was shown to be superior to other functionals in the PBE family in the structural parameters of large organic systems [24] and for metal clusters [25]. For the molecular orbitals and energy calculations of intermediates **I1**, **I2**, **I3** and **I5**, geometry optimizations (GO) were performed with ADF2014 program [26] by using the PBEsol functional with scalar relativistic correction and valence triple- ζ +polarization, relativistically optimized TZP basis sets, with small frozen cores. The molecular orbitals for compounds **2** and **4** and their energies were determined by a geometry optimized calculations that were initiated by using the structures as determined from the crystal structure analyses. The energy profile was computed by scanning the defined reaction coordinate with full geometry optimization of the other degrees of freedom. The transition states are defined as energy maxima along the reaction coordinate scan. The determination of the energy for the transition states is somewhat imprecise because analytic Hessians used to search for transition states in the ADF library failed to calculate the exact transition states. In the transition state search calculation, the transition state geometry reverts back to its intermediate by energy minimization. Our approximate transition state energies, see below, can be safely regarded as upper limits for the true ones. For the first transition state (TS1) scan which lies between intermediate **I2** and intermediate **I3**, it was performed by using the H(1) - Os(3) distance as reaction coordinate. The H(1) is from one of methyl C-H groups that is agostically coordinated to Os(1). For the second transition state (TS2) step, **I3** to **I5**, the reaction coordinate was developed

by progressive removal of the axial CO ligand from the third osmium atom Os(3). For the third transition state (TS3) step, **15** to **2**, it was performed by using the H(2) - Os(2) distance in **15** as reaction coordinate, the H(2) is from one of the methylene C-H groups that is agostically coordinated to Os(3). The intermediates are defined as energy minima along the scan coordinate and are exact within the GO computational model. Electron densities at the bond critical points were calculated by using the Bader Quantum Theory of Atoms in Molecules (QTAIM) model [27].

Results and Discussion

The reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ in CH_2Cl_2 yielded two new complexes: $\text{Os}_3(\text{CO})_{10}(\mu\text{-O}=\text{CCH}_3)(\mu\text{-AuPPh}_3)$, **1** in 37% yield and $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_2(\mu\text{-AuPPh}_3)$, **2** 33% yield. In the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ at room temperature for 4h, the yield of compound **2** was increased to 64% at the expense of **1** (5%) because $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ contains two labile NCCH_3 ligands and fewer CO ligands. Compounds **1** and **2** were both characterized crystallographically, and ORTEP diagrams of their molecular structures are shown in Figures 3 and 4, respectively. Complex **1** contains a triangular cluster of three osmium atoms with a bridging acetyl ligand and a bridging $\text{Au}(\text{PPh}_3)$ group across the Os(1)–Os(2) bond. The non-bridged osmium-osmium bond distances, Os(1) – Os(3) = 2.8716(7) Å and Os(2) – Os(3) = 2.8664(8) Å are nearly identical and are similar to the osmium-osmium bond distances found in $\text{Os}_3(\text{CO})_{12}$ of 2.877(3) Å [28]. The acetyl-bridged osmium - osmium bond distance is significantly longer, Os(1) – Os(2) = 2.9339(7) Å than the other Os – Os bonds. Longer Os - Os bond distances were also found in two previously reported triosmium cluster complexes containing bridging acetyl ligands: $\text{Os}_3(\text{CO})_9(\mu\text{-O}=\text{CCH}_3)(\mu\text{-H})(\text{C}_2\text{H}_4)$, 2.934(1) Å [29] and $\text{Os}_3(\text{CO})_9(\mu\text{-O}=\text{CCH}_3)(\text{H})[\text{CH}_3\text{C}(\text{OCH}_3)]$, 2.909(2) Å [30]. The $\text{Au}(\text{PPh}_3)$

group bridges the same Os – Os bond as the acetyl ligand. Assuming that the Au(PPh₃) group is one-electron donor and acetyl ligand serves as a three-electron donor, then compound **1** contains a total of 48 valence electrons and all metal atoms formally have 18 electron configurations.

Figure 3. ORTEP diagram of the molecular structure of Os₃(CO)₁₀(μ-O=CCH₃)(μ-AuPPh₃), **1**, showing 30% thermal ellipsoid probability. The hydrogen atoms in phenyl groups are omitted for clarity. Selected interatomic bond distances (Å) and angles (°) are as follow: Os(1) – Os(2) = 2.9339(7), Os(1) – Os(3) = 2.8716(7), Os(2) – Os(3) = 2.8664(8), Os(1) – Au(1) = 2.7667(7), Os(2) – Au(1) = 2.7833(7), Os(2) – O(1) = 2.083(11), Os(1) – C(1) = 2.097(14), C(1) – C(2) = 1.45(3), C(1) – O(1) = 1.281(17); C(1) – Os(1) – Os(2) = 66.3(4), O(1) – Os(2) – Os(1) = 67.1(3), Os(1) – C(1) – O(1) = 113.5(9), C(1) – O(1) – Os(2) = 113.1(9).

