Metalloradicals

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Kinetic Destabilization of Metal–Metal Single Bonds: Isolation of a Pentacoordinate Manganese(0) Monoradical

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Abstract: *The 17e$^-$ monoradical [Mn(CO)$_5$] is widely recognized as an unstable organometallic transient and is known to dimerize rapidly with the formation of a Mn−Mn single bond. As a result of this instability, isolable analogues of [Mn(CO)$_5$] have remained elusive. Herein, we show that two sterically encumbering isocyanide ligands can destabilize the Mn−Mn bond leading to the formation of the isolable, manganese(0) monoradical [Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (Ar^{Dipp2} = 2,6-(2,6-(iPr)$_2$C$_6$H$_3$)$_2$C$_6$H$_3$). The persistence of [Mn(CO)$_3$(CNAr^{Dipp2})$_2$] has allowed for new insights into nitrosoarene spin-trapping studies of [Mn(CO)$_5$].*

For decades, transiently generated 17e$^-$ monoradicals have occupied a central role in the development of atom-transfer and radical-mediated processes in organometallic chemistry.[1–3] A prototypical example of this class is the zerovalent manganese pentacarbonyl radical [Mn(CO)$_5$] which has been extensively investigated for its role in radical-type olefin hydrogenation,[4,5] as well as in the photolytic cleavage of the Mn−Mn bond of [Mn$_2$(CO)$_{10}$].[6] Despite these studies, [Mn(CO)$_5$] is well recognized as a highly unstable, organometallic transient, which rapidly dimerizes to [Mn$_2$(CO)$_{10}$] by Mn−Mn bond formation. Accordingly, this instability has necessitated that [Mn(CO)$_5$] be characterized and studied under cryogenic conditions,[7–10] or at higher temperatures by using either ultrafast spectroscopic[11] or nitrosoarene spin-trapping techniques.[12–14] Importantly, efforts to prepare stabilized variants of [Mn(CO)$_5$] by substitution of one or more CO ligands with more encumbering ligands such as phosphines (PR$_3$) have been shown to extend the lifetime of [MnL$_5$]-type radicals to the order of hours in solution.[15–18] However, such derivatized [Mn(CO)$_{5-n}$L$_n$] complexes have remained susceptible to facile dimerization/redistribution processes when concentrated and isolable examples remain unknown. Additionally, investigations into the one-electron activation chemistry of [Mn(CO)$_{5-n}$L$_n$] species with small molecule substrates are limited.[16,17]

Given the challenges faced in exploring the properties of [Mn(CO)$_5$] and related zerovalent [MnL$_5$] complexes, it is notable that they continue to be of significant interest as transient species. For example, [MnL$_5$] monoradicals of the type [Mn(CO)$_3$(bipy)] (bipy = 2,2′-bipyridine) are now recognized as the key intermediates on the pathway to catalyst deactivation (by Mn−Mn bond formation) in electrocatalytic CO$_2$ reduction.[19–21] Accordingly, successful strategies leading to the kinetic stabilization and isolation of such [MnL$_5$] monoradicals, while explicitly preventing the formation of the common Mn−Mn single-bond motif, are of importance in these processes. Furthermore, access to long-lived [MnL$_5$] monoradicals offers a potential avenue for the development of selective, well-defined metal-mediated one-electron transformations. Herein we describe the isolation, structure, and spectroscopic features of the neutral monoradical [Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (Ar^{Dipp2} = 2,6-(2,6-(iPr)$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) featuring two m-terphenyl isocyanide ligands.[22,23] The sterically encumbering nature of these isocyanide ligands effectively prevents the formation of Mn−Mn single bonds, thus rendering this 17e$^-$ radical both isolable in the solid state and persistent in solution. Additionally, as a result of the isolobal analogy between carbon monoxide (CO) and organoisocyanides (C≡NR),[22,24] [Mn(CO)$_3$(CNAr^{Dipp2})$_2$] is a precise electronic structure mimic of archetypical [Mn(CO)$_5$]. Most importantly, a survey of the chemistry accessible to [Mn(CO)$_3$(CNAr^{Dipp2})$_2$] has afforded new insights into classic spin-trapping experiments of [Mn(CO)$_5$] because of the ability to conveniently investigate a kinetically stabilized [MnL$_5$] monoradical under ambient conditions.

