# Formation of a Trimethyldihydroperimidinium Cation from Proton Sponge [1,8-Bis(dimethylamino)naphthalene] during Base-promoted Reactions of Rhodium and Ruthenium Complexes

Sujatha N. Gamage, Robert H. Morris, Steven J. Rettig, David C. Thackray, Ian S. Thorburn, and Brian R. James*

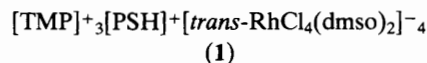*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6*

Proton sponge, in the presence of *mer*-RhCl$_3$(dmso)$_3$ or [RuCl(dppb)]$_2$(μ-Cl)$_3$ (dmso = dimethyl sulphoxide, dppb = Ph$_2$P[CH$_2$]$_4$PPh$_2$), generates (*via* a net hydride loss from one methyl group) the 1,1,3-trimethyl-2,3-dihydro-perimidinium cation, which is isolated as the counter-ion in complexes containing the anions *trans*-[RhCl$_4$(dmso)$_2$]$^-$ and {[RuCl(dppb)]$_2$(μ-Cl)$_3$}$^-$.

We reported recently[1] on the facile dehydrogenation of triethylamine in the presence of *mer*-RhCl$_3$(dmso)$_3$ (dmso = dimethyl sulphoxide), with resulting formation of the ylidic enamine complex RhCl$_3$(dmso)$_2$(σ-CH$_2$CH=NEt$_2$). We now find that the widely employed Aldrich reagent, 'proton sponge' (PS), which we were using to promote formation *via* H$_2$ of monohydride complexes of Rh^{III}, Ru^{III}, and Ru^{II}, equation (1),[2,3] also 'dehydrogenates' with formation of the 1,1,3-trimethyl-2,3-dihydroperimidinium cation (TMP$^+$), equation (2).

$$MX + H_2 \rightarrow MH + X^- + H^+$$

$$M = Rh^{III}, Ru^{III}, \text{ or } Ru^{II}$$

(1)

(2)
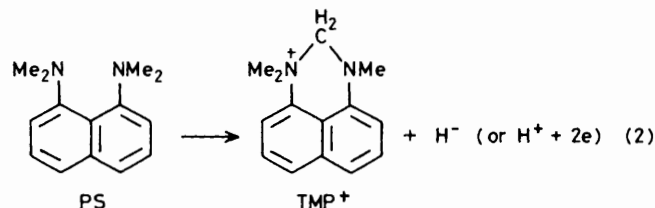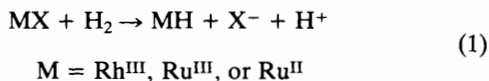
Treatment of a suspension of *mer*-RhCl$_3$(dmso)$_3$ in acetone with proton sponge (Rh:PS 1:0.8) under Ar precipitates an air-stable, orange-brown product, (**1**) (which could be recrystallized from dmso–acetone solutions) and an air-sensitive filtrate. Complex (**1**) has been characterized crystallographically,† and is best written as [C$_{14}$H$_{17}$N$_2$]$^+$$_3$[C$_{14}H_{19}N_2$]$^+$[*trans*-RhCl$_4$(dmso)$_2$]$^-$$_4$, three of the associated cations being TMP$^+$ and one being the protonated form of proton sponge (PSH$^+$).

$$[\text{TMP}]^+{}_3[\text{PSH}]^+[\textit{trans}\text{-RhCl}_4(\text{dmso})_2]^-{}_4$$
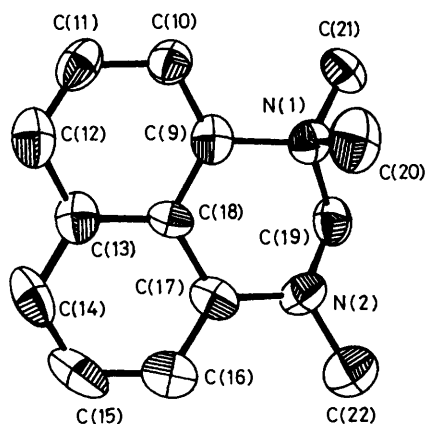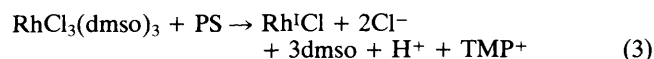
(**1**)

