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Organometallic Complexes of Benzannelated Phospholyls: Synthesis and Characterization of Benzophospholyl and the First *iso*-Benzophospholyl Metal Complexes[†]

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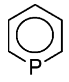
A large-scale synthesis of the benzophospholyl (BP) ligand, **4**, has been developed and employed in the synthesis of a series of manganese and iron complexes. Reaction between Li-BP and $FeCp(CO)_2X$ (X = Br, I) resulted in the formation of $[(\mu_2\text{-BP})Fe_2Cp_2(CO)_4]X$, while reaction of bis(1,1′-benzophospholyl) with $[FeCp(CO)_2]_2$ gave a mixture of isomers of $(\mu_2\text{-BP})_2Fe_2Cp_2(CO)_2$. The phosphine adduct $(BP\text{-}Ph)Mn_2(CO)_9$ was obtained from BP-Ph and $Mn_2(CO)_{10}$ and converted to $(\eta^5\text{-BP})Mn(CO)_3$ upon reaction with organometallic or organic radicals. A synthesis for phenyl-*iso*-benzophosphole (iBP-Ph) has been explored. The compound is highly reactive and polymerizes instantaneously and irreversibly. Polymerization of the iBP precursor was avoided in the novel partially hydrogenated derivative iBP-H_2-Ph. Manganese complexes of iBP, **5**, were obtained by reaction of iBP-H_2-Ph with $Mn_2(CO)_{10}$, resulting in the formation of $(\eta^5\text{-iBP-}H_2)Mn(CO)_3$. Reaction of $(\eta^5\text{-iBP-}H_2)Mn(CO)_3$ with DDQ gave $(\eta^5\text{-iBP})Mn(CO)_3$, the first metal complex of iBP.

Introduction

Phosphorus-containing aromatic heterocycles have attracted much interest for their use as ligands in organometallic complexes[1−5] in particular catalysts.[6−10] Structural diversity of their transition metal complexes has been facilitated by the ability of phospholyls to ligate metals in σ-, π-, and mixed-bonding modes. While phosphinine and phospholyl ligands **1** and **2** have been studied extensively and their high degree of aromaticity has been established experimentally and theoretically,[11−17] very little is known about their benzannelated analogues **3** and **4**, and complexes of **5** are unknown.



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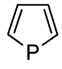

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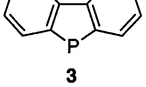

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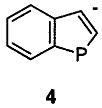

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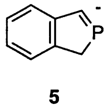

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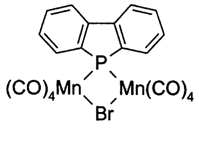
Our research program is concerned with the ligating abilities of ligands **3**−**5**, particularly in complexes of the virtually unexplored anion **4** and its elusive isomer **5**. With respect to the bonding in complexes of dibenzophospholyl (DBP, **3**), we recently reported on the synthesis and characterization of a series of DBP manganese and iron complexes. DBP served as a bridging ligand in the σ-complexes $(\mu_2\text{-DBP})(\mu_2\text{-Br})Mn_2(CO)_8$, **6**, $(\mu_2\text{-DBP})_2Mn_2(CO)_8$, **7**, $(\mu_2\text{-DBP})_2Fe_2Cp_2(CO)_2$, **8**, and $[(\mu_2\text{-DBP})Fe_2Cp_2(CO)_4][X]$ (X = Br, I), **9**, and π-complexes of DBP were not observed.[18,19]



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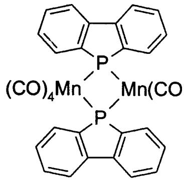

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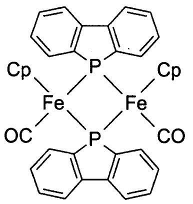

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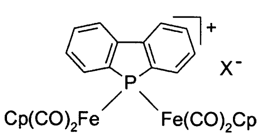

9a: X = Br
9b: X = I

The tendency to form σ-complexes was attributed to the high degree of benzannelation of the phospholyl

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[†] This article is dedicated to Professor Alan H. Cowley, distinguished mentor and friend, on the occasion of his 70th birthday.

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(1) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1.
(2) Mathey, F. *Chem. Rev.* **1988**, *88*, 429.
(3) Mathey, F.; Le Floch, P. *Coord. Chem. Rev.* **1988**, *179−180*, 771.
(4) Mathey, F. *New J. Chem.* **1987**, *11*, 585.
(5) Bansal, R. K.; Heinicke, J. *Chem. Rev.* **2001**, *101*, 3549.
(6) Brown, S. J.; Gao, X.; Harrison, D. G.; Koch, L.; Spence, R. E. v. H.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5445.
(7) Janiak, C.; Lange, K. C. H.; Versteeg, U.; Lentz, D.; Budzelaar, P. H. M. *Chem. Ber.* **1996**, *129*, 1517.
(8) Janiak, C.; Versteeg, U.; Lange, K. C. H.; Weimann; R.; Hahn, I. *J. Organomet. Chem.* **1995**, *501*, 219.
(9) Mathey, F. *J. Organomet. Chem.* **2002**, *646*, 15.
(10) Weber, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 563.

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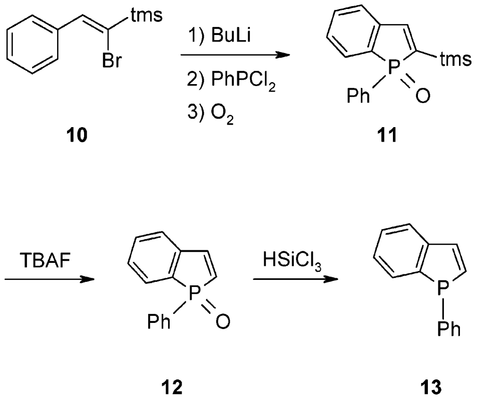
Scheme 1

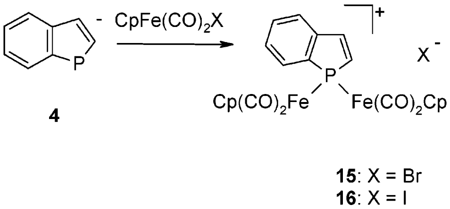


ligand, leading to a decreased ability to bind in a η^5-fashion. Coordination of a metal to the central five-membered ring in DBP would result in a very unfavorable loss of local aromaticity in the six-membered rings. This effect is reduced for the phosphindolyl ligands **4** and **5** because of the lower degree of benzannelation and is absent for the phospholyl ligand **2** because it is not benzannelated. We here report the large-scale synthesis of **4**, its manganese and iron complexes, and the first metal complex of **5**.

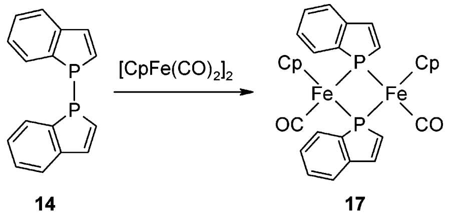
Results and Discussion

Synthesis of Benzophospholyl 4. Several literature procedures are available for the synthesis of **13**, the precursor to **4**. However, they are lengthy or unreliable or give poor overall yields.[20-26] The most promising route was that of Tsuchiya et al.,[24,25] yielding **13** in four steps from commercially available starting materials in reasonable yields. Drawbacks of their strategy include lengthy workup procedures and the formation of varying quantities of the byproduct **12**. Our approach involved the preparation of **11** from **10** by reaction with BuLi, ring closure with $PhPCl_2$, and aerial oxidation. The synthetic sequence was completed by removal of the tms group with TBAF and reduction to **13** using $HSiCl_3$ (Scheme 1).

Scheme 2



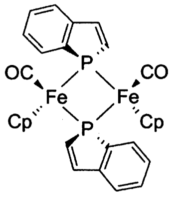
Scheme 3



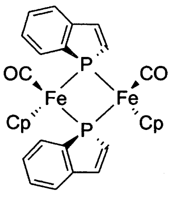
The overall yield was 20%, but more importantly, purification steps were unnecessary for **12** or involved washing of the solid product for **11** or simple recrystallization for **13**, allowing the facile and rapid synthesis of **13** on a 9 g scale. Benzophosphole **13** was readily converted into its anion, **4**, by reaction with metallic lithium, or to the bisphospholyl **14** by quenching **4** with I_2. Both **4** and **14** were most conveniently used in situ. All organic products were characterized using standard ^1H, ^{13}C, and ^{31}P NMR spectroscopies, mass spectrometry, and in the case of **11** and **13**, X-ray crystallography.

Complexes of Benzophospholyl 4. In light of the facile synthesis and high stability of phosphacymantrenes[27,28] and phosphaferrocenes,[29-31] we prepared manganese and iron complexes of **4**. Reaction of **4** with $FeCp(CO)_2X$ (X = I, Br) lead to the isolation of **15** and **16** in high yields (49–74%) (Scheme 2).

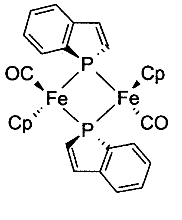
Reaction between **14** and $Fe_2Cp_2(CO)_4$ yielded the metallacycle **17** (Scheme 3). Complex **17** consisted of a mixture of four isomers, **17a–d**, inseparable by column chromatography or crystallization.



17a



17b



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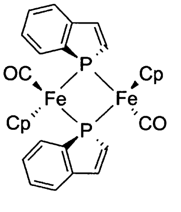

17d

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(11) Clark, T.; Elvers, A.; Heinemann, F. W.; Hennemann, M.; Zeller, M.; Zenneck, U. *Angew. Chem., Int. Ed.* **2000**, *39*, 2087.

(12) Dransfeld, A.; Nyulaszi, L.; Schleyer, P. v. R. *Inorg. Chem.* **1998**, *37*, 4413.

(13) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1997**, *16*, 1543.

(14) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755.

(15) Mathey, F. *J. Organomet. Chem.* **1994**, *475*, 25.

(16) Keglevich, G.; Böcskei, Z.; Kesertii, G. M.; Ujszászy, K.; Quin, L. D. *J. Am. Chem. Soc.* **1997**, *119*, 5095.

(17) Nyulászi, L. *Chem. Rev.* **2001**, *101*, 1229.

(18) Decken, A.; Neil, M.; Bottomley, F. *Can. J. Chem.* **2001**, *79*, 1321.

(19) Decken, A.; Neil, M.; Bottomley, F. *Can. J. Chem.* **2002**, *80*, 55.

(20) Chan, T. H.; Wong, L. T. L. *Can. J. Chem.* **1971**, *49*, 530.

(21) Quin, L. D.; Rao, N. S.; Topping, R. J.; McPhail, A. T. *J. Am. Chem. Soc.* **1986**, *108*, 4519.

(22) Quin, L. D.; Rao, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 5960.

(23) Ashe, A. J.; Savla, P. M. *J. Organomet. Chem.* **1993**, *461*, 1.

(24) Kurita, J.; Ishii, M.; Yasuike, S.; Tsuchiya, T. *Chem. Pharm. Bull.* **1994**, *42*, 1437.

(25) Kurita, J.; Ishii, M.; Yasuike, S.; Tsuchiya, T. *J. Chem. Soc.* **1993**, *17*, 1309.

(26) Nief, F.; Charrier, C.; Mathey, F.; and Simalty, M. *Phosphorus Sulfur* **1982**, *13*, 259.

