Electrophilic (Li^+) acceleration of C–H reductive elimination and oxidative addition reactions of Os(II)/Os(0) nitrosyl complexes†

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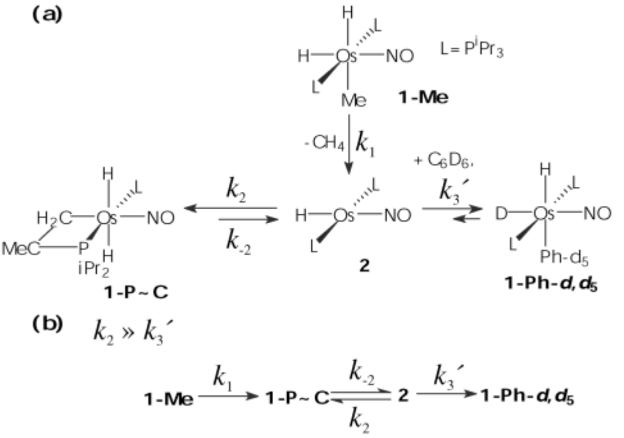
The reductive elimination of methane from *cis,trans*-$Os(H)_2(CH_3)(NO)L_2$ ($L = P^iPr_3$) in benzene is accelerated by added $LiN(SiMe_3)_2$, with ^1H NMR and IR evidence for binding of the lithium electrophile to NO oxygen. Oxidative addition of benzene to the transient $OsH(NO)L_2$, to give *cis,trans*-$Os(H)_2(C_6H_5)(NO)L_2$, is also accelerated by $LiN(SiMe_3)_2$. DFT calculations of the reaction path with and without $LiNMe_2$ show the rate acceleration is due to preferential stabilization of the oxidative addition/reductive elimination transition state, due to the greater back donation to NO in the TS. This is traced, in turn, to the relief of the filled–filled repulsion between the occupied Os d and C–H σ-orbitals by the Li electrophile on NO oxygen.



Scheme 1 The kinetic schemes for generation and reactivity of **2**.

Oxidative addition and reductive elimination reactions at transition metal centers are elementary steps in numerous catalytic cycles[1] and constitute a mechanistic cornerstone of transition metal reactivity. C–H oxidative addition is a common mechanistic solution to selective activation of hydrocarbon substrates,[2] an area currently attracting much interest,[3] and elucidation of factors controlling the facility of the addition process may thus be of importance to the long-standing goal of catalytic alkane functionalization under mild conditions.[4] Formation of secondary bonding interactions to the metal-bound ligands, such as hydrogen bonding, offers a unique opportunity to subtly and easily influence the reactivity at the metal center[5] and conceivably bears a general utility of enhancing catalyst selectivity and/or reaction rates. This study describes significant acceleration of methane reductive elimination and benzene oxidative addition in an Os(II)/Os(0) couple attainable by intermolecular lithium binding to the NO oxygen. This observation is traced by DFT calculations to originate in transition state stabilization *via* relief of filled–filled repulsion between an occupied Os d and the C–H σ-orbital.

We describe first the intrinsic reactivity in the absence of lithium electrophiles. *cis,trans*-$Os(H)_2Me(NO)L_2$ (**1-Me**, $L = P^iPr_3$) is an isolable Os(II) dihydride[6] that undergoes (Scheme 1) irreversible reductive elimination of methane under ambient conditions on a timescale of days in a variety of common organic solvents.[7] The formal Os product {$OsH(NO)L_2$} (**2**) reversibly metallates a phosphine ^{i}Pr group, before subsequently converting completely in C_6D_6 solvent into *cis,trans*-$Os(H)(D)(C_6D_5)(NO)L_2$ (**1-Ph-*d*,*d*$_5$**)[7] *via* benzene C–D oxidative addition. The all-protio complex **1-Ph** was isolated in 66% yield from a thermolysis reaction of **1-Me** in C_6H_6 and was itself found to undergo simultaneous deuteration of the hydride sites and phenyl ligand on prolonged heating in C_6D_6. Although **2** has eluded direct observation even when generated at −40 °C in d_8-PhMe, decomposing then into $OsH(NO)L_3$,[8] its existence was demonstrated by trapping experiments with H_2 and D_2.[7] The low-temperature generation experiment also showed the onset of P^iPr_3 metallation occurring at a temperature of >10 °C lower than that of aromatic C–D activation.

