Notes

One-Step Synthesis of $[HM_3(CO)_{11}]^-$ from $M_3(CO)_{12}$ (M = Fe, Ru, Os) via Unusual Hydride Transfer from 1,3,5-Trimethyl-1,3,5-triazacyclohexane

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*Summary: Reactions of $M_3(CO)_{12}$ and $(MeNCH_2)_3$ (1,3,5-trimethyl-1,3,5-triazacyclohexane) in refluxing n-hexane generate the anionic hydrido clusters $[(\mu\text{-}H)M_3(CO)_{11}]$-$[MeN(MeNCH_2)_2CH]$ (**1** and **2** for M = Fe and Ru, respectively) in good yields, while heating $Os_3(CO)_{12}$ and $(MeNCH_2)_3$ results in fragmentation of the triazacyclohexane ligand to yield the amidino complex $(\mu\text{-}H)Os_3(CO)_9(\mu_3,\eta^2\text{-}CH(NMe)_2)$ (**4**). The Os_3 analogue $[(\mu\text{-}H)Os_3(CO)_{11}][MeN(MeNCH_2)_2CH]$ (**3**) is produced by treatment of $Os_3(CO)_{12}$ with $(MeNCH_2)_3$ in the presence of Me_3NO at room temperature or by treatment of $Os_3(CO)_{11}(NCMe)$ with $(MeNCH_2)_3$ at room temperature. A pathway involving β-hydride abstraction from a CH_2 unit of the bound $(MeNCH_2)_3$ ligand is proposed. The molecular structures of **2** and **4** are determined by an X-ray diffraction study.*

Introduction

The trinuclear cluster anions $[(\mu\text{-H})M_3(CO)_{11}]^-$ of iron group metals (M = Fe,[1] Ru,[2] Os[3]) are important starting compounds for the preparation of a variety of cluster derivatives.[4] In addition, interest has been stimulated by the potential for these compounds to serve as a homogeneous catalyst in hydroformylation,[5] hydrogenation,[6] water-gas shift reactions,[7] etc. There are several literature reports on the syntheses of $[(\mu\text{-H})M_3(CO)_{11}]^-$, all of which involve reactions of $M_3(CO)_{12}$ (and $Fe(CO)_5$) with basic reagents, such as a triethylamine/water mixture in THF,[8] $NaBH_4$ or KH in dry THF,[9] and KOH in alcohol solvents.[10] Usually, subsequent metathesis of small metal countercations by $[Et_4N]^+$ or $[PPN]^+$ species is necessary to obtain stable salts.

The six-membered 1,3,5-trimethyl-1,3,5-triazacyclohexane molecule ($(MeNCH_2)_3$) is an attractive ligand for η^3-metal complexation.[11] For instance, thermolysis of $M(CO)_6$ and $(MeNCH_2)_3$ produces $M(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ (M = Cr, Mo, W) in good yields.[12] In the present research, we explored the reactions of $(MeNCH_2)_3$ with the iron group clusters $M_3(CO)_{12}$, which lead to formation of $[(\mu\text{-H})M_3(CO)_{11}][MeN(MeNCH_2)_2CH]$ quite unusually.

Results and Discussion

Reaction of $Fe_3(CO)_{12}$ and $(MeNCH_2)_3$ in refluxing *n*-hexane for 30 min affords a red precipitate, which is recrystallized from acetone/*n*-hexane to give a crystalline solid of $[(\mu\text{-H})Fe_3(CO)_{11}][MeN(MeNCH_2)_2CH]$ (**1**) in 80% yield (eq 1). Treatment of $Fe_2(CO)_9$ with $(MeNCH_2)_3$ at room temperature also leads to **1** in 49% yield on the basis of the Fe atoms consumed. The ruthenium analogue $[(\mu\text{-H})Ru_3(CO)_{11}][MeN(MeNCH_2)_2CH]$ (**2**) is prepared similarly in 93% yield by heating $Ru_3(CO)_{12}$ and $(MeNCH_2)_3$ in *n*-hexane for 1 h. On the contrary, no reactions occur between $Os_3(CO)_{12}$ and $(MeNCH_2)_3$ in refluxing *n*-hexane. At refluxing toluene temperature, however, fragmentation of the triazacyclohexane ligand

