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Conformational control of nonplanar free base porphyrins: towards bifunctional catalysts of tunable basicity

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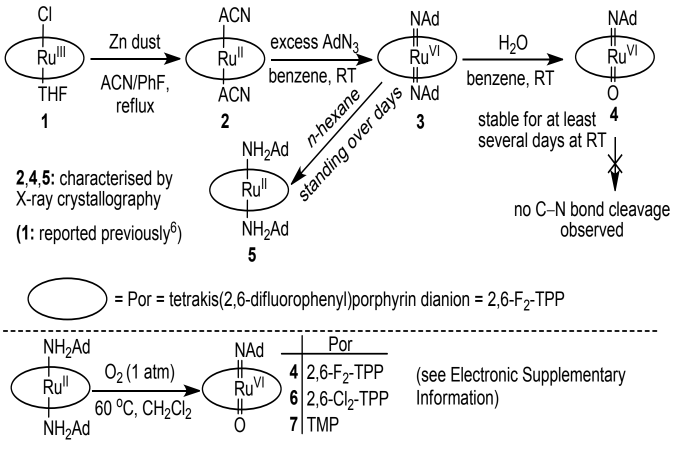
The first crystallographically characterised ruthenium(VI) alkylimido porphyrin competent for aerobic epoxidation and hydrogen atom abstraction

Ka-Pan Shing,[a] Qingyun Wan,[a] Xiao-Yong Chang[a] and Chi-Ming Che*[ab]

The syntheses of [Ru^{VI}(Por)(NAd)(O)] and [Ru^{VI}(2,6-F$_2$-TPP)(NAd)$_2$] were described. [Ru^{VI}(2,6-F$_2$-TPP)(NAd)(O)] capable of catalysing aerobic epoxidation of alkenes has been characterised by X-ray crystallography with Ru=NAd and Ru=O bond distances being 1.778(5) Å and 1.760(4) Å (∠O-Ru-NAd: 174.37(19)°), respectively. Its first reduction potential is 740 mV cathodically shifted from that of [Ru^{VI}(2,6-F$_2$-TPP)(O)$_2$].

Isolation and reactivity studies of metal-imido species are instrumental to understanding burgeoning nitrene-transfer reactions and designing efficient catalysts through structure-reactivity studies. In recent years, intra-[1] and intermolecular[2] C–H amination reactions mediated by late-transition-metal-imido or -alkyliminyl species have garnered much attention,[1,2] but such species are usually short lived in solution. For the literature reported isolable metal-imido/nitrene species, many examples are of low coordination number (2–4);[3] examples of isolable yet reactive 5- and 6-coordinate metal-imido complexes are relatively sparse.[1f,4] Metal-alkylimido complexes, which could readily undergo 1,2-hydride migration and/or C–N bond cleavage,[1a,2d] are intrinsically more unstable than non-aliphatic imide analogues. As to Group-8 alkylimido porphyrins, only [Os^{VI}(4-Cl-TPP)(NBu^t)$_2$] and [Os^{VI}(TTP)(NBu^t)(O)] have been characterised by X-ray crystallography;[5] no X-ray crystal structure has been reported for their Ru counterparts (in contrast to aryl- and sulfonylimides [Ru^{VI}(Por)(NAr)$_2$][4e,f] and [Ru^{VI}(Por)(NSO$_2$Ar)$_2$][4b,d] which could be isolated and purified by chromatography in air). Herein we report a crystallographically characterised Ru(VI) alkylimido porphyrin which can mediate hydrogen atom abstraction and aerobic alkene oxidation reactions.



Scheme 1 Preparation of ruthenium complexes **2–7**.

