η-Tetraphenylphospholyl and η-Tetraphenylarsolyl Derivatives of Manganese, Rhenium, and Iron

By **Edward W. Abel,* Neil Clark,** and **Christopher Towers,** Department of Chemistry, University of Exeter, Exeter EX4 4QD

The tetraphenyl-phospholyl and -arsolyl complexes of manganese and rhenium $[M(CO)_5(\sigma\text{-}EC_4Ph_4)]$ (E = P or As, M = Mn or Re) lose carbon monoxide on heating to yield the corresponding η-phospholyl and η-arsolyl complexes $[M(CO)_3(\eta\text{-}EC_4Ph_4)]$. These products are also obtained by loss of carbon monoxide from the dimers $[\{Mn(CO)_4(EC_4Ph_4)\}_2]$, the action of $Ph_4C_4E{-}EC_4Ph_4$ (E = P or As) upon $[Mn_2(CO)_{10}]$, and by the action of tetraphenyl-1-trimethylsilylarsole upon $[Mn(CO)_5Cl]$. Triphenylphosphine, diphenylacetylene, and the nitrosyl cation all displaced one carbonyl group from the complex $[Mn(CO)_3(\eta\text{-}AsC_4Ph_4)]$. Prolonged heating of the iron complexes $[Fe(CO)_2(\eta\text{-}C_5H_5)(\sigma\text{-}EC_4Ph_4)]$ (E = P or As) caused loss of carbon monoxide and production of the corresponding phospha- and arsa-ferrocenes $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}EC_4Ph_4)]$.

THE neutral phospholes and arsoles are versatile ligands in reactions with metal carbonyls.[1-10] They are formally two-electron donors when only the phosphorus and arsenic lone pairs of electrons are involved in co-ordination,[1-3,9] but four-electron donors when only the diolefin part of the molecule co-ordinates to the metal carbonyl moiety.[1,2,9] When both phosphorus or arsenic and the diolefin are utilised in these ways the ring system is formally a six-electron donor.[1,2,5,6]

In derivatives where there is a single covalent bond between the phosphorus or arsenic and the transition metal of the carbonyl moiety the phosphole or arsole is formally a one-electron donor,[4,7,8] but it is converted into a three-electron donor when the phosphole or arsole heteroatom assumes a bridging role.[7,8] Further, the phosphole and arsole rings can behave as formally five-electron donors [5,7,10] in a manner akin to their nitrogen analogue pyrrole [11,12] and to the homocyclic cyclopentadienyl ring. In one remarkable trinuclear metal complex the phosphole ring system behaves as a formally seven-electron donor ligand.[6]

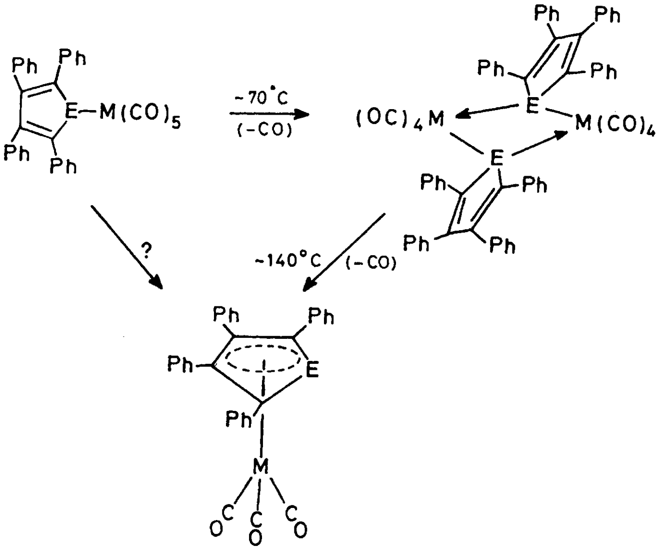
The presence of the pentahapto phospholyl and arsolyl mode of bonding has now been confirmed by *X*-ray diffraction measurements,[7,10] and we report some syntheses and properties of 1—5-η-2,3,4,5-tetraphenylphospholyl and 1—5-η-2,3,4,5-tetraphenylarsolyl derivatives of manganese, rhenium, and iron.

