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Synthesis and reactivity of the osmium methylidene complex $[(C_5Me_5)Os(=CH_2)(dppm)][OTf]$

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Treatment of the hydride complex $(C_5Me_5)Os(dppm)H$, [dppm = bis(diphenylphosphino)methane] with 2 equivalents of methyl trifluoromethanesulfonate (MeOTf) affords the methylidene complex $[(C_5Me_5)Os(=CH_2)(dppm)][OTf]$; 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[1–7] and Fischer–Tropsch[8] reactions. In most cases, the alkylidene ligand is substituted; in contrast, there are relatively few examples of the simplest alkylidene, a terminal methylidene ($=CH_2$) ligand. In 1975, Schrock described the first such complex, $Cp_2Ta(=CH_2)(CH_3)$,[9] and the number of complexes containing a terminal methylidene ligand has slowly grown since.[1,10–19]

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.[13] We now describe the synthesis of an osmium methylidene complex from the reaction of an osmium hydride with methyl trifluoromethanesulfonate (MeOTf).

Treatment of $(C_5Me_5)Os(dppm)H$[20] with 2 equivalents of MeOTf in pentane at room temperature for 18 h affords a yellow powder, which has been identified as the new methylidene compound $[(C_5Me_5)Os(=CH_2)(dppm)][OTf]$ **1**.† The ^1H NMR spectrum of **1** at −30 °C shows that the two hydrogen atoms of the methylidene ligand are inequivalent. In the ^{13}C NMR spectrum of **1**, the methylidene carbon gives rise to a triplet at δ 261.9 (J_{CH} 144 Hz). The inequivalence of the hydrogen atoms is a result of the preferred orientation of the methylidene ligand, which places one hydrogen atom proximal to, and the other distal from, the C_5Me_5 ligand. The same orientation is seen for the methylidene ligands in other $[(C_5R_5)M(=CH_2)L_2]^{n+}$ complexes.[15,17,18]

As the temperature is raised, the methylidene signals in the ^1H NMR spectrum broaden and finally coalesce at 60 °C as rotation of the methylidene ligand around the Os=C bond becomes fast on the NMR time scale. The variable-temperature ^1H NMR line shapes and the simulations of the spectra are shown in Fig. 1. An Eyring plot showed that the activation parameters for rotation of the methylidene ligand in **1** are $\Delta H^\ddagger = 16.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = 5.7 \pm 1.5$ cal mol^{-1} K^{-1}; the free energy of activation is 14.7 ± 0.5 kcal mol^{-1} at 25 °C.

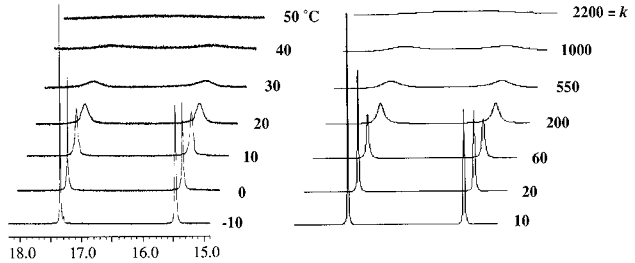


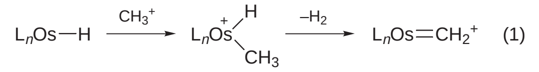
Fig. 1 Variable temperature 500 MHz ^1H NMR line shape for the methylidene protons in **1** (thf-d_8, left) and simulated spectra (right). Rate constants are given in s^{-1}.

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.[15,17,18] For four molecules, however the free energies of activation have been reported: 8.3 ± 0.1 kcal mol^{-1} at −85 °C for $[(C_5Me_5)W(=CH_2)(PPh_3)(CO)_2][AsF_6]$,[15] 9.0 ± 0.1 kcal mol^{-1} at −70 °C for $[(C_5Me_5)W(=CH_2)(PEt_3)(CO)_2][AsF_6]$,[15] 10.7 ± 0.2 kcal mol^{-1} at −28 °C for $[(C_5Me_5)Fe(=CH_2)(dppe)][BF_4]$,[18] and $\geqslant 19$ kcal mol^{-1} at 114 °C for $[(C_5Me_5)Re(=CH_2)(NO)(PPh_3)][PF_6]$.[17]

An X-ray crystallographic study‡ of **1** 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 $Ir(=CH_2)[N(SiMe_2CH_2PPh_2)_2]$,[11] 1.90(2) Å in $[(C_5Me_5)Re(=CH_2)(NO)\{P(OPh)_3\}]^+$,[17] and 1.92(1) Å in $Os(=CH_2)(PPh_3)(NO)Cl$.[14]

Like other cationic methylidene complexes,[14] the methylidene complex **1** is susceptible to attack by nucleophiles. Thus, treatment of **1** with $LiBH_4$ yields the corresponding methyl complex, $(C_5Me_5)Os(dppm)CH_3$.§

