limitations for large molecules. In this case, the molecules smaller than the cavities provide lower capacitive effects than the molecules whose shape allows them to fill the cavities.

The new spreader-bar technique provides a simple way of forming stable nanostructures without chemical polymerization. One can suggest possible applications of this principle in the preparation of artificial receptors (for chemosensors, active phases for chromatography, stereoselective catalysis, and membrane filtration), molecular electronic devices, or other nanostructures.

Experimental Section

The interface with artificial binding sites for barbituric acid was prepared on the gold surface by firstly cleaning it with a hot solution of concentrated H_2SO_4 (3 mL) and 30% H_2O_2 (1 mL), then rinsing with water, and drying. **Caution**: this solution reacts violently with most organic materials and must be handled with extreme care. For the preparation of the artificial receptors by the spreader-bar technique, the electrodes were placed into a solution of dodecanethiol (10 μmolL^{-1}) and thiobarbituric acid (10 mmolL^{-1}) in methanol/water (1/9) for 70 h at 22 °C, then rinsed with chloroform, and dried under nitrogen. The electrodes were further investigated during the following few days; no systematic effect on the surface properties was observed with storage. A coating of the electrodes by other species were performed using the same conditions and with the same concentrations of template and matrix compounds. A mixture of dodecanethiol (10 μmolL^{-1}) and barbituric acid (14 mmolL^{-1}) in the same solvent and coating conditions was used for the preparation of the artificial receptors according to two-dimensional molecular imprinting.

All adsorption measurements were performed at room temperature in the electrolyte consisting of phosphate buffer (5 mmolL^{-1}) and KCl (100 mmolL^{-1}) at pH 5.5. The capacitive method used to study adsorption, as well as essential experimental details, are described in reference [12].

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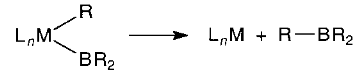
Synthesis and Structures of *cis*- and *trans*-[Os(Bcat)(aryl)(CO)$_2$(PPh$_3$)$_2$]: Compounds of Relevance to the Metal-Catalyzed Hydroboration Reaction and the Metal-Mediated Borylation of Arenes[**]

Clifton E. F. Rickard, Warren R. Roper,* Alex Williamson, and L. James Wright*

Dedicated to Professor Helmut Werner
on the occasion of his 65th birthday

In some discussions of the mechanism of the metal-catalyzed hydroboration of unsaturated hydrocarbons[1, 2] the final step is the reductive elimination of an organoborane from a postulated intermediate **A**, which has both a boryl ligand and a σ-bound carbon ligand (Scheme 1). Theoretical studies of this reaction support the intermediacy of such a metal complex.[3] In related studies arenes and alkenes have been borylated with the metal complexes [CpFe(Bcat)(CO)$_2$], [Mn(Bcat)(CO)$_5$], and [Re(Bcat)(CO)$_5$] (H_2cat = catechol, 1,2-$(HO)_2C_6H_4$) under photolytic conditions.[4] Even alkanes can be functionalized in a similar way with [(C_5Me_5)M(Bcat')$(CO)_n$] (M = Fe, Ru, $n = 2$; M = W, $n = 3$; H_2cat' = 1,2-$(HO)_2C_6H_2$-3,5-Me_2).[5] Although the mechanism of these borylation reactions is not known with certainty, an intermediate of type **A** has been suggested as a reasonable possibility.[5] Despite the obvious significance of characterizing stable examples of metal boryl complexes that also contain a σ-bound carbon ligand, only two rather special examples of such complexes have been described more recently. The first of these is an iridium(IV) complex in which both the boryl and aryl donor atoms are part of a complex chelating ligand system[6] and the second is [Ir(Bcat)(C{CO_2CH_3}=CH{CO_2CH_3})Cl$(PMe_3)_3$] in which the vinyl function arises from insertion of dimethyl acetylenedicarboxylate into an iridium – hydrogen bond.[7]



A

Scheme 1. Reductive elimination of RBR_2 from postulated alkyl, boryl intermediate **A**.

