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Reactions of the Triosmium−Antimony Cluster $Os_3(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$ with Alkynes: C−C Bond Coupling to a Cluster-Bound Phenylene and Catalytic Alkyne Cyclotrimerization

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The reaction of the osmium−antimony cluster $Os_3(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$, **1**, with the terminal alkynes $PhC{\equiv}CH$ and $^tBuC{\equiv}CH$ led to products involving C−C bond coupling with the phenylene ligand on the cluster, viz., $Os_3(\mu\text{-}SbPh_2)(\mu,\eta^2\text{-}HC{=}C(H)Ph)(\mu\text{-}\eta^4\text{-}C_6H_4C(H)CPh)(CO)_7$, **2**, and $Os_5(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3,\eta^3\text{-}C_6H_4)(\mu,\eta^2\text{-}PhC{=}C(H)Bu^t)(CO)_{14}$, **4**. Cluster **1** was also found to be an effective catalyst for the cyclotrimerization of diphenylacetylene to hexaphenylbenzene.

Introduction

One of the reasons for the study of organometallic clusters is their potential as catalysts because of the possibility of synergism among the metal centers.[1] This has resulted in a relatively vast amount of work on the reaction of clusters with organic molecules. In particular, alkynes have generated a lot of interest, as they have been shown to be very reactive with organometallic clusters and they offer a variety of bonding interactions with the metal centers.[2,3] One of the goals in our studies on organometallic clusters has been to investigate the interaction of cluster-bound ligands with other substrates. A particular cluster-bound ligand of interest to us is phenylene (or benzyne). This ligand has been demonstrated to have interesting properties and reactivities. Thus it undergoes exchange of the aryne hydrogens with metal hydrides,[4] can be acylated or alkylated,[5] and can undergo CO insertion reactions.[6] We were interested in examining the possibility of C−C bond coupling reactions involving the phenylene ligand on the cluster $Os_3(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$, **1**.[7] In this paper, we wish to report our investigations on the reactions of **1** with alkynes.

Results and Discussion

The reaction of **1** with PhCCH at 70 °C over 15 h afforded an orange solution from which the major product $Os_3(CO)_7(\mu\text{-}SbPh_2)(\mu,\eta^2{:}\eta^4\text{-}PhC{=}C(H)C_6H_4)(\mu,\eta^1{:}\eta^2\text{-}CH{=}C(H)Ph)$, **2**, was isolated in 65% yield. The molecular structure of **2** is shown in Figure 1, together with selected bond parameters. The molecular structure of **2** reveals that coupling of two alkyne molecules with **1** has occurred, giving rise to two discrete hydrocarbyl ligands. A salient structural feature is the direct coupling of the C_6H_4 phenylene ring with one of the phenylacetylene molecules. The resulting ligand is coordinated in a $\mu,\eta^2{:}\eta^4$ fashion to the Os(2)−Os(3) edge, via an η^2 mode to Os(2) and an η^4 mode to Os(3). The second hydrocarbyl fragment is derived from a second phenylacetylene molecule which has inserted into the osmium−hydride linkage to give a three-electron-donating vinyl $\mu,\eta^1{:}\eta^2\text{-}CH{=}C(H)Ph$ unit; this bonding mode has been encountered, for example, in $Os_3(\mu\text{-}H)(CO)_{10}(\mu_3,\eta^3\text{-}CHCPhCH)$ and $Os_3(CO)_8(\mu_3,\eta^3\text{-}CHCPhCH)(\mu,\eta^2\text{-}PhCCH_2)$.[8,9]

An assignment of the nonphenyl ^1H NMR signals of complex **2** has been made with the aid of two-dimensional homonuclear correlation spectroscopy (COSY) and rotation frame Overhauser enhancement spectroscopy (ROESY). The singlet at δ 7.95 is assigned to the proton H_c (Figure 2); it exhibits the characteristic low-field resonance shift of coordinated alkenyls.[3] The resonances at δ 6.27 and 6.01 are assigned to the two vinyl protons, H_a and H_b, respectively; H_b should exhibit a lower field resonance shift because of deshielding from the neighboring phenyl ring. The resonances from the C_6H_4 moiety are assigned on the basis of their multiplicities and the observation of strong NOE between H_c and H_d, and H_a and H_g, respectively; these are consis-

