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# Expedient Synthesis of a Metallostibine $Os_2(CO)_8(\mu$ -SbPh): An Unusual and Strong Two-electron Donor Ligand

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**Abstract:** A metallostibine  $Os_2(CO)_8(\mu$ -SbPh), **2**, is generated readily and in high yield and purity from the cluster  $Os_3(CO)_{11}(\mu$ -SbPh)(Cl)<sub>2</sub>, **1**, through elimination of the terminal Lewis acid fragment  $Os(CO)_3(Cl)_2$  with activated  $\gamma$ -alumina. Compound **2** is airsensitive in solution but relatively stable as a solid. The Sb atom in **2** adopts a trigonal pyramidal geometry in both the solid and solution states, with an active lone pair. Experimental and computational studies show that **2** is a strong two-electron donor, with a donor strength comparable to that of alkylphosphines.

#### Introduction

Phosphines, arsines and stibines are among the most ubiquitous of ligands in organometallic chemistry. That their stereoelectronic properties can be varied over a wide range through the substituents have made them an important building block in the toolkit of the organometallic chemist. Among them, those in which one or two of the substituents are transition metal fragments are of particular interest and several structural types are known, obtained via a variety of synthetic routes (Figure 1).<sup>[1]</sup>



Figure 1. Known structural types for metallophosphines, -arsines and -stibines.

Most of the studies to date have been on the monometallopnictides (type **A**). Those of type **A1** among them has attacted more interest due to their potential use as metalloligands for the efficient synthesis of bi- and multimetallic complexes.<sup>[2]</sup> Early interests in them were concerned with the conformational impact of a "transition metal gauche effect",<sup>[3]</sup> and the consequent enhanced solution-phase nucleophilicity of the pnictogen atoms and increased tendency towards dimerization or conversion to the electrophilic form **A2**.<sup>[4]</sup> The bimetallopnictides (type **B**) can similarly be either nucleophilic (**B1**) or electrophilic (**B2** or **B3**). Adoption of a pyramidal (**A1** or **B1**) or trigonal planar (**A2**, **B2** or **B3**) geometry at the pnictogen atom (E) depends on whether or not there are acceptor orbitals on the

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metal fragment for the lone pair to be delocalised, the tendency for metal-metal bond formation, and the steric bulk of the ligands (L) coordinated to the metal atom.<sup>[5]</sup>

While there is a fair amount of studies carried out on electrophilic bi-metallopnictides of types B2 and B3,<sup>[1e, 6]</sup> less is known about nucleophilic bi-metallopnictides of type B1. The bimetallophosphines  $Fe_2Cp_2(CO)_2(\mu-CO)(\mu-PR)$  (Cp= $\eta^5$ -C<sub>5</sub>H<sub>5</sub>; R = Cy, Ph, Mes\*; Mes\*=2,4,6-C<sub>6</sub>H<sub>2</sub>'Bu<sub>3</sub>) have been reported, and their chemistry explored quite extensively.<sup>[7]</sup> In contrast, only three metalloarsines of this type, viz., WCoCp(CO)<sub>5</sub>( $\mu$ -CO)[ $\mu$ -AsCH(SiMe<sub>3</sub>)<sub>2</sub>] and Ru<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO)( $\mu$ -AsR) (Cp= $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>; R Me, Ph), have been reported to date.<sup>[8]</sup> Several metallobismuthine complexes of this type are also known, including a number of iron-bismuth ring complexes  $[Fe(CO)_4BiR]_2$  (R = *i*-Bu, Me, Benzyl, Et) and one osmiumbismuth complex  $Os_2(CO)_8(\mu$ -BiPh). These were, however, obtained in low to moderate yields. The former was obtained from the reaction of the anionic complexes [Et<sub>4</sub>N]<sub>3</sub>{Bi[Fe(CO)<sub>4</sub>]<sub>4</sub>} or [Et<sub>4</sub>N]<sub>2</sub>{Bi(Cl)[Fe(CO)<sub>4</sub>]<sub>3</sub>} with organic halides;<sup>[9]</sup> three other miscellaneous reactions also afforded similar ring analogues.[10] The osmium complex was obtained in low yield (5%), presumably via thermal decomposition of Os<sub>3</sub>(CO)<sub>11</sub>(BiPh<sub>3</sub>).<sup>[11]</sup>

