ORGANOMETALLICS

Half-Sandwich Manganese Complexes Bearing Cp Tethered *N*-Heterocyclic Carbene Ligands: Synthesis and Mechanistic Insights into the Catalytic Ketone Hydrosilylation

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S Supporting Information

ABSTRACT: Manganese(I) complexes $[(Cp(CH_2)_nNHC^{Mes})Mn(CO)_2]$ (**2a**, n = 1; **2b**, n = 2) bearing Cp tethered NHC ligands have been prepared in good yield from $[CpMn(CO)_3]$ and *N*-mesitylimidazole as main components, using a novel synthetic strategy based on the anchoring of an imidazolium moiety to the coordinated Cp ligand, followed by an intramolecular photochemical CO substitution for the pendent NHC moiety generated *in situ* upon addition of a base. The catalytic performances of **2a**–**b** in the hydrosilylation of 2-acetonaph-thone with Ph₂SiH₂ were found to be essentially indifferent to the length of the linker between the Cp and the NHC moieties, and lower than the one of the nontethered $[Cp(CO)_2Mn(IMes)]$ (**1**) parent complex. Still, the presence of Cp



tethered NHC ligands allowed isolation and full characterization of monocarbonyl η^2 -silane complexes $[(Cp(CH_2)_nNHC^{Mes})-Mn(CO)(\eta^2-H-SiHPh_2)]$ (8a, n = 1; 8b, n = 2), which are generated upon photochemical reactions of 2a-b with diphenylsilane. Both of these silane complexes are inactive for the catalytic 2-acetonaphthone hydrosilylation process but were found to form catalytically active noncarbonyl species under UV irradiation, being consistent with the Ojima mechanism for ketone hydrosilylation.

INTRODUCTION

The use of organometallic complexes of earth abundant 3d transition metals represents one of the most important aspects of modern homogeneous catalysis. In contrast to the extensive applications of iron-,¹ cobalt-,² and nickel-based³ catalysts, the design of catalytic systems based on organometallic manganese derivatives⁴ has attracted only recently attention, resulting in the spectacular development of highly efficient Mn-catalyzed C–H bond activation,⁵ (de)hydrogenation,⁶ hydrosilylation,⁷ borylation,⁸ CO₂ reduction,⁹ and electrochemical hydrogen production¹⁰ processes.

In a continuation of our work on the hydrosilylation of carbonyl-containing compounds catalyzed by well-defined 3d metal complexes,¹¹ we have recently shown that half-sandwich manganese complex 1 bearing a 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) ligand (Chart 1), easily available from industrially produced cymantrene, $[CpMn(CO)_3]$, is an effective precatalyst for the reduction of a variety of aldehydes and ketones with diphenylsilane at room temperature under UV light irradiation.^{7c} Though the activity of this catalytic system is inferior to the known σ -acyl,¹² π -arene,¹³ salen,^{7e} and especially to the most active to date bis(imino)pyridine manganese catalysts,^{7a,b} it offers a good tolerance toward a variety of sensitive functional groups (ester, nitrile, conjugated or isolated C=C bonds, alkyne, heterocycles).^{7c}

Chart 1. Half-Sandwich Mn^I NHC Complexes Used as Precatalysts for Ketone Hydrosilylation (Mes = 2,4,6-Trimethylphenyl)



During the past decade, it was shown that tethering *N*-heterocyclic carbene (NHC) ligands with η^5 -cyclopentadienyl (Cp) and related η^5 -indenyl (Ind) or η^5 -fluorenyl (Flu) ligands is a viable strategy for increasing the stability of the corresponding transition metal or lanthanide complexes and, in some cases, their catalytic performance.¹⁴ Inspired by this concept, we report herein the synthesis of manganese complexes bearing Cp tethered NHC ligands [(Cp-(CH₂)_nNHC^{Mes})Mn(CO)₂] (**2a**, n = 1; **2b**, n = 2, Chart 1), the comparison of their catalytic performance with regard to

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Scheme 1. Synthesis of Manganese Complexes 2a-b Bearing Cp Tethered NHC Ligands^a



^{*a*}Reagents and reaction conditions: (*a*) 1.1 equiv of *n*-BuLi, THF, -80 °C, 1.5 h; (*b*) 3 equiv of $(CH_2O)_{n}$, -80 °C to RT, 15 h then H₂O at RT; (*c*) 1.2 equiv of SOCl₂, 10% Py, CH₂Cl₂, 0 °C, 30 min; (*d*) 1.3 equiv of *N*-mesitylimidazole, 10% KI, MeCN, 90 °C, 5 days; (*e*) 1.2 equiv of KHMDS, THF, RT, 10–30 min; (*f*) UV irradiation, toluene, 0 °C, 45–90 min; (*g*) 2-2.5 equiv of ethylene oxide, THF, -80 °C to RT, 15 h then H₂O at RT; (*h*) 1.1 equiv of MsCl, 1.5 equiv of Et₃N, CH₂Cl₂, 0 °C, 30 min; (*i*) 1.3 equiv of *N*-mesitylimidazole, toluene, 110 °C, 20 h.

the parent IMes analogue 1, and experimental data relevant to the mechanism of the ketone hydrosilylation process catalyzed by half-sandwich Mn^I NHC complexes.

RESULTS AND DISCUSSION

Synthesis and Characterization of Piano-Stool Mn^I Complexes [(Cp(CH₂)_nNHC^{Mes})Mn(CO)₂] (2a, n = 1; 2b, n= 2) Featuring Cp Tethered NHC Ligands. Literature precedents relative to the syntheses of Cp tethered NHC complexes are all based on the preparation of substituted cyclopentadiene derivatives bearing a pendent imidazolium moiety, followed by complexation of the latter to a transition metal.^{15,16} Here, owing to the excessive availability of $[CpMn(CO)_3]$ precursor, we choose to first anchor the imidazolium moiety to the Cp ligand through a variable length link. In that prospect, selective deprotonation of the Cp ligand in $[CpMn(CO)_3]$ was achieved using *n*-BuLi in THF at -80 °C (Scheme 1).¹⁷ Subsequent treatment of the organolithium derivative [3]Li with either paraformaldehyde¹⁸ or ethylene oxide¹⁹ afforded, after hydrolysis, complexes $4a^{18}$ and 4b in 85% and 91% yield, respectively. The latter were transformed into the corresponding chloride $5a^{18}$ and mesylate 5bderivatives, which were each subjected to nucleophilic substitution with N-mesitylimidazole to provide complexes [6a]Cl and [6b]OMs featuring a pendent mesitylimidazolium moiety attached to the Cp ligand through $-(CH_2)$ - and $-(CH_2)_2-$ (C1 and C2 alkyl) links, respectively. Noticeably, the chloride complex 5a was found to be much less reactive than 5b and the addition of catalytic amounts of potassium iodide (Finkelstein conditions) was necessary to accelerate the process. The treatment of [6a]Cl and [6b]OMs with KHMDS in THF at room temperature led to the formation of the cymantrene derivatives $\left[(Cp(CH_2)_n NHC^{Mes}) Mn(CO)_3 \right] (7a, n)$ = 1; 7b, n = 2) featuring pendent NHCs moieties. They were fully characterized by ¹H and ¹³C NMR spectroscopy, the latter showing, in particular, signals at δ 218.0 and 215.7 ppm for the carbene carbon atoms in 7a and 7b, respectively. Of note is that complex 7b is relatively unstable, slowly decomposing at RT even under an inert atmosphere to give among several decomposition products N-mesitylimidazole and vinylcymantrene, $(\eta^5-C_5H_4CH=CH_2)Mn(CO)_3$ ²⁰ Finally, the formation of the targeted $[(Cp(CH_2)_nNHC^{Mes})Mn(CO)_2]$ (2a, n = 1; 2b, n = 2) was achieved upon UV irradiation of toluene solutions of 7a and 7b, respectively, adjusting a protocol we recently described for the synthesis of $[CpMn(CO)_2(IMes)]$.²¹