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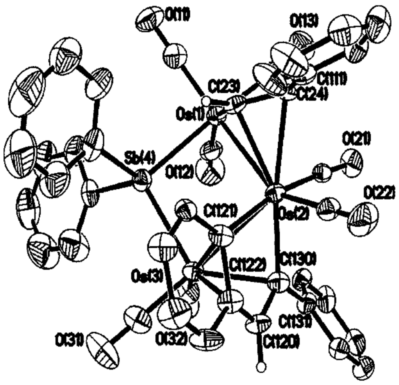

Figure 1. ORTEP plot of **2** (50% thermal ellipsoids; aromatic hydrogens omitted): Os(1)Os(2) 2.9863(4) Å; Os(2)Os(3) 2.8569(4) Å; Os(1)Sb(4) 2.6408(5) Å; Os(3)Sb(4) 2.5902(5) Å; Os(1)C(23) 2.107(7) Å; Os(2)C(23) 2.267(6) Å; Os(2)C(24) 2.377(6) Å; Os(2)C(121) 2.208(6) Å; Os(2)C(130) 2.120(7) Å; Os(3)C(120) 2.252(7) Å; Os(3)C(121) 2.294(6) Å; Os(3)C(122) 2.366(7) Å; Os(3)C(130) 2.258(7) Å; C(23)C(24) 1.395(9) Å; C(120)C(122) 1.434(10) Å; C(120)C(130) 1.409(9) Å; Os(3)Os(2)Os(1) 83.780(10)°; Os(3)Sb(4)Os(1) 96.498(17)°; Sb(4)Os(1)Os(2) 82.360(13)°; Sb(4)Os(3)Os(2) 85.830(13)°.

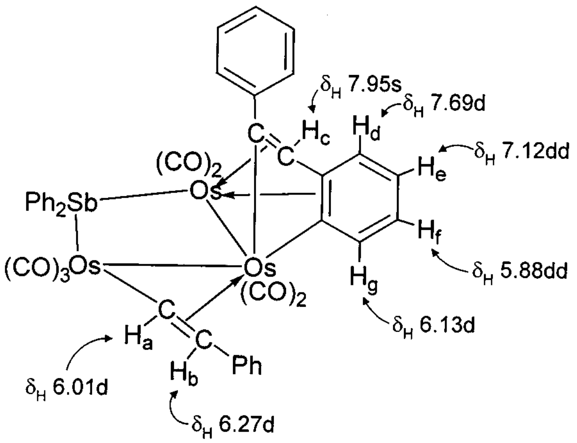

Figure 2. ^{1}H NMR assignment for non-phenyl hydrogens of **2**.

tent with the distances ($H_c\cdots H_d$ = 2.65 Å and $H_a\cdots H_g$ = 2.17 Å) observed in the X-ray crystal structure.

The reaction of **1** with ^{t}BuCCH at 80 °C afforded two orange clusters, $Os_3(\mu\text{-}SbPh_2)[\mu_3,\eta^2\text{-}C{\equiv}CBu^t](CO)_9$, **3**, and minor amounts of the novel cluster $Os_5(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Bu^t)(\mu,\eta^3\text{-}C_6H_4)(CO)_{14}$, **4**. Both were characterized completely, including by single-crystal X-ray crystallography. The ORTEP diagrams showing the molecular structures of **3** and **4**, together with selected bond distances and bond angles, are given below (Figures 3 and 4, respectively). In **3**, the C_6H_4 ring of **1** has been replaced by a ^{t}BuCC group. The acetylenic ligand is considered to be coordinated to the metallic cluster as a five-electron donor via a $\mu_3,\eta^1{:}\eta^2{:}\eta^2$-bonding mode. Such a bonding mode has been observed in similar complexes such as $Os_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}C_2Bu^t)(CO)_9$.[10] The C(1)−C(2) acetylenic bond length (1.339(10) Å) is between that for an sp−sp double and single bond (1.28 and 1.38 Å, respectively)[11] and lies beyond the more “activated” end of the range (1.27−1.32 Å) that has been observed for a number of such group 8 alkyne clusters.[3]