Interestingly, the synthetic methodologies reported for the metallobismuthines could not be used to prepare the corresponding metallostibine analogues. The reason for this may lie with the much stronger donating ability of Sb compared to Bi, making it difficult for the initially formed metallostibine complex to be isolated from the complex reaction mixture without coordination to a metal fragment.[12] The result is that metallostibine complexes of type B1 is the least explored among the group 15 elements. To our knowledge, only one such metallostibine, viz.,  $Fe_2(CO)_8{\mu-Sb[CH(SiMe_3)_2]}$ , has been structurally characterised.<sup>[13]</sup> The bulky CH(SiMe<sub>3</sub>)<sub>2</sub> substituent afforded steric protection of the lone pair on Sb, thus allowing for its isolation. Herein we report the generation and isolation, in high purity and yield, of a metallostibine of type B1 which is sterically less encumbered and has a coordinating ability comparable to that of alkylphosphines.

#### **Results and Discussion**

We recently reported the synthesis of the osmium-antimony carbonyl cluster  $Os_3(CO)_{11}(\mu_3 - SbPh)(CI)_2$ , **1**.<sup>[14]</sup> This cluster can be viewed as an adduct of the metallostibine  $Os_2(CO)_8(\mu - SbPh)$ , **2**, with the electron-deficient fragment  $Os(CO)_3(CI)_2$ . We reasoned that it may be possible to release **2** if it was substituted by other two-electron donors. Cluster **1** failed to react with excess PPh<sub>3</sub> at room temperature but its reaction with PMe<sub>3</sub> indeed afforded **2**, albeit in low yield (< 10%), together with the mononuclear complexes  $Os(CO)_3(CI)_2(PMe_3)_2$ , **4** (Scheme 1). Complex **3** is known,<sup>[15]</sup> and

**4** was characterized spectroscopically and its identity proposed on the basis of the similarity of its IR spectrum with those of other phosphine analogues (Figure S16).<sup>[16]</sup>



Scheme 1. Preparation of 2. Reaction conditions: a. PMe<sub>3</sub> (1.5 equivalents), THF, R.T., 36 h; b. PMe<sub>3</sub> (1.5 equivalents), alumina (100 wt%), THF, 0 °C, 6 h; c. Alumina (2000 wt%), THF, R.T., 20 min.

In the course of chromatographic separation, we observed that activated neutral y-alumina efficiently catalyzed the substitution reaction.<sup>[17]</sup> Thus, in the presence of 100 wt% of neutral  $\gamma$ -alumina,<sup>[18]</sup> the reaction proceeded rapidly even at low temperature (0 °C); the lower reaction temperature disfavored the formation of 4 as well as the thermal decomposition of 1 (Figure S2).<sup>[19]</sup> It was subsequently found that 1 could afford 2 rapidly (20 min at R.T.) and in high yield (91%) simply by stirring with a large excess (2000 wt%) of neutral y-alumina; the phosphine could be dispensed with (Figures S3-S5)! This procedure worked in most of the common solvents, although the reaction rate showed solvent-dependence, with THF being the most favorable among those tested (Figure S6). The role of the  $\gamma$ -alumina is not entirely clear but presumably, it could have acted as a weakly nucleophilic surface to displace 2 from the Os(CO)<sub>3</sub>Cl<sub>2</sub> unit which would be bound as a surface species; in the presence of PMe<sub>3</sub>, complex 3 is formed from it. This is corroborated by the observation that acidic  $\gamma$ -alumina (pH = 6.0 ± 0.5) and basic  $\gamma$ -alumina (pH = 9.5 ± 0.5) showed lower and higher conversion rates, respectively. Brönsted acidic silica, the Lewis acid AICI<sub>3</sub>, and other amphoteric metal oxides with weaker nucleophilic surfaces such as TiO<sub>2</sub> and CeO<sub>2</sub>, did not catalyze the conversion under similar reaction conditions.

