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Oxidative addition across Sb-H and Sb-Sb bonds by an osmium carbonyl cluster: Trapping the intermediate

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ABSTRACT: The cluster $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ oxidatively adds across the Sb-H bond in SbPh_2H to afford the clusters $\text{Os}_3(\text{CO})_{11}(\text{H})(\mu\text{-SbPh}_2)$ and $\text{Os}_3(\text{CO})_{11}(\mu\text{-H})(\mu\text{-SbPh}_2)\text{Os}_3(\text{CO})_{11}$. Similarly, its reaction with Sb_2Ph_4 afforded $\text{Os}_3(\text{CO})_{11}(\mu\text{-SbPh}_2)_2\text{Os}_3(\text{CO})_{11}$ as the major product. In both cases, the intermediate from the oxidative addition reaction was trapped as a $\text{W}(\text{CO})_5$ adduct.

Introduction

Organometallic clusters containing both main group and transition metals are of interest because of their distinctive structural and reactivity patterns which are quite unlike those of their homometallic main group or transition metal cluster analogues. Over the last 18 years, we have focused on the preparation and reactivity studies of osmium-antimony clusters. The choice of osmium rests on its strong metal-metal bond, making it one of the most prolific cluster-forming elements. For example, osmium forms the most number of neutral binary carbonyls, which now include $\text{Os}(\text{CO})_5$, $\text{Os}_2(\text{CO})_9$, $\text{Os}_3(\text{CO})_{12}$, $\text{Os}_4(\text{CO})_x$ ($x = 14, 15, 16$), $\text{Os}_5(\text{CO})_y$ ($y = 16, 18, 19$), $\text{Os}_6(\text{CO})_z$ ($z = 18, 21$), $\text{Os}_7(\text{CO})_{21}$, $\text{Os}_8(\text{CO})_{23}$ and $\text{Os}_{10}(\text{CO})_{26}$.¹ Osmium-antimony clusters have been found to exhibit distinctive reactivity, which are quite different from those of its lighter congeners. For example, $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-SbPh}_2)$, first prepared from a salt elimination reaction between $[\text{HOs}_3(\text{CO})_{11}]^-$ and SbPh_2Cl ,² readily undergoes nucleophilic addition reactions via Os-Os bond cleavage,³ and Sb-C bond cleavage and orthometallation on thermolysis.⁴ The thermolyses of $\text{Os}_3(\text{CO})_{11}(\text{SbPh}_3)$,⁵ and $\text{Os}_3(\text{CO})_{11}(\text{SbMe}_2\text{Ar})$,⁶ also followed very different pathways from their phosphine and arsine analogues.

In contrast to the large number of known cluster compounds of osmium containing the lighter congeners of Group 15, *viz.*, N, P and As, those containing the heavier congeners Sb or Bi are scarce, and even less is known of their reactivity. This is due largely to the relatively difficult syntheses of the ligands (for Sb(III), only the trihalides SbX_3 , $\text{X} = \text{Cl}, \text{Br}$ or I , and SbPh_3 are available commercially), the usually low yields of reactions, and the lack of predictability for thermolytic reactions. The exploration of new, facile syntheses of osmium-antimony carbonyl clusters, especially the higher nuclearity clusters, under mild conditions remains a challenge.

An attractive possibility that has come to our attention is based on reports that the activated osmium cluster $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$, **1**, readily reacted with PPh_2H or AsMe_2H to give $\text{Os}_3(\text{CO})_{11}(\text{PPh}_2\text{H})$,⁷ or $\text{Os}_3(\text{CO})_{11}(\text{H})(\mu\text{-AsMe}_2)$,⁸ respectively, in high yields under am-

bient conditions. It is thus reasonable to expect that **1** may react similarly with SbPh_2H . Similarly, the distibine Sb_2Ph_4 may also be expected to serve as a potential source for the “ SbPh_2 ” moiety through cleavage of the weak Sb-Sb bond.⁹ Examples of the latter acting as ligands, with the Sb-Sb bond remaining intact, has also been reported however.¹⁰ We wish to report here our work on the oxidative addition of **1** with these two substrates as a synthetic route to new osmium-antimony carbonyl clusters, and the trapping of the intermediates of the reactions.