We have previously reported the synthesis of 2,3,4,5-tetraphenylphosphole and 2,3,4,5-tetraphenylarsole derivatives of metal carbonyls of manganese, rhenium, iron, molybdenum, and tungsten, where the ring system is attached to the metal carbonyl moiety solely by a bond from the three-co-ordinate phosphorus or arsenic to the transition metal. In several of these complexes, careful heating causes loss of carbon monoxide, with the phosphorus or arsenic atoms assuming a bridging four-co-ordinate mode.[8] We now report the further loss of carbon monoxide from such compounds with a reversion to a monomeric species containing π-bonded phospholyl and arsolyl ligands.

RESULTS AND DISCUSSION

Both $[M(CO)_5(EC_4Ph_4)]$ and $[\{M(CO)_4(EC_4Ph_4)\}_2]$ (E = P or As, M = Mn or Re) were rapidly converted into the corresponding monomeric tricarbonyl derivatives at high temperature. This was achieved either in xylene under reflux or in a sealed tube under vacuum at 130 °C. Although u.v. irradiation caused a similar conversion, considerable decomposition occurred before the reaction was completed.

Whilst it is possible that some pentacarbonyl molecules lose two carbon monoxide groups to form the tricarbonyl directly, it is more likely that the reaction proceeds *via* the dimers as illustrated in Scheme 1. All four products from Scheme 1 have the expected three bands in the carbonyl-stretching region of their i.r. spectra. Each compound shows a molecular ion (*M*) in its mass spectrum; for the two rhenium complexes these molecular ions are the most intense, but in the manganese compounds the $[M - 3CO]^+$ ions are strongest.

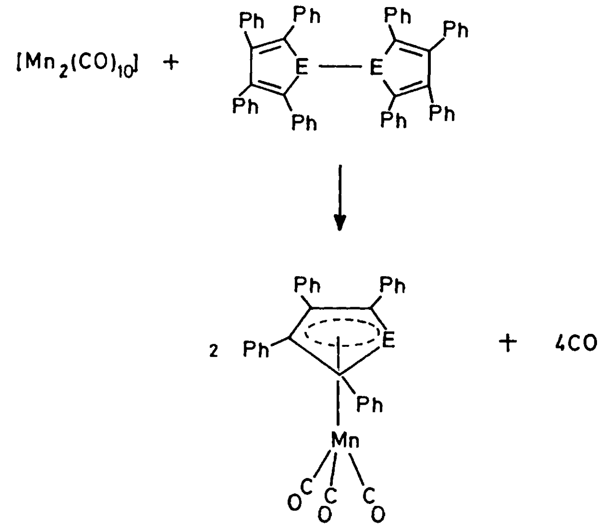


SCHEME 1 E = P or As, M = Mn or Re

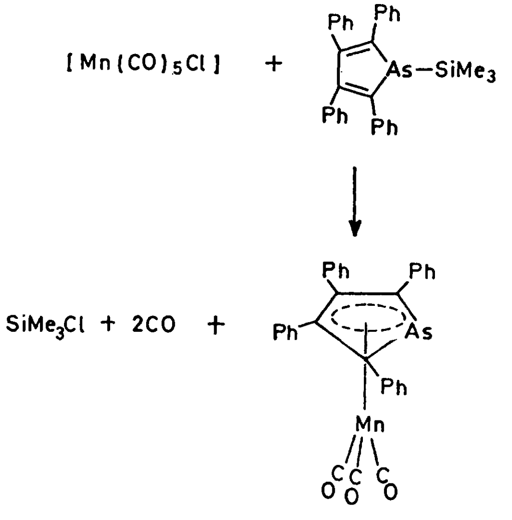
The structure of $[Mn(CO)_3(AsC_4Ph_4)]$ as determined by *X*-ray diffraction [7] contains a planar arsole ring with each phenyl group twisted out of the C_4As plane by *ca.* 40—60°, and the plane containing the three carbon atoms of the carbonyl groups effectively parallel to the heterocyclic ring. Only small differences were observed in the C–C distances of the ring and the As–C(ring) distance of 1.90(2) Å is shorter than the sum of the covalent radii [As–C(sp^2) 1.95 Å]. These facts suggest delocalisation within the arsolyl ring, and whilst photoelectron spectroscopy shows [13] that the phosphole and arsole parent ring systems are not themselves delocalised, calculations suggest that the phospholyl and arsolyl anions should exhibit a large electron delocalisation.[14]

