

Supporting information for the manuscript:

On the Origin of Activity in Cu, Ru, and Os Mediated Radical Polymerization

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I. Determination of K_{ATRP} when ([Mt^zL_n]₀ ≠ [RX]₀)

When an excess of alkyl halide initiator to activator is employed, the values of a function F([XMt^{z+1}L_n]) defined in Eq. (1S) are plotted against time, and K_{ATRP} is obtained from the slope of the linear dependence.

$$\begin{aligned} F\left(\left[XMt^{z+1}L_n\right]\right) &= \left(\frac{[RX]_0 [Mt^z L_n]_0}{\left[Mt^z L_n\right]_0 - [RX]_0} \right)^2 \times \\ &\left(\frac{1}{\left[Mt^z L_n\right]_0^2 \left([RX]_0 - [XMt^{z+1}L_n]\right)} + \frac{2}{[RX]_0 \left[Mt^z L_n\right]_0 \left(\left[Mt^z L_n\right]_0 - [RX]_0\right)} \ln \left(\frac{[RX]_0 - [XMt^{z+1}L_n]}{\left[Mt^z L_n\right]_0 - [XMt^{z+1}L_n]} \right) + \frac{1}{[RX]_0^2 \left(\left[Mt^z L_n\right]_0 - [XMt^{z+1}L_n]\right)} \right) = \\ &= 2k_t K_{ATRP}^2 t + \left(\frac{[RX]_0 [Mt^z L_n]_0}{\left[Mt^z L_n\right]_0 - [RX]_0} \right)^2 \left(\frac{1}{\left[Mt^z L_n\right]_0^2 [RX]_0} + \frac{2}{[RX]_0 \left[Mt^z L_n\right]_0 \left(\left[Mt^z L_n\right]_0 - [RX]_0\right)} \ln \frac{[RX]_0}{\left[Mt^z L_n\right]_0} + \frac{1}{[RX]_0^2 \left[Mt^z L_n\right]_0} \right) \end{aligned} \quad (1S)$$

II. Electronic Spectra

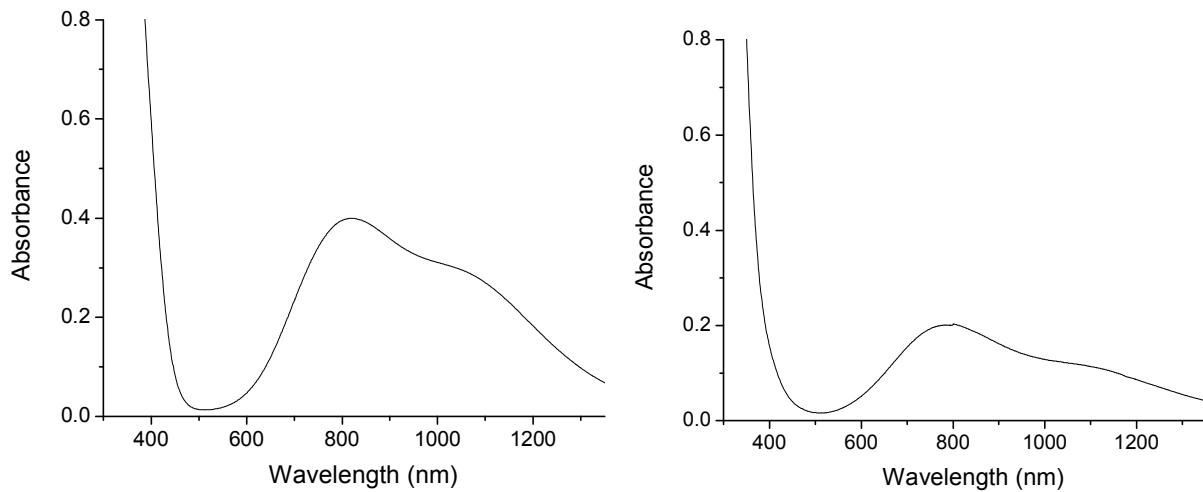


Figure 1S. 1.00 mM electronic spectra of (left) $\text{CuBr}_2(\text{BPMODA})$ and (right) $\text{CuCl}_2(\text{BPMODA})$.

Change in absorbance at 820 and 790 nm, respectively, later followed when determining K_{ATRP} (corresponding Cu^{I} species do not significantly absorb at these wavelengths).

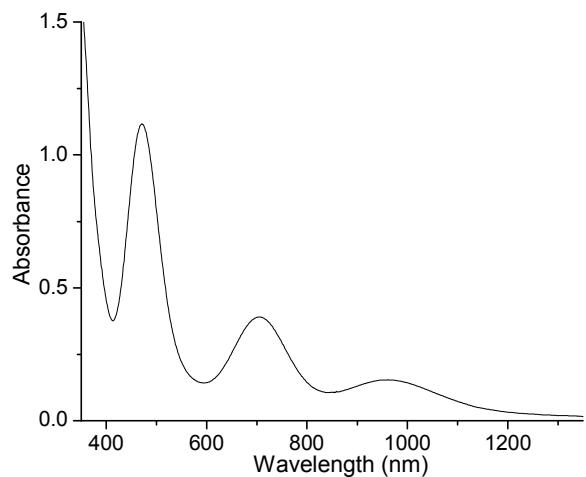


Figure 2S. 1.00 mM electronic spectra of $\text{OsBr}_2(\text{PPh}_3)_3$. Change in absorbance at 705 nm later followed when determining K_{ATRP} (corresponding Os^{III} species does not significantly absorb at 705 nm).

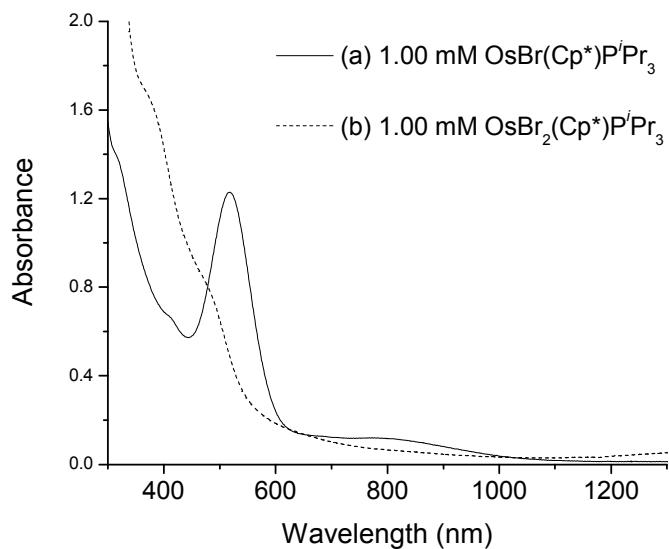


Figure 3S. 1.00 mM electronic spectra of (a) $\text{OsBr}(\text{Cp}^*)\text{P}^i\text{Pr}_3$ and (b) $\text{OsBr}_2(\text{Cp}^*)\text{P}^i\text{Pr}_3$. Change in absorbance at 385 nm later followed for determination of K_{ATRP} .

III. K_{ATRP} Plots

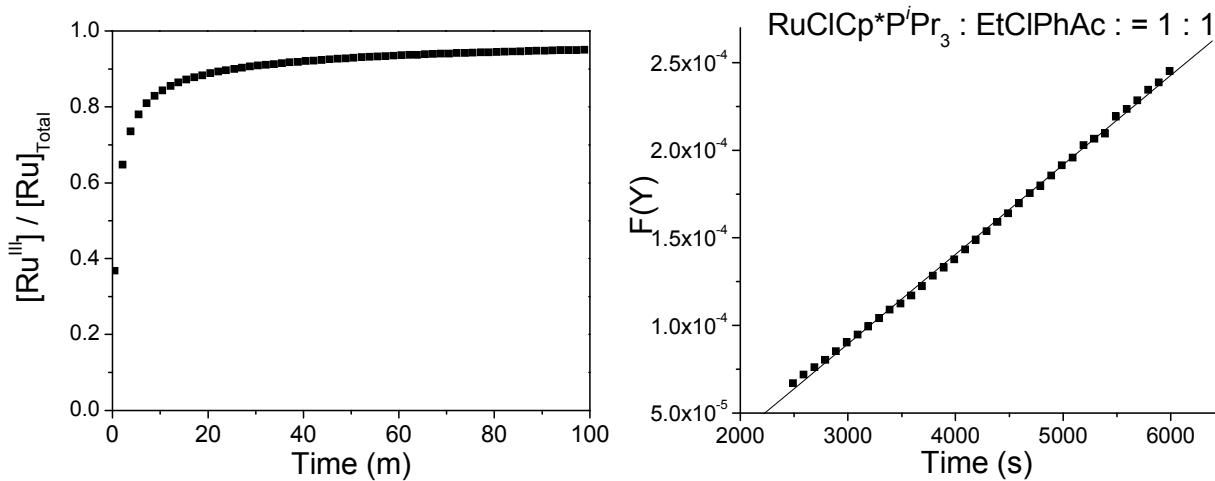


Figure 4S. Determination of K_{ATRP} for the reaction of $\text{RuCl}(\text{Cp}^*)\text{P}^i\text{Pr}_3$ (1.09 mM) with 1 eq. EtClPhAc in THF: a) accumulation of Ru^{III} deactivator with time and b) plot of $F([\text{RuCl}_2(\text{Cp}^*)\text{P}^i\text{Pr}_3])$ against time.