Monoradical [Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (**1**) can be generated by three independent synthetic routes. Oxidation of the sodium salt[25] Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] with 1.0 equivalent of thallium triflate (TlOTf; OTf = [O$_3$SCF$_3$]$^-$) leads to **1** with the loss of Tl metal and NaOTf, whereas comproportionation of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] and the triflate complex [Mn(OTf)(CO)$_3$(CNAr^{Dipp2})$_2$] delivers **1** with only NaOTf as a byproduct. Additionally, **1** can be obtained under photolytic conditions by irradiation of [Mn$_2$(CO)$_{10}$] in the presence of 4.0 equiv of CNAr^{Dipp2}. In all preparations, complex **1** is obtained as a dark-green crystalline solid that possesses limited solubility in alkane solvents, but is well solubilized in both ethereal and aromatic solvents. Of these three methods, comproportionation of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] and [Mn(OTf)(CO)$_3$(CNAr^{Dipp2})$_2$] delivers **1** most cleanly and in the highest yield after isolation (92 %; Figure 1 A). Upon isolation, **1** is stable for days in solution at elevated temperatures (C$_6$D$_6$, 80 °C) and shows no sign of dimerization and/or ligand redistribution when concentrated to a solid.

In both solution and the solid state, complex **1** possesses several spectroscopic and structural features consistent with a d^7 monoradical formulation. The ^{1}H NMR spectrum of **1** in C$_6$D$_6$ features broad, shifted resonance signals characteristic of a paramagnetic species, whereas determination of the

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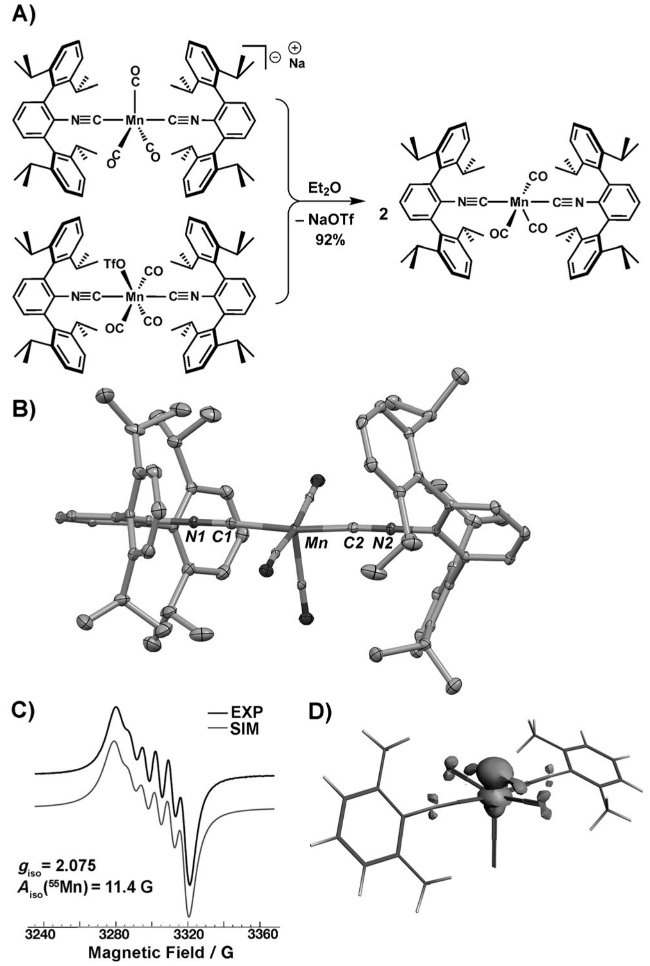


