Synthesis and reactivity of the osmium methylidene complex [(C5Me5)Os(=CH2)(dpmm)][OTf]

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Treatment of the hydride complex (C5Me5)Os(dpmm)H,[dpmm = bis(diphenylphosphino)methane] with 2 equivalents of methyl trifluoromethanesulfonate (MeOTf) affords the methylidene complex [(C5Me5)Os(=CH2)(dpmm)][OTf]; the molecular structure and dynamic NMR behavior of this methylidene complex are described.

Transition metal alkylidenes have been of interest for the last 20 years owing to their role as intermediates in olefin metathesis and Fischer–Tropsch reactions. Most terminal methylidene complexes have been synthesized by one of two routes: by abstraction of a hydride from a methyl group, or by abstraction of a proton from a cationic methyl compound. We now describe the synthesis of an osmium methylidene complex from the reaction of an osmium hydride complex with methyl trifluoromethanesulfonate (MeOTf).

The rotation barrier is a measure of how much the π bonding is weakened upon rotating the methylidene ligand by 90° about the M–C axis. Somewhat surprisingly, the activation entropies and enthalpies of rotation have never been measured for any terminal methylidene complex. For four molecules, however the free energies of activation have been reported: 8.3 ± 0.1 kcal mol\(^{-1}\) at −85 °C for [(C5Me5)W(=CH2)(PPh3)(CO)]\(_2\)AsF\(_6\), 9.0 ± 0.1 kcal mol\(^{-1}\) at −70 °C for [(C5Me5)W(=CH2)(PPh3)(CO)]\(_2\)AsF\(_6\), 10.7 ± 0.2 kcal mol\(^{-1}\) at −28 °C for [(C5Me5)Fe(=CH2)(dppe)]BF\(_4\), and ≥ 19 kcal mol\(^{-1}\) at 114 °C for [(C5Me5)Re(C=CH2)NOPh]PF\(_6\). An X-ray crystallographic study of [(C5Me5)Os(dpmm)H] \(_2\) \(\cdot\) Cl\(_2\) revealed that the Os–C distance for the methylidene ligand is 1.926(9) Å (Fig. 2). This value is comparable to the M–C bond distances seen for other late transition metal methylidene complexes: 1.87(1) Å in Ir(=CH2)[N(SiMe2CH2PPh2)]\(_2\)Cl, 1.90(2) Å in [(C5Me5)Re(=CH2)NO][Pr(OH)\(_3\)]\(_2\), and 1.92(1) Å in Os(=CH2)(PPh3)\(_2\)(NO)Cl. Like other cationic methylidene complexes, the methylidene complex 1 is susceptible to attack by nucleophiles. Thus, treatment of 1 with LiBH\(_4\) yields the corresponding methyl complex, (C5Me5)Os(dpmm)CH\(_3\).

At least two mechanisms could account for the formation of 1 upon treatment of (C5Me5)Os(dpmm)H with MeOTf. In one mechanism, the osmium methyl/hydride intermediate is generated initially, and dihydrogen is lost to form 1.

The free energy of activation is 14.7 ± 0.5 kcal mol\(^{-1}\) at 25 °C. The rotation barrier is a measure of how much the π bonding is weakened upon rotating the methylidene ligand by 90° about the M–C axis. Somewhat surprisingly, the activation entropies and enthalpies of rotation have never been measured for any terminal methylidene complex. For four molecules, however the free energies of activation have been reported: 8.3 ± 0.1 kcal mol\(^{-1}\) at −85 °C for [(C5Me5)W(=CH2)(PPh3)(CO)]\(_2\)AsF\(_6\), 9.0 ± 0.1 kcal mol\(^{-1}\) at −70 °C for [(C5Me5)W(=CH2)(PPh3)(CO)]\(_2\)AsF\(_6\), 10.7 ± 0.2 kcal mol\(^{-1}\) at −28 °C for [(C5Me5)Fe(=CH2)(dppe)]BF\(_4\), and ≥ 19 kcal mol\(^{-1}\) at 114 °C for [(C5Me5)Re(C=CH2)NOPh]PF\(_6\). An X-ray crystallographic study of [(C5Me5)Os(dpmm)H] \(_2\) \(\cdot\) Cl\(_2\) revealed that the Os–C distance for the methylidene ligand is 1.926(9) Å (Fig. 2). This value is comparable to the M–C bond distances seen for other late transition metal methylidene complexes: 1.87(1) Å in Ir(=CH2)[N(SiMe2CH2PPh2)]\(_2\)Cl, 1.90(2) Å in [(C5Me5)Re(=CH2)NO][Pr(OH)\(_3\)]\(_2\), and 1.92(1) Å in Os(=CH2)(PPh3)\(_2\)(NO)Cl. Like other cationic methylidene complexes, the methylidene complex 1 is susceptible to attack by nucleophiles. Thus, treatment of 1 with LiBH\(_4\) yields the corresponding methyl complex, (C5Me5)Os(dpmm)CH\(_3\).

