

# Surface-Mediated Organometallic Synthesis: The Activating Role of Silica for a High-Yield Route to $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ and $[\text{HOs}_3(\text{CO})_{10}\text{Y}]$ ( $\text{Y} = \text{OH}, \text{OR}, \text{Cl}, \text{Br}, \text{I}, \text{O}_2\text{CR}, \text{SCN}$ ) Clusters from $[\text{Os}_3(\text{CO})_{12}]$

Dominique Roberto,\* Elena Lucenti, Carmen Roveda, and Renato Ugo

Dipartimento di Chimica Inorganica, Metallorganica e Analitica and Centro CNR, Università di Milano, Via G. Venezian, 21, 20133 Milano, Italy

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Activation of  $[\text{Os}_3(\text{CO})_{12}]$  by the silica surface via reaction with surface silanol groups provides a new convenient general approach to the selective, high-yield synthesis of various osmium carbonyl clusters such as  $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$  and  $[\text{HOs}_3(\text{CO})_{10}\text{Y}]$  ( $\text{Y} =$  a three-electron donor such as OH, OR, Cl, Br, I,  $\text{O}_2\text{CR}$ , and SCN). These silica-mediated syntheses compare favorably with the more conventional syntheses in solution because (i) differently from other related intermediates used in solution, silica-anchored  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  is easily obtained in quantitative yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  in one step and (ii) the conversion of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  occurs in *one pot* usually in high yields and under mild reaction conditions. In addition, the related species  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ , which can be obtained almost quantitatively by hydrolysis of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ , is even more reactive than its precursor and allows a three-step synthesis of various osmium clusters characterized by excellent total yields from  $[\text{Os}_3(\text{CO})_{12}]$ .

## Introduction

A few years ago, some of us reported the easy and high-yield synthesis of  $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$  by hydrogenation under 1 atm of  $\text{H}_2$  of silica-supported  $[\text{Os}_3(\text{CO})_{12}]$ .<sup>1</sup> The particularly mild pressure required by the synthesis carried out on the silica surface, compared to the high pressure required in inert solvents like octane and xylene in order to obtain similar yields,<sup>2</sup> was later explained by us<sup>3</sup> by the formation of silica-anchored  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  as reactive intermediate. In fact, the starting silica-supported  $[\text{Os}_3(\text{CO})_{12}]$ , which was only deposited on the silica surface as confirmed by its possible extraction with  $\text{CH}_2\text{Cl}_2$ , was activated under reaction conditions (100–150 °C) by interaction with surface silanol groups to give silica-anchored  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ , which was covalently linked to the silica surface via an  $\text{Os}-\text{OSi}\equiv$  bond and, therefore, could not be extracted by simple treatment with solvents.

The easy activation of a rather unreactive molecule such as  $[\text{Os}_3(\text{CO})_{12}]$  is still a difficult task, when total high yields are required. Much work has been devoted to the synthesis of clusters of the type  $[\text{HOs}_3(\text{CO})_{10}\text{Y}]$ .<sup>4</sup> Reactive intermediates such as  $[\text{HOs}_3(\text{CO})_{10}(\text{OCH}=\text{CH}_2)]$ ,<sup>5</sup>  $[\text{Os}_3(\text{CO})_{10}(\text{cyclohexa-1,3-diene})]$ ,<sup>6</sup>  $[\text{Os}_3(\text{CO})_{10}(\text{cyclooctene})_2]$ ,<sup>7</sup> and  $[\text{HOs}_3(\text{CO})_{10}(\text{NCHNMe}_2)]$ <sup>8</sup>

have been synthesized but in 60–76% yields only, starting from  $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ , prepared by hydrogenation of  $[\text{Os}_3(\text{CO})_{12}]$  (73% yield).<sup>9</sup> Other useful labile intermediates are  $[\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]$ ,<sup>10</sup> prepared in 80% yield directly from  $[\text{Os}_3(\text{CO})_{12}]$ , and  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{-CN})_2]$ ,<sup>7,10</sup> obtained via  $[\text{Os}_3(\text{CO})_{10}(\text{cyclooctene})_2]$  or  $[\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]$  with a total yield from  $[\text{Os}_3(\text{CO})_{12}]$  of ~80%.

On the basis of some preliminary evidence of a high reactivity of the surface species  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ <sup>3</sup> which can be easily prepared in almost quantitative yield (97% yield, see Experimental Section) by refluxing an octane solution of  $[\text{Os}_3(\text{CO})_{12}]$  with silica,<sup>11</sup> we extensively investigated the use of the silica surface as a new way to directly activate  $[\text{Os}_3(\text{CO})_{12}]$ . In this work, we describe the easy and high-yield synthesis of  $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$  and  $[\text{HOs}_3(\text{CO})_{10}\text{Y}]$  ( $\text{Y} = \text{OH}, \text{OR}, \text{Cl}, \text{Br}, \text{I}, \text{O}_2\text{CR}, \text{SCN}$ ) directly from  $[\text{Os}_3(\text{CO})_{12}]$ , by using the silica-anchored species  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  as reactive intermediate.

## Results and Discussion

**Synthesis of  $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$  from  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ .** When  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ , prepared from  $[\text{Os}_3(\text{CO})_{12}]$  and silica,<sup>11</sup> is treated with  $\text{H}_2$  (1 atm) at 150 °C for 24 h in a closed reaction vessel (previously described for the reductive carbonylation of silica-supported metal chlorides),<sup>12</sup> the silica changes from yellow to almost white while a pale yellow powder

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**Table 1. Syntheses of Various Clusters Starting from [Os<sub>3</sub>(CO)<sub>12</sub>] via [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)]**

product	reaction conditions	T (°C)	t (h)	total yield from [Os <sub>3</sub> (CO) <sub>12</sub> ] (%) <sup>a</sup>
[H <sub>4</sub> Os <sub>4</sub> (CO) <sub>12</sub> ]	H <sub>2</sub> , 1 atm	150	24	94
[HOs <sub>3</sub> (CO) <sub>10</sub> (OH)]	H <sub>2</sub> O/toluene <sup>b</sup>	95	5	91
[HOs <sub>3</sub> (CO) <sub>10</sub> (OH)]	2 M Na <sub>2</sub> CO <sub>3</sub> (aq)/CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	25	7	79
[HOs <sub>3</sub> (CO) <sub>10</sub> (OH)]	dil HBF <sub>4</sub> (aq)/CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	40	10	78
[HOs <sub>3</sub> (CO) <sub>10</sub> (OBu <sup>n</sup> )]	1-butanol <sup>b</sup>	118	20	84 <sup>c</sup>
[HOs <sub>3</sub> (CO) <sub>10</sub> (OMe)]	methanol and HBF <sub>4</sub> ·Et <sub>2</sub> O <sup>b</sup>	65	24	52 <sup>d</sup>
[HOs <sub>3</sub> (CO) <sub>10</sub> (OPh)]	PhOH/heptane <sup>b,e</sup>	98	5	64
[HOs <sub>3</sub> (CO) <sub>10</sub> Cl]	37% HCl(aq)/CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	40	6	84
[HOs <sub>3</sub> (CO) <sub>10</sub> Br]	48% HBr (aq)/CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	40	7	86
[HOs <sub>3</sub> (CO) <sub>10</sub> (O <sub>2</sub> CCF <sub>3</sub> )]	excess CF <sub>3</sub> CO <sub>2</sub> H/toluene <sup>b</sup>	90	6	70 <sup>f</sup>
[HOs <sub>3</sub> (CO) <sub>10</sub> (O <sub>2</sub> CCH <sub>3</sub> )]	excess CH <sub>3</sub> CO <sub>2</sub> H/toluene <sup>b</sup>	90	10	56 <sup>g</sup>

