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(22) (a) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2a; (b) D. T. Cromer and D. Liberman, *ibid.*, Table 2.3.1.

Synthetic, Physicochemical, and Structural Study of Phosphacymantrenes

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Abstract: The reaction of 1-phenyl-3,4-dimethylphosphole with $Mn_2(CO)_{10}$ at 150 °C in boiling xylene yields 3,4-dimethylphosphacymantrene as the main product together with a heavier complex tentatively identified as (3,4-dimethylphospholyl)-trimanganese dodecacarbonyl. Phosphacymantrene itself and its 3-methyl derivative are analogously prepared starting from 1-phenylphosphole and 1-phenyl-3-methylphosphole, respectively. 3,4-Dimethylphosphacymantrene is acylated on the α carbon by $CH_3COCl-AlCl_3$ in boiling dichloromethane and by $C_6H_5COCl-AlCl_3$ in boiling tetrachlorethane. The phosphorus atom does not react with quaternizing agent nor with mild oxidant such as iodine. On the contrary its reactivity toward nucleophiles is high. In that case the phosphacymantrene moiety is destroyed. For example, *n*-butyllithium with 3,4-dimethylphosphacymantrene yields 1-butyl-3,4-dimethylphosphole. On the basis of the ^{13}C NMR and IR data of the CO groups it appears that the phospholyl nucleus is a weaker electron donor toward the $Mn(CO)_3$ moiety than the cyclopentadienyl nucleus. Phosphacymantrenes are also characterized by a high $^1J(P-C)$ coupling constant (ca. 65 Hz) and a very shielded phosphorus atom. The crystal structure of $[\eta^5-PC_4H(CH_3)_2(COC_6H_5)]Mn(CO)_3$ was determined from three-dimensional x-ray diffraction counter data. The molecule crystallizes with four formula units in the monoclinic space group $P2_1/n$, with $a = 20.995$ (5), $b = 10.869$ (3), $c = 6.784$ (2) Å, and $\beta = 90.17$ (3)°. The final indexes, based on the least-squares refinement of 235 variables for 1047 observations ($I > 3\sigma(I)$), are $R(F_o) = 0.046$, $R_w = 0.056$. The π-bonded phospholyl ring is aromatic but is slightly puckered. The four carbon atoms of the ring are coplanar and the phosphorus atom lies out of this plane by 0.048 Å on the opposite side to manganese. The three bonds C–C (phospholyl ring) are equivalent. Their average length, 1.420 (8) Å, is the same as in several π-bonded cyclopentadienyl rings. The bond P–C (benzoyl) is longer by 0.065 (12) Å than the bond P–C (hydrogen); their average length (1.765 (7) Å) is intermediate between a single and a double bond (P–C). The other parts of the molecule are not altered when compared to other manganese cyclopentadienyl complexes.

In both nitrogen and sulfur organic chemistries, a great emphasis is put on aromatic heterocycles, e.g., pyrrole, pyridine, and thiophene. This is, for a notable part, due to the extreme ease of their functionalization which allows the synthesis of a tremendous array of derivatives. One of the most powerful tools for grafting a functional group onto these rings is the C-electrophilic substitution (e.g., Friedel–Crafts). On the contrary, a rather frustrating situation is encountered when studying the phosphorus analogues of these compounds, namely, phospholes and λ^3 phosphorins; indeed, the synthesis of their functional derivatives is always rather difficult because direct C-functionalization of these rings is impossible (both electrophilic and nucleophilic attacks occur at the phosphorus atom[2,3]). Thus, rather complex procedures were devised to obtain some simple derivatives of these heterocycles. See, for example, ref 4 and 5.

When starting our work on phosphacymantrenes (phos-

pholylmanganese tricarbonyls), we had two ideas in mind: first, to synthesize the first phosphorus heterocycles with a true aromatic chemistry; second, to use an undoubtedly aromatic tricoordinated phosphorus heterocycle as a reference to discriminate between the various "proofs" for and against aromaticity in the phosphole nucleus. Indeed, this last point is still a very controversial matter.[3] For that purpose, we focused our attention on the phospholyl derivatives since the phospholyl anions are isoelectronic with thiophenes and, thus, potentially strongly aromatic.[6] Nevertheless electrophilic attacks always occur at phosphorus in the free anions[7] because of the strong negative charge which is borne by the heteroatom. Thus, we chose more precisely to study the phospholyl π-aromatic complexes. We selected the manganese tricarbonyl derivatives because they were isoelectronic with the long-known thiophenechromium tricarbonyls[8] and because, recently, an arsenic analogue was briefly described.[9] The results of the first ex-

tensive chemical study and of the first structural character-ization of one member of this new family are given hereafter.

Results and Discussion

Synthesis. In a preliminary work,[10] we studied in some depth the reaction of 1-phenyl-3,4-dimethylphosphole (**1**) with de-cacarbonyldimanganese. At 100 °C in cyclohexane under UV irradiation, it gave, beside the classical σ complex axial $LMn_2(CO)_9$ (L = **1**), mainly a σ, π complex **2a** analogous to

1

2a, R = C_6H_5
 b, R = n-C_4H_9
 c, R = t-C_4H_9
 d, R = $Mn(CO)_5$

3   4
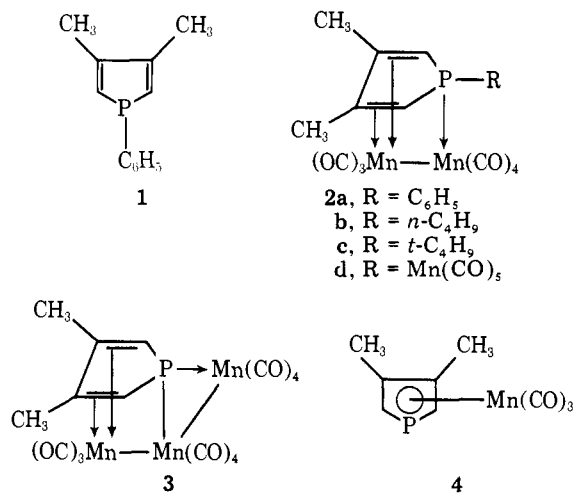
2c, the structure of which was definitively established later by an x-ray study.[11] Complex **2a** reacted with an excess of $Mn_2(CO)_{10}$ at 0 °C under UV to give a new complex in which the P-phenyl bond had been broken. This new complex was thought primarily[10] to have structure **2d** mainly on the basis of its mass spectrum, which showed a very weak peak of m/e 612. However, the x-ray study[11] proved that the correct structure was **3**. This phospholyl complex decomposed upon heating to give inter alia the desired π aromatic complex **4** but we were unable to isolate **4** in the pure state.