A similar delocalisation has been observed [10] for the phospholyl ring in a phosphaferrocene, and this system has further been shown [15] to be ' aromatic ' by acetylation of the phospholyl ring.

In addition to the thermal degradation of the pentacarbonyl complex as indicated in Scheme 1, we have synthesised the phospholyl and arsolyl tricarbonyls of manganese by other methods, *viz.*:



SCHEME 2 E = P or As



SCHEME 3

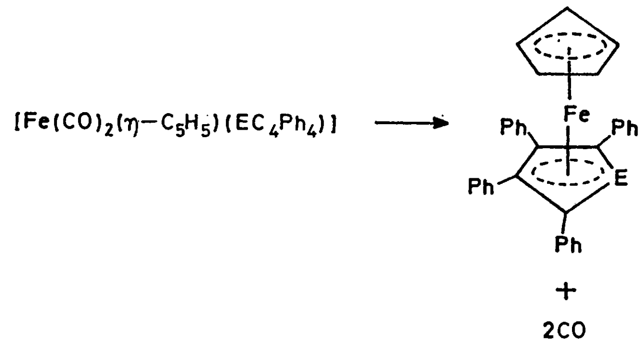
In the reactions represented in Scheme 2 it is possible that the reaction proceeds initially *via* the σ-bonded ring–metal pentacarbonyls and the bridged dimers illustrated in Scheme 1. In Scheme 3 it is likely that the reaction proceeds by initial co-ordination of the silylarsine to the manganese by carbon monoxide displacement, followed by intramolecular elimination of chlorotrimethylsilane.

The trimethyltin derivative [$SnMe_3(AsC_4Ph_4)$] did also react with pentacarbonylchloromanganese to give a low yield of [$Mn(CO)_3(\eta\text{-}AsC_4Ph_4)$], but the reaction was complicated in this case by the formation of [$Mn(CO)_5(SnMe_3)$] in a side reaction.

The compounds [$Fe(CO)_2(\eta\text{-}C_5H_5)(EC_4Ph_4)$] (E = P, As, or Sb), in which the heterocyclic ring is bonded to iron by a σ-(Fe–E) bond, have been reported previously.[4,8] Braye and Joshi [4] attempted the decarbonylation of [$Fe(CO)_2(\eta\text{-}C_5H_5)(PC_4Ph_4)$], but were unable to report the isolation of the phosphaferrocene. We were, however, encouraged by the dominance of the [$Fe(\eta\text{-}C_5H_5)(EC_4Ph_4)$]$^+$ (E = P or As) peaks in the mass spectra of both [$Fe(CO)_2(\eta\text{-}C_5H_5)(PC_4Ph_4)$] and [$Fe(CO)_2(\eta\text{-}C_5H_5)(AsC_4Ph_4)$].

We do note, however, that the iron derivatives [$Fe(CO)_2(\eta\text{-}C_5H_5)(EC_4Ph_4)$] (E = P or As) proved much more thermally stable than the corresponding σ-bonded derivatives of manganese and rhenium, and further we were unable to isolate the phosphole and arsole analogues of the known dialkyl- and diaryl-phosphorus [16] and -arsenic [17] bridged dimers.

Phosphaferrocenes have now been structurally characterised,[10] and we find that prolonged heating of [$Fe(CO)_2(\eta\text{-}C_5H_5)(EC_4Ph_4)$] (E = P or As) does cause the loss of carbon monoxide and the formation of the phospha- and arsa-ferrocenes as illustrated in Scheme 4.

