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Catalytic C–H amination driven by intramolecular ligand-to-nitrene one-electron transfer through a rhodium(III) centre†

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Werner type six-coordinate rhodium(III) complexes coordinated by a planar trianionic ligand and two axial aniline ligands are synthesised. The trianionic ligand behaves as a redox-active ligand to form a ligand radical species upon one-electron oxidation of the complex. The rhodium(III) complexes catalyse C-H amination of external substrates such as xanthene with tosylazide as the nitrene source. DFT-calculation and kinetic deuterium isotope effects indicate that a di-radical rhodium(III) complex formed by one-electron transfer from the redox-active ligand to the nitrene group works as a reactive intermediate to induce aliphatic C-H activation.

Development of catalysts consisting of a redox innocent metal and a redox-active ligand is one of the attractive research subjects in current synthetic organic chemistry as well as coordination chemistry, since such a combination enables us to make use of any metal elements in the periodic table for several types of redox transformation reactions.¹ Typical examples are oxidative addition of Cl_2 and Br_2 to a Zr(rv) (d⁰) centre, aliphatic C–H activation by an Al(m) complex, and dihydrogen production using an Al(m)complex, where the supporting ligands have been demonstrated to participate in the redox processes.²

The C–H amination methodologies have been significantly evolved in the past decade by the advent of redox-active metal catalysts that enable formally one or two electron transfer from the metal centre to the nitrene functional group (Scheme 1(a), path I).³ Such electron transfer adds multiple bond character to the metal-nitrogen moiety. On the other hand, if one can



(path I) and ligand-based redox system (path II). (b) van der Vlugt's intramolecular amination system using ligand-based redox system. (c) Neutral ligand LH₃, [Rh^{III}(L³⁻)(A^X)₂] (**1**^X) and [Rh^{III}(L⁹⁻)(TsN^{•-})(A^X)] (**3**^X) generated by the reaction of **1**^X and tosylazide (A^X = p-X-C₆H₄NH₂).

combine a redox innocent metal with a redox-active ligand in the reaction with nitrene, single-electron transfer from the redoxactive ligand to the nitrene might proceed without change of the oxidation state of the metal centre (Scheme 1(a), path II). In such a case, the generated complex will formally be a metal nitrene radical species with a single bond character supported by a ligand-based radical, thus giving a di-radical complex. Such a nitrene radical complex is expected to have a radical type $C(sp^3)$ -H amination reactivity.⁴ In fact, van der Vlugt and coworkers reported an intramolecular cyclization reaction of 4-azidobutylbenzene via one-electron transfer from a redox-active aminophenol tridentate pincer ligand to the generated nitrene moiety of the substrate (Scheme 1(b)).⁵ The square planar palladium(π) complex has an open-shell singlet character comprising "nitrene radical" and "tridentate ligand radical" to undergo intramolecular radical type C(sp³)-H amination-cyclization reaction without change of the palladium(II) oxidation state.⁵ However, intermolecular C-H amination has yet to be accomplished in the palladium(II) system.



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R₃C—H

R₃C-NHR

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[†] Electronic supplementary information (ESI) available: Experimental details for preparation and DFT calculations (Tables S1–S10, and Fig. S1–S10). CCDC 1535694, 1535696 and 1535697. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc01840a

Recently, we have synthesised a series of late transition-metal complexes $[M(L^{3-})]^-$ (M = Ni²⁺, Cu²⁺, and Pd²⁺) supported by a planar tetradentate ligand (L^{3-}) consisting of a β -diketiminate framework with two aminophenol moieties (Scheme 1(c)).⁶ Oneelectron oxidation of the complexes (both chemically and electrochemically) gave the corresponding ligand-radical complexes $[M(L^{\bullet 2-})]^{2-.6}$ We, therefore, envisioned that the redox-active ligand, L³⁻, can facilitate formation of a nitrene radical complex having metal-nitrene single bond character through ligand to nitrene one-electron transfer when combined with a redox innocent transition metal ion. In this study, we employed rhodium(III) ion as the central metal, since most of the Werner type octahedral rhodium(III) complexes are hardly oxidised to the higher oxidation states.⁷ We herein report the first intermolecular $C(sp^3)$ -H amination with tosylazide catalysed by $[Rh^{III}(L^{3-})(p-X-C_6H_4NH_2)_2]$ (1^X, Scheme 1(c)). DFT calculations indicate that a triplet nitrene di-radical Rh(III) complex works as a reactive intermediate in the C-H amination reaction.

