

# An osmium hydrido methyl species *via* an unconventional methyl transfer†

Dmitry V. Yandulov, John C. Huffman and Kenneth G. Caulton\*

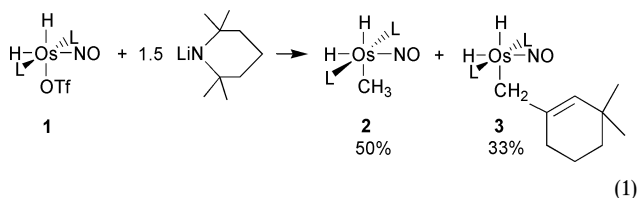
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405-7102, USA

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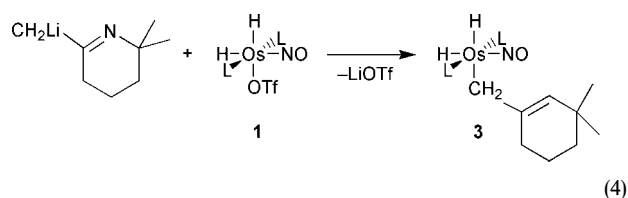
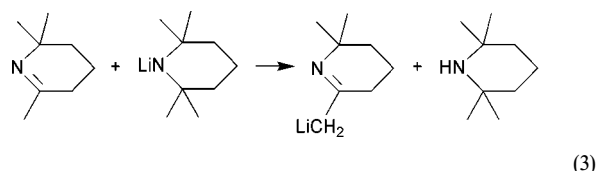
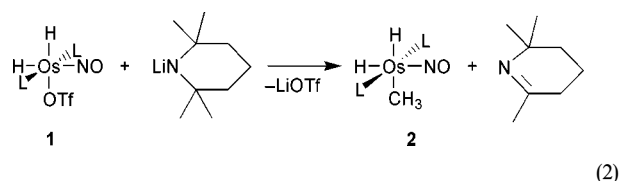
$\text{Os}(\text{H})_2(\text{OTf})(\text{NO})\text{L}_2$  ( $\text{OTf} = \text{O}_3\text{SCF}_3$ ;  $\text{L} = \text{P}^i\text{Pr}_3$ ) reacts with  $\text{Li}(2,2,6,6\text{-tetramethylpiperidide})$  ( $\text{LiTMP}$ ) by *methyl transfer* to give  $\text{Os}(\text{H})_2\text{Me}(\text{NO})\text{L}_2$ . The cyclic imine co-product is rapidly deprotonated by  $\text{LiTMP}$  to give an azaallyl anion that adds to  $\text{Os}(\text{H})_2(\text{OTf})(\text{NO})\text{L}_2$  to give  $\text{Os}(\text{H})_2(\eta^1\text{-C}_8\text{H}_{14}\text{N})(\text{NO})\text{L}_2$ , which was characterized by spectroscopic methods, independent synthesis and X-ray diffraction. Possible reasons for this  $\text{CH}_3^-$  transfer *via*  $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$  cleavage are discussed.

We report a remarkable example where methyl transfer to an electrophilic transition metal complex occurs at 25 °C from lithium 2,2,6,6-tetramethylpiperidide ( $\text{LiTMP}$ ), which is generally considered to be a typical proton-specific Brønsted base,<sup>1–11</sup> although it has been shown to transfer  $\beta\text{-Me}$  at elevated temperature.<sup>12</sup> Reaction of  $\text{Os}(\text{H})_2(\text{OTf})(\text{NO})\text{L}_2$  (**1**,  $\text{L} = \text{P}^i\text{Pr}_3$ ), a molecular triflate species,<sup>13</sup> with 1.5 equiv.  $\text{LiTMP}$  in  $\text{C}_6\text{D}_6$  [eqn. (1)]



gives a modest yield (50% by NMR) of  $\text{Os}(\text{H})_2(\text{CH}_3)(\text{NO})\text{L}_2$ , (**2**), which was independently synthesized by a more conventional method.<sup>14</sup> While this product slowly ( $t_{1/2} \approx 24$  h) eliminates methane, and the resulting  $\{\text{OsH}(\text{NO})\text{L}_2\}$  then oxidatively adds to a C–H bond of benzene, it is sufficiently persistent to allow its characterization<sup>14</sup> with inequivalent hydrides,  $\text{CH}_3$  protons showing coupling to two P and one hydride and diastereotopic  $^i\text{Pr}$  methyl protons.

The surprising results of eqn. (1) are that the amide does not deprotonate  $\text{Os}(\text{H})_2(\text{OTf})(\text{NO})\text{L}_2$  as the major reaction pathway, and that it *does* transfer  $\text{CH}_3^-$ , a process involving  $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$  bond cleavage. This latter supposition was confirmed,<sup>15</sup> and the limited yield of **2** was understood, when it was found that the first mole of amide is converted [eqn. (2)] to imine, by  $\text{CH}_3^-$  transfer, but this imine is rapidly deprotonated by the second mole of lithium amide [eqn. (3)] to give amine and lithium azaallyl. This new lithium alkyl then alkylates another mole of the osmium triflate [eqn. (4)] to form **3**.