At least two mechanisms could account for the formation of **1** upon treatment of $(C_5Me_5)Os(dppm)H$ with MeOTf. In one mechanism [eqn. (1)], an osmium methyl/hydride intermediate is generated initially, and dihydrogen is lost to form **1**.



$$L_nOs{-}H \xrightarrow{CH_3^+} L_n\overset{+}{Os}\begin{smallmatrix}H\\CH_3\end{smallmatrix} \xrightarrow{-H_2} L_nOs{=}CH_2^+ \quad (1)$$

In another mechanism [eqn. (2)], the osmium methyl/hydride intermediate undergoes reductive elimination of methane;

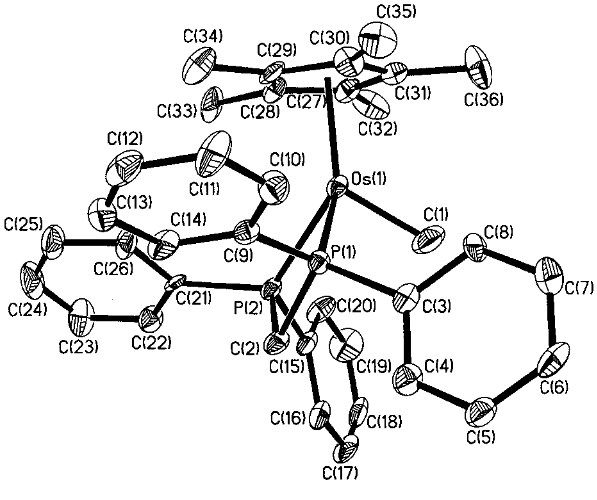
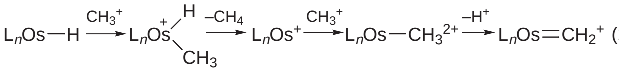


Fig. 2 Crystal structure of $[(C_5Me_5)Os(=CH_2)(dppm)][OTf]$, molecule 1; 35% probability density surfaces are shown. The hydrogen atoms and triflate anion are omitted for clarity.

attack by a second equivalent of MeOTf followed by loss of a proton affords **1**.



$$L_nOs{-}H \xrightarrow{CH_3^+} L_nOs^+\begin{smallmatrix}H\\CH_3\end{smallmatrix} \xrightarrow{-CH_4} L_nOs^+ \xrightarrow{CH_3^+} L_nOs{-}CH_3^{2+} \xrightarrow{-H^+} L_nOs{=}CH_2^+ \quad (2)$$

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 (C_5Me_5)Os(dmpm)H system [dmpm = bis(dimethylphosphino)methane].[21] The mechanism responsible for the formation of **1** was determined by following the reaction of (C_5Me_5)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 (C_5Me_5)Os(dppm)H and MeOTf are allowed to react for only 1 h in pentane, the triflate complex (C_5Me_5)Os(dppm)OTf can be isolated.¶ Subsequent treatment of isolated samples of (C_5Me_5)Os(dppm)OTf with additional MeOTf affords **1** in high yield. These results suggest that **1** 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 **1**: MS(FD); *m/z* 725[M$^+$]. ^1H NMR (thf-d_8, −30 °C): δ 15.49 (td, $^3J_{HP}$ 6.5, $^1J_{HH}$ 1.2 Hz, Os=CH_2), 17.36 (d, $^1J_{HH}$ 1.2 Hz, Os=CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C): δ 261.9 (s, Os=CH_2). ^{19}F NMR (thf-d_8, 25 °C): δ −80.0 (CF_3). $^{31}P\{^1H\}$ NMR (thf-d_8, 25 °C): δ −37.7 (s).

‡ *Crystal data* for **1** at 198 K: monoclinic, space group $P2_1/n$, with a = 11.5525(10), b = 50.217(4), c = 18.410(2) Å, β = 96.866(2)°, V = 10603(2) Å^3, Z = 12, R_1 (obs. data) = 0.0754, wR_2 (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 (C_5Me_5)Os(dppm)H with MeOTf; we have not been able to grow crystals from other solvents. Under these conditions, the crystals obtained were a mixture of **1** with a second compound, the ethylene complex [(C_5Me_5)Os(dppm)(C_2H_4)][OTf], which was evidently generated by alkyl exchange between the diethyl ether solvent and the MeOTf reagent. There are three molecules in the asymmetric unit, but one of these sites is occupied exclusively by the Os=CH_2 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. CCDC 182/1226.

§ *Selected spectroscopic data* for (C_5Me_5)Os(dppm)Me: MS(FD): *m/z* 726[M$^+$]. ^1H NMR (C_6D_6, 25 °C): δ 0.30 (t, J_{HP} 7.9 Hz, Os–CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ −26.8 (t, J_{CP} 8.6 Hz, Os–CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −32.6 (s).

¶ *Selected spectroscopic data* for (C_5Me_5)Os(dppm)(OTf): MS(FD): *m/z* 860[M$^+$]. ^{19}F NMR (C_6D_6, 25 °C): δ −80.0 (s, CF_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −31.0 (s).

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