Terminal and Bridged Phosphole, Arsole, and Stibole Complexes of Molybdenum, Tungsten, Manganese, Rhenium, and Iron

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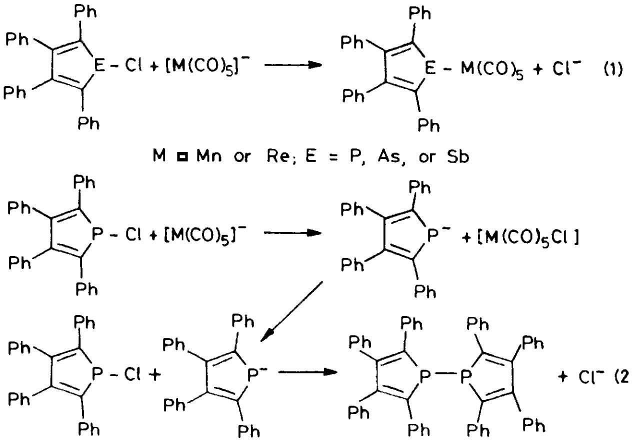
Tetraphenyl-phosphole, -arsole, and -stibole transition-metal complexes containing phosphorus-, arsenic-, or antimony-to-metal σ bonds are reported for molybdenum, tungsten, manganese, rhenium, and iron. The phosphorus- and arsenic-bridged dimers [$\{M(CO)_4(EC_4Ph_4)\}_2$] (E = P or As; M = Mn or Re) have been obtained by controlled decomposition of the corresponding monomeric pentacarbonyls.

A NUMBER of phosphole and arsole complexes of the transition metals have been reported to date.[1-5] These have usually involved the ring system with a phenyl substituent upon the phosphorus or arsenic atom. Thus the metal complexes have normally been restricted either to those involving the use of the ligand as a formally two-electron-donor tertiary phosphine or alternatively as a formally four-electron-donor ring diene. Thus pentaphenylphosphole[1] and 1,2,5-triphenylphosphole[2] have utilized the phosphorus lone pair to form complexes with iron, nickel, and molybdenum carbonyls, and form diene-type complexes with iron carbonyl. Pentaphenylarsole has only been reported to form the cyclic diene complex with iron carbonyl. Mathey[4] has reported the interesting series [$Mn_2(CO)_7$(phosphole)], where the diene part of the phosphole and the phosphorus lone pair are respectively bonded to two different manganese atoms.

Although only two previous complexes[4,5] have been reported where the heteroatom of a phosphole acts as a formally one-electron donor in a simple covalent bond to a transition metal, a number of mononuclear complexes containing comparable bonds are known such as [$Mn(CO)_5\{P(CF_3)_2\}$],[6] [$Mo(CO)_3(\eta\text{-}C_5H_5)\{As(C_6F_5)_2\}$],[7] [$Fe(CO)_2(\eta\text{-}C_5H_5)(AsCl_2)$],[8] and [$Fe(CO)_2(\eta\text{-}C_5H_5)(PPh_2)$].[9] More common, however, are the dimers that are formed by the dialkyl- and diaryl-phosphide and -arsenide groups.[10-12]

RESULTS AND DISCUSSION

The 1-chloro-derivatives of tetraphenyl-phosphole, -arsole, and -stibole react with the pentacarbonyl anions of manganese and rhenium according to equation (1). For the arsenic and antimony complexes, the reactions are virtually quantitative (Table 1). In the case of the phosphole, however, the yields were lower, and the diphosphole and decacarbonyldimanganese were isolated as by-products. Presumably, in this case there was extensive exchange coupling as suggested in equation (2).



The treatment of 1-chlorotetraphenylphosphole, -arsole, and -stibole with either sodium amalgam or lithium wire in tetrahydrofuran gave rise to extremely air-sensitive red solutions[13] of X[EC_4Ph_4] (E = P, As, or Sb; X = Li or Na). Although we were unable to isolate and characterize these salts, the solutions underwent reaction with pentacarbonylchloromanganese to give the heterocycle–pentacarbonylmetal complex as illustrated in equation (3). In this alternative synthetic approach to that of equation (1), yields are somewhat lower (20—40%), possibly due to the incomplete formation of the phosphole, arsole, and stibole anions.