(27) Mathey, F. *Tetrahedron Lett.* **1976**, 4155.

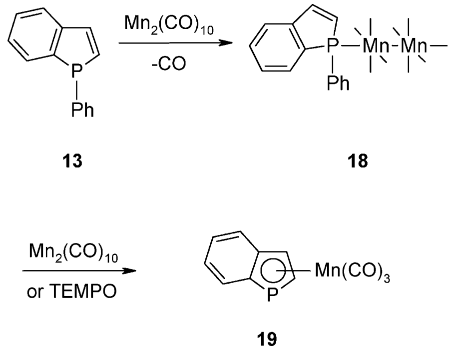
(28) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 5748.

(29) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1977**, *99*, 3537.

(30) Mathey, F. *J. Organomet. Chem.* **1977**, *139*, 77.

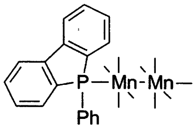
(31) De Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994.

Scheme 4



In both types of complexes, the BP ligand bridges two metal atoms through the phosphorus atom, and bonding involving the ligand π-electron system was not observed. This behavior parallels that of the DBP ligand in the complexes **8** and **9**, as well as the manganese compounds (μ_2-BP)(μ_2-Br)$Mn_2(CO)_8$ and $(\mu_2\text{-BP})_2Mn_2(CO)_8$.[26] Complexes **15**–**17** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopies, mass spectrometry, and microanalysis (**15**) and X-ray crystallography (**16**). Complexes **15**, **16**, and **17** were mildly air and moisture sensitive; **15** and **16** decomposed slowly, especially in the presence of light, while **17** was indefinitely stable under an inert atmosphere. Heating complexes **15**, **16**, and **17** for extended periods yielded intractable decomposition products.

To date, there are no crystallographically authenticated η^5-complexes of **4**.[32] The only account of a π-bonded BP ligand is that of (η^5-BP)$Mn(CO)_3$, **19**.[26] The generation of the benzophosphacymantrene **19** from phosphole **13** and $Mn_2(CO)_{10}$ was in contrast to our earlier observation that reaction between DBP-Ph and $Mn_2(CO)_{10}$ led to the isolation of the phosphine adducts **20** and **21**.[18]



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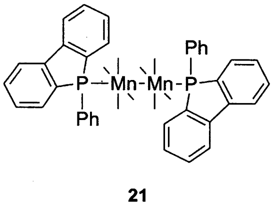

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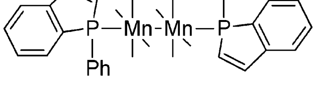
We consequently repeated the original literature procedure and found that heating a mixture of **13** and $Mn_2(CO)_{10}$ for 12 min resulted in the formation of **18** instead of **19** (Scheme 4). The orange-red oil was isolated in 51% yield after flash chromatography and the diphosphine adduct **22** was not observed, in contrast to the formation of the analogous DBP complex **21**.



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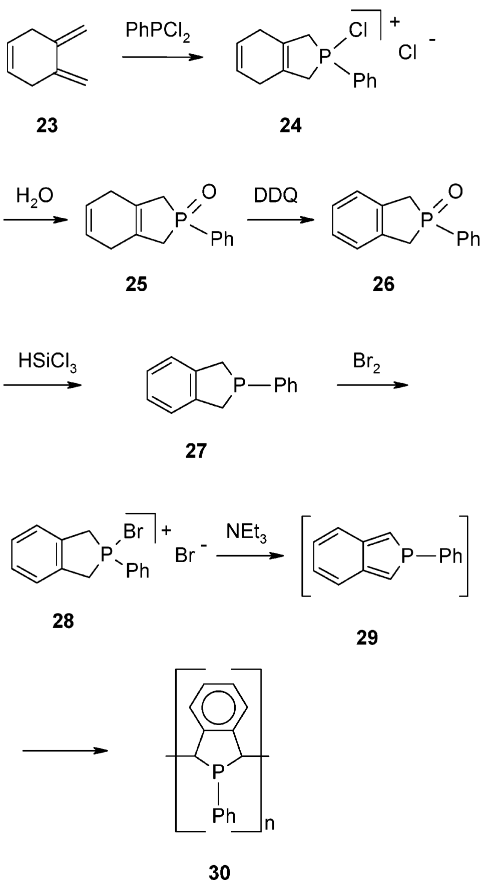
Scheme 5



Heating **18** in refluxing xylenes resulted in decomposition, yielding **13** as the only product containing phosphorus. Liberation of the phosphine ligand was also observed upon heating of the corresponding DBP complexes **20** and **21**. There was no evidence of a thermal conversion of **18** to **19**. However, reaction of **18** with organic or organometallic radicals in xylenes led to the formation of **19**, indicated by a color change of the solutions from orange-red to dark red and confirmed by spectroscopic methods. Compound **19** can also be prepared directly from **13** and $Mn_2(CO)_{10}$ upon extended heating in refluxing xylenes, giving **19** in 17% yield. One may conclude from these findings that **19** is produced by attack of a radical on the hitherto unknown complex **18**, contrary to the previously assumed pathway that involved attack of a radical on **13**.[26] **18** and **19** were characterized by NMR and IR spectroscopies, mass spectrometry, X-ray crystallography, and in the case of **18**, microanalysis.

Attempted Preparation of *iso*-Benzophospholyl 5. There are no literature reports on the synthesis of the *iso*-benzophospholyl ligand **5** or its precursor **29**. We devised a strategy for their preparation starting from **23** (Scheme 5).

On the basis of literature precedence,[33] **23** was converted to **24** by reaction with $PhPCl_2$ in 81% yield.

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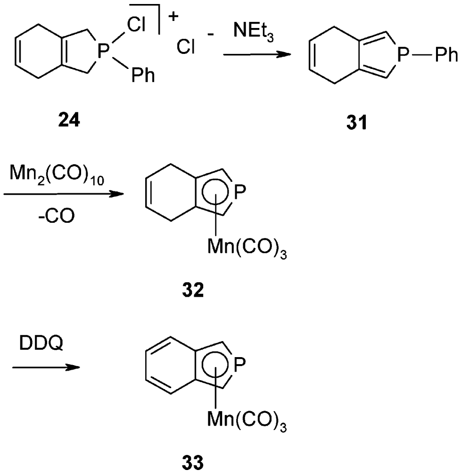
[32] For substituted benzophospholyl complexes see: (a) Niecke, E.; Nieger, M.; Wenderoth, P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 353. (b) Nief, F.; Ricard, L. *J. Organomet. Chem.* **1994**, *464*, 149.

[33] Middlemas, E. D.; Quin, L. D. *J. Org. Chem.* **1979**, *44*, 2587.

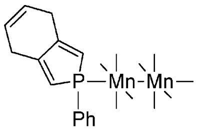
Scheme 6



Hydrolysis gave the phosphine oxide **25** in 48% yield. Aromatization of the six-membered ring was achieved by reaction of **25** with DDQ to give known compound **26**.[33] Reduction with $HSiCl_3$ gave phosphine **27** in 92% yield, and bromination to give **28** was accomplished with either Br_2 or NBS, the former simplifying the workup procedure and furnishing **28** in 78% yield. All products were characterized by spectroscopic means and, in the cases of **25** and **26**, X-ray crystallography. Compound **27** was a highly air-sensitive colorless oil and **28** an air-sensitive orange solid. Completion of the synthesis of **29** involved dehydrobromination of **28**. Consequently, **28** was reacted with an excess of Et_3N, resulting in the immediate discoloration of the orange solution of **28** in CH_2Cl_2, followed by the formation of a pale brown solid precipitate and a pale brown solution. The solid was insoluble in organic solvents. The solution showed no signal in the in situ ^{31}P NMR spectrum, and removal of the solvent and excess Et_3N yielded HEt_3NBr as the only product, identified by ^1H NMR and microanalysis. On the basis of the dramatic color change upon addition of base to **28** and the formation of HEt_3NBr, one must conclude that the dehydrobromination of **28** was successful. These findings suggest that **29** was indeed produced, but immediately polymerized, perhaps to give **30**. It is easily envisaged that the driving force in such a polymerization would be the gain of local aromaticity in the six-membered ring of the *iso*-phosphindole skeleton. The polymerization was irreversible, and the insoluble nature of the polymer prevented further characterization.

Complexes of 5. The highly reactive nature of **29** prevented its use as a starting material in the synthesis of organometallic complexes of **5**, and we turned our attention to precursors of **29** with a partially hydrogenated six-membered ring, eliminating the possibility of polymerization (Scheme 6).

To this end, **24** was dehydrochlorinated with Et_3N to give **31** in 45% yield as a colorless, air-sensitive oil. Dihydro-*iso*-phosphindole **31** was characterized by NMR and IR spectroscopies, mass spectrometry, and high-resolution mass spectrometry. The compound was stable under an inert atmosphere, and formation of a polymer analogous to **30** was not observed, confirming that eliminating the possibility of aromatization of the six-membered ring would increase the stability of the heterocycle. Metal complexation was achieved upon reaction of **31** with $Mn_2(CO)_{10}$, generating **32** as an orange oil in 16% yield after flash chromatography. The above reaction also produced **34** in trace amounts, but the bis adduct **35** was not observed.



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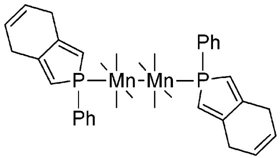

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This behavior was identical to that of BP, **4**, and in contrast to that of DBP, **3**. The final step in the synthesis of a cymantrene analogue of iBP, **5**, was the dehydrogenation of **32** to give **33** as a yellow solid in 32% yield after sublimation. The novel complexes **32** and **33** have been fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopies, mass spectrometry, high-resolution mass spectrometry, and in the case of **33**, IR spectroscopy and X-ray crystallography. Complexes **32** and **33** are air and moisture sensitive, but are indefinitely stable under an inert atmosphere. The isolation of **33** is particularly important because it is the first metal complex of the hitherto unknown ligand **5**.[34] The synthesis of **19** and **33** proves that **4** and **5** form π-complexes with manganese, in contrast to the behavior of **3**, for which only σ-complexes were obtained. This substantiates the notion that the high degree of benzannelation in DBP, **3**, eliminates the possibility of forming η^5-complexes, whereas the monobenzannelated ligands **4** and **5** form stable cymantrene analogues.

Molecular Structures

A thermal ellipsoid plot of **11** is shown in Figure 1, and selected bond distances and angles are presented in Table 3. The phosphindole skeleton is planar and the phosphorus atom tetrahedrally coordinated. The P−C(8) and P−O bond lengths fall within the expected ranges. The five-membered ring contains an isolated C=C double bond, indicated by the short C(2)−C(3) distance of 1.3483(15) Å, and delocalization is not present. The bond lengths within the five-membered heterocycle are comparable to those of **13** (see below), and deformation due to the bulky TMS group is not evident.