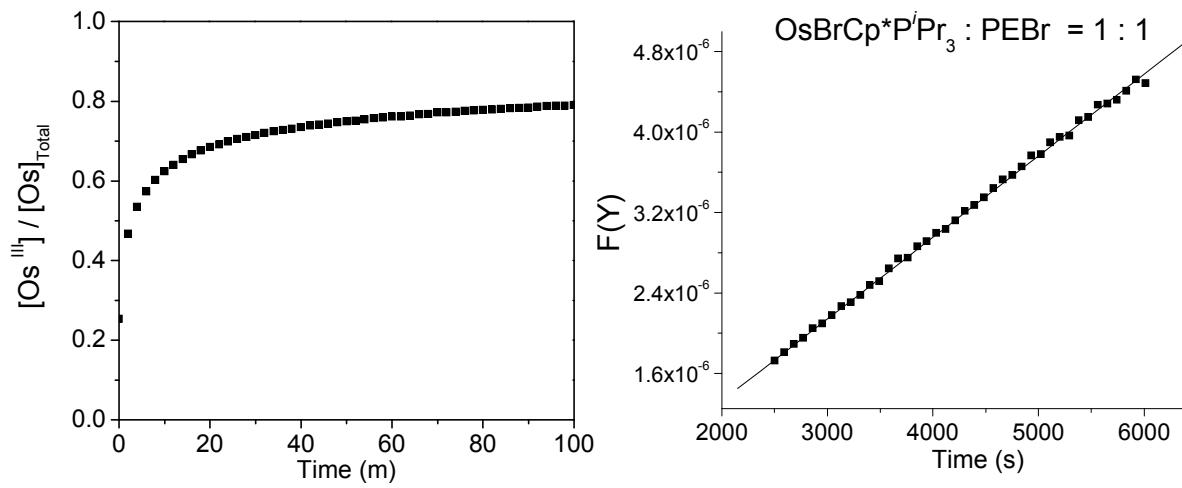


Figure 5S. Determination of K_{ATRP} for the reaction of $\text{OsBr}(\text{Cp}^*)\text{P}^i\text{Pr}_3$ (1.27 mM) with 1 eq. PEBr in THF: a) accumulation of Os^{III} deactivate with time and b) plot of $F([\text{OsBr}_2(\text{Cp}^*)\text{P}^i\text{Pr}_3])$ against time.

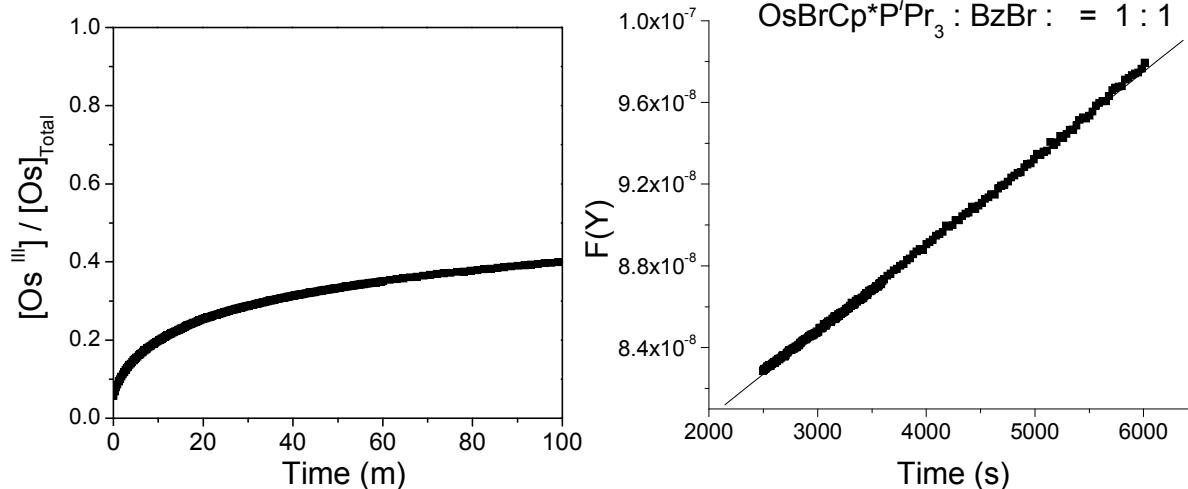


Figure 6S. Determination of K_{ATRP} for the reaction of $\text{OsBr}(\text{Cp}^*)\text{P}^i\text{Pr}_3$ (0.884 mM) with 1 eq. BzBr in THF: a) accumulation of Os^{III} deactivate with time and b) plot of $F([\text{OsBr}_2(\text{Cp}^*)\text{P}^i\text{Pr}_3])$ against time.

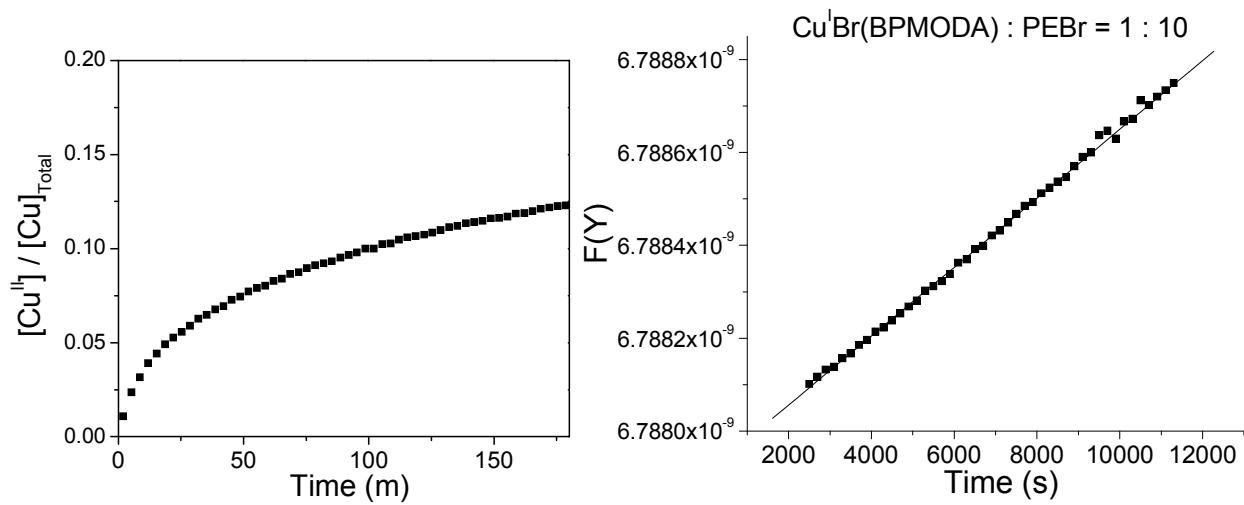


Figure 7S. Determination of K_{ATRP} for the reaction of CuBr(BPMODA) (2.14 mM) with 10 eq. PEBr in THF: a) accumulation of Cu^{II} deactivator with time and b) plot of $F([\text{CuBr}_2(\text{BPMODA})])$ against time.

