

# CHEMISTRY

## A European Journal

A Journal of



### Accepted Article

**Title:** Generation and Reactivity of a One-electron Oxidized Manganese(V) Imido Complex bearing a Macrocyclic Tetraamido Ligand

**Authors:** Tai-Chu Lau, Huatian Shi, Jianhui Xie, William W. Y. Lam, Wai-Lun Man, Chi-Keung Mak, Shek-Man Yiu, and Hung-Kay Lee

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

**To be cited as:** *Chem. Eur. J.* 10.1002/chem.201902405

**Link to VoR:** <http://dx.doi.org/10.1002/chem.201902405>

Supported by  
**ACES**

WILEY-VCH

## COMMUNICATION

# Generation and Reactivity of a One-electron Oxidized Manganese(V) Imido Complex bearing a Macrocyclic Tetraamido Ligand

Huatian Shi,<sup>[a]</sup> Jianhui Xie,<sup>[b]</sup> William W. Y. Lam,<sup>[c]</sup> Wai-Lun Man,<sup>[d]</sup> Chi-Keung Mak,<sup>[a]</sup> Shek-Man Yiu,<sup>[a]</sup> Hung Kay Lee,<sup>[e]</sup> and Tai-Chi Lau\*<sup>[a]</sup>

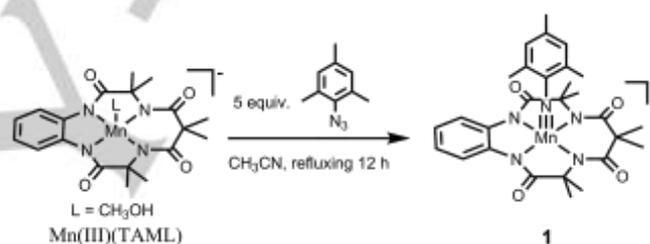
**Abstract:** We report the synthesis and X-ray structure of a new manganese(V) mesitylimido complex bearing a macrocyclic tetraamido ligand (TAML),  $[\text{Mn}^{\text{V}}(\text{TAML})(\text{N-Mes})]^-$  (**1**). **1** is readily oxidized by  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}]^+[\text{SbCl}_6]^-$  and the resulting species readily undergoes H-atom transfer and nitrene transfer reactions.

Manganese(V) imido complexes have been postulated as active intermediates in many useful organic transformation reactions.<sup>1-6</sup> For instance, manganese(V) nitrido complexes bearing porphyrin or salen ligands react with trifluoroacetic anhydride (TFAA) to generate manganese(V) acylimido species, which can transfer the  $\text{CF}_3\text{CON}$  group to alkenes.<sup>1-3</sup> *p*-Toluenesulfonic anhydride is also used to convert chiral manganese(V) salen nitrido complexes to imido species, which can perform asymmetric aziridination of alkenes.<sup>4</sup> Trifluoroacetic acid and  $\text{BF}_3$  have also been employed to convert manganese(V) salen nitrido complexes to imido species which can react with alkenes to give the parent aziridines.<sup>5</sup> Manganese phthalocyanines catalyze intra- and intermolecular  $\text{C}(\text{sp}^3)\text{-H}$  amination reactions and manganese imido/nitrene species are proposed to be active intermediates.<sup>6</sup> In order to directly study the reactivity of these active species, there is a continuing interest in isolating manganese(V) imido complexes. Surprisingly, so far the only isolated and well-characterized manganese(V) imido species are those with corrole and corrolazine ligands. These include  $[\text{Mn}(\text{tpfc})(\text{NAr})]$  (*tpfc* = *tris*(pentafluorophenyl)corrole, Ar = 2,4,6-( $\text{CH}_3$ )<sub>3</sub> $\text{C}_6\text{H}_2$  (Mes), 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$  or *p*-toluenesulfonyl),  $[\text{Mn}(\text{Br}_8\text{tpfc})(\text{NAr})]$  and  $[\text{Mn}(\text{TBP}_8\text{Cz})(\text{NMes})]$  ( $\text{TBP}_8\text{Cz}$  = *octakis*(*p*-*tert*-butylphenyl)corrolazinato).<sup>7,8</sup> Nitrene transfer as well as hydrogen atom transfer (HAT) reactions of these imido complexes have been demonstrated.<sup>7,8</sup>