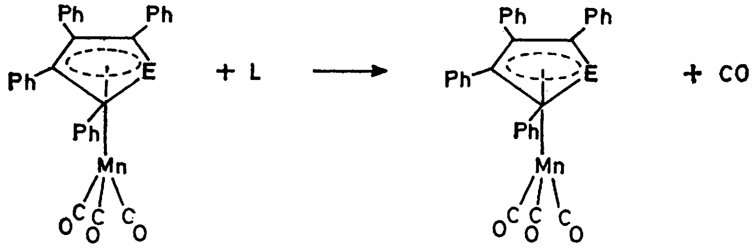


SCHEME 4 E = P or As

It seems likely that Braye and Joshi [4] did synthesise some [$Fe(\eta\text{-}C_5H_5)(PC_4Ph_4)$], but did not take their reaction to completion.

The tetraphenylphospha- and arsa-ferrocenes were red-brown crystalline solids with high melting points. Infrared spectra indicated the complete absence of metal carbonyl groups, and the ^1H n.m.r. spectra gave the expected cyclopentadienyl and phenyl signals in correct relative intensities. Both complexes showed strong molecular ions [$Fe(\eta\text{-}C_5H_5)(EC_4Ph_4)$]$^+$ (E = P or As) in their mass spectra.

Like the corresponding η-cyclopentadienyl complex,[18a] the η-tetraphenylphospholyl- and π-arsolyl-tricarbonylmanganese complexes can undergo a number of carbon-monoxide displacement reactions [18b] as illustrated in Schemes 5 and 6.



SCHEME 5 E = P or As, L = $\mathrm{PPh_3}$; E = As, L = $\mathrm{PhC{\equiv}CPh}$

Although from i.r. evidence cyclo-octene appeared to react in an analogous manner, we were unable to obtain an analytically pure product.

All of these products were obtained in moderate or good yields, in interesting contrast to the low yields[19] from the corresponding reactions of tricarbonyl(η-pyrrolyl)manganese.

EXPERIMENTAL

Reactions were routinely done under an atmosphere of dry oxygen-free nitrogen. Hydrocarbon solvents were dried over fine sodium wire and flushed several times with dry nitrogen in the reaction vessel. σ-Bonded tetraphenylphosphole and -arsole derivatives of manganese, rhenium, and iron were prepared as described previously.[8]

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer, and unless otherwise stated were run in cyclohexane solution. Hydrogen-1 n.m.r. spectra were obtained on Varian 100 or JEOL MH100 instruments, mass spectra on M.S. 902 and VG Micromass spectrometers.

Pyrolysis of the Tetraphenylphosphole and Tetraphenylarsole Pentacarbonyl Complexes of Manganese and Rhenium.—Quantities (*ca.* 1 mmol) of the above four compounds were each heated under reflux in either decane or xylene. After *ca.* 20 min the i.r. spectrum in the metal carbonyl region showed in each case that no σ-bonded pentacarbonyl species remained. The reaction mixture was filtered while hot, solvent removed (45 °C, 0.001 mmHg),* and the residue recrystallised from cyclohexane to give golden yellow crystals of the appropriate η^5-bonded species (Table).

Alternatively, quantities (1 mmol) of the σ-bonded pentacarbonyls were heated *in vacuo* in sealed glass tubes at 120 °C for 1 h. The remaining solids were recrystallised from hexane to give the η^5-bonded tricarbonyl complexes.