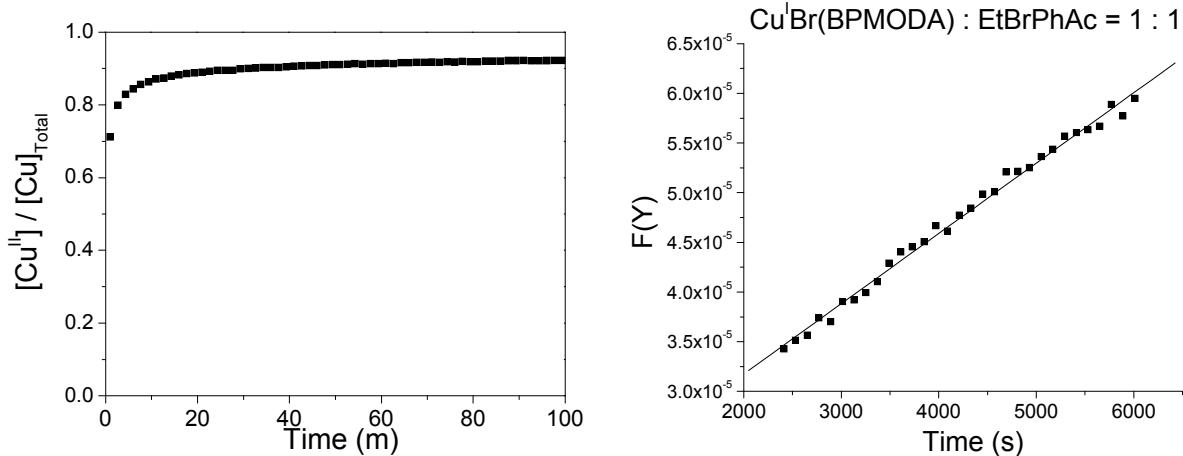


Figure 8S. Determination of K_{ATRP} for the reaction of CuBr(BPMODA) (0.94 mM) with 1 eq. EtBrPhAc in THF: a) accumulation of Cu^{II} deactivator with time and b) plot of $F([\text{CuBr}_2(\text{BPMODA})])$ against time.

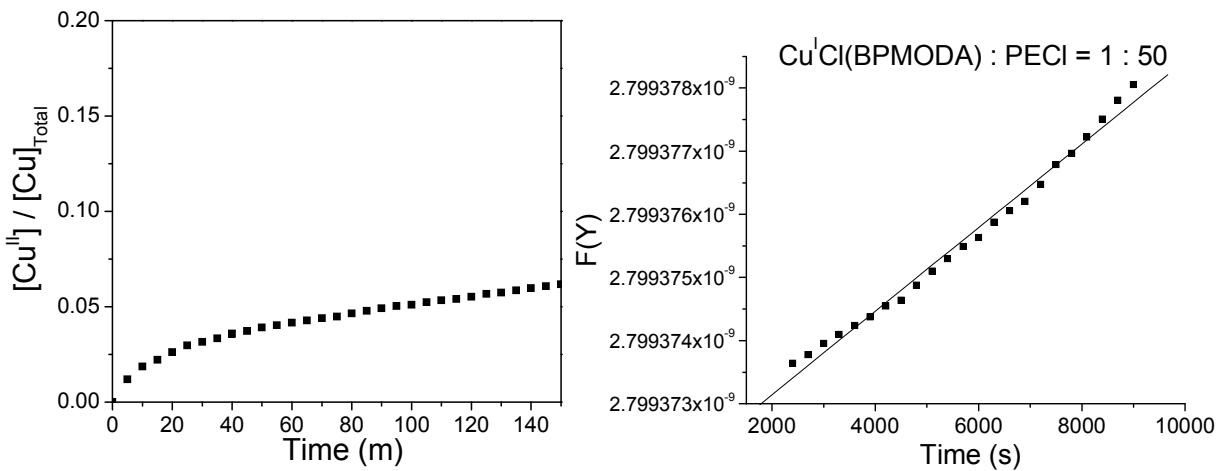


Figure 9S. Determination of K_{ATRP} for the reaction of $\text{CuCl}(\text{BPMODA})$ (1.28 mM) with 50 eq. PECl in THF: a) accumulation of Cu^{II} deactivator with time and b) plot of $F([\text{CuCl}_2(\text{BPMODA})])$ against time.

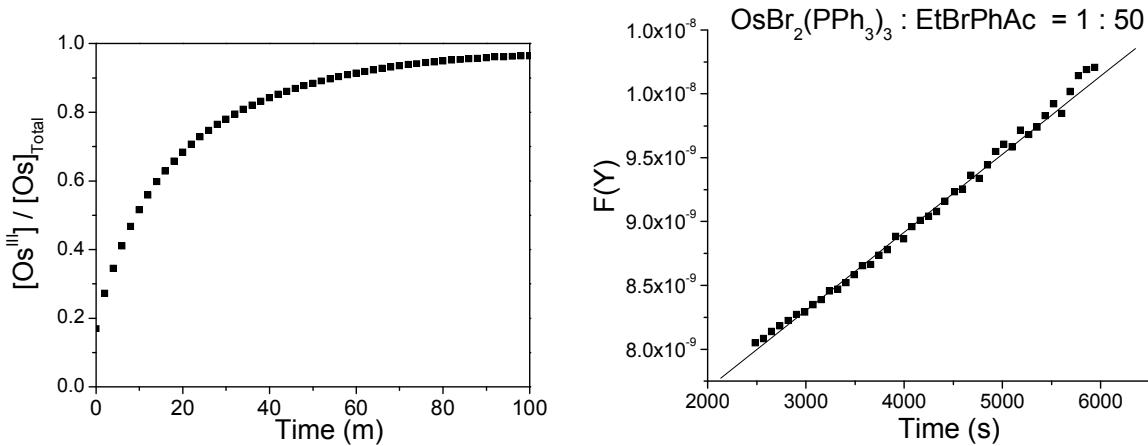


Figure 10S. Determination of K_{ATRP} for the reaction of $\text{OsBr}_2(\text{PPh}_3)_3$ (1.56 mM) with 50 eq. EtBrPhAc in THF: a) accumulation of Os^{III} deactivator with time and b) plot of $F([\text{OsBr}_3(\text{PPh}_3)_3])$ against time.

IV. Polymerization Data

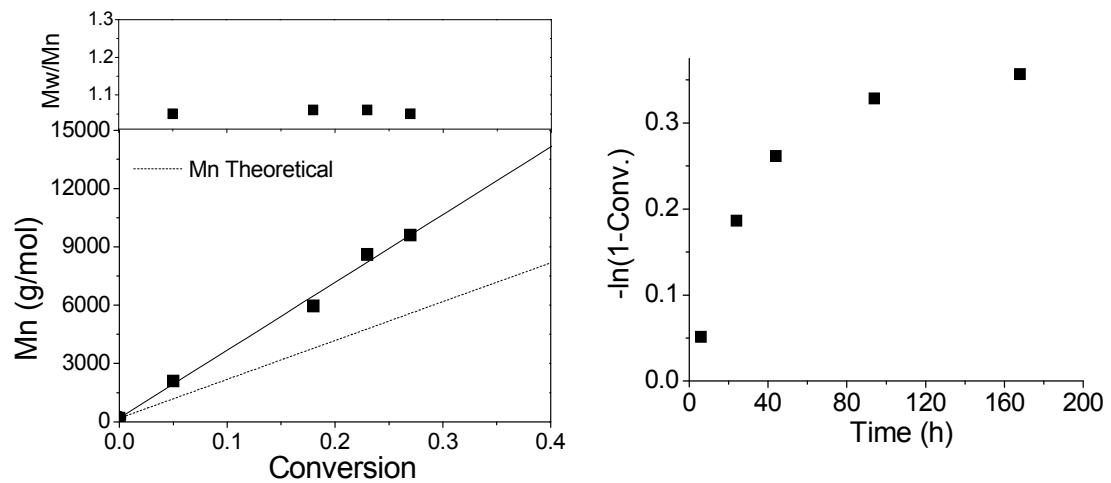


Figure 11S. [Sty] : [PEBr] : [OsBrCp*P*i*Pr₃] : [OsBr₂Cp*P*i*Pr₃] = 200 : 1 : 1 : 0.1, 60°C, bulk, 10 % diphenyl ether internal standard.

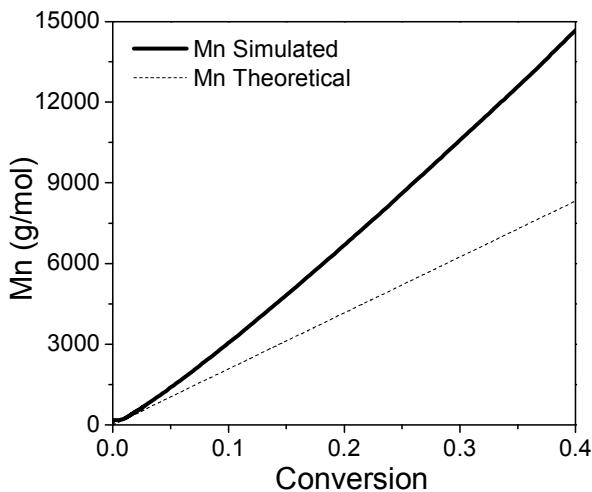


Figure 12S. PREDICI Simulation of Os catalyzed ATRP of Sty; $[Sty] : [PEBr] : [Mt^z] : [Mt^{z+1}] = 200 : 1 : 1 : 0.1$, $60^\circ C$, bulk; $K_{ATRP} = 3 \times 10^{-5}$, $k_{act} = 30 M^{-1}s^{-1}$, $k_{deact} = 1 \times 10^6 M^{-1}s^{-1}$, $k_p = 340 M^{-1}s^{-1}$, $k_t = 1 \times 10^8 M^{-1}s^{-1}$, $k_{t0} = 1 \times 10^9 M^{-1}s^{-1}$ (where k_p is the styrene propagation rate constant¹, k_t is the termination rate constant for polymeric radicals,² k_{t0} is the termination rate constant for small molecular radicals,^{3,4} and where k_{act} and k_{deact} were estimated from other catalysts with similar K_{ATRP} values^{5,6}).