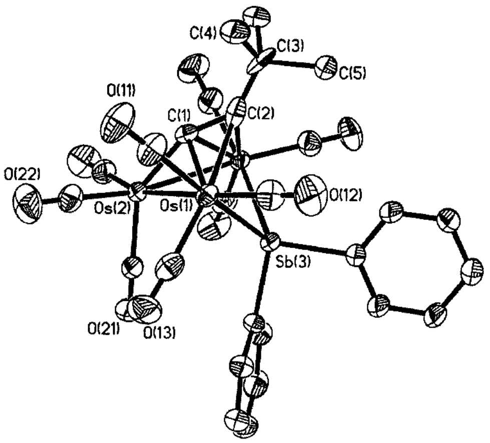

Figure 3. ORTEP plot of **3** (50% thermal ellipsoids; hydrogens omitted): Os(1)Os(2) 2.8945(3) Å; Os(1)Sb(3) 2.6598(4) Å; Os(1)C(1) 2.283(4) Å; Os(1)C(2) 2.422(6) Å; Os(2)C(1) 1.967(7) Å; C(1)C(2) 1.339(10) Å; C(2)C(3) 1.391(12) Å; Os(1)Os(2)Os(1′) 77.835(10)°; Sb(3)Os(1)Os(2) 78.511(10)°.

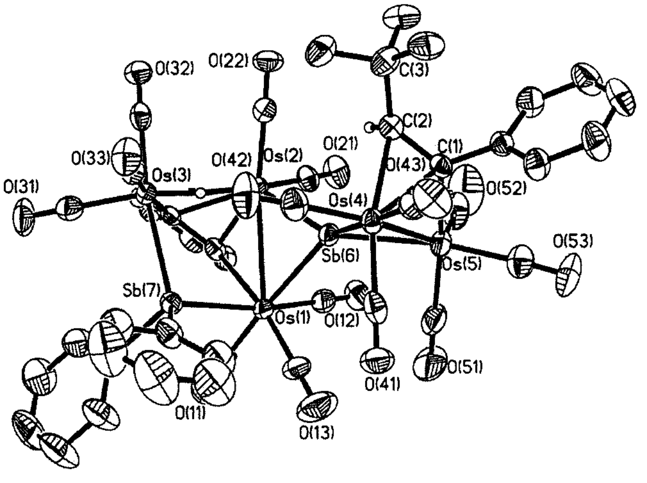

Figure 4. ORTEP plot of **4** (50% thermal ellipsoids; organic hydrogens omitted): Os(1)Os(2) 2.9393(4) Å; Os(2)Os(3) 2.9371(4) Å; Os(4)Os(5) 2.8688(4) Å; Os(1)Sb(6) 2.7805(5) Å; Os(2)Sb(6) 2.5812(5) Å; Os(4)Sb(6) 2.6726(5) Å; Os(5)Sb(6) 2.6390(5) Å; Os(1)Sb(7) 2.6846(5) Å; Os(3)Sb(7) 2.6527(5) Å; C(1)C(2) 1.421(9) Å; C(2)C(3) 1.561(10) Å; Os(3)Os(2)Os(1) 88.039(10)°; Sb(7)Os(1)Os(2) 84.541(13)°; Sb(6)Os(1)Os(2) 53.564(11)°; Sb(6)Os(2)Os(1) 60.069(13)°; Sb(7)Os(3)Os(2) 85.147(13)°; Sb(6)Os(4)Os(5) 56.746(12)°; C(1)C(2)C(3) 131.1(6)°.

The metal core of **4** consists of a closed triosmium unit linked by a μ_4-Sb atom to a diosmium unit. The ^{1}H NMR spectrum shows a singlet resonance at −14.25 ppm, which is indicative of a bridging metal hydride. Although not located directly in the electron density difference map, potential energy calculations suggest that it bridges the Os(2)−Os(3) edge.[12] As may be expected, the C(1)−C(2) bond length (1.421(9) Å) is between the ranges of carbon−carbon $sp^2{-}sp^2$ double and single bonds (1.32 and 1.48 Å, respectively).[11]

