

Electronic Effects of Aminoindenyl Ligands Coordinated to Manganese: Structures and Properties of a Mn^0 Metalloradical and Bimetallic $\text{Mn}^{-\text{I}}/\text{Mn}^{\text{I}}$ Adduct

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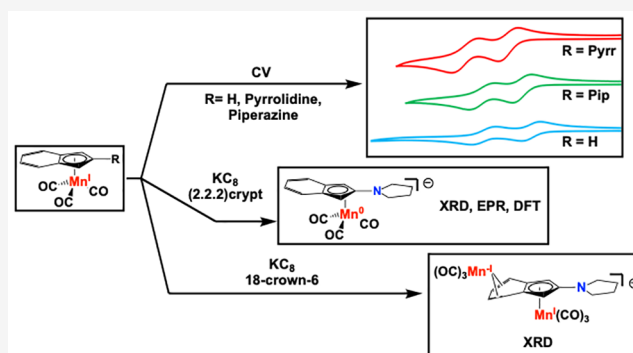
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ABSTRACT: Studying the redox behavior of Earth-abundant metal complexes and understanding their reactivity under reducing conditions is of fundamental importance for activating small molecules. We present the electrochemical behavior and reactivity of amine-functionalized indenylmanganese(I) complexes that form the piano-stool complexes $\text{Mn}^{\text{I}}(\text{CO})_3(\text{Ind}^{\text{R}})$ (R = pyrrolidinyl, piperazinyl), which exhibit two cathodic redox waves via cyclic voltammetry (CV). Electrochemical, spectroscopic, and structural comparisons of these complexes with undecorated indenyl species reveal that the pyrrolidine-substituted tricarbonylmanganese complex $\text{MnInd}^{\text{Pyr}}$ is the most electron-rich due to favorable π -donor effects from the amine to the ring system. These results are also strongly supported by DFT computations. Although CV studies show clean redox behavior, reaction outcomes in the presence of common chemical reductants are strongly dependent on the reagents used. The reduction of $\text{MnInd}^{\text{Pyr}}$ with KC_8 in the presence of the encapsulating agent 2,2,2-Crypt led to the formation of a rare Mn^0 metalloradical, $[\text{K}(2,2,2\text{-Crypt})][\text{MnInd}^{\text{Pyr}}]$, which was characterized by single-crystal X-ray diffraction, EPR spectroscopy, IR spectroscopy, and DFT calculations. Attempts to isolate a doubly reduced $\text{Mn}^{-\text{I}}$ adduct in the presence of 18-crown-6 resulted in indenide anion loss that generated a mixed-valence $\text{Mn}^{-\text{I}}/\text{Mn}^{\text{I}}$ adduct, where the two metal centers were bound to a single indenyl moiety. This study emphasizes the dramatic differences between observing redox-reversible behavior on the electroanalytical scale and performing preparative-scale reduction reactions with alkali metals and encapsulating agents, as these reagents have a profound impact on the reaction outcome.



INTRODUCTION

Piano-stool complexes containing Earth-abundant metals and cyclopentadienyl (Cp) or indenyl (Ind) ligands have attracted renewed interest for small-molecule activation in recent years due to their redox stability and role as electrocatalysts in the reduction of protons to hydrogen and carbon dioxide to formic acid.^{1–7} Under oxidative conditions, the indenyl group has also been identified as a “non-innocent” ligand at iron. It triggers an η^5 – η^6 hapticity shift coupled with metal hydride migration to the η^5 -Cp ring, yielding a complex with very weak homolytic C–H bond strength.⁸ We recently reported that protonation at the carbon atom on the Cp ring is thermodynamically favored during H_2 production electrocatalysis, even in the presence of pendant amines directly attached to Cp.⁵ These counterintuitive findings suggest that amine-functionalized $\text{M}(\text{Cp})$ and $\text{M}(\text{Ind})$ complexes may exhibit chemically “non-innocent” reactivity that remains underexplored for small-molecule activation under positive or negative electrical bias.

It is known that tricarbonyl piano-stool complexes $\text{M}(\text{Cp}^{\text{R}})(\text{CO})_3$ and $\text{M}(\text{Ind}^{\text{R}})(\text{CO})_3$ (M = Mn, Fe) exhibit divergent electrochemical activity. The oxidation of cymantrenes

($\text{Cp}^{\text{R}}\text{Mn}(\text{CO})_3$) has been studied as a function of the Cp ring substitution pattern (R = H, NH_2 , Me_5) to generate stable radical cations.^{9,10} However, the cathodic electrochemistry of $\text{CpMn}(\text{CO})_3$ reveals a very negative and irreversible single-electron reduction (-2.9 V vs $\text{Fc}^{+/0}$, THF).¹¹ In contrast, isostructural $\text{IndMn}(\text{CO})_3$ has two cathodic and electrochemically reversible redox couples (-2.3 V and -2.5 V vs $\text{Fc}^{+/0}$, THF);¹² the stability of these anions suggests that the CO ligands remain coordinated to Mn and an η^5 – η^3 haptotropic shift (i.e., ring slippage) becomes important to accommodate the influx of electrons after the second reduction event. Evidence for $[\text{IndMn}(\text{CO})_3]^-$ and $[\text{IndMn}(\text{CO})_3]^{2-}$ was only reported based on solution-phase spectroscopic data and reactivity studies.¹² With iron, The 1e^- reduction of

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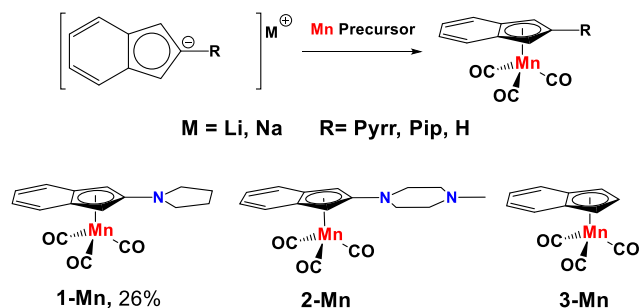
isostructural $\text{IndFe}(\text{CO})_3^+$ results in CO release, with the CO dissociation rate constant being 10^6 slower than that for the corresponding $\text{CpFe}(\text{CO})_3^+$ complex.¹³ This observation was coined an “inverse indenyl effect” from DFT calculations, where a π^* LUMO on the indenyl benzene ring generates a ligand-based radical that tempers ligand dissociations at Fe.