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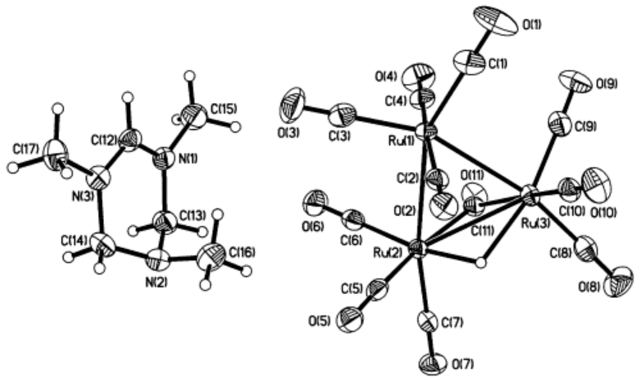
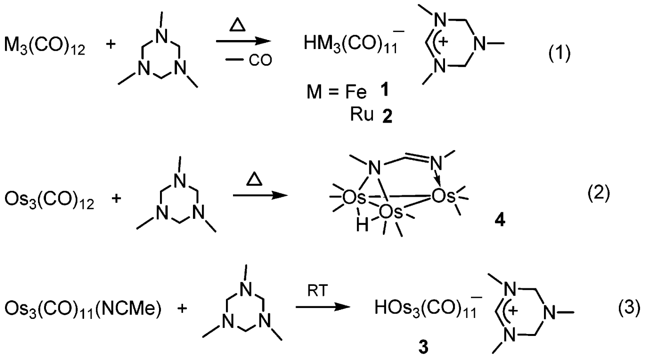


Figure 1. Molecular structure of **2**. Selected bond distances (Å): Ru(1)−Ru(2) = 2.8368(4), Ru(1)−Ru(3) = 2.8450(5), Ru(2)−Ru(3) = 2.8144(4), Ru(2)−C(11) = 2.084(4), Ru(3)−C(11) = 2.085(4), C(11)−O(11) = 1.178(5), C(12)−N(3) = 1.312(5), C(12)−N(1) = 1.308(6), C(14)−N(3) = 1.473(5), C(13)−N(1) = 1.476(6), C(14)−N(2) = 1.430(6), C(13)−N(2) = 1.442(6). Selected bond angles (deg): Ru(1)−Ru(2)−Ru(3) = 60.45(1), Ru(1)−Ru(3)−Ru(2) = 60.16(1), Ru(2)−Ru(1)−Ru(3) = 59.38(1), Ru(2)−C(11)−Ru(3) = 84.9(2), Ru(2)−C(11)−O(11)= 137.1(3), Ru(3)−C(11)−O(11) = 137.9(3), N(1)−C(12)−N(3) = 123.2(4), C(12)−N(1)−C(13) = 118.8(4), C(12)−N(3)−C(14) = 119.6(4).

takes place to yield the amidino complex (μ-H)$Os_3(CO)_9$(μ_3,η^2-CH(NMe)$_2$) (**4**) in 61% yield (eq 2) after separation by TLC. It is obvious that thermal dissociation of a carbonyl ligand from $M_3(CO)_{12}$ is essential to initiating the reaction, and activation of the more robust Os−CO bond requires a higher temperature.[13] Thus, the acetonitrile-substituted labile cluster $Os_3(CO)_{11}(NCMe)$ reacts with $(MeNCH_2)_3$ facilely at room temperature to produce [(μ-H)$Os_3(CO)_{11}$][MeN(MeNCH$_2$)$_2$CH] (**3**) in 61% yield (eq 3). An alternative method is by slow addition of Me_3NO (to remove CO) into a mixture of $Os_3(CO)_{12}$ and $(MeNCH_2)_3$ at room temperature to afford **3** in 80% yield.



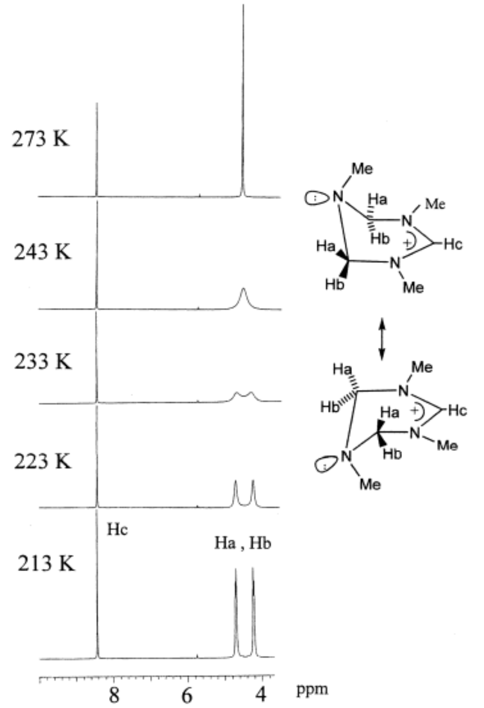


Figure 2. Variable-temperature 500 MHz ^1H NMR spectra for **2** in $(CD_3)_2CO$. Only the CH and CH_2 resonances of the [MeN(MeNCH$_2$)$_2$CH]$^+$ cation are displayed for comparison. The other resonance peaks are basically unchanged.

