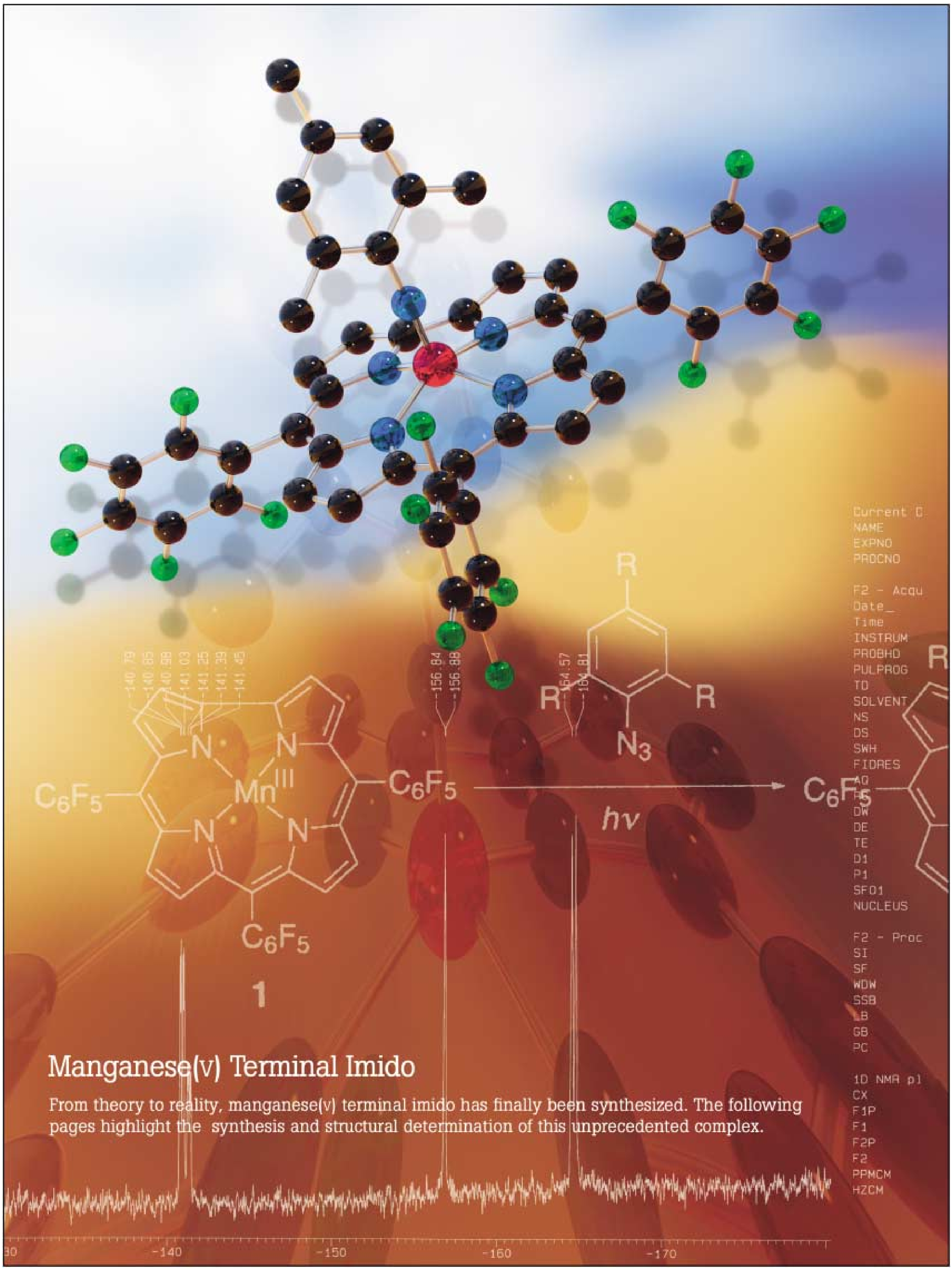


Manganese(V) Terminal Imido

From theory to reality, manganese(V) terminal imido has finally been synthesized. The following pages highlight the synthesis and structural determination of this unprecedented complex.