Compound **2** contains a triangle of three osmium atoms with a triply bridging methylidyne ligand and is structurally similar to the triosmium cluster complex Os₃(CO)₉(μ₃-CH)(μ-H)₃ [31], except that it has one bridging Au(PPh₃) group in the place of one of the

bridging hydrido ligands of $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_3$. Both of these methylidyne complexes contain 48 valence electrons and the Os – Os and Os – C(1) bond distances in both compounds are very similar: for **2**: Os(1) – Os(2) = 2.8967(4) Å, Os(1) – Os(3) = 2.8943(4) Å, Os(2) – Os(3) = 2.8910(5) Å; Os(1) – C(1) = 2.093(7) Å, Os(2) – C(1) = 2.077(7) Å, Os(3) – C(1) = 2.112(8) Å, and for $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_3$: Os – Os(ave) = 2.893(2) Å; Os – C(ave) = 2.101(2) Å.

Figure 4. ORTEP diagram of the molecular structure of $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_2(\mu\text{-AuPPh}_3)$, **2**, showing 25% thermal ellipsoid probability. The hydrogen atoms in phenyls are omitted for clarity. Selected interatomic bond distances (Å) and angles ($^\circ$) are as follow: Os(1) – Os(2) = 2.8967(4), Os(1) – Os(3) = 2.8943(4), Os(2) – Os(3) = 2.8910(5), Os(2) – Au(1) = 2.7786(4), Os(1) – Au(1) = 2.7468(4), Os(1) – C(1) = 2.093(7), Os(2) – C(1) = 2.077(7), Os(3) – C(1) = 2.112(8), Os(1) – H(2) = 1.908(5), Os(3) – H(2) = 1.823(5), Os(2) – H(3) = 1.630(6), Os(3) – H(3) = 1.784(5), C(1) – H(1) = 0.911(5); Os(1) – Os(2) – Os(3) = 60.011(11), Os(2) – Os(1) – Os(3) = 59.897(12), Os(1) – C(1) – Os(2) = 88.0(3), Os(2) – C(1) – Os(3) = 87.3(3), Os(1) – C(1) – Os(3) = 87.0(3).

It is proposed that compounds **1** and **2** are formed by two competing processes, see Scheme 1. In both cases the first step appears to be a displacement of the NCCH₃ ligand that is accompanied by the oxidative addition of the Au – C bond of the (CH₃)Au(PPh₃) to one of the osmium atoms. An initial intermediate formulated “Ph₃PAuOs₃(CO)₁₁(CH₃)”, **I1** is anticipated in the reaction of Os₃(CO)₁₁(NCCH₃) with (CH₃)Au(PPh₃). ¹H NMR spectra of the reaction solution showed an initial formation of two resonances, $\delta = 0.95$ and 0.86 , that could be attributed to complexes with terminally-coordinated methyl groups, see Scheme 1.

Scheme 1. Os₃(CO)₁₁(NCCH₃) reaction pathways with (CH₃)Au(PPh₃) at room temperature.

It appears that **I1** exists as a mixture of two isomers, **I1-a** and **I1-b**. There are few examples of well characterized triosmium cluster complexes containing terminally coordinated methyl ligands, but the compound Os₃(CO)₉[μ-η²-C₇H₃(2-CH₃)NS](μ-CH₂)(CH₃) is one good example which showed the resonance of the Os bonded methyl group at $\delta = 1.03$ [32]. Intermediate **I1**

subsequently undergoes methyl migration/insertion of a CO ligand into the Os-CH₃ bond resulting in the formation of an acetyl ligand that ultimately becomes the bridging acetyl ligand in **1** as indicated by the formation of its acetyl methyl resonance at $\delta = 2.19$ in the ¹H NMR spectrum. Alternatively, **11** can eliminate CO and proceed to **2** via a series of CH bond cleavage steps with the loss of an additional CO ligand as observed by the accompanying appearance of its ¹H NMR resonances at $\delta = 10.59$ (dd), -21.11 (dd).

Additional details about this transformation were obtained by a ¹H NMR study of the reaction of Os₃(CO)₁₀(NCCH₃)₂ with (CH₃)Au(PPh₃). The ¹H NMR spectra of the reaction of Os₃(CO)₁₀(NCCH₃)₂ with (CH₃)Au(PPh₃) as a function of time are shown above in Figure 2. The spectrum taken at 6 min shows a prominent resonance at $\delta = -3.62$. This is attributed to an intermediate triosmium species formulated as Os₃(CO)₁₀(μ-AuPPh₃)(μ-CH₃), **12** containing an agostic-coordinated bridging methyl group, see Scheme 2.