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(34) For complexes of substituted neutral and cationic *iso*-benzophospholyl ligands see: (a) Gudat, D.; Lewall, B.; Nieger, M.; Detmer, I.; Szarvas, L.; Saarenketo; P.; Marconi, G. *Chem. Eur. J.* **2003**, *9*, 661. (b) Gudat, D.; Holderberg, A. W.; Korber, N.; Nieger, M.; Schrott, M. Z. *Naturforsch., B*: Chem. Sci. **1999**, *54*, 1244. (c) Gudat, D.; Hap, S.; Szarvas, L.; Nieger, M. *Chem. Commun.* **2000**, 1637. (d) Gudat, M.; Nieger, M.; Schmitz, K.; Szarvas, L. *Chem. Commun.* **2002**, 1820. (e) Gudat, M.; Schrott, M.; Bajorat, V.; Nieger, M.; Kotila, S.; Fleischer, R.; Stalke, D. *Chem. Ber.* **1996**, *129*, 337. (f) Gudat, M.; Hap, S.; Nieger, M. *J. Organomet. Chem.* **2002**, *643*, 181. (g) Hap, S.; Nieger, M.; Gudat, D.; Betke-Hornfeck, M.; Schramm, D. *Organometallics* **2001**, *20*, 2679. (h) Bajko, Z.; Daniels, J.; Gudat, D.; Hap, S.; Nieger, M. *Organometallics* **2002**, *21*, 5182. (i) Gudat, D.; Nieger, M.; Schrott, M. *Chem. Ber.* **1995**, *128*, 259. (j) Gudat, M. Schrott, M.; Nieger, M. *Chem. Commun.* **1995**, 1541.

Table 1. Crystal Data and Structure Refinement for 11, 13, 16, and 18

	11	**13**	**16**	**18**
formula	$C_{17}H_{19}OPSi$	$C_{14}H_{11}P$	$C_{22}H_{16}Fe_2IO_4P$	$C_{23}H_{11}Mn_2O_9P$
fw	298.38	210.20	613.92	572.17
cryst size, mm	0.075 × 0.150 × 0.375	0.10 × 0.28 × 0.28	0.175 × 0.275 × 0.35	0.175 × 0.45 × 0.525
color and habit	colorless irregular	colorless irregular	Orange, irregular	yellow, irregular
temperature, K	173(1)	173(1)	173(1)	173(1)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclininc	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2(1)2(1)2(1)$	$Pnma$	$C2/c$
a, Å	6.8785(3)	6.2210(8)	12.9436(10)	27.659(2)
b, Å	22.5058(9)	8.1465(11)	12.5339(10)	13.1728(9)
c, Å	10.9140(4)	21.881(3)	13.3180(10)	13.1654(9)
α, deg	90	90	90	90
β, deg	106.811(1)	90	90	100.556(3)
γ, deg	90	90	90	90
V, Å^3	1617.35(11)	1108.9(3)	2160.6(3)	4715.6(6)
Z	4	4	4	8
μ, mm^{-1}	0.237	0.208	2.872	1.190
θ range, deg	1.81 to 32.50	1.86 to 32.48	2.19 to 32.50	1.50 to 32.50
no. of data measd	17 783	9387	22 627	25 934
no. of unique data/R(int)	5781/0.0197	3832/0.0642	4048/0.0333	8487/0.0233
no. of restr/params	0/257	0/181	0/189	0/316
S^a (GOF) on F^2	0.964	1.056	1.085	1.134
R1^b ($I > 2\sigma(I)$)	0.0367	0.0624	0.0302	0.0519
wR2^c (all data)	0.0996	0.1657	0.0791	0.1750
$\Delta_{\sigma\max}$, $\Delta_{\sigma\min}$, e Å^{-3}	0.519, −0.183	0.731, −0.336	2.107, −0.683	1.802, −0.655

[a] $S = (\Sigma[w(F_o^2 - F_c^2)^2/(n - p))^{1/2}$. [b] $R1 = \Sigma||(F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[wF_o^4])^{1/2}$, where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$. For **11**, $a = 0.0619$, $b = 0$; for **13**, $a = 0.0962$, $b = 0$; for **16**, $a = 0.0392$, $b = 1.2121$; for **18**, $a = 0.0986$, $b = 0$.

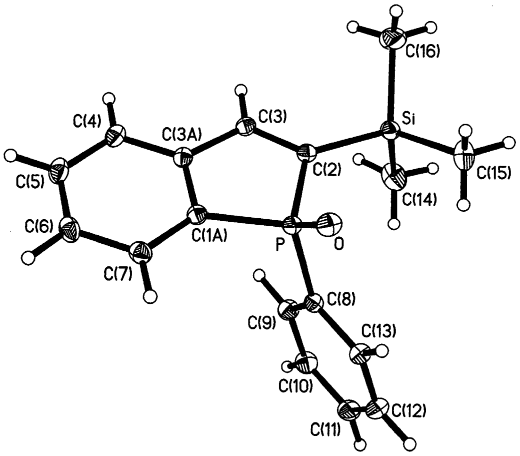

Figure 1. View of **11** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

A thermal ellipsoid plot of **13** is presented in Figure 2, and selected bond distances and angles are summarized in Table 4. The planar phosphindole skeleton contains a localized C═C double bond between C(2) and C(3) (1.326(4) Å) similar to that in **11**. The P−C(8) bond measures 1.852(2) Å, slightly elongated in comparison to the phosphine oxide derivative **11** (1.8045(11) Å).

A thermal ellipsoid plot of the cation of **16** is depicted in Figure 3, and selected bond distances and angles are presented in Table 5. The phosphindolyl fragment lies on a mirror plane, placing the phosphorus atom in a tetrahedral environment. The ∠Fe−P−Fe measures 125.04(3)° and is identical to those observed in **9a** and **9b**. However, the P−Fe (2.2690(4) Å) and Fe−Cp (Cp = centroid of the cyclopentadienyl ring) (1.717 Å) distances are slightly shorter than the corresponding distances in **9a** (P−Fe = av 2.29 Å, Fe−Cp = 1.73 Å) and **9b** (P−Fe = av 2.30 Å, Fe−Cp = 1.73 Å), most likely due to the reduced steric demand of the benzophospholyl ligand compared to the dibenzophospholyl ligand. The Fe···Fe distance is 4.026 Å, and therefore no direct Fe−Fe interactions are observed. The iodide anion forms five hydrogen bonds at 3.035 Å (H(2)), 3.084 Å (H(11) and H(11a)), and 3.187 Å (H(8) and H(8′)). There are no additional interionic contacts.

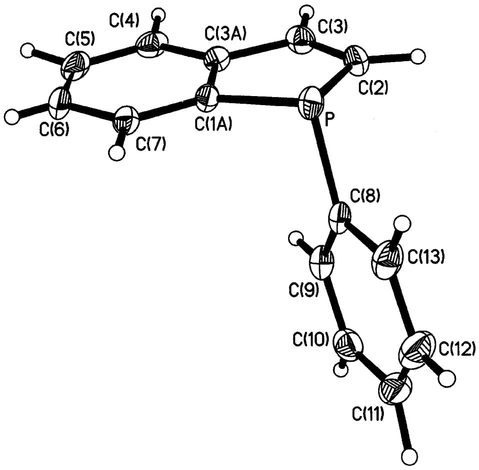

Figure 2. View of **13** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

A thermal ellipsoid plot of **18** is shown in Figure 4, and selected bond distances and angles are presented in Table 6. The phosphine ligand is in an axial position as expected for a bulky ligand, and the P−Mn−Mn moiety is almost linear (177.69(2)°). The P−Mn (2.2326(7) Å) and Mn−Mn distances (2.8870(5) Å) compare favorably with those in **20** (P−Mn = 2.2480(13) Å, Mn−Mn = 2.9198(10) Å) and **21** (P−Mn = 2.2223(7) and 2.2309(7) Å, Mn−Mn = 2.8937(5) Å).

A thermal ellipsoid plot of **19** is shown in Figure 5, and selected bond distances and angles are presented in Table 7. The crystal lattice contains two independent molecules per asymmetric unit, and their metric parameters are almost identical. The ligand skeleton is

Table 2. Crystal Data and Structure Refinement for 19, 25, 26, and 33

	19	**25**	**26**	**33**
formula	$C_{11}H_6MnO_3P$	$C_{14}H_{15}OP$	$C_{14}H_{13}OP$	$C_{11}H_6MnO_3P$
fw	272.07	230.23	228.21	272.07
cryst size, mm	0.3 × 0.15 × 0.15	0.075 × 0.4 × 0.4	0.1 × 0.4 × 0.45	0.2 × 0.225 × 0.4
color and habit	yellow, irregular	colorless, irregular	colorless, plate	yellow, parallelepiped
temperature, K	198(1)	198(1)	198(1)	198(1)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	9.0111(7)	9.7371(10)	10.0213(8)	9.0278(4)
b, Å	9.9967(8)	8.3018(9)	10.8751(9)	9.9626(5)
c, Å	13.0257(10)	14.4596(15)	11.3060(9)	13.1254(6)
α, deg	68.697(1)	90	87.160(2)	68.895(1)
β, deg	81.642(1)	99.411(2)	74.814(2)	81.148(1)
γ, deg	89.513(2)	90	88.958(2)	89.337(1)
V, Å^3	1080.34(15)	1153.1(2)	1187.65(17)	1086.97(9)
Z	4	4	4	4
μ, mm^{-1}	1.354	0.213	0.206 mm	1.346
θ range, deg	1.70 to 27.50	2.35 to 24.96	1.87 to 27.50	1.68 to 27.49
no. of data measd	7558	5601	8327	7615
no. of unique data/R(int)	4726/0.0204	1944/0.0212	5220/0.0131	4749/0.0170
no. of restr/params	0/289	0/205	0/393	0/337
S^a (GOF) on F^2	1.036	1.090	1.068	1.060
R1^b ($I>2\sigma(I)$)	0.0393	0.0362	0.0348	0.0243
wR2^c (all data)	0.1191	0.1009	0.0983	0.0698
$\Delta_{\sigma\max}$, $\Delta_{\sigma\min}$, e Å^{-3}	0.895, −0.663	0.408, −0.198	0.443, −0.130	0.322, −0.219

[a] $S = (\sum[w(F_o^2 - F_c^2)^2/(n - p))^{1/2}$. [b] $R1 = \sum||(F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = (\sum[w(F_o^2 - F_c^2)^2/\sum[wF_o^4])^{1/2}$, where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$. For **19**, $a = 0.0745$, $b = 0.6516$; for **25**, $a = 0.0617$, $b = 0.276$; for **26**, $a = 0.0609$, $b = 0.2234$; for **33**, $a = 0.0386$, $b = 0.2151$.