The loss of methane from **1-Me** in C_6D_6 occurs in a clean first-order reaction (studied through up to four half-lives) and is unaffected by the presence of 10 equiv. of added L, speaking against phosphine dissociation preceding methane elimination,[9] a conclusion reinforced by the DFT calculations below. An Eyring plot of the first-order rate constants measured over a 33 °C interval[7] gave activation parameters for methane reductive elimination from **1-Me** as $\Delta H^{\ddagger}_1 = 26.7(8)$ kcal mol^{-1} and $\Delta S^{\ddagger}_1 = +8(3)$ cal mol^{-1} K^{-1}. The evolution of the products resulting from the decay of **1-Me** in C_6D_6 proceeds according to Scheme 1(a) and is graphically depicted in Fig. 1(a). The available data do not permit a unique simultaneous fitting of the three rate constants, k_2, k_{-2} and pseudo-first order k_3'; however, the assumption $k_2 \gg k_3'$ simplifies the kinetic scheme to that shown in Scheme 1(b), while allowing a reasonable agreement with experimental data [solid lines in Fig. 1(a)] to be obtained by describing the evolution of **1-P~C** and **1-Ph-*d*,*d*$_5$** with well-known rate expressions[10] that utilize only the effective $k_4' = k_3' \cdot k_{-2}/k_2$, k_1 and the mass balance condition in the steady-state approximation for the concentration of the unobserved **2**. Rate constants k_4' determined from a least-squares fitting of the experimental data show a linear dependence on the C_6D_6 concentration (in C_6D_{12}) and give a moderate kinetic isotope effect $k_4'(C_6H_6)/k_4'(C_6D_6)$ (both [C_6D_6] and [C_6H_6] are 3.0 M in C_6D_{12}) of 3.2(9) at 47 °C.[11] C–H bond breaking has therefore progressed only

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† Electronic supplementary information (ESI) available: full experimental and computational details. See http://www.rsc.org/suppdata/nj/b2/b200180m/

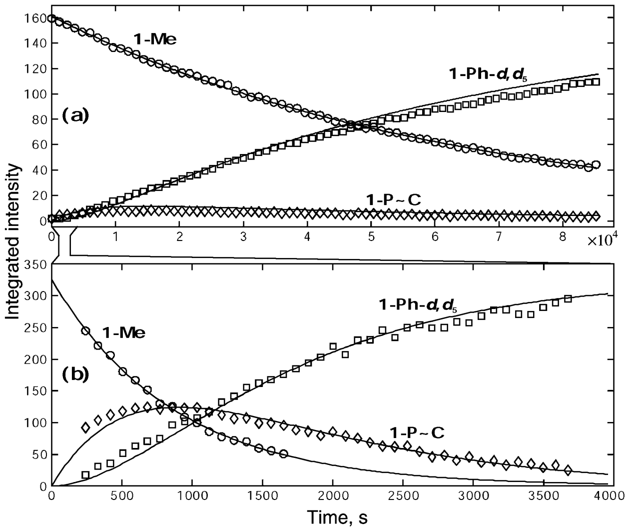


Fig. 1 Decay of **1-Me** and evolution of **1-P ~ C** and **1-Ph-*d*,*d*$_5$** during thermolysis of **1-Me** in C_6D_6 at 29 °C at total [Os] = 29.9 mM measured by ^{1}H NMR (*a*) in the absence of added Lewis acid and (*b*) in the presence of 2.5 equiv. of $(Me_3Si)_2NLi$ (note the timescale expansion). Least-squares fits of experimental data are shown with solid lines.