We report herein the synthesis and characterization of a new manganese(V) imido complex bearing the macrocyclic tetraamido ligand TAML,  $[\text{Mn}^{\text{V}}(\text{TAML})(\text{N-Mes})]^-$  (Mes = mesityl). The tetraanionic TAML ligand is known to stabilize metal complexes in high oxidation states.<sup>9</sup> The oxo analog of this complex,  $[\text{Mn}^{\text{V}}(\text{TAML})(\text{O})]^-$ , has been reported by Fukuzumi and Nam.<sup>9e</sup>

$[\text{Mn}^{\text{V}}(\text{TAML})(\text{N-Mes})]^-$  is highly stable and unreactive towards common organic substrates. However, it readily undergoes one-electron oxidation and the resulting species is highly reactive towards nitrene transfer and HAT reactions.

The manganese(V) mesitylimido complex,  $[\text{Mn}^{\text{V}}(\text{TAML})(\text{N-Mes})]^-$  (**1**) is prepared according to **Scheme 1**.



**Scheme 1.** Synthesis of **1**.

**1** is isolated as the  $\text{PPh}_4^+$  salt. The complex is diamagnetic, as evidenced by the sharp resonances in the normal region in the  $^1\text{H}$  NMR spectrum, consistent with its formulation as a  $d^2$  Mn(V) complex (**Figure S1**). The electrospray ionization mass spectrum (ESI/MS) of **1** in  $\text{CH}_3\text{CN}$  exhibits a predominant parent peak (*M*) at  $m/z = -558.3$  (**Figure S2**). The cyclic voltammetry (CV) in  $\text{CH}_3\text{CN}$  shows a reversible oxidation wave at  $\square 0.49$  V (vs  $\text{Fc}^{+/0}$ ,  $\Delta E = 80$  mV) and an irreversible reduction wave at  $\square 1.32$  V (**Figure S3**).

The molecular structure of **1** has been determined by X-ray crystallography (**Figure 1**). The complex has a distorted square pyramidal geometry, with the TAML ligand in the equatorial plane and a mesitylimido ligand in the axial position. The Mn center is 0.56 Å out of the plane defined by four N atoms of the TAML ligand. The Mn- $\text{N}_{\text{imido}}$  distance is 1.610 (2) Å, which is similar to those of  $[(\text{tpfc})\text{Mn}(\text{NMes})]$  (1.613 Å)<sup>7a</sup> and  $[(\text{TBP}_8\text{Cz})\text{Mn}(\text{NMes})]$  (1.595 Å and 1.611 Å),<sup>8</sup> consistent with a  $\text{M}=\text{NMes}$  triple bond. In accordance with this triple bond character, the Mn1-N5-C20 angle is close to linear (175.6°).

[a] H. Shi, C. K. Mak, S. M. Yiu, T. C. Lau  
Department of Chemistry, City University of Hong Kong  
Tat Chee Avenue, Kowloon Tong, Hong Kong SAR, China.  
E-mail: bhtclau@cityu.edu.hk

[b] J. Xie  
School of Chemistry and Chemical Engineering  
Hefei University of Technology  
Hefei 230009, P. R. China.

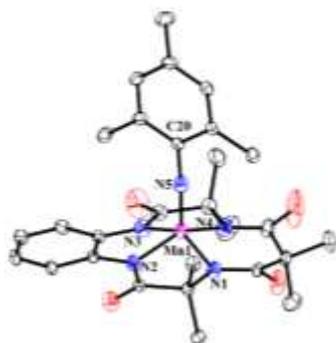
[c] W. W. Y. Lam  
Department of Food and Health Sciences  
Technological and Higher Education Institute of Hong Kong  
Tsing Yi Road, Hong Kong SAR, China.

[d] W. L. Man  
Department of Chemistry, Hong Kong Baptist University  
Kowloon Tong, Hong Kong SAR, China.

[e] H. K. Lee  
Department of Chemistry, The Chinese University of Hong Kong  
Shatin, New Territories, Hong Kong SAR, China.

Supporting information for this article is given via a link at the end of the document.

