Imido Complexes

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On the Mechanism of the Reaction of Organic Azides with Transition Metals: Evidence for Triplet Nitrene Capture**

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Organic azides (RN_3) have received extensive attention recently because of their central role in several "spring-loaded" reactions that have been dubbed "click chemistry".[1–4] In organometallic chemistry, azides have been used

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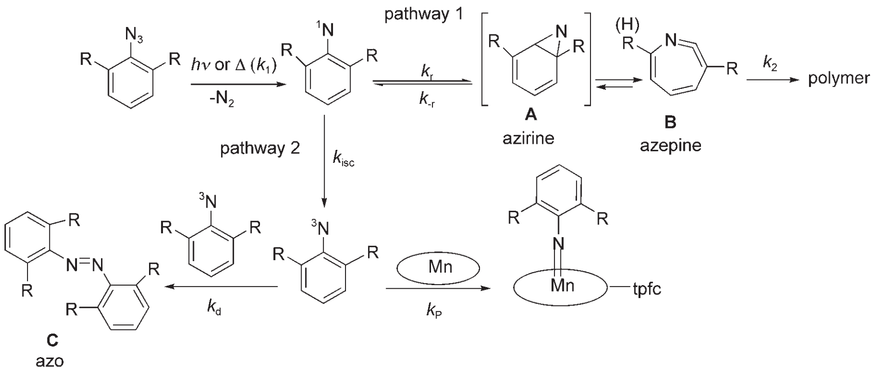
extensively for the preparation of imido (M=NR) complexes, in which dinitrogen is released as byproduct.[5,6] As part of our interest in developing nitrene (NR) transfer to organic substrates by transition-metal catalysis, we have used aryl azides, which are quite stable and easy to make,[7,8] to prepare mononuclear terminal imido complexes of manganese(v) and chromium(v) corroles.[9,10] Despite many known reactions of organic azides with transition metals, little is known about the reaction mechanism. Organoazido metal complexes have been proposed to initially form for coordinatively unsaturated metal complexes.[11–14] However, only in two instances have such complexes been characterized and shown to proceed to the imido product upon heating or photolysis, presumably via a four-membered metallacycle.[15–17] Herein we report a novel mechanism for the reaction of aryl azides with manganese corroles in which the metal does not form an organoazido complex.



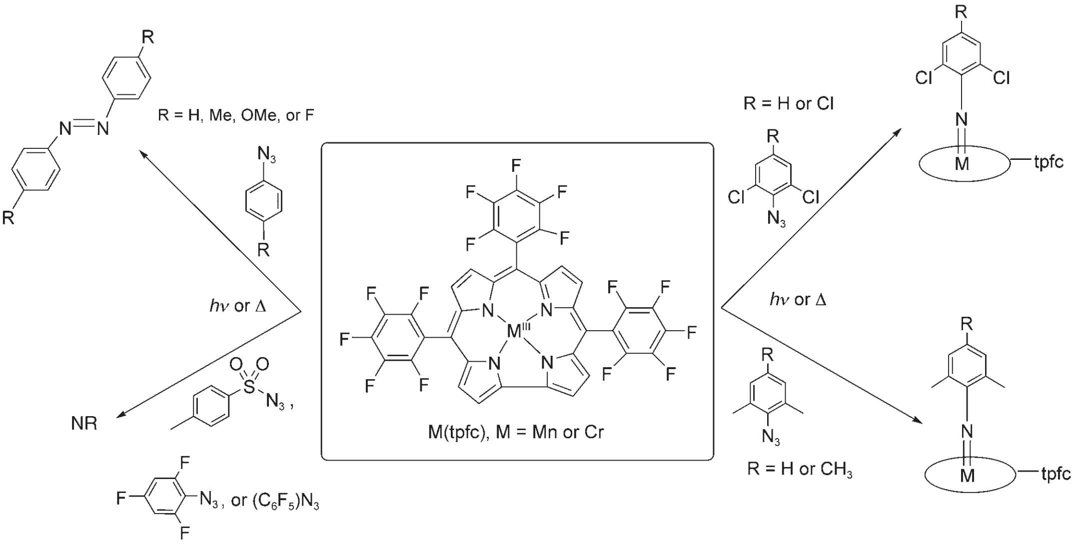
Scheme 2. Mechanism of the reaction of organic azides with [Mn^{III}(tpfc)].

Encouraged by the successful synthesis of terminal imido manganese(v) complexes from mesityl azide and trichlorophenyl azide,[9] we explored the utility and generality of this reaction (Scheme 1). We noted that *ortho* substitution is mandatory, as is thermal or photochemical activation. Phenyl azide with substituents in the *para* position as well as the electron-withdrawing sulfonyl azide did not produce imido metal complexes.