In neither synthetic pathway, however, was there any

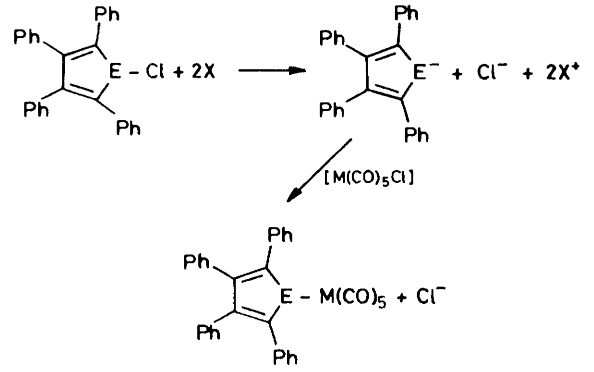
TABLE 1

The complexes [$M(CO)_5(EC_4Ph_4)$] (E = P, As, or Sb; M = Mn or Re) [a]

Complex	Yield (%)	M.p. (θ_c/°C)	Analysis (%) Found C	H	Required C	H	$\tilde{\nu}$(CO) [b]/cm^{-1}			
[$Mn(CO)_5(PC_4Ph_4)$]	65	157—158	68.2	3.7	68.1	3.5	2 111(4)	2 032(9.6)	2 024(10)	2 002(9.4)
[$Mn(CO)_5(AsC_4Ph_4)$]	85	170—172	63.6	3.1	63.3	3.2	2 105(6)	2 026(9)	2 017(10)	1 999(7)
[$Mn(CO)_5(SbC_4Ph_4)$]	92	141—142	59.3	2.9	58.9	3.0	2 096(4)	2 016(8)	2 007(10)	1 998(7)
[$Re(CO)_5(PC_4Ph_4)$]	69	134—135	55.8	2.8	55.5	2.8	2 134(4)	2 037(9.8)	2 029(10)	1 996(9.7)
[$Re(CO)_5(AsC_4Ph_4)$]	90	162	52.6	2.3	52.3	2.6	2 124(3)	2 033(9)	2 022(10)	1 992(7)
[$Re(CO)_5(SbC_4Ph_4)$]	91	101—105 (decomp.)	49.6	2.3	49.3	2.5	2 118(3)	2 026(9)	2 016(10)	1 996(8)

[a] All complexes are yellow or yellow-orange. [b] In n-hexane; relative intensities are given in parentheses.

observable formation of the tetracarbonylmetal dimers. These complexes thus join the small group of organophosphido- and organoarsenido-metal pentacarbonyl derivatives which do not undergo spontaneous dimerization on formation. This is presumably due to the very large protective bulk of the substituted ring system, and also possibly due to some electronic stabilization conferred by the heterocyclic ring system.



(3)

E = P, As or Sb; M = Mn or Re; X = Li or Na

those formed by dialkyl- or diaryl-phosphines and -arsines. No antimony-bridged metal carbonyl derivatives of the stiboles could be isolated, since both heat and irradiation appeared to cause their complete decomposition.

Although molecules of the type $[M(CO)_5X]$ have formal C_{4v} symmetry, this assumes a point mass for X. The phosphole, arsole, and stibole pentacarbonylmetals all have four strong, and well resolved, metal–carbonyl stretching modes in their i.r. spectra. Whilst the nature of the two A_1 modes would be unchanged, the bulky nature of the ring and the pyramidal configuration of the heteroatom would remove formal C_{4v} symmetry, and with it the usual degeneracy of the E mode, thus resulting in the well resolved two middle bands of the four reported for each complex of this type reported in Table 1. Other examples[14] of bulky groups causing such a reduced symmetry in $[M(CO)_5X]$ complexes have been reported.

Although we were unable to sublime these heterocyclemetal pentacarbonyls on a conventional vacuum line at temperatures low enough to prevent their decomposition to dimers, it was nevertheless possible to obtain good mass spectra. All complexes showed molecular ions (P^+) corresponding to $[M(CO)_5(EC_4Ph_4)]^+$, and the subsequent stepwise loss of CO down to $P - 5CO$. The ions corresponding to $[M(EC_4Ph_4)]^+$ and $[M(CO)_3(EC_4Ph_4)]^+$ were intense, and presumably involved the Ph_4C_4E ring attached to the transition metal in an η^5 mode as already shown[15] for the $[Mn(CO)_3(AsC_4Ph_4)]$ neutral molecule.