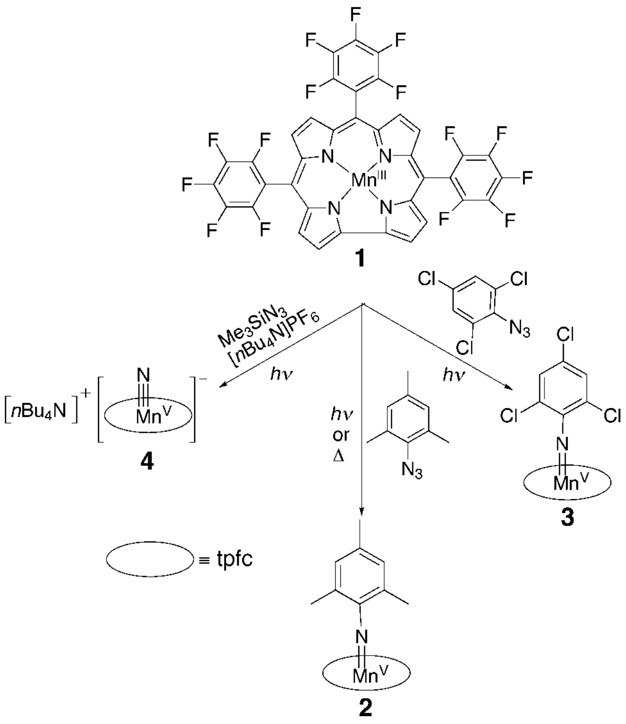
The Elusive Terminal Imido of Manganese(V)**

Rebecca A. Eikey, Saeed I. Khan, and
Mahdi M. Abu-Omar*

The discovery that a (nitrido)manganese(V) porphyrin[1] can be activated for the aziridination of cyclooctene with trifluoroacetic anhydride (tfaa) has stimulated the development of several catalytic[2–4] and stoichiometric methods[5] for metal-mediated nitrene [NR] group transfer. The catalytic tosylamidation of alkanes by PhI = NTs in the presence of manganese(III) pophyrins has also been reported.[6] A major goal of research on the use of catalytic manganese(III) and stoichiometric high-valent manganese(V) species is the identification of reaction intermediates. (Imido)manganese(V) compounds have been proposed as the active species responsible for the delivery of the nitrene group to double bonds,[1,7] similar to what has been postulated for the related metal-mediated oxygen-atom-transfer reaction.[8] Thus, it is not surprising that while many structures of (nitrido)manganese(V) complexes are known,[9] neither structures nor definitive spectroscopic characterizations of (imido)manganese(V) complexes are available.[7,10] Herein, we describe the preparation, molecular structure, and preliminary reactivity studies of novel (imido)manganese(V) corrole complexes. To our knowledge, this report constitutes the first structure of a terminal imido complex of manganese(V).[7,11]

Corroles, one-carbon atom short analogues of porphyrins, have been shown to stabilize high oxidation states of various transition metals.[12] The ambiguity of assigning oxidation states that is characteristic of octaalkylcorroles[13] has been eradicated by the introduction of the electron-poor 5,10,15-tris(pentafluorophenyl)corrole (H_3(tpfc), tpfc = the trianion) by Gross and co-workers.[14] Recently, Gross and Gray and their co-workers extended the chemistry of manganese corroles beyond the trivalent state by preparing (halo)manganese(IV),[12c] (oxo)manganese(V),[12b] and (nitrido)manganese(V)[12c] corroles. The manganese(IV) corroles were structurally characterized, but the manganese(V) corroles were identified spectroscopically.

Following the literature precedent of using NaN_3 and irradiation in the preparation of high-valent nitrido complexes,[9c] we have prepared (imido)manganese(V) corroles from the one-pot reaction of organic azides[15–17] with (tpfc)manganese(III) complex **1** under photolysis (Scheme 1). The reaction of **1** with 2,4,6-trimethylphenyl azide yields the corresponding manganese(V) imido complex **2** under photolytic as well as under thermal conditions. However, the reaction of **1** with 2,4,6-trichlorophenyl azide affords the desired product **3** only under photolysis. Interestingly, when trimethylsilyl azide (tmsa) was employed as the nitrene [NR] source, the (nitrido)manganese(V) corrole **4**, was isolated upon the addition of a salt, [nBu$_4$N][PF$_6$]. The nitrido complex has been prepared previously by the action of NaN_3 followed by photolysis.[12c] Complexes **2** and **3** are easily purified by chromatography to afford red microcrystalline solids in excellent and consistent overall yields of 80–70 %.



Scheme 1. Synthesis of **2**, **3**, and **4** from [Mn^{III}(tpfc)].

