are typical of 5-exo adducts and the respective coupling constants derived from decoupling experiments and computer-simulated spectra confirm the exo configuration in all cases.

In contrast, the cyclopentadienyl complex I undergoes carbonyl substitution to form initially the dicarbonyl derivative $C_5H_5Fe(CO)_2S_2CNR_2$, in which the dithiocarbamate ligand is monodentate (Table I). The infrared spectra (Table I) show the presence of two bands in the 1000 cm^{-1} region confirming monodentate bonding. However, on standing in dichloromethane solution, $C_5H_5Fe(CO)_2S_2CNEt_2$ undergoes further carbonyl substitution to form $C_5H_5Fe(CO)S_2CNEt_2$ (Table I), where there is only one carbonyl stretching mode and only one CS stretching mode in the 1000 cm^{-1} region confirming that the dithiocarbamate ligand is bidentate.

The successive reactions of the dithiocarbamate anion with $[C_5H_5Fe(CO)_3]^+$ to form first $C_5H_5Fe(CO)_2S_2CNR_2$ followed by $C_5H_5Fe(CO)S_2CNR_2$ contrasts with the behavior of $C_5H_5Fe(CO)_2Cl$ that forms $C_5H_5Fe(CO)_2S_2CNR$[21] and of $[C_5H_5Fe(CO)_2]_2$ that forms $C_5H_5Fe(CO)S_2CNR_2$ directly with no evidence for intermediate formation of $C_5H_5Fe(CO)_2S_2CNR_2$.[22]

Registry No. 5-*exo*-$C_7H_9NCSFe(CO)_3$, 83951-02-4; 5-*exo*-$C_7H_9SCNFe(CO)_3$, 83951-03-5; 5-*exo*-$C_7H_9NCSeFe(CO)_3$, 90064-79-2; 5-*exo*-$C_7H_9SeCNFe(CO)_3$, 90064-80-5; 5-*exo*-$C_7H_9NO_2Fe(CO)_3$, 90064-81-6; 5-*exo*-$C_7H_9N_3Fe(CO)_3$, 90130-02-2; 5-*exo*-$C_7H_9NCOFe(CO)_3$, 90064-82-7; 5-*exo*-$C_7H_9IFe(CO)_3$, 90064-83-8; 5-*exo*-$C_7H_9S_2CNMe_2Fe(CO)_3$, 90064-84-9; 5-*exo*-$C_7H_9S_2CNEt_2Fe(CO)_3$, 90064-85-0; 5-*exo*-$C_7H_9S_2CNPr_2Fe(CO)_3$, 90064-86-1; 5-*exo*-$C_7H_9S_2CN(CH_2CH_2)_2OFe(CO)_3$, 90064-87-2; $C_7H_9Fe(CO)_2I$, 12108-27-9; 5-*exo*-$C_6H_7NCSFe(CO)_3$, 83951-00-2; 5-*exo*-$C_6H_7SCNFe(CO)_3$, 83951-01-3; 5-*exo*-$C_6H_7NCSeFe(CO)_3$, 90064-88-3; 5-*exo*-$C_6H_7SeCNFe(CO)_3$, 90064-89-4; 5-*exo*-$C_6H_7NO_2Fe(CO)_3$, 90064-90-7; 5-*endo*-$C_6H_7NO_2Fe(CO)_3$, 90130-03-3; 5-*exo*-$C_6H_7N_3Fe(CO)_3$, 83576-99-2; 5-*exo*-$C_6H_7NCOFe(CO)_3$, 90064-91-8; 5-*exo*-$C_6H_7IFe(CO)_3$, 68193-47-5; 5-*exo*-$C_6H_7S_2CNMe_2Fe(CO)_3$, 90064-92-9; 5-*exo*-$C_6H_7S_2CNEt_2Fe(CO)_3$, 90064-93-0; 5-*exo*-$C_6H_7S_2CNPr_2Fe(CO)_3$, 90064-94-1; 5-*exo*-$C_6H_7S_2CN(CH_2CH_2)_2OFe(CO)_3$, 90064-95-2; $C_6H_7Fe(CO)_2I$, 12107-39-0; $C_5H_5Fe(CO)_2NCS$, 12317-60-1; $C_5H_5Fe(CO)_2SCN$, 12317-59-8; $C_5H_5Fe(CO)_2NCSe$, 90064-96-3; $C_5H_5Fe(CO)_2SeCN$, 33179-83-8; $C_5H_5Fe(CO)_2S_2CNMe_2$, 75900-10-6; $C_5H_5Fe(CO)_2S_2CNEt_2$, 82404-91-9; $C_5H_5Fe(CO)_2S_2CNPr_2$, 90064-97-4; $C_5H_5Fe(CO)_2S_2CN(CH_2CH_2)_2O$, 90064-98-5; $C_5H_5Fe(CO)S_2CNEt_2$, 63989-04-8; $[C_7H_9Fe(CO)_3]BF_4$, 12212-05-4; $[C_5H_5Fe(CO)_3]PF_6$, 38834-26-3; $[C_6H_7Fe(CO)_3]BF_4$, 33678-01-2.

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Synthetic, Structural, and Chemical Study of Some η^5-Phosphacyclohexadienyl Complexes with Iron and Manganese

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The reaction of $Mn_2(CO)_{10}$ with 4,5-dimethyl-1,2-diphenyl-1,6-dihydrophosphorin *P*-sulfide (5) (HL=S) gives $HL{\rightarrow}Mn_2(CO)_9$ (8) through reduction–complexation of the P=S bond and (η^5-L=S)$Mn(CO)_3$ (9) through metalation and η^5-C_5 complexation of the dihydrophosphorin ring. Upon heating the $HL{\rightarrow}Mn_2(CO)_9$ complex undergoes an orthometalation of the *P*-phenyl substituent with loss of $HMn(CO)_5$. The reaction of $Mn_2(CO)_{10}$ with the corresponding oxide (HL=O) (12) gives only the η^5-C_5 complex (η^5-L=O)$Mn(CO)_3$ (13), in high yield, since the P=O bond cannot be reduced. Similarly, HL=O reacts with $[CpFe(CO)_2]_2$ to give (η^5-L=O)FeCp (14). The reaction of this sandwich complex with *n*-butyllithium leads to a replacement of the P–Ph by a P–*n*-Bu substituent. The acylation by $CH_3COCl + AlCl_3$ takes place selectively on the Cp ring. The X-ray crystal structure of 14 shows that the Fe–C distances range from 2.05 to 2.13 Å for the heterocycle and from 2.06 to 2.11 Å for the cyclopentadienyl ring. The two planes are nearly parallel (dihedral angle = ~2.2°). The phosphorus atom is out of the C_5 plane by 0.733 (3) Å on the opposite side of iron, and the folding of the heterocyclic ligand around the C–C_α axis is 38.5°. There is no direct interaction between the iron atom and the endo phosphoryl oxygen.