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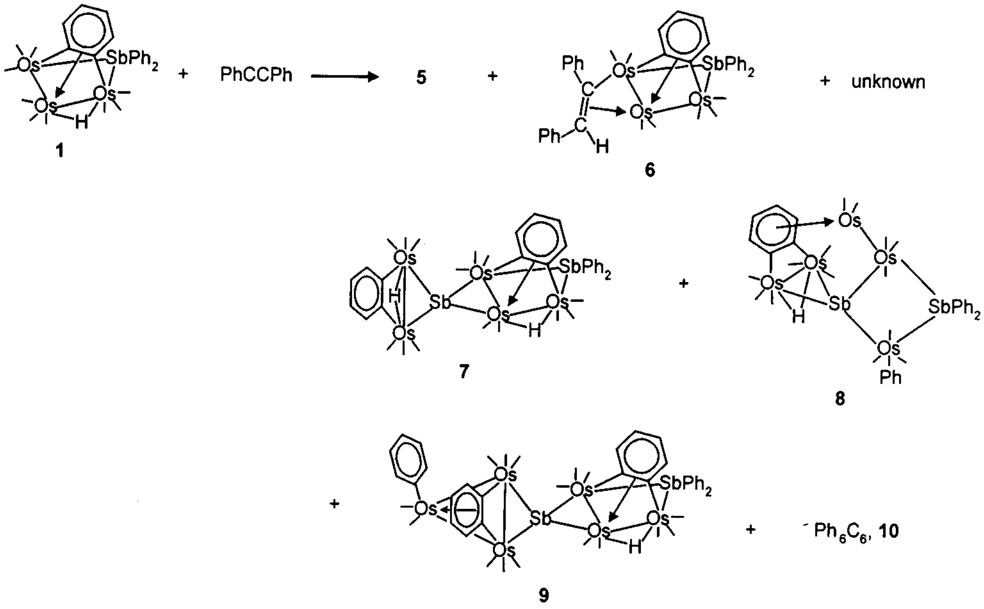
Scheme 1. Reaction of 1 with PhCCPh[a]



[a] Percent yields for clusters calculated with respect to amount of **1** used.

Table 1. Cyclotrimerization Reactions of PhCCPh

run no.	cluster	amt of PhCCPh	temp (°C)	yield of 10	TON[a]
1	**1** (8.2 mg, 7.0 μmol)	85.2 mg, 478 μmol	70	5.9 mg, 6.9%	1.6
2	**1** (13.0 mg, 11.0 μmol)	61.8 mg, 347 μmol	100	8.6 mg, 14%	1.5
3	**5** (12.7 mg, 11.0 μmol)	62.6 mg, 351 μmol	100	3.2 mg, 5.1%	0.5
4	**1** (11.8 mg, 10.0 μmol)	44.0 mg, 247 μmol	150	38.5 mg, 88%	7.2
5	**5** (8.2 mg, 9.0 μmol)	52.8 mg, 296 μmol	150	7.0 mg, 13%	1.5

[a] TON (catalytic turnover number) = moles of product/moles of catalyst.

Cluster **4** is structurally very similar to $Os_5(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}C_6H_4)(\mu,\eta^2\text{-}C_6H_4)(CO)_{14}$, **7**, which has been observed in the reaction of **1** with alkenes and dienes[13] and with diphenylacetylene (see later). The main structural difference is the replacement of the bridging phenylene and hydride in **7** by the $\mu,\eta^1{:}\eta^2$ vinylic group in **4**, which has resulted in a shorter Os(4)−Os(5) distance in **4** (2.8688(4) Å) compared to that in **7** (3.0305(5) Å). Given the structural similarities between **4** and **7**, it is conceivable that **7** may have been the precursor to **4**. This would have required deorthometalation of the phenylene ring on the diosmium unit as well as insertion of the alkyne into the resultant Os−Ph bond. However, on heating **7** and ^{t}BuCCH at 100 °C, monitoring by IR spectroscopy showed that there was no reaction even after 15 h. On the other hand, heating **4** alone at 100 °C led to decomposition to some unidentified products.

The reaction of **1** with an equimolar amount of PhCCPh at 90 °C in a Carius tube afforded a dark red solution that, upon separation by TLC, afforded (besides unconsumed **1**) six cluster products and hexaphenylbenzene, **10** (Scheme 1). All the cluster products have been identified, except for the unknown red compound that eluted as band 4. This was separable from **6** only after repeated TLC with hexane as eluant. The mass spectrum of this product showed a cluster of peaks at *m/z* 1864; on standing for several days, a new cluster of peaks centered at *m/z* 1330 corresponding to **6** appeared. Thus band 4 seemed to decompose slowly to **6**.

