Communication

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Facile Rh-C Bond Cleavage of Rhodium(III) Benzyl Porphyrin Complex in DMSO with Strong Bases

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Abstract: Rhodium-carbon bond cleavage represents an essential step for small molecule activation and transformation by rhodium porphyrin complexes. This article reports on a new method for the cleavage of porphyrin rhodium(III)-carbon bonds in DMSO solvent with strong bases. UV-Vis, *in situ* ^{1}H NMR spectrum and GC-MS analysis confirmed generation of rhodium(I) species and monodeuterated toluene. Mechanistic studies revealed that strongly reducing $CD_3SOCD_2^-$, formed *in situ* from DMSO-d_6 and strong bases, promoted Rh-C bond cleavage.

Keywords: porphyrin · reduction · Rh-C bond cleavage · rhodium

Rhodium(III) and related group nine Co(III) and Ir(III) porphyrin complexes are drawing increasing interest in view of their rich reactivities toward various substrates.[1,2] Our research interest lies in exploring the scope and mechanism of small molecule activation and catalytic transformations,[2h,l,3] of which the cleavage of M-X (X=C, O, N, *etc.*) bonds stands as an essential step for efficient and selective conversion. A remarkable scope of C-H[4] and C-C[1d,j,5] bond activation of organic molecules to form organo-rhodium porphyrin complexes were reported. However, the high stability of resulting Rh-C bonds inhibits further applications in catalytic transformations.

Current state-of-the-art methods for cleaving Rh-C bonds can be classified into homolytic and heterolytic pathways. Photolysis of rhodium alkyl porphyrin complexes is a well-established method for homolytic cleavage of Rh-C bonds to generate porphyrin rhodium(II) metallo-radicals.[6] We have recently reported visible light induced Rh-C bond cleavage at ambient temperature in a catalytic Si-C bond hydroxylation process.[3b] Study of heterolytic Rh-C bond cleavage is relatively rare.[7] Groves[1h,1i] and our group[3b]achieved Rh-C bond cleavage via an intramolecular S_N2 pathway in basic benzene and DMSO solutions. In this communication, we report a unique Rh-C bond cleavage reactivity of a rhodium benzyl porphyrin complex in DMSO with strong bases.

The complex, benzylrhodium(III) tetra (*p*-sulfonatophenyl) porphyrin ((TSPP)Rh^{III}-Bn), was synthesized from (TSPP)Rh^{I} and $PhCH_2Br$.[3b] Heating a DMSO-d_6 solution containing (TSPP)Rh-Bn and excess NaOMe at 80 °C under argon resulted in a color change from orange to brown over a period of 12 h. The intensity of UV-Vis absorption peaks corresponding to (TSPP)Rh-Bn (λ_{max} = 424, 536 nm) decreased as the reaction proceeded (Figure 1). Concomitantly, red-shifted Soret and Q bands

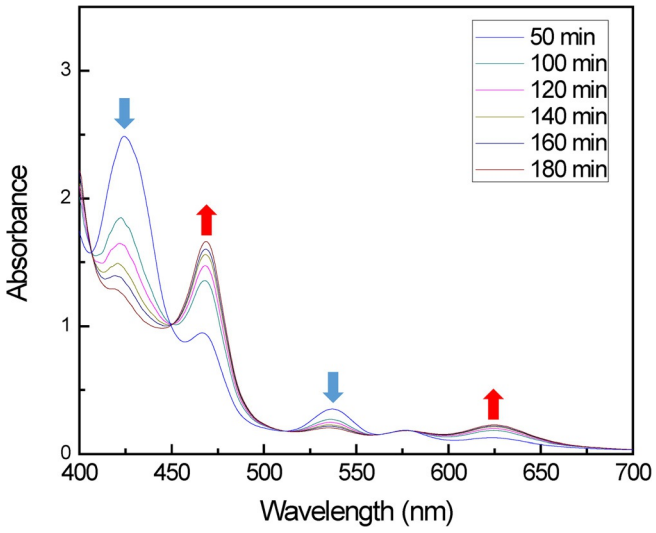

Figure 1. UV-Vis spectral changes of a DMSO-d_6 solution containing 3×10^{-5} mol L^{-1} of (TSPP)Rh-Bn and 6×10^{-3} mol L^{-1} of NaOMe under room temperature.[8]

(λ_{max} = 468, 624 nm) assigned to a new species arose with isosbestic points at 407, 449, 513, 565 and 580 nm. *In situ* ^{1}H NMR monitoring revealed the gradual consumption of (TSPP)Rh-Bn, together with the appearance of a singlet at 7.92 ppm and a 1:1:1 triplet at 2.27 ppm (J = 2 Hz), with integral ratio 4:1, assigned to pyrrole CH of