Complexes 2a and 2b were isolated in 73% and 61% yield, respectively, after purification by column chromatography and crystallization (global yield of ca. 50% starting from cymantrene) and were fully characterized by spectroscopic methods and single-crystal X-ray diffraction analyses. Their IR spectra in toluene solution display two characteristic intense $v_{\rm CO}$ bands (2a: 1924, 1857 cm⁻¹; 2b: 1918, 1851 cm⁻¹). The alkyl spacers between Cp and NHC ligands appear as a singlet at δ 3.47, and two multiplets at δ 2.98, and δ 1.70 ppm in the ¹H NMR spectra for **2a** and **2b**, respectively, while the carbene carbon atoms appear as very characteristic singlets at δ 207.7 ppm, and δ 207.0 ppm, respectively, in the ¹³C{¹H} NMR spectra. In passing, complexes 2a and 2b represent the first examples of complexes exhibiting Cp tethered aryl-substituted NHC ligands,²² 2a featuring in addition the first example of a C1 linker-based Cp tethered NHC ligand.

Perspective views of complexes 2a and 2b are shown in Figures 1 and 2, respectively.



Figure 1. A perspective view of complex **2a** (30% probability ellipsoids; only one of the two independent molecules in the unit cell is shown).



Figure 2. A perspective view of complex 2b (30% probability ellipsoids).

Both piano-stool Mn^I complexes show the usual pseudooctahedral geometry around the manganese atom, the substituted η^{5} -Cp ring being bounded in a *pseudo*-facial manner, the remaining CO and NHC ligands having mutually cis arrangements. The $Mn-C_{carbene}$ bond lengths being of 1.964(2) and 1.963(2) Å for the two independent molecules in the unit cell for 2a, and 1.989(2) Å for 2b, are slightly shorter than the corresponding one in the nontethered parent IMes complex 1 (2.003(3) Å).²³ In complex 2a, which exhibits the most configurationally stable five-membered metallocycle, the NHC ligand adopts a vertical orientation²⁴ ({ $cnt_{Cp}-Mn1-C3-N1$ } = 174.4° and -178.8° for two independent molecules in the unit cell). In the case of complex 2b, the orientation of the NHC moiety is slightly deviated from *vertical* position, {cnt_{Cp}-Mn1-C3-N1 = 162.0°, as it was found in the [(Cp-NHC)Fe-(CO)I] parent complex previously reported by Royo et al.²

Comparison of the Catalytic Performance of the Mn^I NHC Complexes 1, 2a, and 2b in Ketone Hydrosilylation. The activity of the Mn^I complexes 2a and 2b bearing Cp tethered NHC ligands has been evaluated in the ketone hydrosilylation with diphenylsilane under the same conditions as the ones previously reported for complex $1,^{7c}$ using 2-acetonaphthone as a benchmark substrate (Table 1). At 1 mol

Table 1. Hydrosilylation of 2-Acetonaphthone with Ph_2SiH_2 Catalyzed by Manganese NHC Complexes 1, 2a, and $2b^a$

complex	catalyst (mol %)	time (h)	yield (%) ^b
1	1.0	2	>98
	0.5	2	98
	0.1	24	96
2a	1.0	2	56
	0.5	24	92 ^c
	0.1	24	33
2b	1.0	2	66
	0.5	24	98
	0.1	24	29

^{*a*}Reaction conditions: 2-acetonaphthone (0.5–2 mmol), 1 equiv of Ph_2SiH_2 , toluene (1–4 mL, 0.5 M substrate concentration), UV irradiation (350 nm), 25 °C. ^{*b*}NMR yield of the corresponding alcohol (average of two runs) after basic hydrolysis (2 M NaOH_{aq}, MeOH, 30 min, 25 °C). ^{*c*}98% yield after 48 h of reaction.

% loading, both complexes were found to be active in this reaction under UV irradiation, albeit they exhibited a lower efficiency than the parent IMes complex 1. The catalytic charge was reduced to 0.5 mol %, still leading to an almost quantitative yield of product after 24 h for complexes 1 and 2b, and 48 h for complex 2a. Finally, using only 0.1 mol % of catalysts TON of ca. 960, 330, and 290 were achieved for complexes 1, 2a, and 2b, respectively, after 24 h of reaction. It is noteworthy that those TON values are significantly higher than the ones observed (up to 50) for related Fe^{II11k} and Ni^{II11h,22b} NHC precatalysts. Though the rate of ketone hydrosilylation catalyzed with complexes 1 and 2a–b is typically lower than that for other manganese catalysts, ^{7,12,13} only the most active to date bis(imino)pyridine manganese catalysts are more efficient than 1 in terms of TON (up to 6200).^{7a,b}

Insights into the Mechanism of Mn^I NHC Catalyzed Ketone Hydrosilylation through the Stoichiometric Reactivity of the Complexes 2a–b with Diphenylsilane. In order to shed light on the mechanism of the hydrosilylation of carbonyl compounds catalyzed by Mn^I NHC complexes, additional stoichiometric experiments were carried out. First of all, it has been observed that UV irradiation of a solution of 1 in toluene in the presence of 2 equiv of diphenylsilane leads to the gradual consumption of the starting material—according to IR spectroscopy monitoring—without formation of any welldefined organometallic species. To our delight, under the same reaction conditions, the Cp tethered NHC complexes 2a-b cleanly afforded the products $[(Cp(CH_2)_nNHC^{Mes})Mn (CO)(\eta^2-H-SiHPh_2)]$ (8a, n = 1; 8b, n = 2) of photochemical substitution of CO for diphenylsilane (Scheme 2), belonging to

Scheme 2. Synthesis of η^2 -Silane Complexes 8a–b



the family of well-known half-sandwich manganese silane complexes.^{25,26} Both compounds were isolated in good yields and were fully characterized by spectroscopic methods, supplemented for **8b** by a single-crystal X-ray diffraction analysis.