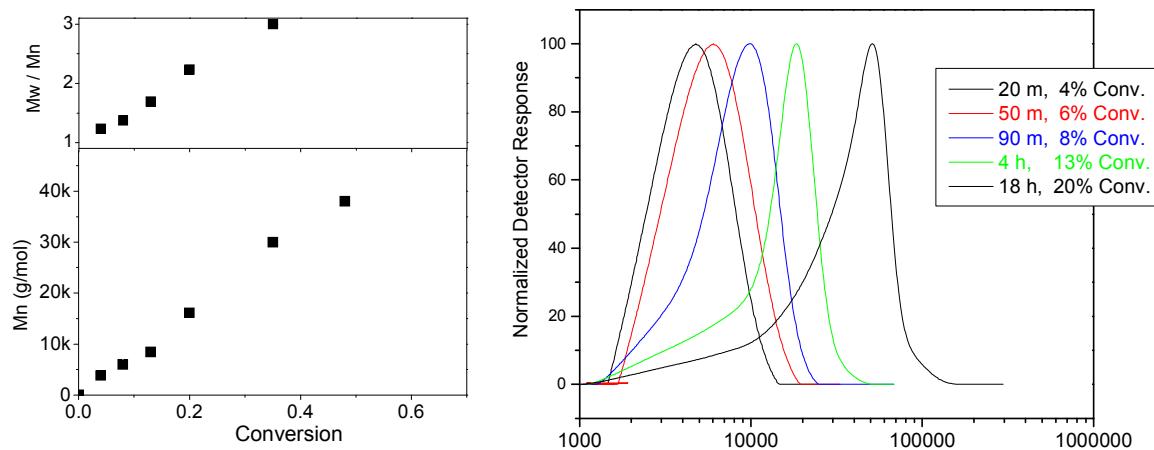


Figure 13S. $[Sty] : [OsBr(Cp^*)P^iPr_3] : [V-70] = 200 : 1 : 2/3$, $60^\circ C$, bulk, 10 % diphenyl ether internal standard.

V. Chain End Analysis

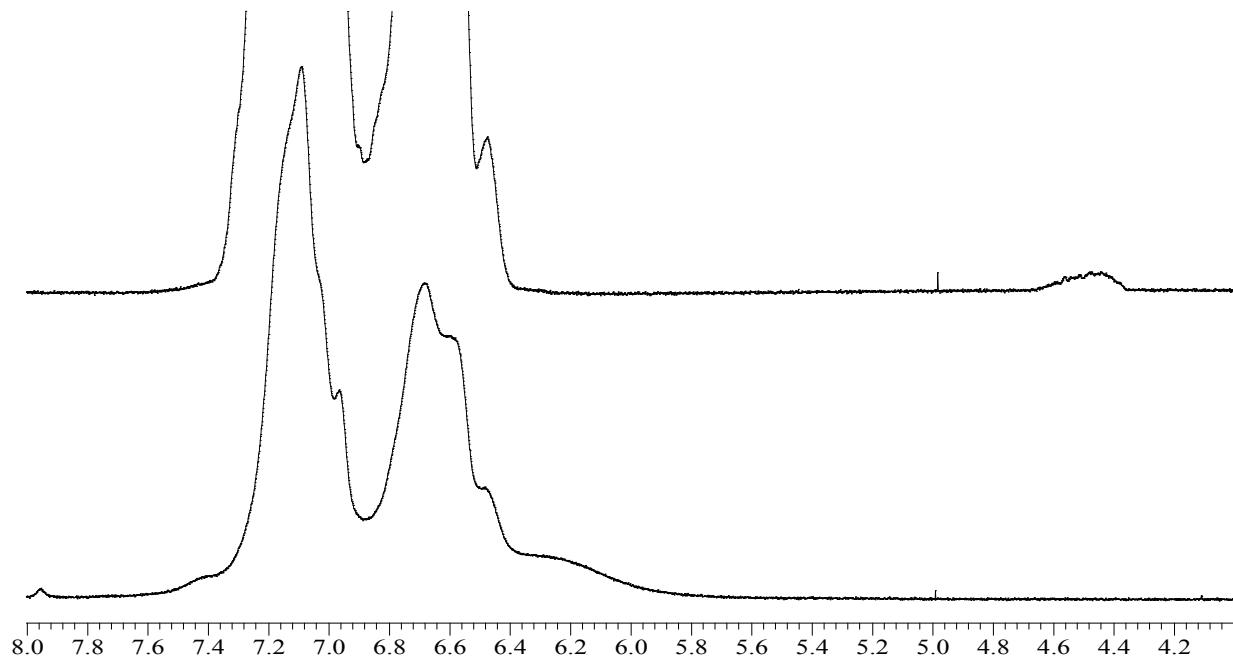


Figure 14S. 300 MHz ^1H NMR spectra in $(\text{CD}_3)_2\text{CO}$ of (top) PSty-Cl macroinitiator generated under ATRP conditions ([Sty]: $[\text{OsCl}_2(\text{PPh}_3)_3]$: $[\text{PECl}] = 200 : 1 : 1$, 100 °C, bulk, 30 min), ~4200 g/mol; and (bottom) polystyrene generated under OMRP conditions ([Sty]: $[\text{OsCl}_2(\text{PPh}_3)_3]$: $[\text{AIBN}] = 200 : 1 : 2/3$, 100 °C, bulk, 30 min), ~10,000 g/mol.

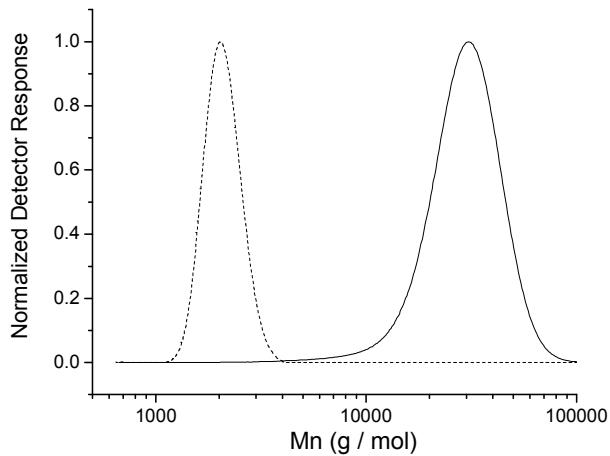


Figure 15S. (dashed line) Polystyrene macroinitiator (PSty-Br) generated under ATRP conditions with $\text{OsBr}(\text{Cp}^*)\text{P}^i\text{Pr}_3$ ($[\text{Sty}] : [\text{PEBr}] : [\text{Os}^{II}] = 200 : 1 : 1$, 60°C , bulk, 6 h.); (solid line) $\text{CuBr}(\text{BPMDOA})$ chain extended polystyrene ($[\text{Sty}]:[\text{PSty-Br}]:[\text{CuBr}]:[\text{CuBr}_2]:[\text{BPMODA}] = 200 : 1 : 1 : 0.1 : 1.1$, 100°C , bulk, ~ 20 h).

VI. PREDICI Simulations Concerning Coupled ATRP/OMRP Equilibria.

With the ultimate objective of identifying how the interplay of OMRP and ATRP might effect the determination of K_{ATRP} in this manuscript, a series of styrene polymerizations was modeled using PREDICI. First, a large range of equilibrium and rate constants was identified for which the fraction of Mt-capped living chains varied from $\sim 0.4\% - 50\%$ during the polymerization, the latter being the maximum value possible for a system employing $1 : 1 = \text{Mt} : \text{R-X}$ (note, it was observed experimentally that $\leq 1\%$ of the living chains in ATRP experiments with Os were actually Os-capped). Constant values of k_{act} , k_{deact} , and therefore K_{ATRP} ($10 \text{ M}^{-1}\text{s}^{-1}$, $1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, 1×10^{-5} , respectively) were employed in all the simulations. Meanwhile, several different values of K_{OMRP} were studied, and several values of k_c and k_{diss} were used for each value of K_{OMRP} . In this way, the

relative concentration of R-X and R-Mt in the polymerization could effectively be governed (Table 1S).

