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# Intra- and Intermolecular Activation of Carbon–Hydrogen Bonds in a Tetrakis(trimethylphosphine)osmium(II) System

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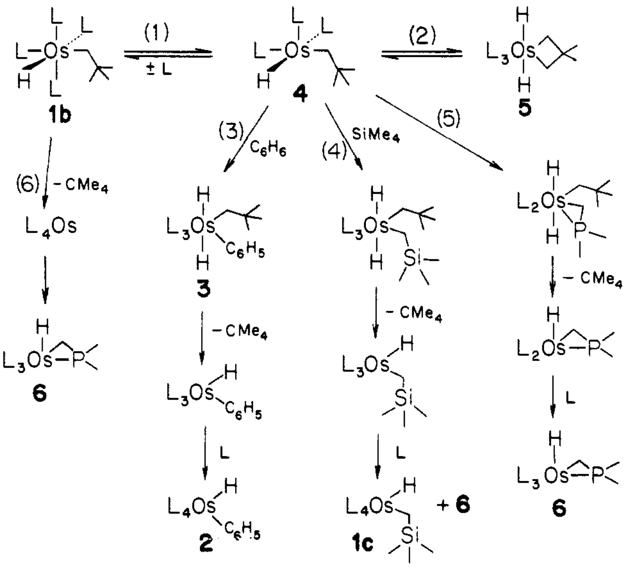
The mild intermolecular activation of carbon–hydrogen bonds in saturated hydrocarbons by soluble transition-metal complexes has recently been achieved,[1] but several fascinating aspects of this reaction are not yet understood. Most of the well-defined examples of this reaction and all examples that yield ($\eta$-1-alkyl)metal hydride complexes involve starting materials containing one or two cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) ligands, the steric and electronic effects of which are not clear. The reported reactions favor intermolecular over intramolecular activation for reasons which are not fully understood. Our interests in other aspects of hydrocarbon activation chemistry[2] and in synthetic organoosmium chemistry in particular led us to investigate the possibility of C–H bond activation by non-Cp-containing osmium–phosphine complexes.[3]

We wish to report the mild activation of carbon–hydrogen bonds, both intramolecularly (intra) and intermolecularly (inter) by an intermediate generated by the thermolysis of *cis*-$L_4Os(H)R$ ($L = P(CH_3)_3$: $R = CH_3$, **1a**; $R = CH_2C(CH_3)_3$, **1b**; $R = CH_2Si(CH_3)_3$, **1c**).[4] In particular, thermolysis of **1b** at 80 °C results in C–H bond activation in the coordinated neopentyl (Np) group, in arenes, in tetramethylsilane ($Me_4Si$), and in trimethylphosphine (L). The intermolecular activation of alkanes in our system has remained elusive. A rather complex mechanistic picture, summarized in Scheme I, is emerging from this study. Particularly to be noted is that, first, our data are most consistent with Os(IV) and not Os(0) intermediates in all but the slowest process, second, the activation of trimethylphosphine has been found to proceed by two distinct paths, depending on conditions, one via Os(IV) and the other via Os(0), and third, a crudely defined "order of relative reactivity" is observed of intra Np > inter arene > inter $Me_4Si$ > intra L Os(IV) > intra L Os(0) > inter alkane (unobserved).

**Scheme I**



Thermolysis of **1b** in benzene at 70 °C proceeds as shown in steps 1–3 of Scheme I to yield **2**,[5] with no other products detectable by $^1H$ NMR spectroscopy. Disappearance of **1b** is cleanly first order over three half-lives,[6] with an observed rate constant of $4.20 \times 10^{-4}$ s$^{-1}$. That an Os(IV) intermediate, presumably **3**, is involved and not an Os(0) species formed by NpH reductive elimination prior to benzene activation is substantiated by several lines of evidence. Use of $C_6D_6$ as solvent reveals a kinetic isotope effect, $k_H/k_D = 2.2$, consistent with formation of **3** as the rate-limiting step. A plot of $1/k_{obsd}$ vs. $1/[C_6H_6]$ for reactions carried out in cyclohexane-$d_{12}$ is linear as required by this mechanism. Finally, the following set of experiments corroborates that both $C_6H_6$ and NpH are present on the metal at the same time at some point, presumably in **3**. When the pyrolysis is conducted in $C_6D_6$, the hydride ligand in **2** is 87% deuterated as determined by $^1H$ and $^2H$ NMR, and the NpH is 12% $d_1$ by mass spectral analysis. Starting material **1b** shows no significant incorporation of deuterium throughout the reaction, and product **2**-$d_6$ exhibits no H/D exchange with $C_6H_6$ as solvent upon heating for 100 h at 80 °C. Thermolysis of a 1:1 mixture of **1b** and $L_4Os(D)[CH_2C(CH_3)(CD_3)_2]$, **1b**-$d_7$, in $C_6H_6$ at 80 °C yielded the expected products but with no detectable neopentane-$d_1$, consistent with no crossover before or during the reductive elimination.