At least two mechanisms could account for the formation of 1 upon treatment of (C5Me5)Os(dpmm)H with MeOTf. In one mechanism, the osmium methyl/hydride intermediate is generated initially, and dihydrogen is lost to form 1.

In another mechanism, the osmium methyl/hydride intermediate undergoes reductive elimination of methane;
attack by a second equivalent of MeOTf followed by loss of a proton affords I.

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\begin{align*}
\text{L}_2\text{Os}^+ &\rightarrow \text{L}_2\text{Os}^- + \text{H}^- \\
\text{H}^- + \text{Me}^- &\rightarrow \text{L}_2\text{Os}^- + \text{CH}_3^+ \\
\text{L}_2\text{Os}^- &\rightarrow \text{L}_2\text{Os}^+ + \text{CH}_3^+ \\
\text{L}_2\text{Os}^+ &\rightarrow \text{L}_2\text{Os}^+ + \text{CH}_3^+ \\
\end{align*}
\] (2)

In both of these mechanisms, the first step is formation of an osmium methyl/hydride cation. This step has precedence in our study of the analogous (C₅Me₅)Os(dppm)H system [dppm = bis(dimethylphosphino)methane]. The mechanism responsible for the formation of I was determined by following the reaction of (C₅Me₅)Os(dppm)H with MeOTf in a sealed NMR tube. As judged by ¹H NMR spectroscopy, no dihydrogen is generated, but a peak attributable to methane (δ 0.11) grows in during the course of the reaction. On a preparatory scale, if (C₅Me₅)Os(dppm)H and MeOTf are allowed to react for only 1 h in pentane, the triflate complex (C₅Me₅)Os(dppm)OTf can be isolated. Subsequent treatment of isolated samples of (C₅Me₅)Os(dppm)OTf with additional MeOTf affords I in high yield. These results suggest that I is generated by the second of the two mechanisms shown above.

Further studies of these new osmium complexes are in progress.

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**Notes and references**

† Selected spectroscopic data for I: MS(FD): m/z 725[M⁺]. ¹H NMR (thf-d₈, -30 °C): δ 15.49 (td, 3JHP = 17.36 Hz, Os–CH₃), 15.36 (d, 1JHP = 15.4 Hz, Os–CH₃), 15.30 (s, Os–CH₃), 13C{¹H} NMR (CD₂Cl₂, 25 °C): δ 26.8 (t, 3JCP = 8.6 Hz, Os–CH₂), 19F NMR (CD₂Cl₂, 25 °C): δ −80.0 (s, CF₃), 31P{¹H} NMR (CD₂Cl₂, 25 °C): δ −31.0 (s).

‡ Crystal data for I at 198 K: monoclinic, space group P2₁/n, with a = 11.5525(10), b = 50.217(4), c = 18.410(2) Å, β = 96.866(2)°, V = 10625.2 Å³, Z = 12, R₁ (obs. data) = 0.0754, wR₂ (all data) = 0.2182 for 1078 parameters and 101 restraints refined against 18671 unique data. The crystal chosen was grown from diethyl ether by treating (C₅Me₅)Os(dppm)H with MeOTf; we have not been able to grow crystals of this compound exclusively by the Os–CH₃ complex. The metric parameters discussed in the text are for this molecule. The presence of the ethylene complex in the sample was confirmed by NMR spectroscopy and by mass spectrometry.

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¶ Selected spectroscopic data for (C₅Me₅)Os(dppm)Me: MS(FD): m/z 726[M⁺]. ¹H NMR (CD₂Cl₂, 25 °C): δ 0.30 (t, 3JHP = 7.9 Hz, Os–CH₃), 13C{¹H} NMR (CD₂Cl₂, 25 °C): δ 26.8 (t, 3JCP = 8.6 Hz, Os–CH₂), 19F{¹H} NMR (CD₂Cl₂, 25 °C): δ −32.6 (s).

§ Selected spectroscopic data for (C₅Me₅)Os(dppm)OTf: MS(FD): m/z 860[M⁺], ¹F NMR (CD₂Cl₂, 25 °C): δ −80.0 (s, CF₃), 31P{¹H} NMR (CD₂Cl₂, 25 °C): δ −31.0 (s).

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