

## Synthesis, Characterization, and Ring-Opening Metathesis Polymerization Activity of Pentamethylcyclopentadienyl Osmium Complexes

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Olefin metathesis reactions are widely-used in industry.<sup>1</sup> The largest application of this reaction is found in the Shell Higher Olefin Process (SHOP), which produces more than  $10^5$  tons of  $C_{10}$ - $C_{20}$  alkenes annually.<sup>2</sup> One subset of olefin metathesis reactions is known as ring-opening metathesis polymerization (ROMP), in which a cyclic alkene, such as norbornene, is metathesized to form a ring-opened polymer.



Homogeneous ROMP is used industrially to produce specialty polymers such as polycyclooctene (polyoctenamer), polydicyclopentadiene, and polynorbornene. Polynorbornene,  $(C_7H_{10})_n$  ( $n > 20,000$ ), in particular, is a highly porous polymer capable of absorbing of up to fifteen times its weight in solvent.<sup>3,4</sup>

In 1965, the later transition metal salts  $RuCl_3$ ,  $OsCl_3$ , and  $IrCl_3$  were found to be active ROMP catalysts.<sup>5</sup> In contrast to the early transition metal ROMP catalysts, these late transition metal catalysts are effective in the presence of oxygen and water.<sup>6</sup> For these catalysts, however, the catalytically active species has never been observed. Consequently, Grubbs's recent synthesis of isolable ruthenium carbene complexes, with the general formula  $RuCl_2(PR_3)_2(=CHR')$ , which are active ROMP catalysts for the polymerization of norbornene and other monomers, has attracted much interest.<sup>7-15</sup>

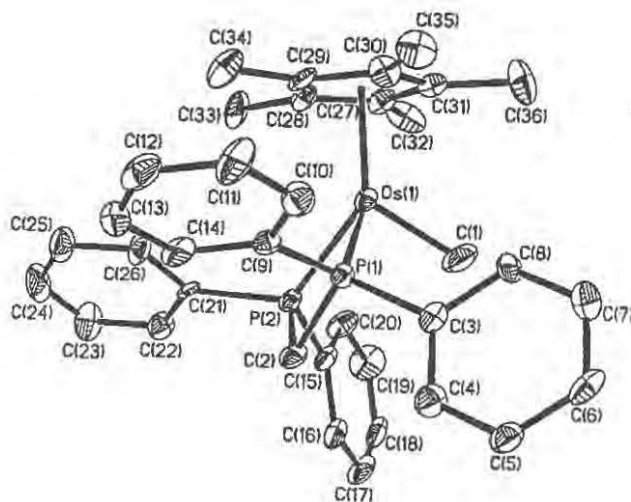
Several osmium carbene complexes are known,<sup>16,17</sup> but few studies of their ROMP catalytic ability have been described.<sup>18-21</sup> In fact, few studies of osmium compounds other than  $OsCl_3$  as ROMP catalysts have been reported.<sup>22-25</sup>

We find that the dinuclear complex  $Cp^*_2Os_2Br_4$  ( $Cp^*$  = pentamethylcyclopentadienyl)<sup>26</sup> and related mono(pentamethylcyclopentadienyl)osmium compounds are catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene. The most active catalyst prepared to date is made by treatment of  $Cp^*_2Os_2Br_4$  with methylaluminumoxane. The  $^{13}C\{^1H\}$  NMR spectra show that the polymer is slightly blocky and that *cis* double bonds predominate. The polynorbornadiene produced is insoluble in organic solvents but is swelled by many of them.

