Synthesis and Crystallographic Characterization of New Manganese(I) Complexes of Donor-Functionalized Indenes

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Treatment of 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**2**[H]) with BrMn(CO)$_5$ provided κ^2-*P,N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_3$Br (**4**) in 73% yield. Addition of either AgBF$_4$ or AgSO$_3$CF$_3$ to **4** yielded the corresponding inner-sphere tetrafluoroborate (**5a**) and triflate (**5b**) complexes in 62% and 65% yield, respectively. Deprotonation of **4**, **5a**, or **5b** produced an intractable mixture of products. The cationic complex [κ^2-*P,N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_4$]$^+$BF$_4^-$ (**6**) was prepared in 30% yield by treating BrMn(CO)$_5$ with AgBF$_4$, followed by the addition of **2**[H]. The benzocymantrene η^5-[**2**]Mn(CO)$_3$ was prepared in 56% yield via reduction of η^5-(2-NMe$_2$-3-P(S)^{i}Pr$_2$-indenyl)Mn(CO)$_3$ with Cl$_3$SiSiCl$_3$. Compound **2**[Li] reacts with BrMn(CO)$_5$ to give a complex product mixture, from which **4** and [κ^2-*P,N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_4$]$^+$-[Mn$_2$(CO)$_8$(μ-P^{i}Pr$_2$)]$^-$ (**7**) were isolated. 2-Dimethylaminoindene (**1**[H]) was silylated to give 1-SiMe$_3$-2-NMe$_2$-indene (**8**[H]) in 93% yield. Treatment of **8**[Li] with ClP^{i}Pr$_2$, followed by the addition of BrMn(CO)$_5$, afforded κ^2-*P,N*-(1-SiMe$_3$-2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn(CO)$_3$Br (**10**) in 27% yield. Alternatively, addition of **8**[Li] to BrMn(CO)$_5$ followed by the addition of ClP^{i}Pr$_2$ generated a mixture of products, from which the substituted 1,1′-biindene *rac*-(2-NMe$_2$-3-SiMe$_3$-C$_9$H$_5$)$_2$ (*rac*-**12**) was isolated. Treatment of **1**[Li] with BrMn(CO)$_5$ provided η^5-(2-NMe$_2$-indenyl)Mn(CO)$_3$ (**11**) in 41% yield. Single-crystal X-ray diffraction data for **4**·0.5C$_7$H$_8$, **5a**·0.5C$_7$H$_8$, **5b**, **6**, η^5-[**2**]Mn(CO)$_3$, **7**·0.5C$_7$H$_8$, **10**, **11**, and *rac*-**12** are reported.

Introduction

With the goal of identifying new classes of transition metal complexes that are capable of mediating synthetically useful chemical transformations, we have recently initiated a research program focused on exploring the coordination behavior and reactivity properties of complexes supported by new ligands derived from 2-dimethylaminoindene (**1**[H]), including the "P,N" ligands **2**[H] and **2′**[H], as well as the "P(S),N" ligand, **3**[H] (Scheme 1).[1] These new multifunctional ligands strategically incorporate hard and soft donor fragments fused to an unsaturated carbocyclic backbone,[2] in anticipation that such a combination of chemically diverse donor groups will allow for the binding of a range of metal fragments, as well as allowing for the rational construction of heteropolynuclear metal complexes.[3]

In a synthetic survey involving Rh(I), we established that **2**[H] can be used in the preparation of cationic

Scheme 1
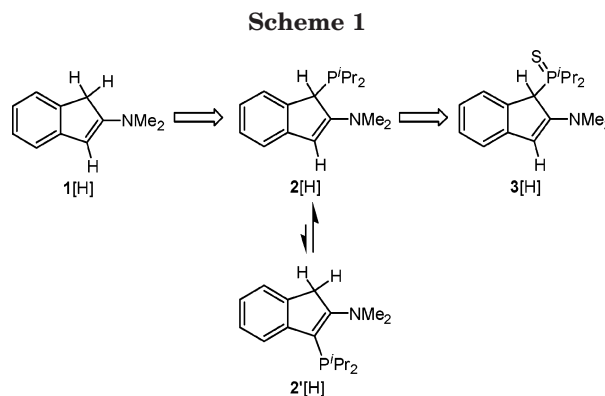
κ^2-[*P,N*]Rh(I) complexes, as well as the zwitterionic complex κ^2-[*P,N*-**2**]Rh(η^4-COD). In the latter species, the carbocyclic backbone serves as an anionic charge reservoir, rather than as a locale for metal binding.[1a] The ligand **3** also exhibits unusual coordination behavior, forming the neutral κ^2-[*C,S*-**3**]Rh(η^4-COD) complex in which the Rh(I) fragment is coordinated in an η^1-fashion to the indenyl ring as well as to the phosphine sulfide group.[1c] We are in the process of expanding our synthetic survey to incorporate metal fragments from across the transition series; in the context of Mn(I), we have demonstrated that **3**[Li] reacts cleanly with BrMn(CO)$_5$ to yield η^5-[**3**]Mn(CO)$_3$.[1c] Building upon these results,

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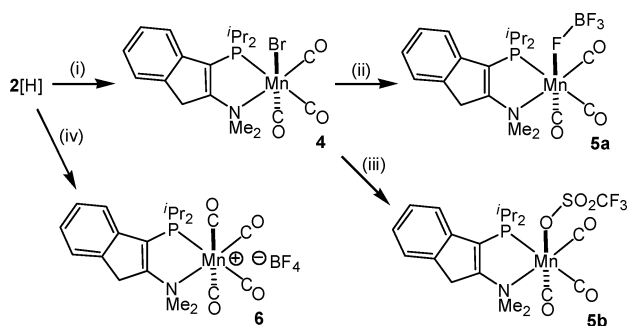† Dalhousie University.
‡ University of Alberta.

(1) (a) Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618. (b) Cipot, J.; Wechsler, D.; Stradiotto, M.; McDonald, R.; Ferguson, M. J. *Organometallics* **2003**, *22*, 5185. (c) Wechsler, D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Chem. Commun.* **2004**, 2446.
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(3) Wheatley, N.; Kalck, P. *Chem. Rev.* **1999**, *99*, 3379.

Scheme 2 [a]

[a] Reagents: (i) BrMn(CO)$_5$; (ii) AgBF$_4$; (iii) AgSO$_3$CF$_3$; (iv) BrMn(CO)$_5$/AgBF$_4$.
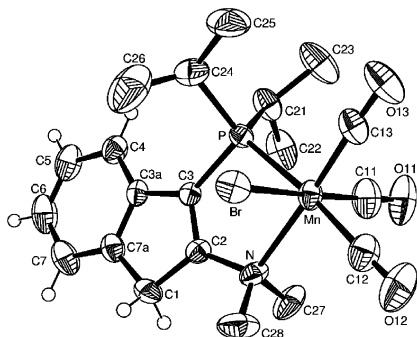

Figure 1. ORTEP for **4**·0.5C$_7$H$_8$, shown with 50% displacement ellipsoids (*P*2$_1$/*c* polymorph). Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected bond lengths (Å) for **4**·0.5C$_7$H$_8$: Mn−Br 2.5218(8); Mn−P 2.346(1); Mn−N 2.211(4); Mn−C11 1.805(6); Mn−C12 1.877(5); Mn−C13 1.791(5); C1−C2 1.505(6); C2−C3 1.340(5); N−C2 1.457(5); P−C3 1.803(4).

herein we report our progress in developing further the Mn(I) coordination chemistry of **2**[H] and related ligands.

Results and Discussion

Synthesis and Reactivity of κ^2-[*P,N*]Mn Complexes. In light of the established ability of coordinatively and electronically unsaturated Mn(CO)$_n$ complexes to bind and/or activate E−H bonds (E = H, B, C, Si, etc.),[4] five-coordinate Mn cations supported by **2**[H] or **2′**[H] were identified as appealing synthetic targets that might also function as precursors to the 16-electron zwitterion, κ^2-[*P,N*-**2**]Mn(CO)$_3$.[5] Treatment of **2**[H] with BrMn(CO)$_5$ provides **4** as an analytically pure orange solid in 73% isolated yield (Scheme 2). The single-crystal X-ray structure of **4**·0.5C$_7$H$_8$ (*P*2$_1$/*c* polymorph) is presented in Figure 1, and relevant crystallographic parameters are collected in Table 1. Both NMR spectroscopic and X-ray crystallographic data confirm that **2**[H]

has undergone a structural rearrangement, such that the ligand **2′**[H] is coordinated to Mn through the P- and N-donors in **4**. Although we have been unable to identify an analogous crystallographically characterized κ^2-[*P,N*]Mn(I) chelate complex from the literature, the interatomic distances within the Mn coordination sphere in **4** are comparable to reported values.[6] In keeping with the greater *trans*-influence of P-donors relative to N-donors, the Mn−C12 distance (*trans* to P) in **4** is lengthened relative to the Mn−C13 distance (*trans* to N). We have also obtained crystallographic data for the *P*2$_1$ polymorph of **4**·0.5C$_7$H$_8$ (Table 1); the salient structural features observed in this polymorph mirror those found in the *P*2$_1$/*c* polymorph of **4**·0.5C$_7$H$_8$.