The synthetic procedure for $\mathbf{1}^{\mathbf{X}}$ is outlined in Scheme 2. First, $[Rh^{I}(LH_{2}^{-})(cod)]$ (cod = 1,5-cyclooctadiene) was prepared by treating $[Rh^{I}(cod)Cl]_{2}$ with LH₃ in the presence of an equimolar amount of Et₃N in THF. The crystal structural analysis of $[Rh^{I}(LH_{2}^{-})(cod)]$ showed that the Rh ion is coordinated with the two nitrogen atoms of mono-deprotonated ligand $\mathrm{LH_2}^-$ at the β-diketiminate moiety and 1,5-cyclooctadiene in a $η^2$ -π-coordination mode to adopt a square planer geometry, where the two phenol groups remain uncoordinated (Scheme 2 and Fig. S1, ESI⁺). The overall geometry around the Rh center is close to those of $[Rh^{I}{\kappa^{2}(N,N)}-(Ar)NC(Me)CHC(Me)N(Ar)}(cod)]$ (Ar = 2,6-dimethylphenyl) and $[Rh^{I}{\kappa^{2}(N,N)-(C_{6}F_{5})NC(Me)CHC(Me)N(C_{6}F_{5})}(cod)].^{8}$ Then, $[Rh^{I}(LH_{2}^{-})(cod)]$ was converted to 1^{X} by treating it with 2 equiv. of *p*-substituted anilines A^{X} (*p*-X-C₆H₄NH₂; **1**^H (X = H), **1**^{Cl} (X = Cl), and $1^{OMe} (X = OMe)$ in the presence of 2 equiv. of Et₃N as a base in THF under air. The obtained complexes were characterised by ¹H NMR and FAB-mass spectra as well as elemental analysis. 1^x was EPR silent and exhibited the sharp ¹H NMR signals in the diamagnetic region from 0 to 10 ppm and no absorption band in a near-IR to IR region (see the Experimental section in the ESI,[†] and Fig. S2). As shown in Fig. 1(a), the crystal structure of 1^H reveals that the Rh center adopts a slightly distorted octahedral geometry comprising a planar tetradentate ligand L³⁻ in the basal plan and two aniline ligands in the axial positions. The metrical oxidation states that defined by Brown⁹ were -1.68 (ring A) and -1.74 (ring B) for 1^H. Above observation indicates that $\mathbf{1}^{\mathbf{X}}$ is best described as a Rh(\mathbf{III}) complex coordinated with the trianionic L^{3-} ligand. Two electron oxidation from Rh(1) to Rh(III) took place during the treatment under air.



Fig. 1 Crystal structures of (a) $\mathbf{1}^{H}$ and (b) $[\mathbf{1}^{H}]$ SbF₆. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths are shown in the right.

Cyclic voltammogram of $\mathbf{1}^{\mathbf{X}}$ in CH₂Cl₂ was measured in a range from -1.5 to +1.5 V vs. Fc/Fc⁺. $\mathbf{1}^{\mathbf{H}}$ exhibited two reversible redox couples at $E_{1/2} = 0.22$ and 0.62 V vs. Fc/Fc⁺ (Fig. 2) and one irreversible oxidation process at $E^{\text{pa}} = +1.34$ V in a range from -1.5 to +1.5 V in CH₂Cl₂ (CV from -1.5 to +1.5 V is give in Fig. S3, ESI[†]). The redox potentials are relatively close to those of the two redox waves that observed for Et₄N[Cu^{II}(L³⁻)] (-0.06 and 0.46 V) and Et₄N[Ni^{II}(L³⁻)] (0.04 and 0.54 V).⁶ Furthermore, $\mathbf{1}^{OMe}$ and $\mathbf{1}^{Cl}$ gave very similar redox couples at 0.22 and 0.61 V for $\mathbf{1}^{OMe}$ and 0.26 and 0.67 V for $\mathbf{1}^{Cl}$ (Fig. S4, ESI[†]). Thus, these redox couples are safety assigned as the consecutive ligand-based oxidation from L³⁻ to L^{•2-} and to L⁻.

