Manganese(I) Complex with Monodentate Arylisocyanide Ligands Shows Photodissociation Instead of Luminescence

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ABSTRACT: Recently reported manganese(I) complexes with chelating arylisocyanide ligands exhibit luminescent metal-to-ligand charge-transfer (MLCT) excited states, similar to ruthenium(II) polypyridine complexes with the same d6 valence electron configuration used for many different applications in photophysics and photochemistry. However, chelating arylisocyanide ligands require substantial synthetic effort, and therefore it seemed attractive to explore the possibility of using more readily accessible monodentate arylisocyanides instead. Here, we synthesized the new Mn(I) complex [Mn(CNdippPhOMe2)6]PF6 with the known ligand CNdippPhOMe2 = 4-(3,5-dimethoxyphenyl)-2,6-diisopropylphenylisocyanide. This complex was investigated by NMR spectroscopy, single-crystal structure analysis, high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) measurements, IR spectroscopy supported by density functional theory (DFT) calculations, cyclic voltammetry, and time-resolved as well as steady-state UV–vis absorption spectroscopy. The key finding is that the new Mn(I) complex is nonluminescent and instead undergoes arylisocyanide ligand loss during continuous visible laser irradiation into ligand-centered and charge-transfer absorption bands, presumably owed to the population of dissociative d–d excited states. Thus, it seems that chelating bi- or tridentate binding motifs are essential for obtaining emissive MLCT excited states in manganese(I) arylisocyanides. Our work contributes to understanding the basic properties of photoactive first-row transition metal complexes and could help advance the search for alternatives to precious metal-based luminophores, photocatalysts, and sensors.

1. INTRODUCTION

Metal-to-ligand charge-transfer (MLCT) excited states play a key role in many coordination complexes and organometallic compounds because they enable a range of different applications in photophysics and photochemistry. Precious and rare elements such as ruthenium(II),1–5 osmium(II),6–10 rhenium(I),11–19 or iridium(III)20,21 in polypyridine or cyclometalating coordination environments often feature a long-lived MLCT excited state,22,23 whereas among first-row d6 transition metal elements, this is yet a very rare occurrence. Iron(II) is by far most investigated in this regard,29–45 yet only a handful of iron(II) complexes with MLCT lifetimes in the nanosecond time regime are known.29,30,42 Building on early reports of hexakis(arylisocyanide) manganese(I) complexes with a focus on UV–vis absorption and electrochemical properties,46–53 we recently discovered that manganese(I) complexes with chelating bi- and tridentate ligands have luminescent and photoredox active MLCT states.54 Until now, the synthesis of these chelates has remained laborious,55 and therefore it seemed attractive to explore the possibility of using more directly accessible monodentate arylisocyanides for manganese(I) complexes with luminescent MLCT states. Recently, there has been increased interest in first-row transition metal elements, partly because they are cheaper and more abundant than the traditionally used metals from the platinum group,56 and because they seem to offer ample opportunities for groundbreaking discoveries.57–60 Advances in ligand design, photophysical techniques, and theoretical understanding61 have made an unexpectedly broad range of transition metals in different oxidation states useable for photophysical or photochemical applications. In particular, luminescent first-row transition metal complexes with V,62–65 Cr,66–74 Mn,75–77 Fe,78–82 Co,83,84 Ni,85–88 and Cu89–98 with different types of electronically excited states featuring promising photoreactivity and photoluminescence behavior have been discovered recently.57,58,60,99,100

As early as 1977, Mann, Gray, and Hammond reported on tungsten(0) arylisocyanide complexes that showed MLCT...
luminescence in solution at room temperature. More recently, the GRAY group revisited this topic and discovered a whole range of $[\text{W(CNAr}_{	ext{yl}})]_{6}$ complexes with outstanding photoluminescence properties and very strong photoreducing behavior with applications in catalysis. In addition to disopropyl substituents at the ortho-position to the ligating isocyanide functional group, the attachment of further phenyl rings at the para-position proved valuable to enhance the chemical stability and the photophysical properties of this compound class, for example in $[\text{W}-(\text{CNdippPhOMe}_{2})_{6}]$ (CNdippPhOMe$_2$ = 4-(3,5-dimethoxyphenyl)-2,6-disoproplyphenylisocyanide). This specific tungsten(0) complex featured a high photoluminescence quantum yield (0.42) paired with a long MLCT lifetime (1.65 μs in toluene at room temperature), hence our interest in this particular ligand for manganese(II).

In the recent past, other oxidation states of manganese received attention in the context of photoluminescence; for instance, many manganese(II) compounds are known to emit in the solid state. Furthermore, a bis-(tris(carbene)borate) manganese(IV) complex featured dual luminescence from LMCT (ligand-to-metal charge-transfer) and metal-centered (MC) excited states. At present, the photophysical properties of manganese(II) isocyanide complexes seems underexplored yet, particularly in comparison to isoelectronic iron(II) polypyridines. 34,38 −3c,150 the basis def2-mSVP(C,H,N,O)150 and def2-mTZVP(Mn)151 more than twice higher than the solubility in water at room temperature and seems incorrect.

Elemental analyses were performed using a vario MICRO cube CHN element analyzer from Elementar. Samples were burned in sealed tin containers using a stream of oxygen.

High-resolution ESI mass spectra were recorded on a Bruker maXis 4G ESI-Q-TOF spectrometer under direct injection conditions with CH$_3$CN as a solvent.

IR spectra were recorded on a Shimadzu IRTracer-100 with QATR 10 spectrometer. Signal intensities are marked as vs (very strong), s (strong), m (medium), w (weak), br (broad), and vw (very weak).

X-ray powder diffraction (XRPD) measurements were performed with a STOE STADI P diffractometer with a microfocused Cu Kα radiation source ($\lambda = 1.542\AA$) equipped with a Dectris Mythen 1K detector.