The structure of 2 has been confirmed by a single crystal Xray diffraction study; the ORTEP plot depicting its molecular structure is shown in Figure 2, together with selected bond parameters. The geometry about the antimony atom is pyramidal, with retention of the metal-metal bond between the osmium atoms. This is clearly indicative that the antimony atom possesses a lone pair of electrons. The only other crystallographically characterized metallostibine complex of type B1, viz., Fe<sub>2</sub>(CO)<sub>8</sub>{µ-Sb[CH(SiMe<sub>3</sub>)<sub>2</sub>]}, existed as two forms in solution - a closed form with an Fe-Fe bond of type B1, and an open form without an Fe-Fe bond of type B2. Both forms were isolated and characterized spectroscopically, though it was proposed that the open form could gradually convert to the closed form.<sup>[13b,20]</sup> It was also reported that the species  $W_2(CO)_{10}(\mu$ -Sb<sup>t</sup>Bu), a reaction intermediate which was not isolated but characterized through its adducts with PPh<sub>3</sub> and W(CO)<sub>5</sub>, interconverted between a closed form with a W-W bond (type **B2**) and an open form without a W-W bond (type **B1**); the antimony was Lewis basic and acidic, respectively.<sup>[21]</sup>



**Figure 2.** ORTEP plot showing the molecular structure of **2**. Thermal ellipsoids are drawn at the 30% probability level. Organic hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–Os2 = 2.935(2), Os2–Sb5 = 2.7294(17), Os1–Sb5 = 2.7472(17), Os1–Sb5–Os2 = 64.80(5), Os1–Sb5–C51 = 104.8(4), Os2–Sb5–C51 = 108.8(4).

In contrast to these iron- and tungsten-metallostibines, which were neither strongly nucleophilic nor electrophilic, the NMR spectrum of 2 showed only one set of peaks, indicating the presence of only one form in solution. A computational study with DFT showed that a type B2 form of 2 lies ~64 kJ mol-1 higher in energy. These suggest that the same form persists in solution; the pattern for the CO stretches in the calculated IR spectrum for the B1 form was also in good agreement in the experimental spectrum (Figure S7). The metallostibine 2 did not react with PMe<sub>3</sub>, indicating that it was not electrophilic. The adoption of the pyramidal B1 form presumably stems from the saturated nature of the Os<sub>2</sub>(CO)<sub>8</sub> moiety and the strength of the Os-Os bond. We thus believe that, like in the case of the monometallopnictides, this Os<sub>2</sub>(CO)<sub>8</sub> moiety is important to the electron donating ability of 2. There appears, however, to have been no previous measurement of the "nucleophilicity enhancement" of bi-metallopnictides, partly because of the lack of suitable model molecules. We attempted to evaluate the donor ability of 2 in several ways.

The donor ability of group 15 ligands have been quantified via Tolman's electronic parameter ( $\chi$ ), via the shift in the CO stretching frequency of Ni(CO)<sub>3</sub>(L) (where L = two-electron donor ligand) relative to that for L = P<sup>t</sup>Bu<sub>3</sub>.<sup>[22]</sup> Complexes such as M(CO)<sub>5</sub>(L) (where M = Cr, Mo, W) and Rh(Cl)(CO)<sub>2</sub>(L) have also been used as proxies for the acutely toxic Ni complexes.<sup>[23]</sup> A more recent alternative measure of donor ability is the use of <sup>13</sup>C chemical shifts for two-electron donor ligands such as phosphines and N-heterocyclic carbenes (NHCs).<sup>[24]</sup> Good linear correlations have been reported between the  $\delta_{CO}$  in Ni(CO)<sub>3</sub>(L) with (a) the  $\nu_{CO}(A_1)$  (r = 0.962), and (b) the *cis* carbonyl chemical shifts ( $\delta_{CO}$ <sup>*cis*</sup>) in M(CO)<sub>5</sub>(L) complexes (M = Cr, r = 0.983; M = Mo, r = 0.993).<sup>[25]</sup>

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As expected, the metallostibine **2** was found to react readily with  $W(CO)_5(NCCH_3)$  to afford the adduct  $Os_2(CO)_8(\mu_3$ -SbPh) $W(CO)_5$ , **5** (Scheme 2). The metallostibine **2** in the resulting adduct cannot be displaced by PMe<sub>3</sub> under similar reaction conditions to that for the generation of **2** from **1**, and may be ascribed to the lower electrophilicity of the W centre in **5**; its structure has also been determined crystallographically (Figure S1).



Scheme 2. Preparation of 5.