<sup>a</sup> Isolated yield, the intermediate [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] being obtained in 97% yield from [Os<sub>3</sub>(CO)<sub>12</sub>]. <sup>b</sup> Reaction carried out under 1 atm of N<sub>2</sub>. <sup>c</sup> [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)], 3%, is also obtained. <sup>d</sup> [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] (15%) is also obtained. <sup>e</sup> By using a molar ratio PhOH:Os<sub>3</sub> = 300:1. <sup>f</sup> Traces of [Os(CO)<sub>3</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>] are also obtained. <sup>g</sup> [Os(CO)<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>], 6%, is also obtained.

sublimes on the cold part of the reaction vessel. Extraction with dichloromethane of the sublimate and the silica powder affords pure [H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub>] in 97% yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 94%, Table 1).

This surface-mediated synthesis is the best method to prepare [H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub>] from [Os<sub>3</sub>(CO)<sub>12</sub>] under mild conditions. In fact, [H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub>] is obtained in 71% yield by working in octane at 100 °C under high H<sub>2</sub> pressure (120 atm),<sup>2</sup> while similar yields (68%) are reached in the previously reported silica-mediated synthesis by direct hydrogenation (1 atm) of silica-supported [Os<sub>3</sub>(CO)<sub>12</sub>].<sup>1</sup> This latter method has the disadvantage of requiring a very long reaction time (5 days) due to the necessity of working at relatively low temperatures (100 °C) in order to avoid sublimation of [Os<sub>3</sub>(CO)<sub>12</sub>].<sup>1</sup> In the present synthesis, the intermediate [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], which is anchored to the silica surface via an Os–OSi≡ bond, does not sublime and therefore it is possible to work at a temperature high enough to obtain higher yields of [H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub>] in a much shorter reaction time.

**Synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] from [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)].** The synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] was reported to occur in solution by direct reaction of [Os<sub>3</sub>(CO)<sub>12</sub>] with NaBH<sub>4</sub> (27% yield)<sup>13</sup> or by hydrolysis of the reactive species [HOs<sub>3</sub>(CO)<sub>10</sub>(OCH=CH<sub>2</sub>)] (36% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 20%),<sup>5</sup> [Os<sub>3</sub>(CO)<sub>10</sub>(cyclohexa-1,3-diene)] (20% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 9%),<sup>6</sup> and [HOs<sub>3</sub>(CO)<sub>10</sub>(NCHNMe<sub>2</sub>)] (60% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 33%).<sup>8</sup> Recently, [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] was obtained in fair total yields (56%) by reaction of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] with aqueous HF.<sup>14</sup> The evidence of a rather easy hydrolysis of the Os–OSi bond<sup>3</sup> prompted us to investigate a new synthetic route still starting from [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] but using milder reaction conditions than dissolution of silica by treatment with aqueous HF.

When yellow [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] is stirred at 95 °C under N<sub>2</sub>, in a biphasic solvent system, water/toluene, the silica powder and the organic phase become white and yellow, respectively, due to the formation of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)], which goes in the organic phase. After 5 h, the reaction is complete, affording [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] in 94% yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 91%; Table 1).

The rate of hydrolysis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] is dependent on the temperature. For example, [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] is obtained in only 68% yield after 7 h at 65 °C whereas only traces are formed after 24 h at 40 °C. However, the rate can be increased by base and acid catalysis (Table 1). By working at room temperature with a biphasic solvent system aqueous, Na<sub>2</sub>CO<sub>3</sub> (2 M)/CH<sub>2</sub>Cl<sub>2</sub>, [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] is obtained in 81% yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] = 79%) after only 7 h. Similarly, by using the biphasic solvent system water/CH<sub>2</sub>Cl<sub>2</sub> in the presence of a few drops of HBF<sub>4</sub>, a 80% yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] = 78%) is obtained after 10 h at 40 °C.

Therefore, total yields of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] from [Os<sub>3</sub>(CO)<sub>12</sub>] are much higher (78–91%, Table 1) than those previously reported (9–33%),<sup>5–6,8,13,14</sup> and reaction conditions are very mild. As we will see later, [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] is another useful intermediate for the synthesis of various [HOs<sub>3</sub>(CO)<sub>10</sub>Y] species where Y is an anionic nucleophile.

**Synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OR)] (R = Me, Bu, Ph).** Direct reaction of [Os<sub>3</sub>(CO)<sub>12</sub>] with alcohols at elevated temperatures (typically 140–170 °C) gives [HOs<sub>3</sub>(CO)<sub>10</sub>(OR)] derivatives in variable yields (10, 46, 48, and 81% with R = Me, CHMe<sub>2</sub>, Ph, and 2-naphthyl, respectively).<sup>15</sup> The same clusters can be prepared in high yields under less severe reaction conditions with a multistep process involving as intermediates [Os<sub>3</sub>(CO)<sub>10</sub>(cyclohexa-1,3-diene)],<sup>6</sup> [Os<sub>3</sub>(CO)<sub>10</sub>(cyclooctene)<sub>2</sub>],<sup>7</sup> [Os<sub>3</sub>(CO)<sub>10</sub>(CH<sub>3</sub>CN)<sub>2</sub>],<sup>7</sup> or [HOs<sub>3</sub>(CO)<sub>10</sub>(NCHNMe<sub>2</sub>)].<sup>8</sup> However, since three or four steps are required starting from [Os<sub>3</sub>(CO)<sub>12</sub>], total yields are never excellent (10–48% for R = Me, Ph).<sup>6,8,15</sup> Therefore, we investigated the direct reaction of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] with alcohols in order to obtain a high yield and *one-pot* synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OR)] species.

**(i) From [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)].** When a slurry of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] in 1-butanol is stirred under N<sub>2</sub> at reflux temperature (118 °C) for 10 h, previously unreported [HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)] is obtained in 59% yield along with minor amounts (2% yield) of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)], due to some water present on the silica surface. Addition of fresh 1-butanol to the unreacted [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], followed by reflux for another 10 h, gives more [HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)] (87% final yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 84%; Table 1). These results