Results and discussion

The literature method for the preparation of the secondary stibine SbPh_2H was by the reduction of SbPh_2Cl with LiAlH_4 at -78°C followed by a vacuum distillation, to afford it as a colorless, air-sensitive oil.¹¹ To simplify the procedure, we have re-optimized the reaction conditions so that it could be carried out at room temperature and the product obtained by extraction with dry hexane and kept as such, thus avoiding distillation and hence decomposition. The ^1H NMR spectrum of this solution indicated that it was pure enough for subsequent use, and the concentration was estimated by ^1H NMR integration, using pyrazine as internal standard (Figure S1). The distibine Sb_2Ph_4 has been reported to be obtainable, usually as a side product, from the reaction of the stibide Ph_2Sb^- with 1,2-dibromoethane or 1,2-dichloroethane; the stibide Ph_2Sb^- being obtainable by sodium reduction of SbPh_3 in liquid ammonium.¹² A rational synthesis is via the metathesis of SbPh_2H and PhLi in dioxane.¹¹ Given the convenient synthesis of SbPh_2H described above, we decided on its deprotonation with $n\text{-BuLi}$ to produce the stibide Ph_2Sb^- ,¹³ followed by its reaction with SbPh_2Cl (Scheme 1). This has proven to be more convenient in work-up and higher in yield than the reported methods. Owing to the air-sensitive property of Sb_2Ph_4 , it was only characterized by its ^1H NMR spectrum (Figure S2).

Scheme 1

The room temperature reaction of **1** with SbPh_2H , in dry DCM or THF, afforded the clusters $\text{Os}_3(\text{CO})_{11}(\text{H})(\mu\text{-SbPh}_2)$, **2**, and $\text{Os}_3(\text{CO})_{11}(\mu\text{-H})(\mu\text{-SbPh}_2)\text{Os}_3(\text{CO})_{11}$, **3**; the analogous reaction with the distibine Sb_2Ph_4 afforded $\text{Os}_3(\text{CO})_{11}(\mu\text{-SbPh}_2)_2\text{Os}_3(\text{CO})_{11}$, **6**, together with trace amounts of the known cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-SbPh}_2)_2$, **5** (Scheme 2).

Scheme 2

Cluster **2** has previously been prepared by the carbonylation of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-SbPh}_2)$, **4**, and was only characterized spectroscopically. We have now characterized it by a single crystal X-ray crystallographic analysis. Unlike the arsenic analogue $\text{Os}_3(\text{CO})_{11}\text{H}(\mu\text{-AsMe}_2)$, which was found to be unstable on silica, losing a CO ligand on exposure to light,⁸ cluster **2** is relatively more stable but does decarbonylate quantitatively to **4** under refluxing DCE. An ORTEP plot showing the molecular structure of **2** is shown in Figure 1. It has the same structure as the arsenic analogue; an Os-Os bond has been cleaved and the Os_3Sb metal core adopts a puckered four-membered ring structure. The hydride ligand is in a terminal coordination mode, and is consistent with the singlet ^1H resonance at δ -8.39 ppm.

Figure 1. ORTEP plot showing the molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level, with organic hydrogen atoms omitted for clarity. Selected bond lengths (Å): Os(1)-Sb(4) = 2.6891(5), Os(1)-Os(2) = 2.9977(4), Os(2)-Os(3) = 2.9542(4), Os(3)-Sb(4) = 2.6309(5).