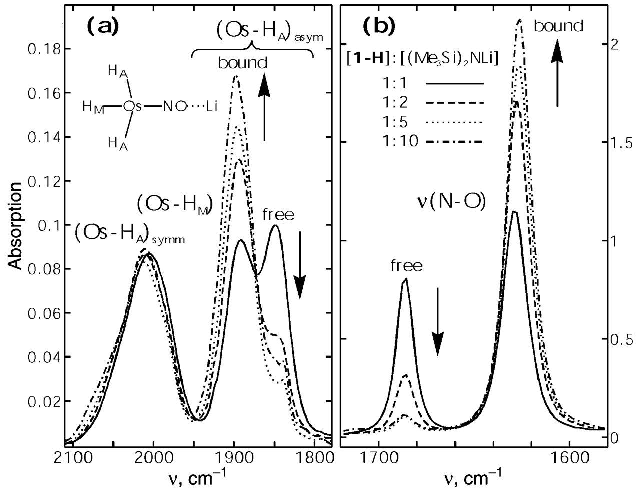


Fig. 2 IR spectra of **1-H** in *n*-heptane at 20 °C [ν(Os–H) (*a*) and ν(N–O) (*b*) regions] recorded in the presence of increasing amounts of $(Me_3Si)_2NLi$, with band assignments, all normalized to a **1-H** concentration of 61.3 mM and with solvent spectrum subtracted. The actual **1-H** concentrations are 61.3 (——), 65.7 (------), 61.3 (········) and 30.7 (-·-·-) mM.

moderately at the transition state (TS). The temperature dependence of $k_4 = k_4'/[C_6D_6]$ evaluated over the same 33 °C interval gave $\Delta H^{\ddagger}{}_4 = 20(1)$ kcal mol^{-1} and $\Delta S^{\ddagger}{}_4 = -13(4)$ cal mol^{-1} K^{-1} for the conversion of **1-P~C** to **1-Ph-*d*,*d*$_5$**. These quantities correspond to the sum of the thermodynamic parameters governing the equilibrium between **1-P~C** and **2** and the activation parameters for oxidative addition of C_6D_6 to **2**, that is, $\Delta H^{\ddagger}{}_4 = \Delta H^{\circ}{}_{-2} + \Delta H^{\ddagger}{}_3$ and $\Delta S^{\ddagger}{}_4 = \Delta S^{\circ}{}_{-2} + \Delta S^{\ddagger}{}_3$. Therefore, $\Delta H^{\ddagger}{}_3$ for the oxidative addition of C_6H_6 to **2** can be estimated as $\Delta H^{\ddagger}{}_3 < 17$ kcal mol^{-1} from $\Delta H^{\circ}{}_{-2} > 2.1$ kcal mol^{-1} [12] and $\Delta H^{\ddagger}{}_4(C_6H_6) = \Delta H^{\ddagger}{}_4 - 0.7$ kcal mol^{-1}, which corrects the $\Delta H^{\ddagger}{}_4$ value measured for the addition of C_6D_6 for the observed kinetic isotope effect[11] to give the $\Delta H^{\ddagger}{}_4(C_6H_6)$ value, for the addition of C_6H_6. A moderately positive $\Delta S^{\circ}{}_{-2}$ for the phosphine demetallation would additionally lower the value of $\Delta S^{\ddagger}{}_3$, consistent with an associative mechanism of formation of **1-Ph-*d*,*d*$_5$** from **2**.