Figure 1. An ORTEP view of the 1,1,3-trimethyl-2,3-dihydroperimi-dinium cation (TMP$^+$) within complex (1). Relevant dimensions (Å or °) are: N(1)–C(9) 1.510(10), N(1)–C(21) 1.497(10), N(1)–C(20) 1.528(11), N(1)–C(19) 1.521(11), N(2)–C(19) 1.422(12), N(2)–C(22) 1.445(12), N(2)–C(17) 1.393(11), N(1)–C(19)–N(2) 108.8(7), C(17)–N(2)–C(22) 120.2(9), C(17)–N(2)–C(19) 115.7(8), C(22)–N(2)–C(19) 116.0(8), C(9)–N(1)–C(21) 113.6(7); other angles at N(1) are in the range 107.7(7)—110.0(7).

The TMP$^+$ cation is shown in Figure 1.‡ The bond lengths and angles of the Me$_2$N$^+$–CH$_2$–NMe moiety are consistent with single bond character for all bonds to N.§

The structure of the PSH$^+$ cation agrees with those published earlier, the non-detected proton being 'mopped-up' between the two nitrogens (N · · · H$^+$ · · · N),[4] while structural data for the *trans*-anion with S-bonded sulphoxide ligands also correspond well with the literature data.[5]

The basic stoicheiometry of the rhodium reaction is governed by the chemistry shown in equations (3) and (4); the nature of the air-sensitive solution (a presumed Rh^I product) has not been elucidated.
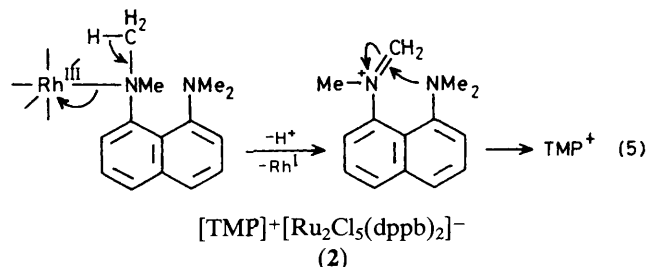
$$RhCl_3(dmso)_3 + PS \rightarrow Rh^ICl + 2Cl^-$$
$$+ 3dmso + H^+ + TMP^+ \qquad (3)$$

$$RhCl_3(dmso)_3 + Cl^- \rightarrow RhCl_4(dmso)_2^- + dmso \qquad (4)$$

A plausible mechanism for formation of TMP$^+$, analogous to that suggested for formation of the enamine complex,[1] involves replacement of the labile O-bonded dmso of RhCl$_3$(dmso)$_3$[6] by the amine, followed by deprotonation and concerted electron transfer to the Rh^{III}; the resulting transient enamine could undergo cyclization *via* intramolecular nucleophilic attack, equation (5).

The TMP$^+$ cation has also been found as the counter ion with a trichlorobridged diruthenate(II) anion containing 1,4-bis(diphenylphosphino)butane (dppb). The complex [TMP]$^+$[Ru$_2$Cl$_5$(dppb)$_2$]$^-$ (2) was isolated following an overnight, room temperature reaction between the

[TMP]$^+$[Ru$_2$Cl$_5$(dppb)$_2$]$^-$
(2)

formally mixed-valence diruthenium(III,II) compound [RuCl(dppb)]$_2$(μ-Cl)$_3$, (3),[7] and proton sponge (Ru$_2$: PS 1 : 3) in toluene under 1 atm H$_2$. Crystallographic analysis of complex (2) (recrystallized from CH$_2$Cl$_2$–acetone) again revealed the presence of the TMP$^+$ cation.† We had anticipated formation of the PSH$^+$ salt, which would have been equally compatible with the elemental analysis and conductivity data, and because we had previously isolated the complex [DMAH]$^+$[Ru$_2$Cl$_5$(dppb)$_2$]$^-$ (DMA = N,N'-dimethylacetamide) by stoicheiometric reduction of the mixed valence compound with H$_2$ in DMA, equation (6).[8] In this reaction, the DMA solvent acts as a base, presumably to assist in the initial heterolytic activation of H$_2$ (equation 1). In the toluene reaction, the proton sponge is clearly able to provide more than the required one reducing equivalent per Ru^{III}Ru^{II} (which is actually a valence-delocalized species[7]); the nature of the other Ru products has not been elucidated.