The IR spectra of 8a and 8b in THF solution show a single medium intensity $v_{\rm CO}$ band at 1969 and 1961 cm⁻¹, and a weak broad v_{SiH} band at 2075 and 2090 cm⁻¹, respectively. For both complexes, the ¹H and ¹³C{¹H} spectra show four different signals for C-H moieties of the Cp ligand and two signals for the Cortho-Me and Cmeta-H fragments of the Mes group as a consequence of the Mn atom being stereogenic. Silane protons in the ¹H NMR spectrum of **8a** appear as singlets at δ 5.51 and -10.48 ppm corresponding to the free and coordinated Si-H entities, respectively. As for complex 8b, the corresponding signals appear at 5.22 and -10.49 ppm as doublets with ${}^{2}J_{\rm HH}$ of 4.0 Hz. The ${}^{1}J_{SiH}$ coupling constants in 8a and 8b—obtained from the corresponding ²⁹Si satellite signals in the ¹H spectra are of 195.0 and 198.5 Hz for the free Si-H bond, and 47.4 and 47.6 Hz for coordinated Si-H bond in 8a and 8b, respectively. The latter values indicate that complexes **8a–b** are closer from

silane σ -complexes with 3c-2e⁻ Mn-Si-H bonds than from Mn^{III} silylhydrides.²⁷

A perspective view of complex **8b** is given in Figure 3. The hydrogen atoms H1 and H2 associated with the diphenylsilane



Figure 3. A perspective view of complex 8b (ellipsoids are show at the 30% probability level).

moieties were clearly located from a Fourier difference map. Their coordinates were refined with fixed isotropic thermal parameters, leading to reasonable Mn-H and Si-H bond distances by reference to the corresponding bond distances determined by neutron diffraction on parent complexes.^{25e,26} The position of H2 bridging the Si1-Mn1 vector (Mn1-H2 = 1.47(3) Å, Si1-H2 = 1.74(3) Å) speaks again for 8b being a silane σ -complex. The Si-H bond adopts a horizontal coordination mode, $\{cnt_{Cp}-Mn1-Si1-H2\} = 112.8^{\circ}\}$, the hydrogen atoms H1 and H2 being relatively in a cis position $({H1-Si1-Mn1-H2} = 84.1^{\circ})$ (Figure 3). The pseudooctahedral environment around the Mn is complemented by the Cp tethered NHC ligand and the remaining CO ligand. The Mn- $C_{carbene}$ bond distance of 1.986(2) Å is similar to the corresponding one in complex 2b, and the orientation of the NHC ligand becomes even more deviated from vertical (torsion angle { cnt_{Cp} -Mn1-C3-N1} = -141.5°), probably to accommodate a greater steric volume of the silane ligand compared to CO.

Regarding the catalytic hydrosilylation of 2-acetonaphthone, we have observed that both complexes 8a and 8b are totally ineffective in the absence of UV light (0.5 M solution of 2acetonaphthone in toluene, 1 equiv of Ph₂SiH₂, 1% catalyst loading, 25 °C) for up to 16 h of reaction, ruling out the possibility of a direct S_N2-type outer-sphere mechanism.²⁸ Gratifyingly, the reaction rapidly started upon switching on the UV irradiation, leading after 2 h to ca. 60% of ketone conversion as estimated by the decrease of the $v_{C=0}$ peak area of the ketone substrate. This observation suggests that silane σ complexes 8a-b are the primary products of photochemical transformation of dicarbonyl NHC complexes 2a-b in the presence of silane, but the real catalytically active species are produced more slowly upon further irradiation, this being consistent with the observation of an induction period for the hydrosilylation of acetophenone catalyzed by complex 1.⁷⁷

In order to get more insights into the reaction mechanism, we have carried out IR monitoring of the 2-acetonaphthone hydrosilylation by **8b** (0.5 M solution of 2-acetonaphthone in toluene, 1 equiv of Ph₂SiH₂, 5% catalyst loading, 25 °C) upon

alternating 20 min periods with and without UV irradiation (see Figure S26). This revealed that the characteristic v_{CO} band of **8b** at 1864 cm⁻¹ gradually decreases during the UV irradiation periods, along with the ketone $v_{C=O}$ peak at 1684 cm⁻¹ and silane v_{SiH} band at 2142 cm⁻¹, consistent with the formation of the resulting silyl ether. It was also found that the reaction proceeds sluggishly when the UV source was off, and that the overall catalyst activity was considerably lower under these interrupted conditions compared to continuous UV irradiation conditions.

The proposed mechanism of ketone hydrosilylation catalyzed by Mn^I NHC complexes is shown in Scheme 3. Clearly, the

Scheme 3. Proposed Catalytic Cycle for the Ketone Hydrosilylation Catalyzed by Mn^I NHC Complexes



remaining CO ligand in 8a-b has to be removed in order to generate the active coordinatively unsaturated manganese species. It is generally admitted that the photochemical dissociation of the last carbonyl ligand in half-sandwich Mn^I complexes is barely possible due to the very strong Mn–CO bond energy.²⁹ However, this process became feasible in the case of half-sandwich Mn^{II} complexes, as indicated by successful high yield photochemical preparation of noncarbonyl silylhydride complexes [Cp(PR₃)₂Mn(H)SiR₃] from [CpMn-(CO)(PR₃)₂] and the corresponding silane.³⁰ On the basis of this, we propose that the photochemical decarbonylation step can indeed occur for Mn^{III} silylhydride species such as [9a–b] which could be reversibly produced in a small amount by oxidative addition of Si–H bond in 8a–b.³¹

The coordination of the ketone substrate to the 16-electron silylhydride intermediates [10a-b] to form [11a-b], followed by a hydride transfer, the reductive elimination of silyl ether from the Mn^{III} intermediates [12a-b], and the coordination of another silane molecule would constitute the catalytic cycle, being in agreement with the classic Ojima mechanism (Scheme 3).^{32,33} The occurrence of the alternative Hofmann–Gade mechanism,³⁴ which is based on the formation of an 18-electron electrophilic silylene dihydride intermediate [(Cp-NHC)(H)₂Mn=SiPh₂] from [10] by α -hydride migration, is

unlikely due to the absence of the dehydrogenative silvlation byproduct 2-NaphC(OSiHPh₂)= CH_2 characteristic for the hydrosilvlation process through this type of mechanism.

CONCLUSIONS

The first examples of Mn^{I} complexes 2a-b bearing Cp tethered NHC ligands have been prepared using a novel synthetic strategy based on the anchoring of an imidazolium moiety to the coordinated Cp ligand, followed by an intramolecular photochemical CO substitution for the pendent NHC moiety generated in situ upon addition of a base prior to irradiation. Though both tethered complexes were less active in ketone hydrosilylation than a parent nontethered IMes analogue 1, we succeeded in isolating the corresponding silane σ -complexes 8a-b, being the primary products of the photochemical CO substitution for diphenylsilane in 2a-b. On the basis of additional experimental data, we proposed the classic Ojima mechanism to be operative in this case, the key step being the formation of a catalytically active noncarbonyl Mn^{III} silylhydride intermediate that would form upon photochemical dissociation of the last CO ligand. Finally, it is also noteworthy that complex 1, easily available in one step from simple IMes and industrially produced cymantrene, can achieve a TON up to 960 in ketone hydrosilylation at room temperature using 1 equiv of diphenylsilane only, thus competing well with other systems based on both noble and base metals. We are currently working on the application of Mn^I NHC complexes for other catalytic transformations, and on the development of efficient catalytic systems for the enantioselective transformations using Mn^I complexes bearing optically active NHC ligands. The results will be reported in due course.