Table 3. Selected Distances (Å) and Angles (deg) for 11

P−O	1.4859(8)	O−P−C(1A)	116.05(5)
P−C(1A)	1.8032(11)	O−P−C(2)	118.30(5)
P−C(8)	1.8045(11)	C(1A)−P−C(2)	93.76(5)
P−C(2)	1.8056(11)	C(3)−C(2)−P	108.07(8)
C(2)−C(3)	1.3483(15)	C(3)−C(2)−Si	126.79(8)
C(2)−Si	1.8725(11)	P−C(2)−Si	124.93(6)
C(3)−C(3A)	1.4821(14)	C(2)−C(3)−C(3A)	116.9(1)
C(3A)−C(1A)	1.3984(15)	C(1A)−C(3A)−C(3)	112.73(9)
		C(3A)−C(1A)−P	108.49(7)

Table 4. Selected Distances (Å) and Angles (deg) for 13

P−C(2)	1.815(3)	C(2)−P−C(1A)	89.40(12)
P−C(1A)	1.821(2)	C(2)−P−C(8)	102.78(12)
P−C(8)	1.842(2)	C(1A)−P−C(8)	104.16(10)
C(2)−C(3)	1.326(4)	C(3)−C(2)−P	113.0(2)
C(3)−C(3A)	1.471(4)	C(2)−C(3)−C(3A)	113.9(2)
C(3A)−C(1A)	1.403(3)	C(1A)−C(3A)−C(3)	113.0(2)
		C(3A)−C(1A)−P	110.15(16)

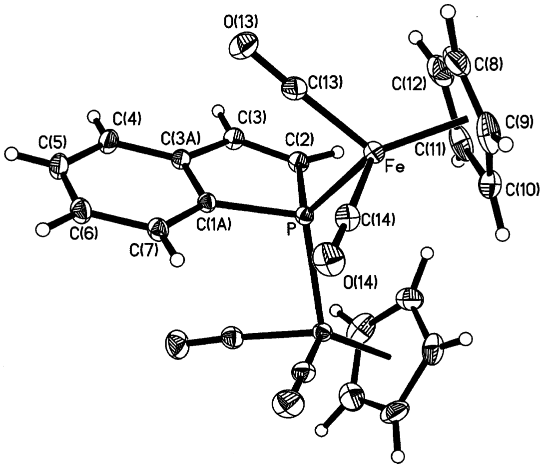

Figure 3. View of the cation of **16** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

Table 5. Selected Distances (Å) and Angles (deg) for 16

Fe−P	2.2690(4)	C(2)−P−Fe	109.15(3)
P−C(2)	1.798(2)	C(1A)−P−Fe	108.66(3)
P−C(1A)	1.813(2)	Fe#1−P−Fe	125.04(3)
C(2)−C(3)	1.338(3)	C(3)−C(2)−P	111.64(18)
C(3)−C(3A)	1.450(3)	C(2)−C(3)−C(3A)	114.6(2)
C(3A)−C(1A)	1.400(3)	C(1A)−C(3A)−C(3)	113.7(2)
		C(3A)−C(1A)−P	109.21(16)

planar and bond delocalization in the five-membered ring evident by the small deviation in inter atom distances, ranging from 1.405(4) Å (C(2)−C(3)) to 1.430(4) Å (C(3a)−C(1a)) for C−C bonds and 1.777(3) Å (P(1)−C(2)) to 1.796(3) Å (P(1)−C(1a)) for the P−C bonds.[35] The metal atom is coordinated to all five atoms in the heterocycle, but slightly displaced away from C(1a) and C(3a), resulting in a slipped η^5-complex with bond lengths ranging from 2.148(3) Å (Mn(1)−C(3)) and 2.153(3) Å (Mn(1)−C(2)) to 2.236(3) Å (Mn(1)−C(3A)) and 2.257(2) Å (Mn(1)−C(1A)). The Mn(1)−P(1) bond measures 2.3833(8) Å, and the distance between the centroid of the five-membered ring and the metal atom is 1.799 and 1.803 Å for the two independent molecules, respectively. There is no significant deviation in the Mn−CO bond lengths (av 1.796 Å), and the orientation of the $Mn(CO)_3$ tripod is analogous to that in substituted (η^5-indenyl)$Mn(CO)_3$ complexes[36−40] and (η^5-2-methylin-

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(35) A very small disorder in one of the independent molecules, interconverting the atom sites for P(2) and C(13), could not be modeled properly. The disorder is evident by the observation of three peaks in the Fourier difference map near C(13) and two peaks near P(2) and results in the elongation of all bonds involving C(13). Bond lengths for the disordered molecule have not been included in the discussion.

(36) Honan, N. B.; Atwood, J. L.; Bernal, I.; Hermann, W. A. *J. Organomet. Chem.* **1979**, *179*, 403.

(37) Tamm, M.; Bannenberg, T.; Baum, K.; Frohlich, R.; Steiner. T.; Meyer-Friedrichsen, T.; Heck, J. *Eur. J. Inorg. Chem.* **2000**, 1161.

(38) Qian, C.; Guo, J.; Sun, J.; Chen, J.; Zheng, P. *Inorg. Chem.* **1997**, *36*, 1286.

(39) Plenio, H.; Burth, D. Z. *Anorg. Allg. Chem.* **1996**, *622*, 225.

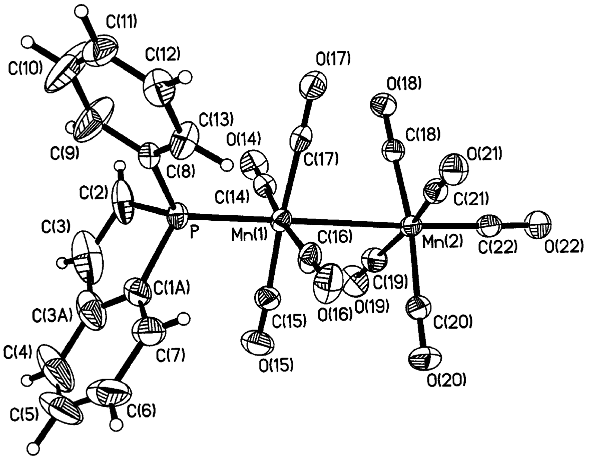

Figure 4. View of **18** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

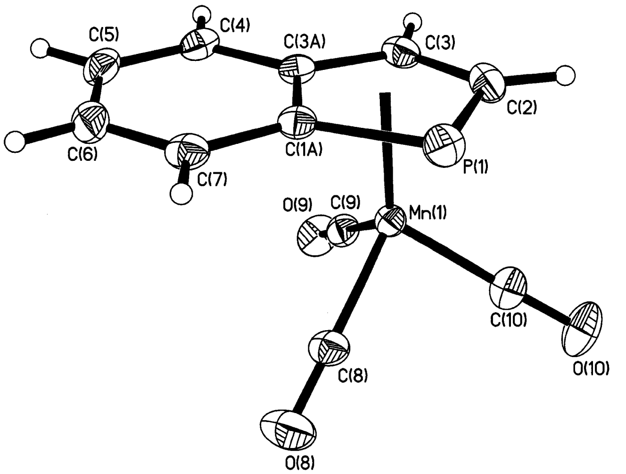

Figure 5. View of one of the independent molecules of **19** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

Table 6. Selected Distances (Å) and Angles (deg) for 18

P−C(2)	1.790(3)	C(2)−P−C(1A)	94.82(19)
P−C(1A)	1.805(3)	C(2)−P−C(8)	101.48(16)
P−C(8)	1.811(2)	C(1A)−P−C(8)	103.01(12)
C(2)−C(3)	1.415(8)	C(2)−P−Mn(1)	116.46(10)
C(3)−C(3A)	1.517(9)	C(1A)−P−Mn(1)	117.58(10)
C(3A)−C(1A)	1.378(6)	C(8)−P−Mn(1)	119.54(8)
P−Mn(1)	2.2326(7)	P−Mn(1)−Mn(2)	177.69(2)
Mn(1)−Mn(2)	2.8870(5)	C(3)−C(2)−P	104.7(4)
		C(2)−C(3)−C(3A)	118.7(4)
		C(1A)−C(3A)−C(3)	109.0(4)
		C(3A)−C(1A)−P	111.5(3)

dolyl)Mn(CO)$_3$, the only crystallographically characterized nitrogen analogue of **19**.[41] The crystal structure of unsubstituted (η^5-indenyl)Mn(CO)$_3$ is not known.

A thermal ellipsoid plot of **25** is presented in Figure 6, and selected bond distances and angles are summarized in Table 8. The eight carbon atoms of the heterocycle form a planar fragment. The phosphorus atom is displaced by 0.48 Å out of this plane, creating a folding angle of 22.6° with the C(1)−P−C(3) plane. The P−C bonds within the five-membered ring are similar to those in **11** and **13** (P−C(1) = 1.8183(18) Å, P−C(3) = 1.8149(19) Å).

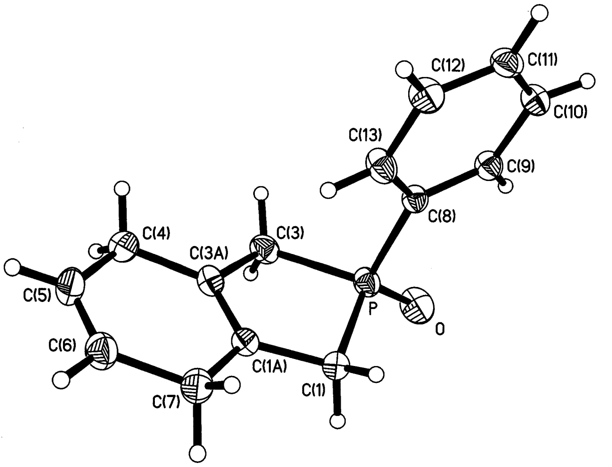

Figure 6. View of **25** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

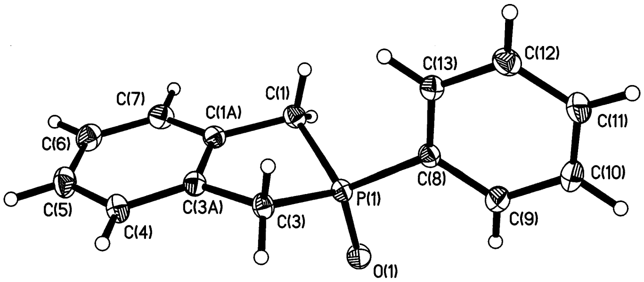

Figure 7. View of one of the independent molecules of **26** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

Table 7. Selected Distances (Å) and Angles (deg) for One of the Independent Molecules of 19

Mn(1)−C(3)	2.148(3)	C(2)−P(1)−C(1A)	88.68(14)
Mn(1)−C(2)	2.153(3)	C(3)−C(2)−P(1)	114.3(2)
Mn(1)−C(3A)	2.236(3)	C(2)−C(3)−C(3A)	112.2(3)
Mn(1)−C(1A)	2.257(2)	C(3)−C(3A)−C(1A)	112.2(2)
Mn(1)−P(1)	2.3833(8)	C(3A)−C(1A)−P(1)	112.6(2)
Mn(1)−C(10)	1.785(3)		
Mn(1)−C(9)	1.799(3)		
Mn(1)−C(8)	1.805(3)		
P(1)−C(2)	1.777(3)		
P(1)−C(1A)	1.796(3)		
C(2)−C(3)	1.405(4)		
C(3)−C(3A)	1.424(4)		
C(3A)−C(1A)	1.430(4)		

Table 8. Selected Distances (Å) and Angles (deg) for 25

P−O	1.4698(13)	O−P−C(8)	111.76(8)
P−C(8)	1.8067(16)	O−P−C(3)	118.81(9)
P−C(3)	1.8149(19)	C(8)−P−C(3)	106.45(8)
P−C(1)	1.8183(18)	O−P−C(1)	117.90(9)
C(1)−C(1A)	1.498(2)	C(8)−P−C(1)	105.36(8)
C(1A)−C(3A)	1.348(2)	C(3)−P−C(1)	94.53(8)
C(3)−C(3A)	1.504(2)	C(1A)−C(1)−P	104.20(11)
		C(3A)−C(1A)−C(1)	116.23(15)
		C(3A)−C(3)−P	104.12(12)
		C(1A)−C(3A)−C(3)	115.96(15)

A thermal ellipsoid plot of **26** is depicted in Figure 7, and selected bond distances and angles are presented in Table 9. The crystal lattice consists of two independent molecules per asymmetric unit, differing only in the folding angle of the five-membered ring. As with **25**, the eight carbon atoms of the heterocycle form a planar

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(40) Plenio, H.; Burth, D. *Organometallics* **1996**, *15*, 1151.