Scheme 2. Schematic of the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$.

The assignments of the methyl, methylene, and methyldyne ligand resonances in this work are firmly established based on the elegant work by Shapley in his studies of the $\text{Os}_3(\text{CO})_9(\text{“CH}_4\text{”})$ family of compounds [9,21]. Agostically, coordinated methyl groups exhibit resonance shifts upfield from TMS.¹⁵ In the next step, the agostic CH bond of the methyl group is cleaved and another intermediate formulated as $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-H})(\mu\text{-AuPPh}_3)$, **I3**, with inequivalent methylene protons is formed showing resonances at 4.55 ppm (dt, $^2J_{\text{H-H}} = 12$ Hz, $^3J_{\text{H-H}} = 2$ Hz, $^4J_{\text{P-H}} = 2$ Hz) and 5.62 ppm (dd, $^2J_{\text{H-H}} = 12$ Hz, $^3J_{\text{H-H}} = 3$ Hz) and a hydride resonance at -20.19 ppm is formed. This step was analyzed computationally, see below. During this period, the resonances of compound **2** (the major final product) appear and grow in intensity. Compound **2** is formed by the loss of a CO ligand from **I3** and a C-H activation of one of the CH bonds of the bridging CH_2 ligand. This transformation was also analyzed computationally, see below. Additional resonances appear at 20 min into the reaction at 4.61 ppm ($^2J_{\text{H-H}} = 8$ Hz) and 6.32 ($^2J_{\text{H-H}} = 8$ Hz) ppm. These are attributed to an intermediate formulated as $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-AuPPh}_3)_2$, **I4**. **I4** can be isolated in low yield (approx. 2%) by TLC and was shown to contain two $\text{Au}(\text{PPh}_3)$ groups on the basis of its mass spectrum, $m/z = 1785$. Finally, small resonances appear at $\delta = 11.94$ (methyldyne) and -22.50 (hydride) which are attributed to a final product formulated as $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})(\mu\text{-AuPPh}_3)_2$, **3**. The low-field resonance in **3** is due to a triply bridging methyldyne ligand formed by the loss of a CO ligand from **I4** and a CH activation of one of the CH bonds of the bridging methylene ligand, see Scheme 2. Compound **3** can also be obtained independently in a good yield (55%) together with the known compound of $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_3$ ²¹ (17% yield) by thermal disproportionation of compound **2** at 125 °C in

octane solvent. Compound **3** was further characterized by single-crystal X-ray diffraction analysis and an ORTEP diagram of its molecular structure is shown in Figure 5.

Compound **3** is structurally similar to that of **2** with a triply-bridging CH (methyldidyne) ligand except that it has a second bridging Au(PPh₃) group in place of one of the bridging hydride ligands in **2**. An interesting structural feature is the existence of a significant Au – Au bonding interaction between the two Au(PPh₃) groups, Au(1) – Au(2) = 3.0559(7) Å. This Au – Au distance is even shorter than those observed in other structurally similar polynuclear metal carbonyl complexes containing two Au(PPh₃) groups, e. g. Ru₃(CO)₉(μ₃-COCH₃)(μ-H)(μ-AuPPh₃)₂, Au – Au = 3.176(1) Å [33], and Ir₄(CO)₁₁(μ-AuPPh₃)₂, Au – Au = 3.2464(13) [34] and Os₄(CO)₁₃(μ-AuPEt₃)₂, Au – Au = 3.128 (1) [35]. Overall, the cluster of **3** can be viewed as a distorted square-pyramidal structure with two osmium and two gold atoms in the base and one osmium Os(3) at the apex.

Figure 5. ORTEP diagram of the molecular structure of $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})(\mu\text{-AuPPh}_3)_2$, **3**, showing 15% thermal ellipsoid probability. The hydrogen atoms on the phenyl groups are omitted for clarity. Selected interatomic bond distances (Å) are as follow: $\text{Os}(1) - \text{Os}(2) = 2.9079(7)$, $\text{Os}(1) - \text{Os}(3) = 2.9121(7)$, $\text{Os}(2) - \text{Os}(3) = 2.9209(7)$, $\text{Os}(1) - \text{Au}(1) = 2.8055(6)$, $\text{Os}(3) - \text{Au}(1) = 2.7481(6)$, $\text{Os}(2) - \text{Au}(2) = 2.7777(7)$, $\text{Os}(3) - \text{Au}(2) = 2.7472(7)$, $\text{Au}(1) - \text{Au}(2) = 3.0559(7)$, $\text{Os}(1) - \text{C}(1) = 2.103(10)$, $\text{Os}(2) - \text{C}(1) = 2.117(11)$, $\text{Os}(3) - \text{C}(1) = 2.075(11)$, $\text{Os}(1) - \text{H}(3) = 1.78(2)$, $\text{Os}(2) - \text{H}(3) = 1.80(2)$, $\text{C}(1) - \text{H}(1) = 0.98(2)$.