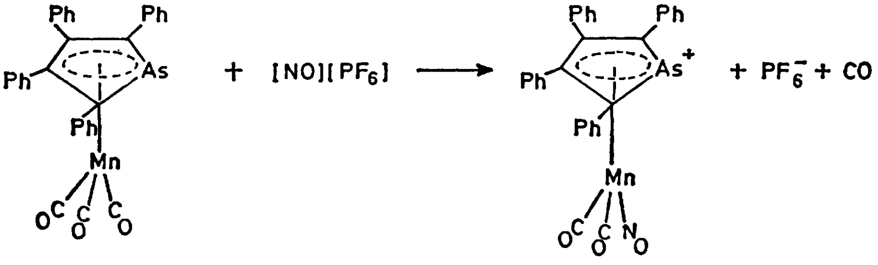
Pyrolysis of the Dimeric Tetraphenylphosphole and Tetraphenylarsole Tetracarbonyl Complexes of Manganese and Rhenium.—The complex $[\{\mathrm{Mn(CO)_4(PC_4Ph_4)}\}_2]$ (0.27 g) was heated under reflux in decane (20 $\mathrm{cm^3}$) for 10 min. After this time the cloudy solution was filtered, and solvent removed (40 °C, 0.001 mmHg). The residue was recrystallised from hexane to give tricarbonyl(1—5-η-2,3,4,5-tetraphenylphospholyl)manganese (0.16 g, 67%) identical to that reported in the Table. In a similar manner pyrolyses of the other dimers $[\{\mathrm{M(CO)_4(EC_4Ph_4)}\}_2]$ (M = Mn, E = As; M = Re, E = P or As) led to the corresponding η^5 tricarbonyl monomeric species in good yield (55—70 %).

Pyrolysis of $[\mathrm{Mn(CO)_5(SbC_4Ph_4)}]$ under various conditions led to no new metal-carbonyl-containing species.

Interaction of $\mathrm{(Ph_4C_4E)_2}$ (E = P *or* As) *and Decacarbonyldimanganese.*—A quantity (0.5 mmol) of $\mathrm{(Ph_4C_4P)_2}$ (0.39 g) or $\mathrm{(Ph_4C_4As)_2}$ (0.43 g) was heated under reflux in xylene (20 $\mathrm{cm^3}$) with decacarbonyldimanganese (0.195 g, 0.5 mmol) for 20 min. After this time each reaction mixture was filtered, solvent removed (45 °C 0.001 mmHg), and the residue recrystallised from hexane to yield $[\mathrm{Mn(CO)_3(\eta\text{-}PC_4Ph_4)}]$ (0.1 g, 23%) or $[\mathrm{Mn(CO)_3(\pi\text{-}AsC_4Ph_4)}]$ (0.17 g, 30%). Each product had an identical melting point, i.r. spectrum, and mass spectrum to the corresponding complex produced by pyrolysis, as in the Table.

Interaction of 2,3,4,5-*Tetraphenyl*-1-*trimethylsilylarsole and Pentacarbonylchloromanganese.*—The arsine (0.25 g, 0.5 mmol) and the chlorocarbonyl (0.11 g, 0.5 mmol) were heated together in dry tetrahydrofuran under reflux. After 2 h all chlorocarbonyl was exhausted. Solvent was removed (20 °C, 0.1 mmHg) and trapped at −150 °C. Recrystallisation of the residue from hexane gave $[\mathrm{Mn(CO)_3(\eta\text{-}AsC_4Ph_4)}]$ (0.07 g, 30%) as characterised in the Table. Gas–liquid chromatography demonstrated the presence of chlorotrimethylsilane in the trapped solvent.

Interactions of Tricarbonyl(1—5-η-2,3,4,5-*tetraphenylarsolyl*)*manganese.*—*With triphenylphosphine.* The tricarbonyl (0.57 g, 1 mmol) and the phosphine (0.26 g, 1 mmol) were irradiated together in hexane solution with a u.v. lamp (24 h). After this time solvent was removed (20 °C, 0.01 mmHg), and the residue recrystallised from hexane–chloroform to produce dicarbonyl(1—5-η-2,3,4,5-



SCHEME 6

---

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

Pyrolysis of $[M(CO)_5(EC_4Ph_4)]$ (E = P or As, M = Mn or Re) to produce the corresponding 1—5-η-phospholyl and 1—5-η-arsolyl metal tricarbonyls