The (imido)manganese complex **2** is sensitive to water and air (the latter is most likely to be as a result of the moisture in air since compound **2** persists for days under ambient atmosphere in dry southern California weather). In solution and in the solid state, **2** is stable for months under dry inert atmosphere. On the other hand, solutions of **3** revert to green Mn^{III} species in a couple of days even under inert atmosphere. A complex mixture of organic products is formed alongside the identifiable azo compound.

The ^{1}H and ^{19}F NMR spectra of both complexes **2** and **3** exhibit sharp resonance signals in the normal range for chemical shifts, consistent with diamagnetic low-spin d^2 manganese (Figure 1) centers. The phenyl proton resonances of the imido ligands are shifted upfield ($\delta = 5.67$ and 6.31 ppm for **2** and **3**, respectively) as a result of the ring current of the corrole macrocycle. Noteworthy is that the green intermediate [(TMP)Mn(=NCOCF$_3$)(OCOCF$_3$)] (TMP = (5,10,15,20-tetramethylporphyrinato)dianion) proposed by Groves and Takahashi to be responsible for [NR] transfer is paramagnetic.[1,18] This high-spin configuration of the Mn^V center could be a result of the weaker π-donation ability of the acylimido ligand or to the porphyrin ligand. Recent DFT calculations on

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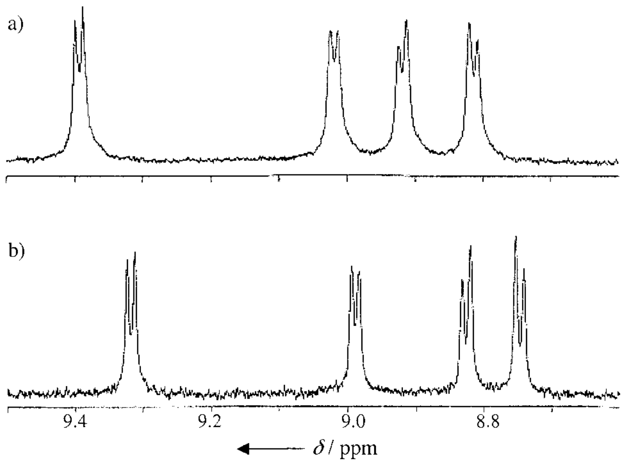


Figure 1. ^{1}H NMR spectra showing the β-pyrrole region of complexes a) **2** and b) **3** in $\mathrm{CD_3CN}$.

(oxo)manganese(v) corrole and porphyrin complexes showed that diamagnetism is expected for corrole and paramagnetism for porphyrin complexes.[19] However, a diamagnetic (oxo)-$\mathrm{Mn^{V}}$(hydroxo) porphyrin intermediate has been recently characterized by ^{1}H NMR spectroscopy.[10] The identification of **2** and **3** as the imido complexes was confirmed by mass spectrometry. The electronic spectra of these complexes exhibit a single Soret band (410 nm) and a Q band at 528 nm. Figure 2 contrasts the UV/Vis spectrum of **2** with that of **1** and **4**. The most relevant changes are the loss of the split Soret band and the band at 470 nm upon formation of manganese(v).

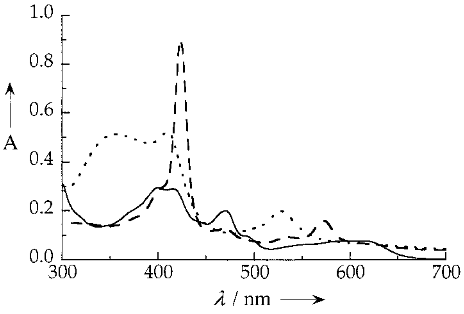


Figure 2. Electronic spectra of a) $[\mathrm{Mn^{III}(tpfc)}]$ (**1**; $1.5\times10^{-5}\,\mathrm{M}$; ——), b) $[\mathrm{Mn^{V}(tpfc)}(N\text{-mesityl})]$ (**2**; $1.6\times10^{-5}\,\mathrm{M}$; ••••), and c) $[\mathrm{Mn^{V}(tpfc)(N)}]^{-}$ (**4**; $1.0\times10^{-5}\,\mathrm{M}$; ----) in acetonitrile.