(41) Jeffreys; J. A. D.; Metters, C. J. *Chem. Soc., Dalton Trans.* **1997**, 1624.

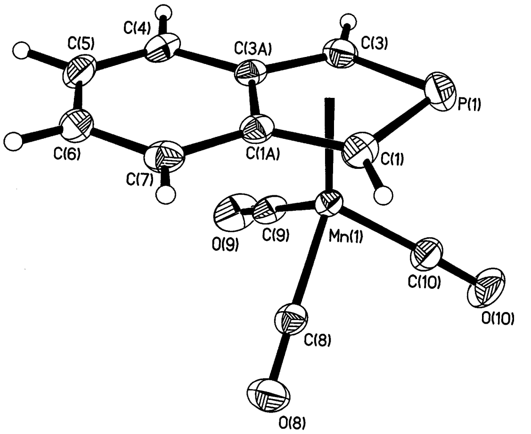

Figure 8. View of one of the independent molecules of **33** showing the atom-numbering scheme. Thermal ellipsoids are at the 30% probability level.

Table 9. Selected Distances (Å) and Angles (deg) for One of the Independent Molecules of 26

P(1)−O(1)	1.4852(10)	O(1)−P(1)−C(8)	111.07(6)
P(1)−C(8)	1.7980(13)	O(1)−P(1)−C(3)	115.00(6)
P(1)−C(3)	1.8083(13)	C(8)−P(1)−C(3)	110.00(6)
P(1)−C(1)	1.8147(14)	O(1)−P(1)−C(1)	113.82(6)
C(1)−C(1A)	1.5112(18)	C(8)−P(1)−C(1)	112.08(6)
C(1A)−C(3A)	1.3950(18)	C(3)−P(1)−C(1)	93.84(6)
C(3)−C(3A)	1.5046(17)	C(1A)−C(1)−P(1)	102.25(9)
		C(3A)−C(1A)−C(1)	114.47(11)
		C(3A)−C(3)−P(1)	102.59(8)
		C(1A)−C(3A)−C(3)	114.56(11)

Table 10. Selected Distances (Å) and Angles (deg) for One of the Independent Molecules of 33

Mn(1)−C(1)	2.1555(16)	C(1)−P(1)−C(3)	89.46(8)
Mn(1)−C(3)	2.1693(16)	C(1)−C(1A)−C(3A)	111.42(14)
Mn(1)−C(1A)	2.2214(14)	C(1A)−C(1)−P(1)	113.54(12)
Mn(1)−C(3A)	2.2255(14)	C(3A)−C(3)−P(1)	113.48(12)
Mn(1)−P(1)	2.3696(5)	C(3)−C(3A)−C(1A)	111.62(14)
Mn(1)−C(10)	1.7885(17)		
Mn(1)−C(8)	1.7983(16)		
Mn(1)−C(9)	1.8032(17)		
P(1)−C(1)	1.7583(19)		
P(1)−C(3)	1.7594(18)		
C(1A)−C(1)	1.426(2)		
C(1A)−C(3A)	1.430(2)		
C(3)−C(3A)	1.424(2)		

fragment. The displacement of the phosphorus atom is much more pronounced than in **25** (0.66 Å for P(1) and 0.61 Å for P(2)), creating a folding angle of 32.9° and 30.0° with the C(1)−P(1)−C(3) or C(11)−P(2)−C(13) plane, respectively. The P−C bonds within the heterocycle are similar to those in **11**, **13**, and **25**, ranging from 1.8083(13) Å (P(1)−C(3)) to 1.8147(14) Å (P(1)−C(1)).

A thermal ellipsoid plot of **33** is shown in Figure 8, and selected bond distances and angles are presented in Table 10. Complex **33** crystallizes with two independent molecules per asymmetric unit that have identical metric parameters within experimental error. The ligand is planar in each case, and a very high degree of bond delocalization is observed. The variation of bond length between the four carbon atoms of the five-membered ring is marginal, ranging from 1.424(2) Å (C(3)−C(3A)) to 1.430(2) Å (C(1A)−C(3A)) and are significantly less that those found for **19**. As with **19**, the metal is slightly displaced away from C(1A)/C(3A), and the metal−C distances consist of a pair of short bonds (Mn(1)−C(1) = 2.1555(16) Å, Mn(1)−C(3) = 2.1693(16) Å) and a pair of long bonds (Mn(1)−C(1A) = 2.2214(14) Å, Mn(1)−C(3A) = 2.2255(14) Å), but the effect is not as prominent as in **19**. The Mn−P distances (2.3696(5) and 2.3725(5) Å) as well as the distances between the centroids of the five-membered ring and the metal atoms (1.794 Å for both molecules) compare favorably to that in **19**. The orientation of the Mn(CO)$_3$ tripod and the Mn−CO distances are the same as in **19**. The similarities between **19** and **33** are further manifested by their respective unit cell parameters, which are virtually identical. The molecular geometry of **33** also compares favorably with that of its recently reported ionic triphenylphosphonio derivative.[34a]

Summary

A large-scale synthesis for 1-phenylphosphindole and its conversion to bis(1,1′-phosphindolyl) and the phosphindolide anion are reported. These compounds have been employed in the synthesis of [(μ_2-BP)Fe$_2$Cp$_2$(CO)$_4$]X (X = Br, I) and (μ_2-BP)$_2$Fe$_2$Cp$_2$(CO)$_2$, where the BP ligand forms σ-bonds, bridging two metal centers and (BP-Ph)Mn$_2$(CO)$_9$, in which the ligand acts as a phosphine. (BP-Ph)Mn$_2$(CO)$_9$ was reacted with organic and organometallic radicals to give the π-complex (η^5-BP)Mn(CO)$_3$. Attempts to isolate 2-phenyl-*iso*-phosphindole failed due to its high reactivity, resulting in spontaneous and irreversible polymerization. These problems were avoided through the synthesis of 2-phenyl-4,7-dihydro-*iso*-phosphindole, which was employed in the preparation of (η^5-iBP-H$_2$)Mn(CO)$_3$. Dehydrogenation of (η^5-iBP-H$_2$)Mn(CO)$_3$ yielded (η^5-iBP)Mn(CO)$_3$, the first metal complex of the hitherto unknown iBP ligand.

Experimental Section

General Considerations. All reactions were carried out under an inert atmosphere of argon using standard Schlenk techniques unless otherwise noted. Solvents were dried and distilled according to standard procedures[42] or directly obtained form a JC Meyer solvent purification system. Organic solvents were degassed using freeze−thaw techniques, and aqueous solutions were purged with argon prior to use. Melting points were measured in open glass capillaries using a Gallenkamp melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 spectrometer at 399.99 and 100.6 MHz, respectively, and referenced relative to the residual solvent signal. ^{31}P NMR spectra were obtained at 161.89 MHz and were recorded relative to external triphenylphosphine (δ = −6.0 ppm). Electron impact (EI) and fast atom bombardment (FAB)$^+$ MS were performed on a Kratos MS-50 mass spectrometer. Helium was used as the bombarding gas. Infrared spectra were obtained on a Bruker IFS 25 instrument using KBr disks. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without purification. Compounds **4**,[26] **10**,[24,25] **26**,[33] FeCp(CO)$_2$I,[43] and FeCp(CO)$_2$Br[44] were prepared according to literature procedures. Flash chromatography was carried out using Merck silica gel (330−400 mesh). Microanalyses were performed by Galbraith Laboratories in Knoxville, TN.

Preparation of 2-Trimethylsilyl-1-phenylphosphindole Oxide (11). *N*-Butyllithium (240 mL, 2.5 M in hexanes, 600 mmol) was added to a solution of **10** (55.6 g, 218 mmol) in ether (2000 mL) at 0 °C. The yellow solution was stirred at

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[42] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980.

[43] King, R. B.; Stone, G. *Inorg. Synth.* **1963**, *7*, 110.

[44] Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1956**, 3030.

room temperature for 2.5 h. A solution of $PhPCl_2$ (43 mL, 313 mmol) in ether (500 mL) was added dropwise at 0 °C over a period of 1 h. The orange suspension was stirred at room temperature for 20 h, followed by addition of ether (5000 mL) and saturated aqueous $NaHCO_3$ (500 mL) while the apparatus was open to the air. The mixture was stirred until all of the solids had dissolved and the layers were separated. The yellow organic phase was washed with saturated aqueous NaCl (500 mL), dried over Na_2SO_4, and filtered, and the solvent was evaporated under reduced pressure to give a wet yellow solid. Hexane (30 mL) was added, and the solid filtered under suction and washed with hexane (2 × 30 mL) to give **11** (51.9 g, 174 mmol, 80%) as a yellow solid. Mp: 135−136 °C. ^{1}H NMR (acetone-d_6): δ 7.86 (s, 1H); 7.70−7.39 (m, 9H); 0.09 (s, 9H). ^{13}C NMR (acetone-d_6): δ 152.9 (d, J_{P-C} 7 Hz); 144.3 (d, J_{P-C} 37 Hz); 142.5 (d, J_{P-C} 59 Hz); 137.0 (d, J_{P-C} 100 Hz); 133.8; 132.8; 132.5 (d, J_{P-C} 95 Hz); 131.6 (d, J_{P-C} 10 Hz); 130.5 (d, J_{P-C} 10 Hz); 129.7 (d, J_{P-C} 12 Hz); 129.2 (d, J_{P-C} 10 Hz); 125.7 (d, J_{P-C} 11 Hz); −0.8. ^{31}P{^{1}H} NMR (acetone-d_6): δ 45 ppm. MS (EI, *m/z* (%), assignment): 298 (42) $\{C_{17}H_{19}OPSi\}^+$ $\{C_8H_5(SiMe_3)P(O)Ph\}^+$; 282 (100) $\{C_{17}H_{19}PSi\}^+$ $\{C_8H_5(SiMe_3)P(Ph)\}^+$; 226 (40) $\{C_{14}H_{11}OP\}^+$ $\{(C_8H_6P)(O)(Ph)\}^+$; 221 (23) $\{C_{11}H_{14}OPSi\}^+$ $\{C_8H_5(SiMe_3)P(O)\}^+$; 210 (36) $\{C_{14}H_{11}P\}^+$ $\{(C_8H_6P)(Ph)\}^+$; 149 (40) $\{(C_8H_6P)(O)\}^+$; 133 (41) $\{C_8H_6P\}^+$; 77 (81) $\{C_6H_5\}^+$; 73 (51) $\{C_3H_9Si\}^+$.