When **1b** was heated at 80 °C in the presence of a 4-fold molar quantity of $P(CD_3)_3$, L′, benzene activation was strongly inhibited, and L′ was incorporated (followed by both $^1H$ and $^{31}P$ NMR) specifically into the positions of the two trans phosphines of **1b** with a rate constant, $k_1$, of $1.1 \times 10^{-3}$ s$^{-1}$. These facts demonstrate the necessity for initial L dissociation (step 1, Scheme I) and indicate that the intermediate retains its stereochemistry and so is probably of square-pyramidal geometry as in **4**. There is a strong effect of steric bulk on the dissociation of L in the initial reaction step, as demonstrated by the temperature required to obtain comparable rates of formation of **2** from **1b**, **1c**, and **1a** ($k_{1b}$(70 °C) = $4.2 \times 10^{-4}$ s$^{-1}$; $k_{1c}$(80 °C) = $9.0 \times 10^{-6}$ s$^{-1}$; $k_{1a}$(105 °C) = $1.2 \times 10^{-6}$ s$^{-1}$, all $k_{obsd}$).

The presence of the intramolecular activation of coordinated Np (path 2, Scheme I) was detected by a deuterium labeling

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[1] For extensive references outlining the development of this subject, see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (b) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. (c) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–133. (d) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994–7001. (e) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235–1236. (f) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929–3939: (g) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190–7191. (h) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620–631. (i) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493. (j) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214–2216.

[2] (a) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076–6077: (b) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795–1803.

[3] (a) Early reported chemistry indicating that osmium should be a good candidate for C–H bond activation: Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1963**, 6017–6027. (b) C–H activation in arenes, acetone, acetonitrile, etc. by Fe– and Ru–phosphine complexes, and indirect observation of arene activation by Os–phosphine complexes: Tollman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080–4089. (c) Directly observed benzene activation in a (benzene)osmium(0) complex; Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793–794. (d) Indirectly observed arene activation in phosphine and phosphite complexes of Ru and Os: Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73–93.

[4] Molecules **1** are prepared by reaction of the appropriate alkyllithium reagent with $L_4Os(H)(OSO_2CF_3)$ (**7**), which is in turn prepared by the reaction of **6** with triflic acid. Compounds **1a**, **1b**, **1c**, and **7** have been characterized with good elemental analyses and consistent $^1H$, $^{31}P$, and, where appropriate, $^2H$ NMR spectra. For example, **1b**: $^1H$ NMR ($C_6D_6$, 270 MHz) $\delta$ −10.4 (dq, $J_{PH}$ = 70.4, 20.5 Hz, OsH), 1.11 (d, $J_{PH}$ = 5.8 Hz, $PMe_3$), 1.36 (d, $J_{PH}$ = 6.0 Hz, $PMe_3$), 1.41 (m, $CH_2$; with $[(CD_3)_3P]_4Os(Np)(H)$ in $C_6D_{12}$, this resonance is visible as a dq, $J_{PH}$ = 11.0, 5.6 Hz), 1.45 (s, $CMe_3$), 1.50 (vt, $J_{PH}$ = 5.2 Hz, *trans*-$Os(PMe_3)_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 109 MHz, internal $PMe_3$ assigned $\delta$ −62.1 as reference) $\delta$ −50.7 (dd, $J_{PP}$ = 20.7, 16.9 Hz, *trans*-$Os(PMe_3)_2$), −58.7 (dt, $J_{PP}$ = 9.2, 20.7 Hz, $PMe_3$ trans to OsH), −63.2 (dt, $J_{PP}$ = 9.2, 16.9 Hz, $PMe_3$ cis to OsH) ppm.

[5] Complex **2** is known,[3c] as is compound **6** (Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547–549).

[6] A slight deviation from first-order behavior after ca. 1.5 half-life can be eradicated by the introduction of 1–3 mol% of neopentyllithium (NpLi). The rate of the reaction is independant of the NpLi concentration. Catalysis by traces of weak acids may be a general feature of the chemistry of these highly basic molecules: Desrosiers, P. J.; Flood, T. C., unpublished results.

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experiment. Randomization of the deuterium throughout the Np group and OsH positions (none into L) of **1b**-$d_7$ was readily followed by $^1$H NMR during thermolysis in $C_6D_{12}$. Mass spectral analysis of NpH resulting from thermolysis of **1b**-$d_7$ in $C_6D_6$ also indicated extensive internal scrambling of the deuterium label within the neopentyl group, presumably through intermediate **5**.

Pyrolysis of **1b** in neat $Me_4Si$ at 80 °C results in a much slower reaction, first order in **1b** ($k_{obsd} = 4.8 \times 10^{-6}$ s$^{-1}$), leading to formation of **1c** but with competitive formation of **6**[5] (path 4, Scheme I). Reaction of **1b** at 80 °C in cyclopentane + ca. 12 mol % of methane leads to formation of only **6** with $k_{obsd} = 2.2 \times 10^{-6}$ s$^{-1}$. We are examining the scope and mechanism of the tetraalkylsilane activation in lieu of the intermolecular alkane activation.