We next consider the effect of Li^+ compounds on reductive elimination from **1**. Examination of ^{1}H NMR data of a large series of *cis,trans*-$Os(H)_2Y(NO)L_2$ complexes (Y = no ligand, halide, pseudohalide, alkyl, aryl, hydride) showed the difference of the hydride chemical shifts $\Delta\delta = \delta H_{trans} - \delta H_{cis}$ (to NO) to follow the opposite trend of the trans-influence of the ligand Y relative to that of the NO ligand,[7] and a considerable increase in the $\Delta\delta$ parameter was observed for several **1-R** complexes in aromatic solvents in the presence of an excess of several lithium alkyls and alkylamides.[13] The significant shifts of the hydride signals of **1-H** effected by the presence of 10 equiv. of $(Me_3Si)_2NLi$ in C_6D_6 were absent in a reaction mixture containing products of partial one-electron reduction of **1-H** with Li–naphthalene–TMEDA in C_6D_6,[13] ruling out the presence of paramagnetic species as the cause of the observed variations in hydride chemical shifts by $LiNR_2$ or LiR′. At the same time, the IR spectrum of **1-Me** in heptane at 20 °C in the presence of 1 equiv of Me_3SiCH_2Li showed a new ν(N–O) band, red-shifted by 60 cm^{-1}, while an analogous $\nu(N\text{–}O)_{bound}$ band was also observed for **1-H** with either Me_3SiCH_2Li or $(Me_3Si)_2NLi$ [$\Delta\nu(N\text{–}O)_{free-bound} = 60$ cm^{-1} for both] and its intensity relative to that of $\nu(N\text{–}O)_{free}$ was found to be concentration-dependent in the latter case [Fig. 2(b)]. All Os–H bands[14] in the new species are blue-shifted [Fig. 2(a)], which rules out an interaction with a hydride based on the conclusions derived from analogous hydrogen-bonding studies[15] of protic acids to (M)(H)NO. The red shift of ν(N–O) is fully consistent with a weakened N–O bond by interaction of electrophilic Li of $(Me_3Si)_2NLi$ with NO oxygen. The latter type of interaction is known to effect a red shift of ν(N–O) ranging from 35 to 264 cm^{-1} for a number of other Lewis acid adducts of metal nitrosyls.[16] Since, in complete analogy to hydrogen bonding, lithium bonding[17] to NO enhances the backbonding from Os to NO, it leads to a weaker N–O but a stronger Os–N bond, which effectively increases the trans-influence of NO, thus explaining the greater $\Delta\delta$ values observed above.

Increased solvation of Li in RLi/R_2NLi by added bases was found to negate the observed increases in hydride $\Delta\delta$ of several **1-R** complexes.[12] For example, $\Delta\delta = 0.17$ ppm of **1-Me** recorded in a homogeneous d_8-THF solution also containing 1.3 equiv. of $(Me_3Si)_2NLi$ and 1.0 equiv. of $LiB[C_6H_3\text{-}3,5\text{-}(CF_3)_2]_4$ is indistinguishable from that recorded in a d_8-THF solution of **1-Me** free of Li sources (0.17 ppm), while presence of 2.5 equiv. of $(Me_3Si)_2NLi$ in a C_6D_6 solution of **1-Me** caused a strong increase in $\Delta\delta$ from 0.18 to 0.37 ppm. The complex **1-CH$_2$SiMe$_3$**, generated from **1-OTf** and excess Me_3SiCH_2Li in d_8-PhMe at −40 °C, showed a $\Delta\delta$ of 2.14 ppm in the presence of 8.6 equiv. of Me_3SiCH_2Li, while an analogous generation experiment using additional TMEDA gave $\Delta\delta = 1.85$ ppm in the presence of 16.4 equiv. of Me_3SiCH_2Li at −40 °C in d_8-PhMe solution also containing 26.4 equiv. of TMEDA. The 20 °C $\Delta\delta$ value of **1-CH$_2$SiMe$_3$** in C_6D_6 is 1.88 ppm and that of pure **1-Me** (0.18 ppm) in d_8-PhMe varies between 0.14 and 0.19 ppm in the −90 to + 60 °C temperature range. Analogous increases in hydride $\Delta\delta$ were also observed with Li salts of less nucleophilic counterions: **1-Me** generated in C_6D_6 from **1-OTf** and 1.2 equiv. of $LiBMe_4$ showed $\Delta\delta = 0.18$ ppm, which increased to 0.25 ppm when 3 equiv. of $LiBMe_4$ were used in an analogous experiment.