In an attempt to access cationic, 16-electron Mn(I) complexes, compound **4** was treated with either AgBF$_4$ or AgSO$_3$CF$_3$ in toluene (Scheme 2). Monitoring (^{31}P NMR) of the reaction mixtures allowed for the loss of the signal attributable to **4** (59.8 ppm) and the appearance of a new signal associated with either **5a** (63.5 ppm) or **5b** (62.6 ppm) to be observed; these complexes were subsequently isolated as analytically pure yellow solids in 62% and 65% yield, respectively. Crystallographic analysis of **5a**·0.5C$_7$H$_8$ and **5b** (Figures 2 and 3; Table 1) revealed both of these complexes to be neutral, six-coordinate 18-electron species, in which the counteranion is coordinated directly to the Mn center. Although Mn(I) complexes featuring either inner-sphere tetrafluoroborate or triflate complexes are known,[7] to the best of our knowledge no crystallographically characterized compounds of this type have been reported. Since the geometric features of the three crystallographically independent molecules of **5a** are similar, the following discussion will be limited to the independent molecule that is depicted in Figure 2. The Mn−F1a distance in **5a** (2.070(3) Å) is only slightly elongated relative to the corresponding distance in FMn(dppe)(CO)$_3$ (2.028(2) Å).[8] As well, the B−F$_{bridging}$ distance (1.465(7) Å) in **5a** is significantly longer than the corresponding B−F$_{terminal}$ distances (av ∼1.33 Å), resulting in a distorted tetrahedral geometry at boron. Taken collectively, these metrical parameters suggest that **5a** is perhaps most appropriately described as a MnF·BF$_3$ adduct, which can be compared to other crystallographically characterized MF·BF$_3$ species.[9] The observation of two resonances at −152.3 and −293.5 ppm (∼3:1 ratio) in the ^{19}F NMR spectrum of **5a** suggests that this structural motif is also maintained in a 1:1 toluene/THF solution.[7c,10] For comparative

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(10) A recently reported PCN-based Rh(III) pincer complex features a coordinated (and fluxional) tetrafluoroborate anion that is displaced by THF at reduced temperatures: Gandelman, M.; Konstantinovski, L.; Rozenberg, H.; Milstein, D. *Chem. Eur. J.* **2003**, *9*, 2595.

Table 1. Crystallographic Data

	$4 \cdot 0.5C_7H_8$	$4 \cdot 0.5C_7H_8$	$5a \cdot 0.5C_7H_8$	$5b$	6	$\eta^5\text{-}[12]Mn(CO)_3$
empirical formula	$C_{23.5}H_{30}BrMnNO_3P$	$C_{23.5}H_{30}BrMnNO_3P$	$C_{23.5}H_{30}BF_4MnNO_3P$	$C_{21}H_{26}F_3MnNO_6PS$	$C_{21}H_{26}BF_4MnNO_4P$	$C_{20}H_{25}MnNO_3P$
fw	540.31	540.31	547.21	563.40	529.15	413.32
cryst dimens (mm)	0.28 × 0.16 × 0.10	0.20 × 0.10 × 0.05	0.62 × 0.52 × 0.16	0.29 × 0.22 × 0.20	0.46 × 0.36 × 0.26	0.35 × 0.30 × 0.12
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	15.525(1)	8.3609(7)	8.1918(6)	11.9460(5)	8.1358(4)	9.0105(5)
b (Å)	8.0752(6)	29.333(2)	15.245(1)	14.3629(6)	19.1164(9)	24.956(1)
c (Å)	20.489(1)	10.0818(8)	62.102(4)	14.5832(6)	15.9808(7)	9.4436(5)
α (deg)	90	90	90	90	90	90
β (deg)	103.634(1)	99.222(2)	93.426(1)	96.9755(8)	96.3604(9)	108.435(1)
γ (deg)	90	90	90	90	90	90
V (Å³)	2496.3(3)	2440.6(3)	7742(1)	2483.7(2)	2470.2(2)	2014.6(2)
Z	4	4	12	4	4	4
ρ_{calcd} (g cm⁻³)	1.438	1.470	1.408	1.507	1.423	1.363
μ (mm⁻¹)	2.217	2.268	0.628	0.739	0.656	0.753
2θ limit (deg)	52.76	50.00	52.78	52.74	52.78	52.78
	$-19 \leq h \leq 19$	$-9 \leq h \leq 9$	$-10 \leq h \leq 9$	$-14 \leq h \leq 14$	$-10 \leq h \leq 10$	$-11 \leq h \leq 11$
	$-10 \leq k \leq 10$	$-32 \leq k \leq 34$	$-19 \leq k \leq 15$	$-17 \leq k \leq 17$	$-23 \leq k \leq 23$	$-31 \leq k \leq 31$
	$-25 \leq l \leq 25$	$-11 \leq l \leq 11$	$-77 \leq l \leq 77$	$-18 \leq l \leq 18$	$-19 \leq l \leq 19$	$-9 \leq l \leq 11$
total data collected	16462	15191	37759	15849	18344	13161
no. of indep reflns	5087	8364	15801	5053	5048	4123
R_{int}	0.0458	0.0639	0.0457	0.0310	0.0240	0.0228
absorp corr	Multiscan (SADABS)	Multiscan (SADABS)	Multiscan (SADABS)	Multiscan (SADABS)	Multiscan (SADABS)	Multiscan (SADABS)
range of transmn	0.8087−0.5757	0.8951−0.6598	0.9063−0.6970	0.8663−0.8142	0.8480−0.7524	0.9151−0.7785
no. of data/restr/params	5087/3/255	8364/7/531	15801/3/911	5053/0/307	5048/0/296	4123/0/237
$R_1 [F_o^2 \geq 2\sigma(F_o^2)]$	0.0521	0.0664	0.0845	0.0379	0.0479	0.0317
$wR_2 [F_o^2 \geq -3\sigma(F_o^2)]$	0.1469	0.1513	0.1918	0.0937	0.1295	0.0873
goodness-of-fit	1.033	1.002	1.121	1.045	1.043	1.048

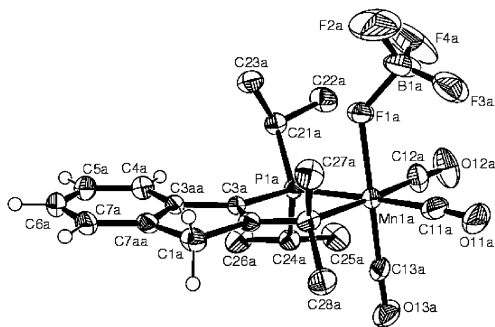|	$7 \cdot 0.5C_7H_8$	10	11	$rac\text{-}12$
empirical formula	$C_{38.5}H_{44}Mn_3NO_{12}P_2$	$C_{23}H_{34}BrMnNO_3PSi$	$C_{14}H_{12}MnNO_3$	$C_{28}H_{40}N_2Si_2$
fw	939.51	566.42	297.19	460.80
cryst dimens (mm)	0.42 × 0.26 × 0.14	0.60 × 0.53 × 0.08	0.53 × 0.26 × 0.26	0.44 × 0.42 × 0.14
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	8.4223(6)	11.5389(7)	6.9708(4)	11.4652(7)
b (Å)	16.235(1)	18.955(1)	7.1061(4)	9.7079(6)
c (Å)	16.356(1)	12.3557(8)	13.3302(7)	24.610(2)
α (deg)	90.742(1)	90	80.2151(8)	90
β (deg)	104.087(1)	105.522(1)	81.6179(8)	95.502(1)
γ (deg)	96.421(1)	90	88.1763(8)	90
V (Å³)	2153.7(3)	2603.8(3)	643.74(6)	2726.6(3)
Z	2	4	2	4
ρ_{calcd} (g cm⁻³)	1.449	1.445	1.533	1.123
μ (mm⁻¹)	0.999	2.173	1.027	0.148
2θ limit (deg)	52.80	52.76	52.74	52.84
	$-10 \leq h \leq 10$	$-14 \leq h \leq 14$	$-8 \leq h \leq 8$	$-14 \leq h \leq 14$
	$-20 \leq k \leq 20$	$-22 \leq k \leq 23$	$-8 \leq k \leq 8$	$-12 \leq k \leq 12$
	$-20 \leq l \leq 20$	$-15 \leq l \leq 15$	$-16 \leq l \leq 16$	$-30 \leq l \leq 30$
total data collected	16679	17411	4725	20951
no. of indep reflns	8756	5332	2605	5592
R_{int}	0.0206	0.0287	0.0145	0.0451
absorp corr	face-indexed	Multiscan (SADABS)	face-indexed	Multiscan (SADABS)
range of transmn	0.8728−0.6790	0.8454−0.3556	0.7761−0.6121	0.9796−0.9379
no. of data/restr/params	8756/3/489	5332/1/284	2605/0/174	5592/0/289
$R_1 [F_o^2 \geq 2\sigma(F_o^2)]$	0.0406	0.0349	0.0241	0.0617
$wR_2 [F_o^2 \geq -3\sigma(F_o^2)]$	0.1272	0.0946	0.0673	0.1928
goodness-of-fit	1.086	1.023	1.084	1.043