Cyclic voltammetry was performed using a Versastat4-200 potentiostat from Princeton Applied Research in a glovebox. A glassy carbon disk electrode served as a working electrode, and two silver wires served as counter and pseudo-reference electrodes. Ferrocene was added as an internal reference ($E_{1/2}$ vs saturated calomel electrode (SCE) in dichloromethane (DCM) = 0.475 V). The solvent was dry and deaerated CH$_2$Cl$_2$ with 0.1 M TBAPF$_6$ (tetra-n-butylammonium hexafluorophosphate) as an electrolyte. Potential sweep rates were otherwise stated, 100 mV s$^{-1}$.

All photophysical measurements were performed, unless otherwise stated, under an Ar atmosphere in either Schlenk or screw cap cuvette with dry and argon-saturated solvents (CH$_3$CN and CH$_2$Cl$_2$).

UV/vis absorption spectroscopy was performed using a Cary 5000 instrument from Varian.

For photostability experiments, a Flame UV/vis spectrometer system from Ocean optics was used with a continuous-wave (cw) laser from Roithner Lasertechnik emitting at 405 nm (optical output up to 375 mA and 526 mW, circular beam dimension with a diameter of 2.5 mm) and a cw-laser emitting at 447 nm (optical output up to 1050 mA and 1.1 W, rectangular beam dimension with a diameter of 2 × 5 mm$^2$). Spectroscopic experiments with that cw-laser as a light source were carried out at 293 K using self-built cuvette holders allowing temperature control and stirring of the solution with a small magnetic stir bar. Photochemical processes involving free radicals and triplet-excited states are usually sensitive to dissolved oxygen. Therefore, oxygen was removed by saturating the solution with argon (for 5 min) before the measurements.

2.2. Single-Crystal X-ray Structure Analysis. $[\text{Mn}-(\text{CNdippPhOMe}_{2})_{6}]PF_6$ was recrystallized from DCM and cyclohexane at room temperature. Single yellow block-shaped crystals were obtained after a few days. A suitable crystal with dimensions 0.20 × 0.16 × 0.12 mm$^3$ was selected, and the crystal was mounted on a mylar loop in perfluoroether oil on a Cu-Stoe diffractometer. The crystal was kept at a steady $T = 150 K$ during data collection. The structure was solved with the olex2.solve 1.2.136 solution program using iterative methods and using olex2.1.5.139 as the graphical interface. The model was refined with ShelXL 2018/3 140 using full-matrix least-squares minimization on F2.

Crystallographic drawings were made with the software packages Mercury141,142 and CRYSTALVIEW.143 Selected crystal data and details of the structure determinations are presented in Tables S1 and S2.

To confirm the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif/.

2.3. Density Functional Theory (DFT) Calculations. All calculations were carried out for the gas phase using the ORCA 4.1.2 package.147−149 Geometry optimization and the calculation of infrared modes were performed with the composite approach PBEPBE3c,150 the basis def2-mSVP(CH$_2$H$_{10}$) and def2-mTZVP(Mn)151 with the atom pairwise dispersion correction with the Becke−Johnson damping scheme (D3BJ)152,153 the geometrical counterpoise correction gCP,154 the RJCOSX approximation, the auxiliary basis def2−SVP,155 fine numerical integration grids (gridS, gridX7, and NoFinalGrid in ORCA 4 nomenclature), and KDIIS+SOSCF. The
Scheme 1. Synthesis of $[\text{Mn(CNdippPhOMe}_2]_{6}\text{PF}_6$
molecules in CH3CN exhibit the expected mass peak for \([M - PF_6]^-\) as well as the mass peaks for \([M - PF_6 - L + CH_3CN]^+\) and \([M - PF_6 - L + CO]^+\) (Figure S8 and Table S3). Over time, the solution stored under ambient conditions and ambient light becomes intensely yellow colored, and measurements performed after a few days exhibit the mass peaks for \([M - PF_6 - L + CH_3CN]^+\), \([M - PF_6 - 2L + 2CH_3CN]^+\), \([M - PF_6 - 3L + 2O]^+\), and \([M - PF_6 - 4L + 2O]^+\), along with some additional minor mass peaks (Figure S9 and Table S3). Evidently, ligand exchange occurs in coordinating CH3CN solvent over time, and furthermore, the presence of oxygen seems to be detrimental.

In the $^1$H NMR spectrum of \([Mn(CNdippPh^{OMe2})_6]PF_6\) in CD$_2$Cl$_2$ (Figures S2 and S3), the coordinating C-atoms of the aromatic isocyanide ligands appear between 170 and 185 ppm in the form of a multiple, likely reflecting an overlay of $^{55}$Mn resonance at -1382 ppm with a linewidth of 42 Hz in the 55Mn NMR spectrum in CD$_2$Cl$_2$ (Figure S6) exhibits a remarkably sharp resonance at -1390 ppm with a linewidth (fwhh) of only 69 Hz, in line with an almost perfect $D_h$ symmetry of the primary coordination sphere around Mn. The observable chemical shift is in the expected range for Mn(I) between -1000 ppm and -1500 ppm and thus confirms the +I oxidation state. This signal is not changing over a few hours in CD$_2$Cl$_2$ at 298 K in the dark, hence ligand exchange is evidently slower in this solvent than in CH$_3$CN. The chemical shift observed for \([Mn(CNdippPh^{OMe2})_6]^+\) (-1390 ppm) lies between the values found for our two previously investigated manganese(I) complexes with chelating arylisocyanides, which featured $^{55}$Mn resonances at -1225 and -1419 ppm, suggesting that the new complex has an electron density at Mn(I) somewhere in between the two previously studied related compounds. More striking is the very large difference in linewidth associated with the $^{55}$Mn resonances, which is only 69 Hz for \([Mn(CNdippPh^{OMe2})_6]^+\) but amounts to 2100 Hz and 5900 Hz in the previously studied chelate complexes, and this reflects the higher symmetry of the new Mn(I) complex with monodentate arylisocyanide ligands. Furthermore, this finding of a relatively narrow $^{55}$Mn resonance bandwidth is similar to the abovementioned other Mn(I) complexes with monodentate arylisocyanide ligands of the type \([Mn(CNR)X]_n\) BF$_4$. For example, \([Mn(CNR)_2]BF_4\) featured its $^{55}$Mn resonance at -1382 ppm with a linewidth of 42 Hz in CH$_3$CN at 298 K.