The molecular structure of **2**, illustrated in Figure 1, was determined by an X-ray diffraction study to evidence the formation of the [MeN(MeNCH$_2$)$_2$CH]$^+$ countercation. The cluster part closely resembles that previously determined for [(μ-H)$Ru_3(CO)_{11}$][PPN],[14] in which the dibridged Ru(2)−Ru(3) distance is slightly but significantly shorter than the other intermetallic distances. The carbonyl C(11)−O(11) bridges the Ru(2)−Ru(3) edge symmetrically, and the dihedral angle between the Ru(2)−C(11)−Ru(3) plane and the triruthenium plane is 102.04°. The [MeN(MeNCH$_2$)$_2$CH]$^+$ cation contains a planar amidinium segment (MeN)$_2$CH$^+$.[15] The N(1)−C(12) and N(3)−C(12) bond distances are 1.308(6) and 1.312(5) Å, respectively, which are ca. 0.1 Å shorter than the remaining N−C bond lengths, ranging from 1.430(6) to 1.476(6) Å. In addition, the C−N−C angles surrounding the N(1) and N(2) atoms are close to 120°, indicating a delocalized double bond over the N(1)−C(12)−N(3) backbone.

Compounds **1**−**3** form deep red crystals, which are only slightly air-sensitive, but they become much more sensitive to oxygen in solution. They dissolve in common polar solvents. Their ^1H and ^{13}C NMR data, as well as the IR spectra in the carbonyl region for the cluster part [(μ-H)$M_3(CO)_{11}$]$^-$, are in close agreement with those recorded in the literature.[1−3] The cation [MeN(MeNCH$_2$)$_2$CH]$^+$ is fluxional in solution. For example, the ^1H NMR spectrum of **2** at −60 °C shows a 1H singlet at δ 8.44 for the cationic C−H resonance, two 2H doublets ($J = 12$ Hz) at δ 4.67 and 4.22 for the CH_2 resonances, a 6H singlet at δ 3.25 and a 3H singlet at δ 2.57 for the CH_3 resonances, and a 1H singlet at δ −12.75 for the μ-H resonance. The CH_2 signals collapse at −40 °C and merge as a singlet above 0 °C (Figure 2). From the coalescence point at ca. 243 K, an approximate value of $\Delta G^\ddagger = 11$ kcal/mol for the ring flipping can be estimated.[16]

Compound **4** forms an air-stable, yellow crystalline solid. The ^1H NMR spectrum shows a 1H singlet at δ

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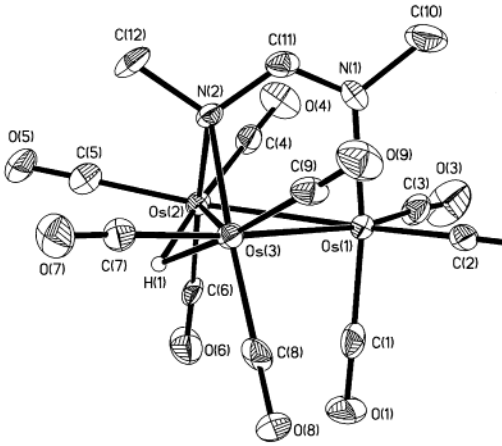
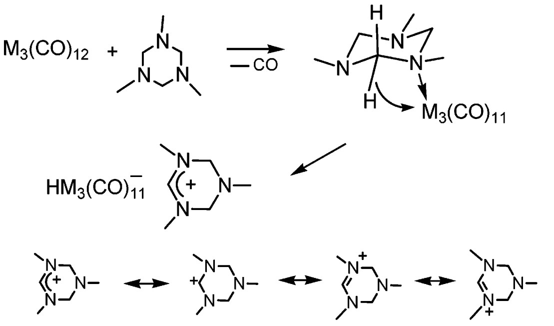