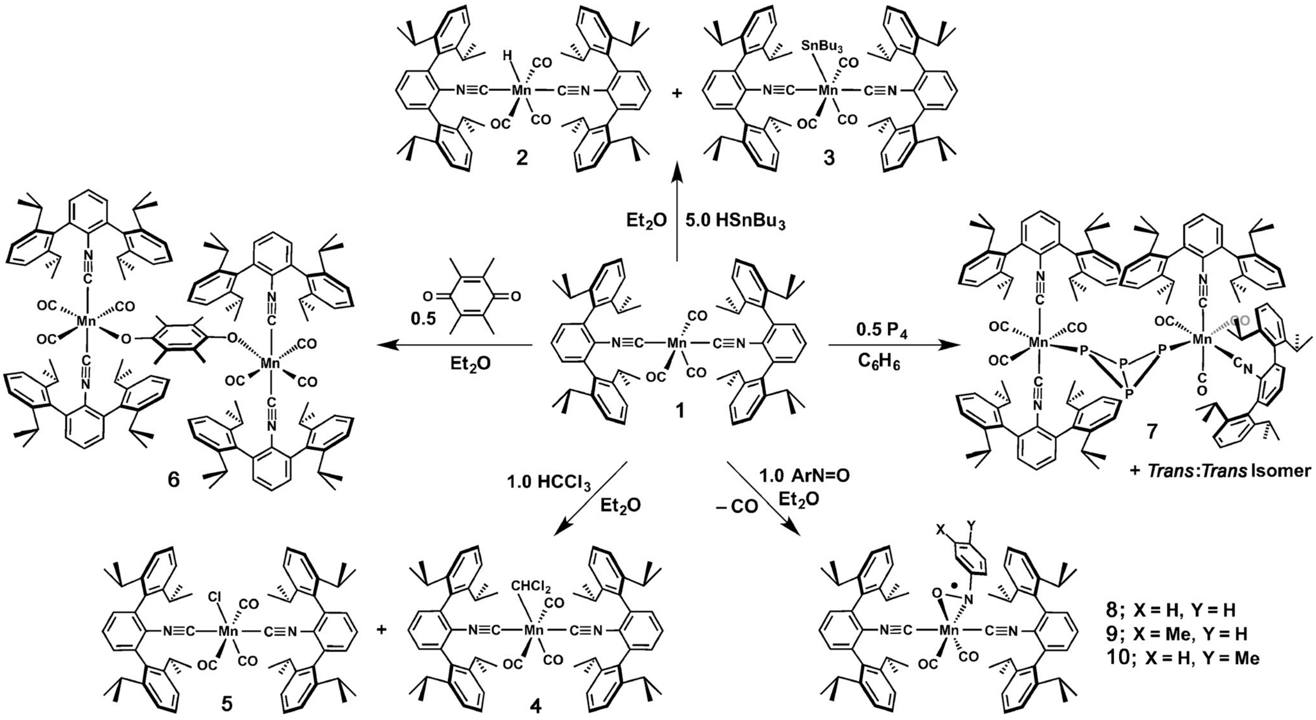
Figure 1. A) Synthesis and B) molecular structure of complex **1**. C) Experimental and simulated room temperature EPR spectrum of **1** in Et$_2$O. D) Spin density plot for the model complex [Mn(CO)$_3$(CNXyl)$_2$].

magnetic moment using the Evans method (C$_6$D$_6$, 20 °C) revealed a μ_{eff} value of 1.89($\pm$0.04) μ_B, indicative of an $S = \frac{1}{2}$ ground state. The room temperature EPR spectrum of **1** (Figure 1 C) supports this assignment and shows a well-resolved six line pattern consistent with a single unpaired electron within a ^{55}Mn $I = 5/2$ spin environment. Importantly, the isotropic g and Mn hyperfine coupling values of $g_{\mathrm{iso}} = 2.075$ and $A_{\mathrm{iso}}(^{55}\mathrm{Mn}) = 11.4$ G are similar to those determined for persistent, but non-isolable, [Mn(CO)$_3$(PR$_3$)$_2$] complexes[15,18] and accordingly reflect the presence of a low-spin, zerovalent Mn center. Additionally, the IR spectrum (C$_6$D$_6$) of **1** features a ν_{CN} band centered at 2048 cm^{-1}. This band is located at an intermediate energy relative to the formally Mn$^{\mathrm{I}}$ and Mn$^{-\mathrm{I}}$ complexes [Mn(OTf)(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$] (2131 cm^{-1}) and Na[Mn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$] (1910 cm^{-1}),[25] respectively, and is likewise indicative of a zerovalent Mn center.