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**Table 2. Syntheses of Various [HO<sub>3</sub>(CO)<sub>10</sub>Y] Clusters Starting from [HO<sub>3</sub>(CO)<sub>10</sub>(OH)]<sup>a</sup>**

product	reaction conditions <sup>b</sup>	T (°C)	t	yield <sup>c</sup> (%)	total yield from [Os <sub>3</sub> (CO) <sub>12</sub> ] (%)
[HO <sub>3</sub> (CO) <sub>10</sub> (OBu <sup>n</sup> )]	<i>n</i> -Butanol	118	10 h	92	84
[HO <sub>3</sub> (CO) <sub>10</sub> (OMe)]	Methanol and HBF <sub>4</sub> ·Et <sub>2</sub> O	65	10 min	90	82
[HO <sub>3</sub> (CO) <sub>10</sub> (OPh)]	PhOH/heptane <sup>d</sup>	98	5 h	97	88
[HO <sub>3</sub> (CO) <sub>10</sub> (OPh)]	PhOH/heptane <sup>d,e</sup>	98	45 min	96	87
[HO <sub>3</sub> (CO) <sub>10</sub> Br]	[NBu <sub>4</sub> ]Br in CH <sub>2</sub> Cl <sub>2</sub> <sup>b,e,f</sup>	40	30 min	80	73
[HO <sub>3</sub> (CO) <sub>10</sub> I]	[NBu <sub>4</sub> ]I in CH <sub>2</sub> Cl <sub>2</sub> <sup>b,e,g</sup>	40	30 min	90	82
[HO <sub>3</sub> (CO) <sub>10</sub> (O <sub>2</sub> CCF <sub>3</sub> )]	CF <sub>3</sub> CO <sub>2</sub> H	25	immediately	100 <sup>23</sup>	91 <sup>h</sup>
[HO <sub>3</sub> (CO) <sub>10</sub> (O <sub>2</sub> CCH <sub>3</sub> )]	excess CH <sub>3</sub> CO <sub>2</sub> H/heptane	78	5 h	90	82
[HO <sub>3</sub> (CO) <sub>10</sub> (SCN)]	[NBu <sub>4</sub> ]SCN in PhH <sup>e,i</sup>	25	2.5 h	87	79

<sup>a</sup> [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] prepared in 91% yield from [Os<sub>3</sub>(CO)<sub>12</sub>] via [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)]. <sup>b</sup> Reaction carried out under 1 atm of N<sub>2</sub>. <sup>c</sup> Isolated yield. <sup>d</sup> By using a molar ratio PhOH:Os<sub>3</sub> = 100:1. <sup>e</sup> In the presence of a few drops of HBF<sub>4</sub>·Et<sub>2</sub>O. <sup>f</sup> By using a molar ratio [NBu<sub>4</sub>]Br:Os<sub>3</sub> = 5:1. <sup>g</sup> By using a molar ratio [NBu<sub>4</sub>]I:Os<sub>3</sub> = 1:1. <sup>h</sup> By using the silica-mediated synthesis of [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] described in the present work. <sup>i</sup> By using a molar ratio [NBu<sub>4</sub>]SCN:Os<sub>3</sub> = 10:1.

would suggest an equilibrium between [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] and alcohols.

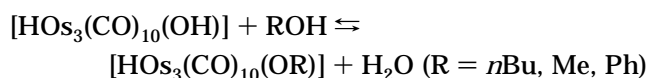
[HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] is quite unreactive when treated with methanol under N<sub>2</sub> at reflux temperature (65 °C). After 10 h, most of the silica-anchored osmium cluster is unaltered, [HO<sub>3</sub>(CO)<sub>10</sub>(OMe)] being obtained in 16% yield only, due to the rather low reaction temperature. However, addition of a few drops of HBF<sub>4</sub>·Et<sub>2</sub>O catalyzes the exchange reaction, affording [HO<sub>3</sub>(CO)<sub>10</sub>(OMe)] in 54% yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 52%), after 24 h (in parallel [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] is obtained in 15% yield; Table 1).

Besides, when a slurry of [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], phenol (molar ratio PhOH:Os<sub>3</sub> = 20:1) and heptane is vigorously stirred at reflux temperature (98 °C) under N<sub>2</sub>, a reaction occurs as shown by the gradual yellow coloring of the heptane solution. The infrared spectrum of this solution, taken after 30 min, shows the presence of the carbonyl bands typical of [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)].<sup>15</sup> However after 4 h, these bands do not grow in intensity. Only addition of more phenol (molar ratio PhOH:Os<sub>3</sub> = 50:1) causes a rapid increase of the intensity of the carbonyl bands in the heptane solution. But, again, the amount of [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)] does not increase after 5 h under reflux, unless more phenol is added. Clearly the reaction of [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] with phenol is also an equilibrium process. This is not surprising since there is also evidence of such an equilibrium for the reaction between silica-anchored [Cp\*Ir(Ph)(PMe<sub>3</sub>)(OSi≡)] and phenol to give [Cp\*Ir(Ph)(PMe<sub>3</sub>)(OPh)].<sup>16</sup>

Therefore, in order to obtain good yields of [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)], a large excess of phenol is necessary. For example, by heating a slurry of [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], phenol (molar ratio PhOH:Os<sub>3</sub> = 300:1), and heptane at reflux temperature for 5 h, [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)] is obtained in 66% yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 64%; Table 1). Higher temperatures (125 °C, using octane instead of heptane) cannot be used, because some [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)] is further converted to [H<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>(OC<sub>6</sub>H<sub>4</sub>)] by *ortho*-metalation.<sup>15</sup>

Because small amounts (3–15% yields) of [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] were produced in parallel during the silica-mediated synthesis of [HO<sub>3</sub>(CO)<sub>10</sub>(OMe)] and [HO<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)], we wondered whether this hydrolysis product of [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], which can be prepared in high yields as reported above, could act as a reactive intermediate of the reaction with ROH species. Its direct reaction with 1-butanol, methanol and phenol was investigated under reflux conditions, using a Markussen

apparatus in order to shift the equilibrium by removing the water produced during the exchange reaction:



**(ii) From [HO<sub>3</sub>(CO)<sub>10</sub>(OH)].** When a solution of [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] in anhydrous 1-butanol is refluxed under nitrogen, [HO<sub>3</sub>(CO)<sub>10</sub>(OBu)] is produced in 100% yield after 10 h, as shown by <sup>1</sup>H NMR spectroscopy (see Experimental Section). Chromatographic purification of the reaction mixture affords [HO<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)] in 92% yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 84%, Table 2).

When a solution of [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] in anhydrous methanol is refluxed for 10 h under nitrogen, [HO<sub>3</sub>(CO)<sub>10</sub>(OMe)] is obtained in only 50% yield, as shown by <sup>1</sup>H NMR spectroscopy from the molar ratio of the H–Os resonance of [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] (δ in CDCl<sub>3</sub> = –12.64 ppm) and [HO<sub>3</sub>(CO)<sub>10</sub>(OMe)] (δ in CDCl<sub>3</sub> = –12.48 ppm). However, addition of a few drops of HBF<sub>4</sub>·Et<sub>2</sub>O catalyzes the exchange reaction affording, after 10 min only, [HO<sub>3</sub>(CO)<sub>10</sub>(OMe)] in 90% yield (isolated yield after chromatographic purification; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 82%; Table 2).

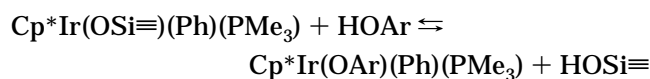
Besides, when a solution of [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] and phenol (molar ratio PhOH:Os<sub>3</sub> = 100:1) in anhydrous heptane is refluxed for 5 h under nitrogen, [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)] is obtained in 97% yield after chromatographic purification (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 88%; Table 2). The exchange reaction is catalyzed by a few drops of HBF<sub>4</sub>·Et<sub>2</sub>O, [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)] being obtained in 96% isolated yield (total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 87%; Table 2) after 45 min only. As in the case of [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], it is necessary to use a large excess of phenol: for instance, by working in anhydrous heptane under reflux for 5 h in the presence of a drop of HBF<sub>4</sub>·Et<sub>2</sub>O but with a 10:1 molar ratio of PhOH:Os<sub>3</sub>, [HO<sub>3</sub>(CO)<sub>10</sub>(OPh)] is obtained in only 60% yield (<sup>1</sup>H NMR yield from [HO<sub>3</sub>(CO)<sub>10</sub>(OH)], see Experimental Section).