In order to get pure samples of **4** by a much simpler method, we decided to reinvestigate the reaction of **1** with $Mn_2(CO)_{10}$ with different experimental conditions. Since it had been shown in the literature that $Mn_2(CO)_{10}$ was able to cleave an As-phenyl bond in boiling xylene (150 °C) without UV irradiation,[12] we reacted **1** with $Mn_2(CO)_{10}$ under these conditions. The reaction gave mainly **4** with yields up to 80% when using equimolar quantities of **1** and $Mn_2(CO)_{10}$. This result was disclosed in a preliminary communication.[13]

The reaction also yielded another much heavier 3,4-di-methylphospholyl complex which was best obtained (~20% yield) when using a ratio $Mn_2(CO)_{10}/1$ = 2. We have tenta-tively identified this complex as **2d** mainly on the basis of its mass spectrum, which is very similar to that of **3** (heavier peak

of m/e 612), of its C, H, Mn, P analysis, which agrees very well with the proposed formula, of its ^{1}H NMR spectrum, which shows that the dienic system is complexed (high shielding of the olefinic protons), and of its ^{31}P chemical shift, which is very close to that of **2a** (δ^{31}P 28.6 ppm), **2b** (δ [31]P 33.9 ppm), and **2c** (δ^{31}P 53.3 ppm). The full comparison between **2d**, **3**, and **4** is made hereafter. **2d**: orange solid; mp 86 °C; highly soluble in organic solvents; eluted on silica gel (Merck 70-230 mesh) by a cyclohexane-benzene mixture (80:20); ^{1}H NMR (CDCl₃, internal Me₄Si) δ 2.17 (s, CH₃), 4.52 (d, J_{H-P} = 31 Hz, CHP); δ^{31}P (external H₃PO₄ + for downfield shifts) 42.4 ppm; IR ν_{CO} (cm⁻¹) 2095 m, 2037 s, 2024 m, 2014 m, 1996 vs (br), 1974 m (br), 1969 m (br), 1954 m (br), 1939 w (br) (decalin). **3**: deep red solid; mp 196 °C dec; low solubility in organic sol-vents; eluted on silica gel by a cyclohexane-benzene mixture (80:20); ^{1}H NMR δ 2.44 (s, CH₃), 3.05 (d, J_{H-P} = 31 Hz, CHP); δ^{31}P 74 ppm; IR ν_{CO} 2077 m, 2032 vs, 2011 w, 1995 vs (br), 1971 w (br) (CHCl₃). **4**: yellow solid; mp 26 °C; sublimes readily under vacuum at room temperature; strong campho-raceous odor like cymantrene itself;[14] high thermal stability; very high solubility in organic solvents; eluted on silica gel by pentane; ^{1}H NMR δ 2.13 (s, CH₃), 4.38 (d, J_{H-P} = 35.5 Hz, CHP); δ^{31}P −46.6 ppm; IR ν_{CO} (cm⁻¹) 2025 s, 1953 vs, 1941 vs (decalin).

On the basis of the ^{1}H NMR spectra it appears that **2d** is (with **4**) one of the decomposition products of **3** upon heating; this fact explains the presence of the m/e 612 peak in the mass spectrum of **3**. Thus we can tentatively summarize our results as in Scheme I. Using the reaction of $Mn_2(CO)_{10}$ with 1-phenylphosphole (**5**) and 1-phenyl-3-methylphosphole (**6**) in boiling xylene, we also prepared phosphacymantrene **7** and its 3-methyl derivative **8**.

5, R = H   7, R = H   yield ~50%
6, R = CH₃   8, R = CH₃   ~40%
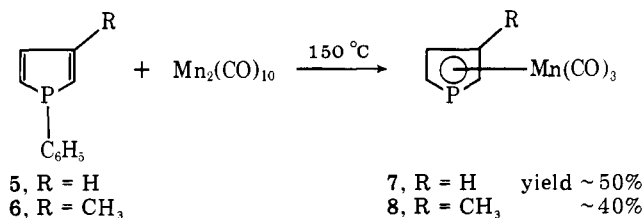
Chemical Reactivity. Since **4** is the most readily available compound in this family all the reactions so far studied were performed with **4**. We have systematically studied the reactions of **4** with some electrophiles and nucleophiles.

C-Acetylation of **4** with CH₃COCl-AlCl₃ takes place easily near room temperature in CH₂Cl₂. On the contrary C-ben-zoylation with C₆H₅COCl-AlCl₃ needs higher temperature (110 °C in (CHCl₂)₂) whereas it goes to completion near room temperature in CS₂ with cymantrene.[15] In the same way we have not succeeded when attempting a C-alkylation of **4** by a C₂H₅Br-AlCl₃ mixture in boiling CH₂Cl₂ whereas numerous successful alkylations of cymantrene have been described in

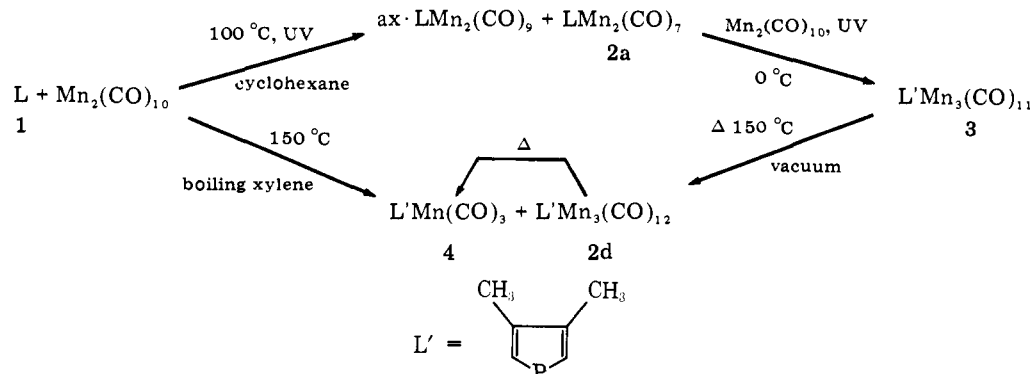**Scheme I.** Reactions of 1-Phenyl-3,4-dimethylphosphole (L) with $Mn_2(CO)_{10}$

L' =

Table I. ^{13}C and ^{31}P NMR of Phosphacymantrenes[a]

| compd		ring carbons δ	J_{C-P}	substituents	CO	δ^{31}P
4	C α	96.8	62	Me 15.0	223.8	−46.6
	C β	111.8	7.7			
7	C α	96.2	65.4		223.2	−25.6
	C β	93.8	7.7			
8	C$_{(2)}$	95.5	62.2	Me 16.2	223.8	−28.7
	C$_{(3)}$	113.9	8.7			
	C$_{(4)}$	94.4	7.8			
	C$_{(5)}$	97.7	63.8			
9	C$_{(2)}$	103.2	63.7	Me 14.1 and 15.3	222.5	−15.8
	C$_{(3)}$	115.3	5.5	*CO*Me 198 J_{C-P} = 23.4		
	C$_{(4)}$	113.9	7.8	CO*Me* 30.2 J_{C-P} = 7.6		
	C$_{(5)}$	97.1	62.3			
10	C$_{(2)}$	111.0	66.6	Me 14 and 15.5	222.5	−22.3
	C$_{(3)}$	113.7	5.0	*CO*Ph 194.1 J_{C-P} = 19.8		
	C$_{(4)}$	111.3	7.8	Ph 138.5, 133,		
	C$_{(5)}$	96.6	64.4	129.3, and 128.4		

[a] δ in parts per million; J in hertz; references internal Me$_4$Si for ^{13}C and external H$_3$PO$_4$ for ^{31}P; δ^{31}P positive for downfield shifts; products in solution in CDCl$_3$.

the literature.[15] An unsuccessful attempt to prepare the 2-CHO derivative by reaction of **4** with Cl$_2$CHOCH$_3$–AlCl$_3$ in boiling tetrachlorethane by analogy with the work of Tirosh et al.[16] on cymantrene is also noteworthy.