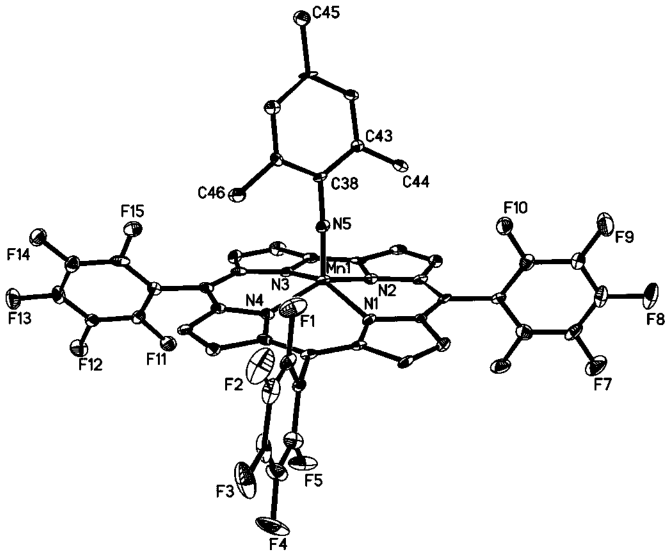
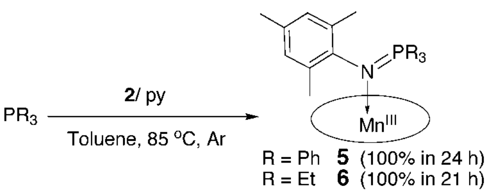


Figure 3. ORTEP diagram (H atoms are omitted for clarity) of **2** (ellipsoids at 50% probability level). Selected bond lengths [Å] and angles [°]: Mn1-N5 1.613(4), $\mathrm{Mn1\text{-}N_{pyrrole}}$ 1.891(4)-1.947(4), N5-C38 1.374(6); C38-N5-Mn1 170.4(4), $\mathrm{N5\text{-}Mn1\text{-}N_{pyrrole}}$ 103.30(19)-106.37(19), and N5-C38-C43 118.9(5).

The molecular structure of **2** was confirmed by single-crystal X-ray analysis (Figure 3).[20] The highlight features of the structure are 1) a five-coordinate manganese(v) center that is located 0.513 Å out of the plane defined by pyrrole nitrogen atoms, 2) a $\mathrm{Mn{\equiv}NR}$ bond length of 1.613(4) Å, and 3) a $\mathrm{Mn\text{-}N\text{-}C_{Ar}}$ bond angle of 170.4(4)°. The $\mathrm{Mn{\equiv}NR}$ distance is slightly longer than what is observed for (nitrido)manganese(v) complexes (the average $\mathrm{Mn{\equiv}N}$ bond for porphyrin and salen complexes is 1.52 Å)[9] and for (oxo)manganese(v) complexes ($\mathrm{Mn{\equiv}O}$ bond of ~1.56 Å).[21] The Mn−NR bond in our compound, however, is significantly shorter than the Mn−O bond observed for a terminal oxo complex of low-valent manganese(iii) (1.80 Å) species,[22] and shorter than the imido bonds in $[\mathrm{Mn^{VII}}(\mathrm{N}t\mathrm{Bu})_3\mathrm{Cl}]$ (the average Mn−NR bond is 1.66 Å).[23] Hence, the Mn−NR bond length and the $\mathrm{Mn\text{-}N\text{-}C_{Ar}}$ bond angle in **2** are well within the range for a $\mathrm{Mn{\equiv}NR}$ triple bond formulation. The average Mn−N bond lengths for the pyrrole nitrogen atoms in **2** (1.916 Å) is the same as those in $[\mathrm{Mn^{III}(tpfc)(OPPh_3)}]$ (1.916 Å).[24] This situation is in contrast to the lengthening of the $\mathrm{Mn{-}N_{pyrrole}}$ distances observed in $[\mathrm{Mn^{IV}(tpfc)Br}]$ (1.925 Å) and $[\mathrm{Mn^{IV}(tpfc)Cl}]$ (1.932 Å)[12c] and to the lengthening of the $\mathrm{Cr{-}N_{pyrrole}}$ distances found in $[\mathrm{(tpfc)Cr^{V}(O)}]$ (1.927–1.943 Å).[25] The cause of this lengthening in the $\mathrm{Mn{-}N_{pyrrole}}$ and $\mathrm{Cr{-}N_{pyrrole}}$ bonds was attributed to the "pronounced doming of the corrole framework" in the manganese(iv) and chromium(v) structures. In our structure, the pyrrole nitrogen atoms are essentially in the same plane as the 19-membered carbon macrocycle. In both **2** and $[\mathrm{(tpfc)Cr^{V}(O)}]$, the metals are displaced out of the plane defined by the pyrrole nitrogen atoms. However, the displacement is larger in $[\mathrm{(tpfc)Cr^{V}(O)}]$ (0.6 Å) resulting in a strong interaction of the bonding orbitals of the pyrrole nitrogen atoms with the π orbitals of the CrO moiety, which results in lengthening of the $\mathrm{Cr{\equiv}O}$ bond (1.57 Å) and doming of the ligand.[25]