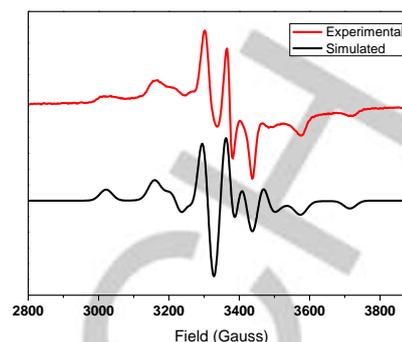
## COMMUNICATION



**Figure 1.** ORTEP plot (30% probability level) of [PPh<sub>4</sub>]**1**. The PPh<sub>4</sub> counter ion and hydrogens have been omitted for clarity.

**1** is stable in the solid state and in CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> solution for days at room temperature. A solution of **1** in CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> is also unreactive towards various organic substrates, such as PPh<sub>3</sub> or phenol for >24 h at 25 °C, as monitored by UV/Vis spectrophotometry. Evidently, the presence of the tetraanionic TAML ligand stabilizes the Mn(V) imido complex. Since the CV of **1** shows a reversible oxidation wave at +0.49 V vs. Fc<sup>+/0</sup>, this suggests that it is possible to oxidize **1** using a suitable oxidant, which should make the resulting imido species more reactive. Nam and coworkers recently reported that one-electron oxidation of [Mn<sup>V</sup>(TAML)(O)]<sup>10</sup> and Fe<sup>V</sup>(TAML)(NTs)]<sup>9g</sup> and the oxidized species become much more reactive.

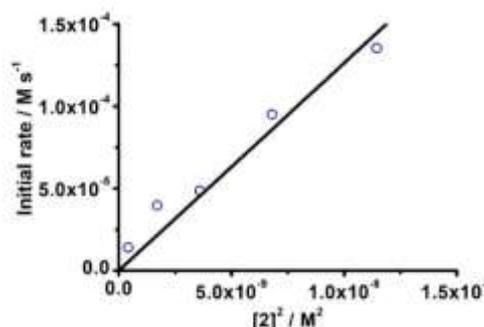
Addition of 1 equiv. of the oxidant [(*p*-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>N]<sup>+</sup>[SbCl<sub>6</sub>]<sup>-</sup> (*E*<sup>0</sup> = 0.67 V vs. Fc<sup>+/0</sup>)<sup>11</sup> in CH<sub>3</sub>CN to **1** at -40 °C to 25 °C produced the one electron oxidized species **2**, with immediate discharge of the blue color of the radical cation (λ<sub>max</sub> at 700 nm) (**Figure S4**). The X-band electron paramagnetic resonance (EPR) spectrum of **2** (CH<sub>3</sub>CN, 4K, **Figure 2**) shows a S = 1/2 signal with an axial splitting pattern that is typical of a manganese(VI) species and is similar to the EPR of the manganese(VI) salen nitrido complex [Mn(Sal<sup>IBu</sup>)N]<sup>+</sup> reported by Storr<sup>13a</sup> as well as two manganese(VI) nitrido complexes reported by Wieghardt.<sup>14</sup> In contrast, one-electron oxidation of the oxo analogue of **1**, [Mn<sup>V</sup>(TAML)(O)] occurs at the TAML ligand to generate [Mn<sup>V</sup>(TAML\*)(O)]; in this case its EPR spectrum shows a typical isotropic ligand radical signal centered at *g* = 2.002.<sup>10</sup> The EPR spectrum of **2** was simulated using a two-component model (Mn(VI) and ligand-based radical, **Figure S5**) with the EasySpin program developed by Stoll.<sup>16</sup> The simulation results show that **2** is predominantly the manganese(VI) species [Mn<sup>VI</sup>(TAML)(N-Mes)] with around 2.5% of the ligand-based radical [Mn<sup>V</sup>(TAML\*)(N-Mes)].



**Figure 2.** Experimental and two-component simulated EPR spectra of **2**. Component 1: Mn(VI) with  $g_{xx} = g_{yy} = 2.001$ ,  $g_{zz} = 1.993$ ;  $A_{xx} = A_{yy} = 134.9$  MHz,  $A_{zz} = 386.7$  MHz; Component 2 (ligand based radical:  $g = 1.991$ ). The ratio between Mn(VI) species [Mn<sup>VI</sup>(TAML)(N-Mes)] and ligand based radical [Mn<sup>V</sup>(TAML\*)(N-Mes)] is 40 : 1.