Numerous η^5-pentadienyl and cyclo-η^5-dienyl complexes of transition metals have been recently described in the literature. Of particular significance to us were the discoveries of "open ferrocenes" (1)[1] and "open cymantrenes" (2).[2] In addition, some λ^5-phosphorin π complexes have been prepared by Dimroth et al.[3,4] and shown to have zwitterionic structure such as 3.[5]

On the other hand, we have found an easy two-step

[†] Laboratoire CNRS-SNPE.

[‡] Université Pierre et Marie Curie.

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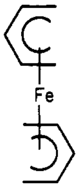
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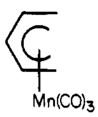
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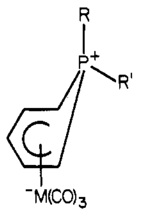
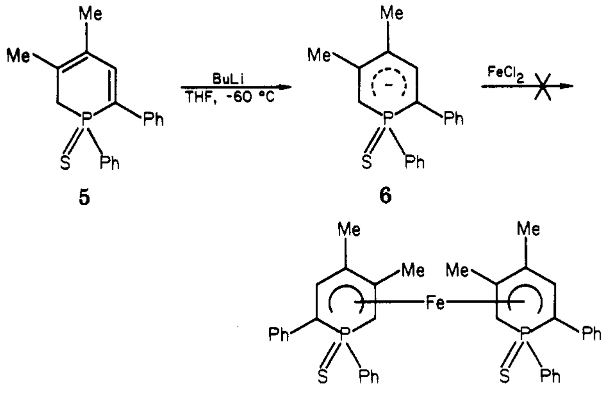

3, M = Cr, Mo, W


4, Y = O, S

access to 1,2-dihydrophosphorins from phospholes.[6,7] These species are readily metalated by BuLi or NaH[7] to give delocalized anions such as 4 that are very similar to pentadienyl or cyclodienyl anions. In consideration of these facts, it appeared that it would be possible to develop interesting coordination chemistry using the 1,2-dihydrophosphorin system. Our first results in that area are described in this paper.

Results and Discussion

Synthesis. Throughout this series of experiments, our starting product was the readily available 1,2-dihydrophosphorin sulfide 5.[6] In a first attempt we metalated 5 with BuLi in order to obtain the corresponding red anion 6 that then was reacted with anhydrous $FeCl_2$. Extensive decomposition took place, and we were unable to isolate the expected product 7.

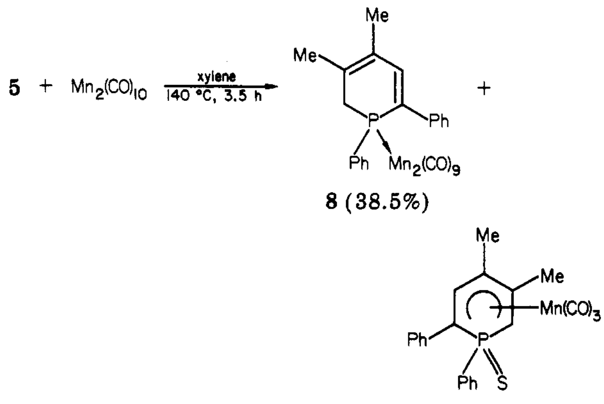


5 6 7

(1)

In the next experiment, instead of using the preformed anion 6, we reacted 5 directly with $Mn_2(CO)_{10}$. The organometallic reagent was expected to perform the necessary proton abstraction while operating under strictly neutral conditions. In fact, the reaction appeared to be very complicated and gave three different products. When stoichiometric amounts of 5 and $Mn_2(CO)_{10}$ were used in boiling xylene for a limited period of time, two main products were obtained (eq 2).

The bright yellow crystalline complex 8 was recovered as the major product by chromatography on silica gel. Its empirical formula was established by mass spectrometry (chemical ionization with NH_3, highest mass *m/e* 658 (M + NH_3, *I* = 100%)) and C, H, P, and Mn elemental analysis. Its IR spectrum was very similar to that of $(Ph_3P)Mn_2(CO)_9$[8] between 1900 and 2100 cm^{-1} (but the CO stretches were shifted toward lower frequencies), and the ^1H and ^{13}C NMR spectra proved unambiguously the presence of the uncomplexed ring. Alper has shown that $Mn_2(CO)_{10}$ can behave as a desulfurizing reagent,[9] and, in this laboratory, we have demonstrated that numerous metal carbonyls $(Fe(CO)_5$,[10] $Mo(CO)_6$,[11] etc.) react with phosphine sulfides (LS) to give phosphine complexes (L→M). Thus, the reduction–complexation observed here is not surprising.



8 (38.5%)

(2)

9 (13.3%)

The second, almost colorless, complex 9 was the desired product. Its empirical formula was established by mass spectrometry (chemical ionization with CH_4, highest mass *m/e* 449 (M + 1, *I* = 87%), base peak *m/e* 364, M − 3CO) and C, H, P, and Mn elemental analysis. Its IR spectrum showed three carbonyl stretches at 2035, 1979, and 1945 cm^{-1} in CCl_4 vs. 2016, 1957, and 1937 cm^{-1} observed for $(\eta^5\text{-}C_5H_7)Mn(CO)_3$.[2] (Obviously the pentadienyl anion is a far better donor than 6.) The ring η^5 complexation was established by ^1H and ^{13}C NMR spectroscopy. This complexation induces strong shieldings at the α- and γ-positions whereas the β-positions are less affected as in pentadienyl complexes.[2] This is the expected consequence of an accumulation of electronic density on the α- and γ-positions (see Table I).