Table 1S. PREDICI simulations for styrene polymerization @ 60 °C.

[Sty]:[PEBr]:[Mt] = 5 M : 0.025 M : 0.025 M

$$K_{ATRP} = 1 \times 10^{-5} \text{ (} k_{act} = 10 \text{ M}^{-1}\text{s}^{-1}, k_{deact} = 1 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \text{)}$$

$k_c (\text{M}^{-1}\text{s}^{-1})$	$k_{diss} (\text{s}^{-1})$	$K_{OMRP} (\text{M}^{-1})$	Fraction of Mt-Capped Living Chains (at 10 % monomer conversion)
1×10^8	1000		1.3%
1×10^6	10		1.3%
1×10^4	0.1	1×10^5	1.3%
1×10^2	0.001		1.3%
10	0.0001		0.4%
1×10^8	100		13%
1×10^4	0.01	1×10^6	12%
1×10^2	0.0001		3%
1×10^8	.001	1×10^{11}	50%

$k_p = 340 \text{ M}^{-1}\text{s}^{-1}$, $k_t = 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, $k_{t0} = 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (where k_p is the styrene propagation rate constant¹, k_t is the termination rate constant for polymeric radicals,² k_{t0} is the termination rate constant for small molecular radicals,^{3,4}

Next, model ATRP experiments with metal catalyst and PEBr initiation (but no monomer) were simulated at room temperature. Contribution from OMRP was included for every entry in Table 1S. Note, that unless trapping of R^\bullet by metal is totally irreversible, the reaction will eventually go to 100% accumulation of the ATRP deactivator. $F(X\text{-Mt})$ vs. time was then plotted according to Eq. (4) for all of these model experiments.

In every case where the fraction of living chains capped by Mt was $\sim 10\%$ or lower for the polymerization experiments (*i.e.*, the first 8 entries of Table 1S), it was found that the function in Eq. (4) was linear with time, and K_{ATRP} determined from the slope was unaffected by the OMRP equilibrium (representative examples are illustrated in Figure 16S). Only when very high values of K_{OMRP} were modeled ($1 \times 10^{11} \text{ M}^{-1}$), such that a large percentage of living chains were Mt-capped, did the function in Eq. (4) become non-linear.

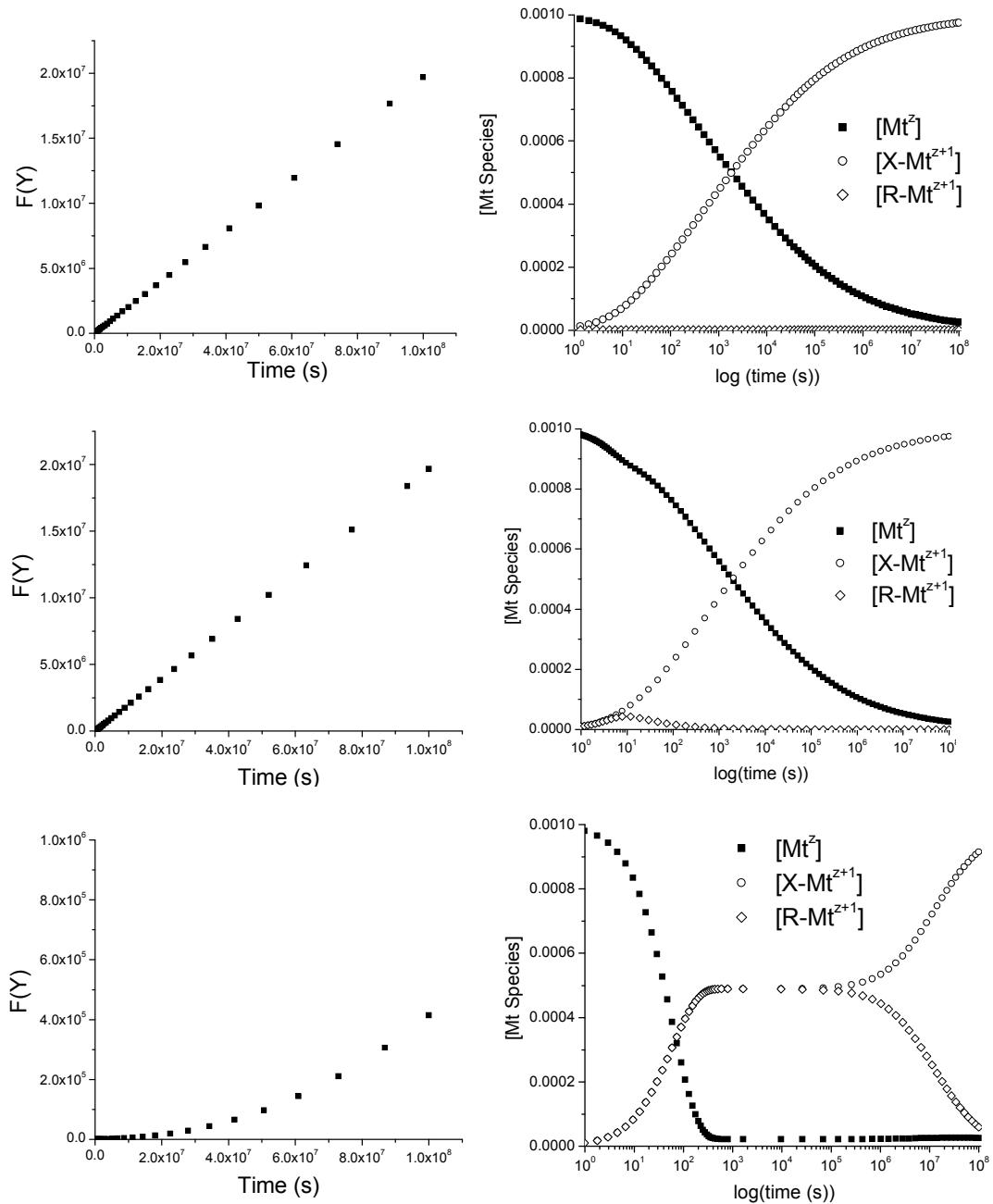


Figure 16S. $[\text{Mt}] = 1 \text{ mM}$, $[\text{PEBr}] = 1 \text{ mM}$, 25°C , $K_{\text{ATRP}} = 1 \times 10^{-5}$, $k_{\text{act}} = 10 \text{ M}^{-1} \text{s}^{-1}$, $k_{\text{deact}} = 1 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$; **Left:** $F(\text{X-Mt})$ vs. time according to Eq. (4); **Right:** Concentration of all Mt species with time; **Top:** $K_{\text{OMRP}} = 1 \times 10^5 \text{ M}^{-1}$, $k_c = 10 \text{ M}^{-1} \text{s}^{-1}$, $k_{\text{diss}} = 0.0001 \text{ s}^{-1}$ (0.4% of living chains Mt-capped in polymerization); **Middle:** $K_{\text{OMRP}} = 1 \times 10^6 \text{ M}^{-1}$, $k_c = 1 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$, $k_{\text{diss}} = 100 \text{ s}^{-1}$ (13% of living

chains Mt-capped in polymerization); **Bottom:** $K_{OMRP} = 1 \times 10^{11} \text{ M}^{-1}$, $k_c = 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, $k_{diss} = .001 \text{ s}^{-1}$ (50% of living chains Mt-capped in polymerization)