An additional resonance at -1387 ppm is observable in the $^{55}$Mn NMR spectrum of \([Mn(CNdippPh^{OMe2})_6]PF_6\) (Figure S6), but its integral is more than 10 times lower than that of the main resonance at -1389 ppm. We tentatively attribute the minor resonance at -1387 ppm to \([Mn(CO)\cdot(CNdippPh^{OMe2})_5]PF_6\), the mass peak of which is furthermore observable in the high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) measurements.

The compound \([Mn(CNdippPh^{OMe2})_6]PF_6\) crystallizes in the P$ar{i}$ space group with Z = 1 molecule in the unit cell. The obtained crystal structure contains 0.8 water and 2 cyclohexane molecules per formula unit. The asymmetric unit consists of the manganese cation, three CNdippPh$^{OMe2}$ ligands, and the PF$_6$$^-\$ anion. The Mn(I) cation is coordinated by six neutral CNdippPh$^{OMe2}$ ligands (Figure 1). The Mn–C bond distances are between 1.878(8) and 1.881(7) Å at 150 K (Table S2).

The slightly distorted octahedral geometry is evident from the small differences in Mn–C bond lengths and the small deviations in the C–Mn–C bond angles from 90° (Table S2). For a more quantitative analysis of the deviation from perfect octahedral symmetry, we employed the $\Sigma$ and $\Theta$ parameters, where $\Sigma$ is a general measure for the deviation from ideal octahedral geometry and $\Theta$ quantifies the distortion from an octahedral toward a trigonal prismatic structure (eq S1 and Table S2).

A perfectly octahedral complex would give $\Sigma = 0$. From the crystal structure of \([Mn(CNdippPh^{OMe2})_6]PF_6\), we obtain $\Sigma = 22.55°$ and $\Theta = 58.37°$, relatively close to $D_h$ symmetry. For reference, the $\Sigma$ and $\Theta$ parameters of \([Mn(CNPh)_6]I_3\) compound has $\Sigma = 25.84°$ and $\Theta = 65.51°$ (Table S2). Furthermore, the structure of \([Mn(CNdippPh^{OMe2})_6]PF_6\) is also somewhat less distorted than the analogous W(0) complex \([W(CNdippPh^{OMe2})_6]\) ($\Sigma = 26.52°$ and $\Theta = 66.33°$, Table S2).

The DFT geometry optimization of \([Mn(CNdippPh^{OMe2})_6]PF_6\) (PBEh-3c/def2-mSVP(C,H,N,O)/def2-mTZV(Pn)) yields similar Mn–C bond lengths as the X-ray crystal structure (Table S2). Furthermore, the DFT-optimized geometry features a similar deviation from ideal octahedral geometry as the X-ray crystal structure (\(\Sigma = 20.83°\) and \(\Theta = 56.41°\), Table S2).

\([Mn(CNdippPh^{OMe2})_6]PF_6\) can be isolated as a yellow crystalline powder by filtration and subsequent drying under air. Not surprisingly, the experimental XRPD pattern of that complex and the free ligand were pattern based on the single-crystal structure (Figure S7), due to the loss of crystal solvents during filtration and air drying. Combustion analysis of the crystalline yellow powder confirms that it is solvent-free.

3.2. Vibrational Spectroscopy and DFT Analysis. Infrared spectra of the complex and the free ligand were measured in the range of 400–3500 cm$^{-1}$ (Figure 2). The C= N stretching frequency (\(\nu(C=N)\) of isocyanides is usually

![Figure 1. Crystal structure of \([Mn(CNdippPh^{OMe2})_6]PF_6\). Hydrogen atoms and solvents (H$_2$O and cyclohexane) are omitted for clarity. Color Code: C (gray), O (red), N (blue), Mn (purple), F (green), and P (orange).](https://doi.org/10.1021/acs.inorgchem.2c01438)
strongly influenced by the metal coordination,\textsuperscript{47,53,54,158,165–180} and this is also the case here. In the IR spectrum of the free ligand, $\nu$(C$\equiv$N) is observed at 2116 cm$^{-1}$, which is nearly the same for the analogous W-complex (2115 cm$^{-1}$), whereas in the complex [Mn(CNdippPhOMe$_2$)$_6$]PF$_6$, it is shifted to 2070 cm$^{-1}$, due to $\pi$-backbonding from the metal center to the $\pi^*$ antibonding orbital of the isocyanide moiety. Furthermore, the respective IR band is significantly broader in the complex than in the free ligand, presumably due to the somewhat distorted octahedral coordination geometry resulting in slightly different metal–ligand bond lengths and angles (Table S2), and consequently to a continuum of slightly differing vibrational frequencies (see below). Another explanation for the broadening could be the fact that the symmetry of the vibrational band in the complex is $T_{1u}$, whereas in the free ligand the symmetry is simply A. Two prominent IR bands at 586 and 789 cm$^{-1}$ appearing in the spectrum of the complex but not in the free ligand are tentatively attributed to Mn(I)-C vibrational modes, in analogy to a recently explored isoelectronic Cr(0) arylisocyanide complex, where the Cr(0)–C vibration appeared at 590 cm$^{-1}$\textsuperscript{67}.