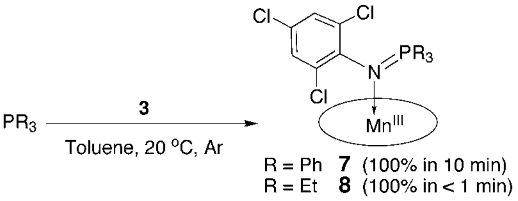
Preliminary investigations of the reactivity of (imido)manganese(v) corroles suggested that olefins are not reactive enough to accept an [NR] group from **2** or **3**. This finding is not surprising, given that $\mathrm{Mn^{III}}$ salen complexes, which are excellent epoxidation catalysts,[26] did not fair well in aziridination reactions.[2b,c] Interestingly, the analogous compound $[\mathrm{(tpfc)Mn^{V}(O)}]$ was shown to be unreactive towards oxygen-atom transfer to alkenes, which suggests that a higher oxidation state of manganese is responsible for catalysis.[12b] However, in the presence of pyridine (py), the terminal mesitylimido group of **2** transfers to organic phosphanes yielding the iminophosphane adduct of manganese(iii) corrole [Eq. (1)]. The UV/Vis spectrum of **5** ($\lambda_{\max}$ in nm = 401



R = Ph **5** (100% in 24 h)
R = Et **6** (100% in 21 h)

(1)

and 421 (split Soret), 493, 607 (Q band)) is similar to that of $[(\text{tpfc})\text{Mn}^{\text{III}}(\text{OPPh}_3)]$.[12b] (The spectra of **5** and **6** are displayed in the Supporting Information.) Even though the reactions of **2** with phosphanes are sluggish, complex **3** with the electron-withdrawing trichlorophenyl substituent is much more reactive and is more sensitive to the nucleophlicity of the R_3P group [Eq. (2)]. This finding is in agreement with electrophilic [NR] group transfer from the manganese(v) center. While [NR] transfer from activated (nitrido)manganese(v) salen complexes[5] and from complex **2** require pyridine as an additive, reactions of complex **3** [Eq. (2)] do not require pyridine, demonstrating the importance of the R substituent on the imido ligand.



R = Ph **7** (100% in 10 min)
R = Et **8** (100% in < 1 min)

(2)

Both of our complexes **2** and **3** are less reactive than their proposed porphyrin and salen counterparts if the latter complexes are indeed the species responsible for nitrene [NR] transfer, which remains to be shown. This difference in reactivity could be a result of the ability of the corrole ligand to stabilize high oxidation state manganese(v) centers, or to the difference in the electron-withdrawing ability of the R substituent on the imido ligand. The latter is an appealing explanation given that complex **3** is more reactive than **2**.

In conclusion, we have described a facile one-step synthesis of novel (imido)manganese(v) complexes containing the electron-poor corrole tpfc as the ancillary ligand. The molecular structure of $[(\text{tpfc})\text{Mn}^{\text{V}}(\text{N-mesityl})]$ is consistent with a low-spin d^2 configuration and a Mn–NR triple bond. Preliminary reactivity studies proved that these new and structurally well-defined (imido)manganese(v) complexes are suitable for [NR]-group transfer only to electron-rich substrates, such as organic phosphanes. The results reported herein set the stage for making and exploring other Mn^{V} and new Mn^{VI} imido species, for designing an efficient catalyst for [NR]-group transfer from organic azides,[27] and for developing the parallel alkylidene/carbene $[CR_2]$ organometallic chemistry.

Experimental Section

Toluene was dried by distillation over CaH_2. Acetonitrile was dried by distillation over CaH_2, deoxygenated, and stored under argon prior to use. For recrystallization purposes, pentane was purified by sulfuric acid before distillation over CaH_2. Photolysis experiments were carried out with a Hanovia Model 73A36 550-W medium pressure mercury lamp at 25 °C.