The one electron-oxidised product of $\mathbf{1}^{\mathbf{H}}$ was obtained by the oxidation with AgSbF₆, and isolated as an SbF₆⁻ salt ([$\mathbf{1}^{\mathbf{H}}$]SbF₆). Crystal structure of [$\mathbf{1}^{\mathbf{H}}$]SbF₆ is shown in Fig. 1(b), which reveals distinct dimensional changes with respect to one of the aminophenolate moieties (ring A). Namely, the diatomic distances of the corresponding bonds of the aminophenolate moieties (rings A and B) in $\mathbf{1}^{\mathbf{H}}$ are nearly equivalent (Fig. 1(a) and Table S1, ESI⁺), whereas ring A and ring B became inequivalent in [$\mathbf{1}^{\mathbf{H}}$]SbF₆; C2–C3, C4–C5, N1–C1 and C6–O1 bonds become shorter, whereas the C1–C2, C3–C4, C5–C6 and C1–C6 are elongated. The results suggest that ring A gets contribution of a quinonoid canonical form upon the oxidation. Such a dimensional change of the aminophenolate moiety also makes the bond length of Rh1–O1 longer from 2.0190(11) Å in $\mathbf{1}^{\mathbf{H}}$ to



Scheme 2 Synthetic scheme of 1^x.



Fig. 2 Cyclic voltammogram of $\mathbf{1}^{H}$ (1.0 mM) in a CH₂Cl₂ solution containing 0.10 M $^{n}Bu_{4}NPF_{6}$ (working electrode = GC, counter electrode = Pt, scan rate = 0.1 V s⁻¹).

2.0402(19) Å in $[1^{H}]$ SbF₆. The metrical oxidation states of ring A and ring B changed from -1.68 and -1.74 to -1.03 and -1.49, respectively, upon the oxidation. The EPR spectrum of $[1^{H}]$ SbF₆ in CH₂Cl₂ at 100 K exhibited a typical signal for an organic radical and the absorption spectrum had a broad band around 2400 nm that is assignable to an inter-valence charge transfer transition (Fig. S2 and S5, ESI†). Furthermore, DFT calculated structure (B3LYP/SDD) of $[1^{H}]$ SbF₆ had a dianionic radical structure of the tetradentate ligand (Fig. S6, the calculation methods are described in the Experimental section in the ESI†). Collectively, the oxidation product can be best described as the Rh^{III}–phenoxyl radical complex [Rh^{III}(L^{•2–})], in which one-electron oxidation takes place at the tetradentate ligand to give L^{•2–} rather than at the metal center.

To examine catalytic activity of **1^H** in C–H amination reaction, we employed xanthene as a substrate and tosylazide (TsN_3) as a nitrene source (experimental procedures are described in the Experimental section in the ESI[†]). Thus, TsN₃ (35.0 µmol) was treated with the substrate (35.0 µmol) in toluene (1 mL) in the presence of Boc₂O (di-tert-butyl dicarbonate, 35.0 μ mol) and 1^H (3.5 µmol, 10 mol%) for 24 h at 100 °C to give N-xanthyl-ptoluenesulfonamide (A) in a 52% yield together with xanthone (B) in a 5% yield (Table 1, entry 1). When the reaction was carried out in the absence of Boc₂O, the reaction did not proceed at all (entry 2). Addition of an excess amount of Boc₂O (5 equiv.) did not improve the product yields (entry 3). Higher product yields were obtained, when 1^{OMe} or 1^{Cl} was employed as the catalyst, but the product selectivity [A/(A + B)] was slightly decreased (entries 4 and 5). When 9,10-dihydroanthracene was used as the substrate under the same conditions as entry 1, anthracene was produced in a 14% yield based on the substrate. The result may indicate that hydrogen atom abstraction from the sp³ carbon of the substrate is involved as a key step, but, in the case of 9,10-dihydroanthracene, aromatization from the generated organic radical intermediate proceeds much faster than the nitrogen rebound process (for detailed mechanistic discussion, see Fig. 4).¹⁰