VII. Theoretical Calculations.

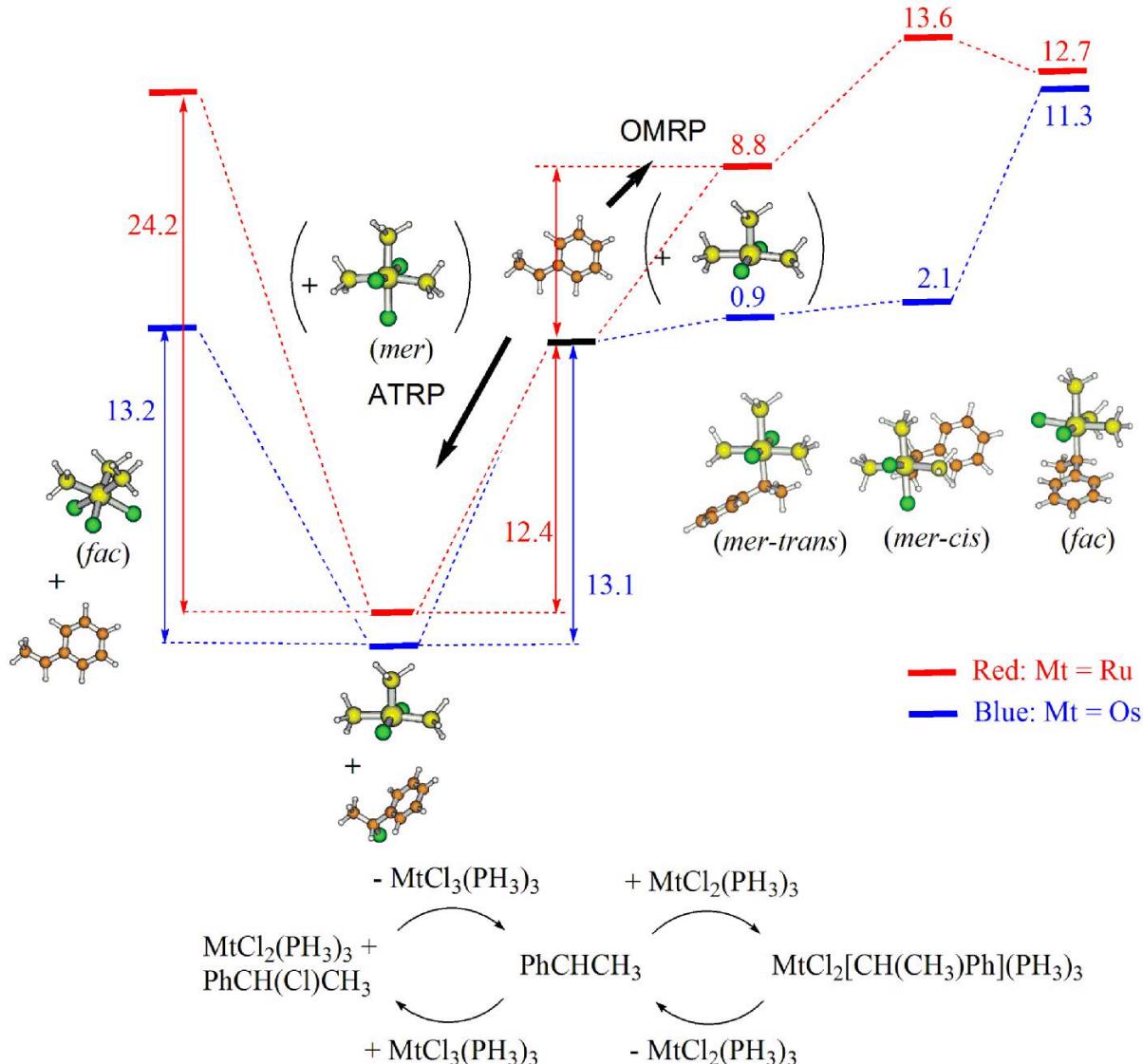


Figure 17S. Relative free energies of Ru and Os complexes used in this theoretical study. The optimized geometries shown are those of the Os systems.

The optimized geometry of the $\text{MtCl}_2(\text{PH}_3)_3$ corresponds very closely to the experimentally available X-ray structure of the Mt^{II} catalyst. For the osmium complex,⁷ the Os-Cl distances [2.383(2) and 2.399(2) Å] and the Os-P distances [2.410(2) and 2.366(2) Å for the equatorial ligands and 2.235(2) Å for the axial ligand] compare very well with those obtained from the DFT optimization. Note in particular that the Os-P distance trend (axial shorter than equatorial) is correctly reproduced by the calculations. The equatorial Cl-Os-Cl angle [160.65(8)°] is equally well reproduced, whereas the P-Os-P angle is substantially smaller in the experimental structure [158.07(7)°], certainly a consequence of the greater steric repulsion between axial and equatorial PPh_3 ligands. There is less steric repulsion for the related complex $[\text{OsCl}_2(\text{PPh}_3)_2(=\text{C=CHCMe}_3)]$, where the vinylidene ligand occupies the axial position [P-Os-P = 168.13(2)°],⁸ and consequently the P-Os-P angle is much closer to that optimized for the $\text{OsCl}_2(\text{PH}_3)_3$ model compound.

The model of the ATRP deactivator, $[\text{MtCl}_3(\text{PH}_3)_3]$, can in principle adopt either a *mer* or a *fac* structure. For osmium, both are represented in crystallographically characterized $[\text{OsX}_3\text{L}_3]$ molecules (X = halogen, L = neutral donor ligand). The *mer* family is larger, suggesting a greater stability for this stereochemistry in general, but a notable example of a *fac* geometry is provided by a tris-phosphine complex, *fac*- $[\text{OsCl}_3(\text{PEt}_2\text{Ph})_3]$.⁹ The DFT calculations indicate that the *fac* isomer is slightly more stable with three PH_3 ligands (see Figure 8). In the *mer* isomer, the chemically inequivalent Os-Cl bonds have distances quite close to each other, as experimentally found for *mer*- $[\text{OsCl}_3\text{py}_3]$ [average 2.36(1) Å]¹⁰ and for *mer,trans*- $[\text{OsCl}_3(\text{PPh}_3)_2(\text{NH}_3)]$ [average 2.362(2) Å].¹¹ The chemically inequivalent Os-P bonds also have closely related distances, which compare with those found in the above mentioned $[\text{OsCl}_3(\text{PPh}_3)_2(\text{NH}_3)]$ [2.411(2) Å]¹² and in the related complex $[\text{OsBr}_3(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$ [2.418(3) Å].¹³ The optimized geometry of *fac*- $[\text{OsCl}_3(\text{PH}_3)_3]$ compares quite well with that experimentally determined for *fac*- $[\text{OsCl}_3(\text{PEt}_2\text{Ph})_3]$,⁹ for which the average Os-

Cl and Os-P distances are 2.446(3) and 2.378(3) Å, respectively. All in all, it seems that this computational level affords optimized geometries in quite close correspondence with experimentally available related ones. A small and systematic error in excess for the bond distances (always contained within less than 0.1 Å) is typical for this computational technique.

Contrary to Os, the *fac*-MtCl₃(PH₃)₃ isomer for the Ru system is much higher in energy than the *mer* isomer. This is in qualitative agreement with the observation that Ru forms a much larger class of *mer*-RuX₃L₃ complexes. A search on the Cambridge Crystallographic Database reveals only two *fac* structures out of 72 hits for neutral RuX₃L₃ molecules, corresponding to compounds where the three L ligands are tied together in a tridentate capping ligand that cannot adapt to the *mer* conformation, *i.e.* L₃ = 1,4,7-trimethyl-1,4,7-triazacyclononane¹⁴ and *N*-(2'-pyridylmethyl)-(2*R*,5*R*)-bis(methyoxyethyl)pyrrolidine.¹⁵

Finally, the model of the OMRP dormant species, [MtCl₂R(PH₃)₃], can adopt in principle either one of three different configurations: *mer,trans*, *mer,cis*, and *fac*. The first one is shown by the DFT calculations to be favored, even though by only a little margin relative to the *fac* structure for the osmium system, as shown in Figure 8. There are no simple structurally characterized alkyl derivatives of Ru^{III} or Os^{III} that can be used for comparison. The closest related example appears to be compound [OsBr(PPh₃)₂(ap-Cl)] where ap-Cl is a doubly deprotonated Cl-substituted arylazophenol (the deprotonated functions are the phenolic OH and an arene through orthometallation).¹³ The calculations indicate that the 1-phenylethyl ligand exerts a significant *trans* influence, since the *trans* Os-Cl (in the *mer,cis* isomer) or Os-P (in the other two isomers) bond is significantly longer than the other bonds of the same type (see Table 3S).

Table 2S. Cartesian coordinates for all DFT-optimized structures.