The ORTEP diagrams for **3** and **6**, together with selected bond parameters, are shown in Figures 2 and 3, respectively. Both clusters consist of an $\text{Os}_3(\text{CO})_{11}$ unit linked by an SbPh_2 moiety to another; an $\text{Os}_3(\text{CO})_{11}(\mu\text{-H})$ unit or an $\text{Os}_3(\text{CO})_{10}(\mu\text{-SbPh}_2)$ unit, for **3** and **6**, respectively. Both clusters are electron-precise. In **3**, as has already been well-documented,¹⁴ the hydride-bridged Os-Os bond (Os(1)-Os(2) = 3.0105(6) Å) is significantly longer than the other two Os-Os bonds (Os(1)-Os(3) = 2.8609(6) Å and Os(2)-Os(3) = 2.8939(6) Å). In **6**, one of the Os-Os bond is not present (Os(1) ... Os(3) = 4.308 Å), as required by the valence electron count. In solution, **6** exists as a mixture of two isomers. This is apparent from its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which showed two sets of resonances in a *ca.* 1:4 ratio. These probably correspond to the $\text{Os}_3(\text{CO})_{11}(\text{SbPh}_2)$ fragment occupying either of two different equatorial positions with respect to the Sb atom in the $\text{Os}_3(\text{CO})_{11}(\mu\text{-SbPh}_2)$ fragment, i.e., one isomer corresponds to that in the solid-state structure, and the other has the positions of the $\text{Os}_3(\text{CO})_{11}(\text{SbPh}_2)$ fragment and CO(33) interchanged. The presence of such isomers has also been observed in other structural analogues, *viz.*, the known clusters $\text{Os}_3(\text{CO})_{10}(\text{H})(\mu\text{-SbPh}_2)(\text{L})$ (where L = PPh₃; AsPh₃; SbPh₃).^{3a} As has already been observed in the simpler $\text{Os}_3(\text{CO})_{11}(\text{L})$ clusters,¹⁵ the SbPh_2 moiety leads to lengthening of the Os-Os bond that is *cis* to it on the $\text{Os}_3(\text{CO})_{11}$ unit; these are the Os(4)-Os(5) and Os(4)-Os(6) bonds of **3** and **6**, respectively.

$\text{SbPh}_2)(\text{L})$ (where L = PPh₃; AsPh₃; SbPh₃).^{3a} As has already been observed in the simpler $\text{Os}_3(\text{CO})_{11}(\text{L})$ clusters,¹⁵ the SbPh_2 moiety leads to lengthening of the Os-Os bond that is *cis* to it on the $\text{Os}_3(\text{CO})_{11}$ unit; these are the Os(4)-Os(5) and Os(4)-Os(6) bonds of **3** and **6**, respectively.

Figure 2. ORTEP plot showing the molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level, with organic hydrogen atoms omitted for clarity. Selected bond lengths (Å): Os(1)-Os(2) = 3.0105(6), Os(2)-Os(3) = 2.8939(6), Os(1)-Os(3) = 2.8609(6), Os(1)-Sb(1) = 2.6744(7), Os(4)-Sb(1) = 2.6391(8), Os(4)-Os(5) = 2.9143(6), Os(5)-Os(6) = 2.8832(6), Os(4)-Os(6) = 2.8498(6).

Figure 3. ORTEP plot showing the molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level, with organic hydrogen atoms omitted for clarity. Selected bond lengths (Å): Os(1)-Os(2) = 2.9837(7), Os(1)-Sb(7) = 2.6928(9), Os(2)-Os(3) = 2.9996(6), Os(3)-Sb(7) = 2.6791(9), Os(3)-Sb(8) = 2.6893(9), Os(4)-Sb(8) = 2.6577(9), Os(4)-Os(5) = 2.8599(7), Os(5)-Os(6) = 2.8890(7), Os(4)-Os(6) = 2.8923(7).

The proposed reaction pathway is common for both substrates (Scheme 3), and involves initial substitution of the CH_3CN ligand in **1** to form intermediate **A**; this is typical of its reactivity pattern with group 15 ligands.^{6,7,8,16} Oxidative addition of the Sb-X bond (where X = H or SbPh_2) across an Os-Os bond generates the intermediate **B**, which carries a lone pair on the trivalent Sb; oxidative addition of M-H bonds (M = Ge, Sn) to clusters have been extensively studied by Adams group.¹⁷ An alternative to **B** would be the species $\text{Os}_3(\text{CO})_{11}(\text{X})(\mu\text{-SbPh}_2)$, **B'**, which would be indistinguishable for X = SbPh_2 , but for X = H, is identical to **2**. This would imply that the formation of **3** involved **2** as the intermediate; that would require a fair amount of rearrangement, and we have also verified that **2** does not react with **1** to afford **3**.