EXPERIMENTAL SECTION

All manipulations were carried out using Schlenk techniques under an atmosphere of dry nitrogen or argon. Dry and oxygen-free organic solvents (THF, Et₂O, CH₂Cl₂, or toluene) were obtained using LabSolv (Innovative Technology) or Braun MB-SPS-800 solvent purification systems. Acetonitrile was distilled over CaH₂ under an argon atmosphere just prior to use. Solvents used for column chromatography (hexane, toluene, or Et₂O) were deoxygenated by nitrogen bubbling during 15–20 min. Deuterated benzene and chloroform used for the NMR experiments were deoxygenated by three freeze–pump–thaw cycles and kept over 4 Å molecular sieves. Technical quality cymantrene purchased as antiknocking essence additive from TPL Region Company (Moscow, Russia) was purified by recrystallization from hexane at -20 °C.²¹ All other reagent grade chemicals purchased from commercial sources were used as received.

Photochemical procedures were performed either in a 250 mL reactor with an immersed 150 W Hg medium pressure lamp TQ150 cooled by a quartz jacket with circulating water (synthesis of 2a-b), or using a homemade external 10 W light source based on 395–405 nm LEDs (synthesis of 8a-b, IR monitoring of catalytic hydrosilylation of 2-acetonaphthone with 8b), or using a Rayonet RPR 100 apparatus (350 nm catalytic hydrosilylation experiments). A liquid nitrogen/ ethanol slush bath was used to maintain samples at the desired low temperature. Chromatographic purifications of the compounds were performed on silica (0.060–0.200 mm, 60 Å) and activated alumina (neutral, 0.050–0.200 mm) obtained from Acros Organics, and flushed with nitrogen just before use.

Solution IR spectra were recorded in 0.1 mm CaF₂ cells using a PerkinElmer Frontier FT-IR spectrometer and given in cm⁻¹ with relative intensity in parentheses. ¹H, ¹³C, and ²⁹Si NMR spectra were obtained on Bruker Avance 400 and Avance III HD 400 spectrometers and referenced to the residual signals of deuterated solvents (¹H and ¹³C) and Me₄Si as internal standard (²⁹Si). High-resolution mass spectra (ESI and DCI modes) were obtained using GCT and Xevo G2

QTof (Waters) spectrometers. Elemental analyses were carried out at the LCC-CNRS (Toulouse, France) using a PerkinElmer 2400 series II analyzer.

Synthesis of $[(\eta^5-C_5H_4CH_2OH)Mn(CO)_3]$ (4a).¹⁸ A solution of *n*-BuLi (13.8 mL of 1.6 M solution in hexanes, 22.0 mmol) was added dropwise over ca. 20 min to a solution of $[CpMn(CO)_3]$ (4.08 g, 20.0 mmol) in THF (30 mL) at -80 °C. The reaction mixture was further stirred at -80 °C for 1.5 h. A suspension of paraformaldehyde (1.8 g, 60.0 mmol) in THF (30 mL) was added slowly to the resulting yelloworange suspension of complex [3]Li maintained at -80 °C, and the reaction mixture was vigorously stirred at this temperature for 4 h, then allowed to warm up slowly to room temperature overnight. Water (3 mL) was added to the solution, and the volatiles were removed under vacuum to afford an orange oil, which was purified by column chromatography on silica $(3 \times 15 \text{ cm})$. Elution with a hexane/Et₂O 10:1 mixture afforded a yellow band of starting cymantrene, followed by an orange band of the product 4a, which was eluted with a hexane/ Et₂O 1:1 mixture. The eluate was evaporated under vacuum to give 4a (3.98 g, 85%) as an orange oil. The spectroscopic data were found in agreement with a previous report.¹⁸ ¹H NMR (400.2 MHz, CDCl₃, 25 °C): δ 4.83 (m, 2H, C₅H₄), 4.70 (m, 2H, C₅H₄), 4.33 (m, 2H, CH₂), 1.70 (br s, 1H, OH). IR (CH₂Cl₂): ν_{OH} 3615 (w) cm⁻¹, ν_{CO} 2020 (s), 1932 cm^{-1} (vs).

Synthesis of $[(\eta^5-C_5H_4CH_2CH_2OH)Mn(CO)_3]$ (4b). To a suspension of complex [3]Li in THF (30 mL) generated from cymantrene (6.12 g, 30 mmol) and n-BuLi (20.6 mL, 33.0 mmol) as described above was added a solution of ethylene oxide in THF (25 mL of 2.5-3.3 M, 62.5-82.5 mmol) slowly at -80 °C. After stirring at -80 °C for 4 h and warming up to the room temperature overnight, the resulting orange solution was hydrolyzed with water (3 mL) and evaporated under vacuum to give a red oil, which was purified by column chromatography on silica $(3 \times 15 \text{ cm})$. Elution with a hexane/ toluene 10:1 mixture afforded a yellow band of starting cymantrene, followed by a red-orange band of the product 4b eluted with a toluene/Et₂O 20:1 mixture. The eluate was evaporated under vacuum to give 4b (6.76 g, 91%) as an orange oil. ¹H NMR (400.2 MHz, CDCl₃): δ 4.72 (m, 2H, C₅H₄), 4.66 (m, 2H, C₅H₄), 3.77 (m, 2H, CH₂CH₂OH), 2.50 (br t, ${}^{3}J_{HH}$ = 5.8 Hz, 2H, CH₂CH₂OH), 1.58 (br s, 1H, OH). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 225.2 (Mn-CO), 103.0 $(C-CH_2)$, 83.3, 82.0 (C_5H_4) , 63.3 (CH_2CH_2OH) , 31.5 (CH₂CH₂OH). IR (CH₂Cl₂): ν_{OH} 3615 (w) cm⁻¹, ν_{CO} 2019 (s), 1931 cm^{-1} (vs).

Synthesis of $[(\eta^5-C_5H_4CH_2CI)Mn(CO)_3]$ (5a). To a solution of 4a (1.91 g, 8.1 mmol) in CH_2Cl_2 (5 mL) was added $SOCl_2$ (0.7 mL, 9.7 mmol) under stirring at 0 °C. Then, pyridine (0.07 mL, 0.81 mmol) was added, and the reaction mixture was stirred at 0 °C until the disappearance of the starting 4a by TLC (ca. 15-20 min). The reaction mixture was then cooled to -80 °C and rapidly filtered through a short column of alumina $(2 \times 3 \text{ cm})$ using CH₂Cl₂ as eluent. The resulting yellow solution was evaporated under vacuum, and the residue was extracted with hexane $(3 \times 10 \text{ mL})$. The extracts were filtered through a short column of silica $(2 \times 4 \text{ cm})$ using hexane as eluent, and the resulting yellow solution was evaporated under vacuum to afford 5a (1.84 g, 90%) as yellow crystals. The spectroscopic data were found in agreement with a previous report.¹⁸¹H NMR (400.2 MHz, CDCl₃, 25 °C): δ 4.90 (m, 2H, C₅H₄), 4.72 (m, 2H, C₅H₄), 4.23 (s, 2H, CH₂). IR (CH₂Cl₂): ν_{CO} 2025 (s), 1938 cm⁻¹ (vs). HRMS (EI): m/z calcd for $C_{10}H_9MnO_4$: 191.9983 [M⁺ - 2CO], found: 192.0021.