TABLE 2

Infrared spectra (cm^{-1}) of the complexes $[\{M(CO)_4(EC_4Ph_4)\}_2]$ (M = Mn or Re; E = P or As) in the metal–carbonyl stretching region

Complex	$\tilde{\nu}$(CO) *			
$[\{Mn(CO)_4(PC_4Ph_4)\}_2]$	2 062(4)	2 018(8)	1 994(8)	1 964(10)
$[\{Mn(CO)_4(AsC_4Ph_4)\}_2]$	2 058(5)	2 009(9)	1 992(7)	1 964(10)
$[\{Re(CO)_4(PC_4Ph_4)\}_2]$	2 079(4)	2 017(9)	1 992(8)	1 949(10)
$[\{Re(CO)_4(AsC_4Ph_4)\}_2]$	2 076(4)	2 005(8)	1 990(8.5)	1 950(10)

* In cyclohexane; relative intensities are given in parentheses.

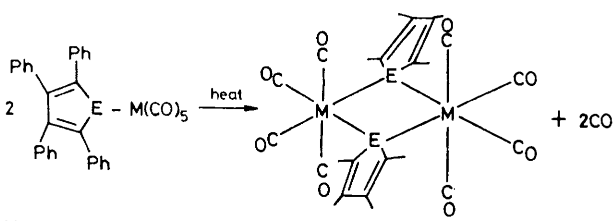
TABLE 3

The complexes $[Fe(CO)_2(\eta\text{-}C_5H_5)(EC_4Ph_4)]$ [a] (E = P, As, or Sb)

			Analysis (%)					
	Yield	M.p.	Found		Required			
Complex	(%)	(θ_c/°C)	C	H	C	H	$\tilde{\nu}$(CO) [b]/cm^{-1}	
$[Fe(CO)_2(\eta\text{-}C_5H_5)(PC_4Ph_4)]$	51	195 (decomp.)	74.8	4.6	74.5	4.4		
$[Fe(CO)_2(\eta\text{-}C_5H_5)(AsC_4Ph_4)]$	72	209—211 (decomp.)	69.0	4.1	69.1	4.1	2 012(8)	1 968(10)
$[Fe(CO)_2(\eta\text{-}C_5H_5)(SbC_4Ph_4)]$	55	127—129 (decomp.)	64.6	4.1	64.2	3.8	2 005(8)	1 960(10)

[a] All complexes are brown, and exhibit a sharp singlet at *ca.* 3.9 p.p.m. (η-C_5H_5) and a multiplet at 6.7—7.3 p.p.m. (C_6H_5) in the ^1H n.m.r. spectra. [b] In hexane; relative intensities are given in parentheses.

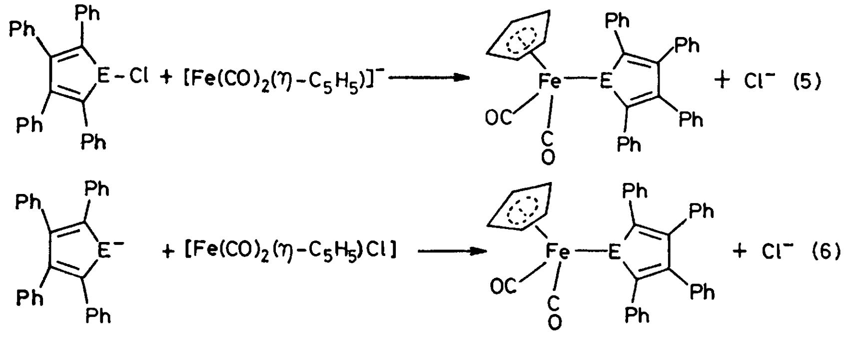
Although these pentacarbonyl complexes are stable as crystals, and in solution at normal temperatures, they easily lose carbon monoxide on heating [equation (4)]. The dimers formed (Table 2) are exactly analogous to those formed by dialkyl- or diaryl-phosphines and -arsines.



(4)