Figure 2. ORTEP for **5a**·0.5C$_7$H$_8$, shown with 50% displacement ellipsoids (only one of three crystallographically independent molecules is shown). Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected bond lengths (Å) for **5a**·0.5C$_7$H$_8$: Mn1a−P1a 2.340(1); Mn1a−N1a 2.175(4); Mn1a−F1a 2.070(3); Mn1a−C11a 1.857(5); Mn1a−C12a 1.808(5); Mn1a−C13a 1.776(5); C1a−C2a 1.523(6); C2a−C3a 1.336(6); N1a−C2a 1.454(5); P1a−C3a 1.808(4); B1a−F1a 1.465(7); B1a−F2a 1.35(1); B1a−F3a 1.330(8); B1a−F4a 1.323(9).
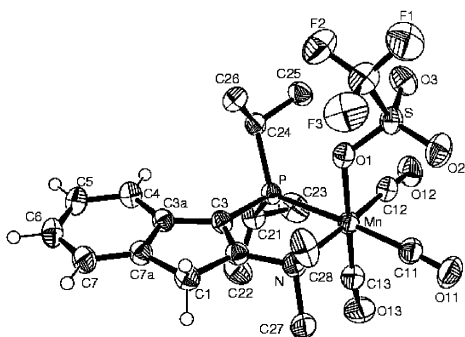

Figure 3. ORTEP for **5b**, shown with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **5b**: Mn−P 2.3419(6); Mn−N 2.209(2); Mn−O1 2.094(2); Mn−C11 1.859(2); Mn−C12 1.806(2); Mn−C13 1.779(3); C1−C2 1.516(3); C2−C3 1.342(3); N−C2 1.450(3); P−C3 1.805(2).
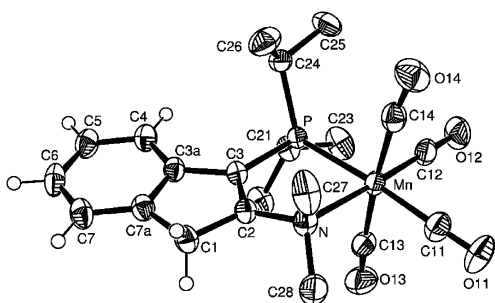

Figure 4. ORTEP for **6**, shown with 50% displacement ellipsoids. Selected hydrogen atoms and the BF$_4^-$ counterion have been omitted for clarity. Selected bond lengths (Å) for **6**: Mn−P 2.3340(7); Mn−N 2.196(2); Mn−C11 1.855(3); Mn−C12 1.803(3); Mn−C13 1.858(3); Mn−C14 1.879(3); C1−C2 1.509(3); C2−C3 1.341(3); N−C2 1.460(3); P−C3 1.789(2).

purposes, the 18-electron cationic species [κ^2-*P*,*N*-(**2′**[H])-Mn(CO)$_4$]$^+$BF$_4^-$ (**6**) was also prepared and crystallographically characterized (Figure 4; Table 1). In contrast to **5a**, complex **6** exhibits a single ^{19}F NMR resonance at −153.1 ppm in dichloromethane. Moreover, the ^{11}B NMR signal for the *coordinated* tetrafluoroborate in **5a** (0.31 ppm, $\Delta\nu_{1/2} = 63$ Hz) is broadened relative to the

signal observed for the *uncoordinated* anion (−0.84 ppm, $\Delta\nu_{1/2} = 29$ Hz) in **6**, in keeping with the reduced local symmetry at the boron center in **5a**. Though we were unable to identify a crystallographically characterized inner-sphere Mn(I) triflate complex from the literature, the Mn−O1 distance (2.094(2) Å) in **5b** can be compared with the related distance (2.04(1) Å) in (F$_5$TeO)Mn-(CO)$_5$.[11] While the Mn−P, Mn−N, and Mn−C distances in **5a**·0.5C$_7$H$_8$, **5b**, and **6** are in general similar to those found in **4**·0.5C$_7$H$_8$, the carbonyl stretching bands in the IR spectrum of **4** (1895, 1926, and 2013 cm^{-1}) appear at lower energy than those observed in the IR spectra of **5a** (1912, 1952, and 2038 cm^{-1}) and **5b** (1916, 1957, and 2036 cm^{-1}),[12] in keeping with the greater electron-withdrawing power of the tetrafluoroborate and triflate anions relative to bromide.
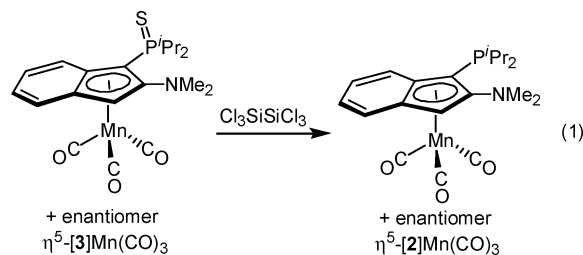
In an effort to assess the lability of the coordinated anions in **5a** and **5b**, these complexes were treated with various two-electron donors (L). Although no changes were observed in the ^{31}P{^{1}H} NMR spectra of either **5a** or **5b** upon dissolution in THF, the addition of 1 equiv of PPh$_3$ to **5a** generated a complex mixture of phosphorus-containing products. Compound **5b** did not react with PPh$_3$ (1 or 2 equiv) at ambient temperature, and upon heating at 60 °C the only new ^{31}P NMR signals observed were those attributable to **2**[H] (19.6 ppm) and **2′**[H] (−2.9 ppm).[1a,b] Complex reactivity was also observed when solutions of **5a** or **5b** were treated with either CH$_3$CN or 4-(dimethylamino)pyridine. In contrast, it is known that (F$_3$CSO$_2$O)Mn(CO)$_5$ reacts cleanly and rapidly with a variety of two-electron donors including THF, CH$_3$CN, and P(*n*-Bu)$_3$ to yield the corresponding [LMn(CO)$_5$]$^+$SO$_3$CF$_3^-$ salts.[7a] Given that treatment of (F$_3$BF)Mn(CO)$_5$ with **2**[H] successfully produces **6**, it is possible that steric factors inhibit the clean formation of the analogous [κ^2-*P*,*N*-(**2′**[H])Mn-(CO)$_3$L]$^+$X$^-$ complexes upon addition of L to either **5a** or **5b**. An additional attempt to prepare a cationic, five-coordinate Mn(I) species by treatment of **4** with Li-(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$ generated a complex mixture of products, including **2**[H] and **2′**[H]. Moreover, efforts to prepare the coordinatively unsaturated zwitterion, κ^2-[*P*,*N*-**2**]Mn(CO)$_3$, via treatment of **4**, **5a**, or **5b** with either *n*-BuLi, NEt$_3$, or K$_2$CO$_3$ were unsuccessful.

Developing Synthetic Routes to η^5-[2]Mn(CO)$_3$. Donor-functionalized planar-chiral cymantrene (i.e., η^5-CpMn(CO)$_3$) derivatives are emerging as effective ancillary supports for a variety of metal-mediated asymmetric transformations.[13] Encouraged by these studies, we have recently established a synthetic pathway to the racemic P(S),N-substituted benzocymantrene η^5-[3]Mn-(CO)$_3$[1c] and are currently developing resolution protocols for this and related planar-chiral metalloligands. In an attempt to transform this complex into the corresponding P,N-substituted benzocymantrene η^5-[2]Mn(CO)$_3$, a toluene solution of η^5-[3]Mn(CO)$_3$ and Cl$_3$SiSiCl$_3$ was heated at 85 °C, and the progress of the reaction was

(11) Abney, K. D.; Long, K. M.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2638.

(12) Ault, B. S.; Becker, T. M.; Li, G. Q.; Orchin, M. *Spectrochim. Acta A* **2004**, *60*, 2567.

(13) (a) Kudis, S.; Helmchen, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 3047. (b) Son, S. U. K.; Park, K. H.; Lee, S. L.; Chung, Y. K.; Sweigart, D. A. *Chem. Commun.* **2001**, 1290. (c) Delacroix, O.; Gladysz, J. A. *Chem. Commun.* **2003**, 665. (d) Lee, J. H.; Son, S. U.; Chung, Y. K. *Tetrahedron: Asymmetry* **2003**, *14*, 2109.

$$\eta^5\text{-}[\mathbf{3}]\text{Mn(CO)}_3 \xrightarrow{\text{Cl}_3\text{SiSiCl}_3} \eta^5\text{-}[\mathbf{2}]\text{Mn(CO)}_3 \quad (1)$$

+ enantiomer   + enantiomer
η^5-[**3**]Mn(CO)$_3$ η^5-[**2**]Mn(CO)$_3$

monitored by use of ^{31}P NMR techniques (eq 1). The slow transformation of η^5-[**3**]Mn(CO)$_3$ (64 ppm) into η^5-[**2**]Mn(CO)$_3$ (−2 ppm) was observed, and quantitative conversion was achieved after 14 days. Following purification, η^5-[**2**]Mn(CO)$_3$ was isolated as an analytically pure, orange-yellow crystalline solid in 56% yield. Solution NMR spectroscopic data fully support the formulation of η^5-[**2**]Mn(CO)$_3$ as a facially bound complex (rather than a κ^2-[*P,N*] species), including the low-frequency ^{31}P NMR chemical shift, and the observation of equivalent NMe ^{1}H and ^{13}C resonances resulting from a rotation/inversion process involving the uncoordinated N-donor fragment that is rapid on the NMR time scale at 300 K. The structure of η^5-[**2**]Mn(CO)$_3$ was also confirmed by an X-ray diffraction study. The crystal structure of η^5-[**2**]Mn(CO)$_3$ is presented in Figure 5 and can be compared with other 2-aminobenzocymantrenes.[1c,14] The relatively short N−C2 distance suggests that the uncoordinated NMe$_2$ fragment in η^5-[**2**]Mn(CO)$_3$ is in partial conjugation with the indenyl framework ($\sum_{\text{angles at N}} \sim 352°$). The Mn−C2 distance in η^5-[**2**]Mn-(CO)$_3$ is also longer than the other four Mn−C$_{\text{indenyl}}$ distances, with the shortest contact existing between Mn and the unsubstituted C1 position. Associated with this structural distortion is the fact that the carbons within the C$_5$ portion of the indenyl ring are not coplanar; the hinge angle (i.e., the difference between the planes defined by {C1, C3, C7a, C3a} and {C1, C2, C3}) in η^5-[**2**]Mn(CO)$_3$ is 8.6(2)°, whereas the fold angle (i.e., the difference between the planes defined by the C$_5$ and C$_6$ rings) is 4.3(1)°.[15]