9, R = CH$_3$ yield ~80%
10, R = C$_6$H$_5$ yield ~70%
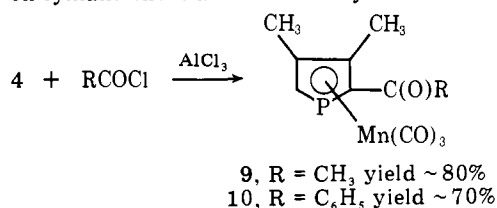
On the basis of these qualitative data, two conclusions are obvious: (a) It is possible to perform electrophilic attacks on the phospholyl ring carbons of **4** and, thus, phosphacymantrenes are, together with phosphaferrocenes,[17] the first carbon–phosphorus heterocycles with a true aromatic chemistry. It is interesting to compare the straightforward behavior of **4** toward acylating agents with the rather complicated reaction of azacymantrene with acetyl chloride. In this latter case a partial decomplexation of the pyrrolyl ring occurs during the acetylation.[18] (b) The reactivity of the phospholyl ring toward electrophiles is much lower than that of the cyclopentadienyl ring in their manganese tricarbonyl complexes. We also decided to check whether or not phosphorus retained some of its nucleophilicity in **4**. For that purpose we studied its reactivity toward benzyl bromide in boiling toluene and toward iodine in boiling CCl$_4$. Both the attempted quaternization and oxidation failed completely. Since it is well known that free phospholes readily react with these reagents,[19] it is obvious from these observations that phosphorus has lost its nucleophilicity upon complexation.

We then turned our attention toward the reactions of nucleophiles with **4**. Since Nesmeyanov and co-workers[20] had described the 2-lithiation of cymantrene by *n*-butyllithium in THF at −40 °C we made a similar experiment with **4**. Contrary to our expectation, we observed a nucleophilic attack at phosphorus with destruction of the phospholyl–Mn bond which yielded 1-butyl-3,4-dimethylphosphole (**11**) characterized as its *P*-sulfide.

yield 68%
(*P*-sulfide)

11
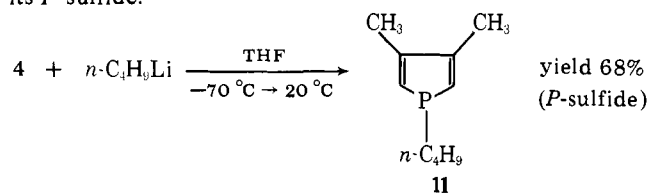
An attempt to trap a hypothetical transient C–Li derivative of **4** by adding benzophenone to the *n*-C$_4$H$_9$Li-4-THF mixture after 3 h at −40 °C failed completely; we just obtained **11** as previously. The high electrophilicity of P in **4** was confirmed by the reactions of **4** with C$_2$H$_5$ONa in THF, (C$_2$H$_5$)$_2$NLi in THF, and even NaCN in ethanol. In every case we observed the destruction of **4** but we were unable to isolate the expected phospholes probably owing to their low stability. At this point, it must be remembered that free phospholes are also attacked at P by nucleophiles but only by the very strong ones such as *n*- and *t*-C$_4$H$_9$Li.[21] Finally the behavior of the phosphorus atom in **4** parallels that of the phosphorus atom in phosphorins[2] (high electrophilicity and low nucleophilicity).

Spectral Data. Numerous ^{1}H NMR, IR, and mass spectral data have been already given in the preliminary communication.[13] The few such data still lacking are given in the Experimental Section. All the ^{13}C and ^{31}P NMR data available are summarized in Table I.

The comparison of the ^{13}C data for cymantrene[22] and phosphacymantrene (**7**) is especially interesting. The CO groups of **7** are shielded by comparison with those of cymantrene (δ^{13}C 224.9) up to the same extent as the CO of acetyl-cymantrene (δ^{13}C 223.2). The comparison of the IR data (ν C=O 2025 and 1938 cm^{-1} for cymantrene;[23] $\nu_{C=O}$ 2032, 1958, and 1954 cm^{-1} for **7**) also suggests that phospholyl is a weaker electron donor than cyclopentadienyl toward the Mn(CO)$_3$ moiety. At the same time the ring carbons of **7** are strongly deshielded by comparison with those of cymantrene (δ^{13}C 83.1). Since it has been shown previously that the reactivity of the ring carbons toward electrophiles was much lower in **7** than in cymantrene, very probably the electron density on these carbons is noticeably lower in **7**. All these combined facts suggest that, even though phosphorus fully participates to the delocalization in the phospholyl ring of **7**, it also acts as a "well" (contrary to its CH counterpart in cymantrene) decreasing the electron density on the other parts of the molecule. The comparison between phospholes and phosphacymantrenes is also especially interesting. Phosphacymantrenes are characterized by a very high (for a P^{III} derivative) $^1J_{P-C}$ coupling constant (ca. 65 Hz) in the same way as phosphorins[24] ($^1J_{P-C}$ ca. 55 Hz) and phosphaferrocenes[17] ($^1J_{P-C}$ ca. 60 Hz) but in sharp contrast with phospholes[25,26] ($^1J_{P-C}$ ca. 5 Hz). In this last case the coupling constants, even somewhat low, are close to those found for classical phosphines[25] ($^1J_{P-C}$ = 12.5 Hz in P(C$_6$H$_5$)$_3$). These results suggest some analogy between the P–C bonds of phosphacymantrenes and phosphorins.