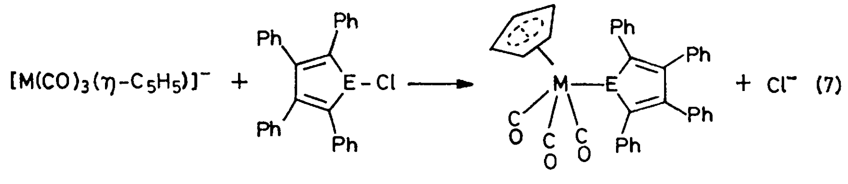
M = Mn or Re; E = P or As

In the syntheses of iron derivatives of the heterocyclic rings, the 1-chloro-phospholes, -arsoles, and -stiboles were treated with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ according to equation (5). Yields in these reactions were only moderate (40—60%) since purification was difficult; further, the alternative syntheses by equation (6) gave yields of only 25—30%. These iron complexes (Table 3) showed the expected two peaks in the carbonyl-stretching region of the i.r. spectra, and their ^{1}H n.m.r. spectra showed a singlet corresponding to the cyclopentadienyl group and a multiplet for the phenyl groups. However, in order to obtain mass spectra of these products, high inlet temperatures (180—200 °C) were necessary, and no molecular ions could be observed. Instead the highest peak for the phosphole and arsole complexes corresponded to the loss of two carbonyl groups leaving the fragment $[Fe(\eta\text{-}C_5H_5)(EC_4Ph_4)]^+$ (E = P or As). These ions are presumably analogous in structure to ferrocene with the phosphorus and arsenic rings η^5-bonded to iron, as in the corresponding azaferrocene.[16] The antimony complex decomposed completely to give no useful mass spectrum.



E = P, As, or Sb

Phosphole, arsole, and stibole compounds of molybdenum and tungsten (Table 4) were obtained according to equation (7). In addition, the single complex $[Mo(CO)_2(\eta\text{-}C_7H_7)(AsC_4Ph_4)]$ was obtained according to equation (8). Whilst the cycloheptatrienyl complex was characterized by analysis and i.r. and ^{1}H n.m.r. spectra, it was not possible to obtain a useful mass spectrum due to low volatility.



M = Mo or W; E = P, As, or Sb

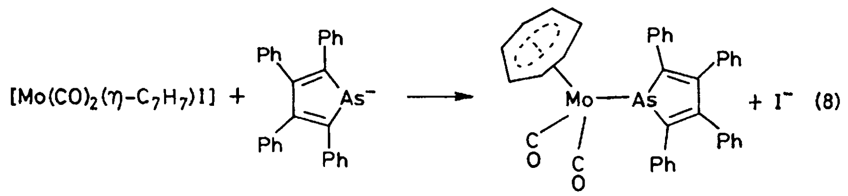


TABLE 4

The complexes $[M(CO)_3(\eta\text{-}C_5H_5)(EC_4Ph_4)]$ [a] (M = Mo or W; E = P, As, or Sb)

Complex	Yield (%)	M.p. (θ_c/°C)	Analysis (%) Found C	Found H	Required C	Required H	$\tilde{\nu}$(CO) [b]/cm^{-1}		
$[Mo(CO)_3(\eta\text{-}C_5H_5)(PC_4Ph_4)]$	68	127 (decomp.)	68.6	4.2	68.4	4.0	2 022(7)	1 950(10)	1 947(8)
$[Mo(CO)_3(\eta\text{-}C_5H_5)(AsC_4Ph_4)]$	73	130—131 (decomp.)	64.2	3.9	63.9	3.7	2 016(7)	1 944(10)	1 941(8)
$[Mo(CO)_3(\eta\text{-}C_5H_5)(SbC_4Ph_4)]$	54	115—120 (decomp.)	60.1	3.7	59.8	3.5	2 004(8)	1 926(10)	1 924(sh)
$[W(CO)_3(\eta\text{-}C_5H_5)(PC_4Ph_4)]$	41	116 (decomp.)	60.4	3.3	60.1	3.5	2 019(8)	1 946(10)	1 943(8)
$[W(CO)_3(\eta\text{-}C_5H_5)(AsC_4Ph_4)]$	52	110—115 (decomp.)	57.0	3.2	56.6	3.3	2 016(7)	1 940(10)	1 938(9)
$[W(CO)_3(\eta\text{-}C_5H_5)(SbC_4Ph_4)]$	55	95 (decomp.)	52.8	3.2	53.2	3.1	2 009(7)	1 924(10)	1 922(sh)

[a] All complexes are yellow, and exhibit a sharp singlet at *ca.* 5.4 p.p.m. (η-C_5H_5) and a multiplet at 6.7—7.5 p.p.m. (C_6H_5) in the ^{1}H n.m.r. spectra. [b] In n-hexane; relative intensities are given in parentheses.

In all of these mononuclear complexes, the ring heteroatom to transition-metal bond undergoes rapid fission with chlorine and with bromine to form the corresponding 1-halogenoheterocycle and the transition-metal complex halide (Table 5).