Our group is interested in preparing amine-functionalized Cp ligands to understand their electronic and secondary coordination-sphere effects in electrocatalytic reactions involving protons and electrons,⁵ and we now report the reactivity of amine complexes $\text{Mn}(\text{Ind}^{\text{R}})(\text{CO})_3$ (R = pyrrolidinyl, piperazinyl) under reducing conditions. Electrochemical studies of $\text{Mn}(\text{Ind}^{\text{R}})(\text{CO})_3$ in the cathodic direction reveal two reversible redox events, with DFT calculations, IR spectra, and molecular structures revealing a correlation between the CO stretching frequency and the π -donor ability of the amine to the indenyl ring. One-electron reduction of $\text{Mn}(\text{Ind}^{\text{Pyr}})(\text{CO})_3$ with KC_8 in the presence of (2,2,2)-crypt generated a rare Mn^0 metal-radical with a partial ring slip character, which was characterized by single-crystal X-ray diffraction and EPR spectroscopy. Conversely, the reduction of $\text{Mn}(\text{Ind}^{\text{Pyr}})(\text{CO})_3$ with KC_8 followed by the addition of 18-crown-6 results in indenide ligand loss and the formation of a bimetallic mixed-valent $\text{Mn}^{\text{I}}/\text{Mn}^{-\text{I}}$ adduct that coordinates to a single Ind^{Pyr} ligand. These results starkly contrast with the “clean” redox behavior via cyclic voltammetry, underscoring the involvement of alkali metals and encapsulating agents during reduction reactions with manganese piano-stool complexes.

RESULTS AND DISCUSSION

The amine-functionalized indene ligands $\text{Ind}^{\text{Pyr}}\text{H}$ and $\text{Ind}^{\text{Pip}}\text{H}$ are easily synthesized via condensation by reacting the corresponding secondary amines with 2-indanone, resulting in air-stable and conveniently handled solids.^{14,16} The procedures for synthesizing piano-stool tricarbonyl complexes $\text{MnInd}^{\text{Pyr}}$, $\text{MnInd}^{\text{Pip}}$,¹⁴ and MnInd^{H} ¹⁵ are all similar, where the first step involves the in situ generation of the indenide via a strong base ($n\text{-BuLi}$ for $\text{MnInd}^{\text{Pyr}}$ and $\text{MnInd}^{\text{Pip}}$) or reductant (Na^0 for MnInd^{H}), followed by the addition of $\text{Mn}(\text{CO})_5\text{Br}$ or $\text{Mn}(\text{CO})_3(\text{py})_2\text{Br}$ to generate the indenylmanganese complexes (Scheme 1). The new indenyl complex in this triad is

Scheme 1. General Synthetic Protocol for Preparing $\text{MnInd}^{\text{Pyr}}$, $\text{MnInd}^{\text{Pip}}$,¹⁴ and MnInd^{H} ¹⁵



$\text{MnInd}^{\text{Pyr}}$, an air-stable solid purified by silica gel column chromatography. This initially elutes $\text{Mn}_2(\text{CO})_{10}$ as a yellow band, followed by the dark orange $\text{MnInd}^{\text{Pyr}}$, indicating that either indenide or $n\text{BuLi}$ may behave as a reductant to convert $\text{Mn}(\text{CO})_5\text{Br}$ to $\text{Mn}_2(\text{CO})_{10}$ and explaining the relatively poor yield of the target compound (26%). $\text{MnInd}^{\text{Pyr}}$, $\text{MnInd}^{\text{Pip}}$ and MnInd^{H} all exhibit characteristic carbonyl IR frequencies that

demonstrate the electron-donating effect of the amine substituent on the ligand (or lack thereof), as shown in Table 1. Based on the experimental CO stretching frequencies, the order of the ligand donor strength is $\text{Ind}^{\text{Pyr}} > \text{Ind}^{\text{Pip}} > \text{Ind}$. DFT¹⁷ frequency calculations of the complexes in acetonitrile ($\omega\text{B97X-V}^{18}/\text{def2-TZVP}+\text{COSMO}(\text{MeCN})^{19,20}$) support this trend, and values are reported in parentheses in Table 1.

Single crystals of $\text{MnInd}^{\text{Pyr}}$ were grown by cooling a concentrated pentane solution of the complex (Figure 1). A structural comparison between $\text{MnInd}^{\text{Pyr}}$ and the known $\text{MnInd}^{\text{Pip}}$ ¹⁴ reveals short C–N bond lengths (1.360(2) and 1.368(4)–1.378(4) Å,¹⁴ respectively) that are on the order of a C=N double bond (average aromatic C=N bond length is 1.336 Å²¹). The dihedral angle between the appended amine and the Cp fragment becomes more planar as the electron donation from the amine increases, forcing the nitrogen into the same plane as the Cp ring (Table 1). These structural data are consistent with the CO stretching frequency data, where the smallest dihedral angle found for the pyrrolidine-appended ligand represents the most electron-donating ligand in the series (Table 1).

Cymantrene ($\text{CpMn}(\text{CO})_3$) has an irreversible reduction potential of -2.9 V vs $\text{Fc}^{+/0}$ in acetonitrile, generating a formally $19e^-$ complex. According to DFT calculations, the electrons populate an antibonding ligand MO,^{22,23} resulting in proposed Cp ring slippage from η^5 to η^3 . Cyclic voltammograms (CVs) recorded under N_2 show that these indenyl complexes have two reversible redox waves centered at ca. -2.3 and -2.5 V (Figure 2). If the potential window for CV is swept too positive (> -1 V), the current response of the second reduction decreases with repeated scans, which may be caused by oxidative degradation that passivates the electrode surface (Figures S1 and S2). In accordance with the IR evidence, the reduction potentials are correlated with the electron-donor capabilities of the indenyl ligand series, where $\text{MnInd}^{\text{Pyr}} > \text{MnInd}^{\text{Pip}} > \text{MnInd}$ (Figure 2). The reduction potentials computed with OT- $\omega\text{B97X-V}/\text{ma-def2-QZVPP}+\text{COSMO-RS}(\text{MeCN})$,^{24–26} shown in parentheses in Table 1, are also in excellent agreement with the experimental values. The DFT geometries of $\text{MnInd}^{\text{Pyr}}$ and the reduced species, shown in Figure 3, show that the first reduction generates a metalloradical, which we describe as having “partial ring slip”, with the Cp ring coordinating somewhere in between η^5 and η^3 . Upon a second reduction, the DFT-calculated geometry distorts fully to an η^3 -configuration.