Synthesis of $[(\eta^5-C_5H_4CH_2CH_2OMs)Mn(CO)_3]$ (5b). To a solution of 4b (7.69 g, 31.0 mmol) and Et₃N (6.5 mL, 46.5 mmol) in CH₂Cl₂ (50 mL) was added MsCl (2.64 mL, 34.1 mmol) dropwise at 0 °C. After stirring the solution at this temperature for 45 min, the reaction was quenched with water (20 mL). The yellow organic phase was separated and washed consequently with 1 M HCl_{aq} (20 mL) and brine (20 mL). The resulting solution was dried over MgSO₄, filtered through Celite, and evaporated under vacuum to give **5b** (9.84 g, 97%) as a yellow powder. ¹H NMR (400.2 MHz, CDCl₃, 25 °C): δ 4.74 (t, ³J_{HH} = 2.1 Hz, 2H, C₅H₄), 4.69 (t, ³J_{HH} = 2.1 Hz, 2H, C₅H₄), 4.32 (t, ³J_{HH} = 6.3 Hz, 2H, CH₂CH₂OMs), 3.01 (s, 3H, CH₃SO₂), 2.72 (t, ³J_{HH})

= 6.3 Hz, 2H, CH₂CH₂OMs). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 224.8 (Mn–CO), 100.2 (C–CH₂), 83.4, 82.3 (C₅H₄), 69.2 (CH₂CH₂-OMs), 37.7 (SO₂CH₃), 31.5 (CH₂CH₂OMs). IR (CH₂Cl₂): ν_{CO} 2022 (s), 1934 cm⁻¹ (vs). Anal. Found: C, 40.54; H, 3.29. Calcd for C₁₁H₁₁MnO₆S (M = 326.2) C, 40.50; H, 3.40.

Synthesis of $[(\eta^5-C_5H_4CH_2Im^{Mes})Mn(CO)_3]CI ([6a]CI)$. A solution of 5a (0.75 g, 3.0 mmol), N-mesitylimidazole (0.73 g, 3.9 mmol), and KI (50 mg, 0.3 mmol) in MeCN (12 mL) was heated at 90 °C until the maximum conversion of 5a was achieved according to the ¹H NMR spectrum of the aliquot (ca. 4-5 days). The volatiles were removed under vacuum, and the residue was dissolved in CH₂Cl₂ (10 mL). The solution was filtered through Celite, and ether (30 mL) was added dropwise under stirring to induce the crystallization of [6a]Cl. The supernatant was removed using a cannula tipped with a filter paper, and the precipitate was washed with ether (20 mL) and dried under vacuum to give [6a]Cl (1.13 g, 84%) as a white powder. Though the product was found to be pure enough according to elemental analysis, its ¹H spectrum is broadened due to the systematic presence of trace amounts of paramagnetic Mn^{II} impurities. ¹H NMR (400.2 MHz, dmso- d_{6} , 25 °C): δ 10.05 (s, 1H, $C\dot{H}_{Im2}$), 8.30 (s, 1H, CH_{Im4,5}), 8.02 (s, 1H, CH_{Im4,5}), 7.14 (s, 2H, CH_{Mes}), 5.56 (m, 4H, $C_{5}H_{4}$), 5.06 (s, 2H, NCH₂), 2.32 (s, 3H, CH_{3para-Mes}), 2.01 (s, 6H, CH_{3ortho-Mes}). ¹³C{¹H} NMR (100.6 MHz, dmso-d₆, 25 °C): δ 224.0 (Mn-CO), 139.7 (C-CH_{3para-Mes}), 137.5 (CH_{Im4,5}), 133.7 (C-CH_{3ortho-Mes}), 130.6 (C_{ipso Mes}), 128.9 (CH_{Mes}), 123.8 (CH_{Im4,5}), 122.9 (CH_{Im2}) , 96.4 $(C-C\dot{H}_2)$, 86.1, 83.1 (C_5H_4) , 45.8 $(NC\dot{H}_2)$, 20.3 $(CH_{3para-Mes})$, 16.9 $(CH_{3ortho-Mes})$. IR (CH_2Cl_2) : ν_{CO} 2027 (s), 1944 cm⁻¹ (vs). Anal. Found: C, 55.92; H, 4.40; N, 5.95. Calcd for

 $C_{21}H_{20}Cl_{0.9}I_{0.1}MnN_2O_3$ (*M* = 448.0) C, 56.31; H, 4.50; N, 6.25. Synthesis of [(η^5 -C₅H₄CH₂CH₂Im^{Mes})Mn(CO)₃]OMs ([6b]OMs). A solution of 5b (0.98 g, 3.0 mmol) and N-mesitylimidazole (0.73 g, 3.9 mmol) in toluene (10 mL) was heated at 110 °C until the maximum conversion of 5b was achieved according to the ¹H NMR spectrum of the aliquot (ca. 20 h). The volatiles were removed under vacuum, and the brown residue was dissolved in CH_2Cl_2 (15 mL). The solution was filtered through Celite, and ether (30 mL) was added dropwise under stirring to induce the crystallization of [6b]OMs. The supernatant was removed using a cannula tipped with a filter paper, and the precipitate was washed with ether (20 mL) and dried under vacuum to give [6b]OMs (1.46 g, 95%) as a light gray powder. ¹H NMR (400.1 MHz, CDCl₃, 25 °C): δ 9.93 (s, 1H, CH_{Im2}), 7.71 (s, 1H, $CH_{Im4,5}$), 7.14 (s, 1H, $CH_{Im4,5}$), 7.00 (s, 2H, CH_{Mes}), 4.86 (m, 4H, $C_5H_4 + NCH_2CH_2$, 4.65 (t, ${}^{3}J_{HH} = 2.0$ Hz, 2H, C_5H_4), 2.96 (t, ${}^{3}J_{HH} =$ 7.2 Hz, 2H, NCH₂CH₂), 2.69 (s, 3H, CH₃SO₃⁻), 2.34 (s, 3H, CH_{3para.Mes}), 2.04 (s, 6H, CH_{3ortho-Mes}). ¹³C{¹H} NMR (100.6 MHz, $C_6D_{6'}^{T}$ 25 °C): δ 224.7 (Mn-CO), 141.3 (C-CH_{3para-Mes}), 139.0 $\begin{array}{l} (CH_{Im4,5}), \ 134.2 \ (C-CH_{3ortho-Mes}), \ 130.8 \ (C_{ipso Mes}), \ 129.9 \ (CH_{Mes}), \\ 123.8 \ (CH_{Im2}), \ 123.7 \ CH_{Im4,5}), \ 99.9 \ (C-CH_2CH_2), \ 83.9, \ 82.6 \ (C_5H_4), \\ 50.9 \ (NCH_2CH_2), \ 40.3 \ (CH_3SO_3^-), \ 29.9 \ (NCH_2CH_2), \ 21.1 \end{array}$ (CH_{3para-Mes}), 17.8 (CH_{3ortho-Mes}). IR (CH₂Cl₂): ν_{CO} 2023 (s), 1937 cm^{-1'} (vs). HRMS (ESI): m/z calcd for C₂₂H₂₂MnN₂O₃: 417.1011 [M⁺], found: 417.1001.

Generation of $[(\eta^5-C_5H_4CH_2NHC^{Mes})Mn(CO)_3]$ (7a) and $[(\eta^5-C_5H_4CH_2CH_2NHC^{Mes})Mn(CO)_3]$ (7b) for NMR Characterization. To a suspension of [6a]Cl (67 mg, 0.15 mmol) in THF (2 mL) was slowly added a solution of KHMDS (0.36 mL of 0.5 M solution in toluene, 0.18 mmol) under stirring at room temperature. The reaction mixture was stirred for 5 min and evaporated under vacuum. The residue was dissolved in dry C_6D_6 (1 mL), and the resulting yellow solution of 7a was filtered through a plug of a glass wool in a Pasteur pipet directly to the NMR tube. The NMR sample of 7b was obtained in the same manner from [6b]OMs (77 mg, 0.15 mmol) and KHMDS (0.33 mL of 0.5 M solution in toluene, 0.165 mmol).