For an ideal octahedral complex of the type [Mn–(C$\equiv$–N–C(Ar))$_6$], six IR-active $T_{1u}$ modes are expected ($\nu$(C$\equiv$N), $\nu$(Mn–C), $\nu$(N–C(Ar)), $\delta$(Mn–C$\equiv$N), $\delta$(C–Mn–C), and $\delta$(C$\equiv$N–C(Ar))).\textsuperscript{179} The infrared spectrum was analyzed only in terms of [Mn–(C$\equiv$N)] core vibrations (Table 1). The core vibrations of [Mn(CNdippPhOMe$_2$)$_6$]\textsuperscript{+} were obtained from DFT calculations (PBEh-3c/def2-mSVP(C,H,N,O)/def2-mTZVP(Mn)) (Figures S11–S14) and compared with the

![Figure 2. Solid-state ATR-IR spectra of the compound [Mn(CNdippPhOMe$_2$)$_6$]PF$_6$ (top) and the free ligand (4) (bottom). The red marked frequencies of the complex are assigned in Table 1.](https://doi.org/10.1021/acs.inorgchem.2c01438)

Table 1. Selected Infrared Vibrational Frequencies for [Mn(CNdippPhOMe$_2$)$_6$]PF$_6$ (Red Marked Frequencies in Figure 2) in Comparison with DFT Calculated Frequencies (PBEh-3c/def2-mSVP(C,H,N,O)/def2-mTZVP(Mn))\textsuperscript{a} Scaled by a Factor of 0.95

| complex                  | mode               | IR$_{exp}$ (cm$^{-1}$) | IR$_{DFT}$ (cm$^{-1}$) |
|--------------------------|--------------------|------------------------|-------------------------|
| [Mn(CNdippPhOMe$_2$)$_6$]PF$_6$ | $\nu$(C$\equiv$N) $T_{1u}$ | 2070                   | 2176 (2973), 2181 (2863), 2184 (1231) and 2184 (2134)\textsuperscript{d} |
|                          | $\nu$(C$\equiv$N) $E_g$     |                        | 2184 (1231),\textsuperscript{d} 2184 (2134)\textsuperscript{d} and 2188 (218) |
|                          | $\nu$(C$\equiv$N) $A_{ig}$     |                        | 2261 (1.07) |
|                          | $\nu$(Mn–C) $T_{1u}$ | 834                    | 789.72 (118), 789.77 (121) and 790.38 (118) |
|                          | $\nu$(Mn–C) $E_g$     | 789                    | 792.46 (0.29) and 792.70 (1.66) |
|                          | $\nu$(Mn–C) $A_{ig}$     | 789                    | 793.12 (0.71) |
|                          | $\delta$(C–Mn–C) and $\delta$(Mn–C$\equiv$N) $T_{1u}$ | 586                    | 599.57 (99), 601.19 (169), 608.21 (41), 610.13 (168), 613.87 (91) and 618.43 (131) |
| [Mn(L$^i$)$_2$]PF$_6$\textsuperscript{47} | $\nu$(C$\equiv$N) $T_{1u}$ | 2081                   | 2083 (vs) |
|                          | Mn–C                 |                        | 584 |
| [Mn(L$^i$)$_3$]PF$_6$\textsuperscript{47} | $\nu$(C$\equiv$N) $T_{1u}$ | 2064                   | 2088 (vs) |
|                          | Mn–C                 |                        | 568 |
| [Mn(CNPh)$_2$]PF$_6$\textsuperscript{47} | $\nu$(C$\equiv$N) $T_{1u}$ | 2088 (vs)              | 2088 (vs) |
|                          | $\nu$(C$\equiv$N) $E_g$     | 2088 (vs)              | 840 (m) |
| [Mn(CNPh)$_3$]Cl$^+$\textsuperscript{53} | $\nu$(C$\equiv$N) $T_{1u}$ | 2084                   | 2084 |
| [Mn(CNPh)$_3$]BF$_4$\textsuperscript{175} | $\nu$(C$\equiv$N) $T_{1u}$ | 2084                   | 2085 (vs) and 1993 (sh) |
| [Mn(CNPh)$_4$]I$^-$\textsuperscript{179} | $\nu$(C$\equiv$N) $T_{1u}$ | 2085 (vs) and 1993 (sh) | 1210 |
|                          | $\nu$(N(isocyanide)-C(phenyl)) $T_{1u}$ | 2085 (vs) and 1993 (sh) | 2085 (vs) and 1993 (sh) |
|                          | $\delta$(Mn–C$\equiv$N) $T_{1u}$ | 600 (vs)              | 600 (vs) |
|                          | $\delta$(Mn–C) $T_{1u}$ | 600 (vs)              | 600 (vs) |
|                          | (multiplet)\textsuperscript{i} |                        | 297 and 319 |
|                          | $\delta$(C–Mn–C) $T_{1u}$ | 113 (w)               | 113 (w) |

\textsuperscript{a}The intensities of the vibrational frequencies obtained from DFT calculations (PBEh-3c/def2-mSVP(C,H,N,O)/def2-mTZVP(Mn)) are indicated in parentheses. (Abbreviations: bend., bending; str., stretching; ip, in-plane). \textsuperscript{b}IR data from previously reported comparable compounds are included for comparison. \textsuperscript{c}of the solid state. \textsuperscript{d}One $T_{1u}$ and $E_g$ modes are mixed together at 2184 cm$^{-1}$ leading to two IR observable modes. \textsuperscript{e}L$^i$ = 5,5’-(2-isocyano-5-methyl-1,3-phenylene)bis(2-(3,5-di-tert-butyl-2-isocyanophenyl)thiophene). \textsuperscript{f}L$^h$ = 2,5-bis(3,5-di-tert-butyl-2-isocyanophenyl)thiophene. \textsuperscript{g}The peak shows a shoulder at lower wavenumbers. \textsuperscript{h}Approximated local symmetry $O_{h}$. \textsuperscript{i}Due to a breakdown of the $T_{1u}$ degeneracy.\textsuperscript{179}
experimentally obtained frequencies (Table 1 and Figures S12–S14). In addition, we compared the assigned vibrational modes with previous reports.