A previous report studied the reduction chemistry of the undecorated indenyl complex MnInd , with magnetic susceptibility measurements, reactivity studies, and EPR spectroscopy supporting the formation of $[\text{MnInd}]^-$; however, its molecular structure remained elusive.¹² In our hands, $\text{MnInd}^{\text{Pyr}}$ can be reduced by one electron to the corresponding Mn^0 anion $[\text{K}(2,2,2\text{-Crypt})][\text{MnInd}^{\text{Pyr}}]$ by the dropwise addition of 1.1 equiv of KC_8 suspended in THF into a stirred solution of $\text{MnInd}^{\text{Pyr}}$ and 2,2,2-Crypt at room temperature (Scheme 2). After workup, this highly sensitive compound was crystallized via vapor diffusion of pentane into a concentrated THF solution, consistently resulting in the cocrystallization of $[\text{MnInd}^{\text{Pyr}}]^-$ and $[\text{K}(2,2,2\text{-Crypt})][\text{Mn}(\text{CO})_5]$ in 36% and 31% yields, respectively, as determined by elemental analysis of the recrystallized bulk product. Unfortunately, all attempts to separate these compounds via washing or recrystallization were unsuccessful due to their extremely similar solubility characteristics. Fortunately, both the dark green Mn^0 and colorless $\text{Mn}^{-\text{I}}$

Table 1. Comparison of Selected Redox Events, IR Stretching Frequencies, and Structural Data^{a,b}

complex	$E_{1/2}$ Red 1 (V vs $\text{Fc}^{+/0}$)	$E_{1/2}$ Red 2 (V vs $\text{Fc}^{+/0}$)	ν_{CO} (cm^{-1} , KBr)	dihedral angle ($^\circ$)	C–N bond length ($\text{\AA}$)
$\text{MnInd}^{\text{Pyrr}}$	−2.34 (−2.23)	−2.55 (−2.58)	1990, 1899 (1986, 1896)	6.9(1) (7.02)	1.360(2) (1.359)
$\text{MnInd}^{\text{Pip}}$	−2.27 (−2.20)	−2.47 (−2.55)	2006, 1907 (1987, 1896)	10.0(3)–12.3(3) ¹⁴ (9.38)	1.368(4)–1.378(4) ¹⁴ (1.378)
MnInd	−2.23 ¹² (−2.08)	−2.46 ¹² (−2.37)	2018, 1929 ¹² (1995, 1906)		
$[\text{MnInd}^{\text{Pyrr}}]^-$			1884, 1807, 1784	14.3(4) (11.1)	1.380(5) (1.371)
$[\text{Mn}_2\text{Ind}^{\text{Pyrr}}]^-$			1973, 1942, 1857, 1832	8.5(4)	1.380(5)

^aComputed data are shown in parentheses below the experimental data (see [DFT Calculations](#) for details). DFT IR frequencies are not shown for the anionic compounds due to their complicated electronic structures. ^bThe dihedral angles are described as the acute angles between the planes N1–C5–C6 and C5–C6–C7, see [Figure 1](#).

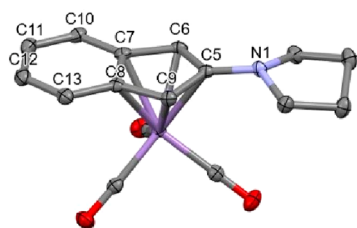


Figure 1. Molecular structure of $\text{MnInd}^{\text{Pyrr}}$ with 50% probability ellipsoids. The dihedral angles in [Table 1](#) are described as the acute angle between the planes N1–C5–C6 and C5–C6–C7.

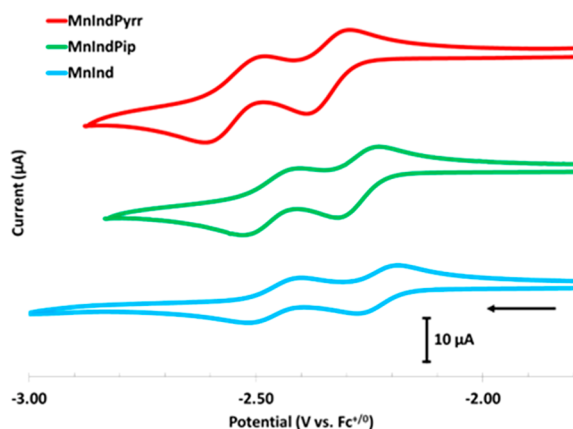


Figure 2. Stacked cyclic voltammograms of 1 mM solutions of $\text{MnInd}^{\text{Pyrr}}$ (red), $\text{MnInd}^{\text{Pip}}$ (green), and MnInd (blue) at 100 mV/s with 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte in MeCN. All CVs are referenced to $\text{Fc}^{+/0}$.

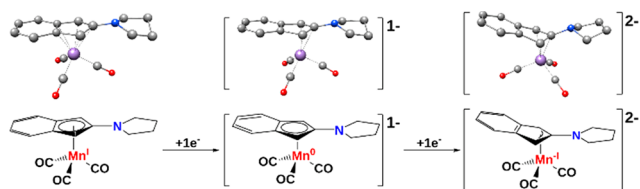


Figure 3. (Top) DFT geometries of $\text{MnInd}^{\text{Pyrr}}$ optimized at the $\omega\text{B97X-V/def2-TZVP+COSMO}(\text{MeCN})$ level of theory. Hydrogen atoms are omitted for clarity. (Bottom) Drawings of each product showing the subtle movement of the ligand from a partial ring slip orientation (middle) to full η^3 -coordination (right).

crystals are easily hand-picked for molecular structure determination by single-crystal X-ray diffraction ([Figures 4](#) and [S3](#)). Evidence for the formation of $[\text{K}(2,2,2\text{-Crypt})][\text{Mn}$

Scheme 2. Reactivity of $\text{MnInd}^{\text{Pyrr}}$ and $\text{Ind}^{\text{Pyrr}}\text{H}$ under Reducing Conditions

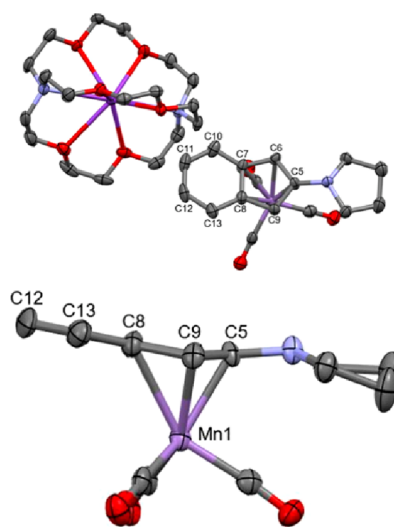
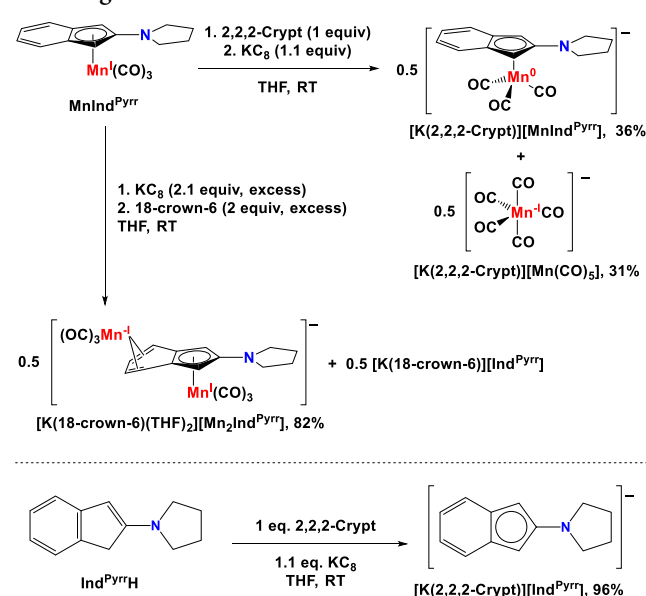


Figure 4. (Top) Molecular structure of $[\text{K}(2,2,2\text{-Crypt})][\text{MnInd}^{\text{Pyrr}}]$ with 50% probability ellipsoids. Hydrogens are omitted for clarity. (Bottom) Side-on view of $[\text{MnInd}^{\text{Pyrr}}]^-$ showing the broken planarity of the five-membered ring.