Clearly, [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] appears to be in this specific synthesis much more reactive than its precursor [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)]. As evidenced from Tables 1 and 2, the best way to attain excellent total yields of [HO<sub>3</sub>(CO)<sub>10</sub>(OR)] (R = alkyl or aryl group) starting from [Os<sub>3</sub>(CO)<sub>12</sub>] involves a three-step route with [HO<sub>3</sub>(CO)<sub>10</sub>(OH)] as final reactive intermediate.

The higher reactivity of [HO<sub>3</sub>(CO)<sub>10</sub>(OH)], compared to that of [HO<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], is not surprising. For instance, in the investigation of olefin hydrogenation by

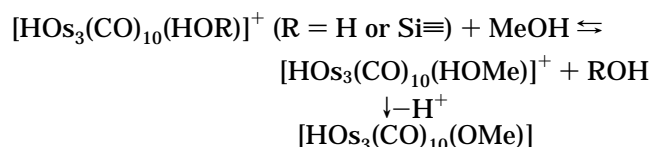
(16) Meyer, T. Y.; Woerpel, K. A.; Novak, B. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 10290.

[ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] or [ $\text{HOs}_3(\text{CO})_{10}(\text{OPh})$ ], it is reported that [ $\text{HOs}_3(\text{CO})_{10}(\text{OPh})$ ] is quickly transformed in solution under 1 atm of hydrogen to [ $\text{H}_2\text{Os}_3(\text{CO})_{10}$ ], while [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] seems to be more stable.<sup>17</sup> In addition, we observed that silica-supported [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ] (prepared by stirring a slurry of [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ],  $\text{CH}_2\text{Cl}_2$ , and silica, followed by evaporation of the solvent) is more easily reduced (1 atm of CO, 200 °C) to [ $\text{Os}_3(\text{CO})_{12}$ ] than silica-anchored [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ].<sup>18</sup> In the present work, the different reactivity could be related to  $\text{HO}^-$  behaving as a better leaving group than the surface  $\equiv\text{SiO}^-$ . In agreement with this hypothesis, it was recently reported that reaction of  $\text{Cp}^*\text{Ir}(\text{OH})(\text{Ph})(\text{PMe}_3)$  with  $\text{PhOH}$  affords easily  $\text{Cp}^*\text{Ir}(\text{OPh})(\text{Ph})(\text{PMe}_3)$  in quantitative yield<sup>19</sup> whereas silica-anchored  $\text{Cp}^*\text{Ir}(\text{OSi}\equiv)(\text{Ph})(\text{PMe}_3)$  is much less reactive, affording only low amounts of the iridium phenoxide (apparent equilibrium quotient,  $K_{\text{app}} = 0.047$ ).<sup>16</sup>



An increase of the acidity of the phenol has a positive effect on the formation of the iridium aryloxide. In fact, silica-anchored  $\text{Cp}^*\text{Ir}(\text{OSi}\equiv)(\text{Ph})(\text{PMe}_3)$  reacts with *p*-nitrophenol to give the corresponding aryloxido complex in quantitative yield.<sup>16</sup>

By analogy, starting from [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ], it is not surprising that  $\text{PhOH}$  can displace the silanolato ligand more easily than the less acidic  $\text{MeOH}$  or  $\text{BuOH}$  (Tables 1 and 2). This kind of exchange reaction is acid-catalyzed, an observation easy to explain because protonation of the osmium cluster ([ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] or [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ]) generates a better leaving group ( $\equiv\text{SiOH}$  vs  $\equiv\text{SiO}^-$  or  $\text{H}_2\text{O}$  vs  $\text{HO}^-$ ):



**Synthesis of [ $\text{HOs}_3(\text{CO})_{10}\text{Y}$ ] ( $\text{Y} = \text{Cl}, \text{Br}, \text{I}$ ).** (i) **From [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ].** Recently, we suggested<sup>3</sup> that [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] could be an intermediate in the formation of traces of [ $\text{HOs}_3(\text{CO})_{10}\text{Cl}$ ]<sup>20</sup> during the reductive carbonylation of silica-supported  $\alpha$ -[ $\text{Os}(\text{CO})_3\text{Cl}_2$ ]<sub>2</sub> under  $\text{CO} + \text{H}_2\text{O}$  (1 atm) at 250 °C.

In fact, when [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] is treated at 40 °C under  $\text{N}_2$  with a mixture of aqueous  $\text{HCl}$  and dichloromethane, the organic phase becomes gradually yellow due to the formation of [ $\text{HOs}_3(\text{CO})_{10}\text{Cl}$ ]. After 6 h, this latter cluster is obtained in 87% yield (total yield starting from [ $\text{Os}_3(\text{CO})_{12}$ ] 84%; Table 1). Similarly, treatment of [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] with a mixture of aqueous  $\text{HBr}$  and dichloromethane, under  $\text{N}_2$  at 40 °C for 7 h, affords [ $\text{HOs}_3(\text{CO})_{10}\text{Br}$ ] in 89% yield (total yield starting from [ $\text{Os}_3(\text{CO})_{12}$ ] 86%; Table 1).

An alternative synthesis of [ $\text{HOs}_3(\text{CO})_{10}\text{Br}$ ], using [ $\text{NBu}_4$ ] $\text{Br}$  instead of aqueous  $\text{HBr}$ , was investigated. No

reaction occurs when a slurry of [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] with a solution of [ $\text{NBu}_4$ ] $\text{Br}$  (molar ratio  $\text{Br}^-:\text{Os}_3 = 10:1$ ) in dichloromethane is heated at 40 °C under  $\text{N}_2$ . Only addition of a drop of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  leads to the formation of some [ $\text{HOs}_3(\text{CO})_{10}\text{Br}$ ] (after 5 h, total yield starting from [ $\text{Os}_3(\text{CO})_{12}$ ] 19%). Similarly, no reaction occurs when a slurry of [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] with a solution of [ $\text{NBu}_4$ ] $\text{I}$  (molar ratio  $\text{I}^-:\text{Os}_3 = 10:1$ ) in  $\text{CH}_2\text{Cl}_2$  is heated at 40 °C under  $\text{N}_2$ . However, addition of a drop of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  leads to the formation of [ $\text{HOs}_3(\text{CO})_{10}\text{I}$ ]. To reach completion, the reaction requires 4 h only, but the workup must be carried out *rigorously* under an oxygen-free atmosphere until pure [ $\text{HOs}_3(\text{CO})_{10}\text{I}$ ] is isolated. In fact, this cluster is easily converted in solution to *fac*-[ $\text{Os}(\text{CO})_3\text{I}_3$ ]<sup>-21</sup> in the presence of excess  $\text{I}^-$  and some air (see Experimental Section). Excess of  $\text{I}^-$  is absolutely necessary since with only 1 equiv of [ $\text{NBu}_4$ ] $\text{I}$  the reaction is extremely slow (see Experimental Section).