The cyclotrimerization of alkynes to form highly substituted benzenes is an intriguing reaction that has continued to be of interest. Although phenylene-containing clusters have been recently reported to be efficient catalysts for alkyne hydrogenation,[14] this is the first instance that we are aware of in which this class of clusters catalyzes alkyne cyclotrimerization. A large variety of organometallic compounds have been reported to catalyze this reaction,[15] but relatively few cluster catalysts are known and even then it is often not clear whether the catalytically active species is indeed a cluster.[16] Among cluster compounds of the group 8 elements, $Fe_3(CO)_{12}$ has been found to be a good catalyst for the cyclotrimerization of PhCCPh to Ph_6C_6.[16a] It has also been shown that $Os_3(CO)_{12}$, **5**, catalyzes the same

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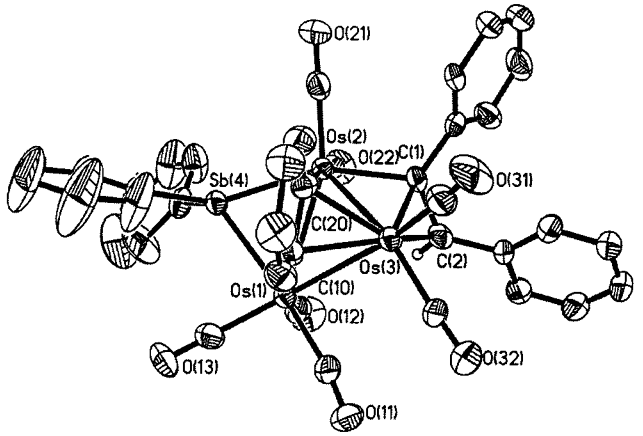

Figure 5. ORTEP plot of **6** (50% thermal ellipsoids; aromatic hydrogens omitted): Os(1)−Os(2) 2.9983(4) Å; Os(1)Os(3) 2.8873(4) Å; Os(2)Os(3) 2.6401(4) Å; Os(1)Sb(4) 2.6957(5) Å; Os(2)Sb(4) 2.5855(5) Å; Os(1)C(10) 2.150(7) Å; Os(2)C(1) 2.149(6) Å; Os(2)C(20) 2.165(7) Å; Os(3)C(1) 2.137(6) Å; Os(3)C(2) 2.240(7) Å; Os(3)C(10) 2.269(6) Å; Os(3)C(20) 2.263(7) Å; C(1)C(2) 1.443(10) Å; C(10)C(20) 1.420(9) Å; Os(1)Os(3)Os(2) 65.521(10)°; Os(3)Os(2)Os(1) 61.216(9)°; Os(3)Os(1)Os(2) 53.263(9)°; Os(2)Sb(4)Os(1) 69.147(14)°.

reaction,[17] and much of the reaction sequence has been worked out.[18] In contrast, $Ru_3(CO)_9(NCCH_3)_3$ reacted with disubstituted alkynes to yield $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6R_3R'_3)$ complexes, which decomposed to yield the free substituted benzene on heating.[19]

Although **5** has been shown to be an effective agent for the cyclotrimerization of diphenylacetylene, no data on the catalytic efficiency was reported. We have therefore investigated this reaction at different temperatures and substrate:catalyst ratio, for both **1** and **5** (Table 1). Under similar conditions, **1** is a more efficient catalyst than **5** for the cyclotrimerization. We have also found that **6** reacted with PhCCPh to afford **10**; it may therefore be an intermediate in the catalytic cycle. This is of significance, as it would support the notion that the active catalyst is a cluster species. In contrast, **7** failed to react with PhCCPh under similar conditions, and the reaction with **8** led to other products but no **10**. Both **7** and **8** have earlier been observed as products from the reactions of **1** with a number of alkenes and dienes, suggesting that they are the result of ligand-assisted cluster condensation.[13] Cluster **9** has been shown in our earlier work to result from the thermolytic decomposition of **1** itself;[7] we have found that it does react with PhCCPh to afford **10**, albeit in very low yield (∼1% after 14 1/2 h at 100 °C), thus suggesting that it is probably not directly involved in the catalytic cycle.

The molecular structure of **6** and selected bond parameters are shown in Figure 5. It may be formally derived from **1** by the replacement of two terminal carbonyls and a hydride by the three-electron donor $\mu\text{-}\eta^2\text{-PhC=C(H)Ph}$ ligand (a σ,π-vinyl system) and formation of an Os−Os bond. The C(1)−C(2) length for the $\mu\text{-}\eta^2\text{-PhC=C(H)Ph}$ ligand (1.443(10) Å) is closer to that of an sp^2-sp^2 single bond length and suggests that the C(1)−C(2) bond has a much reduced multiple-bond character. The most significant feature is the very short Os(2)−Os(3) bond, which, at 2.6401(4) Å, is the shortest Os−Os bond length observed to date for a triosmium cluster. This bond shortening is similar to that in $Os_3(\mu,\eta^2\text{-CPhCHPh})(\mu,\eta^3\text{-}C_3Ph_3)(CO)_8$, in which the Os−Os bridged by a $\mu,\eta^2\text{-PhC=C(H)Ph}$ ligand is also shortened to 2.694(2) Å.[20] These distances are significantly below the range of Os−Os distances (2.814−2.834 Å) found for a number of other triosmium clusters in which an Os−Os edge is bridged by an $\mu\text{-}\eta^2$-alkenyl ligand and a hydride.[8,21]