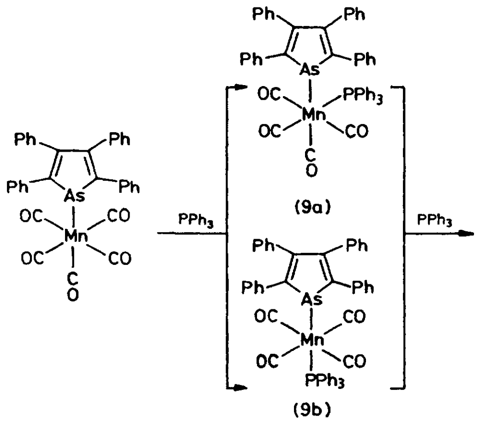
Triphenylphosphine displaces carbon monoxide from pentacarbonyl(2,3,4,5-tetraphenylarsolyl)manganese to form a mixture of two complexes, whose ratio is solvent dependent. These appear to be the two isomers (9a) and (9b). Thus whilst (9a) is the favoured product from *trans*-effect arguments, the formation of (9b) would be less sterically hindered.

TABLE 5

Reagents and products in the halogen fission reactions of the σ-bonded phosphole, arsole, and stibole metal carbonyl derivatives

Reagents	Products *			
$[Mn(CO)_5(PC_4Ph_4)] + Cl_2$	C_4Ph_4PCl	(32)	$[Mn(CO)_5Cl]$	(37)
$[Mn(CO)_5(AsC_4Ph_4)] + Cl_2$	C_4Ph_4AsCl	(36)	$[Mn(CO)_5Cl]$	(23)
$[Mn(CO)_5(SbC_4Ph_4)] + Cl_2$	C_4Ph_4SbCl	(29)	$[Mn(CO)_5Cl]$	(19)
$[Re(CO)_5(PC_4Ph_4)] + Cl_2$	C_4Ph_4PCl	(57)	$[Re(CO)_5Cl]$	(43)
$[Re(CO)_5(AsC_4Ph_4)] + Cl_2$	C_4Ph_4AsCl	(43)	$[Re(CO)_5Cl]$	(56)
$[Re(CO)_5(SbC_4Ph_4)] + Cl_2$	C_4Ph_4SbCl	(76)	$[Re(CO)_5Cl]$	(35)
$[Fe(CO)_2(\eta\text{-}C_5H_5)(PC_4Ph_4)] + Cl_2$	C_4Ph_4PCl	(12)	$[Fe(CO)_2(\eta\text{-}C_5H_5)Cl]$	(34)
$[Fe(CO)_2(\eta\text{-}C_5H_5)(AsC_4Ph_4)] + Cl_2$	C_4Ph_4AsCl	(17)	$[Fe(CO)_2(\eta\text{-}C_5H_5)Cl]$	(49)
$[Fe(CO)_2(\eta\text{-}C_5H_5)(SbC_4Ph_4)] + Cl_2$	C_4Ph_4SbCl	(11)	$[Fe(CO)_2(\eta\text{-}C_5H_5)Cl]$	(21)
$[Mo(CO)_3(\eta\text{-}C_5H_5)(PC_4Ph_4)] + Cl_2$	C_4Ph_4PCl		$[Mo(CO)_3(\eta\text{-}C_5H_5)Cl]$	(17)
$[Mo(CO)_3(\eta\text{-}C_5H_5)(AsC_4Ph_4)] + Cl_2$	C_4Ph_4AsCl		$[Mo(CO)_3(\eta\text{-}C_5H_5)Cl]$	(43)
$[Mo(CO)_3(\eta\text{-}C_5H_5)(SbC_4Ph_4)] + Cl_2$	C_4Ph_4SbCl		$[Mo(CO)_3(\eta\text{-}C_5H_5)Cl]$	(14)
$[W(CO)_3(\eta\text{-}C_5H_5)(PC_4Ph_4)] + Cl_2$	C_4Ph_4PCl		$[W(CO)_3(\eta\text{-}C_5H_5)Cl]$	(34)
$[W(CO)_3(\eta\text{-}C_5H_5)(AsC_4Ph_4)] + Cl_2$	C_4Ph_4AsCl		$[W(CO)_3(\eta\text{-}C_5H_5)Cl]$	(26)
$[W(CO)_3(\eta\text{-}C_5H_5)(SbC_4Ph_4)] + Cl_2$	C_4Ph_4SbCl		$[W(CO)_3(\eta\text{-}C_5H_5)Cl]$	(33)
$[Mn(CO)_5(PC_4Ph_4)] + Br_2$	C_4Ph_4PBr	(27)	$[Mn(CO)_5Br]$	(84)
$[Mn(CO)_5(AsC_4Ph_4)] + Br_2$	C_4Ph_4AsBr		$[Mn(CO)_5Br]$	(76)
$[Mn(CO)_5(SbC_4Ph_4)] + Br_2$	C_4Ph_4SbBr		$[Mn(CO)_5Br]$	(91)
$[Re(CO)_5(PC_4Ph_4)] + Br_2$	C_4Ph_4PBr	(44)	$[Re(CO)_6Br]$	(65)
$[Re(CO)_5(AsC_4Ph_4)] + Br_2$	C_4Ph_4AsBr		$[Re(CO)_5Br]$	(69)
$[Re(CO)_5(SbC_4Ph_4)] + Br_2$	C_4Ph_4SbBr		$[Re(CO)_5Br]$	(78)
$[Fe(CO)_2(\eta\text{-}C_5H_5)(PC_4Ph_4)] + Br_2$	C_4Ph_4PBr	(38)	$[Fe(CO)_2(\eta\text{-}C_5H_5)Br]$	(17)
$[Fe(CO)_2(\eta\text{-}C_5H_5)(AsC_4Ph_4)] + Br_2$	C_4Ph_4AsBr		$[Fe(CO)_2(\eta\text{-}C_5H_5)Br]$	(14)
$[Fe(CO)_2(\eta\text{-}C_5H_5)(SbC_4Ph_4)] + Br_2$	C_4Ph_4SbBr		$[Fe(CO)_2(\eta\text{-}C_5H_5)Br]$	(9)
$[Mo(CO)_3(\eta\text{-}C_5H_5)(PC_4Ph_4)] + Br_2$	C_4Ph_4PBr	(18)	$[Mo(CO)_3(\eta\text{-}C_5H_5)Br]$	

