

Ruthenium vs. Osmium Complexes as Catalysts for Atom Transfer Radical Addition Reactions

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Keywords: ATRA / ATRC / Osmium / Radical reactions / Ruthenium

The catalytic activity of [Cp*OsBr₂(PPh₃)] in conjunction with Mg has been evaluated for atom transfer radical addition (ATRA) and cyclization (ATRC) reactions. The Os complex enabled these reactions to be performed with similar efficiency as that of the analogous Ru complex [Cp*RuCl₂(PPh₃)]. The olefin complex [Cp*OsBr(H₂C=CHPh)(PPh₃)]

was obtained by reduction of [Cp*OsBr₂(PPh₃)] with Mg in the presence of an excess of styrene, whereas an analogous Ru complex was not observed. Kinetic investigations suggest that olefin complexes of Os can form under catalytic conditions.

Introduction

Halogenated compounds can be coupled to olefins by an atom transfer radical addition mechanism. Pioneering studies in this area were performed by Kharasch and his group in the 1940s,^[1] and reactions of this type are commonly referred to as “Kharasch reactions”.^[2] Modern, transition-metal-catalyzed versions of this reaction have found numerous applications in organic synthesis.^[2,3] Copper^[4] and ruthenium complexes^[5,6] typically show the best catalytic performance for ATRA reactions. One of the most active catalysts described so far is the half-sandwich complex [Cp*RuCl₂(PPh₃)] (**1**), which is used in conjunction with either AIBN or Mg.^[6] This catalytic system enables turnover numbers of 1000 or above to be obtained for a number of substrates. Furthermore, it has been successfully applied to atom transfer radical cyclization (ATRC) reactions, which are particularly interesting from a synthetic point of view.^[6a]

The metal-catalyzed atom transfer radical polymerization (ATRP) of olefins is mechanistically closely related to ATRA reactions.^[3b] For the former reaction, it was reported that the Os^{II} complex [Cp*OsBr(PiPr₃)] is a more active catalyst than its Ru analogue [Cp*RuCl(PiPr₃)].^[7] This finding suggested that Os complexes could also be beneficial for ATRA and ATRC reactions. Below we report the results of a study in which we have compared the catalytic activity of the complex [Cp*RuCl₂(PPh₃)] (**1**) with that of its Os analogue [Cp*OsBr₂(PPh₃)] (**2**). Furthermore, we demonstrate that olefin complexes are readily formed in the

case of Os, whereas the analogous Ru complexes are significantly less stable. The implication of this finding for the mechanism of the reaction is discussed.

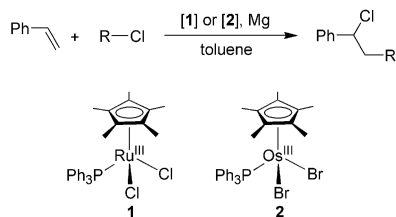
Results and Discussion

First, we have evaluated the catalytic performance of the complexes [Cp*RuCl₂(PPh₃)] (**1**) and [Cp*OsBr₂(PPh₃)] (**2**) for different intermolecular ATRA reactions. Complex **2** is not a perfect analogue of **1**, because – apart from the metal – the halide coligand has also been changed from chloride to bromide. The synthetic chemistry of organometallic Os–Br complexes is much more developed than the chemistry of Os–Cl complexes (the reduction of OsO₄ is more facile with HBr than with HCl).

The halogenated compounds used in our study were ethyl trichloroacetate, ethyl dichloroacetate, and chloroform, and the olefinic reaction partner was styrene. The reactions were performed with substrate concentrations of [styrene] = [R–Cl] = 500 mM in neat toluene with catalyst concentrations of 0.1 and 0.02 mol-%. All reactions were carried out in the presence of an excess of Mg powder. It should be noted that these conditions are not necessarily the optimum conditions for these reactions (faster conversions can be achieved with higher substrate concentrations),^[6a] but the goal of this study was to evaluate the relative performance of the Ru and the Os catalyst. The results of the reactions are summarized in Table 1.