Reduction of [Ru^{III}(2,6-F$_2$-TPP)(Cl)(THF)] [6] (**1**) to air-sensitive [Ru^{II}(2,6-F$_2$-TPP)(ACN)$_2$] (**2**), followed by reaction with excess adamantyl azide (AdN$_3$), gave Ru(VI)-bis(alkylimido) complex [Ru^{VI}(2,6-F$_2$-TPP)(NAd)$_2$] (**3**, Scheme 1). Complex **3** readily underwent hydrolysis to form Ru(VI)-oxo(alkylimido) complex [Ru^{VI}(2,6-F$_2$-TPP)(NAd)(O)] (**4**, which is air-stable in CH$_2$Cl$_2$/C$_6$H$_6$ over days). Previously [Ru^{VI}(Por)(NBu^t)(O)] (Por = 4-Cl-TPP, TPP, 3,4,5-(MeO)$_3$-TPP) were synthesised from [Ru^{VI}(Por)(O)$_2$] and ^{t}BuNH$_2$ via isolation of [Ru^{II}(Por)(NH$_2$Bu^t)] with subsequent oxidation by bromine[7] which requires careful addition of bromine to minimise formation of side product(s). Using **1** as starting material, its reduction to **2** (after overnight reflux) is nearly quantitative, and the reaction of **2** with excess AdN$_3$ in anhydrous benzene afforded **3** with no side product(s) detected. Attempts to obtain the X-ray crystal structure of **3** have not been successful. Layering *n*-hexane on top of a benzene solution of **3** gave diffraction-quality crystals of **4**. Standing a solution of **3** in anhydrous *n*-hexane at RT over days produced [Ru^{II}(2,6-F$_2$-TPP)(NH$_2$Ad)$_2$] (**5**). Complex **4**, and isostructural [Ru^{VI}(Por)(NAd)(O)] (Por = 2,6-Cl$_2$-TPP: **6**, TMP: **7**), could also be prepared through aerobic oxidative deprotonation of [Ru^{II}(Por)(NH$_2$Ad)$_2$] (Scheme 1).

Complexes **2**–**7** were characterised by spectroscopies (see the ESI†) and, for **2**, **4**, **5**, also by X-ray crystallography (Fig. S1, ESI†; Fig. 1 and 2). The ^{1}H NMR spectra of diamagnetic Ru(VI)-alkylimido complexes **3** and **4** exhibit pyrrolic signals (H$_\beta$: 8.70 and 8.91 ppm for **3** and **4**, respectively) that are downfield

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† Electronic supplementary information (ESI) available: Abbreviations, experimental procedures, compound characterisation, Tables S1–S2, Fig. S1–S4 and computational details. CCDC 1972136, 1985960 and 1972138. For ESI and crystallographic data in CIF or other electronic format see DOI:

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shifted from that of diamagnetic Ru(II)-alkylamine complex **5** (H_β: 8.34 ppm). The H_β signal of **3** is slightly upfield shifted from that of **4**, as the former has one extra alkylimido ligand that is more π-basic than the oxo ligand.[5,7] These spectral features are reminiscent of those reported for $[Ru^{VI}(4\text{-}Cl\text{-}TPP)(NBu^t)_2]$ [7b] (not isolated, due to extreme moisture sensitivity), $[Ru^{VI}(Por)(NBu^t)(O)]$ and $[Ru^{II}(Por)(NH_2Bu^t{}_2)]$.[7] In the case of ^{19}F NMR spectra, **3** exhibits a single signal at –108.1 ppm whereas **4** shows two signals at –105.8 and –108.7 ppm, consistent with their molecular symmetry. The MALDI-TOF MS spectra of both **3** and **4** display peaks at *m/z* 1007.1817 attributable to $[Ru(2,6\text{-}F_2\text{-}TPP)(NAd)]$ fragment. In the UV-vis spectrum of **3** (Fig. 3), split Soret bands appear at 410 and 417 nm, which could be originated from two close-lying transitions (π-π*(Por) and π-π*(Ru=NC(Ad))) caused by two bent NAd ligands according to DFT calculations (Fig. S3 and S4, ESI†). Analogous Ru(VI)-bis(imido) porphyrins, such as $[Ru^{VI}(Por)(NSO_2Ar)_2]$ (Por = TPP, TTP, 4-Cl-TPP, TMP, $2,6\text{-}Cl_2\text{-}TPP$, $F_{20}\text{-}TPP$), also exhibit Soret bands in similar spectral region (413–423 nm) in CH_2Cl_2.[4b,d] The UV-vis spectrum of **4** (Fig. 3) shows a Soret band at 411 nm significantly red-shifted from that of the Ru(II) precursor **2** (at 405 nm), as the $(d_{xy})^2(d_\pi)^0$ electronic structure of **4** is deprived of d_π(Ru)-π*(Por) back donation, which narrows the π-π*(Por) energy gap.[8] On going from **2** to the Ru(VI) complex **4**, the β band exhibits a large red shift (from 503 to 553 nm), in accord with other Ru(VI) porphyrins displaying β bands well red-shifted from those of Ru(II) counterparts.[4d,7b,9] The key spectral features of **6** and **7** (see the ESI†) are similar to that of **4** (e.g. the three complexes all exhibited oxidation state marker band at 1014 cm^{-1} in IR spectra and parent-ion peak in HRMS analysis).