The thermal conversion of compound **2** into **3** and $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})_3$ is formally a disproportionation reaction. A possible mechanism for this process is shown in Scheme 3. Competing reductive eliminations of H_2 and “ $\text{HAu(PPh}_3\text{)}$ ”, could generate unsaturated species such as $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-AuPPh}_3)$ and $\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})(\mu\text{-H})$, respectively, which could, in turn, oxidatively re-add $\text{HAu(PPh}_3\text{)}$ [17b] and H_2 , respectively, to yield the observed products.

Scheme 3. A proposed scheme for the disproportionation of **2**.

When compound **2** was heated under 600 psi CO in a solution of octane at 100 °C, it was carbonylated and transformed into three new compounds, $(\text{CH}_3)\text{Os}_3(\text{CO})_{12}\text{AuPPh}_3$ **4**, in 53% yield, $(\text{CH}_3)\text{Os}_2(\text{CO})_8\text{AuPPh}_3$, **5**, in 7% yield and $\text{Os}(\text{CO})_4(\text{PPh}_3)$ [36] **6** in 2% yield. Two other compounds **1** and $\text{Os}_3(\text{CO})_{12}$ were also isolated in low yields, 6% and 2.5% yield respectively. An ORTEP diagram of the molecular structure of **4** is shown in Figure 6.

Figure 6. ORTEP diagram of the molecular structure of **4** showing 30% thermal ellipsoid probabilities. The hydrogen atoms in phenyl groups are omitted for clarity. Selected interatomic bond distances (Å) and angles (°) are as follows: $\text{Os}(1) - \text{Os}(2) = 2.9326(7)$, $\text{Os}(2) - \text{Os}(3) = 2.9058(7)$, $\text{Os}(1) - \text{Au}(1) = 2.6389(7)$, $\text{Os}(3) - \text{C}(1) = 2.11(2)$; $\text{Os}(1) - \text{Os}(2) - \text{Os}(3) = 175.80(3)$, $\text{C}(1) - \text{Os}(3) - \text{Os}(2) = 87.3(5)$, $\text{Au}(1) - \text{Os}(1) - \text{Os}(2) = 83.296(19)$.

Compound **4** contains an open cluster of three osmium atoms having only two Os – Os bonds. The Os – Os distances, $\text{Os}(1) - \text{Os}(2) = 2.9326(7)$ Å and $\text{Os}(2) - \text{Os}(3) = 2.9058(7)$ Å, are similar

to those found in the linear complex $\text{IOs}_3(\text{CO})_{12}\text{I}$, $\text{Os}(1) - \text{Os}(2) = 2.9157(2) \text{ \AA}$ [37]. The Os – Os angle is almost linear, $\text{Os}(1) - \text{Os}(2) - \text{Os}(3) = 175.80(3)^\circ$. A methyl group is terminally coordinated to Os(3), $\text{Os}(3) - \text{C}(1) = 2.11(2) \text{ \AA}$ and a terminally coordinated gold(triphenylphosphine) group is bonded to Os(1), $\text{Os}(1) - \text{Au}(1) = 2.6389(7) \text{ \AA}$, almost perpendicular to the triosmium chain, $\text{Au}(1) - \text{Os}(1) - \text{Os}(2) = 83.296(19)^\circ$. The methyl resonance in **4** appears at $\delta = 0.23$ in the ^1H NMR spectrum. The methyl and gold(triphenylphosphine) groups serve as one electron donors, and the three osmium atoms contain a total of 50 valence electrons; thus, with two Os – Os bonds all of the metal atoms are formally electronically saturated.

An ORTEP diagram of the molecular structure of **5** is shown in Figure 7.

Figure 7. ORTEP diagram of the molecular structure of $(\text{CH}_3)\text{Os}_2(\text{CO})_8(\text{AuPPh}_3)$, **5**, showing 30% thermal ellipsoid probability. The hydrogen atoms in phenyls are omitted for clarity. Selected interatomic bond distances ($\text{\AA}$) and angles ($^\circ$) are as follows: $\text{Os}(1) - \text{Os}(2) = 2.9617(4)$, $\text{Os}(1) - \text{Au}(1) = 2.6508(4)$, $\text{Os}(2) - \text{C}(1) = 2.196(10)$; $\text{C}(1) - \text{Os}(2) - \text{Os}(1) = 90.1(3)$, $\text{Au}(1) - \text{Os}(1) - \text{Os}(2) = 86.941(11)$.