On the other hand the $^3J_{P-C}$ couplings between the methyl

Table II. Relative Coordinates and Thermal Motion Parameters ($\times 10^4$ Å^2)[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0.3758 (1)	0.4703 (1)	0.2012 (1)	375 (7)	416 (8)	372 (7)	15 (8)	7 (5)	−25 (8)
P	0.4302 (1)	0.3862 (2)	−0.0749 (1)	422 (16)	543 (17)	521 (16)	33 (13)	12 (12)	27 (13)
C(2)	0.3547 (4)	0.3238 (8)	−0.0029 (12)	424 (53)	335 (53)	473 (50)	−53 (44)	90 (41)	−104 (43)
C(3)	0.3050 (4)	0.4116 (9)	−0.0081 (11)	423 (57)	492 (60)	334 (48)	−52 (50)	4 (41)	4 (46)
C(4)	0.3277 (4)	0.5289 (9)	−0.0638 (11)	473 (56)	459 (52)	368 (46)	175 (59)	17 (40)	−3 (48)
C(5)	0.3937 (5)	0.5288 (9)	−0.1003 (12)	557 (60)	423 (55)	398 (46)	−27 (55)	35 (41)	−40 (50)
C(6)	0.2362 (5)	0.3851 (12)	0.0197 (17)	460 (67)	915 (97)	712 (79)	−190 (68)	51 (58)	−211 (72)
C(7)	0.2853 (7)	0.6385 (11)	−0.0948 (19)	789 (80)	661 (81)	683 (76)	57 (76)	−109 (71)	196 (63)
C(8)	0.3463 (4)	0.1924 (9)	0.0558 (13)	555 (60)	447 (65)	590 (62)	−130 (48)	169 (48)	−54 (48)
C(9)	0.3809 (4)	0.0975 (9)	−0.0601 (12)	414 (58)	450 (61)	443 (53)	−51 (45)	16 (41)	−73 (47)
C(10)	0.3944 (5)	0.1109 (10)	−0.2571 (14)	585 (67)	552 (64)	503 (70)	54 (55)	78 (50)	−156 (54)
C(11)	0.4246 (5)	0.0181 (13)	−0.3628 (16)	518 (67)	837 (92)	711 (72)	−24 (74)	43 (60)	−248 (77)
C(12)	0.4428 (6)	−0.0851 (12)	−0.2683 (23)	742 (89)	528 (74)	1295 (124)	−38 (65)	148 (81)	−381 (83)
C(13)	0.4290 (6)	−0.1007 (10)	−0.0746 (22)	699 (84)	548 (75)	1188 (110)	20 (67)	21 (78)	141 (78)
C(14)	0.3979 (5)	−0.0112 (9)	0.0346 (17)	712 (71)	387 (63)	763 (69)	−54 (53)	63 (66)	34 (58)
C(15)	0.3888 (4)	0.6218 (9)	0.2961 (13)	593 (62)	408 (61)	534 (53)	75 (51)	−132 (45)	−151 (47)
C(16)	0.3180 (4)	0.4395 (8)	0.3903 (13)	483 (60)	687 (70)	371 (50)	3 (48)	−34 (46)	−83 (45)
C(17)	0.4380 (5)	0.4037 (9)	0.3439 (14)	538 (62)	565 (62)	567 (58)	135 (53)	−65 (50)	−103 (52)
O(1)	0.3966 (3)	0.7191 (6)	0.3495 (11)	932 (58)	484 (51)	1055 (59)	57 (42)	−261 (44)	−323 (43)
O(2)	0.2813 (3)	0.4203 (7)	0.5096 (10)	760 (51)	1466 (79)	593 (56)	−329 (48)	281 (41)	−166 (44)
O(3)	0.4777 (4)	0.3587 (7)	0.4352 (10)	876 (58)	932 (60)	771 (51)	311 (47)	−266 (42)	−17 (45)
O(4)	0.3130 (4)	0.1632 (6)	0.1914 (11)	1514 (69)	522 (46)	1001 (54)	−141 (46)	843 (50)	11 (43)
H(5)	0.408 (6)	0.613 (11)	−0.111 (17)	760[b]					
H(10)	0.375 (6)	0.172 (11)	−0.325 (17)	760					
H(11)	0.424 (5)	0.050 (11)	−0.500 (17)	760					
H(12)	0.456 (5)	−0.139 (11)	−0.370 (16)	760					
H(13)	0.448 (5)	−0.147 (11)	−0.004 (17)	760					
H(14)	0.384 (5)	−0.030 (11)	0.164 (16)	760					
H(61)	0.280 (6)	0.656 (13)	0.811 (17)	760					
H(62)	0.310 (7)	0.700 (12)	−0.078 (21)	760					
H(63)	0.246 (6)	0.634 (12)	0.972 (17)	760					
H(71)	0.211 (6)	0.383 (12)	−0.098 (16)	760					
H(72)	0.211 (6)	0.437 (11)	0.114 (17)	760					
H(73)	0.232 (6)	0.330 (11)	0.089 (18)	760					

[a] The temperature factor is $\exp(-2\Pi^2 \Sigma_i \Sigma_j U_{ij} H_i a^*_i h_j a^*_j)$. Esd's are given in parentheses. [b] The thermal motion for hydrogen was not refined. The value $U_{11} = 0.0760$ Å^2 corresponds to a fixed arbitrary isotropic value of $B = 6.00$ Å^2.

Table III. Description[a] of Thermal Motion for the "Mn(CO)$_3$" Moiety

bond	$U_{z,Mn}$	$U_{z,C}$	$U_{z,O}$	$U_{x,C}$	$U_{x,O}$	w_C	w_O
Mn–C(15)–O(1)	0.0398	0.0334	0.0345	0.0601	0.1065	4.68	5.10
Mn–C(16)–O(2)	0.0379	0.0490	0.0391	0.0526	0.1213	3.74	5.60
Mn–C(17)–O(3)	0.0388	0.0463	0.0463	0.0603	0.1060	4.73	5.08
av	0.0388	0.0429	0.0400	0.0577	0.1113	4.38	5.26

[a] The mean square amplitudes are given in Å^2 in the direction of the bond (U_z), and in a normal direction (U_x) to the bond. w_C and w_O are the root mean square values of the amplitudes of angular motion around manganese for the carbon and the oxygen nuclei; the values are given in degrees.

carbons of **4**, **8**, **9**, and **10** and the phosphorus atom have completely disappeared whereas β-methyl carbons are coupled with phosphorus in the phosphole family ($^3J_{P-C}$ ca. 5 Hz[26]). A conformational origin of this phenomenon is not excluded since the phosphacymantrene ring is almost flat (see the structural features of **10**) contrary to the phosphole ring which is puckered.[27]

When 2,4,6-triphenylphosphorin is π complexed with Cr(CO)$_3$[28] or Mo(CO)$_3$[29] a tremendous high-field shift of the phosphorus atom is observed (ca. 174 ppm). On the contrary only limited shifts of the phosphorus atom either to high fields or to low fields are observed upon P-complexation of this phosphorin by M(CO)$_5$ (M = Cr, Mo, W).[30] Thus the high shielding of the phosphorus atom of phosphacymantrenes and phosphaferrocenes[17] either by comparison with free phospholes or with their complexes is highly significant and is probably characteristic of π-phospha aromatic complexes in general.