Preparation of 1-Phenylphosphindole Oxide (12). TBAF (331 mL, 1.0 M in THF, 331 mmol) was added to a solution of **11** (51.9 g, 174 mmol) in THF (174 mL) and the dark brown solution heated to reflux for 4 h. The mixture was cooled to room temperature, followed by addition of ether (1750 mL) and saturated aqueous $NaHCO_3$ (300 mL), while the apparatus was open to the air. The mixture was stirred for 20 min, and the layers were separated. The yellow organic phase was washed with saturated aqueous NaCl (300 mL), dried over Na_2SO_4, and filtered, and the solvent was evaporated under reduced pressure to give **12** as a brown oil (19.7, 87 mmol, 50%). The crude product was used without further purification. ^{1}H NMR (acetone-d_6): δ 7.90−7.10 (m, 9H); 7.01 (dd, 3.1 Hz, J_{P-H} 16.2 Hz, 1H); 6.55 (dd, 3.5 Hz, J_{P-H} 10.5 Hz, 1H). ^{13}C NMR (acetone-d_6): δ 146.1 (d, J_{P-C} 12 Hz); 143.1 (d, J_{P-C} 31 Hz); 133.9 (d, J_{P-C} 2 Hz); 133.1 (d, J_{P-C} 3 Hz); 131.6 (d, J_{P-C} 10 Hz); 130.5 (d, J_{P-C} 10 Hz); 129.8 (d, J_{P-C} 12 Hz); 129.4 (d, J_{P-C} 10 Hz); 128.6; 127.7; 126.0 (d, J_{P-C} 10 Hz). ^{31}P {^{1}H} NMR (acetone-d_6): δ 37 ppm. MS (EI, *m/z* (%), assignment): 226 (67) $\{C_{14}H_{11}OP\}^+$ $\{(C_8H_6P)(O)(Ph)\}^+$; 210 (39) $\{C_{14}H_{11}P\}^+$ $\{(C_8H_6P)(Ph)\}^+$; 133 (30) $\{C_8H_6P\}^+$; 77 (51) $\{C_6H_5\}^+$.

Preparation of 1-Phenylphosphindole (13). Compound **13** was prepared using a modified literature procedure.[24−26] $SiHCl_3$ (17.6 mL, 174 mmol) was added to a solution of **12** (19.7 g, 87 mmol) in toluene (1750 mL), and the yellow solution was heated to reflux for 1.5 h. The mixture was cooled to 0 °C and hydrolyzed with 2 M NaOH (320 mL), and the layers were separated quickly while the apparatus was open to the air. The yellow organic phase was dried over Na_2SO_4 and filtered, and the solvent evaporated under reduced pressure to give a yellow-brown oil. The product was crystallized from methanol to give **13** (9.2 g, 44 mmol, 50%) as a yellow solid. Mp: 60−62 °C. ^{1}H NMR (acetone-d_6): δ 7.70 (dd, 4.3 Hz, J_{P-H} 11.8 Hz, 1H); 7.66 (d, 7.6 Hz, 1H); 7.48−7.25 (m, 8H); 7.01 (dd, 7.6 Hz, J_{P-H} 39.6 Hz, 1H). ^{13}C NMR (acetone-d_6): δ 145.6 (d, J_{P-C} 6 Hz); 143.8; 139.2; 134.3 (d, J_{P-C} 10 Hz); 133.2 (d, J_{P-C} 15 Hz); 132.6 (d, J_{P-C} 19 Hz); 129.3; 128.9 (d, J_{P-C} 20 Hz); 128.7 (d, J_{P-C} 8 Hz); 128.1; 126.1 (d, J_{P-C} 7 Hz); 124.2. ^{31}P{^{1}H} NMR (acetone-d_6): δ 0 ppm. MS (EI, *m/z* (%), assignment): 210 (20) $\{C_{14}H_{11}P\}^+$ $\{(C_8H_6P)(Ph)\}^+$; 133 (68) $\{C_8H_6P\}^+$; 77 (72) $\{C_6H_5\}^+$.

Preparation of Bis(1,1′-phosphindolyl) (14). A solution of **4** (10 mL, 0.2 M in THF, 2 mmol) was cooled to 0 °C, and $AlCl_3$ (0.089 g, 0.67 mmol) was added. The mixture was stirred at 0 °C for 30 min, and I_2 (0.305 g, 1.2 mmol) was added to give a light yellow-brown suspension. The solvent was removed under reduced pressure, and the oil was dissolved in toluene (20 mL). The crude product solution can be used without further purification. Isolation of **14** was accomplished by filtration of the solution through a sintered glass funnel and removal of the solvent under reduced pressure to give **14** as a yellow oil. An inseparable mixture of diastereomers (meso and racemic) was obtained.[32b] ^{1}H NMR ($CDCl_3$): δ 7.80−6.15 (m). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −19, −24 ppm. MS (EI, *m/z* (%), assignment): 266 (36) $\{C_{16}H_{12}P_2\}^+$ $\{(C_8H_6P)_2\}^+$; 133 (100) $\{C_8H_6P\}^+$.

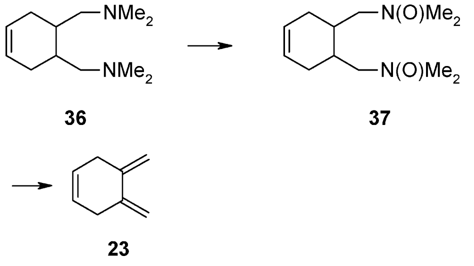
Preparation of [(μ_2-Phosphindolyl)$Fe_2Cp_2(CO)_4$]I (15). A solution of **4** (10 mL, 0.2 M in THF, 2 mmol) was cooled to 0 °C, and $AlCl_3$ (0.089 g, 0.67 mmol) was added. After stirring at 0 °C for 30 min, $FeCp(CO)_2I$ (1.215 g, 4 mmol) was added, producing a red-brown solution with a solid precipitate. The solid was isolated by filtration, washed with hexane, and dried under reduced pressure to give 0.60 g (0.98 mmol, 49%) of **15** as an orange powder. Anal. Found: C, 42.54; H, 3.26. Calcd for $C_{22}H_{16}PFe_2O_4Br$: C, 43.04; H, 2.63. Mp: 179 °C (dec). ^{1}H NMR (acetone-d_6): δ 7.92 (dd, 7.2 Hz, J_{P-H} 7.2 Hz, 1H); 7.79 (d, 7.2 Hz, 1H); 7.64 (dd, 7.6 Hz, J_{P-H} 40.0 Hz, 1H); 7.54−7.45 (m, 2H); 7.33 (dd, 7.4 Hz, J_{P-H} 27.4 Hz, 1H); 5.46 (s, 10H). ^{13}C NMR (acetone-d_6): δ 212.5 (d, J_{P-C} 19 Hz, *CO*); 211.8 (d, J_{P-C} 19 Hz, *CO*); 153.3 (d, J_{P-C} 28 Hz); 145.6 (d, J_{P-C} 20 Hz); 141.3 (d, J_{P-C} 13 Hz); 133.4; 130.7; 128.9 (d, J_{P-C} 14 Hz); 128.3 (d, J_{P-C} 10 Hz); 126.5 (d, J_{P-C} 6 Hz); 88.9. ^{31}P{^{1}H} NMR (acetone-d_6): δ 37 ppm. IR: ν_{CO} 2044 (vs); 2032 (vs); 1999 (vs); 1978 (s). MS (EI, *m/z* (%), assignment): 375 (30) $\{C_{18}H_{16}PFe_2\}^+$ $\{(C_8H_6P)Fe_2Cp_2\}^+$; 310 (76) $\{C_{13}H_{11}PFe_2\}^+$ $\{(C_8H_6P)Fe_2Cp\}^+$; 254 (100) $\{C_{13}H_{11}PFe\}^+$ $\{(C_8H_6P)FeCp\}^+$; 186 (87) $\{C_{10}H_{10}Fe\}^+$ $\{FeCp_2\}^+$; 133 (88) $\{C_8H_6P\}^+$; 120 (25) $\{C_5H_5Fe\}^+$ $\{FeCp\}^+$; 56 (88) $\{Fe\}^+$.

Preparation of [(μ_2-Phosphindolyl)$Fe_2Cp_2(CO)_4$]Br (16). In analogy with the preparation of **15**, reaction of **4** (10 mL, 0.1 M in THF, 1 mmol) and $FeCp(CO)_2Br$ (0.514 g, 2 mmol) gave 0.42 g (0.74 mmol, 74%) of **16** as an orange powder. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and MS were identical to that of **15**.

Preparation of (μ_2-Phosphindolyl)$_2Fe_2Cp_2(CO)_2$ (17). To a solution of **14** in toluene, as obtained above, was added $Fe_2Cp_2(CO)_4$ (0.354 g, 1 mmol), and the mixture was heated to reflux for 1 h to give a dark red-brown suspension. The solvent was evaporated under reduced pressure and the red-brown solid purified by flash chromatography using toluene to give **17** (0.125 g, 222 mmol, 22%) as a green solid. Four inseparable isomers were obtained. Their ^{1}H NMR and ^{13}C NMR data was complicated due to multiple peak overlaps and are reported for the Cp region only. Mp: 195 °C (dec). ^{1}H NMR (C_6D_6): δ 3.82 (s); 3.73 (s); 3.66 (s); 3.57 (s); 3.52 (s). ^{13}C NMR (C_6D_6): δ 81.1, 80.6, 80.3, 80.1, 79.9. ^{31}P{^{1}H} NMR (C_6D_6): δ −26 (d, J_{P-P} 248.2 Hz); −31; −38 (d, J_{P-P} 248.2 Hz); −40; −41. IR: ν_{CO} 2044 (vs); 2032 (vs); 1999 (vs); 1978 (s). MS (EI, *m/z* (%), assignment): 564 (71) $\{C_{28}H_{22}P_2Fe_2O_2\}^+$ $\{(C_8H_6P)_2Fe_2Cp_2(CO)_2\}^+$; 536 (69) $\{C_{27}H_{22}P_2Fe_2O\}^+$ $\{(C_8H_6P)_2Fe_2Cp_2(CO)\}^+$; 508 (82) $\{C_{26}H_{22}P_2Fe_2\}^+$ $\{(C_8H_6P)_2Fe_2Cp_2\}^+$; 375 (62) $\{C_{18}H_{16}PFe_2\}^+$ $\{(C_8H_6P)Fe_2Cp_2\}^+$; 310 (77) $\{C_{13}H_{11}PFe_2\}^+$ $\{(C_8H_6P)Fe_2Cp\}^+$; 254 (100) $\{C_{13}H_{11}PFe\}^+$ $\{(C_8H_6P)FeCp\}^+$; 186 (83) $\{C_{10}H_{10}Fe\}^+$ $\{FeCp_2\}^+$; 133 (81) $\{C_8H_6P\}^+$; 121 (89) $\{C_5H_5Fe\}^+$ $\{FeCp\}^+$; 56 (79) $\{Fe\}^+$.