The X-ray crystal structure of **4** (Fig. 1) features Ru=NAd distance of 1.778(5) Å and Ru=O distance of 1.760(4) Å; the N_5-Ru-O_1 and Ru-N_5-C_{45} angles are 174.37(19)° and 167.7(4)°, respectively, revealing an almost linear axial Ru=N-C(Ad) moiety. In contrast, the X-ray crystal structure of **5** (Fig. 2) shows bent axial Ru-N-C(Ad) moieties (with an angle of 131.2(4)°), coupled with relatively long Ru–N(NH_2Ad) bonds (2.158(4) Å), resembling the structure features of $[Ru^{II}(TMP)(NH_2Bn)_2]$ (axial Ru-N-C(Bn) angle: 118.7(2)°, Ru–N(NH_2Bn) 2.129(2) Å).[10] The lengthened Ru-oxo bond of **4** (1.760(4) Å) compared with that of $[Ru^{VI}(Por)(O)_2]$ (*ca.* 1.72–1.74 Å[9,11]), which is analogous to the longer Os-oxo bond in $[Os^{VI}(TTP)(NBu^t)(O)]$ than in $[Os^{VI}(Por)(O)_2]$ (1.772(7) vs 1.743(3) Å),[5] is suggestive of the strong π-donor strength of NAd ligand. This finding is reflective of π-delocalisation between the metal-alkylimido and metal-oxo units in **4**.

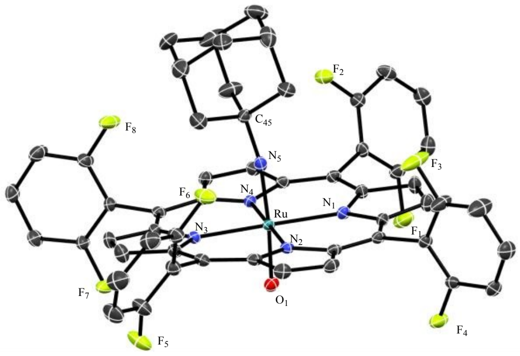

Fig. 1 ORTEP drawing of **4** (thermal ellipsoids drawn at 30% probability level). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Ru–N_1 2.070(4), Ru–N_2 2.065(4), Ru–N_3 2.071(4), Ru–N_4 2.080(4), Ru–N_5 1.778(5), Ru–O_1 1.760(4), N_5-C_{45} 1.416(7); N_5-Ru-O_1: 174.37(19), N_1-Ru-N_5: 91.82(18), N_1-Ru-O_1: 92.00(17), Ru-N_5-C_{45}: 167.7(4).

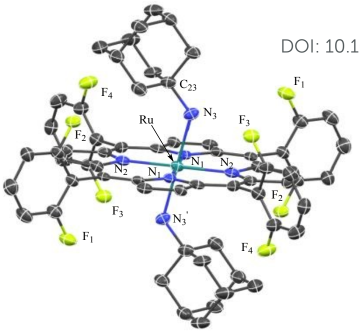

Fig. 2 ORTEP drawing of **5** (thermal ellipsoids drawn at 30% probability level). Hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Ru–N_1 2.045(4), Ru–N_2 2.028(4), Ru–N_3 2.158(4), N_3–C_{23} 1.503(7); N_3-Ru-N_3': 180.0(3), N_1-Ru-N_3: 80.87(17), N_1-Ru-N_3': 99.13(17), Ru-N_3-C_{23}: 132.4(4).