The structure of [Mn<sup>VI</sup>(TAML)(N-Mes)] was investigated by DFT calculation at BP86/def2-TZVP level of theory. The result shows that the structure with doublet ground state is more stable (**Table S1**). The Mn-N<sub>imido</sub> bond length and Mn-N<sub>imido</sub>-C angle of the equilibrium structure are 1.611 Å and 176.42 °, respectively (**Figure S6**). The Mulliken spin population analysis shows that 0.9 spin density ( $\alpha - \beta$ ) is located on the Mn center. On the other hand, only -0.057 spin density is on the N atom of imido group (**Figure S7**), indicating that there is negligible nitrene radical character of the imido group. The calculation results together with the EPR data indicate that the oxidation of **1** is predominantly metal-based and hence **2** may be formulated as a manganese(VI) imido complex, [Mn<sup>VI</sup>(TAML)(N-Mes)], mixed with a small portion of Mn(V) TAML based radical complex, [Mn<sup>V</sup>(TAML\*)(N-Mes)]. These two species are probably in equilibrium as a result of valence tautomerization.<sup>15</sup>

The oxidized species **2** decays slowly at room temperature, as monitored by UV/Vis spectrophotometry (**Figure S8**). The initial rate of the decomposition is second-order with respect to [**2**] (**Figure 3**), indicating that it is a bimolecular process.



**Figure 3.** Plot of initial rate vs [**2**]<sup>2</sup> (slope =  $(1.27 \pm 0.09) \times 10^4$ ;  $r^2 = 0.978$ ).

A neutral dark brown complex **3** could be separated from the decay mixture of **2** by silica column chromatography, with 10% yield based on Mn. The molecular structure of **3** has been determined by X-ray crystallography (**Figure 4**). It shows the addition of two NMe nitrene groups to the *o*-phenylene ring of

## COMMUNICATION

the TAML ligand in **2**, resulting in its conversion into an *o*-benzoquinonediimine moiety. The two imine C-N distances are different; C5-N5 = 1.315 Å, C6-N6 = 1.300 Å. The Mn-N<sub>imido</sub> distance is 1.609 (2) Å, which is the same as that of **1**. **3** is diamagnetic as it shows sharp resonances in the normal range in the <sup>1</sup>H NMR spectrum (Figure S9), consistent with a Mn(V) complex. As the complex is neutral, it requires the presence of an H<sup>+</sup> ion to balance the charge, which is tentatively assigned to N5 since it has a longer C-N bond and a difference peak was successfully assigned to and refined as a hydrogen atom near to N5 in crystal structure refinement. In the proton NMR, the resonance at 9.90 ppm is assigned to the N-H proton. The presence of N-H is also evidenced by a stretch in the IR at 3221 cm<sup>-1</sup>. The ESI/MS of **3** shows a predominant peak at *m/z* = -822.9 (Figure S10), which is assigned to [3-H]<sup>-</sup>. MS/MS of the peak shows a fragment ion at *m/z* = -689.5, which is attributed to the loss of NMe groups bound to the Mn center (Figure S11).

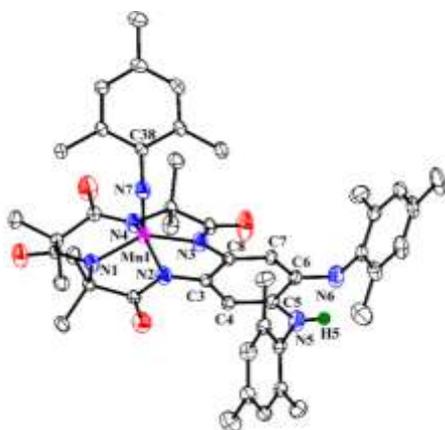
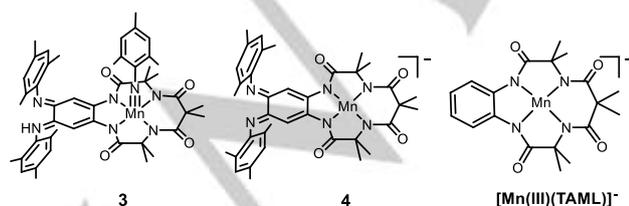