For the addition of ethyl dichloroacetate to styrene at room temp. we found that reactions with the Ru complex **1** were faster than with the Os complex **2**: after 24 h, we observed a full conversion of styrene in the case of complex **1**, whereas a conversion of only 57% was recorded for reactions with complex **2** (Table 1, Entries 1 and 2). At 60 °C,

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Table 1. ATRA reactions of chlorinated compounds to styrene catalyzed by complex **1** or **2** in the presence of Mg.^[a]

Entry	Cat.	RCl	Temp. [°C]	[RCl]/[Cat]	Yield (Conv.) [%]
1	1	CCl ₂ HCO ₂ Et	r.t.	1000:1	84 (>99)
2	2	CCl ₂ HCO ₂ Et	r.t.	1000:1	42 (57)
3	1	CCl ₂ HCO ₂ Et	60	1000:1	84 (>99)
4	2	CCl ₂ HCO ₂ Et	60	1000:1	84 (>99)
5	1	CCl ₂ HCO ₂ Et	60	5000:1	14 (31)
6	2	CCl ₂ HCO ₂ Et	60	5000:1	16 (39)
7	1	CCl ₃ CO ₂ Et	60	1000:1	55 (83)
8	2	CCl ₃ CO ₂ Et	60	1000:1	24 (45)
9	1	CCl ₃ CO ₂ Et	60	5000:1	17 (31)
10	2	CCl ₃ CO ₂ Et	60	5000:1	3 (14)
11	1	CHCl ₃	60	1000:1	28 (47)
12	2	CHCl ₃	60	1000:1	31 (47)

[a] Reaction conditions: [RCl] = 500 mM; [styrene] = 500 mM; [Ru/Os] = 0.50 or 0.10 mM (0.1 or 0.02 mol-%), [Mg] = 100 mg (4.1 mmol), toluene, reaction time 24 h. The data represent averaged values of two independent experiments. Yields and styrene conversions were determined by GC using mesitylene as the internal standard.

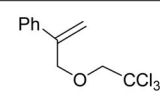
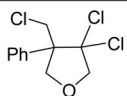
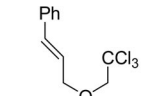
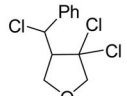
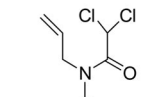
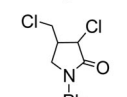
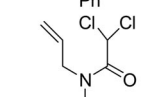
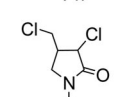
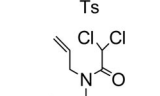
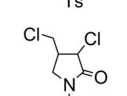
however, the differences in reactivity were much less pronounced, and comparable yields and conversions were obtained for reactions with 0.1 and 0.02 mol-% of catalyst (Table 1, Entries 3–6). Apparently, the Os complex **2** benefits more from the enhanced reaction temperature. A possible explanation is that the reduction of the Os^{III} precursor **2** to a catalytically active Os^{II} species by Mg is relatively slow at room temp. This assumption is substantiated by the following observation: when a toluene solution of the Ru^{III} complex **1** is added to a flask containing Mg, a rapid color change from orange to yellow is observed at room temp. within minutes. In the case of the Os^{III} complex **2**, however, a change in color proceeds slowly within the first hour.

For the reaction of ethyl trichloroacetate with styrene, we found that the Ru complex **1** gave superior results, even at 60 °C (Table 1, Entries 7–10). However, the differences in reactivity were not very pronounced. Comparable yields and conversions were observed for reactions with chloroform as the substrate (Table 1, Entries 11 and 12). For all reactions investigated, the yields were lower than the conversions. This is likely to be a result of the formation of oligomers, a common problem in ATRA reactions.^[4,5]

Next, we tested the performance of the catalysts **1** and **2** in atom transfer radical cyclization (ATRC) reactions. We used two trichloroethyl ethers and three dichloroacetamides as representative substrates. The cyclizations were performed at 60 °C with 1.0 mol-% of the complexes **1** or **2** in the presence of Mg. The results are summarized in Table 2. In most cases the Ru complex **1** gave better results in terms

of yield. On the other hand, the diastereoselectivity was higher for the Os-catalyzed reactions, in particular for the substrate 1-(2,2,2-trichloroethoxy)-3-phenylprop-2-ene (Entry 2). It should be noted, however, that the stereoselectivity was found to change during the course of the reaction. When ATRC reactions with 1-(2,2,2-trichloroethoxy)-3-phenylprop-2-ene were examined after 40 min, both the Ru- and the Os-catalyzed reactions showed a diastereoselectivity of 19:1 (the yields at that point were 61% and 20%, respectively). These results suggest that epimerization processes are occurring, which are more pronounced for reactions with the “faster” Ru catalyst.