Herein we describe 1) the first stable examples of both coordinatively unsaturated and saturated metal complexes containing boryl and simple σ-bound aryl ligands, 2) structure determinations of both *cis* and *trans* isomers of the coordinatively saturated octahedral examples with implications for the bonding characteristics of the Bcat ligand, and 3) the facile

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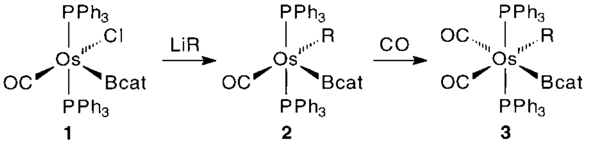
reductive elimination of aryl borane from the *cis* isomer with subsequent oxidative addition of HBcat.

Reaction of the coordinatively unsaturated complex **1**[8] with *o*-tolyllithium in benzene at 5 °C gave the coordinatively unsaturated *o*-tolyl complex **2** as an air-stable solid in high yield (Scheme 2). Remarkably the boryl ligand was not attacked in this reaction. Attempts to synthesize the phenyl and *p*-tolyl analogues were not successful, and the steric protection afforded by the bulkier *o*-tolyl ligand could be important in stabilizing the coordinatively unsaturated **2.** No tractable products from the reaction of the ruthenium complex $[Ru(Bcat)Cl(CO)(PPh_3)_2]$[8] with *o*-tolyllithium could be isolated.



Scheme 2. Synthesis of *o*-tolyl, boryl complexes **2** and **3**. R = *o*-tolyl.

The ^1H and ^{13}C NMR spectra of **2**, both at room temperature and at −40 °C, show two sets of signals for the *o*-tolyl, the Bcat, and the triphenylphosphane ligands in a ratio of approximately 7:2. We interpret this as indicating the presence of two isomers in solution arising from hindered rotation about the osmium-*o*-tolyl bond. Complex **2** reacted rapidly with carbon monoxide to give the corresponding six-coordinate complex **3** in high yield. Solutions of **3** were unstable at room temperature (see following discussion), but a crystal structure determination was carried out on a single crystal grown from toluene/*n*-hexane at −20 °C.[9] The structure (Figure 1) reveals a distorted octahedral arrangement about osmium in which the *o*-tolyl and boryl ligands are mutually *cis* and the phosphane ligands mutually *trans*. The very strong *trans* influence of the boryl ligand is illustrated by the fact that the Os–CO distance *trans* to the boryl ligand (1.964(7) Å) is greater than the corresponding distance for the carbonyl ligand *trans* to the *o*-tolyl ligand (1.904(6) Å). Since *o*-tolyl is recognized as a strong σ-bonding ligand, the observed greater *trans* influence for the Bcat ligand indicates that in this molecule Bcat is not only a good σ-bonding ligand but also a good π acceptor. A consequence of this bonding situation is that a carbonyl ligand *trans* to Bcat can be activated towards nucleophilic attack (see later discussion). Both the boryl ligand and the *o*-tolyl ligand are tilted out of the plane of best fit through the Os, C(1), C(2), C(11), and B atoms by 22.87(13) and 24.96(10)°, respectively. The Os–B distance is 2.155(7) Å, which is longer than those reported for other six-coordinate osmium-Bcat complexes.[8b] The Os–C(11) distance of 2.202(6) Å is at the long end of the range of Os–aryl bond lengths.

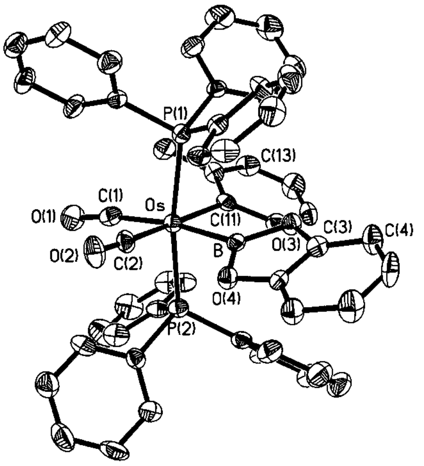
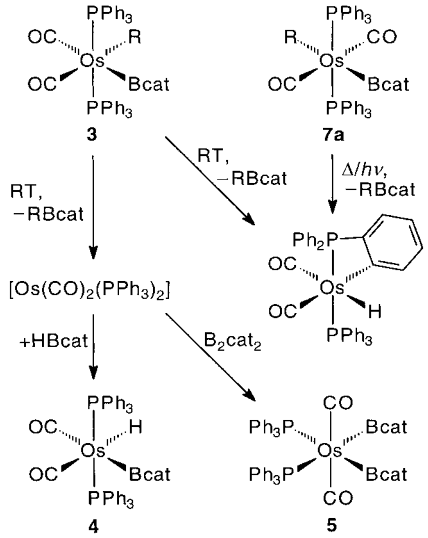