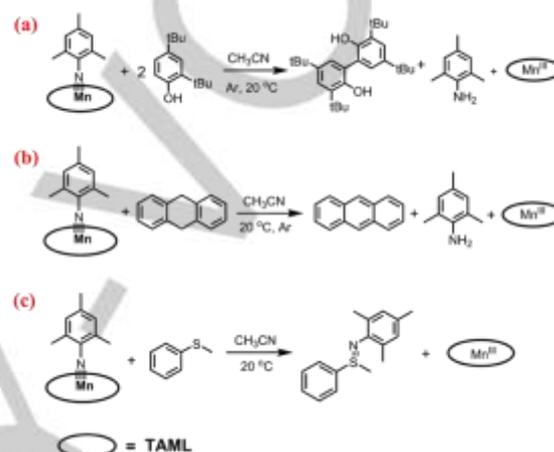
Figure 4. ORTEP plot (30% probability level) of **3**. Hydrogens have been omitted for clarity.

Our results indicate that the decay of **2** occurs initially via intermolecular nitrene transfer. In addition to [3-H]<sup>-</sup>, ESI/MS of the decay mixture of **2** shows the presence of at least two Mn-containing ions at *m/z* = -689.6 and -425.4, which are assigned to complex **4** and [Mn(TAML)]<sup>-</sup>, respectively (Scheme 2, Figure S12). In complex **4**, the two NMe groups are proposed to be both attached to the aromatic ring, since MS/MS does not show the presence of fragment ions arising from the loss of NMe groups (Figure S13). Attempts to isolate PPh<sub>4</sub>[**4**] from the mixture were unsuccessful.



Scheme 2. Decay products of **2**.

Although **2** undergoes intermolecular nitrene transfer reactions with itself, it also reacts readily with various organic substrates if they are present in excess. For instance, it reacts rapidly with 2,4-di-*tert*-butylphenol (20-fold excess) to give the phenol dimer and 2,4,6-trimethylaniline in 25% and 56% yield, respectively, as analyzed by GC-FID and GC-MS (Scheme 3a). The observation of the dimer product indicates that the imido species abstracts a H atom from O-H to generate a phenoxy radical which then rapidly dimerizes.<sup>17</sup> H-atom abstraction by the imido results in the formation of the free aniline.



Scheme 3. HAT and nitrene transfer reaction of **2** with various organic substrates.

**2** also reacts readily with 9,10-dihydroanthracene (DHA); monitoring of the reaction by UV/Vis spectrophotometry reviewed the appearance of characteristic peaks of anthracene (Figure S14). Anthracene (22%) and 2,4,6-trimethylaniline (38%) were also detected and quantified by GC/MS and GC/FID (Scheme 3b). The rate of the reaction is first-order in both [**2**] and [DHA], and the second-order rate constant  $k_2 = 4.79 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at 25.0 °C was obtained. When d<sub>4</sub>-DHA was used as substrate,  $k_2^D = 1.69 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ , this gives a kinetic isotope effect (KIE) of 2.8, which suggests that the rate-limiting step involves C-H bond cleavage, consistent with a HAT mechanism (Figure 5).