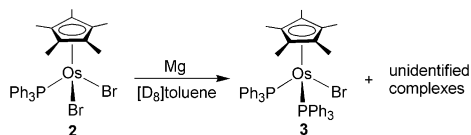
Table 2. ATRC reactions catalyzed by complex **1** or **2** in the presence of Mg.^[a]

Entry	Substrate	Product	Cat.	Yield (Conv.) [%]
1			1	87 (100)
			2	92 (100)
2			1	88 (99) [6:1] ^[c]
			2	78 (91) [15:1] ^[c]
3			1	86 (96) [3.4:1] ^[c]
			2	71 (88) [3.4:1] ^[c]
4 ^[b]			1	58 (73) [4:1] ^[c]
			2	27 (57) [5:1] ^[c]
5			1	91 (100) [2.4:1] ^[c]
			2	81 (83) [2.6:1] ^[c]

[a] Reaction conditions: [substrate] = 100 mM; [Ru/Os] = 1.0 mM (1.0 mol-%), [Mg] = 100 mg (4.1 mmol), [D₈]toluene, 60 °C, reaction time: 24 h. Yields and conversions were determined by NMR spectroscopy using mesitylene as the internal standard. [b] 2.5 mol-% of catalyst was used. [c] Diastereoselectivity.

For ATRA reactions with the catalyst precursor [Cp*₂RuCl₂(PPh₃)] (**1**) it is assumed that the reaction starts by Mg-induced reduction to give an Ru^{II} complex that can reversibly abstract a halogen atom from the substrate.^[8] A likely candidate for the active Ru^{II} catalyst is the 16e⁻ complex [Cp*₂RuCl(PPh₃)], but attempts to prepare this complex on a preparative scale have failed.^[9] However, it was possible to stabilize a structurally related complex by using a sterically very demanding cyclopentadienyl ligand.^[10] In the case of Os, the synthesis and the structure of the 16e⁻ complex [Cp*₂OsBr(PiPr₃)] has been reported,^[11] but, to the best of our knowledge, an analogous PPh₃ complex is not known. We wanted to explore the Mg-induced reduction of complex **2** in more detail. Thus, a [D₈]toluene suspension of **2** (0.025 mmol in 1 mL of solvent) was mixed with an excess of Mg. After 24 h, the Mg was filtered off, and the solution was investigated by NMR spectroscopy. The major

diamagnetic species in solution (36% yield, as determined with the internal standard mesitylene) was found to be the known complex $[\text{Cp}^*\text{OsBr}(\text{PPh}_3)_2]$ (**3**) (Scheme 1).^[12]



Scheme 1. Reduction of complex **2** by Mg.

The reduction of complex **2** with Mg apparently induced a ligand transfer of PPh_3 . We have not tried to optimize this synthetic procedure since complex **3** is more conveniently obtained by reaction of $[\text{Cp}^*\text{OsBr}_2]_2$ with PPh_3 .^[12] However, we have performed a single-crystal X-ray analysis of **3** (Figure 1). For comparison, we have also examined the solid-state structure of the precursor **2** (Figure 2).

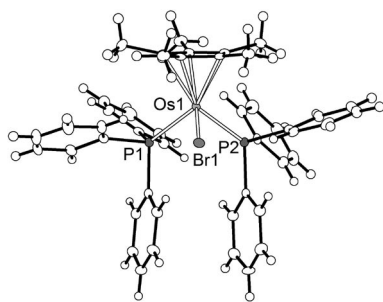


Figure 1. Molecular structure of complex **3** with ellipsoids at the 50% probability level. Only one of the two independent molecules in the unit cell is shown. Selected bond lengths [Å] and angles [°]: Os1–Br1 2.5934(4), Os1–P1 2.3370(9), Os1–P2 2.3313(9); P2–Os1–P1 96.51(3), P2–Os1–Br1 88.61(2), P1–Os1–Br1 93.98(2).