That the reaction of **1** with diphenylacetylene apparently did not afford C−C coupled products involving the cluster-bound phenylene is consistent with the observation made earlier on the related cluster $Os_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9$.[22] The contrasting behavior with the terminal alkynes is interesting and suggests that the acetylenic hydrogen may have a role in effecting C−C coupling with the phenylene; work is currently underway to determine what this role is.

In conclusion, we have found that the osmium−antimony cluster **1** is an effective catalyst for the cyclotrimerization of diphenylacetylene to hexaphenylbenzene. In contrast, its reactions with terminal alkynes led to cluster products with C−C bond formation involving the phenylene ligand.

Experimental Section

General Procedures. All reactions and manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were purified, dried, distilled, and kept under nitrogen prior to use. NMR spectra were recorded on a Bruker ACF 300 MHz NMR spectrometer; 2D experiments were carried out on a Bruker ACF500 MHz NMR spectrometer. EI-MS spectra were acquired on a Micromass VG7035 mass spectrometer. Elemental analyses were carried out by the microanalytical laboratory at the National University of Singapore. Cluster **1** was prepared by the literature method;[7] all other reagents were from commercial sources and used as supplied.

Reaction of 1 with PhCCH. To a Carius tube containing **1** (20.8 mg, 0.018 mmol) and dichloromethane (10 mL) was added PhCCH (10.2 mg, 0.100 mmol). After stirring at 70 °C for 15 h, the color of the solution changed from yellow to orange. Solvent was removed on the vacuum line, and the residue so obtained was redissolved in the minimum volume of dichloromethane and chromatographed on silica TLC plates. Elution with hexane gave unreacted **1** (5.3 mg) and yellow crystals of $Os_3(\mu\text{-SbPh}_2)(\mu,\eta^2\text{-HC=C(H)Ph})(\mu\text{-}\eta^4\text{-}C_6H_4C(H)CPh)(CO)_7$, **2**. Yield = 11.3 mg, 48%. IR (hexane) ν(CO): 2062s, 2023m, 2014vs, 1993w, 1977m, 1956m cm^{-1}. ^{1}H NMR: δ 7.95 (s, 1H), 7.69 (d, 1H), 7.1−7.5 (m, Ph), 7.12 (dd, $^3J_{HH}$ = 9.0 Hz),

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Table 2. Crystal Data for 2, 3, 4, and 6

	2	3	4	6
empirical formula	$C_{41}H_{27}O_7Os_3Sb\cdot 1/2CH_2Cl_2$	$C_{27}H_{19}O_9Os_3Sb$	$C_{44}H_{30}O_{14}Os_5Sb_2$	$C_{39}H_{25}O_7Os_3Sb\cdot 1/4C_6H_{14}$
fw	1366.44	1179.77	1977.18	1319.48
temp, K	223(2)	223(2)	193(2)	223(2)
cryst syst	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$	*Pnma*	*C*2/*c*	$P\bar{1}$
a, Å	9.2354(1)	20.1830(4)	33.7108(12)	9.3913(1)
b, Å	10.0936(2)	13.1745(3)	13.9251(5)	13.5210(1)
c, Å	22.8557(4)	11.1624(2)	21.0185(7)	16.7683(2)
α, deg	101.084(1)	90	90	82.149(1)
β, deg	97.728(1)	90	95.791(1)	85.300(1)
γ, deg	97.503(1)	90	90	72.680(1)
volume, Å^3	2044.86(6)	2968.09(10)	9816.3(6)	2011.72(4)
Z	2	4	8	2
density (calcd), Mg/m^3	2.219	2.640	2.676	2.178
abs coeff, mm^{-1}	10.056	13.751	14.035	10.154
F(000)	1258	2128	7104	1213
cryst size, mm^3	0.28 × 0.07 × 0.05	0.26 × 0.20 × 0.07	0.20 × 0.10 × 0.08	0.30 × 0.20 × 0.10
θ range for data collection, deg	2.08 to 29.32	2.02 to 31.67	2.19 to 31.03	2.12 to 29.08
index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $0 \le l \le 30$	$0 \le h \le 28$, $0 \le k \le 18$, $0 \le l \le 16$	$-47 \le h \le 47$, $0 \le k \le 19$, $0 \le l \le 29$	$-12 \le h \le 12$, $-17 \le k \le 18$, $0 \le l \le 22$
no. of reflns collected	17 316	27 535	86 839	15 383
no. of ind reflns	9695 [*R*(int) = 0.0346]	4904 [*R*(int) = 0.0742]	15176 [*R*(int) = 0.0442]	9442 [*R*(int) = 0.0332]
max. and min. transmn	0.603955 and 0.337559	0.382469 and 0.129349	0.381768 and 0.247246	0.263869 and 0.134745
no. of data/restraints/ params	9695/6/513	4904/0/206	15176/0/590	9442/0/463
goodness-of-fit on F^2	1.056	1.001	0.790	1.048
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0369, wR2 = 0.0735	R1 = 0.0334, wR2 = 0.0710	R1 = 0.0367, wR2 = 0.0634	R1 = 0.0376, wR2 = 0.0893
R indices (all data)	R1 = 0.0556, wR2 = 0.0808	R1 = 0.0437, wR2 = 0.0735	R1 = 0.0658, wR2 = 0.0685	R1 = 0.0524, wR2 = 0.0967
largest diff peak and hole, e Å^{-3}	1.304 and −1.202	1.735 and −1.778	2.749 and −1.285	1.593 and −2.369