Compound **5** contains only two osmium atoms that are joined by a Os – Os single bond, $\text{Os}(1) - \text{Os}(2) = 2.9617(4) \text{ \AA}$. A terminally-coordinated methyl group and a $\text{Au}(\text{PPh}_3)$ group are coordinated to the osmium atoms $\text{Os}(2)$ and $\text{Os}(1)$, respectively, $\text{Os}(2) - \text{C}(1) = 2.196(10) \text{ \AA}$, $\text{Os}(1) - \text{Au}(1) = 2.6508(4) \text{ \AA}$, perpendicular to the Os – Os vector, $\text{C}(1) - \text{Os}(2) - \text{Os}(1) = 90.1(3)^\circ$, $\text{Au}(1) - \text{Os}(1) - \text{Os}(2) = 86.941(11)^\circ$. The methyl resonance in **5** appears at $\delta = 0.26$ in the ^1H NMR spectrum. There are eight linear terminal carbonyl ligands. The CO ligands cis to the metal – metal bond have adopted a staggered rotational conformation. The total valence electron count for the metal atoms in **5** is 34, i.e. both metal atoms have 18 electron configurations.

An osmium group was eliminated from **2** in the formation of **5** in this carbonylation reaction. It observed in the form of the complex $\text{Os}(\text{CO})_4(\text{PPh}_3)$, **6** which contains only one osmium atom that has also captured a PPh_3 ligand that must have been dissociated from an AuPPh_3 group. Compound **6** was characterized crystallographically and an ORTEP diagram of its molecular structure is shown in Figure 8. The metal atom has a trigonal bipyramidal structure, as expected for a structure with five ligands, and the PPh_3 ligand occupies an axial position, $\text{Os}(1) - \text{P}(1) = 2.3904(10) \text{ \AA}$.

Figure 8. ORTEP diagram of the molecular structure of $\text{Os}(\text{CO})_4(\text{PPh}_3)$, **6**, showing 25% thermal ellipsoid probability. The hydrogen atoms in phenyls are omitted for clarity. Selected interatomic bond distances ($\text{\AA}$) and angles ($^\circ$) are as follows: $\text{Os}(1) - \text{P}(1) = 2.3904(10)$, $\text{Os}(1) - \text{C}(1) = 1.914(5)$, $\text{Os}(1) - \text{C}(2) = 1.913(5)$, $\text{Os}(1) - \text{C}(3) = 1.915(4)$, $\text{Os}(1) - \text{C}(4) = 1.940(5)$. $\text{C}(1) - \text{Os}(1) - \text{P}(1) = 87.99(14)$, $\text{C}(1) - \text{Os}(1) - \text{C}(4) = 91.3(2)$.

The first addition of CO to **2** presumably induces shifts the two hydrido ligands back to the methyldyne ligand of **2** leading to the agostic-bridged methyl intermediate **I2** (shown) via the methylene/hydride intermediate **I3**, not shown, see Scheme 4. The second CO addition leads to a shift of the methyl group to a terminal position as found in intermediate **I1**. The third CO addition leads to cleavage of Os - Os and Os - Au bonds with the $\text{Au}(\text{PPh}_3)$ group shifting to a terminal position when the Os_3 cluster opens to yield **4**. Interestingly, it was found that the compounds **5** and **6** were not formed in the reaction of **4** with CO in the presence of PPh_3 . It is possible that they were formed directly from intermediate **I1** by routes involving cleavages of different metal - metal bonds. For example, carbonylation of **I1** by cleavage of the $\text{Os}(2) - \text{Au}$ and $\text{Os}(1) - \text{Os}(2)$ bonds would lead to **4** where the CH_3 and $\text{Au}(\text{PPh}_3)$ groups are separated by an

$\text{Os}(\text{CO})_4$ grouping. On the other hand, cleavage of the $\text{Os}(1) - \text{Os}(3)$, $\text{Os}(2) - \text{Os}(3)$ and $\text{Os}(2) - \text{Au}$ bonds would lead to **5**, where the CH_3 and $\text{Au}(\text{PPh}_3)$ groups lie on adjacent $\text{Os}(\text{CO})_4$ groups, and to **6**, see Scheme 4.

Compound **4** was thermally converted back to a mixture of **1** (50% yield) and **2** (10 % yield) by heating to 97 °C for 2h in heptane solvent. Alternatively, compound **4** was converted back to **1** and **2** in a 10/1 ratio in greater than 90% conversion under irradiation with room light at room temperature over a period of 9 days.

Scheme 4. A schematic of the transformations of **2** by the addition of CO.

In order to learn more about the mechanisms of the decarbonylation **4** to **2** (and in turn the microreverse of the carbonylation of **2** to **4**) in this system, a series of ADF-based DFT computational analyses were performed. The calculations were initiated by obtaining a geometry-optimized structure of the compound formulated above as $\text{Os}_3(\text{CO})_{11}(\text{CH}_3)(\mu\text{-AuPPh}_3)$, **II** containing a 48 electron triangular cluster of three osmium atoms that is formed by the loss of

a CO ligand from **4**. The DFT refined structure of **I1** contains a terminally coordinated methyl group, a bridging Au(PPh₃) group and two bridging CO ligands, Scheme 5.