Although the reduction of η^5-[**3**]Mn(CO)$_3$ to η^5-[**2**]Mn-(CO)$_3$ employing Cl$_3$SiSiCl$_3$ is quantitative, the reaction requires heating for extended periods in order to achieve complete conversion, and a crystallization step is required in order to obtain η^5-[**2**]Mn(CO)$_3$ free of byproducts. Alternative reduction protocols proved ineffective, often resulting in the decomposition of η^5-[**3**]Mn(CO)$_3$. As such, we became interested in establishing other synthetic routes to η^5-[**2**]Mn(CO)$_3$ that avoid phosphine sulfide intermediates. In an effort to prepare η^5-[**2**]Mn-(CO)$_3$ directly, BrMn(CO)$_5$ was treated with **2**[Li] in toluene (Scheme 3). Analysis of the crude reaction mixture (^{31}P NMR) after 20 h revealed the formation of multiple phosphorus-containing products, including those giving rise to resonances at 60 ppm (**4**, ∼20%), 53 ppm (∼70%), −2 ppm (**2**, ∼5%), and −6 ppm (∼5%). A similar product distribution was obtained in toluene, and control experiments ruled out hydrolysis of **2**[Li] by trace moisture. Although the major product of this
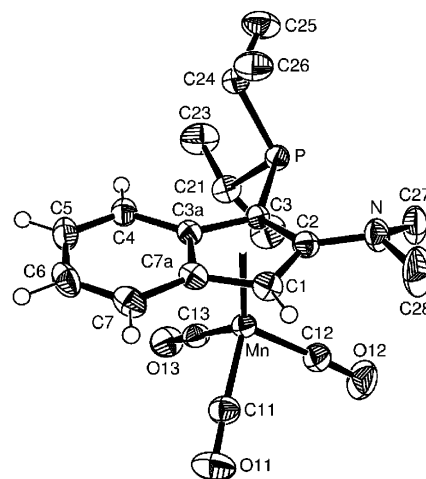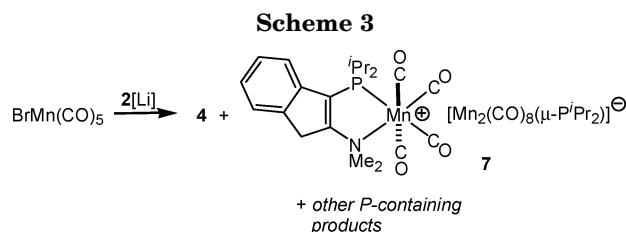

Figure 5. ORTEP for η^5-[**2**]Mn(CO)$_3$, shown with 50% displacement ellipsoids (only one enantiomeric form is shown). Selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for η^5-[**2**]Mn(CO)$_3$: Mn−C1 2.135(2); Mn−C2 2.238(2); Mn−C3 2.181(2); Mn−C3a 2.192(2); Mn−C7a 2.170(2); Mn−C11 1.789(2); Mn−C12 1.790(2); Mn−C13 1.812(2); C1−C2 1.428(2); C2−C3 1.454-(2); N−C2 1.377(2); P−C3 1.837(2).

Scheme 3

BrMn(CO)$_5$ $\xrightarrow{\text{2[Li]}}$ **4** + [cationic complex] [Mn$_2$(CO)$_8$(μ-P^{i}Pr$_2$)]$^{\ominus}$ **7**

+ other P-containing products

reaction could not be isolated in pure form, storage of this reaction mixture at −35 °C for an extended period (>10 months) resulted in the formation of a small quantity of crystalline material that gives rise to ^{31}P resonances at 69 and 217 ppm. The lower frequency resonance coincides with the signal observed for the cationic species **6**. This structural formulation was further substantiated by data obtained from a single-crystal X-ray diffraction study; the crystal structure of this complex (**7**·0.5C$_7$H$_8$) is presented in Figure 6, and relevant crystallographic parameters are provided in Table 1. The metrical parameters within the cationic portion of **7** are identical to those found in **6** and do not warrant further commentary. The [Mn$_2$(CO)$_8$(μ-P^{i}Pr$_2$)]$^-$ counteranion in **7** accounts for the observed high-frequency ^{31}P NMR signal and can be compared with the analogous [Mn$_2$(CO)$_8$(μ-PPh$_2$)]$^-$ anion reported by Mays and co-workers.[16] Efforts to isolate more of **7** from this reaction mixture were unsuccessful, and so we are presently unable to provide additional characterization data for this species. Given the complexity of the reaction mixture that produced **7**, and the lack of supporting experimental data, we are hesitant to propose a detailed mechanistic route to **7**. However, it is possible to envisage the initial formation of the zwitter-ionic species, κ^2-[*P,N*-**2**]Mn(CO)$_4$ (by analogy with κ^2-[*P,N*-**2**]Rh(η^4-COD)[1a]), which decomposes to yield a dimeric form of **2** (vide infra) along with the unsaturated Mn$_2$(CO)$_8$ fragment; the latter could ultimately go on

(14) (a) Plenio, H.; Burth, D. *Organometallics* **1996**, *15*, 1151. (b) Plenio, H.; Burth, D. *Z. Anorg. Allg. Chem.* **1996**, *622*, 225.

(15) For a thorough discussion of structure and bonding phenomena in amino-substituted η^5-indenyl complexes, see: Greidanus, G.; McDonald, R.; Stryker, J. M. *Organometallics* **2001**, *20*, 2492, and references therein.

(16) Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 633.
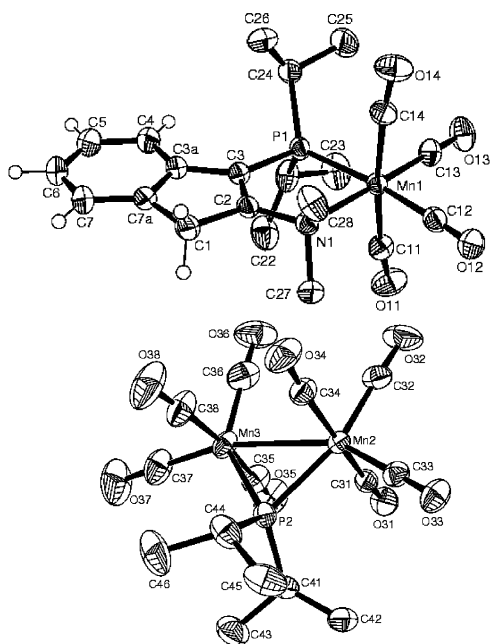
Figure 6. ORTEP of the cation (top) and the anion (bottom) in **7**·0.5C$_7$H$_8$, shown with 50% displacement ellipsoids. Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected bond lengths (Å) for **7**·0.5C$_7$H$_8$: Mn1−P1 2.3373(8); Mn1−N1 2.195(2); Mn1−C11 1.856(3); Mn1−C12 1.856(3); Mn1−C13 1.816-(3); Mn1−C14 1.877(3); N−C2 1.454(3); P−C3 1.797(3); Mn2−Mn3 2.8472(6); Mn2−P2 2.2728(8); Mn3−P2 2.2571(8).

to form the observed [Mn$_2$P]$^-$ counteranion, via some ill-defined P−C bond activation process involving a free or ligated form of **2**. Although we cannot conclusively rule out slow hydrolysis by trace moisture over extended periods as being involved in the formation of **7**, it is worthy of mention that the highly air- and moisture-sensitive **2**[Li] was not hydrolyzed under analogous experimental conditions. The complexity of the reaction mixture generated upon treatment of BrMn(CO)$_5$ with **2**[Li] is in stark contrast to the nearly quantitative yield of η^5-[**3**]Mn(CO)$_3$ that is obtained from the reaction of **3**[Li] with BrMn(CO)$_5$.[1c]

So as to circumvent the use of aggressive lithium-based ligand transfer reagents such as **2**[Li], a silylated derivative of **2** was targeted in anticipation that treatment with BrMn(CO)$_5$ would result in loss of bromosilane, thus directing metal coordination to the carbocyclic ring to give η^5-[**2**]Mn(CO)$_3$.[17] Treatment of **1**[Li] with ClSiMe$_3$ provided **8**[H] in 93% isolated yield as an analytically pure brown solid, which in turn was lithiated followed by quenching with ClP^{i}Pr$_2$ (Scheme 4). Analysis of the resulting product mixture (^{1}H and ^{31}P NMR) confirmed the consumption of the starting materials, and the two new ^{31}P NMR signals observed at 11.8 and −3.2 ppm are tentatively assigned to the isomers **9a**[H]/**9b**[H].[1b] To a solution of **9a**[H]/**9b**[H] was added BrMn(CO)$_5$, and the progress of the reaction was monitored by use of ^{31}P NMR techniques; after 2 h, multiple phosphorus-containing species were observed

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(17) For a report in which a similar synthetic methodology is successfully employed in the synthesis of η^5-indenyl complexes, see: Starzewski, K. A. O.; Kelly, W. M.; Stumpf, A.; Freitag, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2439.