7a: ¹H NMR (400.1 MHz, C₆D₆, 25 °C): δ 6.78 (s, 2H, CH_{Mes}), 6.70 (s, 1H, CH_{Im4,5}), 6.37 (s, 1H, CH_{Im4,5}), 4.51 (s, 2H, C₅H₄), 4.35 (s, 2H, C₅H₄), 3.85 (s, 2H, NCH₂), 2.14 (s, 3H, CH_{3para-Mes}), 2.09 (s, 6H, CH_{3ortho-Mes}). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25 °C): δ 225.2 (Mn–CO), 218.0 (CN₂), 139.0 (C_{ipso Mes}), 137.4 (C–CH_{3para-Mes}), 135.3 (C–CH_{3ortho-Mes}), 129.2 (CH_{Mes}), 120.9, 119.1 (CH_{im4,5}), 102.5 $(C-CH_2)$, 83.7, 81.7 (C_5H_4) , 48.2 (NCH_2) , 21.0 $(CH_{3para-Mes})$, 18.2 $(CH_{3ortho-Mes})$.

7b: ¹H NMR (400.1 MHz, C₆D₆, 25 °C): δ 6.78 (s, 2H, CH_{Mes}), 6.35 (dd, $J_{HH} = 5.3$ Hz, $J_{HH} = 1.5$ Hz, 2H, $CH_{Im4,5}$), 3.97 (t, ³ $J_{HH} = 2.1$ Hz, 2H, C₅H₄), 3.89 (t, ³ $J_{HH} = 2.1$ Hz, 2H, C₅H₄), 3.83 (t, ³ $J_{HH} = 6.9$ Hz, 2H, NCH₂CH₂), 2.38 (t, ³ $J_{HH} = 6.9$ Hz, 2H, NCH₂CH₂), 2.14 (s, 3H, CH_{3para-Mes}), 2.04 (s, 6H, CH_{3ortho-Mes}). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25 °C): δ 225.6 (Mn–CO), 215.7 (CN₂), 139.0 (C_{ipso Mes}), 137.5 (C–CH_{3para-Mes}), 135.3 (C–CH_{3ortho-Mes}), 129.2 (CH_{Mes}), 120.8, 118.6 (CH_{Im4,5}), 103.1 (C–CH₂CH₂), 82.8, 82.0 (C₅H₄), 51.8 (NCH₂CH₂), 30.5 (NCH₂CH₂), 21.0 (CH_{3para-Mes}), 18.1 (CH_{3ortho-Mes}).

Synthesis of $[(\eta^5-C_5H_4CH_2NHC^{Mes})Mn(CO)_2]$ (2a). To a suspension of [6a]Cl (0.76 g, 1.7 mmol) in THF (15 mL) was slowly added a solution of KHMDS (4.1 mL of 0.5 M solution in toluene, 2.04 mmol) under stirring at room temperature. The deep yellow reaction mixture was sonicated for 15 min, then stirred for an additional 15 min and evaporated under vacuum. The orange residue of complex 7a was dissolved in toluene (50 mL), and the resulting solution was transferred via cannula to the photochemical reactor. The reactor was filled with toluene (ca. 200 mL), and the resulting solution was irradiated with UV light at 0 °C under vigorous stirring. IR monitoring showed the gradual transformation of the complex 7a ($\nu_{\rm CO}$ 2021, 1938 cm⁻¹) into the desired 2a ($\nu_{\rm CO}$ 1924, 1857 cm⁻¹), and the irradiation was finished when the bands of the latter ceased to increase (ca. 1.5 h). The resulting orange solution was filtered through a short column of alumina $(3 \times 5 \text{ cm})$ using toluene as eluent and evaporated under vacuum, and the residue was purified by column chromatography on silica $(3 \times 15 \text{ cm})$. Elution with a toluene/hexane 1:1 mixture afforded a yellow band containing an unknown compound discarded based on its IR spectra, followed by an orange band of complex 2a eluted with pure toluene. The eluate was concentrated to ca. 15 mL under vacuum and filtered through Celite, and hexane (50 mL) was added dropwise under stirring to induce the crystallization of 2a finished at -20 °C overnight. The supernatant was removed by decantation, and the precipitate was dried under vacuum to afford 2a (0.464 g, 73%) as a yellow powder. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into the solution of 2a in toluene at room temperature. ¹H NMR (400.1 MHz, C_6D_{62} , 25 °C): δ 6.88 (s, 2H, CH_{Mes}), 6.01 (d, ³J_{HH} = 2.0 Hz, 1H, CH_{Im4,5}), 5.97 (d, ${}^{3}J_{\text{HH}} = 2.0$ Hz, 1H, $CH_{\text{Im}4,5}$), 4.63 (t, ${}^{3}J_{\text{HH}} = 2.1$ Hz, 2H, $C_{5}H_{4}$), 4.15 (t, ${}^{3}J_{HH} = 2.1$ Hz, 2H, $C_{5}H_{4}$), 3.47 (s, 2H, NCH₂), 2.24 (s, 6H, $CH_{3ortho-Mes}$), 2.07 (s, 3H, $CH_{3para-Mes}$). ¹³C{¹H} NMR (100.6 MHz, C_6D_6 , 25 °C): δ 234.7 (Mn–CO), 207.7 (Mn–CN₂), 138.8 (C– CH_{3para-Mes}), 137.1 (C_{ipso Mes}), 136.2 (C-CH_{3ortho-Mes}), 129.4 (CH_{Mes}), 122.8, 118.4 $(CH_{Im4,5})$, 108.9 $(C-CH_2)$, 81.5, 80.0 (C_5H_4) , 46.6 (NCH₂), 21.2 (CH_{3para-Mes}), 18.4 (CH_{3ortho-Mes}). IR (toluene): ν_{CO} 1924 (s), 1857 cm⁻¹ (s). Anal. Found: C, 63.98; H, 4.76; N, 7.49. Calcd for $C_{20}H_{19}MnN_2O_2$ (*M* = 374.3): C, 64.17; H, 5.12; N, 7.48. Synthesis of [(η^5 -C₅H₄CH₂CH₂NHC^{Mes})Mn(CO)₂] (2b). To a

suspension of [6b]OMs (0.72 g, 1.4 mmol) in THF (15 mL) was slowly added a solution of KHMDS (3.4 mL of 0.5 M solution in toluene, 1.68 mmol) under stirring at room temperature. The deep yellow reaction mixture was sonicated for 15 min, then stirred for an additional 15 min and evaporated under vacuum. The orange residue of complex 7b was dissolved in toluene (50 mL), and the resulting solution was transferred via cannula to the photochemical reactor. The reactor was filled with toluene (ca. 200 mL), and the resulting solution was irradiated with UV light at 0 °C under vigorous stirring. IR monitoring showed the gradual transformation of the complex 7b ($\nu_{\rm CO}$ 2019, 1934 cm⁻¹) into the desired **2b** ($\nu_{\rm CO}$ 1918, 1851 cm⁻¹), and the irradiation was finished when the bands of the latter ceased to increase (ca. 45 min). The resulting orange solution was filtered through a short column of alumina $(3 \times 5 \text{ cm})$ using toluene as eluent and evaporated under vacuum, and the residue was purified by column chromatography on silica $(3 \times 15 \text{ cm})$. Elution with a toluene/hexane 1:1 mixture afforded consecutively yellow, orange, and yellow bands containing unknown compounds discarded based on their IR and NMR spectra, followed by an orange band of complex 2b eluted with a toluene/ether 1:1 mixture. The eluate was evaporated under vacuum,