In the mass spectrum of complex 8, the second major peak after the M + NH_3 base peak corresponded to the loss of a $Mn(CO)_5$ unit in the initial structure (m/e 445 (*I* = 38%)). Thus, in order to explain the appearance of side products in the reaction of 5 with $Mn_2(CO)_{10}$, we decided to check the thermal stability of 8. Upon heating 8 in boiling xylene for several hours, the initial ^{31}P NMR peak ($\delta(^{31}P)$ of (8) ~50) slowly disappeared and was replaced by a new peak at ~40 ppm. The same product was also obtained by increasing the reaction time when reacting 5 directly with $Mn_2(CO)_{10}$. This new product appeared to have structure 10. Its empirical formula was established by EI mass spectrometry (highest mass *m/e* 444 (M, *I* = 18%); base peak *m/e* 332 (M − 4CO); chemical ionization with CH_4, highest mass *m/e* 445 (M + 1, *I* = 23%); base peak *m/e* 417 (M + 1 − CO)) and C, H, P, and Mn elemental analysis. The phosphorus ring appeared to be uncomplexed. Indeed, the ^1H and ^{13}C NMR spectra of 8

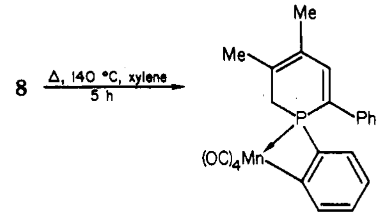


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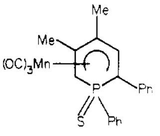
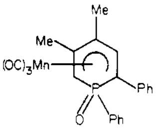
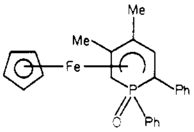
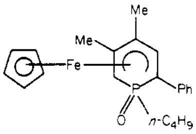
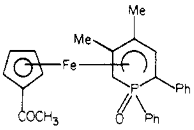
Table I. Selected ^1H, ^{13}C, and ^{31}P NMR Data for Some η^5-Phosphacyclohexadienyl Complexes[a]

	H_α	H_β	$C_\alpha H$	$C_\alpha Ph$	$C_\beta H$	$C_\beta Me$	C_γ	$\delta(^{31}P)$	other data
 9	3.05 (8.8)	5.92 (18.8)	52.07 (76.9)	72.19 (74.5)	106.81 (4.9)	118.20 (~0)	95.0 (9.8)	36.1 (CH_2Cl_2)	δ(CO) 219.56
 13	2.68 (C_6D_6) (2.4)	5.65 (C_6D_6) (21)	52.44 (94)	71.85 (90.3)	106.17 (8.5)	119.17 (2.4)	93.54 (9.8)	21.1 (CH_2Cl_2)	δ(CO) 219.86
 14	b	~5.80	31.96 (98.9)	42.65 (95.2)	87.84 (~3)	98.08 (0)	92.63 (7.3)	19.9 (CH_2Cl_2)	δ(C_5H_5) 76.94 δ(C_5H_5) 4.33
 15	3.68 (10)	5.29 (14.4)	44.95 (90.3)	61.22 (91.6)	89.30 (0)	95.18 (0)	90.54 (11)	4.8 (CH_2Cl_2)	δ(C_5H_5) 75.42 δ(C_5H_5) 4.15
 16	b	5.66	34.20 (98.9)	45.38 (92.8)	88.36 (6.1)	99.66 (0)	92.54 (8.5)	20.4 (CH_2Cl_2)	C-$COCH_3$ 85.36 Cp CH 77.36, 78.09 80.39, 80.88 $COCH_3$ 28.17 $COCH_3$ 200.23

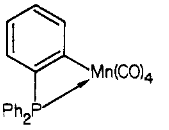
[a] δ in ppm and J(H-P) or J(C-P) in hertz; reference internal Me_4Si for ^1H and ^{13}C and external 85% H_3PO_4 for ^{31}P; δ positive for downfield shifts; unless otherwise noted, products are in $CDCl_3$ solution. [b] Poorly resolved spectrum; probably masked by the Cp peak.

Table II. Atomic Positional Parameters for $FePOC_{24}H_{23}$[a]

atom	x/a	y/b	z/c	B(iso), Å^2
Fe	0	−0.11464 (8)	0	1.84 (4)
P	−0.0468 (3)	0.0505 (2)	0.4946 (3)	1.75 (8)
O	0.0293 (9)	0.0931 (5)	0.6037 (7)	2.7 (3)
C(1)	0.056 (1)	−0.0075 (6)	0.4343 (9)	1.8 (3)
C(2)	−0.016 (1)	−0.0640 (6)	0.3451 (9)	1.9 (3)
C(3)	−0.143 (1)	−0.1026 (7)	0.331 (1)	2.2 (3)
C(4)	−0.205 (1)	−0.0892 (7)	0.418 (1)	2.5 (3)
C(5)	−0.148 (1)	−0.0314 (7)	0.506 (1)	2.5 (4)
C(11)	0.055 (2)	−0.2348 (7)	0.512 (1)	4.7 (5)
C(12)	0.174 (2)	−0.187 (1)	0.541 (1)	4.5 (5)
C(13)	0.183 (2)	−0.1396 (9)	0.636 (1)	4.2 (5)
C(14)	0.074 (2)	−0.159 (1)	0.671 (1)	4.7 (6)
C(15)	−0.010 (2)	−0.2163 (9)	0.592 (2)	5.2 (6)
C(111)	0.2022 (8)	0.0137 (5)	0.4514 (6)	1.9 (2)
C(112)	0.2873 (8)	0.0483 (5)	0.5550 (6)	2.8 (2)
C(113)	0.4244 (8)	0.0651 (5)	0.5723 (6)	4.1 (3)
C(114)	0.4764 (8)	0.0473 (5)	0.4860 (6)	3.4 (3)
C(115)	0.3914 (8)	0.0127 (5)	0.3824 (6)	4.2 (3)
C(116)	0.2543 (8)	−0.0041 (5)	0.3651 (6)	2.7 (2)
C(211)	−0.1529 (8)	0.1238 (4)	0.3890 (7)	2.3 (2)
C(212)	−0.2807 (8)	0.1032 (4)	0.3073 (7)	3.8 (3)
C(213)	−0.3596 (8)	0.1612 (4)	0.2307 (7)	4.7 (3)
C(214)	−0.3107 (8)	0.2398 (4)	0.2358 (7)	3.7 (3)
C(215)	−0.1829 (8)	0.2604 (4)	0.3175 (7)	4.3 (3)
C(216)	−0.1040 (8)	0.2023 (4)	0.3941 (7)	3.4 (3)
Me(3)	−0.201 (2)	−0.1647 (8)	0.238 (1)	3.0 (3)
Me(4)	−0.324 (2)	−0.1409 (9)	0.420 (1)	3.8 (3)