Scheme 4 [a]
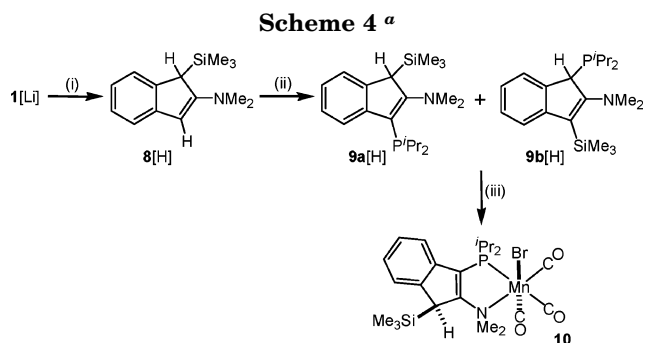
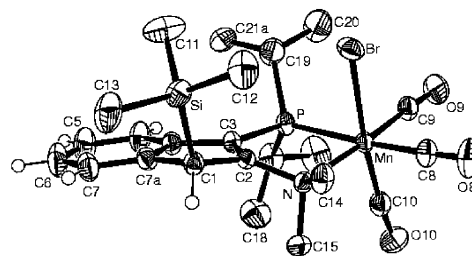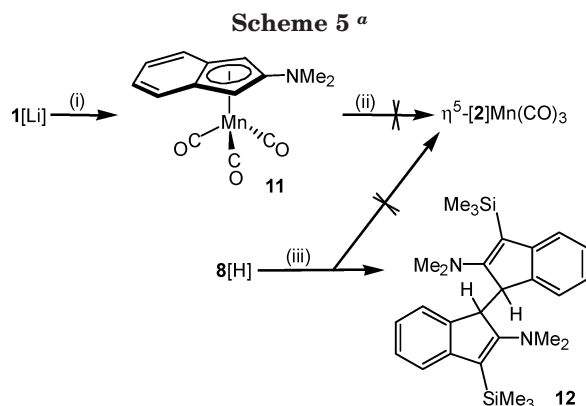[a] Reagents: (i) ClSiMe$_3$; (ii) (a) *n*-BuLi, (b) ClP^{i}Pr$_2$; (iii) BrMn(CO)$_5$.

Figure 7. ORTEP for **10**, shown with 50% displacement ellipsoids. The minor component of the disordered isopropyl carbon atom and selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **10**: Mn−Br 2.5216(4); Mn−P 2.3516(7); Mn−N 2.211(2); Mn−C8 1.834(3); Mn−C9 1.792(3); Mn−C10 1.791(3); Si−C1 1.954-(3); C1−C2 1.495(3); C2−C3 1.354(3); N1−C2 1.468(3); P−C3 1.801(2).

in solution, with none of the resonances corresponding to η^5-[**2**]Mn(CO)$_3$. However, after a total of 18 h a yellow solid precipitated from the reaction mixture, which in turn was isolated (27% yield) and subsequently identified as **10** on the basis of NMR spectroscopic, X-ray crystallographic, and other characterization data. The crystallographically determined structure of **10** is depicted in Figure 7, and relevant crystallographic data are listed in Table 1. The metrical parameters within the Mn coordination sphere of **4** are quite similar to those observed for the silylated analogue, **10**. Similarly, the elongated Si−C$_{indenyl}$ distance (1.954(3) Å) relative to the other Si−C distances (av ∼1.86 Å) in **10** is in keeping with trends observed in crystallographically characterized indenylsilanes.[18] Compound **10** represents one of two possible geometric isomers, with respect to the relative orientation of the SiMe$_3$ fragment and the Br atom. While the other isomer may be present in the crude reaction mixture, it is plausible that the *syn*-geometry exhibited by **10** is in fact the preferable one, with the *trans*-disposition of the silyl fragment, the NC(15)H$_3$ group, and the bromide minimizing unfavorable steric interactions.

Given the preference of Mn to coordinate to the P-donor fragment in **2** and related ligands, alternative synthetic routes to η^5-[**2**]Mn(CO)$_3$ were pursued, involving incorporation of the η^5-Mn(CO)$_3$ fragment into the 2-dimethylaminoindenyl framework, followed by the introduction of the diisopropylphosphino group. Treatment of **1**[Li] with BrMn(CO)$_5$ provided **11** (Scheme 5)

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(18) For example: Stradiotto, M.; Hazendonk, P.; Bain, A. D.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **2000**, *19*, 590, and references therein.

Scheme 5 [a]

[a] Reagents: (i) $BrMn(CO)_5$; (ii) (a) *n*-BuLi, (b) ClP^iPr_2; (iii) (a) *n*-BuLi, (b) $BrMn(CO)_5$, (c) ClP^iPr_2.
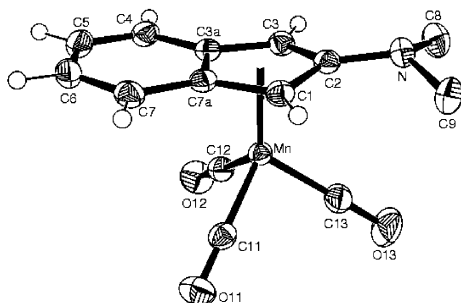
Figure 8. ORTEP for **11**, shown with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **11**: Mn−C1 2.148-(1); Mn−C2 2.248(1); Mn−C3 2.146(2); Mn−C3a 2.179(1); Mn−C7a 2.183(1); N−C2 1.368(2); N−C8 1.457(2); N−C9 1.457(2).

in 41% isolated yield. The apparent C_s symmetry observed in the crystallographically determined structure of **11** (Figure 8, Table 1) is in agreement with the solution ^1H and ^{13}C NMR spectral data obtained for this complex. As was observed for η^5-[**2**]$Mn(CO)_3$ and other 2-aminobenzocymantrenes,[1c,14] bonding between the $Mn(CO)_3$ fragment and the indenyl group **11** deviates significantly from ideal η^5-coordination, with the Mn−C2 distance being significantly longer than the other four Mn−$C_{indenyl}$ distances; the hinge angle in **11** is 10.0(2)°, whereas the fold angle is 3.8(1)°.[15] As well, despite the fact that the N fragment in **11** is pyramidal ($\sum_{angles\ at\ N} \approx 351°$), the rather short N−$C_{indenyl}$ distance (1.368(2) Å) indicates partial conjugation between the nitrogen lone pair and the indenyl system.

In an attempt to install the P-donor fragment, **11** was treated with *n*-BuLi (at −78 °C) and subsequently ClP^iPr_2.[19] Unfortunately, analysis of the crude reaction mixture (^{31}P NMR) revealed the formation of **2**[H], **2′**[H], and numerous other phosphorus-containing products, in the absence of η^5-[**2**]$Mn(CO)_3$. In a final attempt to prepare η^5-[**2**]$Mn(CO)_3$, **8**[Li] was sequentially treated with $BrMn(CO)_5$ and ClP^iPr_2. Once again, the ^1H and ^{31}P NMR spectra of the complex product mixture formed showed no sign of the target compound, η^5-[**2**]$Mn(CO)_3$. Storage of this reaction mixture at −35 °C resulted in the formation of a minute quantity of crystalline material, whose identity as *rac*-**12** was confirmed by a single-
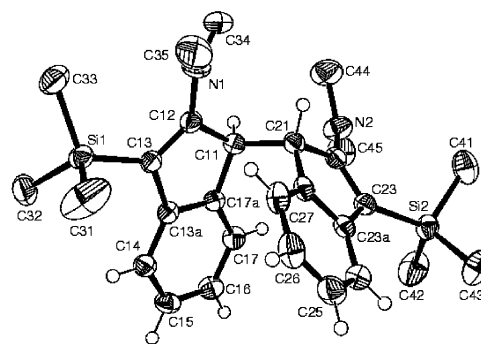
(19) For the lithiation of substituted cymantrenes, see: Ginzburg, A. G. *Russ. Chem. Rev.* **1993**, *62*, 1025.