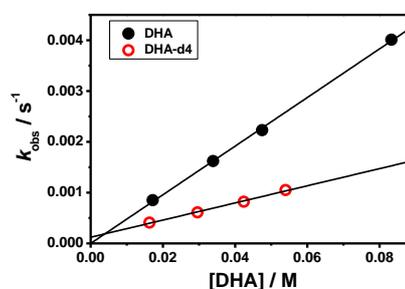


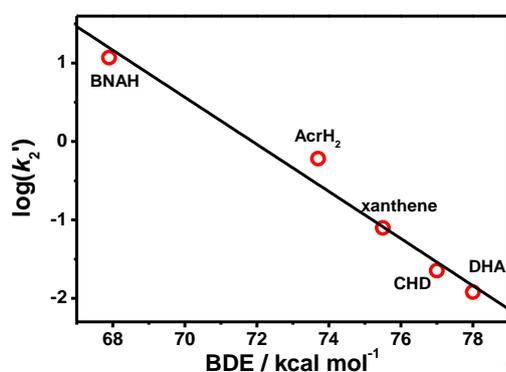
Figure 5. Plots of  $k_{\text{obs}}$  vs [DHA] (closed circle) and [DHA-d<sub>4</sub>] (open circle). DHA: slope =  $(4.79 \pm 0.08) \times 10^{-2}$ , y-intercept =  $-(0.01 \pm 4.20) \times 10^{-5}$ ,  $r^2 =$

## COMMUNICATION

0.999, d<sub>4</sub>-DHA: slope =  $(1.69 \pm 0.07) \times 10^{-2}$ , y-intercept =  $(1.22 \pm 0.26) \times 10^{-4}$ ,  $r^2 = 0.994$ ].

The kinetics for the reaction of **2** with DHA were also carried out as a function of temperature; from the Eyring plot of  $\ln(k_2/T)$  versus  $1/T$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , are found to be  $(14.7 \pm 0.5)$  kcal mol<sup>-1</sup> and  $-(15 \pm 1)$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively (Figure S15). The negative  $\Delta S^\ddagger$  value is consistent with the ordered transition state of a HAT reaction.

The reaction of **2** with various other hydrocarbons with weak C-H bonds were also investigated (Figure S16-S19), and the rate constants were compiled in Table S2. Log  $k_2'$  ( $k_2'$  =  $k_2$  divided by the number of active H) shows a linear correlation with the C-H bond dissociation energy of the substrates, which supports a HAT mechanism for the reaction of **2** with the organic substrates (Figure 6).



**Figure 6.** Plot of  $\log(k_2')$  vs BDEs for the reaction of **2** with various organic substrates in CH<sub>3</sub>CN at 25.0 °C. Slope =  $-0.3 \pm 0.03$ . BNAH = 1-benzyl-1,4-dihydropyridinamide. AcrH<sub>2</sub> = 9,10-dihydro-10-methylacridine. CHD = 1,4-cyclohexadiene.

**2** also undergoes direct nitrene transfer to thioanisole to produce the corresponding sulfilimine (Scheme 3c, Figure S20). The rate of the reaction is first-order in [**2**] and [PhSMe], the second order rate constant  $k_2 = 1.87 \times 10^{-1}$  M<sup>-1</sup> s<sup>-1</sup> at 25.0 °C (Figure S21). The activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were found to be  $(5.8 \pm 0.1)$  kcal mol<sup>-1</sup> and  $-(33 \pm 1)$  cal mol<sup>-1</sup> M<sup>-1</sup>, respectively (Figure S22). The large negative  $\Delta S^\ddagger$  value is consistent with the ordered transition state of a direct nitrene transfer reaction.

The kinetics of the reaction of **2** with various *para*-substituted thioanisoles were also studied (Figure S23-S25). The Hammett plot of the rate constants vs  $\sigma_p^+$  of the substituents gives a  $\rho$  value of  $-1.4 \pm 0.1$ , which is consistent with the electrophilic character of **2** (Figure S26).

In kinetic experiments using low concentrations of **2** and excess substrates, the bimolecular decay reaction of **2** (to generate **3** and **4**) is insignificant and hence clean kinetic behavior was observed. However, when the reaction with various external substrates were carried out on a preparative scale using higher concentrations, the decay reaction of **2** became predominant and hence low yields of products were obtained.

## Conclusions

We have reported a new manganese(V) imido complex bearing the TAML ligand. One-electron oxidation of this complex affords the first example of a manganese(VI) imido species, which readily undergoes novel nitrene transfer reaction with itself and with thioanisoles. It also abstracts H-atom from phenol and hydrocarbons with weak C-H bonds. Compounds of Mn(VI) are rare. Apart from Mn(VI) oxo species, only a few Mn(VI) nitrido species are known.<sup>12-14</sup> However, the reactivity of these complexes towards various substrates has not been investigated. Our work should be a significant contribution to high-valent manganese imido chemistry.