Crystal Structure of Compound 10. The bond lengths were corrected for thermal vibration.[43] (a) For the Mn(CO)$_3$ moiety, it seems reasonable to assume a riding motion of each

carbonyl group around the manganese atom, as indicated by the similarity of the amplitudes of angular motion around Mn for the carbon and oxygen nuclei (root mean square values 4.38 and 5.26°. See Table III). (b) The other bond lengths (with the exception of C-H) were corrected by the rigid-body approximation. The resulting bond lengths and the angles are reported in Table IV.

The molecular structure of **10** is shown in Figure 1 together with the labeling scheme for the atoms. Each nonhydrogen atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density. Figure 2 shows (left) a projection[41] of the molecule on the plane defined by the carbon atoms C(2) to C(5) of the phospholyl ring and (right) a projection of the cyclopentadienylmanganese tricarbonyl molecule[42] on the plane defined by the cyclopentadienyl ring. Both complexes are mononuclear, with an 18-electron closed-shell configuration. Their overall molecular geometries are similar; the projection of one carbonyl intersects a C–C bond in each ring, whereas the two remaining carbonyls are nearly eclipsed with respect to a carbon atom and the phos-

Table IV. Bond Lengths (Å) and Angles (deg)

	uncor	cor for thermal motion	av^a		uncor	av^a
Bond Lengths						
Mn–P	2.379 (2)	2.387		C(5)–H(5)	0.96 (11)	
				C(6)–H(61)	0.95 (11)	
Mn–C(2)	2.155 (8)	2.161		C(6)–H(62)	1.00 (11)	
Mn–C(3)	2.150 (8)	2.159		C(6)–H(63)	0.77 (11)	
Mn–C(4)	2.156 (8)	2.167		C(7)–H(71)	0.82 (12)	
Mn–C(5)	2.176 (8)	2.188	2.169 (4)	C(7)–H(72)	0.85 (14)	
				C(7)–H(73)	0.94 (12)	
Mn–C(15)	1.789 (9)	1.795		C(10)–H(10)	0.90 (11)	
Mn–C(16)	1.800 (8)	1.804		C(11)–H(11)	0.99 (12)	
Mn–C(17)	1.777 (9)	1.783	1.794 (5)	C(12)–H(12)	0.95 (12)	
				C(13)–H(13)	0.79 (11)	
C(15)–O(1)	1.130 (11)	1.136		C(14)–H(14)	0.94 (11)	0.91 (4)
C(16)–O(2)	1.139 (11)	1.149				
C(17)–O(3)	1.146 (12)	1.152	1.146 (7)			
P–C(2)	1.793 (8)	1.808				
P–C(5)	1.737 (10)	1.743	1.765 (7)			
			0.065 (12)^b			
C(2)–C(3)	1.414 (12)	1.419				
C(3)–C(4)	1.414 (13)	1.423				
C(4)–C(5)	1.407 (12)	1.418	1.420 (8)			
C(3)–C(6)	1.486 (14)	1.498				
C(4)–C(7)	1.502 (16)	1.508				
C(8)–C(2)	1.494 (12)	1.502				
C(8)–C(9)	1.488 (12)	1.493	1.500 (6)			
C(8)–O(4)	1.200 (11)	1.211				
C(9)–C(10)	1.374 (12)	1.387				
C(10)–C(11)	1.392 (16)	1.396				
C(11)–C(12)	1.347 (19)	1.354				
C(12)–C(13)	1.357 (21)	1.370				
C(13)–C(14)	1.388 (16)	1.392				
C(14)–C(9)	1.390 (13)	1.398	1.383 (7)			
Bond Angles						
C(2)–P–C(5)		88.5 (4)		C(14)–C(9)–C(10)		119.1 (9)
P–C(2)–C(3)		113.1 (5)		C(9)–C(10)–C(11)		121.3 (9)
C(2)–C(3)–C(4)		111.4 (7)		C(10)–C(11)–C(12)		119.2 (10)
C(3)–C(4)–C(5)		112.3 (8)		C(11)–C(12)–C(13)		120.3 (12)
C(4)–C(5)–P		114.7 (6)		C(12)–C(13)–C(14)		122.1 (11)
				C(13)–C(14)–C(9)		118.0 (10)
P–Mn–C(2)		46.3 (2)				
P–Mn–C(5)		44.6 (2)		C(8)–C(2)–P		122.6 (5)
C(2)–Mn–C(3)		38.4 (3)		C(8)–C(2)–C(3)		124.3 (8)
C(3)–Mn–C(4)		38.3 (3)		O(4)–C(8)–C(2)		121.8 (8)
C(4)–Mn–C(5)		37.9 (3)		O(4)–C(8)–C(9)		120.6 (8)
Mn–C(15)–O(1)		177.6 (6)		C(2)–C(8)–C(9)		117.6 (7)
Mn–C(16)–O(2)		179.8 (6)		C(8)–C(9)–C(10)		122.9 (8)
Mn–C(17)–O(3)		178.8 (6)		C(8)–C(9)–C(14)		118.0 (8)
C(15)–Mn–C(16)		91.0 (4)		C(6)–C(3)–C(2)		125.8 (9)
C(16)–Mn–C(17)		91.9 (4)		C(6)–C(3)–C(4)		122.6 (9)
C(17)–Mn–C(15)		93.9 (4)		C(7)–C(4)–C(3)		123.5 (9)
				C(7)–C(4)–C(5)		124.1 (9)

^{a} The standard deviations of an average value $\bar{l} = \Sigma l_i/n$ were calculated as $\sigma(\bar{l}) = (\Sigma\sigma^2(l_i))^{1/2}/n$. ^{b} The standard deviation of the bond length difference $(l_1 - l_2)$ was calculated by $\sigma^2(l_1 - l_2) = \sigma^2(l_1) + \sigma^2(l_2) - 2\cos(l_1, l_2) = \sigma^2(A) + 2\sigma^2(B)(1 - \cos\beta) + \sigma^2(C)$, where $l_1 = (P-C(2))$, $l_2 = (P-C(5))$, β = angle $(C(2)PC(5))$, and $\sigma(A)$, $\sigma(B)$, $\sigma(C)$ are the standard deviations for the positions of $C(2)$, P, $C(5)$.

phorus atom of the phospholyl ring and to two carbon atoms of the cyclopentadienyl ring, respectively. No pseudosymmetry is observed in either molecule.