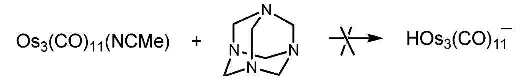
Figure 3. Molecular structure of **4**. Selected bond distances (Å): Os(1)−Os(2) = 2.7899(5), Os(1)−Os(3) = 2.7834(5), Os(2)−Os(3) = 2.7890(5), Os(1)−N(1) = 2.143(8), Os(2)−N(2) = 2.179(7), Os(3)−N(2) = 2.178(7), C(12)−N(2) = 1.49(1), C(11)−N(2) = 1.40(1), C(11)−N(1) = 1.28(1), C(10)−N(1) = 1.46(1). Selected bond angles (deg): Os(1)−Os(2)−Os(3) = 59.86(1), Os(1)−Os(3)−Os(2) = 60.09(1), Os(2)−Os(1)−Os(3) = 60.06(1), Os(2)−N(2)−Os(3) = 79.62(2), C(12)−N(2)−C(11) = 110.4(7), N(1)−C(11)−N(2) = 121.7(8), C(11)−N(1)−C(10) = 118.5(8).

Scheme 1



8.91, a 1H singlet at δ −11.04, and two 3H singlets at δ 3.40 and 3.24. Due to the absence of diagnostic spectral features to reveal the structure of **4**, an X-ray diffraction study was conducted. There are two independent but structurally similar molecules in the asymmetric unit, and one of these is illustrated in Figure 3. The molecule consists of a triangular cluster of three $Os(CO)_3$ units bridged by a hydrido and an amidino ligand on opposite sides of the Os_3 triangle.[17] The three Os−Os bond lengths are about equal, being 2.786 ± 0.003 Å. Each osmium atom is bonded to three terminal carbonyl groups with the Os−C−O angles ranging from 175.3(9)° to 179.2(9)°. The amidino group caps one Os_3 face and formally donates five electrons to the cluster, where the N(2) atom may be considered to act as a three-electron donor symmetrically spanning the Os(2)−Os(3) edge, with the average Os−N(2) distance of 2.18 Å, and the N(1) atom as a two-electron donor coordinated to the Os(1) atom with the distance of 2.143(8) Å. The geometry about the N(1) atom is essentially planar. The C(11)−N(1) length of 1.28(1) Å is characteristic of a C−N double bond, which is 0.12 Å shorter than the C(11)−N(2) length of 1.40(1) Å.

A plausible reaction mechanism to account for the formation of **1**−**3** is depicted in Scheme 1. It formally involves η^1-coordination of triazacyclohexane substituting for a CO (or NCMe) ligand, followed by β-hydride abstraction from a CH_2 group to generate the anionic hydrido cluster. The latter process is likely driven by formation of a stable $[MeN(MeNCH_2)_2CH]^+$ cation with charge delocalization over the planar (sp^2) N−C−N backbone. Since tetraazaadamantane is unable to form a planar $(CH_2N)_2CH^+$ segment, it is not surprising that tetraazaadamantane shows no reactions with $Os_3(CO)_{11}(NCMe)$ even at 80 °C (eq 4).



(4)

In conclusion, reaction of triazacyclohexane with $M_3(CO)_{12}$ of iron group metals represents a novel method for the synthesis of $[(\mu\text{-H})M_3(CO)_{11}]^-$. It is simple and convenient, and the pure solid salt is readily obtained. We are currently investigating whether this synthetic method can be extended to other metal carbonyl systems.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques.[18] The metal carbonyls were purchased from Strem or Aldrich. $Os_3(CO)_{11}(NCMe)$ was prepared by literature methods.[19] 1,3,5-Trimethyl-1,3,5-triazacyclohexane ($(MeNCH_2)_3$) (from TCI) was dried over 3 Å molecular sieves before use. Anhydrous trimethylamine *N*-oxide was obtained from $Me_3NO\cdot 2H_2O$ (98%, Aldrich) by sublimation at 110 °C under vacuum. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Kieselegel, DGF_{254}). ^1H and ^{13}C NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 and 125.7 MHz, respectively. Fast-atom-bombardment (FAB) mass spectra were recorded on a Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Thermal Reaction of $Fe_3(CO)_{12}$ and $(MeNCH_2)_3$. $Fe_3(CO)_{12}$ (100 mg, 0.20 mmol), $(MeNCH_2)_3$ (85 μL, 0.60 mmol), and freshly distilled *n*-hexane (5 mL) were placed in a Schlenk tube. The mixture was heated to reflux under dinitrogen for 30 min, at which point a deep red precipitate was produced, and the IR spectrum of the solution showed no absorptions due to the starting cluster. After cooling to room temperature, the supernatant was removed by a syringe, and the solid washed with *n*-hexane (3 × 1 mL). The product was dried under vacuum and then recrystallized from acetone/*n*-hexane at room temperature, affording deep red crystals of $[(\mu\text{-H})Fe_3(CO)_{11}][MeN(MeNCH_2)_2CH]$ (**1**; 97 mg, 80%). IR (CH_2Cl_2, νCO): 2064 (vw), 1992 (vs), 1974 (s), 1900 (sh), 1694 (w) cm^{-1}. ^1H NMR (CD_3COCD_3, −50 °C): δ 8.44 (s, 1H, CH), 4.70 (br, 2H, CH_2), 4.23 (br, 2H, CH_2), 3.27 (s, 6H, Me), 2.61 (s, 3H, Me), −15.02 (s, μ-H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 23 °C): δ 229.3 (br, CO), 154.5 (*C*H), 67.6 (N*C*H$_3$), 40.0 (*C*H$_2$, N*C*H$_3$).