* Percentage yields are given in parentheses.



Reaction of the isomer mixture with further PPh_3 produces a single disubstituted product. The three strong i.r. bands of this product suggest that they may be the $2A' + A''$ modes of the *fac* form (9c), but two other alternative *mer*-isomer structures are also possible.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran (thf) and diglyme were distilled from lithium tetrahydridoaluminate(III), chlorinated solvents from phosphorus pentaoxide, and all other solvents were dried over fine sodium wire.

All i.r. spectra were run in cyclohexane solution on a Perkin-Elmer 257 instrument.

1-Chloro-2,3,4,5-tetraphenyl-phosphole, -arsole, and -stibole were prepared [1b] from 1,4-dilithiotetraphenylbutadiene (*via* diphenylacetylene), and phosphorus, arsenic, and antimony trichlorides respectively.

Interaction of Pentacarbonylmanganate(1—) *and* 1-*Chloro*-2,3,4,5-*tetraphenylphosphole*.— Decacarbonyldimanganese (0.5 mmol) was converted into the sodium salt by stirring with excess of liquid sodium–mercury amalgam in thf (10 cm³) for 2 h. After this time, excess of amalgam was removed and the phosphole (1 mmol) was added with stirring. On completion of the addition the mixture was stirred for 1 h. After vacuum removal of solvent, the residue was extracted and crystallized from hexane. The product was then chromatographed on Florisil, and elution with hexane gave three pure fractions. The first two products were $[Mn_2(CO)_{10}]$ and 1,1′-bi(2,3,4,5-tetraphenylphosphole) followed by orange pentacarbonyl(2,3,4,5-tetraphenylphospholyl)manganese (Table 1).

In the corresponding reaction with the pentacarbonylrhenate anion, chromatography yielded only trace amounts of the parent carbonyl and the bi(phosphole), the main product being yellow pentacarbonyl(2,3,4,5-tetraphenylphospholyl)rhenium (Table 1).

Interaction of Pentacarbonylmanganate(1—) *and Pentacarbonylrhenate*(1—) *with* 1-*Chloro*-2,3,4,5-*tetraphenyl-arsole and -stibole*.—The experimental methods employed in these reactions were exactly analogous to the phosphole reactions reported above, but chromatography was unnecessary for purification of the products. Thus, simple recrystallization of the reaction residue from hexane yielded in each case a pure sample of the appropriate yellow or orange product in high yield. No bi(arsoles) or bi(stiboles) were formed in observable quantities.