Scheme 5. A schematic of the transformations of **4** to **2** by the elimination of CO ligands. The Red atoms and bonds show where the ligand eliminations occurred in the computational analyses.

The structure **I1** lies 17.3 kcal/mol higher in energy than **4**, see Figure 9 which shows an energy profile of the overall reaction. Compound **I1** loses one CO ligand at the neighboring osmium atom of the gold-bridged Os – Os bond and is transformed to **I2** which contains an agostically coordinated bridging methyl group across the gold-bridged Os – Os bond. Intermediate **I2** lies 23.1 kcal/mol higher in energy than **I1**. The Os – C and Os – H distances to the agostically coordinated C – H bond are 2.44 Å and 1.96 Å, respectively. The C – H bond distance of the agostically coordinated C – H bond is 1.16 Å in length. The blue contour of HOMO-21 of **I2** shows the nature of the bonding of the agostically coordinated C-H group to the osmium atom Os(1), see Figure 10. The C-H bond forms a three-center interaction with the osmium atom in the left hand side in Figure 10. In order to obtain evidence about the character of the metal - agostic

CH bond interactions, the electron densities in this region of the molecule were calculated by using the Quantum Theory of the Atoms in Molecules (QTAIM) model.²⁶

Figure 9. An energy level diagram showing the energies of the intermediates and transition states for the decarbonylation of **4** to **2** along the reaction coordinate.

The electron density at the QTAIM bond critical point (bcp) of the agostically coordinated C-H bond, C(1)-H(1), was calculated to be $0.213 \text{ e}^-/\text{Bohr}^3$. This is slightly less than the values for the two uncoordinated C-H bonds, C(1) – H(2), $0.261 \text{ e}^-/\text{Bohr}^3$ and C(1) – H(3) bonds, $0.265 \text{ e}^-/\text{Bohr}^3$. There was a bcp between the osmium atom Os(1) and the agostic hydrogen atom H(1), Os(1)···H(1) having the electron density $0.063 \text{ e}^-/\text{Bohr}^3$. Clearly, there was significant shift of electron density from the agostic C-H bond toward the associated osmium atom Os(1). There was no bcp calculated between Os(1) and C(1), but there was one between Os(2) – C(1) at 0.090

e^-/Bohr^3 . These numbers compare favorably with those calculated for agostic CH bonding situations involving single metal atoms [38].

Figure 10. The HOMO-21 of the intermediate **I2** with sketch showing QTAIM electron densities (e^-/Bohr^3) at selected bond critical points on the right.

Intermediate **I2** was smoothly converted to the methylene/hydride containing intermediate **I3** via a 20 kcal/mol transition state TS1 by cleavage of the agostic CH bond of the methyl group. The hydrido ligand assumed a position bridging on the neighboring Os – Os bond and the resultant methylene group assumed a bridging position on the Au(PPh₃) bridged Os – Os bond. The HOMO-4 of **I3** shows the nature of a three-center Os – C – Os bonding interaction between two osmium atoms of the cluster and the carbon atom of the bridging CH₂ group by the red contour, see Figure 11.

Figure 11. The HOMO-4 of the intermediate **I3** with a sketch showing QTAIM electron densities (e^-/Bohr^3) at selected bond critical points on the right.

The Os – C distances to the bridging CH_2 group are both 2.19 Å and are similar to those found for the triosmium complexes $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)(\mu\text{-H})_2$, 2.151(5) Å and 2.150(6) Å and $\text{Os}_3(\text{CO})_9(\text{PPh}_3)(\mu\text{-CH}_2)(\mu\text{-H})_2$, 2.140(6) Å and 2.171(6) Å.²⁰ The QTAIM electron densities at the Os - C bcps to the bridging CH_2 group for **I3** were 0.101 e^-/Bohr^3 and 0.100 e^-/Bohr^3 . The transformation of **I3** into **2** involves two steps: 1) loss of a CO ligand from the CO-rich $\text{Os}(\text{CO})_4$ group which leads to an intermediate **I5** containing an agostically-coordinated triple bridging CH_2 ligand; and 2) the cleavage of the agostic C-H bond of triple bridging CH_2 ligand with formation of the triple bridging methylidyne (CH) ligand and a bridging hydrido ligand on the third Os – Os bond. In step (1), the transformation was simulated computationally by progressively removing the axially coordinated CO ligand proximate to the CH_2 ligand from the

third osmium atom. As this removal progressed, the CH_2 ligand shifted toward this osmium atom Os(3). After passing over transition state **TS2**, the calculation formed a stable minimum with the geometry-optimized structure for **I5** shown in Figure 12.