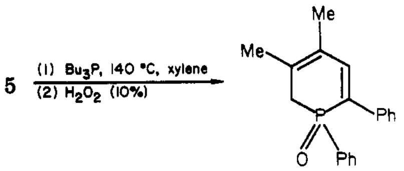
[a] The estimated standard deviation of the least significant digit is given in parentheses. Derived or group atom positions for hydrogen atoms are given as supplementary material.

and 10 were very similar. The IR spectrum of 10 in cyclohexane showed terminal carbonyls at 2060 (m), 1990 (s), 1980 (s), and 1945 (s) cm^{-1} and no acyl group. In fact, this spectrum is very similar to that of complex 11 that has been prepared by thermolysis of Me–Mn(CO)$_4$(PPh$_3$).[12] Such internal metalation is very common in manganese carbonyl chemistry.



11

In view of these results, it was obvious that if we wanted to obtain products such as 9 in high yields, it was necessary to prevent the major side reaction, i.e., the reduction–complexation of the P═S group by $Mn_2(CO)_{10}$. Thus, we decided to study the reaction of the P-oxide 12 with $Mn_2(CO)_{10}$. Since our synthesis of 1,2-dihydrophosphorins produces P-sulfides such as 5 directly, we first converted 5 into 12 through a reduction–oxidation procedure.



12 (80%)

As expected, the reaction of 12 with $Mn_2(CO)_{10}$ in boiling toluene produced exclusively the π-complex 13. Of course, the ^1H and ^{13}C NMR spectra of 9 and 13 are very similar (see Table I). We then extended this reaction to the

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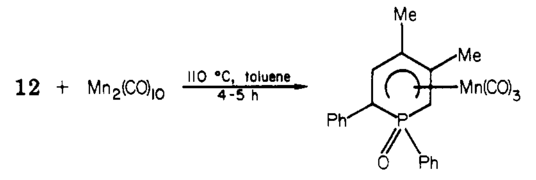
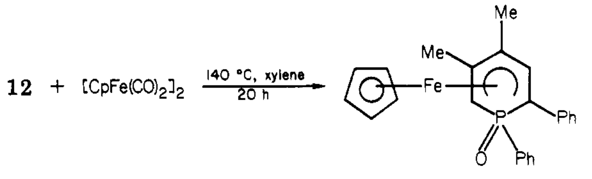
[12] McKinney, R. J.; Hoxmeier, R.; Kaesz, H. D. *J. Am. Chem. Soc.* 1975, *97*, 3059.

synthesis of the sandwich complex **14**.

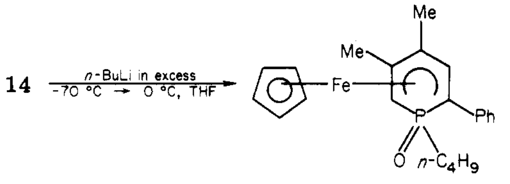


13 (~60%)



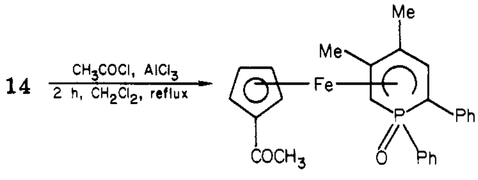
14 (75%)

Chemistry. In order to have an overall view of the chemistry of these new η^5-phosphacyclohexadienyl complexes, we decided to study two key reactions: the reaction with alkyllithiums and the reaction with acyl chlorides (Friedel–Crafts). Our experiments were performed with the readily prepared sandwich complex **14**. The reaction of **14** with *n*-butyllithium led to a P–Ph → P–Bu exchange.



15 (~52%)

The mass spectrum of **15** (EI, 70 eV) shows a molecular ion at *m/e* 394 (*I* = 100%). The ^{1}H NMR spectrum demonstrates that **15** contains butyl, cyclopentadienyl, and phenyl groups in a 1:1:1 ratio. The ^{13}C NMR spectrum shows that the P-*C*(Ph) of **14** at 141.3 ppm [^1J(C–P) = 81.8 Hz] has disappeared and has been replaced by a P-*C*H$_2$-(Bu) at 29.71 ppm [^1J(C–P) = 89.1 Hz]. The formula of **15** is thus unambiguously established and is fully confirmed by the other NMR data (see Table I). This exchange reaction is quite similar to the well-known reaction of Ph$_3$PO with lithium alkyls.[13] On the other hand, the reaction of **14** with CH$_3$COCl + AlCl$_3$ led to acylation of the cyclopentadienyl group.



16 (~48%)

The mass spectrum of **16** (EI, 70 eV) shows a molecular ion at *m/e* 456 (*I* = 100%). The IR spectrum demonstrates that the acylation has indeed taken place [ν(CO) 1660 cm^{-1} in KBr]. Finally, the ^{13}C NMR spectrum of **16** shows an unaltered phosphorus heterocycle, whereas the cyclopentadienyl group now gives five different peaks (see Table I). This means that the acylation has occurred on the cyclopentadienyl group.

The full selectivity of the synthesis of **16** means that the electron-withdrawing P(O)Ph group completely deactivates the η^5-pentadienyl moiety of **14** toward electrophilic substitution.