From **B**, coordination of the Sb atom onto a neighbouring Os via Os-Os bond cleavage would give **2** or **5**.^{3a} Alternatively, it can coordinate to another “Os₃(CO)₁₁” fragment (cluster **1** is the synthetic equivalent for this synthon) to afford **3** or **6**. As one may expect, the former, intramolecular, rearrangement, should be more favourable. Consistent with this is the observation that **3** was only obtained as a minor product and its yield decreased when a larger excess of SbPh₂H is used. For X = SbPh₂, on the other hand, the formation of **5** from **B** would require an additional isomerisation step about the Os carrying the terminal SbPh₂ ligand so that it is *trans* to the μ-X moiety and hence *cis* to an Os-Os bond. This requirement favours the formation of **6** over **5**.

Scheme 3

We have also attempted to monitor the reaction of **1** with SbPh₂H by ¹H NMR spectroscopy; two equivalents of the latter was used in order to suppress the formation of **3** (Figures 4 and S3). Four resonances were observed in the hydride region 10 min after mixing the reagents at 0 °C, at δ = -8.72, -9.90, -17.1 and -18.50 ppm. The lowest field resonance can be assigned to **2**, and the one to highest field tentatively assigned to the intermediate **B**; the remaining two smaller resonances were transients and have not been assigned. The spectrum remained little changed at this temperature even after *ca.* 205 min at 0 °C, indicating a slow reaction rate. On raising to room temperature, the intensities of the resonances for **2** and **B** increased over time, the sum of their intensities (wrt the residue peak of d₂-dichloromethane) reaching a maximum after *ca.* 2.5 h. After that, the amount of **2** increased at the expense of **B**; the sum of their intensities remained nearly constant, indicating the conversion of **B** to **2**, and **B** completely disappeared after about 30 h. A new resonance at δ = -18.95 ppm, assignable to **3**, also became more obvious after 2.5 h at room temperature, but the intensity remained nearly constant over time. This assignment for **3** is also supported by a repeat NMR experiment in which, after 20 h at room temperature, when the resonance at δ = -18.50 ppm was prominent, addition of a further quantity of **1** resulted in the rapid disappearance of this resonance (*ca.* 10 min), accompanied by a slight increase in the resonance at δ = -18.95 (Figure S4).

Figure 4. ¹H NMR spectrum of the reaction of **1** with SbPh₂H in d₂-DCM, monitored over time. (a) after 10 min at 0 °C; (b) after 205 min

at 0 °C; warmed to r.t. and then (c) after 10 min; (d) after 1 h; (e) after 2.5 h; and (f) after 31 h.

The intermediate **B** is interesting as it can be viewed as a stibine in which one of its substituent is a bulky organometallic cluster. The above reaction pathway also suggests that **B** may be trapped chemically. Indeed, the reactions with the stibine or distibine in the presence of W(CO)₅(NCCH₃), afforded the heteronuclear clusters Os₃(CO)₁₁(μ-H)(μ-SbPh₂)W(CO)₅, **7**, or Os₃(CO)₁₁(μ-SbPh₂)₂W(CO)₅, **8**, respectively, albeit in low yields. Both clusters have been completely characterized, including by single crystal X-ray crystallographic studies; the ORTEP plots showing their molecular structures, together with selected bond parameters, are given in Figures 5 and 6, respectively. The overall structures of **7** and **8** are very similar. Both have the Ph₂SbW(CO)₅ group *cis* to the μ-X moiety; this is consistent with the proposed structure for the intermediate **B**. As in the case of its analogue **6**, cluster **8** also exists as a mixture of two isomers in solution, as is evident from its ¹H and ¹³C{¹H} NMR spectra.