PhCH₃
scf done: -310.233367

C	-0.483361	-1.714286	0.775012
C	-1.336181	-1.758383	2.004434
H	-0.870755	-1.231068	2.851066
H	-2.316394	-1.283199	1.846368
H	-1.519078	-2.789283	2.320937
H	-0.156288	-2.659102	0.347122
C	-0.067900	-0.528464	0.122194
C	-0.430873	0.769673	0.584556
C	-0.005730	1.911531	-0.080257
C	0.793778	1.815040	-1.226611
C	0.746013	-0.597210	-1.046231
C	1.165097	0.549221	-1.702518
H	-1.050219	0.865492	1.471496
H	-0.297321	2.889787	0.294142
H	1.123094	2.712746	-1.742221
H	1.785323	0.464927	-2.591390
H	1.037793	-1.575823	-1.420935

PhCH₃Cl
scf done: -771.844959

C	0.359849	1.286079	0.543196
C	0.295902	1.358526	2.058592
C1	2.111756	1.374412	0.022821
H	-0.089519	2.180813	0.107221
C	-0.302511	0.065423	-0.034698
H	-0.751977	1.357367	2.375108
H	0.791142	0.497634	2.513810
H	0.774489	2.268890	2.425963
C	0.132196	-1.221977	0.294676
C	-0.521216	-2.337619	-0.213753
C	-1.620597	-2.183089	-1.057289
C	-2.057669	-0.906175	-1.393031
C	-1.398491	0.211163	-0.885866
H	0.999668	-1.347201	0.936234
H	-0.170680	-3.332013	0.045420
H	-2.129716	-3.056039	-1.454027
H	-2.909061	-0.776416	-2.054117
H	-1.738974	1.207965	-1.154525

RuCl₂(PH₃)₃
scf done: -2043.837930

Ru	-0.008648	-0.011620	-0.000555
P	0.015540	-0.006552	2.357691
P	0.306193	-0.006635	-2.337826
P	-2.172452	-0.408570	-0.134461
C1	0.601893	-2.371018	0.037224
C1	-0.148523	2.404352	-0.009120
H	-3.042666	0.704915	-0.186946
H	-2.665860	-1.144353	-1.238051
H	-2.797590	-1.146648	0.898578
H	-0.576313	-1.065613	3.083478
H	-0.499992	1.092172	3.080967
H	1.304957	-0.060048	2.935078
H	-0.194085	-1.064350	-3.131324
H	-0.113876	1.093232	-3.118808
H	1.656801	-0.063070	-2.751945

mer-RuCl₃(PH₃)₃
scf done: -2504.057540

Ru	-0.007357	-0.008451	0.000680
P	-0.015083	-0.017061	2.375376
P	2.379129	0.030685	-0.222939
P	-0.457391	0.022186	-2.330761
C1	0.149045	-2.390795	-0.033898
C1	0.377476	2.375306	-0.015893
C1	-2.383268	0.110729	0.225088
H	-1.204035	1.124915	-2.786730
H	-1.234334	-1.047205	-2.814815
H	0.571944	0.021771	-3.303192
H	-0.689881	-1.095601	2.977821
H	-0.662173	1.076706	2.980636
H	1.177309	-0.031909	3.139001
H	3.077635	-1.192729	-0.298667
H	3.117625	0.677314	0.789600
H	2.917535	0.695133	-1.344270

fac-RuCl₃(PH₃)₃
scf done: -2504.040180

Ru	-0.004504	0.012379	0.005681
P	-0.000120	0.012951	2.358696
P	2.252152	0.023048	-0.660577
C1	-0.319611	-0.036715	-2.401368
P	-0.204943	-2.340376	-0.151369
C1	0.4888540	2.340455	0.380949
C1	-2.401345	-0.045494	0.390028
H	-0.466677	-1.134706	3.038306
H	-0.821500	0.999151	2.927363
H	1.198809	0.228886	3.077493
H	2.774897	-1.120457	-1.305441
H	3.281819	0.239351	0.284763
H	2.559724	1.013697	-1.606441
H	-1.275119	-2.770379	-0.950498
H	0.853487	-3.092295	-0.708518
H	-0.434284	-3.097839	1.018989

mer-trans-RuCl₂[CH(Me)Ph](PH₃)₃
scf done: -2354.082184

C	0.045294	-0.008997	-0.029773
C	0.022614	-0.003947	1.363922
C	1.214521	-0.008885	2.116212
C	2.431924	-0.023322	1.407220
C	2.455260	-0.028618	0.011091
C	1.263322	-0.021698	-0.715832
C	1.154803	-0.036804	3.615385
C	2.241409	-0.910502	4.251968
Ru	0.999555	1.940667	4.542825
P	0.867211	4.271654	5.769165
C1	3.328431	2.138600	5.124251
C1	-1.362303	2.102631	4.122290
P	1.478217	3.067909	2.499694
P	0.467843	0.836478	6.570562
H	0.169237	-0.417200	3.903726
H	2.243936	-1.904843	3.782154
H	3.240870	-0.482216	4.147452
H	2.075397	-1.056919	5.324732
H	3.370548	-0.033626	1.953505
H	3.410029	-0.044402	-0.508903
H	1.282247	-0.030516	-1.802355
H	-0.891152	-0.009285	-0.582090
H	-0.928465	0.013834	1.889405
H	-0.344755	4.996714	5.875556
H	1.250742	4.357991	7.129314
H	1.680156	5.334436	5.307008
H	0.617649	2.886331	1.399274
H	1.502986	4.484679	2.522405
H	2.726335	2.851258	1.884080
H	-0.160035	-0.428611	6.506785
H	1.494008	0.531913	7.493716
H	-0.441756	1.459916	7.454969

mer-cis-RuCl₂[CH(Me)Ph] (PH₃)₃

scf done: -2354.078968

C	-0.017543	-0.016522	0.008464
C	-0.017396	0.005428	1.404167
C	1.188277	0.012915	2.106446
C	2.430908	0.014244	1.443240
C	2.406564	-0.024990	0.033995
C	1.203019	-0.039381	-0.671076
C	3.719586	0.003524	2.216227
Ru	4.709035	1.975441	2.335326
P	6.347253	1.179462	3.846836
C	4.713654	-1.047561	1.690323
Cl	5.380055	4.282459	3.166214
Cl	6.296114	1.714340	0.564662
P	3.161213	2.493817	4.083748
P	3.416659	3.091171	0.673262
H	3.490522	-0.250070	3.257339
H	4.225316	-2.033579	1.675117
H	5.068735	-0.825963	0.683206
H	5.598263	-1.129963	2.328407
H	3.343772	-0.048777	-0.514398
H	1.219410	-0.074831	-1.757565
H	-0.954141	-0.029532	-0.541930
H	-0.957618	0.000411	1.949928
H	1.166229	-0.012105	3.193536
H	2.034714	3.350216	0.836041
H	3.866008	4.403763	0.424887
H	3.393919	2.584035	-0.638667
H	6.333010	-0.121647	4.410444
H	7.662424	1.183823	3.339500
H	6.552052	1.915495	5.034318
H	2.184408	1.554163	4.496379
H	3.689326	2.825143	5.347681
H	2.320434	3.609738	3.899163

fac-RuCl₂[CH(Me)Ph] (PH₃)₃

scf done: -2354.077410

C	0.007047	0.206318	0.608845
C	0.329701	0.089002	1.969044
C	1.637732	-0.160714	2.356655
C	2.683385	-0.304789	1.396507
C	2.327937	-0.182048	0.022614
C	1.015667	0.067937	-0.355587
C	4.015892	-0.613546	1.818968
Ru	4.843236	1.931754	2.382357
P	4.129219	1.766577	4.560990
C	5.064082	-1.194124	0.920311
P	6.198439	3.698071	2.732480
Cl	6.805738	0.683210	3.280657
P	3.094623	3.166103	1.533047
Cl	5.669768	2.081913	0.056761
H	4.148990	-0.806489	2.881597
H	4.837055	-2.258487	0.738386
H	5.125637	-0.688497	-0.045555
H	6.044327	-1.127970	1.394964
H	3.099478	-0.272674	-0.733511
H	0.769942	0.155257	-1.410573
H	-1.017824	0.398887	0.304839
H	-0.448978	0.181072	2.721645
H	1.877510	-0.276911	3.410925
H	5.846059	4.969218	2.215728
H	6.517339	4.084442	4.056337
H	7.488335	3.560330	2.193592
H	3.932828	0.480896	5.121321
H	4.960410	2.286640	5.580758
H	2.908242	2.346973	5.000491
H	2.343339	2.642840	0.458889
H	2.014295	3.585558	2.354163
H	3.403383	4.427667	0.971930