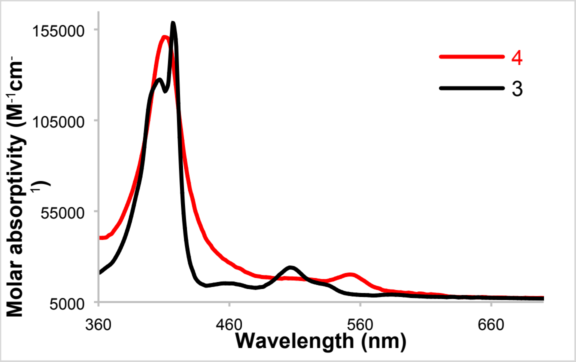

Fig. 3 UV-vis spectra of **3** and **4** in CH_2Cl_2.

We recorded the cyclic voltammograms of the oxo(alkylimido) complexes **4**, **6** and **7** and also the dioxo counterpart $[Ru^{VI}(2,6\text{-}F_2\text{-}TPP)(O)_2]$ (Fig. 4). Notably, the 1st reduction potential $E_{p,c}$ of **4** is –1.52 V (*vs* Fc^+/Fc), which is cathodically shifted by 740 mV compared with that of $[Ru^{VI}(2,6\text{-}F_2\text{-}TPP)(O)_2]$ (–0.78 V), revealing that substitution of the oxo ligand with alkylimido (NAd) ligand has a significant effect on this redox process and suggesting that the alkylimido ligand is a much stronger π-base. A less significant effect was observed by changing the porphyrinato ligand in $[Ru^{VI}(Por)(NAd)(O)]$, as is evident from the similar 1st reduction potential $E_{p,c}$ of –1.52, –1.53, and –1.69 V for Por = $2,6\text{-}F_2\text{-}TPP$ (in **4**), $2,6\text{-}Cl_2\text{-}TPP$ (in **6**), and TMP (in **7**), respectively. This is consistent with the metal-centred Ru(VI) to Ru(V) reduction.

DFT calculations were conducted on **3** and **4** to gain insight into their electronic structures. The optimised structure of **4** shows consistence with the crystal structure (Fig. S2, ESI†). It can be noted that hyper-conjugation effect of the Ad group destabilises π^*(O-Ru-NAd) orbital (Fig. 5), which is conceived to be responsible for the diminished reactivity of **4** compared

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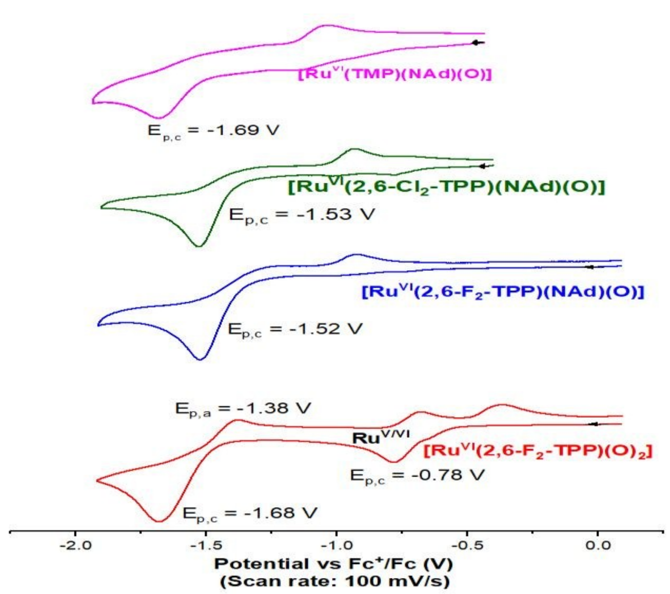


Fig. 4 Cyclic voltammograms recorded in CH_2Cl_2 with 0.1 M [^{n}Bu$_4$N]PF_6.

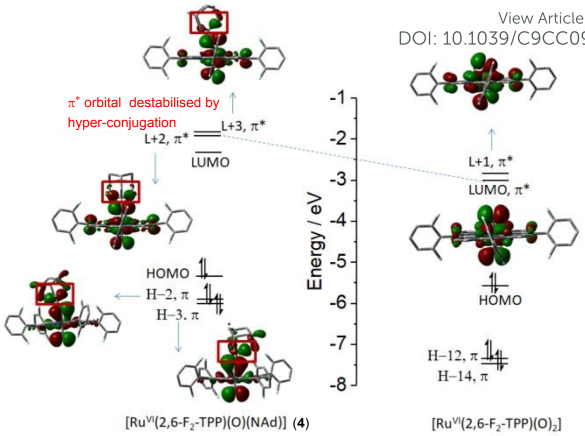


Fig. 5 DFT-calculated molecular orbitals of **4** and [Ru^{VI}(2,6-F_2-TPP(O)$_2$].