Figure 5. ORTEP plot showing the molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level, with organic hydrogen atoms omitted for clarity. Selected bond lengths (Å): Os(1)-Os(2) = 3.0290(2), Os(1)-Os(3) = 2.8785(2), Os(2)-Os(3) = 2.8936(3), Os(1)-Sb(1) = 2.6953(3), Sb(1)-W(1) = 2.8017(3)

Figure 6. ORTEP plot showing the molecular structure of **8**. Thermal ellipsoids are drawn at the 50% probability level, with organic hydrogen atoms omitted for clarity. Selected bond lengths (Å): Os(1)-Os(3) = 2.9940(3), Os(1)-Sb(5) = 2.6797(5), Os(1)-Sb(6) = 2.6870(4), Os(2)-Os(3) = 2.9611(4), Os(2)-Sb(5) = 2.6850(5), W(4)-Sb(6) = 2.7984(4).

Concluding remarks

In this work, we have described a facile approach to osmium-antimony carbonyl clusters through the reaction of the lightly-stabilised cluster, $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)_3$, with a secondary stibine or a distibine. These reactions proceed via oxidative addition across the Sb-H or Sb-Sb bond, and we have shown that the proposed intermediate contains a trivalent Sb moiety, which can be observed by NMR and also trapped chemically. We believe that this intermediate can be viewed as a bulky tertiary stibine, with an organometallic cluster serving as a substituent, and may be employed as such; work on this is currently underway.

Experimental section

General Data. All manipulations were carried out in an argon atmosphere with standard schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)_3$, **1**,¹⁸ SbPh_2Cl ,¹⁹ and $\text{W}(\text{CO})_5(\text{NCCH}_3)_3$,²⁰ were prepared as described in the literature. The TLC plates used were from a commercial source (silica gel 60 F254, Merck Co.). ^1H NMR spectra were recorded on Bruker AV 300 or BBF O1 400 spectrometers and the chemical shifts referenced to residual solvent peaks in the respective deuterated solvents. Infrared spectra were acquired as CH_2Cl_2 solutions on a Bruker ALPHA FTIR spectrometer. High-resolution mass spectra were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were performed by the microanalytical laboratories at the Nanyang Technological University or the National University of Singapore.

Preparation of SbPh_2H : To a suspension of LiAlH_4 (60 mg, 1.6 mmol) in ether (40 ml) was added a solution of SbPh_2Cl (720 mg, 2.3 mmol) in ether (20 ml). Excessive stirring was avoided as it would hinder the sedimentation of LiAlH_4 in the process of purification. After 1 h of gentle stirring at room temperature, the solvent volume was reduced to ca. 1 ml under vacuum, and then extracted with dry hexane (20 ml). The precipitate was allowed to settle to the bottom and the supernatant carefully transferred with a pipette into a Carius tube. The crude product solution was stored at 4 °C for subsequent use. ^1H NMR (C_6D_6): δ 7.45-7.55 (dd, 4H, $^3J_{\text{H,H}} = 2.1$ Hz, PhH), 7.25-7.35 (m, 6H, PhH), 5.70 (s, 1H, SbH).

Preparation of Sb_2Ph_4 : The Ph_2SbH solution in hexane (20 ml, ca. 0.10 M, 2.0 mmol), prepared as described above, was transferred to a 150 ml carius tube followed by the addition of THF (30 ml). Then *n*-BuLi solution in hexane (1.6 M, 1.2 ml, 1.9 mmol) was added dropwise to the above solution maintained at -78 °C. The color immediately changed from colorless to dark red. Ph_2SbCl (0.62 g, 2.0 mmol) was then slowly added, after which the reaction mixture was allowed to warm up to room temperature. The colour of the solution changed gradually to yellow over a period of 20 min. The solvent was removed in vacuo and the residue extracted with dry ether (20 ml). The ether solution was kept at -30 °C overnight from which yellow Sb_2Ph_4 crystallized out. Yield: 0.70 g, 63 %. ^1H NMR (C_6D_6) δ 7.53-7.56 (dd, 8H, $^3J_{\text{H,H}} = 1.8$ Hz, PhH), 6.99-7.04 (m, 12H, PhH).