The phospholyl ring is not strictly planar; it is slightly bent around the axis defined by the C(2) and C(5) atoms. The carbon moiety of the ring is planar within experimental error (root mean square deviation 0.001 Å) but the phosphorus atom lies out of this carbon mean plane by 0.048 (2) Å, on the opposite side to manganese. The dihedral angle between the mean plane C(2) to C(5) and the plane C(2)–P–C(5) is 2.15°. The whole deformation is similar to that found in phosphaferro-

cene.[17] The three carbon–carbon bond lengths in the phospholyl ring are equivalent and their mean value, 1.420 (8) Å, is close to several values found in cyclopentadienyl rings π bonded to manganese (see Table V). On the other hand, the bond lengths P–C(2) [1.808 (8) Å] and P–C(5) [1.743 (10) Å] are inequivalent. This inequivalence is surprisingly large especially since the C–C distances in the phospholyl ring are identical within experimental error. The difference in P–C bond lengths probably follows from the difference in environment of the two carbon atoms, C(2) being bound to a benzoyl group and C(5) to a hydrogen. In contrast, phos-

Table V. Comparison of Average Bond Lengths (Å) Found in Some Related Compounds

compd	(C–C) ring	Mn–C (ring)	Mn–C (carbonyl)	C–O	Mn–Ω^a	Mn–P	ref
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	1.42 ± 0.03	2.165 ± 0.025	1.80 ± 0.02	1.15 ± 0.03	1.80		42
$(\eta^5\text{-}C_6H_7)Mn(CO)_3{}^b$	1.401 ± 0.014	2.177 (5)	1.789 ± 0.009	1.158 ± 0.012	1.686		49
$[\eta^5\text{-}PC_4H(CH_3)_2(COC_6H_5)]\text{-}Mn(CO)_3{}^c$	1.420 (8)	2.169 (4)	1.794 (5)	1.146 (7)	1.757 (1)^d	2.387 (2)	this work
$Mn(NO)(CO)_2(P(C_6H_5)_3)_2$						2.278 (5)	50
$Mn(NO)(CO)_3P(C_6H_5)_3$						2.305 (4)	51
$Mn(NO)(CO)(5\text{-}exo\text{-}CH_3\text{-}C_5H_5)P(C_6H_5)_3$						2.285 (2)	52

^{a} Mn–Ω represents the distance of manganese to the π-cyclopentadienyl mean plane. ^{b} Values uncorrected for thermal motion. ^{c} The standard deviations of an average value ($\bar{l} = \Sigma l_{i/n}$) were calculated as $\sigma(\bar{l}) = (\Sigma\sigma^2(l_i))^{1/2}/n$. ^{d} Mn–$\Omega$ represents the distance of manganese to the carbon moiety C(2) to C(5) of the phospholyl ring.
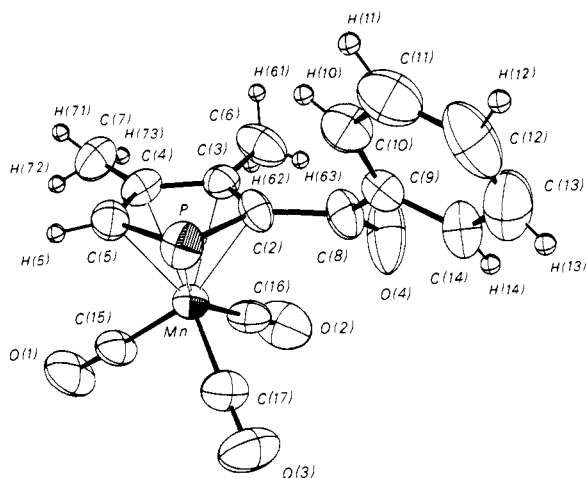

Figure 1. ORTEP drawing of the molecule 10. The thermal ellipsoids of the nonhydrogen atoms are for a 50% probability.

Figure 2. Projection of the phosphacymantrene molecule on the plane defined by the four carbon atoms C(2)–C(5) (left). Projection of the cyclopentadienylmanganese tricarbonyl molecule (ref 42) on the plane defined by the cyclopentadienyl ring (right). Both ORTEP projections are drawn on the same scale in a similar orientation for the carbonyls.

phaferrocene[17] has equivalent phosphorus–carbon bonds (1.758 (5) and 1.768 (5) Å, values not corrected for thermal motion). In compound 10, the phosphorus–carbon bond lengths are intermediate between single-bond values found in tertiary phosphines and double-bond values found in phosphonium ylides (1.85 and 1.661 (8) Å[44,45]). The shorter distance P–C(5) is closer to the phosphorus–carbon bond lengths found in another aromatic ring containing one phosphorus atom, e.g., 2,6-dimethyl-4-phenylphosphorin (1.74 Å).[46] The longer distance P–C(2) is closer to the bond lengths found in 1-benzylphosphole (1.783 Å)[47] and aluminum tris(dibenzoylphosphide) (1.772 (2) Å).[48]

The phospholyl ring is π bonded to the manganese atom in the same manner as a cyclopentadienyl ring. The four Mn–C (phospholyl ring) bond lengths are equivalent and similar to Mn–C (cyclopentadienyl ring) values found in $[(C_5H_5)\text{-}Mn(CO)_3]$.[42] The Mn–P bond is weaker than a P-bonded manganese-triphenylphosphine bond (see Table V). The manganese is somewhat nearer to the planar carbon moiety of the phospholyl ring, 1.758 (1) Å. This value is intermediate between those found in cyclopentadienyl and cyclohexadienyl rings π bonded to manganese.

No anomalies are observed in the geometry of the carbonyl and the benzoyl groups, when compared to related structures. The mean plane of the carbon atoms of the phospholyl ring is nearly parallel to the two planes defined by C(15), C(16), C(17), and O(1), O(2), O(3); the dihedral angles are 1.33 and 1.80°. The manganese atom lies above those planes by 0.991 (1) and 1.604 (1) Å, respectively. The ketone group is strictly planar, and the benzene ring is planar within experimental error; the dihedral angle between them is 29.96° (see Table
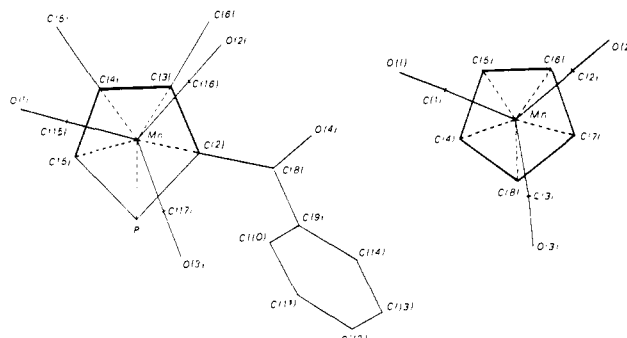
VI). Finally, all nonbonded distances less than 3 Å are listed in Table VII. None of these distances is abnormally short. There is no indication of strong intermolecular forces, which could induce molecular deformations.

Experimental Section

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL PS 100 FT spectrometer by Mrs. Mankowski-Favelier. The spectral data which are not given hereafter are presented in ref 13. The starting phospholes 1, 5, and 6 were prepared according to ref 21 and 31. All the experiments are conducted under argon.