$$[RuCl(dppb)]_2(\mu\text{-}Cl)_3 + 0.5H_2 \xrightarrow[20\,°C]{DMA}$$
$$(3)$$
$$[DMAH]^+[Ru_2Cl_5(dppb)_2]^- \qquad (6)$$
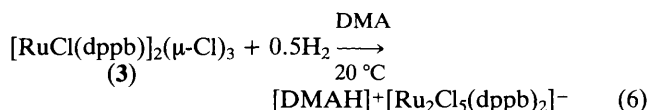
The bond lengths and angles of the TMP$^+$ cation within (2), because of the disorder problem, show minor differences to those of the cation within (1), which are considered more credible. Structural details of the [Ru$_2$Cl$_5$(dppb)$_2$]$^-$ anion within (2) will be presented elsewhere, but the basic form of two octahedral Ru^{II} centres sharing a common (μ-Cl)$_3$ face with each P atom being *trans* to chloride agrees with that predicted, for example, by ^{31}P{^{1}H} n.m.r. spectroscopy [δ(CD$_2$Cl$_2$) singlet at 53.6 ppm downfield from 85% H$_3$PO$_4$].[8]

‡ The n.m.r. assignments (the atom numbering scheme is that in Figure 1) were based on ^{1}H, ^{13}C{^{1}H}, and HETCOR data on (1), PS, and PSH$^+$. ^{1}H N.m.r. (CD$_3$)$_2$SO: δ 8.09 (1H, m, 11-H), 8.00 (1H, d, 10-H), 7.78—7.56 (3H, m, 12- to 15-H), 7.06 (1H, d, 16-H), 5.00 (2H, s, CH$_2$), 3.35 (3H, s, NMe), 3.26 (6H, s, N$^+$Me$_2$); ^{13}C{^{1}H} (CD$_3$)$_2$SO: δ 139.8, 139.3 (C-9, -17), 134.0 (C-18), 129.8—125.9 (C-11, -12, -15), 118.7 (C-10, -14, -16), 114.6 (C-13), 77.9 (CH$_2$), 51.3 (N$^+$Me$_2$), 37.1 (NMe).

§ Preliminary i.r. and ^{1}H n.m.r. data for (1) had initially been considered consistent with the presence of a rhodium carbene (Rh=C=N) complex (S. N. Gamage, R. H. Morris, and B. R. James, Proc. XIIth Intern. Conf. Organomet. Chem., Vienna, 1985, p. 185).

References

1 S. N. Gamage, R. H. Morris, S. J. Rettig, and B. R. James, *J. Organomet. Chem.*, 1986, **309**, C59.

2 B. R. James, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, London, 1982, vol. 8, p. 285.

3 T. W. Dekleva, I. S. Thorburn, and B. R. James, *Inorg. Chim. Acta*, 1985, **100**, 49.

4 D. Pyzalska, R. Pyzalski, and T. Borowiak, *J. Cryst. Spectrosc.*, 1983, **13**, 211; M. R. Truter and B. L. Vickery, *J. Chem. Soc., Dalton Trans.*, 1972, 395.

5 B. R. James, R. H. Morris, F. W. B. Einstein, and A. Willis, *J. Chem. Soc., Chem. Commun.*, 1980, 31.

6 B. R. James and R. H. Morris, *Can. J. Chem.*, 1980, **58**, 399.

7 I. S. Thorburn, S. J. Rettig, and B. R. James, *Inorg. Chem.*, 1986, **25**, 234.

8 B. R. James, A. Pacheco, S. J. Rettig, I. S. Thorburn, R. G. Ball, and J. A. Ibers, *J. Mol. Catal.*, in the press; I. S. Thorburn, Ph.D. Dissertation, University of British Columbia, 1985.