and the residue was crystallized from a CH₂Cl₂/hexane mixture at -20 °C to afford complex **2b** (0.33 g, 61%) as an orange microcrystalline powder. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into the solution of **2b** in CH₂Cl₂ at room temperature. ¹H NMR (400.2 MHz, C₆D₆, 25 °C): δ 6.90 (s, 2H, CH_{Mes}), 6.20 (d, ³J_{HH} = 1.9 Hz, 1H, CH_{Im4,5}), 6.10 (d, ³J_{HH} = 1.9 Hz, 1H, CH_{Im4,5}), 6.10 (d, ³J_{HH} = 2.1 Hz, 2H, C₅H₄), 2.98 (m, 2H, NCH₂CH₂), 2.17 (s, 3H, CH_{3para-Mes}), 2.12 (s, 6H, CH_{3ortho-Mes}), 1.70 (m, 2H, NCH₂CH₂). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25 °C): δ 234.2 (Mn–CO), 207.0 (Mn–CN₂), 138.7 (C–CH_{3para-Mes}), 138.1 (C_{ipso Mes}), 136.4 (C–CH_{3ortho-Mes}), 129.6 (CH_{Mes}), 51.6 (NCH₂CH₂), 27.0 (NCH₂CH₂), 21.2 (CH_{3para-Mes}), 18.4 (CH_{3ortho-Mes}). IR (toluene): ν_{CO} 1918 (s), 1851 cm⁻¹ (s). Anal. Found: C, 64.63; H, 5.18; N, 7.06. Calcd for C₂₁H₂₁MnN₂O₂ (*M* = 388.4): C, 64.95; H, 5.45; N, 7.21.

Synthesis of $[(\eta^5-C_5H_4CH_2NHC^{Mes})(CO)Mn(\eta^2-H-SiHPh_3)]$ (8a). A solution of complex 2a (113 mg, 0.3 mmol) and Ph₂SiH₂ (0.11 mL, 0.6 mmol) in toluene (15 mL) was irradiated by UV light using a custom LED-based apparatus under vigorous stirring. IR spectroscopy monitoring showed the gradual decrease of $\nu_{\rm CO}$ bands of **2a** ($\nu_{\rm CO}$ 1924, 1857 cm⁻¹) and the appearance of a $\nu_{\rm CO}$ band of the resulting complex **8a** ($\nu_{\rm CO}$ 1870 cm⁻¹). After complete conversion of the starting 2a (ca. 2 h), the solvent was evaporated under vacuum and the residue was extracted with a Et₂O/hexane 1:1 mixture (2×10 mL). The extracts were filtered through Celite and concentrated under vacuum to ca. 30% of volume to induce the precipitation of 8a finished at -20 °C overnight. The supernatant was removed, and the precipitate was washed with pentane $(2 \times 3 \text{ mL})$ and dried under vacuum to afford 8a (129 mg, 81%) as a yellow powder. ¹H NMR (400.1 MHz, C₆D₆, 25 °C): δ 7.85 (d, ³J_{HH} = 7.2 Hz, 4H, Ph), 7.30– 7.18 (m, 5H, Ph), 7.15-7.10 (m overlapped with residual solvent protons, 1H, Ph), 6.77 (s, 1H, CH_{Mes}), 6.42 (s, 1H, CH_{Mes}), 6.05 (br s, 1H, $CH_{Im4,5}$), 6.02 (s, 1H, $CH_{Im4,5}$), 5.51 (s with a satellite d, ${}^{1}J_{SiH}$ = 195 Hz, 1H, Ph₂SiH), 4.75 (s, 1H, C₅H₄), 4.38 (s, 1H, C₅H₄), 4.09 (s, 1H, C_5H_4), 3.64–3.53 (s overlapped with m, 3H, C_5H_4 + NCH₂), 2.17 (s, 3H, $CH_{3ortho-Mes}$), 2.04 (s, 3H, $CH_{3para-Mes}$), 1.88 (s, 3H, $CH_{3ortho-Mes}$), -10.48 (s with a satellite d, $^{2}J_{SiH} = 47.6$ Hz, 1H, Mn– H). $^{13}C{}^{1}H{}$ NMR (100.6 MHz, $C_{6}D_{6}$, 25 °C): δ 232.9 (Mn–CO), 206.8 (Mn-CN₂), 147.4, 145.6, 138.4, 135.5, 135.0 (C-CH_{3nara-Mest} C_{ipso Mes}, C-CH_{3ortho-Mes}), 136.5 (C_{ipso Ph}), 136.3, 134.9 (CH_{Mes}), 129.5, 129.4, 127.7, 127.6, 127.5, 127.4 (CH_{Ph}), 123.3, 118.6 (CH_{Im4,5}), 108.4 $(C-CH_2)$, 82.6, 81.9, 81.2, 80.9 (C_5H_4) , 46.7 (NCH_2) , 21.1 $(CH_{3para-Mes})$, 18.7, 18.3 $(CH_{3ortho-Mes})$. ²⁹Si (¹H-²⁹Si HMQC) NMR (79.5 MHz, C₆D₆, 25 °C): δ 18.0. IR (THF): ν_{SiH} 2075 (w br.), ν_{CO} 1869 cm⁻¹ (m). HRMS (DCI CH₄): m/z calcd for C₃₁H₃₀MnN₂OSi: 529.1508 [M⁺ – H], found: 529.1506.