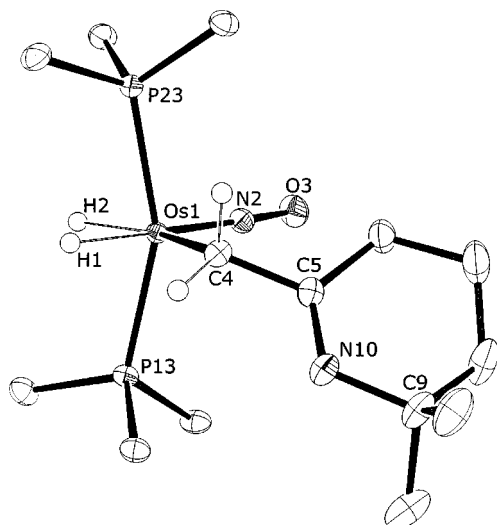


Although increasing the amount of  $\text{LiTMP}$  in eqn. (1) from 1.5 to 6 equiv. per Os does not significantly increase the **2** : **3** ratio, reacting **1** with 2 equiv. of  $\text{LiTMP}$  in the presence of 2.2 equiv. of 1,2-dehydro-2,5,5-trimethylpiperidine in  $\text{C}_6\text{D}_6$  quantitatively yields **3**.

Compound **3**, isolated in 69% yield, was characterized by spectroscopic data<sup>14</sup> (diastereotopic  $^i\text{Pr}$  methyl protons and inequivalent hydrides, but mirror symmetry for the TMP-derived ligand), and X-ray crystallography<sup>16</sup> (Fig. 1). The structure determination shows that NO does not bend to accommodate an  $\eta^3$  binding mode for the new, potentially polydentate ligand. The independent synthesis of **3** verifies the sequence of reactions in eqns. (3) and (4) and shows that imine production in eqn. (1) suppresses methyl transfer by  $\text{LiTMP}$  reacting faster with imine [eqn. (3)] than with  $\text{Os}(\text{H})_2(\text{OTf})(\text{NO})\text{L}_2$  [eqn. (2)]. Most significantly, this represents a direct determination that the  $\text{LiTMP}$  is the source of  $\text{CH}_3^-$  in eqn. (2) because the ligand in **2** has only 8 carbons in contrast to the 9 in  $\text{LiTMP}$ . The structure determination also reveals the nitrogen (*i.e.*, all hydrogens were detected) and also one C=N double bond within the ring. DFT calculations replicate the significant bending of ligands away from the nitrosyl, an effect we attribute to rehybridization of the  $d_\pi$  orbitals to enhance the metal  $\pi$  donation to NO.<sup>17</sup>

Why does  $\text{LiTMP}$  act, in such an unusual manner, to deliver  $\text{CH}_3^-$  to osmium in this case? It is clear that, in spite

† Electronic supplementary information (ESI) available: synthetic procedures and spectroscopic data for **2** and **3**. See <http://www.rsc.org/suppdata/nj/b0/b004484i/>



**Fig. 1** ORTEP representation of  $\text{Os}(\text{H})_2(\text{C}_8\text{H}_{14}\text{N})(\text{NO})(\text{P}^i\text{Pr}_3)_2$ ; phosphine methyls and selected hydrogens are omitted for clarity; ellipsoids are drawn at 50% probability. Selected bond lengths/Å and angles  $\text{Os}-\text{N}2 = 1.7748(16)$ ,  $\text{Os}-\text{C}4 = 2.2396(19)$ ,  $\text{N}10-\text{C}5 = 1.2804(25)$ ,  $\text{N}10-\text{C}9 = 1.4840(26)$ ;  $\text{P}13-\text{Os}-\text{P}23 = 157.78(2)$ ,  $\text{N}2-\text{Os}-\text{C}4 = 104.15(7)$ ,  $\text{Os}-\text{C}4-\text{C}5 = 118.25(13)$ ,  $\text{N}2-\text{Os}-\text{H}1 = 175.2(8)$ ,  $\text{N}2-\text{Os}-\text{H}2 = 102.3(9)$ ,  $\text{H}1-\text{Os}-\text{H}2 = 72.9(11)$ .

of the triflate leaving group encouraging an open coordination site at Os, the potential Os-amide product would encounter large steric resistance due to the two bulky phosphines *cis* to any available coordination site. Secondary modes of reaction thus have a chance to be explored by the reactants. In the case of an amide, a nitrogen lone pair can compensate for the departing carbanion (*i.e.*,  $\text{E}_{1\text{cb}}$  mechanism). Still, since this is the reverse of the normal nucleophilic addition to a keto or imine carbon, the reaction implies significant electrophilicity at the osmium in  $\text{Os}(\text{H})_2(\text{NO})\text{L}_2^+$ . The detailed reaction pathway of this nucleophilic methyl transfer event remains to be explored.

Given the widespread use of bulky amides, such as hexaalkyldisilazides, to stabilize transition metal complexes<sup>18–20</sup> and main group compounds<sup>21</sup> with low coordination numbers and increasing use of 2,2,6,6-tetramethylpiperidine in a similar fashion,<sup>22–25</sup> the methyl anion transfer reactivity reported here deserves wider consideration.

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