Figure 1. Molecular structure of **3** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Os–B 2.154(7), Os–C(1) 1.964(7), Os–C(2) 1.903(6), Os–C(11) 2.202(6), Os–P(1) 2.4060(17), Os–P(2) 2.4050(17); C(1)-Os-B 169.6(3), P(1)-Os-P(2) 171.50(6), C(1)-Os-C(2) 88.1(2), C(1)-Os-C(11) 95.1(2), C(2)-Os-B 82.9(2), C(11)-Os-B 94.0(2), C(2)-Os-C(11) 176.5(2).

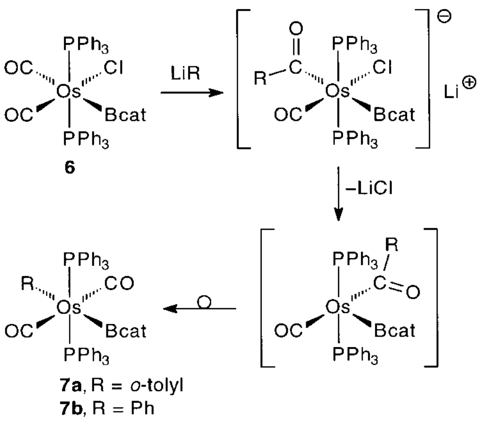
Complex **3** eliminated *o*-tolylBcat slowly at room temperature in benzene to give $[Os(CO)_2(PPh_3)_2]$, which could not be isolated, and in the absence of a further reactant orthometalation occurred to give $[Os(C_6H_4PPh_2)H(CO)_2(PPh_3)]$ (Scheme 3).[10] Complex **3** is therefore a convenient precursor for $[Os(CO)_2(PPh_3)_2]$, which can react with suitable compounds in situ before orthometalation can occur. Examples are the oxidative addition with HBcat to give **4**,[11] and with B_2cat_2 to give the bis(Bcat) complex **5**.



Scheme 3. Reductive elimination of *o*-tolylBcat from *o*-tolyl, boryl complexes. R = *o*-tolyl.

These two reactions, reductive elimination of arylborane and the oxidative addition of HBcat, model two consecutive steps in the catalytic cycle often proposed for transition metal catalyzed hydroboration.[2] The elimination of *o*-tolylBcat from **3** in $CDCl_3$ at 24 °C was monitored by ^1H NMR spectroscopy. After approximately 100 min half of complex **3** had undergone elimination, and this was accompanied by formation of $[OsCl_2(CO)_2(PPh_3)_2]$ from the reaction of $[Os(CO)_2(PPh_3)_2]$ and the solvent. The reductive elimination of *o*-tolylBcat from **3** was suppressed at temperatures at or below −20 °C.

A geometrical isomer of complex **3** with *o*-tolyl and Bcat ligands located mutually *trans* can be prepared as shown in Scheme 4. Carbonylation of complex **1** gave the *cis* complex



Scheme 4. Postulated mechanism for formation of the *trans* isomer **7**.

6.[11] Reaction of **6** with *o*-tolyllithium yielded **7a**. We propose that the reaction proceeds initially by nucleophilic attack of *o*-tolyl anion at the activated carbonyl ligand *trans* to Bcat. Subsequent loss of the chloro ligand forms a neutral complex in which the acyl ligand may adopt either an η^1 or η^2 bonding mode. An alternative possibility is that the acyl oxygen atom may interact weakly with the boron atom, thereby controlling the geometry of the intermediate and so influencing the specificity of the observed product. Reverse migratory insertion occurs such that the *o*-tolyl group assumes the position *trans* to the Bcat ligand giving the observed isomer **7a** (Scheme 4). Complex **6** reacted in the same way with PhLi to give **7b.**