These experiments clearly point to the electrophilic Li in RLi/R_2NLi as causing the observed changes in hydride $\Delta\delta$ and the IR frequency shifts, and allow us to rule out participation of the nucleophilic centers in RLi/R_2NLi, since their reactivity or at least steric accessibility increases upon strong solvation of Li and subsequent disaggregation.[18] The Li acid primarily used in this study, $(Me_3Si)_2NLi$, is a well-known Lewis acid,[19] and the proposed mode of interaction of RLi/R_2NLi with **1-R**, *via* coordination of Li to the nitrosyl oxygen, is closely related to the well-known coordination of organic carbonyl functionalities by Li in R_2NLi.[20] Such interactions constitute an integral part of enolization reaction mechanisms,[20a,b] pre-coordination of carbonyl moieties at Li in solution is often observed and leads to ν(C=O) frequency reduction[20] and several such complexes have been structurally characterized.[20c] The low magnitude of the ν(NO) frequency shift observed here (60 cm^{-1}) rules out net addition of the N–Li moiety across the N–O bond.[21]

Most significantly, the sequence of reactions in Scheme 1(a) was found to be strongly accelerated by the presence of 2.5 equiv. of $(Me_3Si)_2NLi$ at 29 °C [Fig. 1(b)], while 10 equiv. caused the reactions rates to become immeasurably fast. The presence of this amide resulted in no net chemical transformation of reactants or products, other than the conversion of **1-Me** to **1-Ph-*d*,*d*$_5$**, *via* intermediacy of **1-P∼C** as seen in the absence of Li. Quantitative evaluation of k_1 and k_4' in the presence of 2.5 equiv. of $(Me_3Si)_2NLi$ gave the net effects of Li to be $k_1(\text{Li})/k_1 = 72$ and $k_4'(\text{Li})/k_4' = 6$. Since the (population-weighted) $\Delta\delta$ value of the hydride signals of **1-Me** remained constant throughout its decay, all nitrosyl complexes present in solution appear to bind $(Me_3Si)_2NLi$ with very similar equilibrium constants, and therefore the enhanced rate constants correspond to the population-weighted averages of those involving free and fully lithium-bonded complexes.[22] Consistent with the above evidence against participation of the nucleophilic centers of RLi/R_2NLi in causing the hydride $\Delta\delta$ and ν(NO) frequency shifts, similar rate enhancements were observed in the presence of electrophilic centers with more "innocent" nucleophiles. For example, the ethyl analog of **1-Me**, **1-Et**, generated *in situ* from **1-OTf** and a slight excess of $LiBEt_4$ in C_6D_6,[23] underwent first-order reductive elimination of ethane with a rate 3.6 times faster than that measured for pure **1-Et** at 28 °C, an effect ascribable to either a small amount of $LiBEt_4$ or 1 equiv. of BEt_3 present. In summary, the $LiN(SiMe_3)_2$ results demonstrate that enhancing the π-accepting properties of NO by coordination of an electrophile to the oxygen significantly accelerates C–H reductive elimination and, as corroborated by the DFT calculations[24] below, C–H oxidative addition processes.