The IR absorption at 2064 cm<sup>-1</sup> for **5** has been identified as the A<sub>1</sub> mode for the W(CO)<sub>5</sub> fragment, by comparison with the calculated spectrum.<sup>[26]</sup> This is tabulated together with the same vibrational mode for a series of phosphine and stibine analogues W(CO)<sub>5</sub>(L) [**5n**, where L = P(OMe)<sub>3</sub> (**a**); PPh<sub>3</sub> (**b**); SbPh<sub>3</sub> (**b**'); PMe<sub>3</sub> (**c**); SbMe<sub>3</sub> (**c**'); P'Bu<sub>3</sub> (**d**); P'Bu<sub>3</sub> (**e**); 1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene (IMes) (**f**) (Table 1). The lower vibrational frequency for **5** suggests that the metallostibine **2** is a strong donor ligand, with donor strength more like the alkylphosphines; the calculated values are also supportive of this (Figure S13). Similarly, the <sup>13</sup>C chemical shift for the carbonyl ligand that is *cis* to the metallostibine ligand in **5** is to lower field than most of the complexes **5n**, lying in between that of **5d** (L = P'Bu<sub>3</sub>) and **5e** (L = P'Bu<sub>3</sub>) (Table 1 and Figure S14).

Table 1.  $v_{\rm CO}(A_1)$  and  $\delta_{\rm CO}{}^{\rm cs}$  for 5 and 5n, and calculated HOMO energies for the corresponding free ligands.

Complex	Ligand (L)	ν <sub>co</sub> (A <sub>1</sub> ) (cm <sup>-1</sup> ) <sup>[a]</sup>	δco <sup>cis</sup> (ppm) <sup>[b]</sup>	Еномо (ev) <sup>[c]</sup>
5	2	2064	198.3	-6.07
5a	P(OMe) <sub>3</sub>	2079	195.3	-6.87
5b'	SbPh₃	2072	196.3	-6.24
5b	$PPh_3$	2072	197.4	-6.00
5c'	SbMe <sub>3</sub>			-6.19
5c	PMe <sub>3</sub>	2069	197.1	-6.19
5d	P <sup>n</sup> Bu <sub>3</sub>	2067	197.5	-5.72
5e	P <sup>t</sup> Bu <sub>3</sub>	2064	199.4	-5.67
5f	IMes	2059	-	-

[a] A<sub>1</sub> mode of the W(CO)<sub>5</sub> fragment, recorded in dichloromethane solutions. [b] <sup>13</sup>C chemical shifts of the *cis* carbonyl ligands in the W(CO)<sub>5</sub> fragment in CDCI<sub>3</sub>. [c] Calculated HOMO energies of the optimized structures of the free ligands L. We have also calculated the HOMO energies for the free ligands using DFT with the B3LYP density functional. The HOMO corresponds to the lone pair and thus the energy of the HOMO may be expected to reflect  $\sigma$ -donating ability. In comparison with the free phosphines and stibines, that for **2** lies between those of PMe<sub>3</sub> and P<sup>*n*</sup>Bu<sub>3</sub>; the aryl phosphine PPh<sub>3</sub> does not appear to follow the trend, probably due to significant delocalization of the phosphorus lone pair into the aromatic ring.<sup>[27]</sup> The energies of the HOMO for some related metallopnictides, *viz.*, M<sub>2</sub>(CO)<sub>*n*</sub>(*μ*-EPh) (where E = P, Sb; M = W, n = 10; M = Os or Fe, n = 8) were also computed (Figure S17 (b)), although all except **2** presented in this work (when M = Os, E = Sb, n = 8) have only been observed as their coordination complexes.<sup>[28]</sup> A comparison shows that the Os(CO)<sub>4</sub> metallo-fragment is more electron-rich than W(CO)<sub>5</sub> and Fe(CO)<sub>4</sub>.

The steric bulk of **2** has also been evaluated using its percent buried volume (%  $V_{Bur}$ ) in **5**;<sup>[29]</sup> it is less bulky (20.5%) than PPh<sub>3</sub> (23.2%), Fe<sub>2</sub>(CO)<sub>8</sub>{ $\mu$ -Sb[CH(SiMe<sub>3</sub>)<sub>2</sub>]} (25.4%) and P<sup>*t*</sup>Bu<sub>3</sub> (27.2%) (Figure S18).