For the complex [Mn(CNdippPhOMe2)_6]^+ (approximated local symmetry Oh), two symmetrical Raman-active (A_1g and doubly degenerate E_g) and one asymmetrical IR-active (triply degenerate T_{1u}) metal–ligand stretching modes (υ(Mn–C)) are expected. DFT vibrational analysis reveals a splitting of the IR-active υ(Mn–C) T_{1u} mode into three stretching modes with observable Mn motion in the x, y, and z directions for [Mn(CNdippPhOMe2)_6]^+ (Table 1 and Figures S12–S14) at 789.72, 789.77, and 790.38 cm⁻¹, probably because of the small deviation from an ideal octahedral symmetry (Table S2). These modes are forming one band at 790 cm⁻¹ in a simulated IR spectrum (Figure S11).

A complex with Oh symmetry should furthermore exhibit one Raman-active (triply degenerate T_{2g}) and one IR-active (triply degenerate T_{1u}) metal–ligand bending mode (δ(Mn–C≡N) as well as for δ(C–Mn–C)). The calculations reveal between 599 and 618 cm⁻¹ six-core vibration bending modes in x, y, and z directions with dominant Mn motions (Table 1). Specifically, these modes are at 599.57, 601.19, 608.21, 610.13, 613.87, and 618.43 cm⁻¹. It seems that these modes originate from the combination of the δ(Mn–C≡N) and δ(C–Mn–C) bending modes, related to the fact that the complex shows deviation from ideal octahedral geometry (Table S2). All computed modes form together one band at 610 cm⁻¹ in a simulated IR spectrum (Figure S11) and correspond to the expected T_{1u} bending mode.

Finally, the υ(C≡N) T_{1u} mode is also split into a few IR-active motions in x, y, and z directions. The IR-active modes can be identified in DFT calculations at 2176 and 2181 as well as at 2184 and 2184 cm⁻¹ due to a mixing of one T_{1u} and one E_g motion (Table 1 and see SI, Figures S12–S14). These modes are forming one intense broad band at 2181 cm⁻¹ in a simulated IR spectrum (Figure S11) and correspond also to an expected T_{1u} stretching mode.

On the basis of these DFT results supported by literature reports, the most relevant vibrational modes observed experimentally for [Mn(CNdippPhOMe2)_6]PF_6 can be assigned (Table 1). The calculated T_{1u} modes are split into three components due to small deviations from the Oh symmetry but these splittings cannot be observed experimentally. The observed band at 2070 cm⁻¹ is attributed to the υ(C≡N) T_{1u} mode, calculated to appear at ca. 2181 cm⁻¹. This assignment is in agreement with several similar manganese(I) isocyanide complexes, which exhibit this mode between 2064 and 2088 cm⁻¹. The respective IR band exhibits a weak shoulder at lower wavenumbers, which is also reported in the literature, and which results from some deviation from linearity of the CNR axis at the N-atom.

The X-ray crystal structure of [Mn(CNdippPhOMe2)_6]PF_6 shows that such a distortion is indeed present in the solid state. Alternatively, the respective IR shoulder could stem from a CO vibration of [Mn(CO)(CNdippPhOMe2)_5]PF_6, for which the 55Mn NMR spectrum in Figure S6 provides some evidence (see above). The prominent broad band at 834 cm⁻¹ is attributable to the PF_6 anion, supported also by the fact that for [Mn(CNPh)_6]PF_6 this frequency is reported at 840 cm⁻¹. The υ(Mn–C), δ(Mn–C≡N), and δ(C–Mn–C) T_{1u} modes resulting from the octahedral coordination skeleton of [Mn(CNdippPhOMe2)_6]PF_6 are observed at 789 and 586 cm⁻¹ and can be assigned to the calculated IR-active T_{1u} modes at ca. 790 (υ(Mn–C) T_{1u}) and ca. 610 (δ(Mn–C≡N) and δ(C–Mn–C) T_{1u}) cm⁻¹. In the two previously investigated manganese(I) complexes with bidentate and tridentate isocyanides ligands, Mn–C vibrations at 586 and 584 cm⁻¹ were found.

The cyclic voltammogram of [Mn(CNdippPhOMe2)_6]PF_6 in dry and deaerated CH_2Cl_2 containing 0.1 M TBAPF_6 at 20 °C, recorded with a scan rate of 100 mV s⁻¹, shows a weak shoulder at lower wavenumbers, which is also reported in the literature, and which results from some deviation from linearity of the CNR axis at the N-atom. The X-ray crystal structure of [Mn(CNdippPhOMe2)_6]PF_6 shows that such a distortion is indeed present in the solid state. Alternatively, the respective IR shoulder could stem from a CO vibration of [Mn(CO)(CNdippPhOMe2)_5]PF_6, for which the 55Mn NMR spectrum in Figure S6 provides some evidence (see above). The prominent broad band at 834 cm⁻¹ is attributable to the PF_6 anion, supported also by the fact that for [Mn(CNPh)_6]PF_6 this frequency is reported at 840 cm⁻¹. The υ(Mn–C), δ(Mn–C≡N), and δ(C–Mn–C) T_{1u} modes resulting from the octahedral coordination skeleton of [Mn(CNdippPhOMe2)_6]PF_6 are observed at 789 and 586 cm⁻¹ and can be assigned to the calculated IR-active T_{1u} modes at ca. 790 (υ(Mn–C) T_{1u}) and ca. 610 (δ(Mn–C≡N) and δ(C–Mn–C) T_{1u}) cm⁻¹. In the two previously investigated manganese(I) complexes with bidentate and tridentate isocyanides ligands, Mn–C vibrations at 586 and 584 cm⁻¹ were found. For [Mn(CNPh)_6]I, splitting into the two T_{1u} bending modes δ(Mn–C≡N) (600 cm⁻¹) and δ(C–Mn–C) (113 cm⁻¹) was reported. As mentioned above, in our calculations, these two modes appear together around 610 cm⁻¹ (see gifs in the SI).