The X-ray crystal structure of **7a** is shown in Figure 2. The geometry about osmium is a distorted octahedron in which the two carbonyl ligands are mutually *trans* and the Bcat ligand is *trans* to the *o*-tolyl ligand. Both the Bcat and the *o*-tolyl ligands are tilted out of the plane of best fit through the Os, C(1), C(2), C(11), and B atoms by 16.72(41) and 36.82(40)°, respectively. The Os–B distance of 2.132(7) Å is close to that of complex **3**. However, the Os–C(11) distance of 2.277(5) Å is significantly greater than that of complex **3** (2.202(6) Å), illustrating again the very strong *trans* influence of the Bcat ligand relative to the carbonyl ligand.

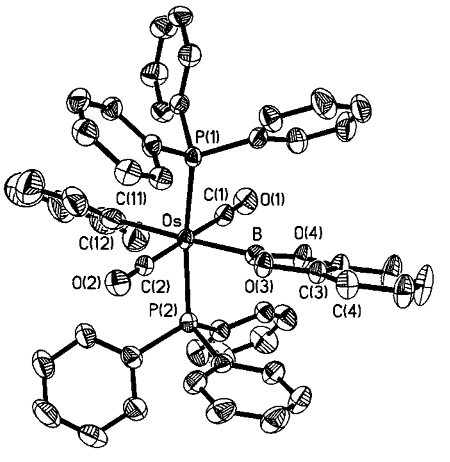


Figure 2. Molecular structure of **7a** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Os–B 2.132(7), Os–P(1) 2.3791(17), Os–P(2) 2.3874(17), Os–C(1) 1.952(7), Os–C(2) 1.930(7), Os–C(11) 2.277(5); C(1)-Os-B 88.5(3), P(1)-Os-P(2) 169.76(5), C(1)-Os-C(2) 178.6(3), C(1)-Os-C(11) 94.2(3), C(2)-Os-B 91.8(3), C(11)-Os-B 175.5(3), C(2)-Os-C(11) 85.6(3).

Complex **7a** is considerably more robust with respect to reductive elimination of *o*-tolylBcat than complex **3**. Unchanged **7a** was recovered after heating under reflux in benzene for 2 h. However, formation of $[\mathrm{Os(C_6H_4PPh_2)H(CO)_2(PPh_3)}]$ occurred when the boiling solution was irradiated with a 1000-W tungsten–halogen lamp (see Scheme 3). Presumably, under these conditions the molecule rearranges to form the *cis* isomer **3**, which immediately reductively eliminates *o*-tolylBcat and undergoes orthometalation. These observations indicate that the requirement for facile reductive elimination is that the aryl and Bcat ligands be adjacent to one another. Complex **3** is therefore a useful model for a key intermediate proposed in both metal-catalyzed hydroboration and aryl borylation.