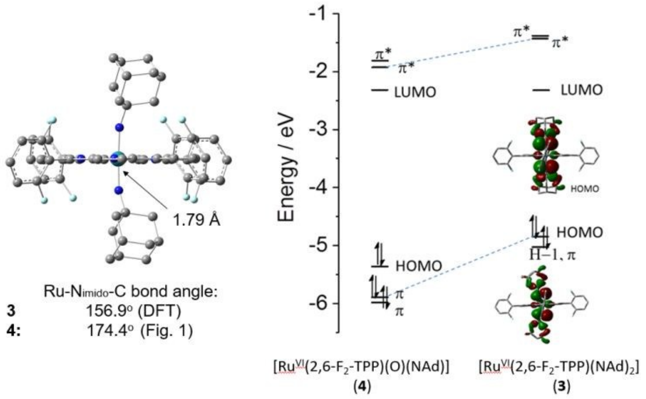
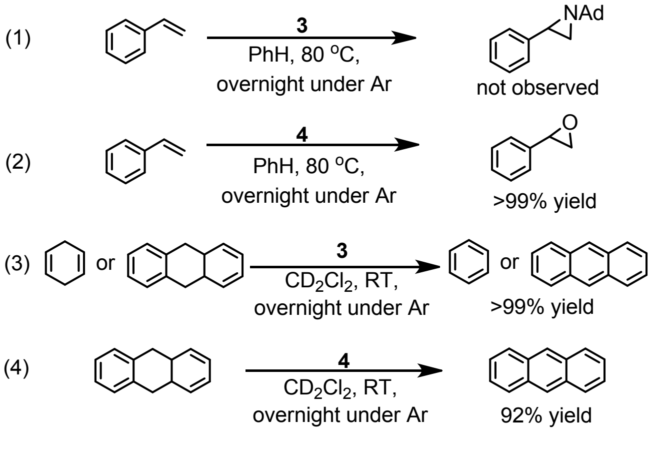


Fig. 6 DFT-optimised structure of **3** and comparison of its molecular orbitals with **4**.



Scheme 2 Reactivity studies involving **3** and **4**. Yield: based on [product]/[Ru] (see ESI†).

with [Ru^{VI}(2,6-F_2-TPP)(O)$_2$] towards reduction. On the other hand, the calculated Ru=NAd bond distance and Ru-N-C(Ad) angle in **3** are 1.79 Å and 156.9°, respectively (Fig. 6). The MO diagram of **3** shows that its π orbitals are at higher energies than that in **4** (*ca*. +1.0 eV), suggesting that the higher basicity of NAd in **3** causes a greater susceptibility to protonation.

We examined the stoichiometric reactions of the alkylimido complexes **3** and **4** with styrene (Scheme 2). Complex **4** reacted with styrene at 80 °C to give epoxidation product, but neither **3** nor **4** was reactive towards aziridination of styrene,[12] unlike the sulfonyl- and arylimido complexes [Ru^{VI}(Por)(NSO$_2$Ar)$_2$] and [Ru^{VI}(Por)(NAr)$_2$] which can undergo alkene aziridination reactions.[4b,d,h] The higher reactivity of the sulfonyl- and arylimido complexes can be attributed to the elevated electrophilicity resulting from π-delocalisation between the N_{imido} and SO_2Ar/Ar groups and higher one-electron reduction potential (e.g., $E_{1/2}$ = −0.34 and −0.27 V vs. Fc$^+$/Fc for [Ru^{VI}(2,6-Cl_2-TPP)(NTs)$_2$] and [Ru^{VI}(TPP)(NTs)$_2$], respectively[4d]); sterics might also play a role due to less bulky SO_2Ar/Ar groups than adamantyl group. The N_{imido}–C_{Ar} and N_{imido}–S_{Ts} bonds in [Ru^{VI}(TPP)(NAr)$_2$] (Ar = 3-(CF_3)$_2$-C_6H_3) and [Ru^{VI}(TMP)(NMs)$_2$] were reported to be 1.361(6)[4f] and 1.60(2) Å,[4g] respectively, and these values are in between those of N–C(sp^2) and N=C(sp^2) (*ca*. 1.28–1.42 Å) or N–S(sp^3) and N=S(sp^3) (*ca*. 1.53–1.73 Å).