### 3.3. Electrochemistry

The cyclic voltammogram of [Mn(CNdippPhOMe2)_6]PF_6 in dry and deaerated CH_2Cl_2 containing 0.1 M TBAPF_6 shows an oxidation wave at 1.21 V vs SCE (E_{1/2}), which can be attributed to the one-electron oxidation of Mn(I) to Mn(II) (Figure 3A). A value of E_{1/2} = 1.22 V was determined by differential pulse voltammetry (Figure 3B). In the potential range between 0 and −2.3 V vs SCE (Figure S15), no redox waves are detectable, and thus the reduction potentials of the coordinated ligands cannot be determined under these conditions. [Mn(CNdippPhOMe2)_6]PF_6 undergoes a second one-electron oxidation at E_{1/2} = 1.74 V vs SCE, likely attributable to the redox couple Mn(II)/Mn(III) (Figure S15). The shape of the wave in Figure 3A and the peak–current ratio indicate a quasi-reversible chemical and electrochemical process. The difference between the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials (peak-to-peak separation, ΔE_p) is 92 mV (at a scan rate of 100 mV s⁻¹) instead of the expected 57 mV for a one-electron process at 25 °C, and the ratio of the anodic and cathodic peak currents is not equal to one (I_{pa}/I_{pc} ≠ 1).

To investigate the electrochemical reversibility of the single electron transfer process at 1.21 V in more detail, the cyclic voltammogram was measured at different scan rates (Figure 3B). The shape of the wave in Figure 3A and the peak–current ratio indicate a quasi-reversible chemical and electrochemical process. The difference between the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials (peak-to-peak separation, ΔE_p) is 92 mV (at a scan rate of 100 mV s⁻¹) instead of the expected 57 mV for a one-electron process at 25 °C, and the ratio of the anodic and cathodic peak currents is not equal to one (I_{pa}/I_{pc} ≠ 1).
SCE in CH₂Cl₂ due to the stronger electron-donating oxidation of Mn(I) to Mn(II) occurs already at 0.47 V vs SCE (isocyanophenyl)thiophene). In [Mn(CNMe)₆]PF₆, the CNdippPhOMe₂ makes oxidation easier compared to the based and furthermore that the arylisocyanide ligand by the observation that the peak-to-peak separation gets larger suggests electrochemical quasi-reversibility, further confirmed against this background, it seems plausible that the absorption band observable for [Mn(CNdippPhOMe₂)₆]PF₆ at 278 nm is predominantly due to intraligand (IL) transitions (π → π*), whereas the band at 370 nm could be due to a delocalized MLCT or a mixed MLCT/IL transition.

In CH₂Cl₂, the band at 278 nm has an extinction coefficient (ε) of 1.5 × 10⁴ M⁻¹ cm⁻¹, whereas the band at 370 nm shows a slightly lower ε-value of 1.4 × 10⁴ M⁻¹ cm⁻¹. For [Mn(CNPh)₆]PF₆, a second one-electron wave was detected at 234 (ε = 7.5 × 10⁴ M⁻¹ cm⁻¹) with shoulders at 234 (ε = 7.1 × 10⁴ M⁻¹ cm⁻¹) and 249 nm (ε = 5.1 × 10⁴ M⁻¹ cm⁻¹) was assigned to an intraligand (IL) transition (π → π*), whereas a band centered at 322 nm (ε = 6.6 × 10⁴ M⁻¹ cm⁻¹) with a shoulder at 340 nm (ε = 6.1 × 10⁴ M⁻¹ cm⁻¹) was attributed to MLCT (dπ → π*) transitions.

Our previously reported Mn(I) compounds [Mn(Ltri)₂]PF₆ and [Mn(Lbi)₃]PF₆ in CH₂Cl₂ showed absorption bands near 400 nm with similar extinction coefficients ((2−4) × 10⁴ M⁻¹ cm⁻¹) and were likewise assigned to MLCT transitions. Against this background, it seems plausible that the absorption band observable for [Mn(CNdippPhOMe₂)₆]PF₆ at 278 nm is predominantly due to intraligand (IL) transitions (π → π*), whereas the band at 370 nm could be due to a delocalized MLCT or a mixed MLCT/IL transition.

Continuous photoexcitation into the band at 370 nm or into its tail at 410 nm causes a decrease of the absorption band at 370 nm and leads to the appearance of a shoulder near 425 nm, both in CH₃CN and in CH₂Cl₂ (green traces in Figure 4). This behavior is observable under laser irradiation (Figure 4A) as well as under illumination with the Xenon lamp of a commercial fluorimeter (Figure 4B), suggesting that photoinduced ligand dissociation occurs.

In contrast to our previously reported manganese(I) and isoelectronic chromium(0) complexes with chelating arylisocyanide ligands, [Mn(CNdippPhOMe₂)₆]PF₆ does not show any detectable photoluminescence, neither in solution at room temperature (both in CH₃CN and CH₂Cl₂) nor at 77 K in a 2-methyl-THF glass. Consequently, we explored whether there are any dark (i.e., nonluminescent) states that could be detectable prior to the abovementioned photodecomposition. Light-induced ligand dissociation typically occurs from dissociative metal-centered excited states, and those states are usually nonemissive. However, all our attempts to detect any such dark state with ns, ps, and fs laser transient absorption spectroscopy were unsuccessful. These findings are reminiscent of photoCORM behavior, such as observed, for Mn(I/II) potentials reported for our previously investigated [Mn(Ltri)₃]PF₆ and [Mn(Lbi)₃]PF₆ compounds (1.00 and 1.05 V vs SCE in CH₂Cl₂). L tri = 5,5′-(2-isocyno-5-methyl-1,3-phenylene)bis(2-(3,5-di-tert-butyl-2-isocynanophenyl)thiophene), L bi = 2,5′-bis(3,5-di-tert-butyl-2-isocynanophenyl)thiophene. In CH₂Cl₂ (5 × 10⁻³ M) with TBACIO₄ (0.1 M) as the supporting electrolyte.