DFT calculations (Fig. 3, which illustrates structures with lithium, together with *changes* in structural parameters caused by lithium) of the Li-free oxidative addition of either methane or benzene to the model $OsH(NO)(PH_3)_2$ reproduce well the experimental $\Delta H^{\ddagger}_1 = 26.7(8)$ kcal mol^{-1} as $\Delta(E + \text{ZPE})^{\ddagger}_1 = 25.9$ kcal mol^{-1} and the kinetic isotope effect for oxidative addition of benzene to **2**[11], with the computed $\Delta(E + \text{ZPE})^{\ddagger}_3 = 10.8$ kcal mol^{-1}, as compared to the experimental estimate $\Delta H^{\ddagger}_3 < 17$ kcal mol^{-1}. No significant lengthening of Os–P distances was found at the transition state (TS) for methane elimination, consistent with the reaction not requiring initial loss of phosphine from **1-Me**. No η^2-C, C-benzene adduct was located at the given level by optimizing the TS for benzene reductive elimination towards the product, indicating that such a structure can at best be a very shallow minimum.

The monomeric Me_2NLi was next used to model the effect of the experimental Li electrophile $(Me_3Si)_2NLi$ and it was found to form strongly bound Li···O(N) adducts with each stationary-point structure; Fig. 3 shows the binding energy for each ground state (GS) and transition state. The $\Delta\nu(\text{N–O}) = 86$ cm^{-1} computed for the $L = PH_3$ model of **1-Me** and monomeric Me_2NLi is greater than the experimental value of 60 cm^{-1}, suggesting that an oligomeric $(Me_3Si)_2NLi$ structure may be involved in lithium bonding in the experimental system, and therefore the computed effects of the Li···O(N) interactions are somewhat overestimated. In complete analogy with hydrogen bonding, the presence of Li···O(N) interactions in every case increases the backbonding from Os to NO π^*, causing an increase in ν(NO) of 86–111 cm^{-1} in all structures in Fig. 3; the apparently highly flexible square-planar structure of $OsH(NO)(PH_3)_2$[7] undergoes strong bending of ∠H–Os–N in response to bending of ∠Os–N–O, while the distorted[14] structures of the $L = PH_3$ models of **1-Me** and **1-Ph** undergo additional compression of the cis angles ∠H–Os–H and ∠H–Os–C due to the effective increase of the π-acidity of NO.

Energetically, lithium binding to NO effects a kinetically very significant stabilization of both transition states by 2.8–3.7 kcal mol^{-1} (E + ZPE) relative to both minimum structures, while stabilizing $OsH(NO)(PH_3)_2$ relative to the ground state Os(II) species by only 0.3 (**1-Me**) and 0.9 (**1-Ph**) kcal mol^{-1}. Thus, model calculations qualitatively reproduce the observed rate-accelerating effect of lithium binding to NO on methane reductive elimination from **1-Me**. They also predict a greater effect on k_1 [$\Delta\Delta(E + \text{ZPE})^{\ddagger}_1 = -3.6$ kcal mol^{-1}] than on $k_4' = k_3' \cdot k_{-2}/k_2$ [$\Delta\Delta(E + \text{ZPE})^{\ddagger}_4 = -3.1$ kcal mol^{-1} by app-