Compound **6** apparently arises from two independent paths. Pyrolysis of **1b** in cyclopentane at 80 °C to produce **6** is retarded by the addition of excess L up to a point, after which the rate becomes independent of [L] ($k_{obsd} = 6.8 \times 10^{-7}$ s$^{-1}$). A kinetic isotope effect, $k_H/k_D$, of 1.7 is observed in the absence of added L (using $[(CD_3)_3P]_4Os(H)[CH_2C(CH_3)_3]$), but *no* isotope effect is found in the presence of a large excess of added L′. These results are most consistent with the operation of path 5 in the absence of added L and path 6 in its presence. All reactions of **4** are suppressed by a large excess of free L, to the point that the very slow direct reductive elimination of NpH from **1b** becomes evident.

This $L_4Os(II)$ system is a rare example of soluble, mononuclear, noncyclopentadienyl-containing metal complexes which undergo a rich variety of C–H bond activation reactions that are amenable to close mechanistic scrutiny. Comparison of this chemistry to that of other reported molecules may afford answers to some of the remaining intriguing questions regarding this important reaction type. Additional investigations of the scope and mechanism of C–H bond activation in this system and analogous Os(II) complexes with other phosphine ligands are under way.

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## Naturally Occurring Benzoporphyrins: Bacterial Marker Pigments?

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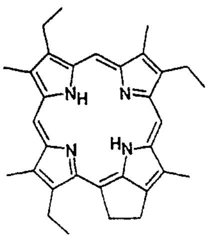
The occurrence of sedimentary porphyrins with rhodo-type electronic spectra,[1] showing a bathochromic effect and intensity increase in band III, in comparison with those of other widely occurring porphyrins of structural types represented by **1** and **2**, has been recognized for over 50 years.[2] Mass spectrometric studies[3] of isolated fractions enriched in rhodo-type components, and subsequent comparison of electronic spectra with those of synthesized compounds,[4] indicated that these components might be monobenzoporphyrins. Other evidence was given by oxidation of isolated fractions to mixtures of products containing 1*H*-benzopyrrole-2,5-dione.[5] It has been suggested that a sedimentary Diels–Alder reaction involving a vinyl $\beta$-substituent and $\beta$–$\beta'$ double bond of one of the tetrapyrroles with a dienophile and subsequent aromatization could account for the formation of the proposed benzene ring.[6]



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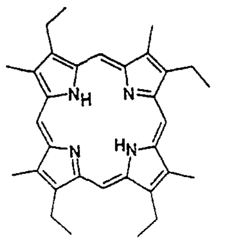

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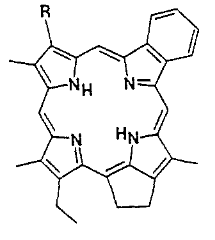

3a : R = $C_2H_5$
3b : R-$CH_3$

An alternative suggestion is intramolecular cyclization of two $\beta$-substituents, e.g., a methyl and an adjacent propionic acid chain, followed by dehydration and dehydrogenation.[7,8] In this paper we report (i) the first isolation of individual components of this type from a crude oil (Boscan; Cretaceous, Venezuela), (ii) confirmation that these components, the two most abundant rhodoporphyrins in the oil, are monobenzoporphyrins, and (iii) their structural assignment as **3a**,**b** by $^1$H NMR, using decoupling and nuclear Overhauser effect (NOE) studies at 400 MHz. Attention was focused on isolating components containing an exocyclic ring (cf. **1**) to identify the specific pyrrole carrying the rhodofying moiety and to attempt to provide information about a possible origin for the sedimentary components in terms of precursor biological pigments, since no tetrapyrrole with a benzene ring (or dihydro or tetrahydro counterpart) at $\beta,\beta'$ positions has been reported in organisms.

The isolation procedure was developed from that used previously[9] and involved flash silica chromatography[10] of the crude oil, followed by demetalation (methanesulfonic acid 98%, $N_2$, 100 °C, 4 h) of the porphyrin-containing fraction (mainly $V = 0$). Further flash chromatography afforded a fraction enriched in rhodoporphyrins (ca. 15%). Two stages of preparative HPLC, involving normal phase (Spherisorb S 5W; 250 × 10 mm i.d.), followed by reverse phase (Spherisorb S 5 ODS2; 250 × 10 mm i.d.), allowed isolation of a number of components including **3a** and **3b** (ca. 1% of total porphyrins). Both **3a** and **3b** have mass ($M^{+\cdot}$, $m/z$ 484 and 470, respectively) and electronic spectra ($\lambda_{max}$ 505, 542, 574, 628 nm; relative intensity 69, 100, 43, 23, Soret 407 nm) consistent with rhodoporphyrins containing an exocyclic alkano ring.

Examination of the Zn$^{II}$ complex of **3a** by $^1$H NMR (Figure 1, Table I) revealed the presence of 2$\beta$-ethyls, 3$\beta$-methyls, and 3-meso protons. The presence of a $\beta,\beta'$-fused benzene ring and the $CH_2CH_2$ moiety in the alkano ring was confirmed by decoupling and NOE difference experiments. Furthermore, con-

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(1) For rhodoporphyrins band III > IV > II > I, for **1** IV > I > II > III, and for **2** IV > III > II > I.

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