3.4. Optical Spectroscopy. The UV–vis spectrum of [Mn(CNdippPhOMe₂)₆]PF₆ exhibits two absorption band maxima at 278 nm and 370 nm (Figure 4, blue line), similar to [Mn(CNPh)₆]Cl. Thus, the yellow color stems from the broad absorption band maximizing at 370 nm, which tails into the violet region and which is not present in the UV–vis spectrum of the free ligand (Figure 4B, black trace). In CH₂Cl₂, the band at 278 nm has an extinction coefficient (ε) of 1.5 × 10⁴ M⁻¹ cm⁻¹, whereas the band at 370 nm shows a slightly lower ε-value of 1.4 × 10⁴ M⁻¹ cm⁻¹. For [Mn(CNPh)₆]Cl in ethanol/methanol/diethyl ether (8:2:1), an absorption band at 225 nm (ε = 7.5 × 10⁴ M⁻¹ cm⁻¹) with shoulders at 234 and 249 nm (ε = 5.1 × 10⁴ M⁻¹ cm⁻¹) was assigned to an intraligand (IL) transition (π → π*), whereas a band centered at 322 nm (ε = 6.6 × 10⁴ M⁻¹ cm⁻¹) with a shoulder at 340 nm (ε = 6.1 × 10⁴ M⁻¹ cm⁻¹) was attributed to MLCT (dπ → π*) transitions. Against this background, it seems plausible that the absorption band observable for [Mn(CNdippPhOMe₂)₆]PF₆ at 278 nm is predominantly due to intraligand (IL) transitions (π → π*), whereas the band at 370 nm could be due to a delocalized MLCT or a mixed MLCT/IL transition.

Continuous photoexcitation into the band at 370 nm or into its tail at 410 nm causes a decrease of the absorption band at 370 nm and leads to the appearance of a shoulder near 425 nm, both in CH₃CN and in CH₂Cl₂ (green traces in Figure 4). This behavior is observable under laser irradiation (Figure 4A) as well as under illumination with the Xenon lamp of a commercial fluorimeter (Figure 4B), suggesting that photoinduced ligand dissociation occurs.

In contrast to our previously reported manganese(I) and isoelectronic chromium(0) complexes with chelating arylisocyanide ligands, [Mn(CNdippPhOMe₂)₆]PF₆ does not show any detectable photoluminescence, neither in solution at room temperature (both in CH₃CN and CH₂Cl₂) nor at 77 K in a 2-methyl-THF glass. Consequently, we explored whether there are any dark (i.e., nonluminescent) states that could be detectable prior to the abovementioned photodecomposition. Light-induced ligand dissociation typically occurs from dissociative metal-centered excited states, and those states are usually nonemissive. However, all our attempts to detect any such dark state with ns, ps, and fs laser transient absorption spectroscopy were unsuccessful. These findings are reminiscent of photoCORM behavior, such as observed, for

| Table 2. Electrochemical Potentials of [Mn(CNdippPhOMe₂)₆]PF₆ in Comparison with Similar Compounds from the Literature |
|-----------------|-----------------|-----------------|-----------------|
| compound        | E¹/² (Mn(I)/II) vs SCE(V) | E¹/² (Mn(II)/III) vs SCE(V) |
| [Mn(CNdippPhOMe₂)₆]PF₆ | 1.21            | 1.74            |
| [Mn(Ltri)₂]PF₆  | 1.00            |                  |
| [Mn(Lbi)₃]PF₆  | 1.05            |                  |
| [Mn(CNdippPhOMe₂)₆]PF₆ | 1.01            | 1.91            |
| [Mn(CNMe₅)₆]PF₆ | 0.47            | 1.59            |

“In (dry and deaerated) CH₂Cl₂ at 20 °C with TBAPF₆ (0.1 M) as the supporting electrolyte. Only observable during one cycle (irreversible). L tri = 5,5′-(2-isocyno-5-methyl-1,3-phenylene)bis(2-(3,5-di-tert-butyl-2-isocynanophenyl)thiophene), L bi = 2,5′-bis(3,5-di-tert-butyl-2-isocynanophenyl)thiophene. In CH₂Cl₂ (5 × 10⁻³ M) with TBACIO₄ (0.1 M) as the supporting electrolyte.”

Figure 4. UV/vis absorption spectra of [Mn(CNdippPhOMe₂)₆]PF₆ in dry and argon-saturated (A) CH₂Cl₂ and (B) CH₃CN before (blue) and after (green) irradiation with the Xenon lamp of (A) a spectrofluorometer or (B) a picosecond laser. The UV/vis spectrum of the free ligand in CH₂Cl₂ is included in (A). The absorbance axes (colored in green) apply to all measured spectra.
example, in tricarbonyl manganese(I) complexes of the type [Mn(CO)₃(Rbpy)Br] (Rbpy = 4,4′-disubstituted-2,2′-bipyridyl ligand, where R = tBu, H or CF₃). Upon photoexcitation, these complexes undergo loss of one CO ligand on the femtosecond time scale, followed by solvent coordination on the picosecond time scale. The proposed mechanism of CO extrusion involves ultrafast internal conversion from an initially populated MLCT excited state to a dissociative ligand-field (d−d) excited state.

Table 3. Comparison of [Mn(CNdippPhOMe2)₆]PF₆ to Related Mn(I) Compounds with Tris(bidentate) and Bis(tridentate) Coordination Environments

| Compound | Ligand structure | UV/Vis λₘₐₓ | υ(C≡N) | T₁₀ / cm⁻¹ |
|----------|-----------------|------------|-------|-----------|
| [Mn(CNdippPhOMe2)₆]PF₆ | ![Ligand structure](image) | 278 nm (ε = 1.5 · 10⁵ M⁻¹ cm⁻¹) 370 nm (ε = 1.4 · 10⁵ M⁻¹ cm⁻¹) | 2070 |
| [Mn(L⁵)₂]PF₆ | ![Ligand structure](image) | 258 nm (ε = 1.1 · 10⁵ M⁻¹ cm⁻¹) 327 nm (ε = 0.65 · 10⁵ M⁻¹ cm⁻¹) 392 nm (ε = 0.29 · 10⁵ M⁻¹ cm⁻¹) | 2081 |
| [Mn(L⁶)]PF₆ | ![Ligand structure](image) | 253 nm (ε = 0.99 · 10⁵ M⁻¹ cm⁻¹) 308 nm (ε = 0.81 · 10⁵ M⁻¹ cm⁻¹) 380 nm (ε = 0.29 · 10⁵ M⁻¹ cm⁻¹) | 2064 |