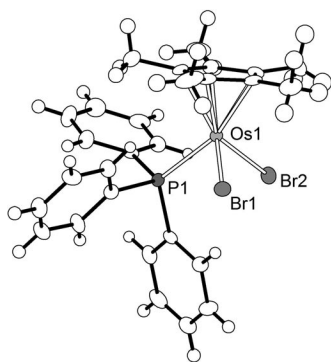
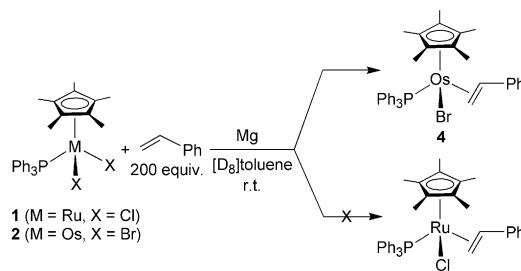


Figure 2. Molecular structure of complex **2** with ellipsoids at the 50% probability level. Selected bond lengths [Å] and angles [°]: Os1–Br1 2.5110(9), Os1–Br2 2.4955(8), Os1–P1 2.3379(1); P1–Os1–Br1 88.49(5), P1–Os1–Br2 88.50(5), Br2–Os1–Br1 97.81(3).

Both complexes show the expected three-legged piano-stool geometry. The Os–Br and Os–P bond lengths observed for **3** (Figure 1) are very similar to those found for the analogous complex $[\text{Cp}\text{OsBr}(\text{PPh}_3)_2]$ ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$).^[13] The Os–Br bond lengths [2.5110(9) and 2.4955(8) Å] of the Os^{III} complex **2** are shorter than that

found for the Os^{II} complex **3** [2.5934(4) Å]. A similar shortening has been observed for the analogous Ru complexes $[\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)]$ [Ru–Cl 2.4042(5) and 2.3775(5) Å]^[6a] and $[\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2]$ [Ru–Cl 2.4583(6) Å].^[14]

We have also investigated the reduction of the complexes **1** and **2** with Mg in the presence of an excess of styrene (Scheme 2). This experiment was performed to evaluate the possibility that the hypothetical intermediates $[\text{Cp}^*\text{MX}(\text{PPh}_3)]$ are stabilized by coordination to the olefinic substrate. As before, the reactions were performed in deuterated toluene to allow in situ NMR analyses. For reactions with the Os complex **2**, we observed the formation of a new complex **4** with a ^{31}P NMR signal at $\delta = 7.4$ ppm. In the ^1H NMR spectrum, this complex showed three well-defined signals at $\delta = 5.71$ (dd), 2.91 (ddd), and 2.47 (ddd) ppm, which suggests the presence of coordinated styrene (the signals of “free” styrene can be observed at $\delta = 6.82$, 5.86, and 5.35 ppm). The description of **4** as an olefin complex with the formula $[\text{Cp}^*\text{OsBr}(\text{H}_2\text{C}=\text{CHPh})(\text{PPh}_3)]$ was also supported by the ^{13}C NMR spectroscopic data. For reactions with the Ru complex **1** we did not find evidence for the formation of a diamagnetic styrene complex (the ^1H NMR spectrum showed no signals between $\delta = 2$ and 3 ppm). It is interesting to note that olefin complexes of the formula $[\text{Cp}^*\text{RuCl}(\text{H}_2\text{C}=\text{CHR})(\text{PPh}_3)]$ ($\text{R} = \text{CN}, \text{COCH}_3$) have been prepared by reaction of $[\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2]$ with the respective olefin in thf .^[15] We have attempted a similar reaction with styrene: complex $[\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2]$ (0.020 mm) was mixed with styrene (0.050 mm) in $[\text{D}_8]\text{thf}$, and a ^1H NMR spectrum was recorded after 4 h. As before, we did not observe signals corresponding to an olefin complex. These results suggest that the hypothetical styrene complex $[\text{Cp}^*\text{RuCl}(\text{H}_2\text{C}=\text{CHPh})(\text{PPh}_3)]$ is significantly less stable than complexes with electron-deficient olefins such as acrylonitrile or 3-buten-2-one, a finding that is in line with what has been observed for other late-transition-metal complexes.^[16]



Scheme 2. Reduction of the complexes **1** and **2** by Mg in the presence of an excess of styrene.