Experimental Section

2: To a rapidly stirred suspension of **1** (166 mg, 0.185 mmol) in benzene at 5 °C was slowly added a solution of *o*-tolyllithium in diethyl ether (0.75 M, 0.32 mL, 0.24 mmol). The mixture was allowed to warm to room temperature and was then stirred for 30 min. During this time the starting material dissolved to form a cloudy orange solution. The benzene was then reduced to a volume of 1 mL in vacuo, and *n*-hexane was added to precipitate **2** as a yellow solid. This was collected and washed with ethanol and *n*-hexane. Yield 162 mg (92 %); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, –40 °C, TMS): major isomer: $\delta = 0.31$ (s, 3 H, $\mathrm{C_6H_4}\mathit{CH_3}$), 5.23 (d, $J = 7.2$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.10 (t, $J = 7.1$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.45 (d, $J = 7.3$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.58 (t, $J = 7.1$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.88 (m, 4 H, Bcat), 7.25–7.41 (m, 30 H, $\mathrm{PPh_3}$); minor isomer: $\delta = 0.15$ (s, 3 H, $\mathrm{C_6H_4}\mathit{CH_3}$), 5.72 (d, $J = 7.1$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.53 (t, $J = 7.1$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.66 (t, $J = 7.0$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.79 (m, 2 H, Bcat), 6.97 (m, 3 H, Bcat with $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 7.16–7.23 (m, $\mathrm{PPh_3}$); ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$, –40 °C, TMS): major isomer: $\delta = 24.65$ (s, $\mathrm{C_6H_4}\mathit{CH_3}$), 110.17 (Bcat), 118.99 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 120.28 (s, Bcat), 121.80 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 127.54 (t′,[12] $^{2,4}J$(C,P) = 9 Hz, *o*-$\mathrm{PPh_3}$), 129.59 (s, *p*-$\mathrm{PPh_3}$), 131.13 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 132.06 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 132.66 (t′, $^{1,3}J$(C,P) = 49 Hz, *i*-$\mathrm{PPh_3}$), 134.43 (t′, $^{3,5}J$(CP) = 10 Hz, *m*-$\mathrm{PPh_3}$), 148.89 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 150.20 (s, Bcat), 180.03 (t, ^2J(C,P) = 13 Hz, *i*-$\mathit{C_6}\mathrm{H_4CH_3}$), 196.66 (t, ^2J(C,P) = 8 Hz, CO); minor isomer: $\delta = 18.07$ (s, $\mathrm{C_6H_4}\mathit{CH_3}$), 119.91 (s, Bcat), 121.11 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 127.42 (*o*-$\mathrm{PPh_3}$), 128.81 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 129.19 (s, *p*-$\mathrm{PPh_3}$), 133.68 (t′, $^{1,3}J$(C,P) = 50 Hz, *i*-$\mathrm{PPh_3}$), 133.91 (t′, $^{3,5}J$(C,P) = 10 Hz, *m*-$\mathrm{PPh_3}$), 140.56 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 149.88 (s, Bcat), 171.07 (t, ^2J(C,P) = 12 Hz, *i*-$\mathit{C_6}\mathrm{H_4CH_3}$), other signals not observed; IR (Nujol): $\tilde{\nu} = 1903$ cm^{-1} (vs, CO); elemental analysis calcd for $\mathrm{C_{50}H_{41}BO_3OsP_2}$ (%): C 63.03, H 4.34; found: C 62.88, H 4.54.

3: Complex **2** (150 mg, 0.157 mmol) was dissolved in benzene (10 mL) to give a yellow solution through which a stream of CO gas was passed for 5 s, turning the solution colorless. The volume of the benzene was reduced to about 1 mL in vacuo, and *n*-hexane was added to precipitate **3** as a white solid, which was collected and washed with ethanol and *n*-hexane. Yield 137 mg (89 %); ^{1}H NMR: $\delta = 1.96$ (s, 3 H, $\mathrm{C_6H_4}\mathit{CH_3}$), 6.17 (t, $J = 7.2$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.46 (d, $J = 7.4$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.63 (t, $J = 7.1$ Hz, 1 H, $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$), 6.79 (m, 4 H, Bcat), 7.05–7.23 (m, 31 H, $\mathrm{PPh_3}$ and $\mathrm{C_6}\mathit{H_4}\mathrm{CH_3}$); ^{13}C{^{1}H} NMR: $\delta = 33.13$ (s, $\mathrm{C_6H_4}\mathit{CH_3}$), 110.74 (s, Bcat), 119.87 (s, Bcat), 122.35 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 122.60 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 127.22 (t′, $^{2,4}J$(C,P) = 9 Hz, *o*-$\mathrm{PPh_3}$), 127.35 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 129.41 (s, *p*-$\mathrm{PPh_3}$), 133.47 (t′, $^{1,3}J$(C,P) = 54 Hz, *i*-$\mathrm{PPh_3}$), 133.69 (t′, $^{3,5}J$(C,P) = 10 Hz, *m*-$\mathrm{PPh_3}$), 145.37 (t, ^2J(C,P) = 11 Hz, *i*-$\mathit{C_6}\mathrm{H_4CH_3}$), 147.84 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 148.98 (s, $\mathit{C_6}\mathrm{H_4CH_3}$), 149.64 (s, Bcat), 183.37 (t, ^2J(C,P) = 7 Hz, CO), 186.09 (t, ^2J(C,P) = 7 Hz, CO); IR (Nujol): $\tilde{\nu}$ 1997 (vs), 1937 cm^{-1} (vs, CO); elemental analysis calcd for $\mathrm{C_{51}H_{41}BO_4OsP_2}$ (%): C 62.45, H 4.21; found: C 62.15, H 4.23.