An isolable osmium methylidene complex can be synthesized by addition of two equivalents of MeOTf (OTf = trifluoromethanesulfonate) to the hydride complex  $Cp^*Os(dppm)H$  (dppm = bis(diphenylphosphino)methane). After 1 h,  $Cp^*Os(dppm)OTf$  is formed, and if the solution is stirred for 18 h, the cationic methylidene complex  $[Cp^*Os(dppm)(=CH_2)][OTf]$  is formed (Figure 1). Variable temperature  $^1H$  NMR studies of this methylidene complex show that  $\Delta H^\ddagger = 16.4 \pm 0.5$  kcal / mol and  $\Delta S^\ddagger = 5.7 \pm 1.5$  cal / mol K for rotation of the methylidene ligand, giving a  $\Delta G^\ddagger = 14.7 \pm 0.5$  kcal / mol at 25 °C. This rotational barrier is comparable to those of  $\Delta G^\ddagger = 10.7 \pm 0.2$  kcal / mol at 25 °C and  $\geq 19$  kcal

/ mol at  $\sim 119$  °C for the  $M=CH_2$  bond in  $[Cp^*Fe(=CH_2)(dppe)][BF_4]^{27}$  ( $dppe$  = bis(diphenylphosphino)ethane) and  $[Cp^*Re(=CH_2)(NO)(PPh_3)][PF_6]^{28}$  respectively.

Aqua complexes with the formula  $[Cp^*Os(dmpm)(OH_2)][OTf]$  and  $[Cp^*Os(dppm)(OH_2)][OTf]$  can be generated by addition of water to the respective triflate



**Figure 1.**

complexes  $Cp^*Os(dmpm)OTf$  and  $Cp^*Os(dppm)OTf$ . Addition of dialkylmagnesium reagents to the triflate complexes results in the formation of  $Cp^*Os(dmpm)R$  and  $Cp^*Os(dppm)R$  compounds, where  $R = Me$  or  $Et$ . The methyl complex  $Cp^*Os(dppm)Me$  can also be made by addition of  $LiBH_4$  to  $[Cp^*Os(=CH_2)(dppm)][OTf]$ .

Protonations of the osmium(II) alkyls with the carbon acid  $CH_2(O_2SCF_3)_2$  have been studied. For  $Cp^*Os(dmpm)Me$ , the initial organometallic product formed by protonation at  $-130$  °C is the alkyl / hydride cation,  $[Cp^*Os(dmpm)MeH]^+$ ,<sup>29</sup> but above  $-110$  °C, this species converts to the alkylidene cation  $[Cp^*Os(dmpm)(=CH_2)]^+$ . At the same time, some of the fluorochlorocarbon solvent,  $CDFCl_2$ , is converted to  $CDHfCl$ . Protonation of the analogous complexes  $Cp^*Os(dmpm)Et$  and  $Cp^*Os(dppm)Me$  affords the alkylidene cations,  $[Cp^*Os(dppm)(=CH_2)]^+$  and  $[Cp^*Os(dmpm)(=CHCH_3)]^+$ ; hydride / chloride exchange with the solvent occurs in these reactions as well.

Treatment of  $Cp^*Os(NO)Br_2$ <sup>30</sup> with  $NaBH_4$  yields the dihydride  $Cp^*Os(NO)H_2$ .<sup>31</sup> The dihydride loses  $H_2$  over several days in solution to form  $[Cp^*Os(\mu-NO)]_2$ ; this dinuclear compound can also be formed directly by reduction of  $Cp^*Os(NO)Br_2$  with zinc powder. Treatment of  $Cp^*Os(NO)Br_2$  with  $MgR_2$  affords the monoalkylated products  $Cp^*Os(NO)RBr$ , where  $R = Me$ ,  $CH_2SiMe_3$ ,  $Ph$ , or  $o-Tol$ . The slow ligand substitution kinetics of this reaction prevent the formation of dialkyls of stoichiometry  $Cp^*Os(NO)R_2$ , even after long reaction times or when a large excess of alkylating agent is used. Dialkyls such as  $Cp^*Os(NO)Me_2$  can, however, be obtained by treatment of  $Cp^*Os(NO)MeBr$  with silver trifluoromethanesulfonate followed by addition of dimethylmagnesium.

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