#### Conclusions

We have shown that the metallostibine **2** can be isolated in high purity and yield. It is a very strong donor ligand, with a donor ability that is greater than phosphines such as PPh<sub>3</sub> and PMe<sub>3</sub>, and yet is sterically less bulky than PPh<sub>3</sub>. Together with the fact that it is stable in the solid state, the metallostibine **2** should be useful in the preparation of multimetallic clusters. The findings also alter the prevailing view that stibines are weaker electron donating ligands than phosphines. Metallostibines such as **2** represent a new class of two-electron donor ligands  $[M_2(L)_n(\mu rSbR)]$ , with electron donating ability that should be tunable via the substituent R as well as the ligands L and the metal M. Both sets of investigations are currently underway.

#### **Experimental Section**

General Methods. All reactions were carried out under an argon atmosphere with standard Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Compound 1 was prepared through an adapted method from literature.<sup>[14]</sup> The tungsten complexes 5a-f were prepared according to literature method.<sup>[30]</sup> All activated neutral, basic, and weakly acidic  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Brockmann activity I, particle size: 150 mesh, pore size: 58 Å) were purchased from Sigma-Aldrich and used as received without further activation. TLC separations were carried out on 20 x 20 cm<sup>2</sup> plates coated with silica gel 60 F254 under ambient conditions while the neutral γ-Al<sub>2</sub>O<sub>3</sub> column purifications carried out in glovebox with dry solvents as eluents. NMR spectra were recorded on a 400 MHz NMR spectrometer at room temperature unless otherwise specified. All <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to the residual proton resonance, and the <sup>13</sup>C resonance, of the deuterated solvent used; <sup>31</sup>P chemical shifts were referenced to external 85% aq. H<sub>3</sub>PO<sub>4</sub>. High-resolution mass spectra were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were carried out in-house.

Reaction of 1 with PMe<sub>3</sub> in the absence of  $Al_2O_3$ : Cluster 1 (20 mg, 17  $\mu$ mol) was dissolved in dry THF (8 ml) and PMe<sub>3</sub> (2.0 mg, 25  $\mu$ mol) was

dropwise added. The reaction mixture was stirred at room temperature for 36 h to give a yellow solution; IR monitoring showed **1** was completely consumed. The solvent was then removed and the residue separated by TLC on silica with DCM/hexane (2:1, v/v) as the eluent to give two separable bands. The first, colorless, band was identified as  $Os(Cl)_2(CO)_2(PMe_3)_2$ , **4** ( $R_f = 0.35$ ; yield = 4.0 mg, 49%). IR (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 2033s, 1960s cm<sup>-1</sup>. <sup>1</sup>H(<sup>31</sup>P) NMR (CDCl<sub>3</sub>)  $\delta$  1.78(s, 18H, P(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -33.34. ESI-MS<sup>+</sup> (*m*/z): 488 [M+H<sub>3</sub>O]<sup>+</sup>, 434 [M-Cl]<sup>+</sup>. The second, colorless, band was identified as the known  $Os(Cl)_2(CO)_3(PMe_3)$ , **3** ( $R_f = 0.25$ ; yield = 2.0 mg, 27%). IR (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 2127m, 2054s, 2012m cm<sup>-1</sup>. <sup>1</sup>H NMR (*d*-THF)  $\delta$  1.80 (s, 9H, P(CH<sub>3</sub>)<sub>3</sub>). When the residue was separated on neutral  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> column with DCM/Hex (1:10, v/v) as eluent, the first fraction, yellow solution, afforded small amount of **2** (not quite pure as determined by IR spectrum; yield < 1.0 mg, < 10%).

**Reaction of 1 with PMe**<sub>3</sub> in the presence of Al<sub>2</sub>O<sub>3</sub> (100 wt%): Cluster 1 (20 mg, 17 µmol) was dissolved in dry THF (8 ml) at 0 °C. To the yellowish solution PMe<sub>3</sub> solution in toluene (0.1 M) (0.2 ml, 20 µmol) and neutral  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (20 mg) were sequentially added. The reaction mixture was stirred at 0 °C for 6 h to give a light yellow solution; IR monitoring showed 1 was completely consumed. The solvent was then removed and the residue subjected to a neutral  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> column with dry DCM/Hex (1:10, v/v) as eluent to give 2 in the first fraction (Yield = 10 mg, 72%). Then the eluent was changed to DCM/Hex (1:3, v/v) to give 3 (Yield = 6.0 mg, 82%) and further 4 (trace amount, unweighed).