Figure 12. The HOMO-33 of the intermediate **I5** with sketch showing QTAIM electron densities (e^-/Bohr^3) at selected bond critical points on the right.

The HOMO-33 of **I5** shows the nature of the bonding of the triple bridging CH_2 ligand to the triosmium cluster. One of the C-H bonds, $\text{C}(1) - \text{H}(2)$ has formed an agostic interaction to the third metal atom by using an sp-hybridized carbon orbital that simultaneously bonds the CH_2 group to the $\text{Au}(\text{PPh}_3)$ bridged Os – Os bond. The agostic C-H bond distance in **I5** is 1.20 Å while the uncoordinated C-H bond distance is 1.10 Å. The agostic $\text{Os} \cdots \text{C}$ and $\text{Os} \cdots \text{H}$ bond distances are 2.35 Å and 1.91 Å, respectively. The QTAIM electron density of the agostic C - H bond at its bcp was calculated to be $0.196 \text{ e}^-/\text{Bohr}^3$. The QTAIM electron density for the uncoordinated C - H bond, was $0.270 \text{ e}^-/\text{Bohr}^3$. There was an $\text{Os} \cdots \text{H}$ bcp of $0.072 \text{ e}^-/\text{Bohr}^3$.

between the metal atom Os(3) and the agostic hydrogen atom which once again shows there is a significant transfer of electron density from the agostic C-H bond toward the metal atom.

In the final step **I5** was converted smoothly to **2** via a small transition state **TS3**, +13.3 kcal/mol. Structure **2** lies 4.1 kcal/mol lower in energy than **I5**. The HOMO-4 which shows the bonding of the triply-bridging methylidyne ligand to the cluster together with a schematic of **2** showing selected QTAIM electron densities is shown in Figure 13.

Figure 13. The HOMO-4 of the product **2** with sketch showing QTAIM electron densities (e⁻/Bohr³) at selected bond critical points on the right.

The Os – C bond distances to the triply bridging methylidyne ligand are 2.14 Å and are very similar to those observed for **2** in the crystal structure analysis, Os(1) – C(1) = 2.103(10), Os(2) – C(1) = 2.117(11), Os(3) – C(1) = 2.075(11), see above. The QTAIM electron densities of the Os – C bonds at bcps were calculated to be 0.111, 0.111 and 0.118 e⁻/Bohr³; the bcp for the remaining C-H bond is normal at 0.263 e⁻/Bohr³.

The loss of each CO ligand and the cleavage of each CH bond, except for the last one, each produces an increase in the total energy of the system, so overall the conversion of **4** to **2** results in a net increase of approximately 64 kcal/mol. Due to complexity of the system and inherent ambiguity in the accuracy of DFT model, this value is probably only qualitatively correct, see Figure 9. The geometrical features of the various species involved are likely to be considerably more accurate.

Summary and Conclusions

It has been shown that $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ reacts with $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ by the loss of the NCCH_3 ligand and the oxidation-addition of the Au-C bond to the methyl group to the osmium atoms. This is followed by methyl migration/CO insertion to yield the product **1** or a series of decarbonylations to yield the co-product **2**. The yield of **2** was higher in the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with $(\text{CH}_3)\text{Au}(\text{PPh}_3)$. Time-dependent ^1H NMR measurements confirmed a series intermediates containing methyl and methylene ligands en route the methyldidyne complex **2** via a series of CO dissociation steps. Interestingly, the reverse process (CH bond formations) was achieved by CO additions to compound **2**. In addition, the Os - Au and Os - Os bonds were cleaved to form the two open OsAu cluster complexes **4** and **5**. The open cluster **4** was converted back to compounds **1** and **2** via decarbonylation processes. DFT computational analyses revealed a plausible mechanism for the processes that proceeds via a series reversible C-H activations that involve intermediates containing bridged species having agostic CH interactions with the metal atoms in the cluster. In addition, when compound **2** was heated to 125 °C in solution, the digoldtriosmium compound **3** was formed via ligand exchange between the AuPPh_3 and H ligands or more likely by a reversible elimination and re-addition of H_2 and “ HAuPPh_3 ” to the appropriate intermediates, see Scheme 3. We believe that $(\text{CH}_3)\text{Au}(\text{PPh}_3)$ will serve as a viable

mimic for CH₄ for studies of its activation and transformations. It is very likely that the activation/transformation of methyl groups at triangular trinuclear metal sites in other polynuclear metal complexes will proceed similarly and these might serve as reasonable models for similar transformations on the triangular {111} faces of metal surfaces.

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Supporting Information: (1) Details and results of the DFT computational analyses. (2) Details of the crystallographic analyses. (3) Cif files for the structural analyses have been deposited with the Cambridge Crystallographic Data CCDC 1405087-1405091 for compound **1** – **6**. Copies of this information may be obtained from The Director, CCDC at [www: http://www.ccdc.cam.ac.uk/pages/Home.aspx](http://www.ccdc.cam.ac.uk/pages/Home.aspx).