Results presented herein and the scope of the reaction (Scheme 1) gave valuable insight into the mechanism of the reaction of organic azides with transition-metal corroles. Our mechanistic proposal is presented in Scheme 2. On thermal or photochemical decomposition of aryl azide, singlet nitrene is formed and dinitrogen extruded.[18,19] The singlet nitrene then decomposes along two pathways. The first is cyclization to azepine **B** via azirine **A** as a steady-state intermediate.[20] The ultimate fate of the azepine is polymerization.[19] However, in highly dilute solutions, polymerization of **B** is suppressed and it reverts to singlet nitrene, which relaxes by intersystem crossing (isc) to the lower-energy triplet state.[21] The final thermodynamic product is azo compound **C**, assumed to form by dimerization of triplet nitrene.[22] This second pathway, isc of singlet nitrene to triplet, is responsible for the formation of the imido manganese complex in our system and is most consistent with the observed scope of the reaction (Scheme 1) and kinetic data, as detailed below.

Ortho substituents are mandatory for the formation of imido metal complexes in this system. This is in agreement with results showing that singly *ortho*-substituted singlet aryl nitrenes cyclize away from the substituent,[23] and *ortho* methylation increases the rate of intersystem crossing.[21] Furthermore, the lack of reaction with fluorinated phenyl azides and sulfonyl azide is consistent with these substituents destabilizing the open-shell singlet nitrene.[24] Indeed, under our reaction conditions only starting material was recovered with these substrates (Scheme 1).

The kinetics of imido metal formation were studied in detail for the reaction of mesityl azide (MesN$_3$) with [Mn^{III}(tpfc)]. Changes in the UV/Vis spectra for a typical reaction are displayed in Figure 1. The disappearance of the bands at



Scheme 1. Scope of the reaction of aryl azides with transition-metal corroles.

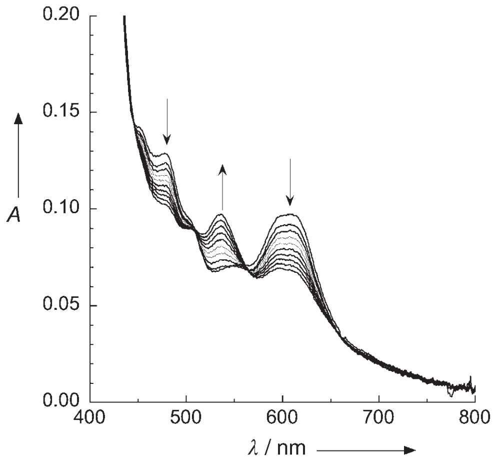


Figure 1. UV/Vis spectral changes for the reaction of [Mn^{III}(tpfc)] (15 μM) with mesityl azide (2.1 mM) in toluene at 80 °C recorded every 6 min.

479 and 609 nm and appearance of the band at 536 nm are indicative of a change in the oxidation state from Mn^{III} to Mn^{V}. The tight isosbestic points at 510 and 565 nm demonstrate clean conversion without significant accumulation of an intermediate.

The progress of the reaction was monitored at 536 nm with [Mn^{III}(tpfc)] limiting and MesN$_3$ in excess. The experimental reaction rate was found to be first-order in mesityl azide (Figure 2) and exhibited a complex dependence on the concentration of the manganese complex. A simplified rate law that includes the reaction steps described in Scheme 2 is given in Equation (1).

$$\frac{dc_{[\mathrm{Mn^{V}imide}]}}{dt} = \frac{k_1 k_\mathrm{P} c_{[\mathrm{Mn(tpfc)}]} c_{\mathrm{MesN_3}}}{k_\mathrm{P} c_{[\mathrm{Mn(tpfc)}]} + k_\mathrm{d} c_{{}^3\mathrm{NMes}}} \tag{1}$$

Under conditions where $k_\mathrm{P} c_{[\mathrm{Mn(tpfc)}]} \gg k_\mathrm{d} c_{{}^3\mathrm{NMes}}$, the rate law simplifies to $dc_{[\mathrm{Mn^{V}{=}NR}]}/dt = k_1 c_{\mathrm{MesN_3}}$ and the rate is zeroth-order in the concentration of the manganese corrole. However, as the reaction proceeds and [Mn(tpfc)] is consumed, the above assumption is no longer valid and the kinetics divert from zeroth order. This expectation is consistent with the time profiles shown in Figure 2 A, which are linear over the initial 30 % of the reaction (ca. 0.02 ΔOD) and deviate from zeroth order in the later stages. The experimental time profiles do not fit an exponential pseudo-first-order equation (see Supporting Information). Furthermore, under no circumstance would the reaction rate be independent of the metal concentration if an organoazido adduct was formed initially or the metal corrole reacted directly with the organic azide. Similar kinetic behavior was observed when reaction progress was followed at 479 nm, which corresponds to the disappearance of the Mn^{III} reactant (see Supporting Information).