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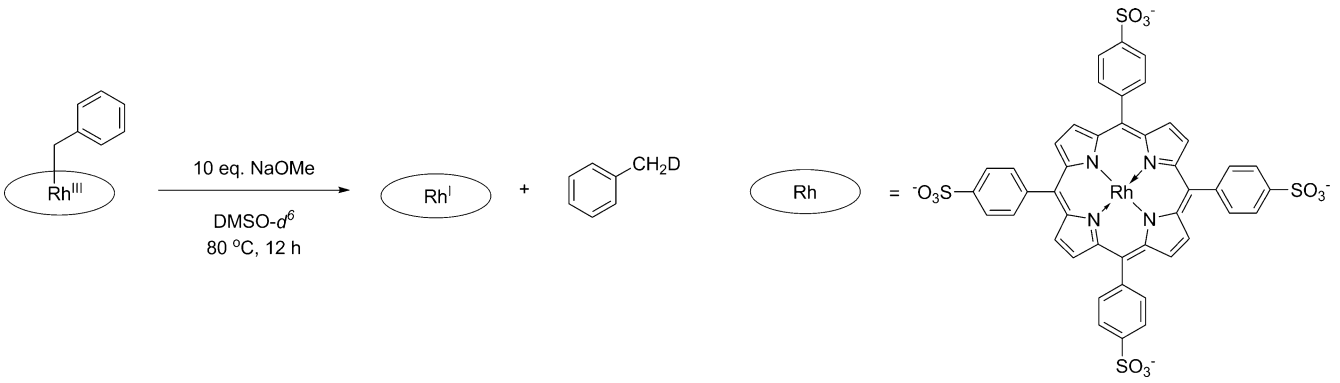

Scheme 1. NaOMe-promoted Rh-C bond cleavage of (TSPP)Rh-Bn in DMSO-d_6.

(TSPP)Rh^{I} and benzyl CH_2 of $PhCH_2D$, respectively (Scheme 1). GC-MS analysis confirmed the mono-deuterated nature of toluene product. Performing the reaction in normal DMSO, on the other hand, led to exclusive formation of $PhCH_3$ at a much faster rate than that in DMSO-d_6 (complete conversion was achieved within 5 min in DMSO-h_6 at room temperature; see Supporting Information), confirming the origin of the deuterium in $PhCH_2D$ to be DMSO solvent.

To establish the mechanism, the role of NaOMe was probed by comparison studies. Treatment of a DMSO-d_6 solution of (TSPP)Rh-Bn with NaOMe at room temperature caused an upfield shift of porphyrin and benzyl resonances; for example, resonances of pyrrole CH and benzyl CH_2 shifted from 8.60 and −4.59 ppm to 8.33 and −5.26 ppm, respectively (see Supporting Information for detailed NMR characterization data). Similar upfield shifts were observed upon addition of pyridine (py) or PPh_3 to (TSPP)Rh-Bn (albeit less pronounced), suggesting that the upfield shift resulted from MeO^- coordination to Rh^{III}. Ligand-induced homolysis of analogous porphyrin cobalt(III)-carbon bonds are well documented.[9] However, donor ligands other than NaOMe (py, NEt_3, $PhCH_2NH_2$, and PPh_3) were ineffective in promoting this transformation, despite that coordination was observed in all four cases (Table 1, entries 2, 4–6). Moreover, blocking the vacant coordination site of (TSPP)Rh-Bn with py prior to addition of NaOMe had no apparent inhibitory effect on the formation of (TSPP)Rh^{I} and $PhCH_2D$ (Table 1, entry 3). These evidences collectively argue against a coordination-induced Rh-C bond scission mechanism.

Subsequently, we investigated the role of NaOMe as a base to deprotonate DMSO. It is well known that DMSO can react with strong bases to give the strongly reducing $CH_3SOCH_2^-$ anion,[10] which is capable of reducing O_2 and organic substrates via single electron transfer.[11] Meanwhile, alkylcobalamins[12] and organocobalt phthalocyanines,[13] analogous to organorhodium porphyrins,[14] have been shown to undergo Co–C bond cleavage upon single electron reduction, affording Co(I) complexes

Table 1. Reaction of various ligands or bases with (TSPP)Rh-Bn in DMSO-d_6.[a]

Entry	Ligand or base	Products[b]
1	NaOMe	(TSPP)Rh^{I}, $PhCH_2D$
2	py	(TSPP)Rh(py)-Bn
3	py + NaOMe	(TSPP)Rh^{I}, $PhCH_2D$
4	NEt_3	(TSPP)Rh(NEt_3)-Bn
5	$PhCH_2NH_2$	(TSPP)Rh(NH_2CH_2Ph)-Bn
6	PPh_3	(TSPP)Rh(PPh_3)-Bn
7	LDA	(TSPP)Rh^{I}, $PhCH_2D$
8	LiHMDS	(TSPP)Rh^{I}, $PhCH_2D$
9	KOH(saturated)	27% (40%, 3d), (TSPP)Rh^{I}, $PhCH_2D$

[a] Reaction conditions: 10 eq. ligand or base, Ar atmosphere, 80 °C, 12 h. [b] Determined by ^{1}H NMR and GC-MS; yield >95% unless specified.

and organoradicals. Hence, various strong bases of comparable or superior basicity than NaOMe were tested (Table 1, entries 7–9). It should be noted that the sterically bulky amides, including lithium diisopropylamide (LDA) and lithium bis(trimethylsilyl)amide(LiHMDS), were also found to be highly effective, affording the products (TSPP)Rh^{I} and $PhCH_2D$ quantitatively (Table 1, entries 7–8). This result also rules out a coordination-induced mechanism. Retarded conversion was observed for KOH (Table 1, entry 9), which is presumably due to its low solubility in DMSO. In parallel to the applicability of various strong bases, the sulfoxide moiety in DMSO was found to be crucial for the reduction. Solvents without sulfoxide functional groups, including protic (CD_3OD, D_2O) and polar aprotic solvents (DMF) led to no conversion (Table 2, entries 2–4); however, tetrahydrothiophene-1-oxide was found to be as effective as DMSO-d_6 for this reaction (Table 2, entry 5).