Reaction of **1 with SbPh_2H :** Cluster **1** (50 mg, 54 μmol) was dissolved in dry DCM (10 ml). To this was added the crude Ph_2SbH /hexane solution (50 μl , ca. 50 μmol). The resulting yellow mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue separated by silica TLC. Elution with DCM/Hexane (1:1, v/v) afforded two main bands.

The first, light yellow, band was identified as $\text{Os}_3(\text{CO})_{11}(\text{H})(\mu\text{-SbPh}_2)$, **2** ($R_f = 0.75$; yield = 36 mg, 61%). IR (CH_2Cl_2): $\nu(\text{CO})$

2117m, 2077s, 2046s, 2034vs, 2015m, 1991m. 1970w cm^{-1} ; ^1H NMR (C_6D_6): 7.7 (d, 2H), 7.4-7.5 (d, 2H), 6.9-7.0 (m, 6H), -8.39 (s, 1H, OsH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 176.74 (br, CO), 174.63 (CO), 169.41 (CO), 136.49 (Ph), 133.37 (Ph), 130.30 (Ph), 129.43 (Ph), 129.13 (Ph), 128.56 (Ph), 127.74 (Ph), 120.88 (Ph). Anal. Calcd for $\text{C}_{23}\text{H}_{11}\text{O}_{11}\text{Os}_3\text{Sb} \cdot 0.3(\text{THF})$: C 24.7, H 1.2%. Found: C 24.7, H 0.9%. HRMS(ESI⁺) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{23}\text{H}_{12}\text{O}_{11}\text{Os}_3\text{Sb}^+$): 1155.835, found, 1155.830.

The second, dark yellow, band afforded a small amount of a dark yellow product $\text{Os}_3(\text{CO})_{11}(\mu\text{-H})(\mu\text{-SbPh}_2)\text{Os}_3(\text{CO})_{11}$, **3** ($R_f = 0.60$; yield = 11 mg, 24%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2142w, 2103w, 2093s, 2060s, 2051m, 2016vs cm^{-1} ; ^1H NMR (C_6D_6) δ 7.65 (d, 6H), 7.02 (t, 4H), -18.89 (s, 1H, OsHOs). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): 185.26 (4C, CO), 181.06 (4C, CO), 173.09 (2C, CO), 173.07 (2C, CO), 172.28 (1C, CO), 172.25 (1C, CO), 168.89 (2C, CO), 168.33 (2C, CO), 162.69 (1C, CO), 162.67 (1C, CO), 162.40 (1C, CO), 162.33 (1C, CO), 134.80 (Ph), 132.31 (Ph), 129.47 (Ph), 128.66 (Ph). Anal. Calcd for $\text{C}_{34}\text{H}_{11}\text{O}_{22}\text{Os}_6\text{Sb}$: C 20.1, H 0.6%. Found: C 20.1, H 0.6%. HRMS(ESI⁺) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{34}\text{H}_{12}\text{O}_{22}\text{Os}_6\text{Sb}^+$): 2035.647, found, 2035.647.

Thermolysis of **2:** A solution of **2** (30 mg, 26 μmol) in 1,2-dichloroethane (10 ml) was refluxed for 12 h. After the solvent was removed under reduced pressure, TLC separation with DCM/hexane (1:4, v/v) as the eluent yielded an orange band of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-SbPh}_2)_2$, **4** ($R_f = 0.40$; yield = 25 mg, 85%), which was identified by its IR and ^1H NMR data with the literature values.²

Reaction of **1 with Sb_2Ph_4 :** To a solution of **1** (30 mg, 33 μmol) in dry DCM (10 ml) was added Sb_2Ph_4 (18 mg, 33 μmol). The resulting yellow mixture was stirred at room temperature for 48 h. TLC separation of the residue after solvent removal, with DCM/hexane (1:1, v/v) as the eluent, gave two yellow bands.