The facile formation of the styrene complex $[\text{Cp}^*\text{OsBr}(\text{H}_2\text{C}=\text{CHPh})(\text{PPh}_3)]$ (**4**) has potential implications for the mechanism of Os-catalyzed ATRA reactions since olefin complexes are possible intermediates, which could inhibit the reaction.^[17] To investigate this issue in more detail, we have performed a kinetic study of the Os-catalyzed ATRA reaction of ethyl trichloroacetate with styrene. The reactions were performed with a fixed concentra-

tion of $[\text{Cl}_3\text{CCO}_2\text{Et}] = 100 \text{ mM}$ and $[\mathbf{2}] = 0.50 \text{ mM}$ in the presence of Mg powder. The styrene concentrations were varied from 12.5 mM to 3.2 M, and the initial rate of the reaction was calculated from the yields obtained at nine different times within the first 25 min. For comparison, we have performed reactions with the Ru complex **1** under otherwise identical conditions. The results are summarized in Figure 3.

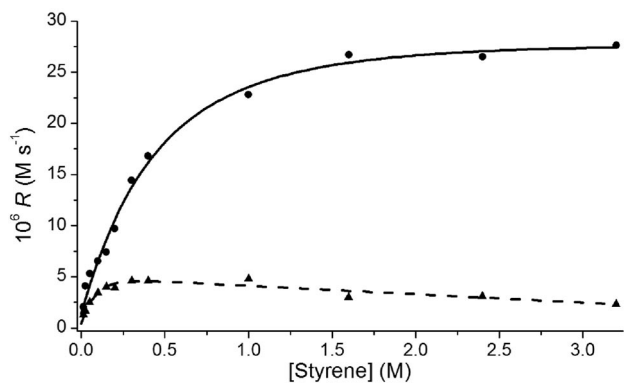


Figure 3. Observed initial reaction rates vs. initial styrene concentrations for the ATRA of ethyl trichloroacetate to styrene catalyzed by the Ru^{III} complex **1** (dots) or by the Os^{III} complex **2** (triangles) in the presence of Mg. Reaction conditions: [ethyl trichloroacetate] = 100 mM; [Ru/Os] = 0.50 mM, [Mg] = 100 mg, toluene, 60 °C. Yields were determined by GC using mesitylene as the internal standard.

For reactions with the Ru catalyst **1** one observes a nearly linear correlation between the initial reaction rate and the styrene concentration for $[\text{styrene}] \leq 200 \text{ mM}$. This result is in line with what we observed previously for kinetic studies carried out at 35 °C.^[8] At higher styrene concentrations, however, the reaction rates level off with saturation occurring at $[\text{styrene}] \approx 2 \text{ M}$. Such a saturation is expected because the high styrene/ $\text{Cl}_3\text{CCO}_2\text{Et}$ ratio favors oligomeric side products.^[18] Reactions with the Os complex **2** were slower than those with the Ru complex **1**. Importantly, the reaction rates started to level off at much lower styrene concentrations, and concentrations of above 1 M led to a decrease in the rate.

In addition, we have investigated the catalytic activity of the isolated styrene complex **4**, using the addition of ethyl dichloroacetate to styrene ($[\text{styrene}] = 500 \text{ mM}$, $[\text{Cl}_2\text{HCCO}_2\text{Et}] = 500 \text{ mM}$, $[\mathbf{4}] = 0.50 \text{ mM}$) as a test reaction.^[19] The initial rate of the reaction was found to be $1.3(\pm 0.2) \times 10^{-5} \text{ M s}^{-1}$, which is lower than that observed for reactions with the catalyst precursor **2** [$2.4(\pm 0.3) \times 10^{-5} \text{ M s}^{-1}$].

The results suggest that Os-catalyzed ATRA reactions of halogenated compounds with styrene can be inhibited by the formation of olefin complexes, in particular when the reactions are performed with high concentrations of styrene. One should point out, however, that we have only indirect evidence for the relevance of styrene complexes under catalytic conditions, and alternative explanations for the observed data cannot be ruled out.

Conclusions

We have studied the catalytic activity of the Os complex $[\text{Cp}^*\text{OsBr}_2(\text{PPh}_3)]$ (**2**) in conjunction with Mg for intra- and intermolecular atom transfer radical reactions. It was found that the complex is a potent catalyst, which enables the ATRA and ATRC reactions to be performed in an efficient manner. However, under the conditions studied, its activity was either similar or lower than that of $[\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)]$ (**1**). It is thus not justified to use a more expensive and toxic Os complex for these types of reactions. The isolation of $[\text{Cp}^*\text{OsBr}(\text{H}_2\text{C}=\text{CHPh})(\text{PPh}_3)]$ (**4**) shows that olefin complexes are more likely to form in reactions with Cp^*Os catalysts, and this should be considered for future studies with Os-catalyzed polymerization reactions.^[17,20]