Reactant	Product [a]	Reaction conditions	Yield (%)	M.p. (θ_c/°C)	Analysis (%) [b]		$\tilde{\nu}$(CO) [c]/ cm^{-1}	Significant ions in mass spectrum [d]
$[Mn(CO)_5(PC_4Ph_4)]$	$[Mn(CO)_3(\eta\text{-}PC_4Ph_4)]$	Refluxing decane, 20 min	49	120—122	71.0 (70.7)	3.8 (3.8)	2 034 (10), 1 969 (7), 1 955 (8)	526, $[Mn(CO)_3(PC_4Ph)]^+$ (21) 470 $[Mn(CO)(PC_4Ph_4)]^+$ (30) 442, $[Mn(PC_4Ph_4)]^+$ (100) 387, $[C_4Ph_4P]^+$ (26) 178, $[C_2Ph_2]^+$ (10)
	$[Mn(CO)_3(\eta\text{-}PC_4Ph_4)]$	Refluxing xylene, 15 min	45	121				
	$[Mn(CO)_3(\eta\text{-}PC_4Ph_4)]$	*In vacuo*, 120 °C, 1 h	43	120				
$[Mn(CO)_5(AsC_4Ph_4)]$	$[Mn(CO)_3(\eta\text{-}AsC_4Ph_4)]$	Refluxing decane, 20 min	58	127	64.9 (65.3)	3.6 (3.5)	2 024 (10), 1 960 (7.5), 1 944 (8)	570, $[Mn(CO)_3(AsC_4Ph_4)]^+$ (35) 514, $[Mn(CO)(AsC_4Ph_4)]^+$ (43) 486, $[C_4Ph_4As]^+$ (100) 178, $[C_2Ph_2]^+$ (16)
	$[Mn(CO)_3(\eta\text{-}AsC_4Ph_4)]$	*In vacuo*, 115 °C, 1 h	57	124—127				
$[Re(CO)_5(PC_4Ph_4)]$	$[Re(CO)_3(\eta\text{-}PC_4Ph_4)]$	Refluxing xylene, 25 min	43	119			2 029 (10), 1 957 (8), 1 939 (9.5)	658, 656, $[Re(CO)_3(PC_4Ph_4)]^+$ (100) 630, 628, $[Re(CO)_2(PC_4Ph_4)]^+$ (42) 602, 600, $[Re(CO)(PC_4Ph_4)]^+$ (19) 574, 572, $[Re(PC_4Ph_4)]^+$ (74) 356, $[C_4Ph_4]^+$ (32) 178, $[C_2Ph_2]^+$ (27)
	$[Re(CO)_3(\eta\text{-}PC_4Ph_4)]$	*In vacuo*, 120 °C, 1 h	55	119	56.8 (56.6)	3.5 (3.0)		
$[Re(CO)_5(AsC_4Ph_4)]$	$[Re(CO)_3(\eta\text{-}AsC_4Ph_4)]$	Refluxing decane, 25 min	61	129—130	54.2 (53.1)	3.2 (2.9)	2 028 (10), 1 952 (9), 1 937 (9.5)	702, 700, $[Re(CO)_3(As_4C_4Ph_4)]^+$ (100) 674, 672, $[Re(CO)_2(AsC_4Ph_4)]^+$ (45) 646, 644, $[Re(CO)(AsC_4Ph_4)]^+$ (21) 618, 616 $[Re(AsC_4Ph_4)]^+$ (95) 356, $[C_4Ph_4]^+$ (53) 178, $[C_2Ph_2]^+$ (32)
	$[Re(CO)_3(\eta\text{-}AsC_4Ph_4)]$	Refluxing xylene, 20 min	39	129				

[a] The ^1H n.m.r. spectra of all four products in deuteriochloroform showed only the phenyl multiplet in the region δ = 6.7—7.3, and no other peaks. [b] Calculated values are given in parentheses. [c] Relative peak heights are in parentheses. [d] *m/e* Values with relative intensities in parentheses.

tetraphenylarsolyl)(triphenylphosphine)manganese (0.58 g, 72%), as a yellow crystalline solid, m.p. 244 250 °C, which was sparingly soluble in hexane but appreciably soluble in more polar solvents such as chloroform {Found: C, 71.8; H, 4.2. $[Mn(CO)_2(PPh_3)(\eta\text{-}AsC_4Ph_4)]$ requires C, 71.6; H, 4.4%}. The complex showed only two peaks in the metal carbonyl region of its i.r. spectrum at 1 931 (10) and 1 872 (9) cm^{-1}, and a complex aryl multiplet in its ^1H n.m.r. spectrum at δ = 6.3—7.5.