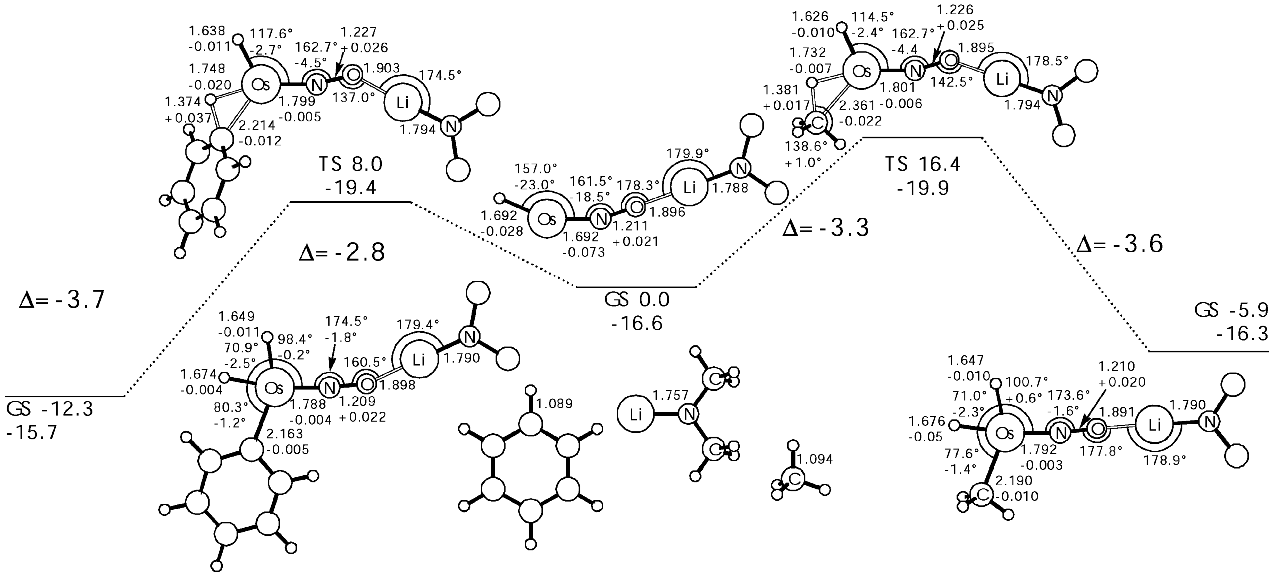
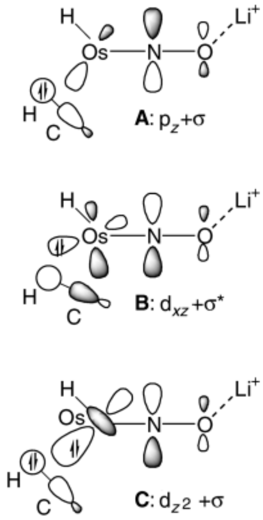


Fig. 3 Computed structures (B3LYP, polarization functions used on all metal-bound atoms and Os) involved in C–H oxidative addition of methane and of benzene to $OsH(NO)(PH_3)_2$ in the presence of Li···ON interactions with Me_2NLi: selected bond distances (Å), angles (°), and their changes relative to the structures without Li···ON bonding (directly underneath), as well as ZPE-corrected relative energies (kcal mol^{-1}) and binding energies of Me_2NLi (directly underneath). Δ denotes the reduction in $\Delta(E + \text{ZPE})^{\ddagger}$ upon coordination of Li to NO. *trans*-PH_3 groups and CH_3 hydrogens are omitted for clarity.



Scheme 2

proximating the effect of Li-bonding on the equilibrium constant k_{-2}/k_2 to the computed stabilization of $OsH(NO)(PH_3)_2$ relative to the $L = PH_3$ model of **1-Me**] in accord with experiment. They therefore allow us to attribute the observed enhancement of k_4' primarily to the effective increase in k_3 for benzene oxidative addition to **2**.

The electrophile-induced acceleration of *both* oxidative addition and reductive elimination is surprising, since it might have been expected to have complementary effects on these opposing redox processes if lithium influenced primarily one ground state. The observed result comes from the major influence being in fact on the TS. Formation of the strongest Li···O(N) bonding with the TS structures is the direct consequence of the greater back donation from Osd_{z^2} to NO π* already present (**C** in Scheme 2), which makes the NO oxygen the most nucleophilic at the TS, relative to both minima. Such increase in the backbonding to the π-accepting ligand in the TS has long been recognized[25] as an important orbital interaction in oxidative *addition* to d^8 square-planar complexes. Presence of the Li···O(N) interaction results in an effective increase of the π-acidity of NO. In the TS, this slightly enhances the electron donation from σ_{CH} to Os p_z (**A**) and diminishes the backbonding from the filled Osd_{xz} to σ_{CH}* (**B** in Scheme 2). However, the dominating effect of the Li···O(N) interaction lies in decreasing the four-electron repulsion between the filled Osd_{z^2} and the σ_{CH} (**C** in Scheme 2), which allows for improved Os···C and Os···H bonding (see bond length changes in Fig. 3) and causes a net stabilization of the TS energy relative to the GS.