(CO)₅] is also supported by the CO stretching frequencies of [Mn(CO)₅][−] in the FTIR spectrum.²⁷ Solution-phase ⁵⁵Mn NMR spectra of the cocrystallized mixture in THF-*d*₈ exhibited a characteristic ⁵⁵Mn NMR signal for [Mn(CO)₅][−] at −2691 ppm²⁸ along with a second peak at −2919 ppm (Figure S8), which we speculate to be the dianion [MnInd^{Pyrr}]^{2−} that we have been unable to isolate or characterize any further.

The molecular structure of [K(2,2,2-Crypt)][MnInd^{Pyrr}] is shown in Figure 4. Notably, structurally characterized monometallic Mn⁰ metalloradicals remain very rare and typically require significant steric protection to avoid dimerization.^{29–33} Structural analysis shows that the [K(2,2,2-Crypt)][MnInd^{Pyrr}] complex does not fully represent an indenyl ring slip to a standard η³-indenyl configuration, but 1e[−] reduction certainly introduces structural distortions to the system. The C–N bond slightly elongates from 1.360(2) Å to 1.380(5) Å, which correlates well with the DFT-computed value (1.371 Å; Table 1). The dihedral angle increases from 6.9(1)° to 14.3(4)° (DFT value of 11.1°), which would be expected due to the increase in electronic repulsion with the presence of an additional electron. Interestingly, the ring slippage appears somewhere between an η³- and η⁵-indenyl configuration, where the ring has broken planarity but the C–C bond lengths for atoms C5 through C13 are nearly unchanged between MnInd^{Pyrr} and [MnInd^{Pyrr}][−], suggesting that the ring aromaticity is preserved (Table 2). The most

Table 2. Comparison of C–C and Mn–C Bond Length Data (Å) for [MnInd^{Pyrr}] and [MnInd^{Pyrr}][−]

atom 1	atom 2	[MnInd ^{Pyrr}] (Å)	[MnInd ^{Pyrr}] [−] (Å)
C5	C6	1.428(2)	1.426(6)
C6	C7	1.440(2)	1.445(6)
C7	C8	1.436(2)	1.428(7)
C8	C9	1.437(2)	1.448(6)
C9	C5	1.437(2)	1.420(5)
C7	C10	1.427(2)	1.395(7)
C10	C11	1.359(2)	1.383(7)
C11	C12	1.430(3)	1.392(8)
C12	C13	1.367(2)	1.388(7)
C13	C8	1.428(2)	1.403(6)
Mn1	C7	2.167(1)	2.472(5)
Mn1	C8	2.180(1)	2.471(5)
Mn1	C9	2.159(1)	2.201(4)
Mn1	C5	2.249(1)	2.200(4)
Mn1	C6	2.146(1)	2.195(5)

dramatic changes occur in the bond lengths between the Mn center and the carbons of the fused six-membered and Cp rings (Mn1–C7 and Mn1–C8), which elongate by ca. 0.30 Å upon reduction from MnInd^{Pyrr} to [MnInd^{Pyrr}][−]. These elongations correlate well with the DFT-computed values of ca. 0.33 Å for the complex solvated in acetonitrile.

The X-band EPR spectrum of [K(2,2,2-Crypt)][MnInd^{Pyrr}] in 2-MeTHF glass at 77 K is shown in Figure 5. DFT calculations indicate that the residual unpaired spin density is located mainly at the Mn center, with small residual spin density on the six-membered ring of the indenyl ligand and the carbonyl ligands (Figure 5, bottom left). A best fit is achieved in the simulated EPR spectrum when 80% of the spectrum is attributed to a ⁵⁵Mn-centered radical (*g* = 1.997, 1.968, and 2.000) and 20% of the spectrum attributed to a second very similar ⁵⁵Mn center (*g* = 1.996, 1.977, and 2.007). The sum of

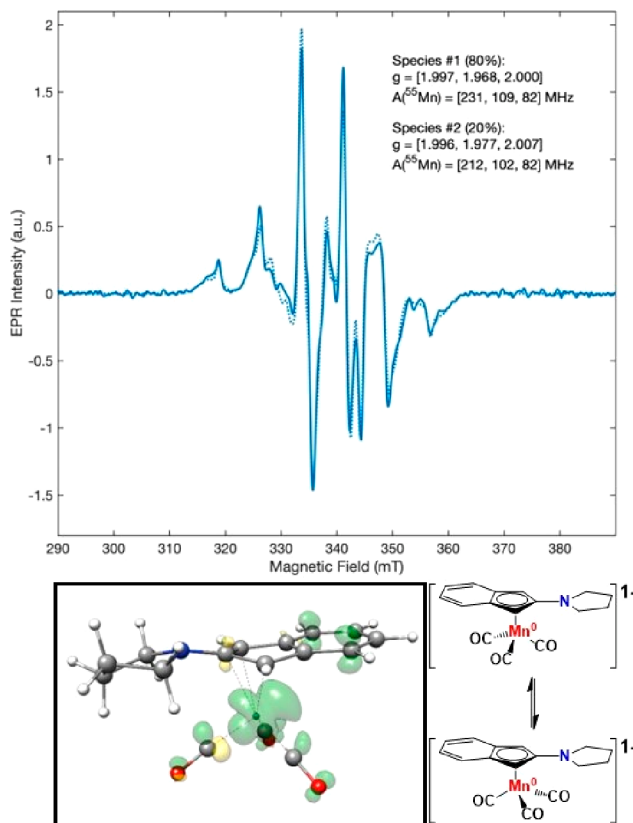


Figure 5. (Top) Experimental (solid line) and simulated (dotted line) X-band EPR spectra of [K(2,2,2-Crypt)][MnInd^{Pyrr}] in 2-MeTHF, including *g*-values and hyperfine tensors (*A*) for both ⁵⁵Mn centers. (Bottom) Computed residual spin density of [MnInd^{Pyrr}][−] (isosurface value of 0.005 e Bohr^{−1/2}) and its proposed conformers in the EPR sample.

these contributions is shown in Figure 5 as the dotted line. Based on the extremely similar *g*-values and coupling constants for these two complexes, we suggest that two energetically similar conformers of [MnInd^{Pyrr}][−] exist in the glass, where the indenyl ligand ring is rotated relative to the three CO ligands of the piano-stool base (Figure 5, bottom right). This behavior has some precedent, as low-spin [CpMn^{II}(CO)₂(IMes)][BF₄] was found to have two different *g*₃ values, which were ascribed to either two conformations in frozen solution or positional differences between the cation and the counteranion.³⁴ However, in our case, we also cannot exclude the possibility of other another EPR-active molecule contaminating the sample.