The first band, obtained in trace amounts, was identified as the known cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-SbPh}_2)_2$, **5**, by comparing its IR spectral values with the literature.^{2b}

The second band, major product, was identified as $\text{Os}_3(\text{CO})_{11}(\mu\text{-SbPh}_2)_2\text{Os}_3(\text{CO})_{11}$, **6** ($R_f = 0.50$; yield = 20 mg, 53 %). IR (CH_2Cl_2): $\nu(\text{CO})$ 2123s, 2101s, 2083s, 2050vs, 2039s, 2014s, 1981w, 1942w cm^{-1} . ^1H NMR (C_6D_6 , major isomer) δ 6.81-6.96 (m, 12H), 6.98-7.04 (dd, 4H), 7.36-7.39 (dd, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , major isomer): 187.13 (4C, CO), 179.50 (2C, CO), 177.34 (4C, CO), 174.73 (4C, CO), 172.22 (2C, CO), 170.65 (2C, CO), 168.24 (2C, CO), 164.34 (2C, CO), 135.27 (Ph), 135.10 (Ph), 131.52 (Ph), 130.21 (Ph), 129.14 (Ph), 128.96 (Ph), 128.10 (Ph), 123.55 (Ph). Anal. Calcd for $\text{C}_{46}\text{H}_{20}\text{O}_{22}\text{Os}_6\text{Sb}_2 \cdot 0.8(\text{THF})$: C 25.0, H 1.1%. Found: C 25.3, H 0.9%. HRMS(ESI⁺) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{46}\text{H}_{21}\text{O}_{22}\text{Os}_6\text{Sb}_2^+$): 2308.615, found, 2308.611.

Reaction of **1, $\text{W}(\text{CO})_5(\text{NCCH}_3)_3$ and SbPh_2H :** Cluster **1** (60 mg, 65 μmol) and $\text{W}(\text{CO})_5(\text{NCCH}_3)_3$ (24 mg, 65 μmol) were dissolved in dry DCM (10 ml). To this was added the crude Ph_2SbH /hexane solution (0.65 ml, ca. 65 μmol). The resulting yellow mixture was stirred at room temperature for 26 h. The solvent was removed under reduced pressure and the residue separated by silica TLC. Elution with DCM/Hexane (1:2, v/v) afforded several bands.

The first, light yellow, band was identified as **2** ($R_f = 0.65$; yield = 40 mg, 57%).

The second, light yellow, band was identified as unconsumed $\text{W}(\text{CO})_5(\text{NCCH}_3)_3$, which gradually decomposed in DCM solution.

The third, light yellow, band was identified as $\text{Os}_3(\mu\text{-H})(\text{CO})_{11}(\mu\text{-SbPh}_2)\text{W}(\text{CO})_5$, **7** ($R_f = 0.35$; yield = 5.0 mg, 5.2%). IR (CH_2Cl_2):

$\nu(\text{CO})$ 2140w, 2092s, 2063vs, 2038w, 2028w, 2011m, 1985w, 1930vs cm^{-1} ; ^1H NMR (C_6D_6) δ 7.70 (d, 4H), 7.10 (t, 4H), 7.02 (t, 2H), -18.89 (s, 1H, OsHOs). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): 201.14 (1C, CO), 199.16 (4C, CO), 185.82 (2C, CO), 181.52 (2C, CO), 173.27 (2C, CO), 172.90 (1C, CO), 169.44 (1C, CO), 168.66 (1C, CO), 163.21 (1C, CO), 162.45 (1C, CO), 135.27 (Ph), 131.58 (Ph), 129.07 (Ph), 128.73 (Ph). Anal. Calcd for $\text{C}_{28}\text{H}_{11}\text{O}_{16}\text{Os}_3\text{SbW}$: C 22.7, H 0.8%. Found: C 23.0, H 1.0%. HRMS(ESI^+) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{28}\text{H}_{12}\text{O}_{16}\text{Os}_3\text{SbW}^+$): 1479.746, found, 1479.750.