An alternative method to prepare **1** is by stirring a suspension of $Fe_2(CO)_9$ (100 mg, 0.27 mmol) and $(MeNCH_2)_3$ (114 μL, 0.81 mmol) in *n*-hexane (7 mL) at room temperature for 3 h

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(17) An analogous complex $HOs_3(CO)_9(NPhC(Ph)NH)$ was prepared by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with amidine (NHPhC(Ph)=NH). Burgess, K.; Holden, H. D.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1983**, 1199.

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under dinitrogen. Compound **1** (54 mg, 49% based on Fe atom) was obtained after recrystallization from acetone/*n*-hexane.

Thermal Reaction of $Ru_3(CO)_{12}$ and $(MeNCH_2)_3$. $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol), $(MeNCH_2)_3$ (60 μL, 0.43 mmol), and freshly distilled *n*-hexane (5 mL) were refluxed under dinitrogen for 1 h, producing a deep red precipitate. The reaction was worked up in a fashion identical with that above. The product was recrystallized from CH_2Cl_2/*n*-hexane at room temperature to afford deep red crystals of $[(\mu\text{-H})Ru_3(CO)_{11}][MeN(MeNCH_2)_2CH]$ (**2**; 110 mg, 93%). Anal. Calcd for $C_{17}H_{15}N_3O_{11}Ru_3$: C 27.57, H 2.04, N 5.67. Found: C 27.43, H 2.17, N 5.72. MS (FAB): *m*/*z* 587 [$M^- - CO$, ^{102}Ru]. IR (THF, νCO): 2072 (vw), 2004 (vs), 1984 (s), 1956 (m), 1710 (w), 1690 (w) cm^{-1}. ^1H NMR (CD_3COCD_3, −90 °C): δ 8.44 (s, 1H, CH), 4.67 (d, 2H, $J = 12$ Hz, CH_2), 4.22 (d, 2H, $J = 12$ Hz, CH_2), 3.25 (s, 6H, Me), 2.57 (s, 3H, Me), −12.75 (s, μ-H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, −90 °C): δ 272.7 (μ-CO), 210.2, 209.3, 203.1, 203.0, 197.4, 192.9 (CO), 153.3 (*C*H), 66.2 ($=N\text{-}CH_3$), 39.6 (CH_2), 39.4 ($N\text{-}CH_3$).

Thermal Reaction of $Os_3(CO)_{12}$ and $(MeNCH_2)_3$. $Os_3(CO)_{12}$ (30 mg, 0.03 mmol), $(MeNCH_2)_3$ (14 μL, 0.1 mmol), and toluene (8 mL) were introduced into a Schlenk flask, and the mixture was heated to reflux for 4 h under dinitrogen. The solution was cooled to room temperature, and the solvent removed under vacuum. The residue was separated by TLC with an *n*-hexane/dichloromethane (4:1) eluant. Isolation of the material forming the third yellow-orange band afforded $(\mu\text{-H})Os_3(CO)_9(\mu_3,\eta^2\text{-}CH(NMe)_2)$ (**4**; 16 mg, 61%). Anal. Calcd for $C_{12}H_8N_2O_9Os_3$: C, 16.11; H, 0.90; N, 3.13. Found: C, 16.09; H, 0.97; N, 3.09. MS (FAB): *m*/*z* 900 (M^+, ^{192}Os). IR (hexane, νCO): 2084 (m), 2052 (s), 2020 (s), 1992 (s), 1978 (s), 1952 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ 8.91 (s, 1H, CH), 3.40 (s, 3H, Me), 3.24 (s, 3H, Me), −11.04 (s, μ-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 188.8, 181.8, 179.1, 178.5, 178.0 (CO), 181.0 (*C*H), 64.4, 51.4 (CH_3). The remaining minors bands were not characterized.