(ii) **From [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ].** [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ], obtained in high yields from [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ], reacts with [ $\text{NBu}_4$ ] $\text{Br}$  (molar ratio  $\text{Br}^-:\text{Os}_3 = 5:1$ ), at 40 °C in dichloromethane added with a drop of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ , affording [ $\text{HOs}_3(\text{CO})_{10}\text{Br}$ ] in less than 30 min (80% yield; total yield starting from [ $\text{Os}_3(\text{CO})_{12}$ ] 73%; Table 2). Besides, [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ] reacts readily with only 1 equiv of [ $\text{NBu}_4$ ] $\text{I}$  when dissolved in dichloromethane in the presence of a drop of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  as catalyst. After less than 30 min at 40 °C under  $\text{N}_2$ , [ $\text{HOs}_3(\text{CO})_{10}\text{I}$ ] is obtained (yield 90%; total yield starting from [ $\text{Os}_3(\text{CO})_{12}$ ] 82%; Table 2). Since there is no excess of iodide ion, the work-up can be easily carried out in air.

In the synthesis of [ $\text{HOs}_3(\text{CO})_{10}\text{Br}$ ] starting from [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ], best yields are reached when working in the presence of an aqueous phase. This observation and the much higher reactivity of [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ] compared to [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] suggest that [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ] could be the real reactive intermediate formed *in situ* when working with [ $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ ] in the presence of an acidic aqueous phase.

The above described preparations of [ $\text{HOs}_3(\text{CO})_{10}\text{X}$ ] ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) clusters are by far better than those previously described (total yields from [ $\text{Os}_3(\text{CO})_{12}$ ],  $\text{Y} = \text{Cl}$ , 35–55%;  $\text{Y} = \text{Br}$ , 30–40%;  $\text{Y} = \text{I}$ , 40–69%).<sup>5–8,10,22</sup>

**Synthesis of [ $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CR})$ ] ( $\text{R} = \text{Me}, \text{CF}_3$ ).** Derivatives of the type [ $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CR})$ ] ( $\text{R} = \text{Me}, \text{CF}_3, \text{Et}, \text{Ph}$ ) were first prepared in high yields (90%; total yields starting from [ $\text{Os}_3(\text{CO})_{12}$ ] 40%) by reaction of [ $\text{Os}_3(\text{CO})_{10}(\text{cyclohexa-1,3-diene})$ ] with an excess of  $\text{RCO}_2\text{H}$  in refluxing cyclohexane.<sup>6</sup> Addition of excess  $\text{CF}_3\text{CO}_2\text{H}$  to a solution of either [ $\text{HOs}_3(\text{CO})_{10}(\text{OCH}=\text{CH}_2)$ ] or [ $\text{HOs}_3(\text{CO})_{10}(\text{NCHNMe}_2)$ ] also gives [ $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CCF}_3)$ ] in almost quantitative yield (total yields starting from [ $\text{Os}_3(\text{CO})_{12}$ ] ~55%).<sup>5,8</sup> Moreover, it was reported that dissolution of [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ] in  $\text{CF}_3\text{CO}_2\text{H}$  at room temperature affords [ $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CCF}_3)$ ] quantitatively whereas the related reaction with  $\text{CH}_3\text{CO}_2\text{H}$  is quite slow (50% conversion after 46 days at room temperature);<sup>23</sup> however, when this synthesis was reported, it had the inconvenience that [ $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ ] could be prepared only in low yields from [ $\text{Os}_3(\text{CO})_{12}$ ] (9–27%).<sup>6,13</sup>

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**(i) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ .** No reaction occurs when a slurry of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  in  $\text{CF}_3\text{CO}_2\text{H}$  is stirred under  $\text{N}_2$  for 3 days at room temperature. Only at 90 °C,  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  reacts with an excess of  $\text{CF}_3\text{CO}_2\text{H}$  in toluene, affording  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CCF}_3)]$  (72% yield after 6 h, total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  70%; Table 1) along with traces of  $[\text{Os}(\text{CO})_3(\text{O}_2\text{CCF}_3)_2]$ .<sup>24</sup> Similarly,  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  reacts with an excess of  $\text{CH}_3\text{CO}_2\text{H}$  in refluxing toluene, affording  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CCH}_3)]$  (58% yield after 10 h; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  56%; Table 1) along with minor amounts of  $[\text{Os}(\text{CO})_3(\text{O}_2\text{CCH}_3)_2]$ <sup>25</sup> (6% yield after 10 h). The formation of some  $[\text{Os}(\text{CO})_3(\text{O}_2\text{CCF}_3)_2]$  and  $[\text{Os}(\text{CO})_3(\text{O}_2\text{CCH}_3)_2]$  is not surprising since they are produced in high yields by thermal treatment (160–185 °C) under  $\text{N}_2$  of  $[\text{Os}_3(\text{CO})_{12}]$  with  $\text{CF}_3\text{CO}_2\text{H}$ <sup>24</sup> and  $\text{CH}_3\text{CO}_2\text{H}$ ,<sup>25</sup> respectively.

**(ii) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ .** We further reinvestigated the reactivity of  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  with  $\text{CH}_3\text{CO}_2\text{H}$ . The reaction is very slow at room temperature, as previously reported.<sup>23</sup> However, by heating an excess of  $\text{CH}_3\text{CO}_2\text{H}$  in heptane under reflux,  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CCH}_3)]$  is obtained in 90% yield after 5 h (total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  82%; Table 2). Therefore, to prepare from  $[\text{Os}_3(\text{CO})_{12}]$  selectively and in high total yields  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CR})]$  species, it is more convenient to use  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  as reactive intermediate.

**Synthesis of  $[\text{HOs}_3(\text{CO})_{10}(\text{SCN})]$ .**  $[\text{HOs}_3(\text{CO})_{10}(\text{SCN})]$  has recently been prepared by reaction of  $[\text{HOs}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]\text{BF}_4$ , obtained by acidification of  $[\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})]$ ,<sup>26</sup> with  $[\text{Bu}_4\text{N}][\text{SCN}]$  in dichloromethane at room temperature (56% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  45%).<sup>27</sup>

**(i) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ .** When  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  is treated with a benzene solution of  $[\text{Bu}_4\text{N}][\text{SCN}]$  (molar ratio  $[\text{SCN}]^- : \text{Os}_3 = 10:1$ ) acidified with a few drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ , a very slow reaction occurs. After 2 days, only traces of  $[\text{HOs}_3(\text{CO})_{10}(\text{SCN})]$  are obtained.

**(ii) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ .** As in the case of other nucleophiles (e.g., alcohols, halides, and acetates),  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  is much more reactive than  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ . In fact,  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ , dissolved in anhydrous benzene, reacts readily with  $[\text{Bu}_4\text{N}][\text{SCN}]$  (molar ratio  $[\text{SCN}]^- : \text{Os}_3 = 10:1$ ) in the presence of a few drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  as catalyst. After 2.5 h at room temperature under nitrogen,  $[\text{HOs}_3(\text{CO})_{10}(\text{SCN})]$  is obtained in 87% yield (total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  79%; Table 2). The reaction is very sensitive to the acidity of the reaction medium, as observed by monitoring the formation of  $[\text{HOs}_3(\text{CO})_{10}(\text{SCN})]$  by infrared spectroscopy. If the amount of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  is too small, the reaction is slow, with the limiting case of lack of reaction without acid (see Experimental Section).