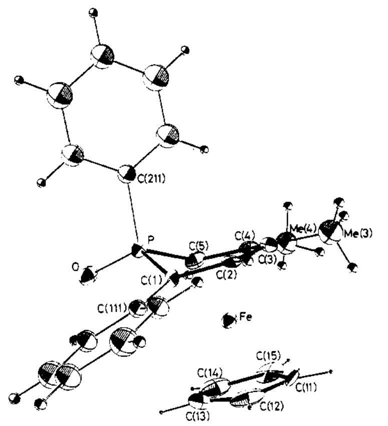


Figure 1. ORTEP view of the molecule with thermal ellipsoids at the 35% probability level (Johnson, C. K. ORTEP, Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965).

X-ray Crystal Structure of 14. The crystal consists of discrete molecules. The closest non-hydrogen contact between molecules is 3.23 Å, between atoms C$_2$ and O. A view of a molecule and the system used in labeling the principal atoms is shown in Figure 1. Selected distances and angles are presented in Table VI.

Coordination Sphere around the Fe Atom. The cyclopentadienyl ligand is approximately in an eclipsed configuration with respect to C$_2$–C$_3$–C$_4$ of the C$_5$P heterocycle. Only the five carbon atoms of the latter ligand are coordinated to Fe; these Fe–C distances range from 2.05 to 2.13 Å for the heterocycle and from 2.06 to 2.11 Å for the cyclopentadienyl ring. The former may be compared with "open ferrocenes" such as bis(2,4-dimethylpentadienyl) iron[14] or with bis(cyclo-η^5-dienyl)iron compounds such as [Fe(η^5-C$_7$H$_7$)(η^5-C$_7$H$_9$)][15] or [Fe{(η^5-6-*t*-C$_4$H$_9$-1,3,5-(CH$_3$)$_3$C$_6$H$_3$}$_2$][16] in which Fe–C distances range from 2.058 to 2.122, 2.035 to 2.126, and 2.047 to 2.135 Å, respectively; the latter may be compared with ferrocene (Fe–C(av) = 2.064 (3) Å, gas-phase electron diffraction,[17] or 2.010–2.054 Å, X-ray diffraction[18]).

The distances from Fe to the planes through the five carbon atoms of the heterocyclic ligand and those of the cyclopentadienyl ligand are 1.489 (1) and 1.702 (1) Å, respectively. These are similar to comparable distances in an "open ferrocene" of 1.46 Å[14] and in ferrocene of 1.66[17] or 1.65 Å.[18] In the title compound these two planes are nearly parallel; the angle between normals to these planes is 2.2°, in contrast to the "open ferrocene" mentioned above,[14] for which the comparable angle is 15°. Neither phosphorus nor oxygen are coordinated to Fe; both are on the opposite side to Fe of the plane through the carbon atoms of the heterocyclic ligand at distances to Fe of 2.784 and 3.66 Å, respectively.

The Heterocyclic Ligand. The five carbon atoms of the C$_5$P ring are nearly coplanar; the greatest deviation from their least-squares plane is 0.044 Å (C$_4$). The C–C distances average 1.43 (2) Å, somewhat longer than 1.40 Å, the average C–C distance within the five coordinated carbon atoms of the η^5-C$_7$H$_7$ ligand in Fe(η^5-C$_7$H$_7$)(η^5-

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Table VI. Selected Interatomic Distances and Angles for $FePOC_{24}H_{23}$

Distances (Å)			
Fe···P	2.784 (3)	C(1)-C(2)	1.44 (1)
Fe-C(1)	2.126 (9)	C(1)-C(111)	1.50 (1)
Fe-C(2)	2.048 (10)	C(2)-C(3)	1.42 (2)
Fe-C(3)	2.099 (11)	C(3)-C(4)	1.46 (2)
Fe-C(4)	2.054 (11)	C(3)-Me(3)	1.50 (2)
Fe-C(5)	2.093 (11)	C(4)-C(5)	1.41 (2)
Fe-C(11)	2.067 (11)	C(4)-Me(4)	1.52 (2)
Fe-C(12)	2.086 (11)		
Fe-C(13)	2.082 (13)	C(11)-C(12)	1.41 (2)
Fe-C(14)	2.110 (13)	C(11)-C(15)	1.42 (2)
Fe-C(15)	2.064 (11)	C(12)-C(13)	1.40 (2)
		C(13)-C(14)	1.39 (2)
O-P	1.479 (8)	C(14)-C(15)	1.42 (2)
P-C(1)	1.795 (11)		
P-C(5)	1.758 (12)		
P-C(211)	1.837 (8)		
Angles (deg)			
O-P-C(1)	115.7 (5)	C(2)-C(1)-P	116.3 (8)
O-P-C(5)	115.9 (5)	C(111)-C(1)-P	123.0 (7)
C(1)-P-C(5)	94.8 (5)	C(111)-C(1)-C(2)	119.0 (7)
O-P-C(211)	108.8 (4)	C(1)-C(2)-C(3)	126.5 (10)
C(1)-P-C(211)	110.9 (4)	C(2)-C(3)-C(4)	118.7 (10)
C(5)-P-C(211)	110.2 (4)	Me(3)-C(3)-C(2)	119.9 (11)
		Me(3)-C(3)-C(4)	120.9 (11)
C(15)-C(11)-C(12)	107.5 (13)	C(3)-C(4)-C(5)	119.7 (11)
C(11)-C(12)-C(13)	108.1 (13)	Me(4)-C(4)-C(3)	120.5 (12)
C(12)-C(13)-C(14)	109.1 (15)	Me(4)-C(4)-C(5)	119.6 (11)
C(13)-C(14)-C(15)	107.9 (13)	C(4)-C(5)-P	124.4 (9)
C(14)-C(15)-C(11)	107.3 (13)		

C_7H_9),[15b] or 1.411 (7) Å, the average distance for the ten coordinated carbon atoms of $(2,4\text{-}C_7H_{11})_2Fe$;[14] however, it is comparable to the value of 1.428 (5) Å found for the average distance in (2,3,4-trimethylpentadienyl)ruthenium[19] or 1.424 (8) Å found in $Ru(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$.[20] A pattern of C–C bond distances is found in the pentadienyl ligands of $Nd(2,4\text{-}C_7H_{11})_3$,[21] a shorter "external set" (C_1–C_2 and C_4–C_5 averaging 1.373 (12) Å and a longer "internal set" (C_2–C_3 and C_3–C_4) averaging 1.421 (12) Å. However, this pattern is found neither in bis(2,3,4-trimethylpentadienyl)ruthenium[19] nor in the chromium phosphorin complexes,[5,22] nor is it found in the title compound. The precision of this determination does not allow speculation about contributing resonance structures.