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Compound	1	2	3
Empirical formula	Os ₃ AuPO ₁₁ C ₃₀ H ₁₈	Os ₃ AuPO ₉ C ₂₈ H ₁₈	Os ₃ Au ₂ P ₂ O ₉ C ₄₆ H ₃₂
Formula weight	1353.08	1297.06	1755.19
Crystal system	Triclinic	Orthorhombic	Triclinic
Lattice parameters			
<i>a</i> (Å)	9.3218(7)	17.1603(5)	12.0351(6)
<i>b</i> (Å)	13.0462(10)	14.3830(5)	17.9004(9)
<i>c</i> (Å)	14.3573(11)	25.7235(8)	22.0930(11)
α (deg)	93.720(2)	90.00	89.326(1)
β (deg)	94.647(1)	90.00	78.026(1)
γ (deg)	104.564(1))	90.00	89.105(1)
<i>V</i> (Å ³)	1677.8(2)	6349.0(3)	4655.3(4)
Space group	<i>P</i> $\bar{1}$ (#2)	<i>Pbca</i> (#61)	<i>P</i> $\bar{1}$ (#2)
Z value	2	8	4
ρ_{calc} (g / cm ³)	2.25	2.772	2.504
μ (Mo K α) (mm ⁻¹)	7.081	7.081	7.081
Temperature (K)	294(2)	294(2)	294(2)
2 Θ_{max} (°)	52.82	52.48	55.94
No. Obs. (<i>I</i> > 2 σ (<i>I</i>))	5091	5249	12496
No. Parameters	416	389	1123
Goodness of fit (GOF)	1.054	1.106	0.978
Max. shift in cycle	0.000	0.003	0.001
Residuals*: <i>R</i> ₁ ; <i>wR</i> ₂	0.0535; 0.1430	0.0357; 0.0677	0.0449; 0.0865
Absorption Correction,	Multi-scan	Multi-scan	Multi-scan
Max/min	1.000 / 0.141	1.000 / 0.268	1.000 / 0.475
Largest peak in Final			
Diff. Map (e ⁻ / Å ³)	2.927	1.618	1.861

Table 1. Crystallographic Data for Compounds 1- 6.

$$*R = \sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{hkl} |F_{\text{obs}}|; R_w = [\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{hkl} w F_{\text{obs}}^2]^{1/2};$$

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

Table 1 (continued).

Compound	4	5	6
Empirical formula	Os ₃ AuPO _{12.5} C ₃₁ H _{16.5}	Os ₂ AuPO ₈ C ₂₇ H ₁₈	Os ₁ PO ₄ C ₂₂ H ₁₅
Formula weight	1387.48	1078.82	564.54
Crystal system	Monoclinic	Monoclinic	Triclinic
Lattice parameters			
a (Å)	9.9834(5)	12.8857(7)	9.9300(9)
b (Å)	16.1827(8)	17.9703(9)	10.5341(9)
c (Å)	22.3716(11)	13.8285(7)	10.8638(9)
α (deg)	90.00	90.00	91.132(2)
β (deg)	90.374(1)	113.0920(10)	112.736(2)
γ (deg)	90.00	90.00	93.529(2)
V (Å ³)	3614.2(3)	2945.6(3)	1044.93(16)
Space group	<i>P</i> 2(1)/n (#14)	<i>P</i> 2(1)/n (#14)	<i>P</i> $\bar{1}$ (#2)
Z value	4	4	2
ρ _{calc} (g / cm ³)	2.550	2.336	1.794
μ (Mo Kα) (mm ⁻¹)	7.081	7.081	7.081
Temperature (K)	294(2)	294(2)	294(2)
2Θ _{max} (°)	52.46	54.12	55.5
No. Obs. (I > 2σ(I))	6246	5543	4471
No. Parameters	444	353	313
Goodness of fit (GOF)	1.063	1.026	1.099
Max. shift in cycle	0.000	0.019	0.001
Residuals*: R ₁ ; wR ₂	0.0551; 0.1513	0.0328; 0.0833	0.0281; 0.0613
Absorption Correction,	Multi-scan	Multi-scan	Multi-scan
Max/min	1.000 / 0.322	1.000 / 0.465	1.000 / 0.638
Largest peak in Final			
Diff. Map (e ⁻ / Å ³)	2.808	2.041	1.080

$$*R = \sum_{hkl} (|F_{obs}| - |F_{calc}|) / \sum_{hkl} |F_{obs}|; R_w = [\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2 / \sum_{hkl} w F_{obs}^2]^{1/2};$$

$$w = 1/\sigma^2(F_{obs}); GOF = [\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2 / (n_{data} - n_{var})]$$