Preparation of 1-Phenylphosphindole Dimanganese Nonacarbonyl (18). A solution of **13** (1.05 g, 5 mmol) in xylenes (20 mL) was added to a solution of $Mn_2(CO)_{10}$ (1.95 g, 5 mmol) in xylenes (30 mL). The resultant orange solution was heated to reflux for 12 min to give an orange suspension. The mixture was cooled to room temperature and filtered through a sintered glass funnel, producing a red-orange solution. The solvent was evaporated under reduced pressure and the red-orange oil purified by flash chromatography using a 4:1 mixture of hexanes/ether to give **18** (1.45 g, 2.5 mmol, 51%) as a red-orange oil. Anal. Found: C, 48.05; H, 1.94. Calcd for $C_{21}H_{11}PMn_2O_9$: C, 48.28; H, 1.94. Mp: 140 °C. ^{1}H NMR (acetone-d_6): δ 8.18 (ddd, 4.0 Hz, 7.0 Hz, J_{P-H} 12.6 Hz, 1H);

Scheme 7



7.80 (dd, 2.0 Hz, J_{P-H} 11.6 Hz, 1H); 7.78 (dd, 1.2 Hz, J_{P-H} 11.6 Hz, 1H); 7.75−7.71 (m, 1H); 7.64−7.59 (m, 3H); 7.48 (dd, 8.0 Hz, J_{P-H} 65 Hz, 1H); 7.51−7.48 (m, 3H). ^{13}C NMR (acetone-d_6): δ 223.8 (br, *C*O); 143.5 (d, J_{P-C} 17 Hz); 141.1 (d, J_{P-C} 2 Hz); 141.2 (d, J_{P-C} 50 Hz); 134.5 (d, J_{P-C} 42 Hz); 133.3 (d, J_{P-C} 43 Hz); 132.2 (d, J_{P-C} 2 Hz); 131.5 (d, J_{P-C} 2 Hz); 131.3 (d, J_{P-C} 10 Hz); 130.5 (d, J_{P-C} 13 Hz); 130.2 (d, J_{P-C} 10 Hz); 129.5 (d, J_{P-C} 10 Hz); 126.5 (d, J_{P-C} 6 Hz). ^{31}P{^{1}H} NMR (acetone-d_6): δ 73 ppm. IR: ν_{CO} 1922 (s); 1944 (s); 1968 (s); 1992 (s); 2018 (s); 2090 (m). MS (EI, *m*/*z* (%), assignment): 460 (5) $\{C_{19}H_{11}PMn_2O_5\}^+$ $\{(C_8H_6P)(Ph)Mn_2(CO)_5\}^+$; 432 (23) $\{C_{18}H_{11}PMn_2O_4\}^+$ $\{(C_8H_6P)(Ph)Mn_2(CO)_4\}^+$; 377 (20) $\{C_{18}H_{11}PMnO_4\}^+$ $\{(C_8H_6P)(Ph)Mn(CO)_4\}^+$; 349 (18) $\{C_{17}H_{11}PMnO_3\}^+$ $\{(C_8H_6P)(Ph)Mn(CO)_3\}^+$; 321 (15) $\{C_{16}H_{11}PMnO_2\}^+$ $\{(C_8H_6P)(Ph)Mn(CO)_2\}^+$; 293 (10) $\{C_{15}H_{11}PMnO\}^+$ $\{(C_8H_6P)(Ph)Mn(CO)\}^+$; 266 (22) $\{C_{16}H_{12}P_2\}^+$ $\{(C_8H_6P)_2\}^+$; 265 (25) $\{C_{14}H_{11}PMn\}^+$ $\{(C_8H_6P)(Ph)Mn\}^+$; 244 (23) $\{C_{10}H_6PMnO_2\}^+$ $\{(C_8H_6P)Mn(CO)_2\}^+$; 216 (30) $\{C_9H_6PMnO\}^+$ $\{(C_8H_6P)Mn(CO)\}^+$; 210 (54) $\{C_{14}H_{11}P\}^+$ $\{(C_8H_6P)(Ph)\}^+$; 188 (30) $\{(C_8H_6P)Mn\}^+$; 149 (100) $\{(C_8H_6P)(O)\}^+$; 133 (22) $\{C_8H_6P\}^+$; 77 (26) $\{C_6H_5\}^+$.

Preparation of η^5-Phosphindole Manganese Tricarbonyl (19). Compound **19** was prepared using a modified literature procedure.[26] A solution of **13** (1.05 g, 5 mmol) in xylenes (20 mL) was added to a solution of $Mn_2(CO)_{10}$ (1.95 g, 5 mmol) in xylenes (30 mL), and the resultant orange solution was heated to reflux for 3 h to give a dark red-brown suspension. The mixture was cooled to room temperature and filtered through a sintered glass funnel, producing a dark red solution. The solvent was evaporated under reduced pressure and the red oil purified by flash chromatography using hexanes to give **19** (0.230 g, 0.85 mmol, 17%) as a red solid. ^{31}P{^{1}H} NMR (acetone-d_6): δ −53 ppm. ^{1}H NMR, MS, and IR matched the reported literature data.[26]

Preparation of η^5-Phosphindole Manganese Tricarbonyl (19) via 18. Procedure A: A solution of **18** (0.1 g, 0.175 mmol) and $Mn_2(CO)_{10}$ (0.068 g, 0.175 mmol) in xylenes (7 mL) was heated to reflux for 2 h to give **19**, the only product containing phosphorus as determined by in situ ^{31}P NMR. Procedure B: A solution of **18** (0.075 g, 0.138 mmol) and TEMPO (0.022 g, 0.138 mmol) in xylenes (5.5 mL) was heated to reflux for 2 h to give **19**, the only product containing phosphorus as determined by in situ ^{31}P NMR.

Preparation of 4,5-Dimethylenecyclohexene (23). 23 was prepared using a modified literature procedure (see Scheme 7).[33] ***Caution*:** Pyrolysis of **37** can lead to explosions, and for safety reasons the scale was decreased and the synthesis carried out as follows. A solution of **36** (23.03 g, 117 mmol) in methanol (49.2 mL) was cooled to 0 °C, and H_2O_2 (32.8 mL, 30% solution in water, 289 mmol) was added, followed by a second portion (32.8 mL, 30% solution in water, 289 mmol) 3 h later. The solution was stirred for 36 h at room temperature, after which the pH was neutral as indicated by pH paper. Excess H_2O_2 was destroyed by stirring the reaction mixture with Pt/C (30 mg), until the evolution of oxygen ceased (48 h). The solid precipitate was removed by filtration and the filtrate concentrated under reduced pressure to give **37** (7 g, 31 mmol, 26%) as a clear highly viscous pale yellow oil. The crude material and hydroquinone (0.020 g) were added to a pyrolysis apparatus, consisting of a 100 mL reaction flask, short path distillation head, 100 mL receiving flask, and 500 mL vacuum ballast. The pressure was adjusted to ~100 mmHg using a partially opened valve connecting a water aspirator and a three-way valve, which was connected to a Hg manometer and the vacuum adapter of the pyrolysis apparatus. The reaction flask was heated to ~100−120 °C in a sand bath, and the receiving flask was cooled in an acetone/LN2 bath. At the onset of pyrolysis, the highly viscous mixture released large quantities of gases, followed by a rapid decrease in viscosity. After completion of the reaction, water (6.7 mL) was added to the pyrolysate and the two layers were separated. The organic layer was washed with water (2 × 2.2 mL), cold 5% HCl (2.2 mL), saturated $NaHCO_3$ (2.2 mL), and saturated NaCl (2.2 mL). The crude product was dried over 4 Å molecular sieves for 20 min and decanted to give **23** (0.312 g, 2.94 mmol, 10%) as a colorless liquid, used immediately in the preparation of **24**.

Characterization of 37. ^{1}H NMR ($CDCl_3$): δ 5.72 (s, 2H); 3.68 (d, *J* 12 Hz, 2H); 3.28 (s, 6H); 3.18 (s, 6H); 3.06 (d, *J* 12 Hz, 2H); 2.90 (s, 2H); 2.52 (d, *J* 18 Hz, 2H); 1.94 (d, *J* 18 Hz, 2H). ^{13}C NMR ($CDC1_3$): δ 126.3 (s); 72.6 (s); 60.4 (s); 58.9 (s); 31.3 (s); 30.9 (s). MS (EI, *m*/*z* (%) assignment): 228 (26) $\{C_{12}H_{24}N_20_2\}^+$.

Preparation of 2-Phenyl-1,3,4,7-tetrahydro-*iso*-phosphindolenium Chloride (24). Compound **24** was prepared according to a modified literature procedure.[33] Under exclusion of light, $PhPCl_2$ (0.44 mL, 327 mmol) was added to a mixture of freshly prepared **23** (0.312 g, 2.94 mmol) and BHT (0.004 g) in ligroin (1.6 mL). The mixture was allowed to stand at room temperature for 5 days, producing a pale yellow solid precipitate. The solid was isolated by filtration and washed with hexane (3 × 0.5 mL) to give **24** (0.674 g, 2.38 mmol, 81%) as a pale yellow fine solid, used immediately in the preparation of **25** and **31**. ^{1}H NMR (CD_2Cl_2): δ 8.08 (dd, *J* 7.2 Hz, J_{P-H} 17.1 Hz, 2H); 7.60−7.72 (m, 3H); 5.84 (s, 2H); 4.05 (d, J_{P-H} 8.7 Hz, 4H); 2.96 (s, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.7.

Preparation of 2-Phenyl-1,3,4,7-tetrahydro-*iso*-phosphindole 2-Oxide (25). Compound **25** was prepared using a modified literature procedure.[33] **24** (0.674 g, 2.38 mmol) was added to a saturated $NaHCO_3$ solution (2.14 mL) at 0 °C, forming an insoluble oil. The resulting mixture was extracted with $CHCl_3$ (6 × 1.1 mL), and the organic phases were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give **25** (0.262 g, 1.14 mmol, 48%) as a pale yellow solid. The ^{1}H, ^{13}C, and ^{31}P NMR matched the reported literature data.[33]

Preparation of 2-Phenyl-*iso*-phosphindoline (27). To a solution of **26** (0.347 g, 1.52 mmol) in toluene (31 mL) was added $HSiCl_3$ (0.31 mL, 3.04 mmol) and the resulting clear solution heated to reflux for 1.5 h. The mixture was cooled to room temperature and quenched with 2 M NaOH (5.6 mL). The organic layer was separated, washed with a saturated Na_2CO_3 solution (2.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give **27** (0.297 g, 1.40 mmol, 92%) as a colorless oil. ^{1}H NMR (C_6D_6): δ 7.31 (s, 2H); 6.97 (m, 7H); 3.19 (m, 2H); 2.96 (d, J_{P-H} 17.2 Hz, 2H). ^{13}C NMR (C_6D_6): δ 142.1 (s); 141.2 (s); 136.6 (d, J_{P-H} 4.6 Hz); 131.66 (s); 128.6 (d, J_{P-H} 9.6 Hz); 127.0 (s); 126.65 (s); 32.7 (d, 495 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −14.0. MS (EI, *m*/*z* (%) assignment): 212 (76) $\{C_{14}H_{13}P\}^+$ $\{C_8H_8PPh\}^+$; 181 (19) $\{C_{14}H_{13}\}^+$ $\{C_8H_8Ph\}^+$; 135 (39) $\{C_8H_8P\}^+$; 104 (36) $\{C_8H_8\}^+$; 77 (23) $\{C_6H_5\}^+$.

Preparation of 2-Bromo-2-phenyl-*iso*-phosphindolenium Bromide (28). To a solution of **27** (0.078 g, 0.368 mmol) in CH_2Cl_2 (2.0 mL) was added Br_2 (6.75 mL, 0.109 M in CH_2Cl_2, 0.735 mmol) to give a dark orange solution. The mixture was concentrated under reduced pressure to give an orange oil, which was dissolved in CH_2Cl_2 (2.0 mL) and added slowly to hexane (30 mL) to give an orange solid precipitate. The pale orange supernatant was decanted and the solid dried under high vacuum for 5 min to give **28** (0.107 g, 0.288 mmol, 78%)

as an orange solid. ^1H NMR (CD_2Cl_2): δ 7.75 (m, 3H); 7.58 (m, 2H); 7.37 (m, 4H); 3.72 (m, 4H). ^{13}C NMR (CD_2Cl_2): δ 134.6 (s); 133.2 (d, J_{P-C} 9.65 Hz); 130.5 (d, J_{P-C} 10.46 Hz); 129.8 (d, J_{P-C} 12.77 Hz); 129.1 (s); 127.8 (d, J_{P-C} 15.99 Hz); 125.0 (d, J_{P-C} 79.38 Hz); 34.2 (d, J_{P-C} 67.27 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 74.4. IR: 3054 (w); 2958 (m); 2900 (w); 1264 (s); 1180 (m); 1086 (vs); 1026 (s); 920 (m); 802 (vs); 742 (s); 694 (m) cm^{-1}.