Additionally, the reaction was found to be considerably slower in the presence of air (reaching only 70% conversion after 24 h) than under argon atmosphere and completely inhibited by 1 atm of O_2. This result indicates the possible radical nature of the reaction. Indeed, performing the reaction in the presence of 2 eq. of 2,2,6,6-tetramethylpiperidineoxy (TEMPO) resulted in the quantita-

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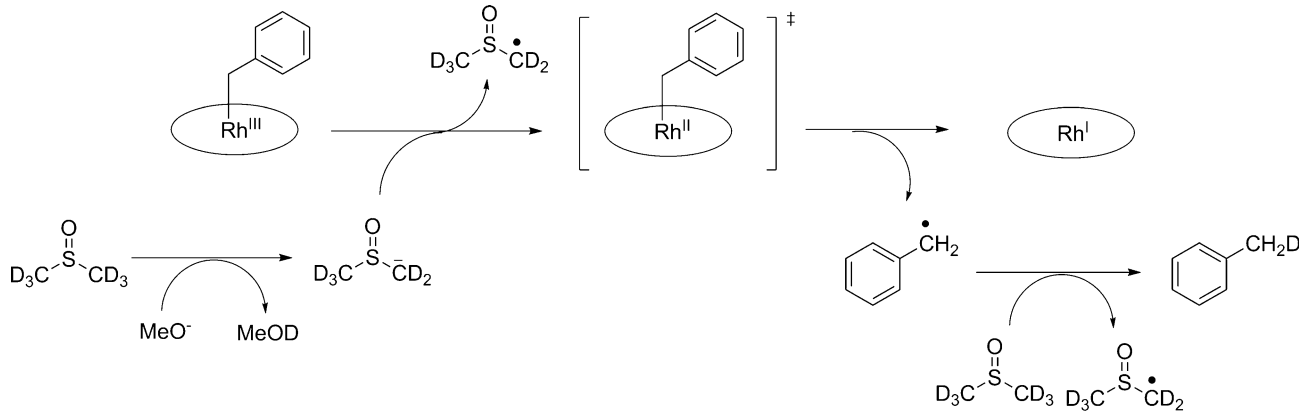

Scheme 2. Proposed mechanism for Rh-C bond cleavage of (TSPP)Rh-Bn in DMSO-d_6.

Table 2. Reaction of NaOMe with (TSPP)Rh-Bn in various solvents.[a]

Entry	Solvent	Product[b]
1	DMSO-d_6	(TSPP)Rh^{I}, $PhCH_2D$
2	CD_3OD	No reaction
3	D_2O	No reaction
4	DMF	No reaction
5		(TSPP)Rh^{I}, $PhCH_3$

[a] Reaction conditions: 10 eq. NaOMe, Ar atmosphere, 80 °C, 12 h. Only highly polar solvents were tested due to limited solubility of (TSPP)Rh-Bn in moderately polar and non-polar solvents. [b] Determined by ^{1}H NMR and GC-MS; yield >95% unless specified.

tive formation of *N*-benzyloxy-2,2,6,6-tetramethylpiperidine (evidenced by HRMS, see Supporting Information), supporting the formation of a benzyl radical intermediate after Rh^{II}-Bn bond cleavage.

Based on the above results, we propose the following mechanism, as depicted in Scheme 2. Deprotonation of DMSO-d_6 by NaOMe led to $CD_3SOCD_2^-$, which further underwent single electron transfer to (TSPP)Rh^{III}-Bn. Homolysis of resulting Rh^{II}-Bn intermediate gave (TSPP)Rh^{I} and a benzyl radical, which subsequently abstracted a deuterium atom from DMSO-d_6 to afford $PhCH_2D$.

In conclusion, we developed a new method for the cleavage of porphyrin rhodium(III)-carbon bond using a strong reductant, $CD_3SOCD_2^-$, generated *in situ* from the solvent DMSO-d_6 and strong bases. Further efforts to construct catalytic cycles utilizing the highly reactive rhodium(I) porphyrin and organoradicals are currently underway.[15]

Acknowledgement

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[15] Similar to its TSPP analog, the tetraphenylporphyrin (TPP) rhodium benzyl complex (TPP)Rh-Bn underwent reductive Rh-C bond cleavage with NaOMe in DMSO-d_6 to afford (TPP)Rh^{I} quantitatively, along with $PhCH_2D$ in ~50% yield. See Supporting Information for details.

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