Interaction of Pentacarbonylchloromanganese and 2,3,4,5-Tetraphenyl-phosphole, -arsole, and -stibole Anions.—The appropriate chloroheterocycle (1-chloro-2,3,4,5-tetraphenylphosphole, -arsole, or -stibole) (0.1 mmol) was dissolved in thf (30 cm^3) and stirred with excess of 3% sodium-mercury amalgam (30 g). In all cases, after 3 h, the solution had turned very dark red, and excess of amalgam was removed to leave an extremely air-sensitive solution of the appropriate heterocycle anion. To this was added [Mn(CO)$_5$Cl] (1 mmol) in thf (10 cm^3) with rapid stirring. The mixture was stirred for another hour, filtered, and the solvent removed *in vacuo*. Recrystallization of the three individual products gave respectively pentacarbonyl(2,3,4,5-tetraphenylphospholyl)manganese (22%), pentacarbonyl-(2,3,4,5-tetraphenylarsolyl)manganese (34%), and pentacarbonyl(2,3,4,5-tetraphenylstibolyl)manganese (18%), identical to the samples characterized in Table 1.

Pyrolysis of Pentacarbonyl(2,3,4,5-tetraphenylphospholyl)-manganese.—The complex (0.29 g, 0.5 mmol) was heated gently under reflux in hexane (30 cm^3) for 24 h. The resulting solution was filtered whilst still hot, and slow removal of solvent in a stream of nitrogen caused deposition of golden-yellow crystals of bis[tetracarbonyl(2,3,4,5-tetraphenylphospholyl)manganese] (0.24 g, 90%), m.p. 166—168 °C (decomp) (Found: C, 69.2; H, 3.5. $C_{64}H_{40}Mn_2O_8P_2$ requires C, 69.3; H, 3.60%). The product had four sharp metal–carbonyl stretching modes in the i.r. spectrum (Table 2).

The conditions of the above pyrolysis were repeated with the corresponding arsole derivative, and the corresponding complexes of rhenium. All gave dimerization reactions and the characteristic i.r. spectra of these dimeric products are in Table 2.

Interaction of Dicarbonyl(η-cyclopentadienyl)ferrate(1−) and 1-Chloro-2,3,4,5-tetraphenyl-phosphole, -arsole, and -stibole.—Bis[dicarbonyl(η-cyclopentadienyl)iron] (0.5 mmol) was converted into the anion by stirring with excess of sodium–mercury amalgam in thf (25 cm^3). After 2 h, the excess of amalgam was removed and the appropriate chloroheterocycle (1 mmol) in thf (10 cm^3) was added with stirring. After 1 h the mixture was filtered and the solvent removed *in vacuo*. The residue was taken up in the minimum quantity of hexane and chromatographed on a Florisil column. Elution with hexane gave some of the parent binuclear complex and then the appropriate product [Fe(CO)$_2$(η-C$_5$H$_5$)(EC$_4$Ph$_4$)] (E = Ph, As, or Sb) (Table 3). In the phosphole reaction a band eluted between the two carbonyl products was identified as the bi(phosphole) $(Ph_4C_4P)_2$ (9%).

Interaction of Dicarbonylchloro(η-cyclopentadienyl)iron and 2,3,4,5-Tetraphenyl-phosphole, -arsole, and -stibole Anions.—The appropriate chloroheterocycle (1 mmol) was used to prepare the anion as described above, and to this was added [Fe(CO)$_2$(η-C$_5$H$_5$)Cl] (1 mmol) in thf (10 cm^3). After 1 h, solvent and unchanged [Fe(CO)$_2$(η-C$_5$H$_5$)Cl] were removed at 60 °C (0.01 mmHg).* Recrystallization of the three individual products gave respectively dicarbonyl-(η-cyclopentadienyl)(2,3,4,5-tetraphenylphospholyl)iron (21%), dicarbonyl(η-cyclopentadienyl)(2,3,4,5-tetraphenylarsolyl)iron (30%), and dicarbonyl(η-cyclopentadienyl)-(2,3,4,5-tetraphenylstibolyl)iron (25%), identical to the samples characterized in Table 3.