The observed kinetics were successfully modeled with the kinetic simulation program KINSIM.[25,26] Figure 3 A shows the simulated time profiles for [Mn^{III}(tpfc)], [Mn^{V}(tpfc)], azo compound, azepine, and polymer arising from the azepine. The rate constants used in association with Scheme 2 as the reaction mechanism are given in the caption of Figure 3. The rate constant for the thermal decomposition of mesityl azide

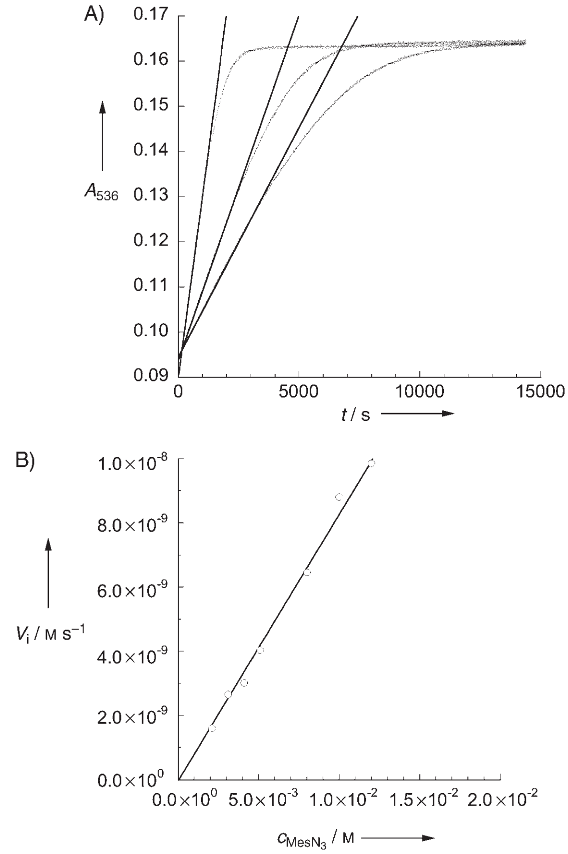


Figure 2. A) Time profiles for the reaction of [Mn(tpfc)] (15 μM) and mesityl azide (3, 5, and 12 mM) in toluene at (80.0 ± 0.2) °C. The linear fit is over the initial 30 % of the reaction to illustrate zeroth-order kinetics that deviate from linearity in the later stages of the reaction. B) A plot of the initial rate V_i versus the mesityl azide concentration showing first-order dependence on the azide concentration.

(k_1) was determined experimentally herein (Figure 2 B); the rate constant for intersystem crossing (k_isc) was taken from published data,[27] and the rate constants for triplet nitrene dimerization to give the azo compound (k_d) and for polymerization of azepine (k_2) were set to the diffusion limit (8.0×10^9 M^{-1} s^{-1}). The remaining three rate constants were floated to give the best fit to the experimental profiles. The agreement between experimental and simulated kinetics is illustrated in Figure 3 B and the Supporting Information. It is worth noting that formation of the azo compound sets in after the initial 30 % of reaction, which agrees with the observed kinetic behavior (see above). Nevertheless, GC-MS analyses of reaction mixtures at the end of the reaction show only azide, and only at longer decomposition times is the azo compound detected (see Supporting Information). This apparent contradiction is most likely due to low concentrations of the azo compound (below the GC-MS detection threshold) on the reaction timescale (2 h).

To date, the reaction of organic azides with transition-metal complexes to give imido metal compounds has been accepted to proceed via an organoazido metal intermediate. While this mechanism holds true in many instances and has been demonstrated in a couple of reaction systems, it is not exclusive.[15–17] We have described herein a new mechanism