The fourth, dark yellow, band was identified as **3** (R_f = 0.30; yield = 7.0 mg, 13%).

Reaction of 1, $\text{W}(\text{CO})_5(\text{NCCH}_3)$ and Sb_2Ph_4 : To a solution of **1** (60 mg, 65 μmol) and $\text{W}(\text{CO})_5(\text{NCCH}_3)$ (24 mg, 65 μmol) in dry DCM (10 ml) was added Sb_2Ph_4 (36 mg, 65 μmol). The resulting yellow mixture was stirred at room temperature for 96 h. After solvent removal, the was separated by TLC. Elution with DCM/Hexane (2:3, v/v) afforded several bands.

The first band, obtained in trace amounts, was identified as **5**.

The second, light yellow, band was identified as unconsumed $\text{W}(\text{CO})_5(\text{NCCH}_3)$.

The third, light yellow, band was identified as $\text{Os}_3(\text{CO})_{11}(\mu\text{-SbPh}_2)_2\text{W}(\text{CO})_5$, **8** (R_f = 0.50; yield = 5.0 mg, 4.4%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2122s, 2082s, 2061w, 2048w, 2038s, 2022w, 2003m, 1976w, 1927s cm^{-1} ; ^1H NMR (C_6D_6 , major isomer) δ 7.54 (d, 4H, PhH), 7.08-7.11 (q, 4H, PhH), 6.82-6.95 (m, 12H, PhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , major isomer): 201.41 (1C, CO), 198.97 (4C, CO), 188.01 (2C, CO), 180.27 (1C, CO), 177.55 (2C, CO), 174.97 (2C, CO), 172.31 (1C, CO), 171.27 (1C, CO), 168.50 (1C, CO), 164.50 (1C, CO), 135.57 (Ph), 135.24 (Ph), 131.39 (Ph), 130.10 (Ph), 129.05 (Ph), 128.46 (Ph), 128.16 (Ph), 123.23 (Ph). Anal. Calcd for $\text{C}_{40}\text{H}_{20}\text{O}_{16}\text{Os}_3\text{Sb}_2\text{W}$: C 27.4, H 1.2%. Found: C 27.7, H 1.4%. HRMS(ESI^+) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{40}\text{H}_{21}\text{O}_{16}\text{Os}_3\text{Sb}_2\text{W}^+$): 1754.720, found, 1754.720.

The fourth, orange, band was identified as **6** (R_f = 0.40; yield = 20 mg, 27%).

Crystallographic Analyses. Diffraction-quality crystals were obtained by slow evaporation of solvent from solutions in hexane/dichloromethane solvent mixtures at room temperature. The crystals were mounted onto quartz fibres, and the X-ray diffraction intensity data were measured with a Bruker Kappa diffractometer equipped with a CCD detector, employing Mo K α radiation (λ = 0.71073 Å), with the SMART suite of programs.²¹ All the data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.²² Structural solution and refinement were carried out with the SHELXTL suite of programs.²³ The structures were solved by direct methods or Patterson maps to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The crystals of **3** and **6** were found to be twinned; the twin law and cell parameters were determined using the programs CELL_NOW,²⁴ and the reflection data were processed and corrections applied using the program TWINABS.²⁵ A dichloromethane solvate was found for the crystal of **3**, and a thf with partial occupancy (fixed at 0.8) for the crystal of **6**. All non-hydrogen atoms were refined with anisotropic thermal parameters. Metal hydrides were placed by potential energy calculations using the XHYDEX program,²⁶ and were refined riding on an Os atom to which they were attached, with fixed isotropic thermal parameters. Crystal data, data collection parameters, and refinement data are summarized in Table S1.

Supporting Information

Crystallographic tables and CIF files for all structures; all NMR, IR and HR-MS spectra, and elemental analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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