Since these indenyl complexes exhibited two reversible redox events on the CV time scale, the chemical reduction of MnInd^{Pyrr} with more than one equivalent of KC₈ was explored (Scheme 2). The room-temperature addition of a THF suspension of a twofold excess of KC₈ to a solution of MnInd^{Pyrr} in THF under an N₂ atmosphere *before* the addition of an encapsulating agent resulted in the immediate formation of suspended graphite (C₈) and solution darkening. Next, the solution was treated with a twofold excess of 18-crown-6, filtered through Celite, and a red-orange oil was obtained after solvent removal. This solution was crystallized via pentane vapor diffusion into a THF solution at −35 °C, and single-crystal X-ray diffraction revealed the unusual bimetallic mixed-valent manganese complex [K(18-crown-6)(THF)₂][Mn₂Ind^{Pyrr}] (Figure 6) with the loss of an indenide anion

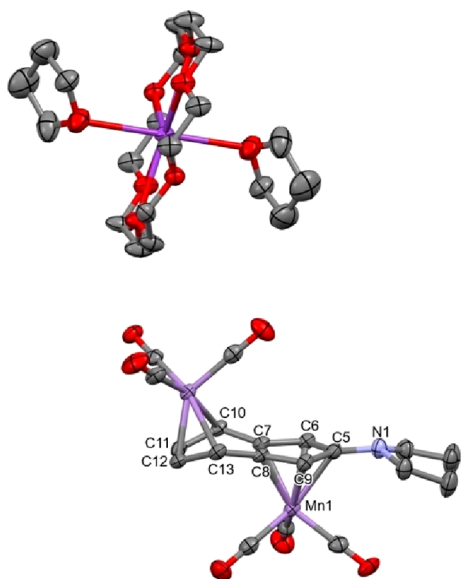


Figure 6. Molecular structures of $[K(18\text{-crown-6})(\text{THF})_2][\text{Mn}_2\text{Ind}^{\text{Pyr}}]$ with 50% probability ellipsoids. Hydrogens and disordered THF are omitted for clarity.

(Scheme 2, bottom). Although additional characterization via ^1H NMR spectroscopy was achieved, separation to yield an analytically pure product proved challenging, which will be described in detail later. To the best of our knowledge, there are no other structurally authenticated group 7 compounds that form similar bimetallic structural motifs sharing a single indene ligand. Expanding a CCDC structural search to group 8 metals reveals a bimetallic “double decker” Ru complex, where a $\text{Cp}^*\text{Ru}^{\text{II}}$ moiety coordinates to the $\eta^5\text{-Cp}$ face of indene and a $\text{Cp}^*\text{Ru}^{\text{II}}$ moiety coordinates to the $\eta^6\text{-arene}$ ring of indene.³⁵

To verify the stability of the indenide anion that is released upon the formation of $[K(18\text{-crown-6})(\text{THF})_2][\text{Mn}_2\text{Ind}^{\text{Pyr}}]$, free ligand $\text{Ind}^{\text{Pyr}}\text{H}$ was directly reacted with KC_8 and (2,2,2)-crypt in THF to generate $[K(2,2,2\text{-crypt})][\text{Ind}^{\text{Pyr}}]$ (Scheme 2, bottom). Concentrating and cooling the reaction solution resulted in the crystallization of the analytically pure product in a 96% yield. The obtained crystals were suitable for single-crystal X-ray diffraction (SCXRD, Figure S4), and the free indenide was structurally distinct from the coordinated ligand. The C–N bond length is 1.381(8) Å, and the indenyl ring is nearly planar with a dihedral angle of 0.2(4)°. ^1H NMR spectra support the planarization of this molecule, where the protons of the six-membered ring generate a symmetric AA’BB’ splitting pattern (Figure S9).

After $\text{MnInd}^{\text{Pyr}}$ was reduced with 2.1 equiv of KC_8 and 2 equiv of 18-crown-6 was added to the reaction mixture, ^1H NMR spectra of the reduction mixture in $\text{THF-}d_8$ recorded after the mixture was washed with diethyl ether to remove traces of $\text{Ind}^{\text{Pyr}}\text{H}$ show a clean mixture of $[\text{Mn}_2\text{Ind}^{\text{Pyr}}]^-$ and $[\text{Ind}^{\text{Pyr}}]^-$ (Figure S13). Due to the incredibly similar solubility profiles of the reduction products, the yield of $[\text{Mn}_2\text{Ind}^{\text{Pyr}}]^-$ (82%) was determined by ^1H NMR spectroscopy of the crude reaction mixture, with addition of 1,3,5-trimethoxybenzene as an internal standard (Figure S11). Furthermore, $[\text{Mn}_2\text{Ind}^{\text{Pyr}}]^-$ is partly soluble in diethyl ether, and cooling a concentrated solution of this mixture for several days at -35°C led to the crystallization of milligram quantities of X-ray-quality crystals of the bimetallic complex $[K(18\text{-crown-6})][\text{Mn}_2\text{Ind}^{\text{Pyr}}]$ without THF coordinated to 18-crown-6 in the crystal lattice

(Figure 7). This result emphasizes the dynamic solvation–desolvation behavior of this complex, which further compli-

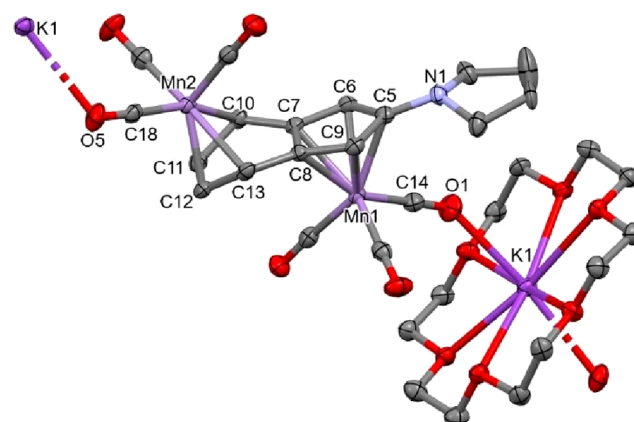
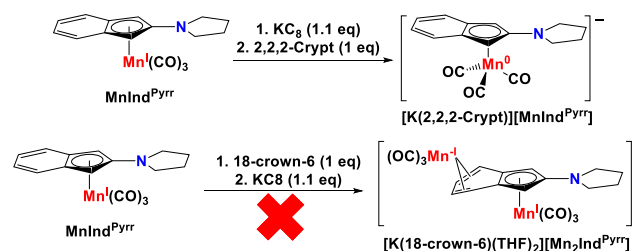