The comparable C–C distance in two similar heterocyclic ligands, the chromium tricarbonyl complexes of 1,1-dimethoxy-2,4,6-triphenyl-λ^5-phosphorin and of 4-*tert*-butyl-1,1-difluoro-2,6-diphenyl-λ^5-phosphorin,[5,22] is 1.40 (2) and 1.43 (1) Å, respectively. In these latter two complexes the coordinated carbon atoms are somewhat less coplanar; the rings are somewhat boat-shaped with phosphorus at distances of 0.440 or 0.450 Å and γ-carbon at distances of 0.169 or 0.068 Å from a plane through the remaining four carbon atoms. For such a plane in the title compound, the phosphorus and carbon atoms are at distances of 0.733 (3) and 0.06 (1) Å, also somewhat boat-shaped, and the normal to the C_1–P–C_5 plane forms an angle of 38.5° with the normal to the C_5 plane. This is the same angle found in the deformation of the sixth carbon atom from the plane of five coordinated carbon atoms in an (η^5-cyclohexadienyl)tricarbonylchromium(O) complex[23] (38.6°).

Those carbon atoms having an attached methyl group have smaller C–C–C bond angles (119 and 120° rather than 126°); this effect has been discussed previously.[14,24,25] The shortest Fe–C distances to the heterocycle are to C_2 and C_4 (2.05 Å); the shortest Fe–C distances in the bis(cyclo-η^5-dienyl)iron complexes are also to C_2 and C_4,[15,16] 2.04 Å (av) and 2.05 Å (av).

Both methyl groups and the phenyl group attached to C_1 are bent out of the ligand plane in a direction toward the iron atom by 4°, 9°, and 13°. Such tilts toward the metal would enable the ligand to direct better its p orbitals toward the metal;[26] they are indeed also found in the "open ferrocenes",[14] in other η^5-dienyl ligands,[1,19,20] and, although in $Fe(C_5(CH_3)_5)_2$ the methyl groups are bent away from the metal,[27] in ferrocene the hydrogen atoms are displaced toward the Fe atom.[17,28,29] For $[M(2,4\text{-}C_7H_{11})_2]$ (M = V, Cr, Fe) complexes[19] this tilt averages about 9°.

The plane of the phenyl group on phosphorus is nearly perpendicular to the C_5 plane (93°), and the plane of the phenyl group on C_1 is more nearly coplanar (18°) with the latter. The two phenyl rings are nearly perpendicular to each other (93°). The angle between normals to the plane of the phenyl group on phosphorus and to a pseudo mirror plane passing through P, C3, Fe is 31°.

Phosphorus is at the center of a distorted tetrahedron; the C–P–C angle is most acute (94°), the three angles involving the phenyl carbon atom are nearly tetrahedral (109–111°), and the remaining two are between tetrahedral and trigonal (115, 116°). The C–P–C angle is somewhat smaller than those for phosphorin complexes with tricarbonylchromium[5,22] (103, 106°) or for uncomplexed phosphorinanones[30] (100–102°) or uncomplexed phos-

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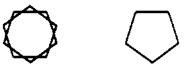
phorinanes[31] (100°) or their salts[32] (104, 105°). The P–C distances within the heterocycle are nearly equal, 1.80 (1) and 1.76 (1) Å, and somewhat longer than for the "phosphorin complexes" cited above, 1.69 and 1.70 Å for the 4-*tert*-butyl-1,1-difluoro-2,6-diphenyl-λ^5-phosphorin ligand and 1.76 and 1.77 Å for the 1,1-dimethoxy-2,4,6-triphenyl-λ^5-phosphorin ligand. P–C distances of 1.79–1.80 Å are found in the uncomplexed phosphorus heterocycles.[31,32]

The P–O distance is the same, 1.479 (8) Å, as that found in *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxide,[31] 1.483 (2) Å; herein the P–C(phenyl) distance, 1.805 (2) Å, is somewhat shorter than that found in the title compound, 1.837 (8) Å.

The Cyclopentadienyl Ligand. The ligand is a planar regular pentagon within the estimated error (greatest deviation from the plane is 0.02 (2) Å, and average C–C distance is 1.41 Å). Thermal ellipsoids for these atoms are rather large compared with the other ones of the molecule, indicating probable disorder.

Vibrational ellipsoids resemble those found in the bis(cyclopentadienyl) complexes of Fe, Co, and Mg.[18] In the title compound the ligand could be described as a regular pentagon, C–C = 1.42 Å, which occupies two different positions. A position of $^3/_4$ occupancy is related to another of $^1/_4$ occupancy



approximately by a rotation of roughly 30° about the center of mass. These two are not quite coplanar (1.3°), and one centroid is displaced from the other by 0.06 Å.

Experimental Section

NMR spectra (chemical shifts in parts per million from internal Me_4Si for ^1H and ^{13}C and from external 85% H_3PO_4 for ^{31}P; δ positive for downfield shifts in all cases) were recorded on a Bruker WP 80 spectrometer respectively at 80.13, 20.15, and 32.44 MHz. Mass spectral measurements (VG 30F spectrometer) and elemental analyses were carried out by "Service Central de Microanalyse du CNRS" (Lyon). All reactions were run under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh Riedel de Haën).

(1,2-Diphenyl-4,5-dimethyl-1,6-dihydrophosphorin)nonacarbonyldimanganese (8) and (η^5-1,2-Diphenyl-4,5-dimethyl-1-hydrophosphorin 1-sulfide)tricarbonylmanganese (9). A mixture of 2 g (6.45 mmol) of dihydrophosphorin sulfide **5** and 2.52 g (6.45 mmol) of dimanganese decacarbonyl was heated at 120 °C for 5 h in 50 mL of dry degassed xylene. After filtration on sintered glass (*caution*! the black solid thus eliminated is often pyrophoric) and evaporation of xylene, the organic residue was chromatographed with hexane–ether (80:20) to isolate **8** and then with ether to isolate **9** (**9** is eluted after the unreacted starting sulfide **5**).