With diphenylacetylene. The tricarbonyl (0.57 g, 1 mmol) and the acetylene (0.18 g, 1 mmol) were irradiated together in hexane solution with a u.v. lamp (48 h). Solvent was then removed (25 °C, 0.1 mmHg), and the residue recrystallised from methylcyclohexane to give yellow crystals (0.29 g, 40%), m.p. 163—165 °C {Found: C, 73.7; H, 4.3. $[Mn(CO)_2(C_2Ph_2)(\eta\text{-}A_5C_4Ph_4)]$ requires C, 73.3; H, 4.2%}. The complex had two intense peaks in the metal carbonyl region of the i.r. spectrum at 1 939 (10) and 1 899 (8.5) cm^{-1}.

The corresponding experiment with cyclo-octene showed a comparable reaction (from the i.r. spectrum of the product mixture), but we were unable to isolate an analytically pure product.

With nitrosyl hexafluorophosphate. The tricarbonyl (0.57 g, 1 mmol) was dissolved in methyl cyanide (20 cm^3) and to this was added $[NO][PF_6]$ (0.23 g) with vigorous stirring. Gas evolution occurred during the addition, and when it was complete the mixture was filtered and solvent removed (25 °C, 0.001 mmHg). The residue was recrystallised twice from chloroform to give a dark yellow air-sensitive product (0.23 g, 32%), m.p. 127 °C {Found: C, 54.6; H, 3.4. $[Mn(CO)_2(NO)(\eta\text{-}AsC_4Ph_4)][PF_6]$ requires C, 51.4; H, 2.9%}. Somewhat unsatisfactory analytical data for this complex appear to be due to partial decomposition before analysis could be started. The i.r. spectrum showed two metal carbonyl bands at 2 122 and 2 084 cm^{-1} and a single metal nitrosyl absorption at 1 859 cm^{-1}.

Pyrolysis of Dicarbonyl(η-cyclopentadienyl)(2,3,4,5-tetraphenylarsolyl)iron.—The dicarbonyl (200 mg, 0.33 mmol) was dissolved in xylene and heated under reflux (60 h). The resulting mixture was cooled and filtered through Kieselgühr, then concentrated under reduced pressure to a volume of 15 cm^3. Hot hexane (35 cm^3) was added until a yellow solid began to appear. When cool the liquor was decanted, and the residual solid was washed with hexane (2 × 5 cm^3) and dried (20 °C, 0.01 mmHg). This was identified (m.p., ^1H n.m.r. and mass spectra) as a by-product, 1,1′-bi(2,3,4,5-tetraphenylarsole). Another 10 cm^3 of solvent were removed from the decanted liquor at 20 °C (1 mmHg) and the solution kept at 0 °C for 10 h when a further crop of the biarsole was obtained. This procedure of evaporation and cooling was repeated twice after which the total yield of the bis(arsacyclopentadiene) was *ca.* 40 mg. The remaining cloudy liquor was centrifuged for 15 min to give a clear solution which was then kept at 20 °C for 15 h. Red needle-shaped crystals of (η-cyclopentadienyl)(1—5-η-2,3,4,5-tetraphenylarsolyl)iron (70 mg) were obtained, m.p. 247—249 °C (in nitrogen and *in vacuo*) (Found: C, 71.65; H, 4.60. $C_{33}H_{25}AsFe$ requires C, 71.75; H, 4.55%). The crystals grew on the walls of the centrifuge tube and were isolated by decantation and washing with hexane (3 × 5 cm³). There were no absorptions in the carbonyl region of the i.r. spectrum. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: $\delta =$ 4.42 (1 H) (C_5H_5) (sharp singlet) and 6.98—7.12 (4 H) (4 Ph) (multiplet). The molecular ion $[Fe(C_5H_5)(AsC_4Ph_4)]^+$ was the highest peak in the mass spectrum ($m/e =$ 552); the isotope distribution pattern obtained agreed completely with that predicted by computation.