3,4-Dimethylphospholyldodecacarbonyltrimanganese (2d). A mixture of 1 (0.94 g) and $Mn_2(CO)_{10}$ (4 g) in xylene (50 cm^3) is heated at 150 °C with stirring for 4 h. After cooling, the solution is filtrated and evaporated. The residue is chromatographed on silica gel 60 Merck, 70–230 mesh, with benzene–cyclohexane (20:80). Yellow products are eluted first and then an orange oil is obtained ($R_f \sim 0.3$) which crystallizes slowly, mp 86 °C (hexane), yield 0.69 g (22.5%). Anal. Calcd for $C_{18}H_8Mn_3O_{12}P$: C, 35.32; H, 1.32; Mn, 26.93; P, 5.06. Found: C, 35.18; H, 1.34; Mn, 26.81; P, 5.23.

3,4-Dimethylphosphacymantrene (4). A mixture of 1 (1.88 g, 0.01 mol) and $Mn_2(CO)_{10}$ (3.9 g, 0.01 mol) is reacted as above. After filtration and evaporation, the residue is thoroughly extracted with hexane. This extract is chromatographed on silica gel with pentane. The first yellow band is $Mn_2(CO)_{10}$. The second yellow band (which gives a white spot on a TLC sheet with iodine) contains 4 ($R_f \sim 0.46$), yield up to 2 g (80%). The product may be further purified by vacuum sublimation at room temperature under 0.1 mmHg onto a cold finger at −60 °C.

Phosphacymantrene (7). A mixture of 5 (1.6 g) and $Mn_2(CO)_{10}$ (3.9 g) is treated as above. A yellow solid is obtained, mp 56–60 °C, yield 1.2 g (54%). Anal. Calcd for $C_7H_4MnO_3P$: C, 37.87; H, 1.82. Found: C, 37.90; H, 1.86. Mass spectrum (70 eV): m/e 222 ($I = 7\%$, M), 166 ($I = 9\%$, M − 2CO), 138 ($I = 45\%$, M − 3CO), 55 ($I = 100\%$, Mn). Only the main peaks of $m/e \geqslant 55$ are given.

3-Methylphosphacymantrene (8). A mixture of 6 (1.74 g) and

Table VI. Least-Squares Planes[a]

mean plane I through the carbon moiety of the phospholyl ring
$-0.1711X - 0.2215Y - 0.9600Z + 2.0346 = 0$

C(2)*[b]	-0.0003 (79)
C(3)*	0.0007 (79)
C(4)*	-0.0007 (76)
C(5)*	0.0004 (81)
Mn	-1.758 (1)
P	0.048 (2)
C(6)	0.131 (12)
C(7)	0.090 (13)
C(8)	-0.036 (9)
C(15)	-2.786 (9)
C(16)	-2.706 (9)
C(17)	-2.749 (10)
O(1)	-3.397 (7)
O(2)	-3.305 (7)
O(3)	-3.378 (7)

mean plane II through the benzene ring
$-0.8830X - 0.4053Y - 0.2365Z + 7.3908 = 0$

C(9)*	-0.005 (8)
C(10)*	-0.002 (10)
C(11)*	0.015 (11)
C(12)*	-0.017 (12)
C(13)*	0.000 (12)
C(14)*	0.009 (10)
C(8)	0.035 (9)
O(4)	0.566 (8)

mean plane III through the ketone group
$-0.7794X - 0.0768Y - 0.6218Z + 6.0616 = 0$

C(2)*	-0.000 (8)
C(8)*	0.000 (9)
C(9)*	-0.000 (8)
O(4)*	-0.000 (8)
P	-0.984 (3)

plane IV defined by C(15), C(16), and C(17)
$-0.1516X - 0.1984Y - 0.9683Z + 4.5221 = 0$

Mn	0.991 (1)

plane V defined by O(1), O(2), and O(3)
$-0.1521X - 0.2094Y - 0.9659Z + 5.1924 = 0$

Mn	1.604 (1)

dihedral angle (deg) between the planes

I, (C(2), P, C(5))	2.15
I, II	62.10
I, III	41.64
I, IV	1.33
I, V	1.80
II, III	29.96

[a] The equation of each plane is expressed with coordinates (X,Y,Z) referred to an orthogonal system (A,B,C) oriented with respect to the crystallographic axis such that A and B are parallel to a and b, and C is parallel to c^*. [b] Planes are calculated using unit weights for each atom marked with an asterisk.

$Mn_2(CO)_{10}$ (3.9 g) is treated as above. A yellow oil is obtained, yield 1 g (42%). This product seems to be less stable than either **4** or **7**. Mass spectrum: m/e 236 (I = 26%, M), 180 (I = 31%, M $-$ 2CO), 152 (I = 100%, M $-$ 3CO), 55 (I = 39%, Mn).

2-Acetyl-3,4-dimethylphosphacymantrene (9). A mixture of **4** (1.25 g), $AlCl_3$ (2.5 g), and CH_3COCl (2.5 cm³) in methylene chloride (35 cm³) is heated at 40 °C with stirring for 8 h. The solution turns deep red. The mixture is hydrolyzed on ice. The CH_2Cl_2 layer is washed first with aqueous CO_3Na_2, then with water until neutrality. After evaporation, the residue is chromatographed on silica gel with benzene. An orange oil is thus obtained, yield 1.2 g (82%). Anal. Calcd for $C_{11}H_{10}MnO_4P$: C, 45.21; H, 3.45; P, 10.61. Found: C, 45.70; H, 3.63; P, 10.56. Mass spectrum: m/e 292 (I = 19%, M), 236 (I = 22%, M $-$ 2CO), 208 (I = 100%, M $-$ 3CO), 180 (I = 17%, M $-$ 4CO), 125 (I = 9%, 180 $-$ Mn), 70 (I = 18%, CH_3Mn), 55 (I = 41%, Mn).

2-Benzoyl-3,4-dimethylphosphacymantrene (10). A mixture of **4** (1 g), $AlCl_3$ (2 g), and C_6H_5COCl (1 cm³) in tetrachlorethane (40 cm³) is heated at 110 °C with stirring for 6 h. The solution is then worked up as above. The product is eluted with benzene–hexane (50:50). A yellow solid is thus obtained, mp 102 °C (hexane), yield

Table VII. Intermolecular Contacts Less Than 3.0 Å[a]

A	B		
O(1) ⋯ H(11)		1/011	2.73 (11)
O(1) ⋯ H(73)		4/000	2.99 (13)
O(3) ⋯ H(11)		2/0$\overline{1}\overline{1}$	2.80 (12)
O(4) ⋯ H(63)		4/0$\overline{1}$0	2.64 (12)
O(4) ⋯ H(72)		4/0$\overline{1}$0	2.84 (11)
H(5) ⋯ H(13)		1/010	2.84 (16)
H(10) ⋯ H(63)		4/0$\overline{1}\overline{1}$	2.75 (16)
H(11) ⋯ H(14)		1/00$\overline{1}$	2.56 (16)
H(11) ⋯ H(11)		2/0$\overline{1}$2	2.85 (16)
H(13) ⋯ H(5)		1/0$\overline{1}$0	2.84 (16)
H(14) ⋯ H(72)		4/0$\overline{1}$0	2.56 (16)
H(61) ⋯ H(71)		4/00$\overline{1}$	2.64 (18)
H(62) ⋯ H(71)		4/00$\overline{1}$	2.99 (18)

[a] The relative coordinates of the atoms in column A are listed in Table I. The atoms in column B have their atomic parameters specified by I/uvw which denotes how these parameters can be derived from the corresponding atom in the crystal unit: 1, x, y, z; 2, $1 - x$, $1 - y$, $1 - z$; 4, $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$. The u, v, and w code a lattice translation as $ua + vb + wc$.