Single crystals of [Mn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$] (**1**) were reproducibly obtained by crystallization from a layered Et$_2$O/*n*-pentane mixture at −35 °C. In the solid state, **1** adopts a square-pyramidal coordination geometry (Addison-Reedijk τ_5 geometry index[26] = 0.03) with *trans*-spanning CNAr$^{\mathrm{Dipp2}}$ ligands within the equatorial plane (Figure 1 B). This geometry is consistent with a $e(\mathrm{xz,yz})^4 b_2(\mathrm{xy})^2 a_1(\mathrm{z}^2)^1 b_1(\mathrm{x}^2\text{-}\mathrm{y}^2)^0$ d orbital splitting pattern in idealized C_{4v} symmetry, as has been proposed for the ground-state geometry and electronic configuration of the d^7 monoradical [Mn(CO)$_5$].[27] Additionally, the molecular structure of **1** has an average C-Mn-C angle between the axial carbonyl and the basal-plane ligands of 96.4($\pm$2.7)°. This structural property is in excellent agreement with the axial/basal-plane angle of 98° predicted by Hoffmann and Elian for the C_{4v}-symmetric d^7 monoradical [Mn(CO)$_5$], and occurs to maximize π-backbonding interactions between the partially occupied Mn d$_{z^2}$ orbital and the basal-plane ligands.[27] Indeed, a DFT-derived spin-density plot for the model complex [Mn(CO)$_3$(CNXyl)$_2$] (Xyl = 2,6-Me$_2$C$_6$H$_3$) is fully consistent with this prediction and shows that spin density is located predominantly on the Mn center, but is also distributed over the out-of-plane π* orbitals of the basal CO and isocyanide ligands (Figure 1 D). Additionally, it is important to note that [Mn(CO)$_5$] isolated in a CO matrix at 20 K has also been determined to possess an axial/basal-plane angle of 96($\pm$3)° by IR spectroscopy.[10] Accordingly, the spectroscopic and structural features of **1** render it a precise electronic structure analogue to the highly unstable [Mn(CO)$_5$] monoradical.

In addition to serving as an electronic structure model, monoradical **1** mimics the major reactivity patterns established for [Mn(CO)$_5$]. For example, **1** engages in hydrogen-atom abstraction reactions with substrates possessing weak H−E bonds. Treatment of **1** with an excess (> 10 equiv) of HSnBu$_3$ or stoichiometric H$_2$SnPh$_2$ in benzene solution readily affords the monohydride complex [HMn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$] (**2**).[25] However, when **1** is exposed to lower concentrations of HSnBu$_3$ ($\leq$ 5.0 equiv), an equimolar mixture of **2** and the stannyl complex [(Bu$_3$Sn)Mn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$] (**3**) is obtained (Scheme 1). This product distribution indicates that **1** is a highly efficient radical scavenger and intercepts the tri-*n*-butyltin radical at a rate competitive with dimerization to form [Bu$_3$Sn−SnBu$_3$].[28] Similarly, **1** reacts with chloroform (1.0 equiv) in Et$_2$O solution to produce a 1:1 mixture of the dichloromethyl complex [(Cl$_2$HC)Mn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$] (**4**) and the chloride complex [ClMn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$] (**5**), again indicating a competency for both atom-abstraction and radical-scavenger reactivity pathways.

Two molecules of **1** can also cooperatively effect the 2e$^-$ reduction of certain substrates. As shown in Scheme 1, treatment of **1** with tetramethylbenzoquinone (0.5 equiv) gives rise to reductive aromatization and the formation of the diamagnetic, aryloxide-bridged dimer [(μ_2-κ^1:κ^1-OC$_6$Me$_4$O)-{Mn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$}$_2$] (**6**), as determined by ^{1}H NMR spectroscopy and X-ray diffraction. Additionally, **1** reacts quantitatively with P$_4$ (0.5 equiv) at room temperature to produce the P$_4$-butterfly-bridged complex [(μ_2-η^1:η^1-P$_4$){Mn(CO)$_3$(CNAr$^{\mathrm{Dipp2}}$)$_2$}$_2$] (**7**; Scheme 1 and Figure 2 A).[29] Whereas the μ_2-η^1:η^1-P$_4$ butterfly motif is a common structural outcome from the reaction of main-group radicals and anions with P$_4$,[30] it is very rarely observed during the activation of white phosphorus by transition-metal complexes.[31–34]



Scheme 1. The reactivity of complex **1**.

Accordingly, the stability of $17e^-$ **1** in solution, coupled with the sterically encumbering *m*-terphenyl ancillary groups, allows for the selective radical-type,[33] transition-metal-based activation of P_4 under ambient conditions.