To get insight into the C–H amination mechanism, a FABmass spectrum (positive mode) of a mixture of $\mathbf{1}^{H}$ and TsN₃ in toluene was measured (Fig. S7, ESI[†]) to give a peak cluster at m/z = 886.3 with an isotope distribution pattern consisting of a

| Table 1 C-H amination of xanthene with tosylazide catalyzed by 1 ^x | | | | | |
|---|-------------------|---|-----------------------|----------------------|------------------------------|
| Ċ, | + | 0, 100 °C N ₃ S 0 tolu TsN ₃ 100 °C | it. ene ;, 24 h | | + 0 B |
| Entry | Cat. ^a | Additive | \mathbf{A}^{b} (%) | \mathbf{B}^{b} (%) | Selectivity ^c (%) |
| 1 | 1 ^H | Boc ₂ O (10 eq.) | 52 | 5 | 91 |
| 2 | 1 ^H | None | 0 | 0 | — |
| 3 | 1 ^H | Boc_2O (5 eq.) | 52 | 6 | 90 |
| 4 | 1 ^{OMe} | Boc_2O (10 eq.) | 73 | 12 | 86 |
| 5 | 1 ^{CI} | Boc ₂ O (10eq.) | 72 | 21 | 77 |

^{*a*} 10 mol%. ^{*b*} ¹H NMR yield (%). ^{*c*} 100 × A/(A + B).

sum of $[Rh + L + NTs + A^{H} + 2H]^{+}$ and $[Rh + L + NTs + A^{H} + H]^{+}$ in a 60 : 40 ratio.‡ Thus, the catalytic reaction begins from replacement of one of the two aniline ligands (A^{H}) of $\mathbf{1}^{H}$ with TsN₃ to give $[Rh(L)(N_{3}Ts)(A^{H})]$ ($\mathbf{2}^{H}$), where Boc₂O traps the aniline (A^{H}) giving $C_{6}H_{4}$ NHBoc to enhance the binding of TsN₃. The results of both entry 2 in Table 1 and the mass measurements suggest that this replacement process will be slow and the catalytic cycle runs before the second replacement of the remaining aniline ligand with tosylazide. Then, dissociation of dinitrogen (N_{2}) from $\mathbf{2}^{H}$ generates a nitrene bound rhodium complex $[Rh(L)(NTs)(A^{H})]$ ($\mathbf{3}^{H}$) as a key reactive intermediate. Feasibility of the mechanism for the formation of $\mathbf{3}^{H}$ from $\mathbf{1}^{H}$ is supported by DFT calculation shown in Fig. S8 (ESI⁺), where the N₂ elimination proceeds with $\Delta E^{\neq} = 24.3$ kcal mol⁻¹.