Reaction of 1 with THF in the presence of Al<sub>2</sub>O<sub>3</sub> (2000 wt%): Cluster 1 (80 mg, 70  $\mu$ mol) was dissolved in dry THF (15 ml) followed by addition of neutral γ-Al<sub>2</sub>O<sub>3</sub> (1.60 g) in one portion. The suspension was stirred at room temperature for 20 min to give a light yellow solution. The suspension was then filtered and Al<sub>2</sub>O<sub>3</sub> further washed with cold THF (< 0 °C) under inert atomosphere. The solvent of the combined filtrate was removed in vacuo to give 2 in a pure enough form (Yield = 51 mg, 91%). IR (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 2118m, 2076s, 2035s, 2021sh, 2006w, 1990w cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -5 °C) δ 7.39 (d, 2H, Ph-*H*), 7.15 (t, 2H, Ph-*H*), 7.08 (t, 1H, Ph-H). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.35 (dd, 2H, Ph-H), 6.96 (m, 2H, Ph-H), 6.88 (m, 1H, Ph-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, -5 °C): δ(CO) 179.33, 178.80, 174.09, 171.99; δ(Ph-C) 138.40, 128.20, 127.90, 127.38. Anal. Calcd for C14H5O8Os2Sb: C 20.93, H 0.63. Found: C 20.74, H 1.19. ESI-MS+ (m/z): 821  $[M+H_2O]^+$ , 737  $[M-3CO+H_2O]^+$ . Note: This reaction and the subsequent work-up can also be easily performed under ambient conditions using normal THF as solvent, but the purity will be slightly lower due to the moderately air-sensitive nature of 2!

**Reaction of 2 with W(CO)**<sub>5</sub>(CH<sub>3</sub>CN): Cluster 2 (15 mg, 19 µmol) was dissolved in dry THF (8 ml), and W(CO)<sub>5</sub>(CH<sub>3</sub>CN) (10 mg, 27 µmol) was added. The reaction mixture was stirred at room temperature for 12 h to give a yellow solution. The solvent was then pumped off and the residue separated by TLC with DCM/hexane (1:2, v/v) as the eluent to give one main yellow band affording Os<sub>2</sub>W(CO)<sub>13</sub>(µ<sub>8</sub>-SbPh), **5** (R<sub>f</sub> = 0.50; yield = 18 mg, 86%). IR (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 2130s, 2092s, 2064s, 2049s, 2022w, 2008w, 1935s cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.26-7.28(m, 2H, Ph-*H*), 6.88-6.92 (m, 2H, Ph-*H*), 6.81-6.85 (m, 1H, Ph-*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  (CO) 200.91 (1C), 198.25 (4C), 175.02 (2C), 174.86 (2C), 170.94 (2C), 170.10 (2C);  $\delta$  (Ph-*C*) 135.47, 129.27, 129.16, 128.90. Anal. Calcd for C<sub>19</sub>H<sub>5</sub>O<sub>13</sub>Os<sub>2</sub>SbW: C 20.24, H 0.45. Found: C 19.80, H 0.99. ESI-MS<sup>+</sup> (*m/z*): 1128 [M+H]<sup>+</sup>.

CCDC-1534534 (for **5**) and -1534535 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

**Supporting Information** (see footnote on the first page of this article): Crystallographic data of **2** and **5**, IR, NMR and MS spectra of all the new compounds, and details of the DFT calculations.

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**Keywords:** Metallostibine • Stibinidene • Strong two-electron donor • Alkylphosphine • Osmium carbonyl

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- [19] A solution of 2 in dry dichloromethane under an inert atmosphere decomposed within 2 days at R.T., and much more rapidly (< 4 h) in air. Coordinating solvents (THF or MeOH) or heat sped up the decomposition. In the solid state, 2 is stable under ambient conditions for at least 20 days.
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## **Entry for the Table of Contents**

## COMMUNICATION

Strong two-electron donor: The stable metallostibine  $Os_2(CO)_8(\mu$ -SbPh) can be obtained in high yield and purity via a one-step reaction. Experimental and computational data show that its donor strength is comparable to that of alkylphosphines.



#### Metallostibine

Ying-Zhou Li, Rakesh, Ganguly, and Weng Kee Leong\*

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Expedient Synthesis of a Metallostibine  $Os_2(CO)_8(\mu$ -SbPh): An Unusual and Strong Two-electron Donor Ligand