The well-defined and persistent nature of **1** has also allowed for a survey of its reactivity toward nitrosoarenes (ArN=O). These reactions can be viewed as a model system for nitrosoarene spin-trapping studies of $[Mn(CO)_5]$, which provided some of the earliest EPR evidence for the formation of $[Mn(CO)_5]$ radicals in fluid solution.[12–14] It is generally accepted that $[Mn(CO)_5]$ reacts with nitrosoarenes to form simple κ^1-*N* nitroxide–radical spin adducts (that is, $[(\kappa^1\text{-}N\text{-}ArNO)\{Mn(CO)_5\}]$), which give rise to *g* values near that of the free electron (2.002), indicative of NO π^*-system-centered radicals. However, like $[Mn(CO)_5]$ itself, these nitroxide spin adducts are not amenable to isolation and their characterization is limited to EPR spectroscopic detection at temperatures near −30 °C.[12–14] It is therefore significant that treatment of **1** with 1.0 equiv of nitrosobenzene (PhNO) in thawing Et_2O solution produces the η^2-*N*,*O* phenylnitroxide radical complex $[(\eta^2\text{-}N,O\text{-PhNO})Mn(CO)_2(CNAr^{Dipp2})_2]$ (**8**) with loss of one CO ligand as determined by X-ray diffraction (Scheme 1; Figure 2B). Furthermore, this outcome is not limited to nitrosobenzene, as treatment of **1** with either *m*-nitrosotoluene (*m*-TolNO) or *p*-nitrosotoluene (*p*-TolNO) results in the formation of complexes $[(\eta^2\text{-}N,O\text{-}m\text{-TolNO})Mn(CO)_2(CNAr^{Dipp2})_2]$ (**9**) and $[(\eta^2\text{-}N,O\text{-}p\text{-TolNO})Mn(CO)_2(CNAr^{Dipp2})_2]$ (**10**), respectively, with loss of CO.

The structural and spectroscopic features of complexes **8**–**10** are strongly reflective of the presence of η^2-coordinated arylnitroxide radical ligands $[ArNO]^{1-\bullet}$. In the solid state, complexes **8**–**10** feature N−O bond lengths of 1.264(10) Å, 1.284(9) Å, and 1.320(2) Å, respectively, and show a marginal lengthening in response to the inductive properties of the ArNO aryl substituent. However, these bond lengths are all intermediate in value between those typical for NO double (circa 1.19 Å) and single bonds (circa 1.45 Å),[35] and thus provide strong support for a formal NO bond order of 1.5. Additionally, the nitroxide aryl groups in complexes **8**–**10** adopt an in-plane orientation relative to the Mn center (Figure 2B). This feature contrasts distinctly with structurally characterized η^2-*N*,*O* nitrosoarene complexes (such as metalloxaziridines),[36] in which the aryl groups adopt a perpendicular orientation relative to the metal center on account of in-plane $M\rightarrow\pi^*(NO)$ backbonding. Accordingly, the solid-state structures of complexes **8**–**10** strongly suggest that the η^2-ArNO ligands do not bind according to the standard Dewar–Chatt–Duncanson model of $M\rightarrow L$ π backbonding. Rather, the structural properties of **8**–**10** indicate that the η^2-ArNO ligands function as L_2–type, not X_2–type, donors,[37] with an unpaired electron localized in a NO π^* orbital oriented perpendicular to the plane of the Mn center. The room-temperature EPR spectra of complexes **8**–**10** in toluene solution support this description and give rise to g_{iso} values of 2.004, 2.008, and 2.005, respectively, indicative of organic radicals (see Figure 2C for the EPR spectrum of **8** and Figures S2.3 and S2.4 for the spectra of **9** and **10**, respectively). Notably, while persistent nitroxide radical complexes are uncommon, structurally characterized examples exhibiting κ^1-*N*,[36,38,39] κ^1-*O*,[40] and bridging μ-$(1\kappa^1\text{-}N{:}2\kappa^1\text{-}O)$[41] coordination modes have been reported. However, complexes **8**–**10** are unique examples of side-on bound η^2-*N*,*O* nitroxide radicals.