## Conclusion

The facile and quantitative activation of  $[\text{Os}_3(\text{CO})_{12}]$  by the silica surface via reaction with specific surface silanol groups provides a new convenient general route to the selective, high-yield synthesis under mild conditions of various osmium carbonyl clusters such as  $[\text{H}_4\text{-Os}_4(\text{CO})_{12}]$  and  $[\text{HOs}_3(\text{CO})_{10}\text{Y}]$  (Y = a three-electron donor). These silica-mediated syntheses compare favorably with the more conventional syntheses in solution because (i) differently from other intermediates used in solution, the reactive  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  species is easily obtained in one step and in nearly quantitative yield starting from  $[\text{Os}_3(\text{CO})_{12}]$ , and (ii) the reaction can be carried out in *one pot*. In addition,  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  is an excellent precursor of the species  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ , which is obtained almost quantitatively by its hydrolysis. This soluble species is even more reactive than its precursor, allowing excellent total yields of various osmium clusters starting from  $[\text{Os}_3(\text{CO})_{12}]$  in three high-yield steps: formation of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ , hydrolysis to  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ , and finally reaction in solution with the desired nucleophile. Interestingly, the cleavage of Os–OSi or Os–OH bonds by three-electron-donor nucleophiles is usually acid-catalyzed.

The work described here is an additional example of the potential of the silica surface for the activation of rather unreactive species such as  $[\text{Os}_3(\text{CO})_{12}]$ . As in other cases,<sup>12,28–30</sup> high yields and selectivities together with rather mild reaction conditions characterize these new synthetic routes mediated by the silica surface. In this specific work, we have the limitation, from the synthetic point of view, that the formation of silica-anchored  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  species is controlled by the number of specific available silanol groups on the silica surface,<sup>31</sup> so that only loadings of the surface up to 4 wt % Os/SiO<sub>2</sub> have been achieved.<sup>32</sup> However, the simplicity of the two-step (in *one pot*) or three-step (via  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ ) methodology and the very high total yields and selectivities from  $[\text{Os}_3(\text{CO})_{12}]$  make the methodology still rather attractive. In any case, amounts of 200–300 mg of final product can be easily obtained using ~10 g of silica, which can be recycled after workup and completion of the reaction.

The methodology of using the silica-anchored species  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  for the high-yield synthesis of  $[\text{HOs}_3(\text{CO})_{10}\text{Y}]$  species may have a general character with the exception of nucleophiles (Y) sensible to water, such as carbanions, because the presence of some surface water cannot be avoided under our experimental conditions. However, the alternative use of  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ , easily obtainable from the above anchored species and soluble in many organic solvents, can avoid the presence of water, thus extending the methodology to rather unstable nucleophiles.

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## Experimental Section

**General Comments.** SiO<sub>2</sub> (Aerosil 200 Degussa, with a nominal surface area of 200 m<sup>2</sup>/g) was used for the preparation of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)]. [Os<sub>3</sub>(CO)<sub>12</sub>] was prepared according to the literature.<sup>29</sup> Products were purified by recrystallization or by column chromatography, using silica gel 60 (Fluka) or neutral aluminum oxide (Baker). Their purity was then controlled by thin-layer chromatography and by elemental analysis. All the known reaction products were also identified by infrared, proton nuclear magnetic resonance, and mass spectroscopies, their spectra being compared to those of pure samples. The best syntheses for the various osmium carbonyl clusters are described below.

**Preparation of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)].** Typically, [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] was prepared according to the literature<sup>11</sup> by refluxing under N<sub>2</sub> an *n*-octane solution (300 mL) of [Os<sub>3</sub>(CO)<sub>12</sub>] (0.270 g; 0.298 mmol; 2.08 wt % Os with respect to SiO<sub>2</sub>) with silica (pretreated under vacuum, 10<sup>-2</sup> Torr, at 25 °C for 3 h; 8.14 g) until the solvent was decolorized (~10 h). After filtration and washing with hexane (~100 mL), a pale yellow powder of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] was obtained and kept under N<sub>2</sub>. The osmium loading on the silica surface (2.01 wt % Os with respect to SiO<sub>2</sub>) was established by evaporation of the filtrate, which afforded unreacted [Os<sub>3</sub>(CO)<sub>12</sub>] (0.009 g; 3% of the starting [Os<sub>3</sub>(CO)<sub>12</sub>]; therefore, yields of silica-anchored [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] are 97%. In the present work, osmium loadings in the range 1.46–2.04 wt % Os with respect to SiO<sub>2</sub> were used.

**Synthesis of [H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub>].** [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] (7.49 g of powder; 1.90 wt % Os with respect to SiO<sub>2</sub>; 0.729 mmol of Os) was transferred into a cylindrical Pyrex vessel (previously described for the reductive carbonylation of silica-supported metal chlorides at atmospheric pressure),<sup>12</sup> treated in vacuo (10<sup>-2</sup> Torr) at room temperature, and then exposed to H<sub>2</sub> at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put into an oven and heated at 150 °C for 24 h. Extraction of the sublimate and the silica powder with CH<sub>2</sub>Cl<sub>2</sub> (~150 mL) in a Soxhlet, followed by evaporation of the solvent, afforded pure [H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub>] (195 mg; 0.177 mmol; 97% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 94%).

**Synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] from [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)]. (i) by Thermal Hydrolysis.** [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] (7.56 g of powder; 2.04 wt % Os with respect to SiO<sub>2</sub>; 0.783 mmol of Os) was stirred *vigorously*, at 95 °C under N<sub>2</sub>, in the biphasic system H<sub>2</sub>O/toluene (150 and 350 mL, respectively). After 5 h, evaporation of the organic phase afforded [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)], which was recrystallized from pentane (213 mg; 0.245 mmol; 94% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 91%).

**(ii) by Base-Catalyzed Hydrolysis.** [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] (7.56 g of powder; 2.04 wt % Os with respect to SiO<sub>2</sub>; 0.783 mmol of Os) was stirred *vigorously*, at room temperature under N<sub>2</sub>, in the biphasic system 2 M Na<sub>2</sub>CO<sub>3</sub>(aq)/CH<sub>2</sub>Cl<sub>2</sub> (80 and 300 mL, respectively). After 7 h, the CH<sub>2</sub>Cl<sub>2</sub> phase was separated, washed twice with water (2 × 50 mL), and evaporated to dryness, affording [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)], which was recrystallized from pentane (184 mg; 0.211 mmol; 81% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 79%).

**(iii) By Acid-Catalyzed Hydrolysis.** [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] (7.56 g of powder; 2.04 wt % Os with respect to SiO<sub>2</sub>; 0.783 mmol of Os) was stirred *vigorously*, at 40 °C under N<sub>2</sub>, in the biphasic system H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> (90 and 350 mL, respectively) in the presence of 20 drops of 48% aqueous HBF<sub>4</sub>. After 10 h, the CH<sub>2</sub>Cl<sub>2</sub> phase was separated, washed twice with water (2 × 50 mL), and evaporated to dryness, affording [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)], which was recrystallized from pentane (181 mg; 0.207 mmol; 80% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 78%).

**Synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)]. (i) From [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)].** [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] (9.81 g of powder; 1.73 wt % Os with respect to SiO<sub>2</sub>; 0.867 mmol of Os) in anhydrous 1-butanol (400 mL, dried over 3 Å molecular sieves) was

refluxed for 10 h under N<sub>2</sub>. The 1-butanolic solution was separated, fresh 1-butanol (400 mL) was added to unreacted [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], and the reaction mixture was refluxed for another 10 h. The combined 1-butanolic solutions were evaporated, and the residue was chromatographed on a silica column using as eluant pentane, to obtain [HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)] (234 mg; 0.251 mmol; 87% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 84%), and then CH<sub>2</sub>Cl<sub>2</sub>, to obtain [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] (7 mg; 0.009 mmol; 3% yield). The previously unreported [HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)] gave satisfactory elemental analyses (Calcd: C, 18.18; H, 1.09. Found: C, 18.3; H, 1.12). It was characterized by IR [ $\nu$ (CO) in CH<sub>2</sub>Cl<sub>2</sub> 2109 (w), 2069 (s), 2059 (m), 2020 (s), 1998 (m), 1982 (w, sh) cm<sup>-1</sup>], <sup>1</sup>H NMR [in CDCl<sub>3</sub>  $\delta$  -12.53 (s, 1H, OsH), 3.53 (t, 2H, OCH<sub>2</sub>), 1.25 (m, 4H, CCH<sub>2</sub>-CH<sub>2</sub>C), 0.86 (t, 3H, CH<sub>3</sub>) ppm], and mass spectroscopy (*m/e* 926 [M]<sup>+</sup> followed by successive loss of CO groups).

**(ii) From [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)].** A solution of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] (80 mg; 0.091 mmol; prepared by thermal hydrolysis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] as reported above) in anhydrous 1-butanol (60 mL; dried over 3 Å molecular sieves) was refluxed under N<sub>2</sub> in a two-necked flask equipped with a Markussen apparatus. After 10 h, the solution was evaporated to dryness and the residue was chromatographed on a silica column using as eluant pentane, to obtain [HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)] (78 mg; 0.084 mmol; 92% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 84%). This reaction was also followed by taking samples of the reaction mixture, evaporating them, and analyzing them by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>. The molar ratio of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)]/[HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)], obtained from the ratio of the corresponding H–Os signal ( $\delta$  -12.64 ppm for [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] and  $\delta$  -12.53 ppm for [HOs<sub>3</sub>(CO)<sub>10</sub>(OBu<sup>n</sup>)] was 2:1, 1:2, and 0:1, after 2, 5, and 10 h, respectively.

**Synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OMe)]. (i) From [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)].** A suspension of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] (6.94 g of powder; 1.95 wt % Os with respect to SiO<sub>2</sub>; 0.706 mmol of Os) in anhydrous methanol (400 mL) acidified with 20 drops of HBF<sub>4</sub>·Et<sub>2</sub>O complex (85%) was refluxed for 11 h under N<sub>2</sub>. The methanolic solution was separated, fresh methanol (400 mL), acidified with 20 drops of HBF<sub>4</sub>·Et<sub>2</sub>O complex (85%), was added to unreacted [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)], and the reaction mixture was refluxed for another 13 h. The combined methanolic solutions were evaporated, and the residue was chromatographed on a silica column using as eluant pentane, to obtain [HOs<sub>3</sub>(CO)<sub>10</sub>(OMe)] (113 mg; 0.127 mmol; 54% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 52%), and then CH<sub>2</sub>Cl<sub>2</sub>, to obtain [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] (31 mg; 0.035 mmol; 15% yield).

**(ii) From [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)].** A solution of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] (104 mg; 0.119 mmol; prepared by thermal hydrolysis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] as reported above) in anhydrous methanol (60 mL; dried over 3 Å molecular sieves) added with 10 drops of HBF<sub>4</sub>·Et<sub>2</sub>O complex (85%) was refluxed for 10 min under N<sub>2</sub> in a two-necked flask equipped with a Markussen apparatus. The solution was then evaporated to dryness, and the residue was chromatographed on a silica column using as eluant pentane, to obtain [HOs<sub>3</sub>(CO)<sub>10</sub>(OMe)] (94 mg; 0.107 mmol; 90% yield; total yield starting from [Os<sub>3</sub>(CO)<sub>12</sub>] 82%). The reaction was slower without acid. In fact, after 10 h under reflux, a mixture of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] and [HOs<sub>3</sub>(CO)<sub>10</sub>(OMe)] was still present, as shown by infrared spectroscopy in the carbonyl region. Evaporation of the solution to dryness afforded a residue which was analyzed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>. The molar ratio of the H–Os signals corresponding to [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] ( $\delta$  -12.64 ppm) and [HOs<sub>3</sub>(CO)<sub>10</sub>(OMe)] ( $\delta$  -12.48 ppm) was 1:1, indicating that only 50% of [HOs<sub>3</sub>(CO)<sub>10</sub>(OH)] had reacted.

**Synthesis of [HOs<sub>3</sub>(CO)<sub>10</sub>(OPh)]. (i) From [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)].** A suspension of [HOs<sub>3</sub>(CO)<sub>10</sub>(OSi≡)] (9.75 g of powder; 1.93 wt % Os with respect to SiO<sub>2</sub>; 0.960 mmol of Os) and phenol (9.02 g; 95.9 mmol; molar ratio PhOH:Os<sub>3</sub> = 300:1) in heptane (400 mL) was refluxed for 5 h under N<sub>2</sub>. The reaction mixture was filtered, concentrated (~40 mL), cooled to ~-78 °C in order to precipitate most phenol, and filtered

again. Evaporation of the heptane solution afforded  $[\text{HOs}_3(\text{CO})_{10}(\text{OPh})]$  contaminated by minor amounts of phenol which were removed by silica column chromatography using as eluant pentane:  $[\text{HOs}_3(\text{CO})_{10}(\text{OPh})]$  was eluted first (198 mg; 0.211 mmol; 66% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  64%).

**(ii) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ .** A solution of  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  (174 mg; 0.201 mmol) prepared by thermal hydrolysis of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  as reported above and phenol (1.89 g; 20.1 mmol; molar ratio  $\text{PhOH}:\text{Os}_3 = 100:1$ ) in anhydrous heptane (60 mL; dried over 3 Å molecular sieves) was refluxed for 5 h under  $\text{N}_2$  in a two-necked flask equipped with a Markuss apparatus. The solution was evaporated to dryness, and the residue was chromatographed on an aluminum oxide column using as eluant pentane:  $[\text{HOs}_3(\text{CO})_{10}(\text{OPh})]$  was eluted first (184 mg; 0.195 mmol; 97% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  88%). By working under the same reaction conditions but in the presence of 8 drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  complex (85%), the formation of  $[\text{HOs}_3(\text{CO})_{10}(\text{OPh})]$  was complete after 45 min. Purification as described above afforded this cluster in 96% yield (182 mg; 0.193 mmol; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  87%). By working under the same conditions, in the presence of 8 drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ , but using a 10:1 molar ratio of  $\text{PhOH}/\text{Os}_3$ , the formation of  $[\text{HOs}_3(\text{CO})_{10}(\text{OPh})]$  was slower, as shown by infrared spectroscopy in the carbonyl region. Evaporation of the solution to dryness afforded a residue which was analyzed by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$ . The molar ratio of the H–Os signals corresponding to  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  ( $\delta -12.64$  ppm) and  $[\text{HOs}_3(\text{CO})_{10}(\text{OPh})]$  ( $\delta -12.18$  ppm) was 2:3.