Complex 8: yield 1.6 g (38.5%); ^1H NMR (C_6D_6) δ 1.38 (d, J(H–P) = 12.9 Hz, 3 H, Me), 1.54 (s, 3 H, Me), 2.2–3.0 (m, 2 H, CH_2P), 6.54 (d, ^3J(H–P) = 23.4 Hz, 1 H, CH=), 6.8–8.0 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.08 (d, J(C–P) = 2.4 Hz, Me), 21.57 (d, J(C–P) = 7.3 Hz, Me), 40.41 (d, ^1J(C–P) = 31.7 Hz, CH_2P), 223.58 (m, CO); $\delta(^{31}P)$ 48.50 ($CDCl_3$); IR (decalin) ν(CO) 2080 (m), 2005 (s), 1990 (vs), 1968 (s), 1932 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{19}Mn_2O_9P$: C, 52.50; H, 2.97; Mn, 17.19; P, 4.84. Found: C, 52.27; H, 2.87; Mn, 16.53; P, 4.34.

Complex 9: yield 0.4 g (13.8%). Anal. Calcd for $C_{22}H_{18}MnO_3PS$: C, 58.93; H, 4.02; Mn, 12.28; P, 6.92. Found: C, 58.26; H, 4.01; Mn 11.61; P, 6.92.

Complex 10. The same experiment as above was carried out with 2 g of sulfide **5** and 2.8 g (7.1 mmol) of $Mn_2(CO)_{10}$. The xylene solution was refluxed for one night. Complex **10** was formed instead of complex **8** and was purified in the same way: ^1H NMR ($CDCl_3$) δ 1.77 (s, 3 H, Me), 1.87 (s, 3 H, Me), 2.89 (d, ^2J(H–P) = 5.9 Hz, 2 H, CH_2P), 6.95 (d, ^3J(H–P) = 24.4 Hz, 1 H, CH=), 7.0–7.8 (m, 9 H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.06 (s, Me), 22.35 (d, J(C–P) = 5.2 Hz, Me), 33.31 (d, ^1J(C–P) = 30.9 Hz, CH_2P), 217 (m, CO); a doublet at 164.76 ppm (J(C–P) = 8.6 Hz) might be attributed to (Ph)CMn; $\delta(^{31}P)$ 38.4 ($CDCl_3$). Anal. Calcd for $C_{23}H_{18}MnO_4P$: C, 62.16; H, 4.05; Mn, 12.39; P, 6.98. Found: C, 61.18; H, 3.98; Mn, 11.66; P, 7.07.

1,2-Diphenyl-4,5-dimethyl-1,6-dihydrophosphorin Oxide (12). A mixture of 2 g (6.45 mmol) of sulfide **5** and 4 mL of tri-*n*-butylphosphine (16 mmol) was refluxed in 25 mL of xylene for 3 h. Then the solution was cooled in an ice bath, and 40 mL of 10% H_2O_2 was added with stirring. After it had been warmed to room temperature, the solution was washed three times with water and dried with $MgSO_4$. After evaporation, the residue was washed with ether to give 1.57 g (83%) of white crystals of **12**: ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H, Me), 2.56 (s, 3 H, Me), 3.0 (m, 2 H, CH_2P), 6.04 (d, ^2J(H–P) $\approx$ 20 Hz, 1 H, CH=), 7.3 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.51 (s, Me), 22.05 (d, J(C–P) = 9.8 Hz, Me), 37.71 (d, ^1J(C–P) = 72 Hz, CH_2P); δ (^{31}P) 19.9 (CH_2Cl_2); IR (KBr) ν(C=C) 1635, ν(PO) 1168 cm^{-1}; mass spectrum (EI, 70 eV), *m/e* 294 (M, 100%). Anal. Calcd for $C_{19}H_{19}OP$: C, 77.55; H, 6.46; P, 10.54. Found: C, 77.43; H, 6.38; P, 10.38.

(η^5-1,2-Diphenyl-4,5-dimethyl-1-hydrophosphorin 1-oxide)tricarbonylmanganese (13). A mixture of 2 g (6.8 mmol) of oxide **12** and 2.92 g (7.6 mmol) of $Mn_2(CO)_{10}$ was heated at 120 °C for 5 h in dry degassed xylene (50 mL). The solution was cooled, filtered, and evaporated. The residue was chromatographed with ethyl acetate. Complex **13** was recovered as a yellow solid in 67% yield (1.98 g): IR (CCl_4) ν(CO) 2035, 1978, 1942 cm^{-1}; mass spectrum (chemical ionization with CH_4), *m/e* 433 (M + 1, 100%). Anal. Calcd for $C_{22}H_{18}MnO_4P$: C, 61.11; H, 4.17; Mn, 12.73; P, 7.18. Found: C, 60.98; H, 4.20; Mn, 11.62; P, 7.14.

(η^5-1,2-Diphenyl-4,5-dimethyl-1-hydrophosphorin 1-oxide)cyclopentadienyliron (14). A mixture of 3.4 g (0.012 mol) of oxide **12** and 4.8 g (0.014 mol) of $[CpFe(CO)_2]_2$ was refluxed in 500 mL of xylene for 20 h. The solution was cooled, filtered if necessary, and evaporated. The organic residue was chromatographed with ether–ethyl acetate (95:5). Complex **14** was eluted after the starting oxide in 75% yield (~3.6 g): IR (KBr) ν(PO) 1150 cm^{-1}; mass spectrum (chemical ionization with CH_4), *m/e* 415 (M + 1, 100%). Whereas the sample used for that purpose was spectroscopically pure and was also used for the X-ray crystal structure analysis, we have been unable to get satisfactory analytical results (low results for C and Fe and good results for H and P).