6.27 (d, 1H), 6.13 (d, 1H), 6.01 (d, 1H, $^3J_{HH}$ = 14.0 Hz), 5.88 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 9.0 Hz). Anal. Calcd for $C_{41}H_{27}O_7Os_3Sb$: C, 37.19; H, 2.06. Found: C, 37.06; H, 2.21. Presence of dichloromethane in the crystalline samples used for the X-ray diffraction study was confirmed by ^1H NMR.

Reaction of 1 with ^tBuCCH. To a Carius tube containing **1** (56.2 mg, 0.048 mmol) and dichloromethane (10 mL) was added ^tBuCCH (4.1 mg, 0.05 mmol). After stirring at 80 °C for 15 h, the color of the solution changed from yellow to red. Solvent was removed on the vacuum line, and the residue so obtained was redissolved in the minimum volume of dichloromethane and chromatographed on TLC plates. Elution with hexane/CH_2Cl_2 (4:1, v/v) gave unreacted **1** (12.5 mg) and two novel clusters, viz., $Os_3(\mu\text{-}SbPh_2)(\mu_3,\eta^2\text{-}C{\equiv}CBu^t)(CO)_9$, **3** (21.2 mg, 37%), and $Os_5(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3,\eta^3\text{-}C_6H_4)(\mu,\eta^2\text{-}PhC{=}C(H)Bu^t)(CO)_{14}$, **4** (6.8 mg, 14%), as orange crystalline solids.

3: IR (hexane) ν(CO): 2085w, 2060vs, 2044m, 2020vw, 2004s, 1991mw, 1983w, and 1973w cm^{-1}. ^1H NMR: δ 7.6−6.9 (m, aromatic), 1.67 (s, ^tBu). Anal. Calcd for $C_{27}H_{19}O_9Os_3Sb$: C, 27.48; H, 1.62. Found: C, 27.65; H, 1.50.

4: IR (hexane) ν(CO): 2094w, 2084s, 2064w, 2057m, 2039vs, 2027m, 2006w, 1984m, 1970w, 1957w cm^{-1}. ^1H NMR: δ −14.25 (s, 1H, OsHOs). Anal. Calcd for $C_{44}H_{30}O_{14}Os_5Sb_2$: C, 26.73; H, 1.53. Found: C, 26.84; H, 1.75.

Reaction of 1 with PhCCPh. To a Carius tube containing **1** (61.7 mg, 0.053 mmol) and PhCCPh (10.7 mg, 0.060 mmol) was added dichloromethane (10 mL), and the reaction mixture degassed by three freeze−pump−thaw cycles. After stirring for 15 h at 90 °C, the color of the solution changed to dark red. The solvent was removed on the vacuum line, and the residue obtained was redissolved in the minimum volume of dichloromethane and chromatographed on TLC plates. Elution with hexane gave eight bands. The first two bands were identified from their IR spectra as **5** (2.8 mg, 5.8%) and unreacted **1** (15.6 mg), respectively.