Figure 9. ORTEP for *rac*-**12**, shown with 50% displacement ellipsoids. Only one enantiomeric form is shown, and selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for *rac*-**12**: Si1−C13 1.862(3); Si2−C23 1.876(3); N1−C12 1.387(3); N2−C22 1.373(4); C11−C21 1.564(4); C11−C12 1.527(4); C12−C13 1.363(4); C21−C22 1.527(3); C22−C23 1.371(4).

crystal X-ray diffraction study (Figure 9, Table 1).[20] The decomposition of indenyl metal complexes to yield 1,1′-biindenes has been observed previously.[21]

Conclusions

Although isolable five-coordinate, 16-electron [κ^2-*P,N*]-Mn(I) cations supported by **2**[H] and related ligands remain elusive, we have succeeded in preparing and structurally characterizing the unusual six-coordinate, 18-electron Mn(I) species **5a** and **5b**, which feature inner-sphere tetrafluoroborate and triflate ligands. We are hopeful that these complexes will serve as an in-situ source of reactive, low-coordinate [κ^2-*P,N*]Mn(I) cations in the presence of substrates containing E−H bonds, and the reactivity of **5a** and **5b** with such substrates will be the subject of future reports. The results described herein also indicate that the coordination chemistry of **2**, **2**[H], and related ligands with $Mn(CO)_n$ fragments is dominated by the formation of κ^2-[*P,N*] complexes. It appears that the preparation of η^5-$Mn(CO)_3$ derivatives of 2-dimethylaminoindenes is only viable in the absence of an adjacent P-donor fragment (as in the synthesis of **11**) or if a neighboring P-donor fragment is rendered unavailable for binding (as in the sequential conversion of **3**[H] to η^5-[**3**]$Mn(CO)_3$ and then to η^5-[**2**]$Mn(CO)_3$). Reports pertaining to the resolution of η^5-[**2**]$Mn(CO)_3$ and related ancillary ligands and their use in asymmetric catalysis are forthcoming.

Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) was oven dried (130 °C) for 5 days and then evacuated for 24 h prior to use. With the exception of CH_3CN, all nondeuterated solvents were deoxygenated and dried by sparging with N_2 gas, followed by

(20) For the crystal structure of *meso*-1,1′-biindenyl, see: Lustenberger, P.; Joss, S.; Engel, P.; Oesch, N.; Rutsch, W.; Neuenschwander, M. *Z. Kristallogr.* **1979**, *150*, 235.
(21) For example: Huber, T. A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1995**, *14*, 4997.

passage through a double-column solvent purification system provided by mBraun Inc. Tetrahydrofuran and diethyl ether were purified over two alumina-packed columns, while benzene, toluene, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Purification of CH_3CN was achieved by refluxing over CaH_2 for 4 days under N_2. The solvents used within the glovebox were stored over activated 3 Å molecular sieves. The C_6D_6 (Aldrich) was degassed by using three repeated freeze–pump–thaw cycles and then dried over 3 Å molecular sieves for 24 h prior to use; $CDCl_3$ and CD_2Cl_2 (Aldrich) were degassed by using three repeated freeze–pump–thaw cycles, dried over CaH_2 for 7 days, and distilled in vacuo. All commercial reagents were obtained from Aldrich and were used as received, with the exception that $BrMn(CO)_5$, $AgSO_3CF_3$, and $AgBF_4$ were dried in vacuo for 12 h prior to use, and $Li(Et_2O)_{2.5}B(C_6F_5)_4$ was obtained from Boulder Scientific. Compounds **1**[Li],[22] **2**[H],[1a] **2**[Li],[1a] and η^5-[**3**]Mn(CO)$_3$[1c] were prepared employing literature procedures. All ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 160.5, 125.8, 470.6, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe$_4$ (for ^{1}H and ^{13}C), 85% H_3PO_4 in water (for ^{31}P), CFCl$_3$ (for ^{19}F), or BF$_3$ in diethyl ether (for [11]B, with peak width at half-height following the reported chemical shift). In some cases, slightly fewer than expected independent ^{1}H or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^{1}H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC NMR experiments. IR spectra were collected on a Bruker VECTOR 22 FT-IR instrument, employing Nujol mulls. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. All X-ray data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer, using samples that were mounted in inert oil and transferred to a cold gas stream of the diffractometer. Crystal structure diagrams were generated by use of the ORTEP-3 program.[23] During the refinement of the $P2_1$ polymorph of **4**·0.5C$_7$H$_8$, the behavior of the Flack absolute structure parameter (0.217(17)) indicated a degree of racemic twinning in the crystal; the SHELXL-93 TWIN instruction was employed to accommodate this twinning. For complete experimental details and tabulated crystallographic data, see the Supporting Information.

Preparation of κ^2-*P*,*N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn-(CO)$_3$Br (4). To a magnetically stirred solution of **2**[H] (0.17 g, 0.62 mmol) in THF (1.5 mL) was added a slurry of BrMn(CO)$_5$ (0.17 g, 0.62 mmol) in THF (2 mL) via pipet. The reaction mixture was left to stir for 24 h, during which time the mixture became mostly homogeneous. Analysis of the crude reaction mixture (^{31}P NMR) confirmed both the consumption of **2**[H] and the quantitative formation of a single phosphorus-containing species at 59.8 ppm. The reaction mixture was then filtered through Celite, and the resulting dark orange solution was evaporated, leaving **4** as an analytically pure orange powder (0.22 g, 0.45 mmol, 73%). Crystals of **4**·0.5C$_7$H$_8$ (both $P2_1$ and $P2_1$/c polymorphs) suitable for single-crystal X-ray diffraction analysis were grown from toluene at −35 °C. Anal. Calcd for $C_{20}H_{26}O_3PNMnBr$: C: 48.60, H: 5.30, N: 2.83; Found: 48.44, H: 4.94, N: 2.67. ^{1}H NMR (C$_6$D$_6$): δ 7.15−6.99 (m, 4H, Ar−Hs), 2.72 (s, 3H, NMe$_a$), 2.62−2.55 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.46 (s, 2H, CH$_2$), 2.42 (s, 3H, NMe$_b$), 2.35 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.67 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 1.45 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 1.30

(d of d, $^3J_{PH}$ = 16.3 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 0.92 (d of d, $^3J_{PH}$ = 14.7 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me*$_c$-Me$_d$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 174.4 (d, $^2J_{PC}$ = 19.8 Hz, C2), 143.0 (C7a), 140.5 (C3a), 133.1 (d, $^1J_{PC}$ = 21.7 Hz, C3), 127.0, 125.9, 124.7, 122.3 (C4, C5, C6, C7), 58.5 (NMe$_b$), 54.3 (NMe$_a$), 31.8 (d, $^1J_{PC}$ = 22.0 Hz, P(*C*HMe$_a$Me$_b$)), 30.8 (d, $^3J_{PC}$ = 9.0 Hz, C1), 30.4 (d, $^1J_{PC}$ = 24.0 Hz, P(*C*HMe$_c$Me$_d$)), 22.4 (P(CH-*Me*$_a$*Me*$_b$)), 20.9 (P(CH*Me*$_a$Me$_b$)), 19.9 (d, $^2J_{PC}$ = 6.0 Hz, P(CH-*Me*$_c$*Me*$_d$)), 19.5 (P(CH*Me*$_c$*Me*$_d$)). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 59.8. FTIR (cm^{-1}) ν(CO): 2013, 1926, 1895.

Preparation of κ^2-*P*,*N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn-(CO)$_3$FBF$_3$ (5a). To a magnetically stirred solution of **4** (0.025 g, 0.050 mmol) in toluene (3 mL) was added a slurry of AgBF$_4$ (0.010 g, 0.051 mmol) in toluene (1 mL) via pipet. A clear yellow solution resulted, followed by immediate development of a white precipitate. The mixture was stirred for 5 min and then was filtered through Celite to remove the precipitated material. A ^{31}P NMR spectrum of the filtered solution revealed formation of a single new phosphorus-containing product at 63.5 ppm. Solvent and other volatile materials were then removed in vacuo to yield **5a** as an analytically pure yellow powder (0.015 g, 0.031 mmol, 62%). Crystals of **5a** suitable for single-crystal X-ray diffraction analysis were grown from a concentrated toluene solution at room temperature. Anal. Calcd for $C_{20}H_{26}O_3PNMnBF_4$: C 47.93; H 5.23; N 2.79. Found: C 47.91; H 5.41; N 2.95. ^{1}H NMR (C$_6$D$_6$): δ 7.32−6.97 (m, 4H, Ar−Hs), 2.48 (s, 2H, C1-H_2), 2.44 (s, 3H, NMe$_a$), 2.40 (s, 3H, NMe$_b$), 2.29−2.24 (m, 2H, P(C*H*Me$_2$)$_2$), 1.49 (d of d, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 1.20 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.6 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 1.04 (d of d, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 0.80 (d of d, $^3J_{PH}$ = 15.3 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CH*Me*$_c$-Me$_d$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 220.7 (CO), 174.9 (d, $^2J_{PC}$ = 19.7 Hz, C2), 143.2 (d, J_{PC} = 4.6 Hz, C3a or C7a), 139.2 (C7a or C3a), 132.2 (d, $^1J_{PC}$ = 23.4 Hz, C3), 127.2, 126.5, 124.9, 121.7 (C4, C5, C6, C7), 57.0 (NMe$_b$), 52.7 (NMe$_a$), 30.9 (d, $^3J_{PC}$ = 9.1 Hz, C1), 29.8 (d, $^1J_{PC}$ = 19.8 Hz, P(*C*HMe$_a$Me$_b$)), 28.6 (d, $^1J_{PC}$ = 27.5 Hz, P(*C*HMe$_a$Me$_b$)), 20.3 (d, $^2J_{PC}$ = 5.0 Hz, P(CH-*Me*$_a$*Me*$_b$)), 20.0 (d, $^2J_{PC}$ = 5.8 Hz, P(CH*Me*$_c$*Me*$_d$)), 19.6 (P(CH-*Me*$_a$Me$_b$)), 19.3 (P(CH*Me*$_c$*Me*$_d$)). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 63.5. ^{19}F{^{1}H} NMR (1:1 toluene/THF): δ −152.3 (MnFB*F*$_3$), −293.5 (Mn*F*BF$_3$). ^{11}B{^{1}H} NMR (1:1 toluene/THF): δ 0.31 ($\Delta\nu_{1/2}$ = 63 Hz). FTIR (cm^{-1}) ν(CO): 2038, 1952, 1912.