In an analogous pyrolysis we prepared (η-cyclopentadienyl)(1—5-η-2,3,4,5-tetraphenylphospholyl)iron (35% yield), as orange crystals, 227—229 °C (Found: C, 77.4; H, 4.9. $C_{33}H_{25}FeP$ requires C, 77.9; H, 4.9%). There were no absorptions in the metal carbonyl region of the i.r. spectrum. Hydrogen-1 n.m.r. spectrum in $CDCl_3$; $\delta =$ 4.48 (1 H) (C_5H_5) (sharp singlet) and 6.8—7.1 (4 H) (4 Ph) (multiplet). The molecular ion $[Fe(C_5H_5)(PC_4Ph_4)]^+$ was the highest peak in the mass spectrum ($m/e = 508$).

[8/2023 *Received, 21st November,* 1978]

REFERENCES

[1] E. Braye and W. Hubel, *Chem. and Ind.*, 1959, 250.

[2] E. Braye, W. Hubel, and E. Caplier, *J. Amer. Chem. Soc.*, 1961, **83**, 4406.

[3] A. N. Hughes and C. Scrivant, *J. Heterocyclic Chem.*, 1970, **7**, 1.

[4] E. H. Braye and K. K. Joshi, *Bull. Soc. chim. belges*, 1971, **80**, 651.

[5] F. Mathey, *J. Organometallic Chem.*, 1975, **93**, 377; F. Mathey and G. Muller, *ibid.*, 1977, **139**, 77; G. Thiollet, R. Poilblanc, D. Voigt, and F. Mathey, *Inorg. Chim. Acta Letters*, 1978, **30**, L294.

[6] J. M. Rosalky, B. Metz, F. Mathey, and R. Weiss, *Inorg. Chem.*, 1977, **16**, 3307.

[7] E. W. Abel, I. W. Nowell, A. G. J. Modinos, and C. Towers, *J.C.S. Chem. Comm.*, 1973, 258.

[8] E. W. Abel and C. Towers, *J.C.S. Dalton*, 1979, 814.

[9] R. C. Cookson, G. W. A. Fowles, and D. K. Jenkins, *J. Chem. Soc.*, 1965, 6405.

[10] F. Mathey, A. Mitschler, and R. Weiss, *J. Amer. Chem. Soc.*, 1977, **99**, 3537; F. Mathey, *J. Organometallic Chem.*, 1977, **139**, 77.

[11] K. K. Joshi, P. L. Pauson, A. R. Quazi, and W. H. Stubbs, *J. Organometallic Chem.*, 1964, **1**, 471.

[12] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 796.

[13] W. Schafer, A. Schweig, G. Markl, H. Hauptmann, and F. Mathey, *Angew. Chem.*, 1973, **85**, 140.

[14] W. Schafer, A. Schweig, and F. Mathey, *J. Amer. Chem. Soc.*, 1976, **98**, 407.

[15] F. Mathey, *Tetrahedron Letters*, 1976, 4155.

[16] R. G. Hayter, *J. Amer. Chem. Soc.*, 1963, **85**, 3120.

[17] M. Cooke, M. Green, and D. Kirkpatrick, *J. Chem. Soc.* (*A*), 1968, 1507.

[18] (*a*) W. Strohmeier and C. Barbeau, *Z. Naturforsch.*, 1962, **B17**, 848; (*b*) A. Breque and F. Mathey, *J. Organometallic Chem.*, 1978, **144**, C9.

[19] R. B. King and E. Efraty, *J. Organometallic Chem.*, 1969, **20**, 264.