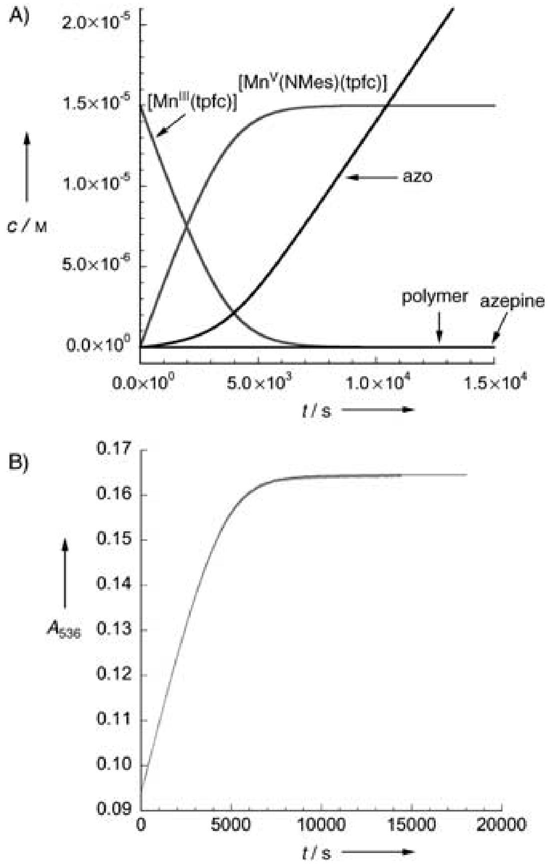


Figure 3. A) Time profiles simulated by the program KINSIM for the reaction of $[\mathrm{Mn^{III}(tpfc)}]$ with mesityl azide according to Scheme 2. Simulation conditions: $c_{[\mathrm{Mn^{III}(tpfc)}]} = 15\ \mu\mathrm{M}$, $c_{\mathrm{MesN_3}} = 5.3\ \mathrm{mM}$, $k_1 = 8.3\times10^{-7}\ \mathrm{s^{-1}}$, $k_{\mathrm{isc}} = 2.0\times10^{7}\ \mathrm{s^{-1}}$,[27] $k_r = 1.0\times10^{10}\ \mathrm{s^{-1}}$, $k_{-r} = 1.0\times10^{7}\ \mathrm{s^{-1}}$, $k_2 = k_d = 8.0\times10^{9}\ \mathrm{M^{-1}\,s^{-1}}$, $k_p = 2.0\times10^{6}\ \mathrm{M^{-1}\,s^{-1}}$. B) Simulated (gray) and experimental (black) data for the formation of $[\mathrm{Mn^V(NMes)(tpfc)}]$ from the reaction of 15 µM [Mn(tpfc)] and 5 mM mesityl azide.

for the reaction of a manganese corrole with aryl azides to give imido metal complexes. In this mechanism, the transition-metal complex captures a triplet nitrene formed by thermal or photochemical activation of the organic azide. The compelling evidence presented for this mechanism is 1) complex dependence of the kinetics on metal concentration with zeroth order over 30 % of the reaction), 2) the kinetics have been modeled successfully for the reaction mechanism described in Scheme 2, and 3) substituents in both *ortho* positions (Me or Cl, but not F) are required. Contrary to conventional wisdom that highly reducing metal complexes are needed for a reaction with organic azides, we have demonstrated that effective imido metal formation via nitrene capture does not require a highly reducing center. Investigations into harnessing this mechanistic paradigm for selective nitrene transfer under thermal or photochemical catalysis are in progress.

Experimental Section

Compounds were prepared and handled by standard vacuum-line and glove-box techniques. Toluene and acetonitrile were predried over molecular sieves and distilled over $\mathrm{CaH_2}$ prior to use. When required, solvents were deoxygenated by freeze/pump/thaw cycles. Deuterated solvents were purchased from Cambridge Isotopes and used without further purification. All other solvents and reagents were of reagent grade and used as received. The syntheses of $\mathrm{H_3(tpfc)}$,[28,29] [Mn(tpfc)],[30] $[\mathrm{Cr(tpfc)(py_2)}]$,[31] [Mn(tpfc)(NMes)][9] (Mes = 2,4,6-$\mathrm{(CH_3)_3C_6H_2}$), [Mn(tpfc)(NAr)][9] (Ar = 2,4,6-$\mathrm{Cl_3C_6H_2}$), [Mn(tpfc)(NAr′)][10] (Ar′ = 2,6-$\mathrm{Cl_2C_6H_3}$), [Cr(tpfc)(NMes)],[10] and [Cr(tpfc)(NAr)][10] followed previously described methods. All azides were prepared by using the Sandmeyer reaction or slight variations thereof.[7,8] Azo compounds were compared to authentic samples. Photolysis experiments were carried out with a Hanovia Model 673A-0360 550 W medium-pressure mercury arc lamp. Rate measurements were carried out by conventional UV/Vis spectroscopy on a Shimadzu UV-2501 spectrophotometer equipped with a temperature-controlled cell holder. Formation of $[\mathrm{Mn^V(NMes)(tpfc)}]$ was monitored at 536 nm, $c_{[\mathrm{Mn(tpfc)}]} = 15$ or 30 µM, and $c_{\mathrm{MesN_3}} = 2.0$–12.0 mM at (80 ± 0.2) °C.

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