Experimental Section

General: The complexes $[\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)]$ (**1**),^[21] $[\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2]$,^[22] and $[\text{Cp}^*\text{OsBr}_2(\text{PPh}_3)]$ (**2**),^[23] were prepared according to literature procedures. The substrates 1-(2,2,2-trichloroethoxy)-2-phenylprop-2-ene,^[5a] 1-(2,2,2-trichloroethoxy)-3-phenylprop-2-ene,^[24] *N*-allyl-2,2-dichloro-*N*-phenylacetamide,^[25] *N*-allyl-2,2-dichloro-*N*-(4-tolylsulfonyl)acetamide,^[26] and *N,N*-diallyl-2,2-dichloroacetamide^[26] for the ATRC reactions were also prepared according to published procedures. Mg powder (>99%) was purchased from Fluka and was agitated by means of a stirring bar under dry dinitrogen for 10 d before use. All ATRA, ATRC, and synthesis reactions were performed in a glove box under dinitrogen. The solvents were collected under dinitrogen from an Innovative Technologies SPS-400-5 solvent system. The commercially available substrates were distilled from appropriate drying agents and stored under dinitrogen. GC measurements were made with a Varian Chrompack CP3-380 apparatus (Chrompack CP-SIL8CB column; 30 m; 250 μm) coupled to an FID detector. The NMR spectra (¹H, ¹³C, ³¹P) were recorded at room temp. with a Bruker AVANCE DPX 400 spectrometer. Chemical shifts are relative to solvent signals as internal references; $\delta(^{31}\text{P})$ are relative to external H_3PO_4 (85% in D_2O). Microanalyses (C, H, N) were performed with an EA 1110 CHN Carlo Erba instrument.

General Procedure for the ATRA Reactions: An aliquot of a stock solution of complex **1** or **2** in toluene (400 μL of a 1.25 mM stock solution) was added to a 1.5 mL vial containing Mg powder (100 mg). The total volume was increased to 800 μL with toluene, and the resulting mixture was stirred at room temp. or 60 °C for 10 min. The reaction was then initiated by addition of 200 μL of a freshly prepared stock solution containing styrene, the chlorinated compound, and mesitylene as an internal standard. The solution was stirred at room temp. or 60 °C, and samples (25 μL) were removed at given times from the reaction mixtures, diluted with non-deoxygenated acetone (500 μL), and analyzed by GC chromatography.

General Procedure for the ATRC Reactions: An aliquot of a stock solution of complex **1** or **2** in $[\text{D}_8]$ toluene (800 μL of a 1.25 mM stock solution) was added to a 1.5 mL vial that contained Mg powder (100 mg). The resulting mixture was stirred at 60 °C for 10 min. The reaction was then initiated by addition of 200 μL of a freshly prepared stock solution containing the substrate and mesitylene as an internal standard in $[\text{D}_8]$ toluene. For *N*-allyl-2,2-dichloro-*N*-(4-tolylsulfonyl)acetamide, a 1.5 mL vial was charged with 2.5 μmol of the solid catalysts **1** (or **2**), 100 mg of Mg, and 800 μL of $[\text{D}_8]$ -

toluene, and the mixture stirred at 60 °C for 10 min, before 200 μL of a freshly prepared stock solution containing the substrate and mesitylene as an internal standard in $[\text{D}_8]$ toluene was added. After 24 h, the reaction mixture was analyzed by ^1H NMR spectroscopy.

Reduction of Complexes 1 and 2 with or without Styrene: Complex 1 or 2 (5.0 μmol) and Mg powder (100 mg) were suspended in $[\text{D}_8]$ -toluene (1.0 mL). If styrene was used, 200 equiv. (1 mmol, 114.6 μL) of it were added. The resulting reaction mixtures were stirred at room temp. for 2 h, and the liquid phase was analyzed by ^1H NMR and ^{31}P NMR spectroscopy.