*In CH₂Cl₂ at 20 °C.*

3.5. Photoinduced Ligand Dissociation. To investigate the photodissociation in more detail, we irradiated [Mn(CNdippPhOMe2)₆]PF₆ in CH₂Cl₂ (Figures 5A and S18A) and in CH₃CN (Figure 5B) with a blue continuous-wave (cw) laser (405 nm, 526 mW). The absorbance at the excitation wavelength was adjusted close to 0.1 (Table S4), resulting in concentrations of 7.29 μM in CH₂Cl₂ (7.15 μM for a second measurement) and 7.13 μM in CH₃CN. The measurements were done at 25 °C and the absorption spectra were measured each 10 s during continuous irradiation at 405 nm.

Based on the series of UV−vis spectra in Figure 5, [Mn(CNdippPhOMe2)₆]⁺ undergoes nearly complete photodegradation within 30 min. Aside from the very prominent absorbance decrease at 370 nm, the absorption band shift from 278 nm to 273 nm seems important, because the free ligand has an absorption band maximum at 273 nm (black trace in Figure 4A). Thus, the spectral evolution over time is compatible with the loss of one or more CNdippPhOMe2 ligands. Furthermore, in CH₃CN, a new absorption band at 425 nm becomes increasingly prominent with increasing irradiation time. When CH₂Cl₂ and CH₃CN solutions of...
[Mn(CNdippPhOMe2)6]PF6 are kept under ambient conditions without direct 405 nm irradiation, the UV–vis absorption spectra show comparatively minor changes over much longer time periods (Figure S19), compatible with the view that ligand loss is phototriggered. MS-ESI-HR measurements of a CH3CN sample prior and after photoirradiation (Figure S10 and Table S3) show that the initially dominant [M − PF6]+ mass peak (relative intensity of 85% with respect to 100% for [M − PF6 − L + CH3CN]; L = CNdippPhOMe2) vanishes with continuing irradiation, finally resulting in relative intensities of 4.3% for [M − PF6]+ and 64% for [M − PF6 − L + CH3CN]+. Furthermore, a new mass peak attributable to [M − PF6 − 2L + 2CH3CN]+ with a relative intensity of 15.7% becomes observable. Collectively, the irradiation experiments and HR-ESI-MS measurements demonstrate that light-induced ligand dissociation from an electronically excited state is much faster than spontaneous ligand dissociation in the electronic ground state.

The prototypical d6 metal compound [Ru(bpy)3]+ is known to undergo photodegradation as well,4,187–189 and consequently it seemed meaningful to compare the photostabilities of [Mn(CNdippPhOMe2)6]PF6 and [Ru(bpy)3]+(PF6)2 in CH3CN under similar conditions (SI pages S27 to S31 and Figures S16B and S20 to S22). The key finding is that in CH3CN our manganese(I) complex undergoes photodegradation far more efficiently than [Ru(bpy)3]+(PF6)2 under these conditions of very intense cw-laser irradiation.

4. CONCLUSIONS

The primary coordination sphere of the [Mn(CNdippPhOMe2)6]PF6 complex comes close to Oh symmetry according to single-crystal X-ray diffraction, 55Mn NMR spectroscopy, IR spectroscopy, and vibrational analysis with DFT calculations. A detailed vibrational analysis permitted the identification of the IR-active and asymmetrical υ(C≡N), υ(Mn−C), δ(C−Mn−C), and δ(Mn−C≡N) vibrational modes (Tiu), and furthermore reveals substantial differences in the π-backbonding interaction between the two previously investigated Mn(I) complexes with chelating isocyanide ligands and the new compound studied here (Table 3). Based on cyclic voltammetry, the Mn(I) center of [Mn(CNdippPhOMe2)6]PF6 is substantially more electron-rich than in previously reported hexakis(arylisocyanide)manganese(I) complexes.46–52 Unlike our recently reported manganese(I) complexes with tris(bidentate) and bis(tridentate) coordination environments (Table 3),54,99 and unlike its third-row congener [W(CNdippPhOMe2)3]+,102–107 the [Mn(CNdippPhOMe2)6]+ complex is nonemissive. Instead, photoirradiation into its lowest energy UV–vis absorption band leads to ligand dissociation, similar to what is well-known from manganese(I) carbonyl compounds.76,119–121,123,125–132 The much weaker ligand field in our 3d6 complex compared to that experienced by W(0) in the same coordination environment likely leads to fast and efficient population of a dissociative metal-centered excited state, which represents a common challenge in first-row transition metal complexes.57,60 The photophysical properties of the new Mn(I) complex differ substantially from those of the recently reported analogous complexes with bi- and tridentate isocyanide ligands (Table 3).52 Aside from the chelating nature of the previously used ligands, their thiophene units in the ligand skeleton likely affect the electronic structures of the resulting Mn(I) complexes.

Thus, our study suggests that monodentate isocyanide ligands are not well suited for obtaining manganese(I) complexes with emissive MLCT excited states. Chelating arylisocyanides, as used previously for chromium(0),66,67 manganese(I) (Table 3),54,99 and molybdenum(0),138,190,191 seem better suited for this purpose.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01438.

Synthesis procedures and characterization of the CNdippPhOMe2 ligand; 1H, 13C, 19F, 31P, and 55Mn NMR spectroscopy of [Mn(CNdippPhOMe2)6]PF6; crystallographic data and crystal structure of the complex; XRPD pattern; HR-ESI-MS measurements of the complex; IR spectra and vibrational analysis; and cyclic voltammetry measurements, photostability studies, and UV–vis absorption spectroscopy of the complex, as well as cartesian coordinates of the optimized structure of the complex (PDF)

Full dynamic figures of the corresponding metal–ligand vibrations (ZIP)

Accession Codes

CCDC 2165895 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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