Preparation of κ^2-*P*,*N*-(2-NMe$_2$-3-P^{i}Pr$_2$-indene)Mn-(CO)$_3$OTf (5b). To a magnetically stirred solution of **4** (0.23 g, 0.46 mmol) in toluene (7 mL) was added a slurry of AgOTf (0.12 g, 0.46 mmol) in toluene (6 mL) via pipet. Immediately, a bright yellow solution formed followed by generation of a white precipitate. The reaction mixture was allowed to stir for 4 h, after which the precipitate was removed by filtration through Celite. Further product was extracted from the solid residue of the filtration by use of THF (4 × 3 mL) until the residue was colorless. The THF extractions were combined with the original toluene filtrate, and all solvent and other volatile materials were removed in vacuo to yield **5b** as an analytically pure yellow powder (0.17 g, 0.030 mmol, 65%). Crystals of **5b** suitable for single-crystal X-ray diffraction analysis were grown from the slow evaporation of toluene at room temperature. Anal. Calcd for $C_{21}H_{26}O_6$-PNMnSF$_3$: C 44.77; H 4.65; N 2.49. Found: C 44.41; H 4.93; N 2.33. ^{1}H NMR (C$_6$D$_6$): δ 7.14−7.11 (m, 2H, Ar−Hs), 7.02−6.99 (m, 2H, Ar−Hs), 2.47 (s, 2H, C1-H_2), 2.41 (s, 3H, NMe$_a$), 2.39 (s, 3H, NMe$_b$), 2.35−2.25 (m, 2H, P(C*H*Me$_2$)$_2$), 1.41 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 1.23 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 1.09 (d of d, $^3J_{PH}$ = 15.4 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 0.85 (d of d, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CH*Me*$_c$-Me$_d$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 174.7 (d, $^2J_{PC}$ = 19.5 Hz, C2), 142.5 (d, J_{PC} = 4.6 Hz, C3a or C7a), 139.5 (d, J_{PC} = 3.3 Hz, C7a or C3a), 132.3 (d, $^1J_{PC}$ = 23.1 Hz, C3), 127.2, 126.4, 124.9, 122.0 (C4, C5, C6, C7), 57.1 (NMe$_b$), 53.3 (NMe$_a$), 30.8 (d, $^3J_{PC}$

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= 9.2 Hz, C1), 29.3 (d, $^1J_{PC}$ = 19.1 Hz, P(CHMe$_c$Me$_d$)), 28.2 (d, $^1J_{PC}$ = 26.6 Hz, P(CHMe$_a$Me$_b$)), 20.2 (d, $^2J_{PC}$ = 6.2 Hz, P(CHMe$_a$Me$_b$) or P(CHMe$_c$Me$_d$)), 20.1 (d, $^2J_{PC}$ = 2.1 Hz, P(CHMe$_c$Me$_d$) or P(CHMe$_a$Me$_b$)), 19.7 (P(CHMe$_a$Me$_b$)), 19.4 (P(CHMe$_c$Me$_d$)). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 62.6. ^{19}F{^{1}H} NMR (1:1 toluene/THF): δ −77.4. FTIR (cm^{-1}) ν(CO): 2036, 1957, 1916.

Preparation of [κ²-*P*,*N*-(2-NMe₂-3-^{i}Pr₂P-indene)Mn-(CO)₄]⁺BF₄⁻ (6). To a magnetically stirred solution of BrMn(CO)$_5$ (0.044 g, 0.16 mmol) in THF (3 mL) was added a slurry of AgBF$_4$ (0.034 g, 0.17 mmol) in THF (3 mL) via pipet. Immediately upon addition of AgBF$_4$ a dark brown precipitate formed from the yellow solution. After 1.5 h the precipitated solid was separated by filtration through Celite. The clear yellow filtrate was then added to a solution of **2**[H] (0.044 g, 0.16 mmol) in THF (3 mL) via pipet. The reaction mixture was monitored periodically (^{31}P NMR) over the following 21 days, after which time all phosphorus-containing intermediates were observed to evolve into a single phosphorus-containing product at 69.8 ppm. The reaction mixture was then filtered through Celite and concentrated in vacuo to a volume of 5 mL. From this solution the product (**6**) was obtained as analytically pure yellow crystals, which were isolated by decanting the supernatant and dried in vacuo (0.025 g, 0.047 mmol, 30%). Anal. Calcd for C$_{21}$H$_{26}$O$_4$PNMnBF$_4$: C 47.67, H 4.95, N 2.65. Found: C 47.42, H 5.24, N 2.72. A sample of these crystals proved suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (C$_6$D$_6$/CD$_2$Cl$_2$, 3:1): δ 7.32 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H4 or H7), 7.20−7.13 (m, 2H, H5 and H6), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H7 or H4), 3.99 (s, 2H, CH$_2$), 2.77 (s, 6H, NMe$_2$), 2.49−2.44 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 1.06 (d of d, $^3J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P(CH*Me*$_a$Me$_b$)$_2$), 0.80 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, P(CHMe$_a$*Me*$_b$)$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 209.7 (CO), 176.3 (d, $^2J_{PC}$ = 16.4 Hz, C2), 143.7 (d, J_{PC} = 6.2 Hz, C3a or C7a), 137.2 (C7a or C3a), 131.8 (d, $^1J_{PC}$ = 32.1 Hz, C3), 128.4, 125.8, 124.8, 122.0 (C4, C5, C6, C7), 60.9 (NMe$_2$), 32.4 (d, $^3J_{PC}$ = 9.1 Hz, C1), 31.1 (d, $^1J_{PC}$ = 26.1 Hz, P(CHMe$_a$Me$_b$)$_2$), 20.5 (P(CH*Me*$_a$Me$_b$)$_2$), 19.6 (P(CHMe$_a$*Me*$_b$)$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 69.3. ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$): δ −153.1. ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): δ −0.84 (Δν$_{1/2}$ = 29 Hz). FTIR (cm^{-1}) ν(CO): 2097, 2028, 1993, 1907.

Preparation of η⁵-[2]Mn(CO)₃. Employing a modification of a literature procedure for the reduction of phosphine sulfides,[24] within the glovebox a solution of η⁵-[**3**]Mn(CO)$_3$ (0.063 g, 0.14 mmol) in toluene (3 mL) was transferred to a resealable reaction vessel charged with a stir bar. A solution of hexachlorodisilane (0.053 g, 0.20 mmol) in toluene (2 mL) was then transferred to the reaction vessel via Pasteur pipet, and the vessel was sealed. The reaction vessel was then transferred from the glovebox to a Schlenk line, covered with aluminum foil, and heated at 85 °C in an oil bath. The progress of the reaction was monitored (^{31}P NMR), and complete conversion to a single phosphorus-containing product at −1.9 ppm was achieved after 14 days. The resulting reaction mixture was then filtered through Celite, and the solvent of the resulting filtrate was removed in vacuo. The residue was subsequently extracted into pentane (3 mL) and filtered through Celite. Storage of the filtrate at −35 °C resulted in the crystallization of η⁵-[**2**]Mn(CO)$_3$ as an analytically pure orange-yellow solid (0.033 g, 0.080 mmol, 56%). Crystals suitable for single-crystal X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C. Anal. Calcd for C$_{20}$H$_{25}$PNO$_3$Mn: C 58.12, H 6.10, N 3.39. Found: C 57.95, H 6.47, N 3.33. ^{1}H NMR (C$_6$D$_6$): δ 7.59 (d, $^3J_{HH}$ = 6.5 Hz, 1H, H4 or H7), 7.23 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H7 or H4), 6.77 (m, 2H, H5 and H6), 4.49 (s, 1H, H1), 2.92 (br m, 1H, C*H*Me$_2$), 2.61 (s, 6H, NMe$_2$), 2.29 (br m, 1H, C*H*Me$_2$), 1.69 (broad d,

J = 16.0 Hz, 3H, CH*Me*$_2$), 1.25 (br s, 3H, CH*Me*$_2$), 1.09 (br d, J = 15.5 Hz, 3H, CH*Me*$_2$), 0.56 (br s, 3H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 225.1 (CO), 140.0 (C2), 126.2, 126.0, 125.4, 125.0 (C4, C5, C6, C7), 105.0 (C3a or C7a), 98.8 (C7a or C3a), 67.4 (d, $^1J_{PC}$ = 44.2 Hz, C3), 61.8 (C1), 43.9 (d, $^4J_{PC}$ = 15.7 Hz, NMe$_2$), 25.5 (d, $^1J_{PC}$ = 12.3 Hz, CHMe$_2$), 23.4 (d, $^2J_{PC}$ = 24.8 Hz, CH*Me*$_2$), 22.9−22.5 (m, CH*Me*$_2$ and C*H*Me$_2$), 20.9−20.4 (m, 2 CH*Me*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −1.9. FTIR (cm^{-1}) ν(CO): 2010, 1926, 1905. Alternative reduction procedures employing Raney nickel[25] proved unsuccessful, resulting in the complete decomposition of η⁵-[**3**]Mn(CO)$_3$.