Figure 7. Molecular structure of $[K(18\text{-crown-6})][\text{Mn}_2\text{Ind}^{\text{Pyr}}]$ with 50% probability ellipsoids. Hydrogens and disorder in the pyrrolidine ring are omitted for clarity.

cates isolation efforts to obtain high quantities of analytically pure product. The axial sites of potassium act as bridges between the $\text{Mn}^{\text{I}}\text{CO}$ and $\text{Mn}^{\text{I}}\text{CO}$ moieties, weakly coordinating to the oxygen atoms of the bound CO ligands and forming an infinite chain in the crystal lattice. The $\text{Mn}^{\text{I}}\text{CO}$ –K contact distance is 2.752(4) Å (O1-K1), and the $\text{Mn}^{\text{I}}\text{CO}$ –K contact distance is 2.810(3) Å (O5-K1). In both the THF-coordinated and solvent-free structures, the Mn-coordinated C=C bonds are lengthened from an average C–C bond of 1.364 Å in the parent $\text{MnInd}^{\text{Pyr}}$ to average distances of 1.434 and 1.432 Å, respectively. In addition, Mn coordination to these alkenes dramatically alters their ^1H NMR chemical shifts, which change from 7.44 and 7.01 ppm in $\text{MnInd}^{\text{Pyr}}$ to 5.80 and 1.88 ppm in $[\text{Mn}_2\text{Ind}^{\text{Pyr}}]^-$. The ^1H NMR spectrum of $[K(18\text{-crown-6})][\text{Mn}_2\text{Ind}^{\text{Pyr}}]$ is shown in Figure S12, confirming the peak assignments of the reaction mixture described above. Therefore, we are confident that this novel bimetallic species reliably forms under conditions where reductant is added before 18-crown-6.

As illustrated in Scheme 2, the order of addition (reducing agent vs encapsulating agent) and the choice of encapsulating agent (2,2,2-Crypt vs 18-crown-6) are important for the reaction outcome. Scheme 3 summarizes the results of other permutations not discussed in Scheme 2. Adding KC_8 before 2,2,2-crypt yields a dark green solution, qualitatively indicating that the formation of $[K(2,2,2\text{-Crypt})][\text{MnInd}^{\text{Pyr}}]$ is not dependent on the reagent order when 2,2,2-Crypt is used. Adding 18-crown-6 before KC_8 generates an intractable mixture

Scheme 3. Reactivity of $\text{MnInd}^{\text{Pyr}}$ with Different Encapsulating Reagents and Orders of Addition



instead of $[\text{K}(\text{18-crown-6})(\text{THF})_2][\text{Mn}_2\text{Ind}^{\text{Pyr}}]$, clearly indicating that the order of addition is essential when using 18-crown-6. Work-up of a reaction mixture containing single equivalents of both KC_8 and 18-crown-6 did not result in a clean mixture of $[\text{K}(\text{18-crown-6})][\text{Mn}_2\text{Ind}^{\text{Pyr}}]$ and $[\text{K}(\text{18-crown-6})][\text{Ind}^{\text{Pyr}}]$, which required the use of a twofold excess of the reductant and the encapsulating agent, as shown in Scheme 2.

CONCLUSIONS

We have explored the cathodic electrochemistry and reactivity of aminoindenyl manganese tricarbonyl complexes. The deviations in planarity between the amine and the Cp ring in the solid state dictate the observed electrochemical and spectroscopic signatures in solution. Increased ligand planarity results in greater π -electron donation from the amine to the Cp ring, boosting the electron density at Mn. The structural, electrochemical, and IR spectroscopic data are all in excellent agreement with the DFT computations. The reaction outcome upon the chemical reduction of $\text{MnInd}^{\text{Pyr}}$ depends on the choice of encapsulating agent, the amount of reductant, and their order of addition. Reduction in the presence of 2,2,2-crypt and $\text{MnInd}^{\text{Pyr}}$ generated a rare Mn^0 metalloradical anion that was characterized by X-ray crystallography and EPR spectroscopy, with DFT calculations showing a predominantly metal-based radical character. The reduction of $\text{MnInd}^{\text{Pyr}}$ in the absence of the encapsulating agent, followed by the addition of 18-crown-6, results in the formation of an unusual mixed-valent complex in which $\text{Mn}^{\text{I}}(\text{CO})_3$ and $\text{Mn}^{-\text{I}}(\text{CO})_3$ moieties are coordinated to a single indenyl ligand. Although the dissociation of the aminoindenyl ligand instead of CO loss diminishes the utility of these compounds as precatalysts for small-molecule activation and electrocatalysis, this study emphasizes that reversible redox activity on the CV time scale does not adequately capture the novel reactivity of indenylmanganate anions in the presence of alkali metal reductants and encapsulating agents.

EXPERIMENTAL SECTION

General Procedures. Compounds were handled under a nitrogen atmosphere in glovebox or via standard Schlenk techniques unless otherwise stated. Commercially available reagents were used as received. $\text{Mn}(\text{CO})_5\text{Br}$ was either obtained from commercial vendors or synthesized as published.³⁶ $\text{Mn}(\text{CO})_3(\text{py})_2\text{Br}$,³⁶ 1-(1*H*-inden-2-yl)-4-methylpiperazine,¹⁴ 1-(1*H*-inden-2-yl)pyrrolidine,¹⁶ η^5 -(2-(*N*-methylpiperazine)-indenyl)-manganese tricarbonyl¹⁴ (Ind^{PipH}), and indenyltricarbonylmanganese¹⁵ (Ind^{PyrH}) were also synthesized as published. Potassium graphite (KC_8) was prepared by agitating potassium chunks and graphite flakes at 150 °C under a vacuum.³⁷ The concentration of $n\text{BuLi}$ was checked using a quantitative no-D NMR experiment with a 1,5-cyclooctadiene (COD) internal standard.^{38,39} THF used in glovebox work was dried and degassed over alumina columns on a solvent purification system and then stored overnight on 10% w/v molecular sieves before use.⁴⁰ Diethyl ether and pentane were dried and degassed over alumina columns on a solvent purification system and directly used without further drying. Solvents used in air-stable reactions were used as received. Column chromatography was performed on silica gel (60 Å, 40–63 μm , Sorbent Technologies). Celite was heated at 140 °C for several hours and then transferred into a glovebox for use. Infrared spectra were recorded on a Thermo Nicolet FT-IR instrument. Elemental analyses were performed by Atlantic Microlab (Norcross, GA) or the Department of Chemistry at the University of Rochester (Rochester, NY).