2: Method A. A solution of mesityl azide (36 mg, 230 μmol) and **1** (18 mg, 21 μmol) in toluene (10 mL) was refluxed under argon for 30 min or until the disappearance of $[\text{Mn}^{\text{III}}(\text{tpfc})]$ as monitored by TLC (12:1 mixture of pentane:diethyl ether). Evaporation of the solvent under reduced pressure followed by column chromatography (silica gel, 60 Å, 12:1 mixture of pentane:diethyl ether) resulted in isolation of **2**. Yield: 16 mg (75%). MS (negative ion FAB): *m/z* (%) 982 (100) $[M^-]$, 848 (33) $[M\text{–Nmes}^-]$; UV/Vis (CH_3CN): λ [nm] ($\log \varepsilon$) = 354 (4.53), 410 (4.53), 528 (4.14); ^{1}H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 9.39$ (d, $J = 4.5$ Hz, 2H), 9.03 (d, $J = 4.1$ Hz, 2H), 8.93 (d, $J = 4.7$ Hz, 2H), 8.82 (d, $J = 4.9$ Hz, 2H), 5.67 (s, 2H), 1.53 ppm (s, 3H), −0.61 (s, 6H); ^{19}F NMR (400 MHz, CD_3CN, 25 °C): $\delta = -140.82$ (d, $J = 20.0$ Hz, 2F), −141.00 (d, $J = 20.0$ Hz, 2F), −141.27 (d, $J = 24.0$ Hz, 1F), −141.41 (d, $J = 24.0$ Hz, 1F), −156.79 to −156.93 (m, $J = 16.0$ Hz, 3F), −164.55 (m, $J = 16.0$ Hz, 3F), −164.79 ppm (m, $J = 20.0$ Hz, 3F).

Method B. A solution of mesityl azide (64 mg, 397 μmol) and **1** (28 mg, 33 μmol) in acetonitrile (5 mL) was photolyzed under argon for 4–5 days. Evaporation of the solvent under reduced pressure and purification of the residue as in Method A resulted in isolation of **2**. Yield: 12 mg (37%).

3: A solution of 2,4,6-trichlorophenyl azide (36 mg, 162 μmol) and **1** (10 mg, 12 μmol) in acetonitrile (2.5 mL) was photolyzed under argon for 4–5 days. Evaporation of the solvent under reduced pressure and purification of the residue as in Method A resulted in isolation of **3**. Yield: 11 mg (81%). MS (negative ion FAB): *m/z* (%) 1043 (9) $[M^-]$, 864 (100) $[MN\text{–}Ar^-]$, 848 (11) $[M\text{–}NAr^-]$; UV/Vis (Toluene): λ [nm] ($\log \varepsilon$) = 396 (4.22), 488 (3.63), 540 (3.75); ^{1}H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 9.31$ (d, $J = 4.5$ Hz, 2H), 8.99 (d, $J = 4.3$ Hz, 2H), 8.83 (d, $J = 4.9$ Hz, 2H), 8.77 (d, $J = 4.9$ Hz, 2H), 6.31 ppm (s, 2H); ^{19}F NMR (400 MHz, CD_3CN, 25 °C): $\delta = -140.31$ (d, $J = 20.0$ Hz, 2F), −140.94 (t, $J = 20.0$ Hz, 3F), −141.47 (d, $J = 24.0$ Hz, 1F), −156.65 (m, $J = 24.0$ Hz, 3F), −164.31 to −164.61 ppm (m, $J = 8.0$ Hz, 6F).

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Light-Harvesting Dendrimers: Efficient Intra- and Intermolecular Energy-Transfer Processes in a Species Containing 65 Chromophoric Groups of Four Different Types[**]

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Dedicated to J. Fraser Stoddart
on the occasion of his 60th birthday

An antenna for light harvesting is an organized system in which several chromophoric molecular species absorb the incident light and channel the excitation energy to a common acceptor component.[1] Light-harvesting antennas are essential devices for natural photosynthetic processes.[2] In the last decade, dendrimers[3] have been extensively used to construct artificial antenna systems as suitable chromophoric groups may be incorporated into their regular branched structures.[4,5] Another interesting aspect of dendrimer chemistry is the presence of internal cavities where ions or neutral molecules can be hosted.[6,7] Energy-transfer processes between the

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