In conclusion, these results show that enhancing the π-accepting properties of a π-acid ligand that directly interacts with a filled metal d orbital involved in four-electron repulsion with a substrate σ-orbital during oxidative addition/reductive elimination results in a significant transition state stabilization, as demonstrated experimentally for the case of C–H activation. While $(Me_3Si)_2NLi$ was found to be an effective and chemically inert Lewis acid in the studied system, lithium-containing acidic catalysts developed by Strauss and coworkers[26] may offer greater compatibility and rate enhancements for controlled application of the principles demonstrated here.

Experimental

A solution of **1-Me** (100 mg, 179 μmol) in benzene (3 mL) was heated at 60–65 °C for 1 h 40 min, filtered through Celite and brought to dryness. The residue was dried at 45 °C/*ca.* 10 mTorr for 2 h and extracted with MeOH. The combined extracts were filtered and concentrated to yield orange crystals after cooling to −40 °C overnight, which were washed with 3 × 5 mL of MeOH at −40 °C, dried *in vacuo* and stored under Ar at −20 °C. Yield 73 mg (118 μmol, 66%). ^{1}H NMR (C_6D_6, 20 °C): δ 7.91 (br s, 2H, o-C_6H_5), 7.16 (approx. t, $J_{H-H} = 6.8$ Hz, 2H, m-C_6H_5), 6.99 (approx. t, $J_{H-H} = 6.9$ Hz, 1H, p-C_6H_5), 2.11 {m, 6H, $P[CH(CH_3)_2]_3$}, 1.09 {dvt, $J_{H-H} = 7.3$ Hz, $N = 14.6$ Hz, 18H, $P[CH(CH_3)_2]_3$}, 1.03 {dvt, $J_{H-H} = 7.3$ Hz, $N = 14.6$ Hz, 18H, $P[CH(CH_3)_2]_3$}, −5.99 (td, $J_{P-H} = 25.4$ Hz, $J_{H-H} = 8.1$ Hz, 1H, ON–OsH), −6.63 (td, $J_{P-H} = 19.0$ Hz, $J_{H-H} = 8.1$ Hz, 1H, Ph–OsH). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 28.5 (s). IR (C_6D_6): 1690 cm^{-1} (υ_{NO}). Anal. found (calcd., %) for $C_{24}H_{49}NOOsP_2$: C 46.25 (46.51), H 7.70 (7.97), N 2.18 (2.26). Selected shifts of hydride NMR signals on deuteration, measured on a mixture of **1-Ph** and **1-Ph-*d*,*d*$_5$**; ^{1}H NMR (C_6D_6, 20 °C): δ[ON–Os(D)–H] − δ[ON–Os(H)–H] = −69.0 ppb, δ[Ph–Os(D)–H] − δ[Ph–Os(H)–H] = −1.0 ppb; ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ[ON–Os(D)–H] − δ[ON–Os(H)–H] = + 63.0 ppb, t, $J_{P-D} = 3$ Hz; δ[Ph–Os(D)–H] − δ[Ph–Os(H)–H] = −30.0 ppb, t, $J_{P-D} = 4$ Hz.

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23 This reaction[13] produced a mixture of **1-H** (21%), OsH(η^2-C$_2$H$_4$)(NO)(P^{i}Pr$_3$)$_2$ (17%), together with **1-Et** and the products of subsequent reactions of **2** (62%), which also contained 0.06 equiv. of LiBEt$_4$ and 1 equiv. of BEt$_3$ (relative to all {Os}NO species present). The $\Delta\delta$ of **1-Et** in this mixture was found to be indistinguishable from that of the pure compound, which is also true for **1-Me** in the presence of an analogously small excess of (Me$_3$Si)$_2$NLi.

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