Band 3 gave orange crystals of $Os_3(\mu\text{-}SbPh_2)(\mu_3,\eta^2\text{-}C_6H_4)(\mu\text{-}PhC{=}C(H)Ph)(CO)_7$, **6**. Yield = 11.2 mg, 16%. IR (hexane) ν(CO): 2078w, 2054m, 2020sh, 1985m, 1963m cm^{-1}. ^1H NMR: δ 8.4−6.5 (m, aromatic), 6.44 (s, CH). Anal. Calcd for $C_{39}H_{25}O_7Os_3Sb\cdot 1/2C_6H_{14}$: C, 37.61; H, 2.40. Found: C, 37.31; H, 2.58. Presence of the hexane solvent of crystallization was confirmed by ^1H NMR spectroscopy.

Band 4 was a red unstable product. Yield = 12.5 mg. IR (hexane) ν(CO): 2065w, 2053m, 2022sh, 2009sh, 1992m, 1963m cm^{-1}. Bands 5, 6, and 7 were identified by the IR and ^1H NMR spectra as the previously reported clusters $Os_5(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}C_6H_4)(\mu,\eta^2\text{-}C_6H_4)(CO)_{14}$, **7** (10.8 mg, 22%), $Os_5(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3,\eta^6\text{-}C_6H_4)(C_6H_5)(CO)_{14}$, **8** (2.0 mg, 4%), and $Os_6(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(\mu_3,\eta^2\text{-}C_6H_4)_2(C_6H_5)(CO)_{16}$, **9** (3.6 mg, 6%), respectively.

Band 8 gave colorless crystals of C_6Ph_6, **10**. Yield = 2.6 mg, 73%. ^1H NMR: δ 6.9−6.8 (m, Ph). MS (EI, 70 eV): *m*/*z* 534.1 (M$^+$), 457.2 ([M − Ph]$^+$), 379.1 ([M − 2Ph]$^+$), 302.0 ([M − 3Ph]$^+$), 231.0 ([M − 4Ph]$^+$). X-ray crystal data: space group *Pna*2$_1$, *a* = 12.1347(11) Å, *b* = 11.7679(11) Å, *c* = 20.6828(19) Å.[23]

Cyclotrimerization Reaction of PhC≡CPh. In a typical reaction, the cluster **1** or **5** and PhCCPh were placed in a Carius tube with hexane (10 mL), degassed by three freeze−pump−thaw cycles, and heated for 15 h. The precipitate obtained was washed with hexane and weighed. For heating at 150 °C, the reaction mixture was placed in a 43 mL capacity autoclave under a stream of nitrogen.

Crystal Structure Determination of 2, 3, 4, and 6. The crystals were grown by slow cooling of CH_2Cl_2/hexane solutions and were mounted onto glass fibers. Crystal data and structure refinement details are given in Table 2. The intensities were measured on a Siemens SMART diffractometer, equipped with

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[23] Bart, J. C. J. *Acta Crystallogr., Sect. B* **1968**, *24*, 1277.

a CCD detector, using Mo Kα radiation ($\lambda = 0.71073$ Å) at 223(2) K (193(2) K for **3**). The data were corrected for Lorentz and polarization effects with the SMART suite of programs,[24] and for absorption effects with SADABS.[25] The final unit cell parameters were obtained by least squares on 8192 (**2** and **6**), 7435 (**3**), or 8016 (**4**) strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs.[26] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All the organic hydrogen atoms were placed in calculated positions. The position of the metal hydride in **4** was located in a low-angle difference map and was refined. A partial molecule of hexane in **6** was located on a crystallographic center of symmetry and modeled isotropically; it was given an occupancy of 0.25. The crystal of **2** contained half a CH_2Cl_2 molecule that was disordered; this was modeled with two sites of equal occupancy, the C−Cl bonds were restrained to be equal and the carbon atoms were given a common isotropic thermal parameter. All non-hydrogen atoms of the main molecules were given anisotropic displacement parameters in the final refinement. Refinements were on $\sum[w(F_o^2 - F_c^2)^2]$. Atomic coordinates are given in the Supporting Information.

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Supporting Information Available: Experimental and refinement details for the crystallographic studies, tables of crystal data and structure refinement, atomic coordinates, isotropic and anisotropic thermal parameters, complete bond parameters, and hydrogen coordinates. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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