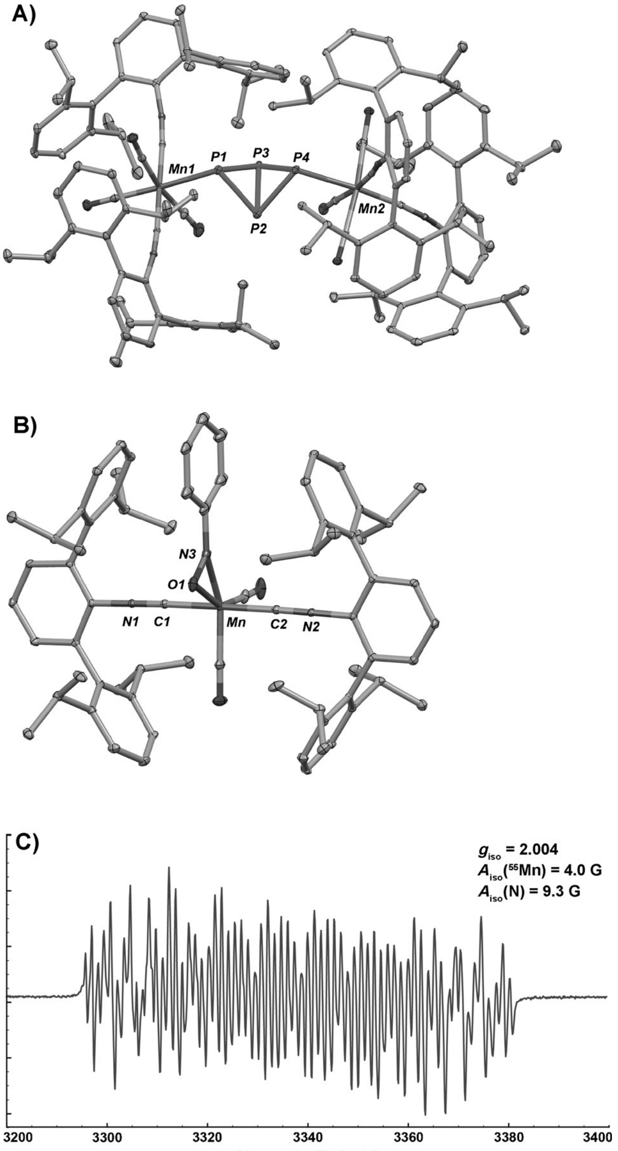


Figure 2. Molecular structures of A) dimer **7** and B) complex **8**. C) Room temperature EPR spectrum of **8** in toluene.

Although it appears that monoradical **1** and transiently generated [$Mn(CO)_5$] display divergent reactivities toward nitrosoarenes, it is important to note that ^{1}H NMR and IR spectroscopy indicated that the formation of complexes **8**–**10** is complete upon mixing. Furthermore, intermediate species indicative of a κ^1-*N* nitroxide radical complex are not detected during these transformations at temperatures as low as −35 °C. To this end, DFT calculations for the conversion of the putative κ^1-*N* nitroxide radical complex [(κ^1-*N*-PhNO)$Mn(CO)_3(CNXyl)_2$] into [(η^2-*N*,*O*-PhNO)$Mn(CO)_2(CNXyl)_2$] and free CO reveal that the process is enthalpically disfavored by 10.2 $kcal\,mol^{-1}$. Similarly, the calculated conversion of [(κ^1-*N*-PhNO)$Mn(CO)_5$] to [(η^2-*N*,*O*-PhNO)$Mn(CO)_4$] and CO is enthalpically disfavored by 5.9 $kcal\,mol^{-1}$.

Based on these results, the formation of complexes **8**–**10** likely arises from a strong kinetic *cis*-CO labilizing effect[42] by an unobserved κ^1-*N*-coodinated arylnitroxide radical (that is, [(κ^1-*N*-ArNO)$Mn(CO)_3(CNAr^{Dipp2})_2$]). Indeed, κ^1-*N* arylnitroxide ligands are expected to exhibit weak σ- and strong π-donor capacity and therefore function as efficient *cis*-labilizing ligands in six-coordinate [$XMnL_5$] complexes.[42–44] However, as the π-acidity properties of isocyanides are known to match those of CO with respect to *cis*-labilizing ability,[43] substitution of isocyanide for CO on the Mn center should not dramatically affect reaction outcomes. Therefore, it is plausible that [(η^2-*N*,*O*-ArNO)$Mn(CO)_4$], rather than [(κ^1-*N*-PhNO)$Mn(CO)_5$], species may more accurately reflect the results of [$Mn(CO)_5$] spin-trapping studies.[12–14] This notion is further supported by the fact that complexes **8**–**10** give rise to Mn and N hyperfine coupling constants (A_{iso}(Mn) ≈ 4.0 G; A_{iso}(N) ≈ 9.0 G) that are markedly similar to those measured during nitrosoarene spin-trapping studies of [$Mn(CO)_5$].[12–14]

This suggestion highlights an important aspect of the ability to isolate monoradical **1** and explore its behavior in a well-defined manner. As the transient nature of [$Mn(CO)_5$] and other organometallic monoradicals has most often precluded systematic studies of their reactivity properties, variants that are kinetically stabilized in both solution and the solid state can be employed to further develop selective transformations. Just as importantly, kinetic stabilization in the manner exhibited by **1** can afford a more detailed assessment of reaction outcomes in such transformations.

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