**Synthesis of  $[\text{HOs}_3(\text{CO})_{10}\text{Cl}]$ .** **(i) from  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ .**  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  (6.30 g of powder; 2.01 wt % Os with respect to  $\text{SiO}_2$ ; 0.642 mmol of Os) was stirred vigorously, at 40 °C under  $\text{N}_2$ , in the biphasic system 37% aqueous  $\text{HCl}/\text{CH}_2\text{Cl}_2$  (50 and 300 mL, respectively). After 6 h, evaporation of the organic phase, followed by recrystallization from pentane, afforded  $[\text{HOs}_3(\text{CO})_{10}\text{Cl}]$  (165 mg; 0.186 mmol; 87% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  84%).

**Synthesis of  $[\text{HOs}_3(\text{CO})_{10}\text{Br}]$ .** **(i) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ .**  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  (6.30 g of powder; 2.01 wt % Os with respect to  $\text{SiO}_2$ ; 0.642 mmol of Os) was stirred vigorously, at 40 °C under  $\text{N}_2$ , in the biphasic system 48% aqueous  $\text{HBr}/\text{CH}_2\text{Cl}_2$  (50 and 300 mL, respectively). After 7 h, evaporation of the organic phase, followed by recrystallization from pentane, afforded  $[\text{HOs}_3(\text{CO})_{10}\text{Br}]$  (178 mg; 0.190 mmol; 89% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  86%).

**(ii) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ .** A  $\text{CH}_2\text{Cl}_2$  solution (60 mL) of  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  (67 mg; 0.077 mmol; prepared by thermal hydrolysis of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  as reported above),  $[\text{NBu}_4]\text{Br}$  (125 mg; 0.387 mmol; molar ratio  $\text{Br}^-:\text{Os}_3 = 5:1$ ), and 8 drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  complex (85%) was refluxed for 30 min under  $\text{N}_2$  and then evaporated to dryness. Extraction with pentane, followed by recrystallization, afforded pure  $[\text{HOs}_3(\text{CO})_{10}\text{Br}]$  (55 mg; 0.060 mmol; 80% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  73%).

**Synthesis of  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$ .** **(i) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ .** A suspension of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  (7.14 g of powder; 1.80 wt % Os with respect to  $\text{SiO}_2$ ; 0.670 mmol of Os) was stirred under  $\text{N}_2$  with a  $\text{CH}_2\text{Cl}_2$  (400 mL) solution of  $[\text{NBu}_4]\text{I}$  (823 mg; 2.23 mmol; molar ratio  $\text{I}^-:\text{Os}_3 = 10:1$ ) added with 16 drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (85%). The reaction was followed by infrared spectroscopy, with monitoring of the increase in intensity of the carbonyl bands of  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$  ( $\nu(\text{CO})$  2113 (w), 2073 (vs), 2065 (s), 2024 (vs), 2007 (sh), 1985 (w)  $\text{cm}^{-1}$ ) in the organic phase. After 4 h, these carbonyl bands did not

grow in intensity. Filtration in a Pyrex Buchner filter funnel under  $\text{N}_2$ , followed by evaporation of the solvent, afforded a residue containing both  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$  and  $[\text{NBu}_4][\text{Os}(\text{CO})_3\text{I}_3]^{21}$  ( $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$  2100 (m), 2018 (s)  $\text{cm}^{-1}$ ). Extraction of the residue with ~80 mL of pentane afforded pure  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$  (89 mg; 0.092 mmol; 41% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  40%).  $[\text{NBu}_4][\text{Os}(\text{CO})_3\text{I}_3]$  was formed during the workup due to the excess of  $\text{I}^-$  and to traces of oxygen. In fact, a blank experiment carried out in air showed that  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$  dissolved in  $\text{CH}_2\text{Cl}_2$  reacts readily with  $[\text{NBu}_4]\text{I}$  (molar ratio  $\text{I}^-:\text{Os}_3 = 10:1$ ) to give  $[\text{NBu}_4][\text{Os}(\text{CO})_3\text{I}_3]$ . Therefore we tried to convert  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  in  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$  by using a stoichiometric amount of  $[\text{NBu}_4]\text{I}$ . However, under these conditions, the formation of  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$  was very slow.

**(ii) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ .** A  $\text{CH}_2\text{Cl}_2$  solution (120 mL) of  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  (156 mg; 0.180 mmol, prepared by thermal hydrolysis of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  as reported above),  $[\text{NBu}_4]\text{I}$  (66 mg; 0.180 mmol), and 6 drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (85%) was refluxed for 30 min under  $\text{N}_2$  and then evaporated to dryness. The resulting yellow residue was treated with pentane (~100 mL) and filtered. The pentane solution was evaporated, affording pure  $[\text{HOs}_3(\text{CO})_{10}\text{I}]$  (158 mg; 0.162 mmol; 90% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  82%).

**Synthesis of  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CR})]$  ( $\text{R}=\text{CH}_3, \text{CF}_3$ ).** **(i) from  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ .**  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  (8.06 g of powder; 1.46 wt % Os with respect to  $\text{SiO}_2$ ; 0.610 mmol of Os) was stirred vigorously, at 90 °C under  $\text{N}_2$ , in  $\text{CF}_3\text{CO}_2\text{H}/\text{toluene}$  (10 and 400 mL, respectively) or  $\text{CH}_3\text{CO}_2\text{H}/\text{toluene}$  (60 and 400 mL, respectively). Filtration, followed by evaporation of the solvent, afforded a residue which was chromatographed on a silica column using as eluant pentane, to obtain  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CR})]$  ( $\text{R}=\text{CH}_3$ , after 10 h, 107 mg, 58% yield, total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  56%;  $\text{R}=\text{CF}_3$ , after 6 h, 141 mg, 72% yield, total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  70%), and then  $\text{CH}_2\text{Cl}_2$ , to obtain  $[\text{Os}(\text{CO})_3(\text{O}_2\text{CCH}_3)_2]$  (12 mg; 6% yield) or  $[\text{Os}(\text{CO})_3(\text{O}_2\text{CCF}_3)_2]$  (traces).

**(ii) From  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ .**  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CCH}_3)]$  was also prepared by refluxing for 5 h under  $\text{N}_2$  a solution of  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  (75 mg; 0.086 mmol),  $\text{CH}_3\text{CO}_2\text{H}$  (3 mL), and heptane (90 mL). Evaporation of the solvent afforded a residue which was chromatographed on a silica column using pentane as eluant to give  $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CCH}_3)]$  (70 mg; 0.077 mmol; 90% yield, total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  82%).

**Synthesis of  $[\text{HOs}_3(\text{CO})_{10}(\text{SCN})]$  from  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$ .** A benzene (60 mL, dried over 3 Å molecular sieves) solution of  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  (133 mg; 0.154 mmol, prepared by thermal hydrolysis of  $[\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)]$  as reported above),  $[\text{NBu}_4][\text{SCN}]$  (462 mg; 1.54 mmol), and 20 drops of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (85%) was stirred at room temperature under  $\text{N}_2$ . After 2.5 h, the solution was evaporated to dryness and the residue was chromatographed on a silica column using as eluant  $\text{CH}_2\text{Cl}_2$ , to obtain  $[\text{HOs}_3(\text{CO})_{10}(\text{SCN})]$  (122 mg; 0.134 mmol; 87% yield; total yield starting from  $[\text{Os}_3(\text{CO})_{12}]$  79%). When a lower amount of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (6 drops) was used, the reaction was slower (22 h, as shown by infrared spectroscopy in the carbonyl region), whereas without acid,  $[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$  did not react.

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