Synthesis of Complex 4: Styrene (800 μL , 6.99 mmol) was added to a suspension of complex 2 (33 mg, 44 μmol) and Mg (300 mg) in toluene (15 mL). The mixture was stirred at 35 °C for 15 h and then filtered through a glass frit. Solvents and excess styrene were removed under vacuum to give complex 4 as a yellow solid. Yield: 27 mg (ca. 75%). ^1H NMR (400 MHz, C_6D_6): δ = 1.23 (d, J = 1.4 Hz, 15 H, C_5Me_5), 2.47 (ddd, J = 15.7, J = 7.7, J = 2.6 Hz, 1 H, $\text{CH}=\text{CH}_2$), 2.91 (ddd, J = 10.2, J = 2.8, J = 2.6 Hz, 1 H, $\text{CH}=\text{CH}_2$), 5.71 (dd, J = 10.2, J = 7.7 Hz, 1 H, $\text{CH}=\text{CH}_2$), 6.98–8.18 (m, 20 H, aromatic) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ = 7.4 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ = 8.98 (s, C_5Me_5), 21.0 (d, J = 4.4 Hz, $\text{CH}=\text{CH}_2$), 41.8 (d, J = 2.9 Hz, $\text{CH}=\text{CH}_2$), 92.1 (d, J = 2.9 Hz, C_5Me_5), 124.8–136.9 (m), 145.9 (s) ppm. Attempts to characterize complex 4 by elemental analysis were unfortunately not successful. We assume that the styrene ligand is partially removed during the drying procedure.

Crystallographic Analyses: Single crystals of complex 2 were obtained by slow vapor diffusion of pentane into a benzene solution of 2. Single crystals of complex 3 were obtained by slow diffusion of hexane at -18 °C into a toluene solution, which was obtained after reduction of complex 2 with Mg and filtration. Intensity data for 2 were collected with an Oxford Diffraction KM-4 CCD dif-

fractometer, whereas in the case of 3 a Bruker APEX II CCD was employed, both having kappa geometry and using graphite-monochromatized Mo- K_α radiation (λ = 0.71073 Å) at low temperature. A summary of the crystallographic data, the data-collection parameters, and the refinement parameters are given in Table 3. Data reduction was carried out with CrysAlis PRO^[27] (2) and EvalCCD^[28] (3) and then corrected for absorption.^[29] Structure solution and refinement were performed with the SHELXTL software package.^[30] The structures were refined by using the full-matrix least-squares routines on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models in calculated positions by using the riding model. CCDC-772348 (2) and -772349 (3) 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.

Acknowledgments

This work was supported by the Swiss National Science Foundation and by the Ecole Polytechnique Fédérale de Lausanne (EPFL). We thank Dr. E. Solari for help with the crystallographic measurements.

Table 3. Crystallographic data for the complexes 2 and 3.

	Complex 2	Complex 3
Empirical formula	$\text{C}_{28}\text{H}_{30}\text{Br}_2\text{OsP}$	$\text{C}_{46}\text{H}_{45}\text{BrOsP}_2$
M_r [g mol^{-1}]	747.51	929.87
Crystal size [mm]	$0.32 \times 0.28 \times 0.17$	$0.31 \times 0.16 \times 0.37$
Crystal system	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/c$
a [Å]	8.7145(2)	17.349(2)
b [Å]	32.4584(8)	10.7211(10)
c [Å]	18.2551(6)	20.5972(17)
α [°]	90	90
β [°]	91.504(3)	101.101(8)
γ [°]	90	90
V [Å ³]	5161.8(2)	3759.4(7)
Z	8	4
ρ_{calcd} [g cm^{-3}]	1.924	1.643
T [K]	140(2)	100(2)
μ [mm^{-1}]	8.114	4.573
θ range [°]	2.64–27.88	3.36–27.51
Reflections collected	12237	86119
Independent reflections	12237	8624
Absorption corrections	semi-empirical	semi-empirical
Max./min. transmissions	1.00000/0.19163	1.0000/0.7237
Data/restraints/parameters	12237/0/579	8624/0/451
Goodness of fit on F^2	1.125	1.242
Final R indices [$I < 2\sigma(I)$]	$R_1 = 0.0517$, $wR_2 = 0.1318$	$R_1 = 0.0297$, $wR_2 = 0.0494$
R indices (all data)	$R_1 = 0.0600$, $wR_2 = 0.1354$	$R_1 = 0.0430$, $wR_2 = 0.0531$
Max. peak/hole [$\text{e} \text{Å}^{-3}$]	4.944/–2.163	0.778/–0.657

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Received: April 8, 2010
Published Online: July 2, 2010