Dehydrobromination of 2-Bromo-2-phenyl-*iso*-phosphindolenium Bromide (28). To a solution of **28** (0.020 g, 0.054 mmol) in CH_2Cl_2 (5 mL) was added NEt_3 (0.04 mL, 0.288 mmol) dropwise. The orange solution slowly changed color to pale brown, and a pale brown solid precipitate was formed. The solid was isolated by filtration and found to be insoluble in all organic solvents. The mother liquor gave no signal in the ^{31}P NMR spectrum. The solvent was evaporated under reduced pressure and the solid identified as $HNEt_3Br$. The ^1H NMR matched the reported literature data. Anal. Found: C, 39.00; H, 7.79. Anal. Calcd for $C_6H_{16}NBr$: C, 39.57; H, 7.69.

Preparation of 2-Phenyl-4,7-dihydro-*iso*-phosphindole (31). To a colorless solution of **24** (0.169 g, 0.59 mmol) in CH_2Cl_2 (5 mL) was added NEt_3 (0.18 mL, 1.27 mmol), resulting in immediate formation of a white vapor and a yellow solution. HCl (3 M, 0.13 mL) was added, the layers were separated, and the yellow organic phase was washed with H_2O until the pH of the aqueous phase was neutral (3 × 0.5 mL). The pale yellow organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a colorless oil. Hexane (0.5 mL) was added, resulting in a colorless solid and a colorless solution. The solution was filtered and concentrated under reduced pressure to give **31** (0.0567 g, 0.267 mmol, 45%) as a colorless oil. ^1H NMR (CD_2Cl_2): δ 7.41 (m, 2H); 7.33 (m, 3H); 6.61 (d, J $_{PH}$ 38.1 Hz, 2H); 5.93 (s, 2H); 3.34 (d, J_{P-H} 3.3 Hz, 4H). ^{13}C NMR (CD_2Cl_2): δ 146.7 (d, J_{P-C} 8.22 Hz); 133.3 (d, J_{P-C} 18.09 Hz); 131.9 (d, J_{P-C} 10.93 Hz); 129.2 (d, J_{P-C} 1.66 Hz); 128.7 (d, J_{P-C} 8.22 Hz); 128.2 (d, J_{P-C} 1.66 Hz); 124.5 (s); 28.7 (d, J_{P-C} 3.84 Hz). ^{31}P NMR (CH_2Cl_2): δ 4.2 (t, J_{P-H} 38.1 Hz). IR: 660 (m), 692 (s), 724 (m), 744 (s), 784 (s), 812 (s), 916 (w), 936 (w), 964 (m), 996 (w), 1096 (m), 1116 (w), 1184 (m), 1228(m), 1264 (w), 1304 (w), 1356 (s), 1420 (s), 1436 (s), 1480 (m), 1572 (w), 1584 (w), 1656 (w), 2812 (m), 2872 (w), 3000 (w), 3028 (m), 3048 (w), 3064 (w) cm $^{-1}$. MS (EI, *m*/*z* (%), assignment): 212 (100) $\{C_{14}H_{13}P\}^+$ $\{(C_8H_8PPh\}^+$; 135 (63) $\{C_8H_8P\}^+$. EI HRMS (*m*/*z*): $\{C_{14}H_{13}P\}^+$ calcd 212.07549, found 212.07475.

Preparation of (η^5-4,7-Dihydro-*iso*-phosphindolyl) Manganese Tricarbonyl (32) and 2-Phenyl-4,7-Dihydro-*iso*-phosphindole Dimanganese Nonacarbonyl (34). A solution of **31** (0.8 g, 3.77 mmol) in xylenes (16 mL) was added to $Mn_2(CO)_{10}$ (0.735 g, 1.88 mmol) in xylenes (16 mL) and the resulting yellow mixture heated to reflux for 1 h. The reaction mixture, consisting of a red solution and a dark solid, was cooled to room temperature and the solvent removed under reduced pressure to give a red oil with a dark solid. The mixture was separated by flash chromatography using a 10:1 mixture of hexane/ether to give **32** (0.163 g, 0.595 mmol, 16%) as an orange oil and trace amounts of **34** as an orange oil.

Characterization of 32. ^1H NMR (CD_2Cl_2): δ 5.96 (s, 2H); 4.54 (d, J_{P-H} 35.6 Hz, 2H); 3.31 (d, J 16.0 Hz, 2H); 3.11 (d, J 16.0 Hz,2H). ^{13}C NMR (CD_2Cl_2): δ 223.7 (s, br); 123.1 (s); 112.1 (d, J_{P-C} 7.24 Hz); 92.2 (d, J_{P-C} 63.4 Hz); 26.6 (s). ^{31}P NMR (CD_2Cl_2): δ −35.3 (t, J_{P-H} 35.1 Hz). IR: ν_{CO} 2016 (s), 1930 (s, br) cm^{-1}. MS (EI, *m*/*z* (%), assignment): 274 (5) $\{C_{11}H_8PO_3Mn\}^+$ $\{(C_8H_8P)Mn(CO)_3\}^+$; 218 (10) $\{C_9H_8POMn\}^+$ $\{(C_8H_8P)Mn(CO)\}^+$; 190 (30) $\{C_8H_8PMn\}^+$ $\{C_8H_8PMn\}^+$. HRMS (EI, *m*/*z*): $\{C_{11}H_8PO_3Mn\}^+$ calcd 273.95917, found 273.95932.

Characterization of 34. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 81.1. IR: ν_{CO} 2088 (s); 2048 (m), 2012 (s); 1980 (br, s), 1932 (m); 1930 (m) cm^{-1}. MS (EI, *m*/*z* (%), assignment): 574 (1) $\{C_{23}H_{13}PO_9Mn_2\}^+$ $\{(C_8H_8PPh)Mn_2(CO)_9\}^+$; 462 (5) $\{C_{19}H_{13}PO_5Mn_2\}^+$ $\{(C_8H_8PPh)Mn_2(CO)_5\}^+$; 434 (5 $\{C_{18}H_{13}PO_4Mn_2\}^+$ $\{(C_8H_8PPh)Mn_2(CO)_4\}^+$; 406 (2) $\{C_{17}H_{13}PO_3Mn_2\}^+$ $\{(C_8H_8PPh)Mn_2(CO)_3\}^+$; 379 (25) $\{C_{18}H_{13}PO_4Mn\}^+$ $\{(C_8H_8PPh)Mn(CO)_4\}^+$; 351 (5) $\{C_{17}H_{13}PO_3Mn\}^+$ $\{(C_8H_8PPh)Mn(CO)_3\}^+$; 323 (4) $\{C_{16}H_{13}PO_2Mn\}^+$ $\{(C_8H_8PPh)Mn(CO)_2\}^+$; 295 (2) $\{C_{15}H_{13}POMn\}^+$ $\{(C_8H_8PPh)Mn(CO)\}^+$; 267 (100) $\{C_{14}H_{13}PMn\}^+$ $\{(C_8H_8PPh)Mn\}^+$; 212 (38) $\{C_{14}H_{13}P\}^+$ $\{C_8H_8PPh\}^+$. HRMS (EI, *m*/*z*): $\{C_{23}H_{13}PO_9Mn_2\}^+$ calcd 573.90582, found 573.90788.

Preparation of (η^5-*iso*-Phosphindolyl) Manganese Tricarbonyl (33). An orange solution of **32** (0.163 g, 0.595 mmol) in benzene (15.5 mL) was added to DDQ (0.155 g, 0.681 mmol). The resulting orange mixture was heated to reflux overnight, producing a dark solid precipitate. The solid was filtered and washed with benzene (3 × 2 mL). The combined organic phases were concentrated under reduced pressure to yield a red oil. Hexane (3 × 2 mL) was added, and the resulting brown solid was removed by filtration to give a yellow solution. The solution was concentrated under reduced pressure to give a yellow oil. The oil was purified by sublimation (0.140 mmHg, 25 °C) onto a coldfinger (12 °C) to give **33** (0.051 g, 0.188 mmol, 32%) as a yellow solid. ^1H NMR (CD_2Cl_2): δ 7.50 (dd, J 2.95 Hz, J_{P-H} 6.71 Hz, 2H); 7.27 (dd, J 2.95 Hz, J_{P-H} 6.71 Hz 2H); 5.19 (d, J_{P-H} 35.2 Hz, 2H). ^{13}C NMR (CD_2Cl_2): δ 223.1 (s, br); 127.1 (s); 126.0 (s); 112.8 (d, J_{P-C} 7.24 Hz); 86.4 (d, J_{P-C} 64.2 Hz). ^{31}P (CH_2Cl_2): δ −1.5 (t, J_{P-H} 34.3 Hz). IR: ν_{CO} 2019 (s), 1939 (s, br) cm^{-1}. MS (EI, *m*/*z* (%), assignment): 272 (26) $\{C_{11}H_6PO_3Mn\}^+$ $\{(C_8H_6P)Mn(CO)_3\}^+$; 216 (44) $\{C_9H_6POMn\}^+$ $\{(C_8H_6P)Mn(CO)\}^+$; 188 (100) $\{C_8H_6PMn\}^+$ $\{C_8H_6PMn\}^+$. EI HRMS (*m*/*z*): $\{C_{11}H_6PO_3Mn\}^+$ calcd 271.94351, found 271.94352.

X-ray Diffraction Experiments. Crystals suitable for diffraction studies were grown by solvent evaporation using CH_2Cl_2 (**25**, **26**) or hexane (**18**) at 25 °C, by solvent diffusion using acetone/pentane (**15**) at −25 °C, or by sublimation at 0.140 mmHg at 25 °C onto a coldfinger at 12 °C (**33**, **19**). Single crystals were coated with Paratone-N oil, mounted using a glass fiber, and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ϖ and θ scans with a scan width of 0.3° and 30 s (**26**, **25**, **13**, **11**), 20 s (**15**), or 10 s (**33**, **18**) exposure times. The detector distance was 6 cm (**25**), 5 cm (**26**, **33**), or 4 cm (**18**, **15**, **13**, **11**). The data were reduced (SAINT)[45] and corrected for absorption (SADABS).[46] The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL).[47] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in Fourier difference maps and refined isotropically.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, bond distances, bond angles, and isotropic and anisotropic displacement parameters. ^{31}P, ^1H, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) *SAINT* 6.02; Bruker AXS, Inc.: Madison, WI, 1997−1999.

(46) Sheldrick, G. *SADABS*; Bruker AXS, Inc.: Madison, WI, 1999.

(47) Sheldrick, G. *SHELXTL* 5.1; Bruker AXS, Inc.: Madison, WI, 1997.