NMR. ^1H and ^{13}C NMR spectra were collected on a Bruker Avance III 500 MHz NMR with autosampler capability using either a 5 mm BBO broadband (^{31}P – ^{109}Ag , ^1H , and ^{19}F) probe or a 5 mm BBFO broadband (^{31}P – ^{15}N plus ^{19}F and ^1H) probe and a 15 mm boron-selective (^{11}B , ^1H , and ^{19}F) probe. ^{55}Mn NMR spectra were obtained on a Bruker Avance III 500 MHz NMR with a 5 mm BBO broadband (^{31}P – ^{109}Ag , ^1H , and ^{19}F) probe at 125 MHz. ^1H and ^{13}C NMR spectra were referenced to residual ^1H and ^{13}C signals in the deuterated solvent, and ^{55}Mn NMR spectra were referenced externally to a freshly prepared saturated solution of KMnO_4 in D_2O set to 0 ppm.^{41,42} Magnetic moments were determined by Evans' method by measuring the paramagnetic shifts of deuterated solvent signals in a known concentration of analyte solution and comparing them with the chemical shift of the deuterated solvent in a flame-sealed capillary tube.^{43,44}

X-ray Diffraction. Single crystals were mounted on a nylon or Kapton loop and cooled to 100 K under a dry nitrogen stream before data collection unless otherwise stated. SCXRD was performed on a Rigaku XtaLAB Synergy-I diffractometer with a HyPIX HPC detector using Cu $K\alpha$. Structures were refined by full-matrix least-squares based on F^2 with all reflections (SHELXTL V5.10; G. Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. The SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI, 1998) absorption correction was applied. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center and are available free of charge through the CCDC online database.

EPR Spectroscopy. Continuous-wave X-band (9.43898 GHz) EPR spectra were collected at 77 K using a Bruker EMXPlus EPR spectrometer with a standard high-sensitivity X-band resonator. Concentrated solutions were suspended in a frozen 2-MeTHF glass and contained in 4 mm OD quartz tubes. The microwave power was typically 0.2 mW. The field was swept by 1000 G centered at 3400 G and modulated at 100 kHz with 4 G amplitude. A time constant of 20.48 ms was used. Spectra were simulated using EasySpin.⁴⁵

Electrochemistry. Cyclic voltammetry experiments were conducted under N_2 at 295 ± 3 K using a standard three-electrode setup consisting of a PEEK-encased glassy carbon working electrode ($\varnothing = 1$ mm) and type 2 graphite rod counter electrode ($\varnothing = 3$ mm). The Ag/AgCl pseudoreference electrode was stored in a glass compartment containing the solvent and the electrolyte and was separated from the bulk solution using a porous glass frit (Coralpor). The working electrode was polished in the glovebox with 0.25 μm diamond polishing paste (Buehler) and lapping oil and thoroughly rinsed with the solvent used in the corresponding experiment. A Gamry Reference 1010B potentiostat and Gamry software were used for data collection and analysis, respectively. Samples contained 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$, organic solvent (3 mL), and 1.0 mM analyte. All CVs are referenced to the $\text{Cp}_2\text{Fe}^{+/0}$ redox couple (0 V).

DFT Calculations. DFT geometry optimizations and frequency calculations were performed with TURBOMOLE ver. 7.5.1⁴⁶ at the $\omega\text{B97X-V}/\text{def2-TZVP}+\text{COSMO}(\text{MeCN})$ level of theory. To reduce the errors from the harmonic approximation, the frequencies were scaled by a factor of 0.95.⁴⁷ Single-point energy calculations on a higher level of theory were performed employing ORCA ver. 5.0.3⁴⁸ with the optimal-tuned (OT)⁴⁹ $\omega\text{B97X-V}$ functional (see the SI for details) and the large ma-def2-QZVP basis set. Thermostatistical corrections were obtained from the calculated frequencies via the modified rigid-rotor-harmonic-oscillator scheme,⁵⁰ and the solvation free energy for the final energy evaluation was obtained with COSMO-RS. For the calculation of reduction potentials, the $\text{Cp}_2\text{Fe}^{+/0}$ reference was explicitly calculated at the same level of theory.

$\text{MnInd}^{\text{Pyr}}$. 1-(1*H*-Inden-2-yl)pyrrolidine (995 mg, 5.37 mmol) was dissolved in THF (25 mL), cooled to -78 °C, and deprotonated with 2.5 M $n\text{BuLi}$ (2.2 mL, 6 mmol, 1.1 equiv). The brown solution turned red and was warmed to room temperature, forming a suspension. This mixture was reacted at room temperature for 1 h, then $\text{Mn}(\text{CO})_5\text{Br}$ (1.48 g, 5.37 mmol) was added as a solid under a positive flow of

nitrogen. Upon addition, the solution became dark orange. This solution was then stirred at room temperature for three days. The solvent was then removed in vacuo and purified by silica gel column chromatography (3 cm × 30 cm column) under air. A 1:10 ethyl acetate/hexane mobile phase eluted a small yellow band ($\text{Mn}_2(\text{CO})_{10}$), followed by a larger orange product band. The yellow band was identified to be $\text{Mn}_2(\text{CO})_{10}$ by unit cell analysis via SCXRD (formed by cooling a concentrated pentane solution to -35°C). The orange solution was not air-stable at room temperature for prolonged periods of time. As soon as the solution was isolated, the solvent was removed on a rotary evaporator, and the product was recrystallized from hexanes in a standard laboratory freezer at -16°C . The crystalline product was air stable enough to dry and isolate on the benchtop (449 mg, 26%). The resultant crystals were suitable for SCXRD. ^1H NMR (500 MHz, CDCl_3) δ 7.44 (dd, $J = 6.6, 3.2$ Hz, 2H, H11, H12), 7.01 (dd, $J = 6.6, 3.1$ Hz, 2H, H10, H13), 4.57 (s, 2H, H6, H9), 3.09–3.03 (m, 4H, H1, H4), 1.97–1.90 (m, 4H, H2, H3). ^{13}C NMR (126 MHz, CDCl_3) δ 25.14, 48.84, 55.56, 76.75, 77.00, 77.25, 99.60, 124.90, 125.38, 133.08, 208.30, 225.41. IR (cm^{-1} , KBr) 2957(w), 2923(w), 2852(w), 1989 (s, CO), 1890(s, CO), 1539(s), 1520(m), 1479(m), 1459(m), 1449(m), 1374(w), 1351(w), 1260(w), 1205(w), 1168(w), 1152(m), 1139(m), 1114(w), 1021(w), 993(w), 898(w), 815(m), 798(m), 738(s), 665(s). Elemental Analysis calculated (%) for $\text{C}_{16}\text{H}_{14}\text{MnNO}_3$: C 59.45, H 4.37, N 4.33. Found (%): C 59.48, H 4.39, N 4.44.