Synthesis of $[(\eta^5-C_5H_4CH_2CH_2NHC^{Mes})(CO)Mn(\eta^2-H-SiHPh_2)]$ (8b). A solution of complex $\mathbf{\hat{2}b}$ (116 mg, 0.3 mmol) and Ph_2SiH_2 (0.11 mL, 0.6 mmol) in toluene (15 mL) was irradiated by UV light using a custom LED-based apparatus under vigorous stirring. IR spectroscopy monitoring showed the gradual decrease of $u_{\rm CO}$ bands of **2b** ($\nu_{\rm CO}$ 1918, 1851 cm⁻¹) and the appearance of a $\nu_{\rm CO}$ band of the resulting complex 8b ($\nu_{\rm CO}$ 1861 cm⁻¹). After complete conversion of the starting 2b (ca. 4 h), the solvent was evaporated under vacuum and the yellow residue was washed with pentane $(2 \times 3 \text{ mL})$ to remove the excess of Ph₂SiH₂. The crude 8b was extracted with a THF/hexane 1:1 mixture $(2 \times 10 \text{ mL})$, and the extracts were filtered through Celite and slowly evaporated under vacuum to induce the crystallization of the product, which was finally washed with pentane $(2 \times 3 \text{ mL})$ and dried under vacuum to afford 8b×0.5THF (144 mg, 83%) as a yellow microcrystalline powder. Single crystals suitable for X-ray diffraction experiment were obtained by slow diffusion of hexane vapors to the solution of 8b in THF at room temperature. ¹H NMR (400.1 MHz, C_6D_6 , 25 °C): δ 7.87 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 2H, Ph), 7.55–7.50 (m, 2H, Ph), 7.28-7.19 (m, 5H, Ph), 7.15-7.09 (m overlapped with residual solvent protons, 1H, Ph), 6.74 (s, 1H, CH_{Mes}), 6.26 (s, 1H, CH_{Im4,5}), 6.23 (s, 1H, CH_{Mes}), 6.08 (s, 1H, $CH_{Im4,5}$), 5.22 (d with a satellite dd, ${}^{1}J_{\text{SiH}} = 198.5 \text{ Hz}, {}^{2}J_{\text{HH}} = 4.1 \text{ Hz}; 1\text{H}, \text{Ph}_{2}\text{SiH}), 4.46 (s, 1\text{H}, C_{5}H_{4}), 4.25$ $(s, 1H, C_5H_4)$, 3.91 $(s, 1H, C_5H_4)$, 3.57 $(m, 2H, OCH_2CH_{2THF})$,

3.35–3.25 (s overlapped with m, 3H, C_5H_4 + NCH₂CH₂), 2.15–2.04 (s overlapped with m, 4H, NCH₂CH₂ + CH_{3para-Mes}), 1.97 (s, 3H, CH_{3ortho-Mes}), 1.79 (s, 3H, CH_{3ortho-Mes}), 1.51–1.40 (m, 3H, NCH₂CH₂ + OCH₂CH₂THF), -10.49 (d with a satellite dd, ²J_{SiH} = 47.4 Hz, ²J_{HH} = 4.0 Hz, 1H, Mn–H). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25 °C): δ 233.6 (Mn–CO), 206.1 (Mn–CN₂), 148.8, 145.7, 138.3, 136.1, 134.9 (C–CH_{3para-Mes}) C–CH_{3ortho-Mes}), 137.9 (C_{ipso Ph}), 136.3, 134.6 (CH_{Mes}), 129.9, 129.6, 127.5, 127.5, 127.2, 126.9 (CH_{Ph}), 122.3, 121.6 (CH_{1m4,5}), 101.0 (C–CH₂), 82.1, 81.6, 80.8, 79.4 (C₅H₄), 67.9 (OCH₂CH_{2THF}), 51.9 (NCH₂CH₂), 27.3 (NCH₂CH₂), 25.9 (OCH₂-CH_{2THF}), 51.9 (NCH₂CH₂), 25.1 C(H_{3ortho-Mes}). ²⁹Si (¹H–²⁹Si HMQC) NMR (79.5 MHz, C₆D₆, 25 °C): δ 16.8. IR (THF): ν_{SiH} 2090 (w br.), ν_{CO} 1871 cm⁻¹ (m). Anal. Found: C, 69.86; H, 6.42; N, 4.94; Calcd for C₃₄H₃₇MnN₂O_{1.5}Si (8b×0.5THF, *M* = 580.7) C, 70.32: H, 6.42: N, 4.82.

General Procedure for Catalytic Hydrosilylation of 2-Acetonaphthone with Mn¹ NHC Complexes. A 10 mL ovendried Schlenk tube containing a stirring bar was charged with Mn^I NHC catalyst (1/2a/2b) (1.0–0.1 mol %). After purging with argon (argon-vacuum 3 cycles), toluene (1–4 mL, 0.5 M substrate concentration) was added, followed by Ph₂SiH₂ (1 equiv) and 2acetonaphthone (0.5–2 mmol). The reaction mixture was irradiated under UV (350 nm) using a Rayonet RPR 100 apparatus. At the end of the reaction, MeOH (2 mL) and 2 M NaOH (2 mL) were added consequently under vigorous stirring. The reaction mixture was stirred for a further 2 h at room temperature and was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated under vacuum. Product yields were determined by ¹H NMR spectroscopy.

Catalytic Hydrosilylation of 2-Acetonaphthone with Silane Complexes 8a and 8b. Silane complexes 8a (5.3 mg, 0.01 mmol) or 8b×0.5THF (5.8 mg, 0.01 mmol) were added to a solution of 2-acetonaphthone (170 mg, 1 mmol) and Ph₂SiH₂ (185 μ L, 1 mmol) in toluene (2 mL), and the resulting yellow solution was stirred for 16 h in the absence of UV irradiation. IR spectral monitoring of the ketone band $\nu_{C=0}$ at 1684 cm⁻¹ showed no substrate conversion. The reaction mixture was then irradiated under vigorous stirring for 2 h with a UV LED-based apparatus, resulting in ca. 60–65% substrate conversion estimated by the decrease of the $\nu_{C=0}$ peak area calculated using PerkinElmer Spectrum 10.4.00 software.

Solution IR Monitoring of the Hydrosilylation of Acetonaphthone Catalyzed by Silane Complex 8b. A solution of 2acetonaphthone (102 mg, 0.6 mmol), Ph₂SiH₂ (110 μ L, 0.6 mmol), and 8b×0.5THF (17.5 mg, 0.03 mmol) in toluene (1.2 mL) was irradiated under vigorous stirring with a UV LED-based apparatus for 20 min periods, followed by 20 min periods of simple stirring. The IR spectra of the reaction mixture after each iteration are shown in Figure S26. The substrate conversion was estimated by the decrease of the ketone $\nu_{C=0}$ peak area calculated using PerkinElmer Spectrum 10.4.00 software.

Details of X-ray Diffraction Experiments for Complexes 2a, 2b, and 8b. Single-crystal X-ray diffraction data collections were carried out on a Bruker D8/APEX II/Incoatec IµS Microsource diffractometer (graphite monochromator, Mo K α radiation, λ = 0.71073 Å). All calculations were performed on a PC compatible computer using the WinGX system.35 The structures were solved using the SIR92 program,³⁶ which revealed, in each instance, the position of most of the non-hydrogen atoms. All the remaining nonhydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses using the SHELX program.³⁷ Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Mn were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. The hydrogen atoms were generally set in idealized positions (R₃CH, C-H = 0.96 Å; R₂CH₂, C-H = 0.97 Å; RCH₃, C-H = 0.98 Å; C(sp²)-H = 0.93 Å; U_{iso} 1.2 or 1.5 times greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached), and their positions were refined as "riding" atoms, expect for H1 and H2 in the structure of 8b, whose positions were inferred from a residual electron density map and refined with a U_{iso} arbitrarily set at 0.05 Å². After completing the initial structure solution for complex **8b**, it was found that 12% of the total cell volume was filled with disordered solvent molecules, which, however, could not be modeled in terms of discrete molecules. The disordered solvent contribution was then subtracted from the observed data using the SQUEEZE procedure.³⁸ CCDC 1497716–1487718 contain the supplementary crystallographic data for the three structures unveiled in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00785.

NMR spectra for all compounds and IR monitoring data for the hydrosilylation of 2-acetonaphthone catalyzed by complex 8b (PDF)

Details of X-ray diffraction experiments for **2a–b** and **8b** (CIF)

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Notes

The authors declare no competing financial interest.

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