Interaction of Tricarbonyl(η-cyclopentadienyl)-molybdate(1−) and -tungstate(1−) with 1-Chloro-2,3,4,5-tetraphenyl-phosphole, -arsole, and -stibole.—Bis[tricarbonyl-(η-cyclopentadienyl)molybdenum] (0.5 mmol) and its tungsten analogue were converted into their respective anions by stirring with excess of sodium amalgam in thf (15 cm^3). After removal of excess of amalgam, the appropriate chloroheterocycle (1 mmol) dissolved in thf (25 cm^3) was added and stirred (1 h). After filtration, solvent was removed from the filtrate *in vacuo* and the residue recrystallized from hexane to produce the yellow air-sensitive products (Table 4).

Interaction of Dicarbonyl(η-cycloheptatrienyl)iodomolybdenum and 2,3,4,5-Tetraphenylarsole Anion.—The arsole anion was prepared on a 0.1 mmol scale in thf as described above. To this was added [Mo(CO)$_2$(η-C$_7$H$_7$)I] (1 mmol) in thf (30 cm^3). The mixture was stirred (1 h), filtered, and the solvent removed from the filtrate *in vacuo*. The residue was taken up in hexane (40 cm^3), filtered, and slow evaporation of the solvent in a stream of nitrogen gave yellow crystals of dicarbonyl(η-cycloheptatrienyl)(2,3,4,5-tetraphenylarsolyl)molybdenum (63% yield), m.p. 65 °C (decomp.) (Found: C, 66.5; H, 3.8. $C_{37}H_{27}AsMoO_2$ requires C, 65.9; H, 4.0%). The complex had two sharp peaks in the metal carbonyl region of its i.r. spectrum [2 007(10) and 1 961(9) cm^{-1}], and the n.m.r. spectrum consisted of a singlet at τ 4.7 (η-C$_7$H$_7$) and a multiplet at τ 2—3 (C$_6$H$_5$) integrating in the ratio *ca.* 1 : 3.

Interaction of σ-Bonded Phosphole, Arsole, and Stibole Metal Carbonyl Complexes with Chlorine and Bromine.—To the metal carbonyl heterocycle complex (0.1 mmol) in hexane (at −10 °C) was added the stoicheiometric quantity of chlorine or bromine in carbon tetrachloride solution. After removal of solvent [25 °C (15 mmHg)], the metal carbonyl halide was carefully sublimed [50 °C (0.01 mmHg)] on to a cold probe, and characterized by its i.r. spectrum in the metal carbonyl region and its mass spectrum. The residue was recrystallized from hexane–chloroform to give the appropriate heterocycle halide characterized by melting point and mass spectrum. Gaps in Table 5 indicate that a particular product of the fission was not obtained in a pure state for characterization.

Interaction of Pentacarbonyl(2,3,4,5-tetraphenylarsolyl)-manganese and Triphenylphosphine.—Equimolar (0.5 mmol) proportions of the two reactants were stirred in thf at 20 °C for 48 h. After this time the i.r. spectrum of the starting carbonyl in the metal–carbonyl stretching region had disappeared completely. Removal of solvent *in vacuo* gave a yellow solid which appeared to be a mixture of the *cis* and *trans* forms of tetracarbonyl(2,3,4,5-tetraphenylarsolyl)-(triphenylphosphine)manganese, with six peaks in its carbonyl spectrum at 2 059(6), 2 020(4), 1 994(8.5), 1 983(10), 1 961(7), and 1 950(7) cm^{-1}. The mixture could not be separated by chromatography. The reaction was repeated under identical conditions in methylene chloride to give the same products, with carbonyl bands at 2 059(6), 2 020(2), 1 994(8.5), 1 983(10), 1 961(7), and 1 950(4) cm^{-1}. The change of solvent has thus changed the proportion of products, and allows the bands at 2 020 and 1 950 cm^{-1} to be assigned to the *trans* isomer and the other bands to be assigned to the *cis* product.

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

The reaction between the two reagents was again repeated with PPh_3 and the carbonyl complex in the mol ratio of 2 : 1 respectively. After 72 h in thf at 20 °C, the solvent was removed *in vacuo* and the residue taken up in a minimum of chloroform and filtered. Hexane was added until precipitation just started. Filtration after 24 h yielded yellow crystals of tricarbonyl(2,3,4,5-tetraphenylarsolyl)bis(triphenylphosphine)manganese (0.09 g, 23%), m.p. 170 °C (decomp.) (Found: C, 73.2; H, 4.8. $C_{67}H_{50}AsMnO_3P_2$ requires C, 73.5; H, 4.6%) with i.r. metal carbonyl bands at 2 022(7), 1 952(10), and 1 916(10) cm^{-1}.

[8/854 *Received*, *8th May*, 1978]

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