Interestingly, complexes **3** and **4** can undergo hydrogen atom abstraction (HAA) reaction with allylic or benzylic hydrocarbons to give **5** bearing coordinated amine ligands, and, for the reaction of **3** (bearing two alkylimido axial ligands) with cyclohexa-1,4-diene/9,10-dihydroanthracene, a quantitative yield of benzene/anthracene (2 equiv. generated per Ru used) was observed as the organic product, respectively (Scheme 2). The reaction of **4** (bearing one alkylimido axial ligand) with 9,10-dihydroanthracene gave anthracene with a yield of 92%. For both **3** and **4**, no oxygen atom transfer reaction with the hydrocarbons was observed, whereas the dioxo complexes [Ru^{VI}(Por)(O)$_2$] typically undergo HAA and radical rebound mechanism to give C–H bond hydroxylation products.

Despite the fact that aerobic epoxidation can be mediated by a cycle involving [Ru^{IV}(Por)(O)] and [Ru^{II}(Por)],[13] exploring other new ruthenium porphyrin systems capable of mediating aerobic epoxidation is of considerable interest. We found that [Ru^{VI}(Por)(NAd)(O)] can mediate epoxidation of a variety of alkenes under aerobic conditions (Table 1), albeit with

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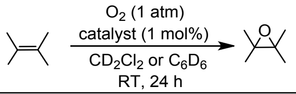
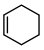
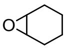
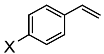
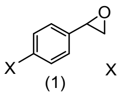
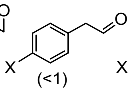
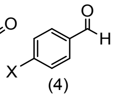
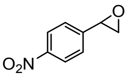
attenuated reactivity. Complex **4** could mediate aerobic epoxidation of cyclohexene, norbornene, and styrenes at RT; better product yield was found for the epoxidation of *p*-nitrostyrene at 40 °C (8 equiv. epoxide product per complex **4**, entry e in Table 1; no other oxidation products were detected). In the cases of electron-rich styrenes such as *p*-(*tert*-butyl)styrene, besides epoxides, benzaldehydes and phenylacetaldehydes were also formed (entry d in Table 1).

Table 1 Aerobic oxidations of alkenes mediated by [Ru^{VI}(Por)(NAd)(O)] (**4**, **6**, **7**).[i]



Entry	Catalyst	Substrate	Product(s) (equiv. per Ru)
a	**4**		 (3)
b	**4**		 (5)
c	**4**	 X = H	 (1)  (<1)  (4)
d	**4**	X = ^{t}Bu	(2) (<1) (4)
e[ii]	**4**	X = NO$_2$	 (8) or (8)[iii]
f	**6**	X = NO$_2$	(1)
g	**7**	X = NO$_2$	(5) or (5)[iv]

[i] Conditions: substrate (0.2 mmol), catalyst (0.002 mmol) and solvent (CD$_2$Cl$_2$, 2 mL). [ii] 40 °C. [iii] 5 atm O$_2$. [iv] C$_6$D$_6$ as solvent.

In summary, [Ru^{VI}(2,6-F$_2$-TPP)(NAd)(O)] (**4**), which was both spectroscopically and crystallographically characterised, is capable of undergoing oxygen atom transfer (but not alkylimido group transfer) to styrene, and can also mediate aerobic epoxidation of alkenes. Electrochemical studies showed that the first reduction of **4** is less thermodynamically favourable compared with the dioxo counterpart [Ru^{VI}(2,6-F$_2$-TPP)(O)$_2$]. [Ru^{VI}(2,6-F$_2$-TPP)(NAd)$_2$] (**3**) is unable to transfer its alkylimido group(s) to styrene, but can undergo HAA reactions with cyclohexa-1,4-diene or dihydroanthracene to give [Ru^{II}(2,6-F$_2$-TPP)(NH$_2$Ad)$_2$] (**5**) and benzene or anthracene.

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Conflicts of Interest

There are no conflicts to declare.

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