Reaction of $Os_3(CO)_{11}(NCMe)$ and $(MeNCH_2)_3$. $Os_3(CO)_{11}(NCMe)$ (30 mg, 0.033 mmol) was dissolved in CH_2Cl_2 (5 mL), and $(MeNCH_2)_3$ (14 μL, 0.1 mmol) was added. The mixture was stirred at room temperature for 30 min to yield a dark red solution, at which point the IR spectrum showed no absorptions due to the starting cluster. The volatile materials were removed under vacuum, and the residue was washed with *n*-hexane (3 × 1 mL) under dinitrogen. The product was recrystallized from acetone/*n*-hexane in a freezer to afford red crystals of $[(\mu\text{-H})Os_3(CO)_{11}][MeN(MeNCH_2)_2CH]$ (**3**; 20 mg, 61%). IR (CH_2Cl_2, νCO): 2040 (w), 2016 (s), 1988 (s), 1952 (m), 1690 (w), 1676 (w) cm^{-1}. ^1H NMR (CD_3COCD_3, 25 °C): δ 8.63 (s, 1H), 4.46 (s, 4H), 3.31 (s, 6H), 2.66 (s, 3H), −13.54 (s, 1H).

Reaction of $Os_3(CO)_{12}$ and $(MeNCH_2)_3$ in the Presence of Me_3NO. $Os_3(CO)_{12}$ (30 mg, 0.033 mmol), $(MeNCH_2)_3$ (28 μL, 0.2 mmol), and CH_2Cl_2 (20 mL) were placed in a Schlenk flask. A solution of Me_3NO (2.7 mg, 0.036 mmol) in CH_2Cl_2 (3 mL) was slowly introduced into the flask over a period of 1 h at room temperature, resulting in a deep red solution. The volatile materials were removed under vacuum, and the residue was washed with *n*-hexane (3 × 1 mL) under dinitrogen. The product was crystallized from acetone/*n*-hexane in a freezer to afford **3** (27 mg, 80%).

Table 1. Crystallographic Data for 2 and 4

	2	**4**
chem formula	$C_{17}H_{15}N_3O_{11}Ru_3$	$C_{12}H_8N_2O_9Os_3$
cryst syst	orthorhombic	triclinic
fw	740.53	894.80
space group	$P2_12_12_1$	$P\bar{1}$
a, Å	11.8166(1)	9.8983(3)
b, Å	11.9664(1)	12.7390(4)
c, Å	17.0426(2)	14.5342(5)
α, deg	90	88.345(1)
β, deg	90	89.073(1)
γ, deg	90	89.957(1)
V, Å^3	2409.86(4)	1831.7(1)
Z	4	4
D_{calc}, g cm^{-1}	2.041	3.245
μ, mm^{-1}	1.916	20.806
R_1/R_{w2}[a]	0.0287/0.0664	0.0399/0.0638
GOF on F^2	1.060	1.198

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma |F_o|$. $R_{w2} = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma w|F_o|^4\}\}^{1/2}$.

Structure Determination for 2 and 4. The crystals of **2** and **4** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on the Nonius KappaCCD and Bruker Smart ApexCCD diffractometers, respectively, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 2.08−27.50° for **2** and 1.40−27.50° for **4**. Of the 20 419 and 24 381 reflections collected for **2** and **4**, 5513 and 8403 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-squares cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package.[20] The data collection and refinement parameters are presented in Table 1. The space group $P2_12_12_1$ for **2** is noncentrosymmetric; thus, in the course of the final structure factor calculation the program calculates the Flack[21] absolute structure factor *x* and its esd. A comparison of *x* with its esd provides an indication as to whether the refined absolute structure is correct or whether it has to be “inverted”. The true value of *x* is close to zero.

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Supporting Information Available: Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters, bond angles, and bond distances of **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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