1 g (70%). Anal. Calcd for $C_{16}H_{12}MnO_4P$: C, 54.26; H, 3.42. Found: C, 54.0; H, 3.26. IR (KBr): ν (CO) 2016, 1950, 1940, and 1650 cm^{-1}. Mass spectrum: m/e 354 (I = 19%, M), 298 (I = 18%, M $-$ 2CO), 270 (I = 100%, M $-$ 3CO), 242 (I = 18%, M $-$ 4CO), 187 (I = 6%, 242 $-$ Mn), 132 (I = 19%, C_6H_5Mn), 77 (I = 7%, C_6H_5), 55 (I = 42%, Mn). ¹H NMR (CDCl₃, Me₄Si): δ 2.20 (s, $CH_3\beta'$), 2.23 (s, $CH_3\beta$), 4.57 (d, J_{H-P} = 36 Hz, Hα'), 7.43 (m, m-,p-C_6H_5), 7.67 (m, o-C_6H_5).

Reaction of 4 with n-Butyllithium. Complex **4** (1 g) is treated by n-BuLi (2.5 cm³, 1.9 M) at -70 °C in THF (25 cm³) with stirring. The mixture slowly comes back to room temperature (1–2 h). Then sulfur (1 g) is added and the mixture is heated at 65 °C for 0.5 h. After the usual workup, the organic residue is chromatographed on silica gel with benzene. A solid is thus obtained, mp 70 °C (hexane), yield 0.55 g (68.7%). This product has the same melting point, R_f, and ¹H NMR spectrum as an authentic sample of 1-butyl-3,4-dimethyl-phosphole sulfide.[31]

X-Ray Data Collection and Processing. Crystals of compound **10**, $[\eta^5$-$PC_4H(CH_3)_2(COC_6H_5)]Mn(CO)_3$, suitable for x-ray study were grown by vacuum sublimation at room temperature. Preliminary precession photographs of the crystals displayed monoclinic symmetry and systematic absences were consistent with the centrosymmetric space group $P2_1/n$ (an alternate setting of $P2_1/c$-C_{2h}^5). The overall mosaicity of the crystals was checked on a Philips PW1100 diffractometer using graphite-monochromated Cu $K\alpha$ radiation; the precise lattice parameters were also determined at 18 ± 2 °C, by a least-squares refinement on the diffractometer settings of 25 high-angle reflections. The values are a = 20.995 (5), b = 10.869 (3), c = 6.784 (2) Å, β = 90.17 (3)°. The calculated density of 1.52 g cm^{-3}, assuming four molecules ($C_{16}H_{12}O_4PMn$, mol wt 354.2) per unit cell (volume 1548 Å³), agrees with an observed value of 1.51 (2) g cm^{-3} as measured by flotation in an aqueous KI solution.

Room temperature (18 ± 2 °C) x-ray diffraction data were collected on a PDP-8/I computer-controlled Picker FACS-1 diffractometer working with graphite-monochromated Mo $K\alpha$ radiation. The pulse height analyzer was set to admit about 95% of the Mo $K\alpha$ peak. Whenever the counting rate exceeded about 7000 counts/s, copper foils were inserted in the diffracted beam; the attenuator factors were 1.606 and 2.672. The crystal used for data collection was cut in a cold room (4 °C) into a nearly spherical shape of an average diameter 0.26 ± 0.01 mm; then it was sealed in a thin-walled glass capillary and mounted on a goniometer head without rotation movements.[32] The mosaicity of the crystal was checked by measuring ω scans on several strong reflections, using a narrow source and an open counter;[33] the peak widths at half-height were always less than 0.15°. The take-off angle was fixed at 1.6°; at this angle, the intensity of the diffracted beam was about 80% of the maximum intensity as a function of take-off angle. The total scan width in the $\theta/2\theta$ mode used was 1.8° + (Mo $K\alpha_1,\alpha_2$ splitting). The fixed scan rate was 2.0°/min. Stationary-counter, stationary-crystal background counts during 20 s were taken at each end of the scan range. The scintillation counter was

set at 23 cm from the crystal; its aperture was adjusted so as to minimize the background count without loss of net peak intensity at the 2σ level.

Three standard reflections measured every 2 h during the entire data collection showed no significant trend in intensity.

The data were processed in a usual way.[34] From the 3696 independent reflections measured up to $\theta = 27°$ ($\sin \theta/\lambda = 0.640$ Å^{-1}, Mo K$\alpha_1 = 0.709$ 30 Å), a set of 1047 reflections ($I > 3\sigma(I)$) was considered as observed. The variance estimated from counting statistics of an integrated intensity I was $\sigma^2(I) = \sigma_{count}^2 + p^2I^2$, where p has a value of 0.05. Lorentz and polarization corrections were applied.

The linear absorption coefficient was $\mu = 9.33$ cm^{-1}. Owing to the spherical shape and the small size of the crystal ($\mu R = 0.12$), the absorption factor is practically constant ($A^* = 1.198-1.197$)[35] over the range of θ used in the data collection, and therefore the intensities were not corrected for absorption effects.

The crystal structure was solved by application of the program MULTAN.[36] Atomic scattering factors were taken from the usual sources.[37] Anomalous dispersion effects were included for the manganese and the phosphorus atoms.[38] The structure was refined with an isotropic thermal motion by the full-matrix least-squares method using the program SFLS-5;[39] the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weights w were taken as $1/\sigma^2(F_o)$. Fourier difference maps then revealed electron density concentrations close to the calculated positions for all hydrogen atoms. An arbitrary isotropic fixed temperature factor ($B = 6$ Å^2) was assigned to each hydrogen atom. Subsequent refinement on all positional parameters with an anisotropic thermal motion for the nonhydrogen atoms converged to values of the agreement factors $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.046$ and $R_w = (\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.056$ for 235 refined parameters with 1047 observed data. The corresponding value of the standard deviation of an observation of unit weight was 0.998. The final difference Fourier maps showed no significant electron density above background.

Table 11 gives the relative atomic coordinates and the thermal motion parameters with their standard deviations. A list of observed and calculated structure amplitudes is available.[40]

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