## Experimental Section

Detailed information on synthesis and general procedures can be found in the Supporting Information. Crystallographic data of **1** and **3** are available at the Cambridge Crystallographic Data Centre (CCDC 1868325 and 1868326).

## Acknowledgements

This research is supported by the Research Grants Council of Hong Kong (CityU 11302917), the Hong Kong University Grants Committee (AoE/P-03-08) and the National Natural Science Foundation of China (21801058). We thank Dr. C. Y. Wong and Dr. K. C. Lau for helpful discussions.

**Keywords:** Manganese complex • Imido transfer • Hydrogen atom transfer

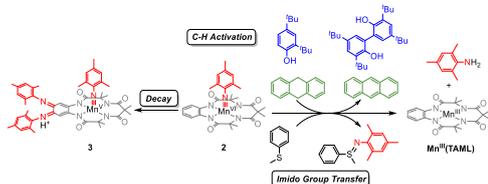
- [1] J. T. Groves, T. Takahashi, *J. Am. Chem. Soc.* **1983**, 105, 2073–2074.
- [2] L. A. Bottomley, F. A. Neely, *J. Am. Chem. Soc.* **1988**, 110, 6748–6752.
- [3] (a) J. Du Bois, J. Hong, E. M. Carreira, M. W. Day, *J. Am. Chem. Soc.*, **1996**, 118, 915–916. (b) J. Du Bois, C. S. Tomooka, J. Hong, E. M. Carreira, *J. Am. Chem. Soc.* **1997**, 119, 3179–3180. (c) J. Du Bois, C. S. Tomooka, J. Hong, E. M. Carreira, M. W. Day, *Angew. Chem. Int. Ed.* **1997**, 36, 1645–1647. (d) J. Du Bois, C. S. Tomooka, J. Hong, E. M. Carreira, *Acc. Chem. Res.* **1997**, 30, 364–272.
- [4] S. Minakata, T. Ando, M. Nishimura, I. Ryu, M. Komatsu, *Angew. Chem. Int. Ed.* **1998**, 37, 3392–3394.
- [5] C.-M. Ho, T.-C. Lau, H.-L. Kwong, W.-T. Wong, *J. Chem. Soc., Dalton Trans.* **1999**, 0, 2411–2414.
- [6] (a) S. M. Paradine, J. R. Griffin, J. Zhao, A. L. Petronico, S. M. Miller, C. M. White, *Nat. Chem.* **2015**, 7, 987–994. (b) J. R. Clark, K. Feng, A. Sookezian and C. M. White, *Nat. Chem.* **2018**, 10, 583–591.
- [7] (a) R. A. Eikey, S. I. Khan, M. M. Abu-Omar, *Angew. Chem. Int. Ed.* **2002**, 41, 3592–3594. (b) N. Y. Edwards, R. A. Eikey, M. I. Loring, M. M. Abu-Omar, *Inorg. Chem.* **2005**, 44, 3700–3708. (c) M. M. Abu-Omar, *Dalton Trans.*, **2011**, 40, 3435–3444. (d) M. J. Zdilla, J. L. Dexheimer, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2007**, 129, 11505–11511. (e) M. J. Zdilla, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2006**, 128, 16971–16979.
- [8] D. E. Lansky, J. R. Kosack, A. A. Narducci Sarjeant, D. P. Goldberg, *Inorg. Chem.*, **2006**, 45, 8477–8479.
- [9] (a) F. T. de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, ; L. Jr. Que, E. L. Bominaar, E. Münck, T. J. Collins, *Science* **2007**, 315,