OsCl₂(PH₃)₃

scf done: -2040.996044

Os	0.000010	0.008660	-0.142987
P	2.345392	0.051462	-0.282118
P	0.000288	-0.197459	2.049875
Cl	-0.001235	2.433950	-0.403690
Cl	0.000929	-2.370778	-0.628928
P	-2.345446	0.049506	-0.281862
H	-0.000073	-1.500291	2.613635
H	1.073658	0.361122	2.789430
H	-1.072450	0.361889	2.789760
H	-3.092328	0.730968	0.708724
H	-3.065058	-1.166615	-0.318993
H	-2.901271	0.678164	-1.419406
H	3.091824	0.731373	0.709892
H	3.065785	-1.164123	-0.321612
H	2.900859	0.682803	-1.418347

mer-OsCl₃(PH₃)₃

scf done: -2501.214468

Os	-0.000003	-0.016402	-0.012470
P	-0.000514	-0.055915	2.360406
P	2.353977	-0.008312	-0.233464
Cl	-0.015431	-2.416860	0.021455
Cl	0.014918	2.379832	0.362127
Cl	0.000743	0.153579	-2.416539
P	-2.353650	0.021069	-0.233216
H	2.888629	1.043155	-1.002582
H	2.924586	-1.125046	-0.876019
H	3.207081	0.073606	0.893634
H	-2.938368	-1.089677	-0.873508
H	-2.875122	1.077679	-1.004309
H	-3.205332	0.115914	0.893946
H	-0.003996	-1.315171	2.995057
H	-1.070171	0.568725	3.037655
H	1.071794	0.563405	3.038254

fac-OsCl₃(PH₃)₃

scf done: -2501.217244

Os	-0.000824	0.012402	-0.000284
P	1.721239	1.172430	1.083189
Cl	1.815403	-0.737402	-1.431469
P	0.360292	-1.958407	1.221784
Cl	-0.391541	2.167863	-1.026623
Cl	-1.567911	-1.240977	-1.377098
P	-1.956193	0.565522	1.166501
H	-2.569609	-0.431974	1.958072
H	-3.040367	0.948441	0.357179
H	-1.954099	1.623316	2.105263
H	2.662061	0.434882	1.838239
H	1.422176	2.181009	2.028435
H	2.587943	1.880664	0.231142
H	0.359918	-3.140326	0.460100
H	1.570602	-2.118869	1.933061
H	-0.549079	-2.323040	2.241543

mer-trans-OsCl₂[CH(Me)Ph] (PH₃)₃

scf done: -2351.257430

C	-0.337994	0.117262	0.115055
C	0.070510	-0.142235	1.437975
C	1.448476	-0.321250	1.665099
C	2.374325	-0.233008	0.622217
C	1.949180	0.033934	-0.679742
C	0.584149	0.207615	-0.926789
C	-0.954148	-0.235179	2.543635
Os	-1.508681	1.683053	3.471709
C	-0.607306	-1.331724	3.567142
H	-1.902284	-0.512729	2.064871
H	-0.393059	-2.280030	3.054487
H	0.259980	-1.071395	4.178685
H	-1.431726	-1.514094	4.266024

H	1.804031	-0.536821	2.668726	H	1.007233	3.069953	1.396017
H	3.431392	-0.380707	0.830695	H	1.726470	4.535928	2.801185
H	2.668594	0.099061	-1.491709	H	3.024971	2.941641	2.138066
H	0.234588	0.407614	-1.936823	H	0.052327	-0.311769	6.804950
H	-1.395847	0.260208	-0.088540	H	1.748635	0.822802	7.491978
Cl	-0.214194	1.365613	5.488046	H	-0.230662	1.690651	7.526248
Cl	-2.900226	2.308290	1.603165	H	-1.919244	1.022838	3.393114
P	0.350252	2.765427	2.483193	H	-2.166235	2.339683	5.076217
P	-3.345335	0.540812	4.387996	H	-1.674128	3.144898	3.155745
P	-2.182716	3.828555	4.601584				
H	-3.130956	4.669493	3.975188				
H	-2.762232	3.789597	5.891039				
H	-1.198240	4.806324	4.882055				
H	0.458216	2.774797	1.079160				
H	0.512701	4.152953	2.726568				
H	1.644883	2.341359	2.841404				
H	-3.773561	-0.651180	3.758620				
H	-3.264863	0.078612	5.721921				
H	-4.600590	1.189970	4.453015				
<i>mer-cis</i> -OsCl ₂ [CH(Me)Ph](PH ₃) ₃							
scf done: -2351.257267							
C	0.007637	-0.188987	-0.090589				
C	-0.049143	-0.219272	1.304154				
C	1.099931	-0.039643	2.095607				
C	2.322892	0.137676	1.418981				
C	2.386231	0.160819	0.025072				
C	1.227496	0.005845	-0.740163				
C	1.017869	-0.060568	3.604417				
C	2.081591	-1.005345	4.209982				
Os	1.040453	1.922899	4.547389				
Cl	0.405054	4.148494	5.564192				
Cl	3.366610	1.970259	5.131204				
P	-1.261800	2.107911	4.019066				
P	1.715876	3.136046	2.617709				
P	0.623093	0.977883	6.655023				
H	0.043065	-0.496346	3.864555				
H	2.012644	-1.996401	3.738918				
H	3.098198	-0.631451	4.074387				
H	1.937462	-1.143916	5.287068				
H	3.236254	0.257637	1.995207				
H	3.347198	0.295960	-0.465458				
H	1.277477	0.023773	-1.825392				
H	-0.901622	-0.332976	-0.669325				
H	-1.003935	-0.409317	1.789914				

fac-OsCl₂[CH(Me)Ph](PH₃)₃
scf done: -2351.242175

C	-0.539223	-0.693710	0.490149
C	-0.208751	-0.636990	1.845116
C	0.994952	-0.053690	2.286788
C	1.862346	0.471318	1.307341
C	1.535590	0.411404	-0.046187
C	0.333952	-0.169475	-0.464016
C	1.334440	-0.050584	3.747811
C	2.759294	-0.560272	4.043798
Os	1.285868	1.972713	4.836032
P	0.889686	3.984998	6.063125
Cl	3.026924	1.634315	6.555816
P	-0.261650	2.579285	3.229928
Cl	2.947015	3.097823	3.470095
P	0.002019	0.743212	6.315441
H	0.621420	-0.723036	4.238293
H	2.911801	-1.510918	3.509654
H	3.532178	0.139774	3.718184
H	2.907155	-0.730590	5.111510
H	2.786397	0.947899	1.616058
H	2.223819	0.822651	-0.780214
H	0.084172	-0.214722	-1.520645
H	-1.473222	-1.156672	0.181399
H	-0.887792	-1.068452	2.578684
H	-0.115429	4.901052	5.663183
H	0.564781	3.908984	7.436927
H	1.984505	4.868389	6.132563
H	0.572578	-0.465786	6.769625
H	-0.348092	1.295487	7.571114
H	-1.277633	0.248506	5.953417
H	0.201824	2.805220	1.918401
H	-1.378934	1.760317	2.947868
H	-0.961379	3.796774	3.431643

Table 3S. Selected bond distances (\AA) and angles ($^\circ$) optimized by DFT.^a

	Mt-Cl	Mt-P	Mt-C	Cl-Mt-Cl	P-Mt-P
MtCl ₂ (PH ₃) ₃	2.420/2.429	2.358/2.350	2.304/2.203 (<i>ax</i>)	168.8/162.3	94.1/93.5
	2.437/2.439	2.358/2.350			94.1/93.5
<i>mer</i> -MtCl ₃ (PH ₃) ₃	2.388/2.401 (<i>t</i>) 2.389/2.410 (<i>c</i>) 2.415/2.425 (<i>t</i>)	2.375/2.364 (<i>t</i>) 2.375/2.364 (<i>t</i>) 2.397/2.373 (<i>c</i>)	96.3/94.8 96.7/94.8 167.0/170.3	95.6/95.4 95.6/95.4 168.9/169.2	171.7/172.9
<i>fac</i> -MtCl ₃ (PH ₃) ₃	2.409/2.419 2.428/2.431 2.428/2.434	2.353/2.342 2.353/2.343 2.366/2.347	91.6/89.4 101.6/96.6 101.6/98.4	93.8/93.6 93.8/93.9 106.3/105.4	168.9/169.2
<i>mer,trans</i> -MtCl ₂ [CH(Ph)CH ₃](PH ₃) ₃	2.404/2.412 2.409/2.417	2.369/2.349 2.382/2.367 2.637/2.517 (<i>c</i>)	2.190/2.202	170.6/171.6	89.5/90.5
					90.2/91.7
<i>mer,cis</i> -MtCl ₂ [CH(Ph)CH ₃](PH ₃) ₃	2.392/2.399 (<i>t</i> -P) 2.542/2.528 (<i>t</i> -C)	2.367/2.347 (<i>t</i>) 2.392/2.369 (<i>c</i>) 2.383/2.377 (<i>t</i>)	2.209/2.196	99.6/97.4	178.6/177.7
					93.1/93.2
					93.3/93.4
<i>fac</i> -MtCl ₂ [CH(Ph)CH ₃](PH ₃) ₃	2.473/2.427 2.493/2.471	2.299/2.311 2.303/2.313 2.254/2.390 (<i>t</i> -C)	2.735/2.298	96.1/88.4	168.0/170.0
					95.4/91.4
					95.5/91.6
					98.8/102.3

^aEach column reports values in the order Ru/Os. ^bThe symbols *c* and *t*, without additional suffix, refer to *cis* and *trans* relative to another ligand of the same type.

Complete reference 50 from main text: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.04*; Gaussian, Inc.: Pittsburgh PA, 2003.

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