[K(18-crown-6)(THF) $_2$][Mn $_2$ Ind $^{\text{Pyr}}_2$]. To a yellow solution of MnInd $^{\text{Pyr}}$ (51.8 mg, 0.160 mmol) in THF (3 mL), KC_8 (45.5 mg, 0.337 mmol) suspended in 1 mL of THF was added dropwise. The reaction mixture was stirred in a 20 mL scintillation vial for 2 h and then filtered through a pad of Celite. To this orange-red solution was added 18-crown-6 (84.7 mg, 0.321 mmol) and the mixture was allowed to stir for 30 min. The solvent was then removed in vacuo, and the resulting dark orange oily solid was washed with diethyl ether (3 × 6 mL) and dried in vacuo. The product yield (82%) was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard (8.1 mg, 0.048 mmol) along with varying amounts of [K(18-crown-6)][Ind $^{\text{Pyr}}$], which was independently synthesized but had to be accounted for in microanalysis (see below). Crystallization of the crude reduction mixture via pentane vapor diffusion into a concentrated THF solution resulted in dark orange-red crystals suitable for XRD. ^1H NMR (500 MHz, THF) δ 5.79 (dd, $J = 5.0, 2.8$ Hz, 2H, H11, H12), 3.62 (s, 2H, H6, H9), 2.70 (td, $J = 5.2, 3.0$ Hz, 4H, H1, H4), 1.86 (d, $J = 2.8$ Hz, 2H, H10, H13), 1.75 (m, 4H, H2, H3). IR (cm^{-1} , KBr) 2961 (m), 2887 (m), 2824 (m), 1972 (m), 1942 (s), 1857 (s), 1832 (m), 1584 (w), 1457 (w), 1352 (m), 1285 (w), 1258 (w), 1107 (s), 962 (m). Elemental Analysis calculated (%) for $[\text{C}_{31}\text{H}_{38}\text{NO}_{12}\text{Mn}_2\text{K}][\text{C}_{25}\text{H}_{38}\text{NO}_6\text{K}]_{0.7}$: C 52.62, H 5.88, N 2.15. Found (%): C 52.92, H 6.18, N 1.97.

[K(18-crown-6)][Mn $_2$ Ind $^{\text{Pyr}}_2$]. The ether washings of the crystallized [K(18-crown-6)(THF) $_2$][Mn $_2$ Ind $^{\text{Pyr}}_2$] were concentrated and then cooled at -35°C for several days, leading to milligram quantities of the THF-free adduct [K(18-crown-6)][Mn $_2$ Ind $^{\text{Pyr}}_2$] that were suitable for X-ray diffraction. The yield was not determined.

[K(2,2,2-Crypt)][Ind $^{\text{Pyr}}_2$]. To a stirred yellow solution of Ind $^{\text{Pyr}}_2$ (49.7 mg, 0.154 mmol) and 2,2,2-Crypt (142 mg, 0.397 mmol) in THF (3 mL) in a 20 mL scintillation vial, KC_8 (55.9 mg, 0.414 mmol) suspended in a 1 mL THF solution was added dropwise. The solution was stirred for 1 h at room temperature and then filtered through a pad of Celite. The solution was concentrated to ca. 2 mL and then stored overnight at -35°C , resulting in the crystallization of the product. The solvent was then decanted and the crystals were dried in vacuo, yielding analytically pure [K(2,2,2-Crypt)][Ind $^{\text{Pyr}}_2$] (88 mg, 96%). ^1H NMR (500 MHz, THF) δ 6.84 (dd, $J = 5.7, 3.1$ Hz, 2H), 6.05 (dd, $J = 5.7, 3.0$ Hz, 2H), 5.21 (s, 2H), 3.26 (s, 12H), 3.20 (t, $J = 4.7$ Hz, 12H), 3.18–3.13 (m, 4H), 2.25–2.20 (m, 12H), 1.90–1.81 (m, 4H). ^{13}C NMR (126 MHz, THF) δ 26.03, 51.13, 54.72, 68.35, 71.06, 79.94, 109.40, 114.99, 131.77, 148.54. IR (cm^{-1} , KBr) 2961 m, 2873 m, 2813 m, 1587 s, 1462 m, 1358 s, 1291 w, 1258 w, 1126 m, 1099 s, 948 m, 933 m. Elemental Analysis calculated (%) for

$\text{C}_{31}\text{H}_{50}\text{KN}_3\text{O}_6$: C 62.07, H 8.40, N 7.01. Found (%): C 62.25, H 8.09, N 6.79.

[K(2,2,2-Crypt)][MnInd $^{\text{Pyr}}_2$]. To a stirred yellow solution of MnInd $^{\text{Pyr}}$ (37 mg, 0.11 mmol) and 2,2,2-Crypt (43 mg, 0.11 mmol) in THF (3 mL) in a 20 mL scintillation vial, KC_8 (17 mg, 0.13 mmol) suspended in a 1 mL THF solution was added dropwise. The mixture was stirred for 2 h and then filtered through a pad of Celite. The solvent was concentrated to ca. 0.5 mL, and the resulting deep green solution was diluted with diethyl ether. The solvent was removed in vacuo, during which the product crystallized as dark green needles. These crystals were washed with diethyl ether, then dried under high vacuum to generate the product (31 mg, 36%) and a nearly equimolar amount of [K(2,2,2-Crypt)][Mn(CO) $_5$] (0.7 equiv) as determined by elemental analysis. Crystals suitable for XRD were grown via pentane vapor diffusion into a concentrated THF solution of [K(2,2,2-Crypt)][MnInd $^{\text{Pyr}}_2$] that also contained colorless crystals of [K(2,2,2-Crypt)][Mn(CO) $_5$]. IR (cm^{-1} , KBr) 2965 w, 2888 w, 2819 w, 1884 s (CO), 1807 m (CO), 1784 m (CO), 1547 w, 1511 w, 1480 w, 1445 w, 1355 m, 1297 w, 1260 w, 1170 w, 1133 m, 1102 s, 950 m, 933 m. Elemental Analysis calculated (%) for $[\text{C}_{34}\text{H}_{53}\text{N}_3\text{O}_9\text{MnK}][\text{C}_{23}\text{H}_{36}\text{N}_2\text{O}_{11}\text{MnK}]_{0.7}$: C 51.46, H 6.74, N 5.27. Found (%): C 51.83, H 6.28, N 5.04. Magnetic moment: $\mu_{\text{eff}} = 1.69 \mu_{\text{B}}$ (THF- d_8).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.2c00463>.

Computed Cartesian coordinates (XYZ)

Electrochemistry, molecular structures, NMR spectra, IR spectra, and DFT computational workflow (PDF)

Accession Codes

CCDC 2202042 and 2202047–2202051 contain 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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