(η^5-1-Butyl-2-phenyl-4,5-dimethyl-1-hydrophosphorin 1-oxide)cyclopentadienyliron (15). A solution of 0.5 g (1.2 mmol) of complex **14** in 25 mL of THF was treated at −70 °C with 5 mL of a 1.5 M solution of *n*-butyllithium (7 mmol) in hexane. The mixture turned red. The temperature then was raised slowly to 25 °C. Hydrolysis was performed with 25 mL of HCl (1N). After evaporation of the THF, the product was extracted from the water layer by dichloromethane. After being dried with $MgSO_4$, the CH_2Cl_2 solution was evaporated and the organic residue chromatographed with ether–methanol (90:10). Complex **15** was recovered after the unreacted starting product in 52% yield (0.25 g): IR (KBr) ν(PO) 1135 cm^{-1}. Anal. Calcd for $C_{22}H_{27}FeOP$: C, 67.01; H, 6.85; P, 7.87. Found: C, 65.79; H, 6.94; P, 6.80 (low results on Fe).

(η^5-1,2-Diphenyl-4,5-dimethyl-1-hydrophosphorin 1-oxide)acetylcyclopentadienyliron (16). A mixture of 0.828 g (2 mmol) of complex **14**, 0.6 g (4.4 mmol) of $AlCl_3$, and 0.16 mL (2.2 mmol) of acetyl chloride was refluxed in 25 mL of dry degassed dichloromethane for 2 h. After hydrolysis with 25 mL of distilled water, the mixture was worked up as usual. The organic product was chromatographed with ether–methanol (90:10). Complex **16** was eluted after the unreacted starting product in 48% yield (0.44 g). Anal. Calcd for $C_{26}H_{25}FeO_2P$: C, 68.42; H, 5.48; Fe, 12.28; P, 6.80. Found: C, 65.48; H, 5.47; Fe, 11.58; P, 6.37.

X-ray Data Collection and Processing. Preliminary unit cell dimensions and symmetry information were derived from

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precession photographs of a red lathe-shaped crystal. Accurate unit cell dimensions, derived from a least-squares refinement of 22 reflections for which 14° < θ < 17°, λ(Mo K$\bar{\alpha}$) = 0.710 69 Å, are as follows: a = 10.428 (4) Å, b = 16.616 (4) Å c = 12.402 (4) Å, β = 111.13 (3)°, D_{exptl} = 1.37 g cm^{-3}, Z = 4, V = 2004.4 Å^3. The space group was determined to be Cc, based on Z and the lack of symmetry in the molecule. Data were collected on a Philips diffractometer equipped with a graphite monochromator, Mo K$\bar{\alpha}$ radiation, using the θ–2θ scan technique, with a scan width of (1 + 0.3 tan θ), a scan rate of 0.01°/s for θ < 18° and 0.007°/s for $\theta \geq$ 18°, 2° < θ < 27°, and background time equal to half the scan time. Intensities of three standard reflections were monitored every 2 h. These showed no appreciable change during the data collection. Data were processed by using a locally written program. No absorption correction was considered to be necessary (μ = 7.0 cm^{-1}, crystal dimensions 0.038 × 0.075 × 0.38 mm). A total of 1974 unique reflections were processed, of which 1362 had $I > 3\sigma(I)$ and were used in subsequent calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2|F_o|$.[33] Atomic scattering factors for neutral Fe, P, O, and C were taken from a recent tabulation,[34] those for H were taken from Stewart et al.,[35] and anomalous dispersion terms for Fe and P were included.[34]

The positions of iron and phosphorus atoms were determined from a Patterson map. All other non-hydrogen atoms were located on subsequent Fourier and difference Fourier maps. The two phenyl groups were treated as rigid hexagons, C–C = 1.395 and C–H = 1.0 Å. Hydrogen atoms of the methyl groups were placed in calculated positions (H–C–H = 109.5°, C–H = 1.0 Å) and were not refined. The remaining hydrogen atoms, which were all located in difference maps, were constrained to be 1.0 Å from their attached carbon atoms. Refinement of 149 parameters led to an agreement index of 0.0611 ($R = \sum||F_o| - |F_c||/\sum|F_o|$) and a weighted index of 0.0805 ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. A final difference electron density map showed no peaks greater than 0.5 e Å^{-3}.

Final positional parameters and their standard deviations are presented in Table II. Thermal parameters for non-hydrogen atoms, parameters for hydrogen atoms, and final values of observed and calculated structure factors are presented in Tables III, IV, and V, respectively, and are available as supplementary material.

Registry No. **5**, 66314-69-0; **8**, 90219-10-6; **9**, 90245-07-1; **10**, 90245-08-2; **12**, 90219-11-7; **13**, 90245-09-3; **14**, 90245-12-8; **15**, 90245-10-6; **16**, 90245-11-7; $Mn_2(CO)_{10}$, 10170-69-1; $[CpFe(CO)_2]_2$, 12154-95-9.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters (Table III), the hydrogen atom parameters (Table IV), and the structure factor amplitudes (Table V) (8 pages). Ordering information is given on any current masthead page.

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A Theoretical Study of the Formation and Reactivity of Substituted Cyclohexadienyliron Complexes. The Structures and Reactivities of Tricarbonyl(2-methoxycyclohexadienyl)iron Cation and Tricarbonyl(1-methyl-4-methoxycyclohexadienyl)iron Cation

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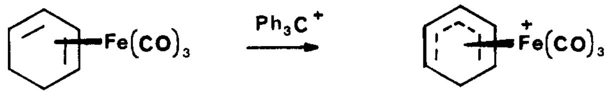
Extended Hückel calculations have been performed to understand the high regioselectivity in the formation and the reactivity of tricarbonyliron cyclohexadienyl cations. The formation of a substituted cyclohexadienyl complex from the diene complex by an hydride abstraction is rationalized. It is found that a distortion of the cyclohexadienyl complex in which the metal is not linked symmetrically to the two ends of the dienyl accounts for the high regioselectivity of the nucleophilic addition to the dienyl. This theoretical analysis is well supported by the structural determination of two cyclohexadienyl complexes: tricarbonyl(2-methoxycyclohexadienyl)iron cation and tricarbonyl(1-methyl-4-methoxycyclohexadienyl)iron cation.

Tricarbonyl(polyene)iron complexes are currently used in synthesis to allow an easy route to functionalized polyenes with special focus on cyclohexa-1,3-diene and cyclohexadienyl cation complexes. Converting one into the other presents some interesting and puzzling problems of regioselectivity.[1,2]

A tricarbonyl(cyclohexa-1,3-diene)iron complex, **1**, is easily converted into a cyclohexadienyl cation complex, **2**,



1 **2**

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