## COMMUNICATION

- 835–838. (b) M. R. Mills, A. C. Weitz, M. P. Hendrich, A. D. Ryabov, T. J. Collins, *J. Am. Chem. Soc.* **2016**, 138, 13866–13869. (c) C. Panda, J. Debgupta, D. D. Díaz, K. K. Singh, S. S. Gupta, B. B. Dhar, *J. Am. Chem. Soc.* **2014**, 136, 12273–12282. (d) E. Kwon, K.-B. Cho, S. Hong, W. Nam, *Chem. Commun.* **2014**, 50, 5572–5575. (e) S. Hong, Y.-M. Lee, M. Sankaralingam, A. K. Vardhaman, Y. J. Park, K.-B. Cho, T. Ogura, R. Sarangi, S. Fukuzumi, W. Nam, *J. Am. Chem. Soc.* **2016**, 138, 8523–8532. (f) S. Hong, K. D. Sutherlin, A. K. Vardhaman, J. J. Yan, S. Park, Y.-M. Lee, S. Jang, X. Lu, T. Ohta, T. Ogura, E. I. Solomon, W. Nam, *J. Am. Chem. Soc.* **2017**, 139, 8800–8803. (g) S. Hong, X. Lu, Y.-M. Lee, M. S. Seo, T. Ohta, T. Ogura, M. Clémancey, P. Maldivi, J.-M. Latour, R. Sarangi, W. Nam, *J. Am. Chem. Soc.* **2017**, 139, 14372–14375.
- [10] D. G. Karmalkar, X. Li, M. S. Seo, M. Sankaralingam, T. Ohta, R. Sarangi, S. Hong, W. Nam, *Chem Eur. J.* **2018**, 24, 17927–17931.
- [11] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, 96, 877–910.
- [12] G. Golubkov, Z. Gross, *J. Am. Chem. Soc.* **2005**, 127, 3258–3259.
- [13] (a) R. M. Clarke, T. Storr, *J. Am. Chem. Soc.* **2016**, 138, 15299–15302; (b) T. Chantarojsiri, A. H. Reath, J. Y. Yang, *Angew. Chem. Int. Ed.* **2018**, 57, 14037–14042.
- [14] J. Bendix, K. Meyer, T. Weyhermglger, E. Bill, N. Metzler-Nolte, K. Wieghardt, *Inorg. Chem.* **1998**, 37, 1767–1775. (b) K. Meyer, J. Bendix, N. Metzler-Nolte, T. Weyhermglger, K. Wieghardt, *J. Am. Chem. Soc.* **1998**, 120, 7260–7270.
- [15] (a) P. Leeladee, R. A. Baglia, K. A. Prokop, R. Latifi, S. P. De Visser, D. P. Goldberg, *J. Am. Chem. Soc.* **2012**, 134, 10397–10400. (b) C. J. Bougher, S. Liu, S. D. Hicks, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2015**, 137, 14481–14487.
- [16] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, 178, 42–55.
- [17] J. P. T. Zaragoza, M. A. Siegler, D. P. Goldberg, *J. Am. Chem. Soc.*, **2018**, 140, 4380–4390.

## COMMUNICATION

## COMMUNICATION



We report the synthesis and X-ray structure of a new Mn(V) mesitylimido(N-Mes) bearing a tetraamido macrocyclic ligand (TAML), Mn(V)(TAML)(N-Mes)<sup>-</sup> (**1**). Upon one electron oxidation, a reactive species Mn(TAML)(N-Mes) (**2**) was generated, which readily undergoes H-atom transfer and nitrene transfer reactions.

Huatian Shi,<sup>[a]</sup> Jianhui Xie,<sup>[b]</sup> William W. Y. Lam,<sup>[c]</sup> Wai-Lun Man,<sup>[d]</sup> Chi-Keung Mak,<sup>[a]</sup> Shek-Man Yiu,<sup>[a]</sup> Hung Kay Lee,<sup>[e]</sup> and Tai-Chi Lau<sup>\*[a]</sup>

Page No. – Page No.  
**Generation and Reactivity of a One-electron Oxidized Manganese(V) Imido Complex bearing a Macrocyclic Tetraamido Ligand**

[a] H. Shi, C. K. Mak, S. M. Yiu, T. C. Lau<sup>\*</sup>  
 Department of Chemistry, City University of Hong Kong  
 Tat Chee Avenue, Kowloon Tong, Hong Kong SAR, China  
 E-mail: bhtclau@cityu.edu.hk

[b] J. Xie  
 School of Chemistry and Chemical Engineering  
 Hefei University of Technology  
 Hefei 230009, P. R. China.

[c] W. W. Y. Lam  
 Department of Food and Health Sciences  
 Technological and Higher Education Institute of Hong Kong  
 Tsing Yi Road, Hong Kong SAR, China.

W. L. Man  
 Department of Chemistry, Hong Kong Baptist University