Reaction of 2[Li] with BrMn(CO)₅. To a magnetically stirred slurry of **2**[Li] (0.15 g, 0.65 mmol) in toluene (3 mL) was added a slurry of BrMn(CO)$_5$ (0.18 g, 0.65 mmol) in toluene (2 mL). After 20 h, ^{31}P NMR analysis of the reaction mixture revealed the formation of multiple phosphorus-containing products giving rise to signals at 60 ppm (∼20%), 53 ppm (∼70%), −2 ppm (∼5%), and −6 ppm (∼5%). Storage of this reaction mixture at −35 °C for 20 h yielded a brown, microcrystalline precipitate which displayed ^{31}P NMR signals at 60 ppm (∼10%) and 53 ppm (∼90%). This solid was isolated, dried in vacuo, and redissolved in toluene (2 mL), and the resulting solution was stored at room temperature. Although no crystalline material was obtained from this solution initially, storage for a prolonged period of time (>10 months) resulted in the formation of a minute quantity of crystalline material, which gave rise to ^{31}P NMR resonances at 217 and 69 ppm (1:1 ratio). The identity of this complex as **7** was determined on the basis of data obtained from a single-crystal X-ray diffraction experiment.

Preparation of 1-SiMe₃-2-NMe₂-indene (8[H]). Although the synthesis of **8**[H] has been alluded to in a previous report,[15] complete synthetic details and structural characterization data were not provided. Compound **1**[Li] (0.31 g, 1.9 mmol) was dissolved in THF (10 mL) and cooled to −80 °C. To this cold, magnetically stirred solution was added freshly distilled ClSiMe$_3$ (0.25 mL, 2.0 mmol) via syringe. The reaction mixture warmed to room temperature over 2 h, and the THF and other volatile materials were removed in vacuo over 16 h. The product was extracted into toluene (12 mL) and isolated from insoluble byproducts by filtration through Celite. The solvent and other volatile materials were removed in vacuo to yield **8**[H] as an analytically pure pale brown solid (0.41 g, 1.8 mmol, 93%). Anal. Calcd for C$_{14}$H$_{21}$NSi: C 72.66; H 9.15; N 6.05. Found: C 72.64; H 9.02; N 5.93. ^{1}H NMR (C$_6$D$_6$): δ 7.32−7.24 (m, 3H, C4-*H*, C5-*H* or C6-*H*, C7-*H*), 7.07 (t of d, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, C6-*H* or C5-*H*), 5.62 (s, 1H, C3-*H*), 3.27 (s, 1H, C1-*H*), 2.35 (s, 6H, N*Me*$_2$), 0.04 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 161.2 (C2), 145.9 (C7a), 139.9 (C3a), 125.4, 122.4, 118.1 (C4, C6, C7), 120.3 (C5), 97.9 (C3), 42.8 (C1), 41.8 (NMe$_2$), −3.2 (SiMe$_3$).

Preparation of κ²-*P*,*N*-(1-SiMe₃-2-NMe₂-3-P^{i}Pr₂-indene)-Mn(CO)₃Br (10). To a magnetically stirred solution of **8**[H] (0.04 g, 0.17 mmol) in THF (2 mL) at 0 °C was added *n*-BuLi (0.11 mL of 1.6 M hexanes solution, 0.17 mmol) via syringe. The reaction mixture immediately turned bright yellow in color. After stirring for 1 h at room temperature, the reaction mixture was cooled to −35 °C and a solution of ClP^{i}Pr$_2$ (0.26 g, 0.17 mmol) in THF (1.5 mL) was added. After 2 h of stirring at room temperature, the THF was removed in vacuo and the residue was extracted into C$_6$D$_6$. ^{1}H and ^{31}P NMR spectral data revealed consumption of the starting materials and formation of two new phosphorus-containing products at +11.8 and −3.2 ppm, tentatively assigned as **9a**[H] and **9b**[H], respectively.[1a,b] The C$_6$D$_6$ solution was then filtered through Celite, and additional product was recovered by washing the Celite filter with 1 mL of C$_6$H$_6$. In a separate vial, a slurry of BrMn(CO)$_5$ (0.047 g, 0.17 mmol) in THF (2 mL) was prepared and added via pipet to the magnetically stirred benzene

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reaction mixture. All solid went into solution and the color darkened to orange. The mixture stirred for 18 h, during which a bright yellow precipitate formed in the dark brown solution. The supernatant was decanted and the yellow solid was dried in vacuo to remove any solvent and other volatile materials, yielding **10** as a yellow powder (0.026 g, 0.046 mmol, 27%). Crystals suitable for single-crystal X-ray diffraction analysis were grown by vapor diffusion of Et_2O into a $CDCl_3$ solution of **10** at room temperature. Anal. Calcd for $C_{23}H_{34}O_3$-SiPNMnBr: C 48.77; H 6.05; N 2.47. Found: C 48.14; H 5.78; N 2.65. Repeat analysis on this complex consistently led to marginally low %C values. ^1H NMR ($CDCl_3$): δ 7.45 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-*H*), 7.28 (d, $^3J_{HH}$ = 7.3 Hz, 1H, C7-*H*), 7.25−7.22 (m, 1H, C6-*H*), 7.15 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C5-*H*), 3.73 (s, 1H, C1-*H*), 3.28 (s, 3H, NMe$_a$), 3.21−3.05 (m, 2H, P(C*H*Me$_a$-Me$_b$)(C*H*Me$_c$Me$_d$)), 2.97 (s, 3H, NMe$_b$), 1.63 (d of d, $^3J_{PH}$ = 14.8 Hz, $^3J_{HH}$ = 7.0 Hz, P(CH*Me$_a$*Me$_b$)), 1.54−1.47 (m, 6H, P(CHMe$_a$*Me$_b$*)(CH*Me$_c$*Me$_d$)), 1.11 (d of d, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 7.2 Hz, P(CHMe$_c$*Me$_d$*)), 0.00 (s, 9H, SiMe$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 180.3 (d, $^2J_{PC}$ = 19.3 Hz, C2), 146.2 (d, $^2J_{PC}$ = 4.7 Hz, C3a), 139.8 (C7a), 127.3 (d, $^1J_{PC}$ = 24.9 Hz, C3), 125.3 (C6), 123.8, 123.7 (C5 and C7), 122.0 (C4), 62.3 (NMe$_a$), 53.1 (NMe$_b$), 42.5 (d, $^3J_{PC}$ = 8.2 Hz, C1), 30.5 (d, $^1J_{PC}$ = 23.8 Hz, P(C*H*Me$_a$-Me$_b$)), 26.1 (d, $^1J_{PC}$ = 24.2 Hz, P(C*H*Me$_c$Me$_d$)), 21.7 (P(CH-Me$_a$*Me$_b$*)), 21.0 (P(CH*Me$_a$*Me$_b$)), 19.9 (d, $^2J_{PC}$ = 7.0 Hz, P(CH-*Me$_c$*Me$_d$)), 19.5 (P(CHMe$_c$*Me$_d$*)), 0.0 (SiMe$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.2. FTIR (cm^{-1}) ν(CO): 2012, 1926, 1895.

Preparation of η^5-(2-NMe$_2$-indenyl)Mn(CO)$_3$ (11). To a magnetically stirred slurry of **1**[Li] (0.48 g, 0.29 mmol) in Et_2O (30 mL) was added a slurry of BrMn(CO)$_5$ (0.80 g, 0.29 mmol) in Et_2O (10 mL) via pipet. A ruby red, cloudy mixture formed immediately. After stirring for 16 h, the reaction mixture lightened in color to yellow, with a fine white precipitate apparent. The mixture was then filtered through Celite, and the solvent was removed in vacuo. The product was extracted from the residue by repeated benzene extractions to a total volume of 30 mL. The benzene solvent was removed in vacuo, and the residual solid was washed with pentane (3 × 5 mL). The remaining solid was dried in vacuo, yielding **11** as an analytically pure yellow powder (0.35 g, 0.12 mmol, 41%). Crystals suitable for single-crystal X-ray diffraction analysis were grown from a concentrated pentane solution of the solid at room temperature. Anal. Calcd for $C_{14}H_{12}O_3NMn$: C 56.58; H 4.07; N 4.71. Found: C 56.77; H 3.82; N 4.87. ^1H NMR (C_6D_6): δ 7.17−6.76 (m, 4H, Ar−*H*s), 4.08 (s, 2H, C1-*H* and C3-*H*), 2.11 (s, 6H, NMe$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 225.5 (CO), 135.3 (C3a and C7a), 125.3 (C4 and C7 or C5 and C6), 125.1 (C5 and C6 or C4 and C7), 99.7 (C2), 55.2 (C1 and C3), 39.4 (NMe$_2$). FTIR (cm^{-1}) ν(CO): 2013, 1935, 1919.

Supporting Information Available: Tabulated single-crystal X-ray diffraction data for **4**·0.5C$_7$H$_8$, **5a**·0.5C$_7$H$_8$, **5b**, **6**, η^5-[**2**]Mn(CO)$_3$, **7**·0.5C$_7$H$_8$, **10**, **11**, and *rac*-**12** are available free of charge via the Internet at http://pubs.acs.org.

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