The active species 3^{H} can be a closed-shell singlet (3^{H} -CSS) like [Rh^{III}(L³⁻)(NTs)(A^H)] or an open-shell singlet di-radical (3^H-**OSS**) or a triplet di-radical $(3^{H}-T)$ of $[Rh^{III}(L^{\bullet 2-})(N^{\bullet-}Ts)(A^{H})]$. The DFT calculation study (B3LYP/SDD) indicated that 3^H-OSS and 3^H-T were close to each other in energy but energetically more stable than 3^H-CSS by 13.6 and 13.7 kcal mol⁻¹, respectively. The spin density plots of 3^H-OSS and 3^H-T are shown in Fig. 3(a) and (b), respectively, where one radical delocalizes over the redox-active tetradentate ligand to make it dianion radical structure as L^{•2-} and another radical localizes at the nitrene nitrogen atom in both structures.§ The extent of the radical delocalization on the tetradentate ligand is quite close to that of $[1^{H}]^{+}$ (one-electron oxidized complex of 1^{H} , Fig. 1b). Therefore, the formation of the diradical species (3^H-OSS or 3^H-T) involves an intramolecular one-electron transfer from the trianionic tetradentate ligand L³⁻ to the nitrene nitrogen atom without change of the oxidation state of Rh^{III} center. The calculated TsN-Rh^{III} bond length are 1.90 Å for 3^H-OSS and 1.99 Å for 3^H-T, respectively, which are significantly longer than the Rh^{III}=N double bond length in a tetrahedral complex of [Rh^{III}(NAd)(PhB(CH₂PPh₂)₃)] (1.780(2) Å, Ad = adamantyl).¹¹ Thus, the calculation study suggests that TsN-Rh^{III} bond has a single bond character. The calculated SCF energy profile for the C-H amination of xanthene with 3^H-T is displayed in Fig. 4.¶ The optimized structures of the intermediates and transition states involved in the pathways are provided in Fig. S9 (ESI[†]). The first step of the amination involves intermolecular H-atom abstraction from xanthene by the nitrene radical complex of 3^H-T to yield an intermediate 4^H and the xanthene radical $(-20.1 \text{ kcal mol}^{-1})$. This step requires a transition state **TS2** with a barrier of 10.8 kcal mol^{-1} . Then, a



Fig. 3 Spin density plots of (a) open-shell singlet $(3^{H}-OSS)$ and (b) triplet $(3^{H}-T)$ of active oxidant. The color in blue represents positive regions and the color in orange represents negative regions.





subsequent radical rebound process takes place *via* a transition state **TS3** with a low barrier of 1.1 kcal mol⁻¹ to yield **5^H**, where **TS3** and **5^H** are singlet species. When a 1 : 1 mixture of xanthene (17.5 µmol) and dideuterated-xanthene (xanthene-*d*₂, 17.5 µmol) were employed under the same conditions as entry 1 of Table 1, a kinetic isotope effect (KIE) of 5.0 was observed, which was nearly the same to the calculated KIE value of 5.7 at 375 K (Fig. S10, experimental procedures are described in the Experimental section in the ESI†). These results strongly support that the amination reaction involves a hydrogen atom abstraction process from the sp³ carbon of the substrate.

In summary, Werner type six-coordinate rhodium(III) complexes coordinated with a redox-active tetradentate ligand (L^{3-}) and anilines (A^{X}) axial ligands were found to undergo the ligand-based oxidation with electrochemical and chemical methods to give a ligand radical species, which was supported by spectroscopic, electrochemical, X-ray crystallographic, and computational studies. The complexes are capable to catalyze the intermolecular C-H amination reaction of xanthene with tosylazide. The DFT calculations indicated that one electron transfer from the tetradentate ligand to the nitrene nitrogen atom gives a reactive intermediate that possesses a di-radical character with Rh^{III}-N single bond. The kinetic deuterium isotope effect (KIE) revealed the C-H amination involved hydrogen abstraction from the substrate. Although the substrate scope was limited, this study expands ligand-based C-H activation chemistry using redox-non-innocent metal ions.

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Notes and references

‡ The appearance of the additional protons to $[Rh + L + NTS + A^H]$ suggests that the $[Rh(L)(NTS)(A^H)]$ might abstract hydrogen atom from the solvent. § The extent of the one radical localization on the nitrene nitrogen atom is 85%. Rh atom has only 5% and 6% spin density in **3^H-OSS** or **3^H-T**, respectively. The rest is on $-SO_2$ - group of Ts moiety in the both structure. ¶ The C-H amination profile with **3^H-OSS** is identical with that with **3H-T**.

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