7a: A colorless solution of **6** (0.415 g, 0.449 mmol) in benzene (25 mL) was cooled to 5 °C. A solution of *o*-tolyllithium in diethyl ether (0.75 M, 0.78 mL, 0.58 mmol) was added slowly to the rapidly stirred solution, and the resulting mixture was pale yellow and cloudy. The mixture was allowed to

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warm to room temperature and then stirred for 30 min. The volatiles were removed in vacuo and the resultant solid dissolved in dichloromethane (15 mL). Ethanol (7 mL) was then added and the dichloromethane removed in vacuo to precipitate a white solid, which was collected and washed with ethanol and *n*-hexane. The solid was recrystallized from dichloromethane/ethanol to give pure **7a**. Yield 0.324 g (74 %); ^{1}H NMR (24 °C): $\delta = 1.74$ (s, 3 H, $C_6H_4CH_3$), 6.33 (t, $J = 6.8$ Hz, 1 H, $C_6H_4CH_3$), 6.72 (m, 2 H, Bcat), 6.80 (m, 3 H, Bcat and $C_6H_4CH_3$), 6.85 (d, $J = 6.8$ Hz, 1 H, $C_6H_4CH_3$), 7.08 – 7.25 (m, 30 H, PPh_3); $^{13}C\{^1H\}$ NMR (24 °C): $\delta = 31.17$ (s, $C_6H_4CH_3$), 110.27 (s, Bcat), 119.85 (s, Bcat), 122.55 (s, $C_6H_4CH_3$), 124.13 (s, $C_6H_4CH_3$), 127.47 (t′, $^{2,4}J(C,P) = 9$ Hz, *o*-PPh_3), 127.98 (s, $C_6H_4CH_3$), 129.48 (s, *p*-PPh_3), 133.60 (t′, $^{3,5}J(C,P) = 9$ Hz, *m*-PPh_3), 134.70 (t′, $^{1,3}J(C,P) = 51$ Hz, *i*-PPh_3), 146.47 (t, $^2J(C,P) = 9$ Hz, *i*-C_6H_4Me), 149.41 (s, $C_6H_4CH_3$), 149.84 (s, $C_6H_4CH_3$), 150.35 (s, Bcat), 189.75 (t, $^2J(C,P) = 7$ Hz, CO), 192.71 (t, $^2J(C,P) = 7$ Hz, CO); IR (Nujol): $\tilde{\nu} = 1941$ (vs), 2038 cm^{-1} (w, CO); elemetal analysis calcd for $C_{51}H_{41}BO_4OsP_2 \cdot 1.2\,CHCl_3$ (%): C 55.77, H 3.78; found: C 55.74, H 3.82.

5: A mixture of **3** (89 mg, 0.091 mmol) and B_2cat_2 (60 mg, 0.25 mmol) was dissolved in benzene (10 mL) and stirred at room temperature for 16 h. The benzene was removed from the resulting orange solution, and then dichloromethane (10 mL) was added. The resultant suspension was filtered through Celite, and ethanol (5 mL) was added to the filtrate. The dichloromethane was removed in vacuo to give **5** as a white precipitate which was collected and washed with ethanol. Yield 46 mg (50 %); ^{1}H NMR: $\delta = 6.69$ (m, 4 H, Bcat), 6.82 (m, 4 H, Bcat), 7.08 – 7.18 (m, 18 H, PPh_3), 7.30 (m, 12 H, PPh_3); $^{13}C\{^1H\}$ NMR: $\delta = 110.71$ (s, Bcat), 120.04 (s, Bcat), 127.86 (t′, $^{2,4}J(C,P) = 10$ Hz, *o*-PPh_3), 129.49 (s, *p*-PPh_3), 133.20 (t′, $^{3,5}J(C,P) = 12$ Hz, *m*-PPh_3), 136.40 (m, *i*-PPh_3), 150.17 (s, Bcat), 189.76 (t, $^2J(C,P) = 8.5$ Hz, CO); IR (Nujol): $\tilde{\nu} = 1963$ cm^{-1} (vs, CO); elemental analysis calcd for $C_{50}H_{38}B_2O_6OsP_2$ (%): C 59.54, H 3.80; found: C 59.30, H 3.51.

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[9] Data for the X-ray structure analyses: **3**: Crystals from chloroform/toluene (– 20 °C), $C_{51}H_{41}BO_4OsP_2 \cdot C_7H_8$ ($M_r = 1072.92$); crystal dimensions 0.15 × 0.08 × 0.05 mm; triclinic; space group $P\bar{1}$; $a = 12.06320(10)$, $b = 13.7859(2)$, $c = 15.2392(2)$ Å, $\alpha = 73.9760(10)$, $\beta = 86.6520(10)$, $\gamma = 85.8510(10)°$, $Z = 2$, $V = 2427.51(5)$ Å^3, $\rho_{calcd} = 1.468$ g cm^{-3}; $T = 203$ K; $2\theta_{max} = 50°$; total reflections 22 672 of which 8466 were unique ($R_{int} = 0.0703$); Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); empirical absorption correction ($\mu = 2.740$ mm^{-1}, $T_{min}/T_{max} = 0.6840/0.8752$). The structure was solved by Patterson methods and refined by full matrix least squares on F^2 on all data. The asymmetric unit cell contains one molecule of **3** and one molecule of toluene. $R_1 = 0.0473$ for the 6469 observed data ($I > 2\sigma(I)$) and $wR_2 = 0.0845$ for all data. Goodness of fit (F^2) = 1.035. **7a**: Crystals from chloroform/*n*-hexane, $C_{51}H_{41}BO_4OsP_2 \cdot CHCl_3$ ($M_r = 1100.16$); crystal dimensions 0.42 × 0.27 × 0.09 mm; triclinic; space group $P\bar{1}$; $a = 10.6356(5)$, $b = 14.5521(7)$, $c = 19.4083(9)$ Å, $\alpha = 68.9500(10)$, $\beta = 76.4950(10)$, $\gamma = 73.2160(10)°$, $Z = 2$, $V = 2655.5(2)$ Å^3, $\rho_{calcd} = 1.376$ g cm^{-3}; $T = 203$ K; $2\theta_{max} = 55.02°$; total reflections 22 438 of which 11 362 were unique ($R_{int} = 0.0366$); Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); empirical absorption correction ($\mu = 2.652$ mm^{-1}, $T_{min}/T_{max} = 0.4021/0.7963$). The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 on all data. The asymmetric unit cell contains one molecule of **7a** and one molecule of chloroform split between two sites; $R_1 = 0.0557$ for the 10 128 observed data ($I > 2\sigma(I)$) and $wR_2 = 0.1640$ for all data. Programs used: SHELXS-97 (structure solution) and SHELXL-97 (structure refinement). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-104 125 (**3**) and CCDC-104 126 (**7a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] The notation t′ indicates that the signal has apparent multiplicity; $^{n,m}J(C,P)$ is the sum of the two coupling constants $^mJ(C,P)$ and $^nJ(C,P)$ as explained in: S. M. Maddock, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1996**, *15*, 1793 – 1803.

Thermally Stable Heterobinuclear Bivalent Group 14 Metal Complexes $Ar_2M{-}Sn[1,8\text{-}(NR)_2C_{10}H_6]$ (M = Ge, Sn; Ar = 2,6-$(Me_2N)_2C_6H_3$; R = CH_2tBu)**

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Homobinuclear tin(II) compounds $Sn_2R'_4$, free of bridging ligands, and their germanium(II) analogues have attracted much attention.[1] The first such crystallographically characterized compound **I** was reported 25 years ago,[2] followed more recently by **II**,[3] **III**,[4] and **IV**.[5] Only one example of a crystalline, bivalent bis[tin(II)] compound with different ligands attached to each tin atom, namely, the thermally labile **V**, had previously been described.[6] In **I** – **III** and **V**, the Sn–Sn distance *l* was in the range 2.77 – 2.91 Å (cf. 2.81 Å in tetrahedral tin), while in **IV** (which has close Sn ··· F contacts) the tin – tin distance of 3.64 Å is too large for significant Sn ··· Sn bonding. Each of **I** – **IV**, unlike **V**, was either partially (**III** > **I**[1]) or completely dissociated in toluene or methylcyclohexane. There was some evidence for formation of the transient

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