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HALOGENATION, THALLIATION AND MERCURIATION OF TRIPHENYL PHOSPHONIUM AND DIMETHYLSULPHONIUM CYCLOPENTADIENYLIDES

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Abstract—The reactions of triphenylphosphonium and dimethylsulphonium cyclopentadienylides with various electrophilic species have been studied in both acidic and neutral media. The dominant reaction type is that of addition rather than substitution. Attack is principally at C2 in the sulphonium derivative but at C3 in the phosphonium compound due mainly to steric factors. Thalliation and mercuriation reactions were studied in detail by NMR methods and the products of the reactions identified.

During the past decade, interest has grown in the structure and reactivity of cyclopentadienylides.[1] These derivatives are considered to be resonance hybrids of the ylide and ylene structures shown below.

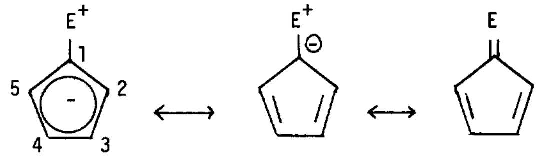
Yoshida *et al.*[2a,b] have shown that the contributions of the ylide form in the ground states of II and III are 84 and 83% respectively from semi-empirical MO calculations. In addition, Cl appears to have the greatest electron density, whereas C2 is the favoured position for electrophilic attack as deduced from superdelocalisabilities and localisation energies.[3] The latter postulate has received justification from a number of sources. Thus Ramirez and Levy[4] had earlier reported that I reacted with diazonium salts exclusively at the 2 position, the product being identified by chemical synthesis. Nitrosation,[5] and nitration of I[3] and acetylation of III[6] followed a similar substitution pattern. The products were characterised by their NMR spectra. The cyclopentadienylides did not undergo Diels–Alder reactions,[3] but underwent instead Michael addition reactions, providing further evidence against the existence of a significant ylene structural contribution. The regiospecificity of the above reactions leads to the conclusion that they are dominated by electronic rather than steric effects, particularly in view of known preference for tetraphenylmethane to undergo 4-substitution.[7] More recently, Freeman and Lloyd[8] showed that triphenylphosphonium 2,4-diphenylcyclopentadienylide was acetylated both in the 3 and 5 positions. Further evidence that regiospecificity at C2 is not always found comes from the recent work of Holy *et al.*[9] who showed from X-ray crystallographic studies that mercuric salts reacted with I specifically at C3, the result being interpreted in terms of steric hindrance between the HgX_2 and the bulky Ph_3P substituent.

The work reported here deals in detail with reactions of I and III with mercury(II) and thallium(III) salts and other simple electrophilic reagents.

RESULTS AND DISCUSSION

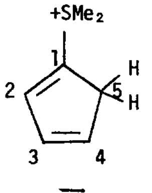
Reactions with trifluoroacetic and acetic acids

The reactions of I and III were studied in detail. The NMR spectrum of freshly crystallised III in CF_3CO_2H was run after 10 min (Fig.(1)). The spectrum comprises a multiplet (3H) at $\delta = 6–7.3$ ppm, an apparent quartet ($J = 1.2$ Hz) at 3.07 (2H) and a singlet at 2.67 ppm (6H). In addition, a small singlet appeared at 2.42 ppm. The spectrum did not change over a period of three days. In general, the spectrum resembled that expected for structure IV, the hydrogen at C2, being proximate to the positively charged SMe_2 group, would appear downfield from those at C3 and C4. Thus the peak at

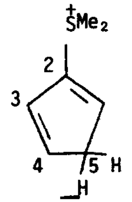


a b c

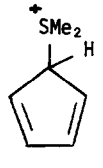
E = Ph_3P(I)
nPr_3P(II)
Me_2S(III)



IV



V



VI

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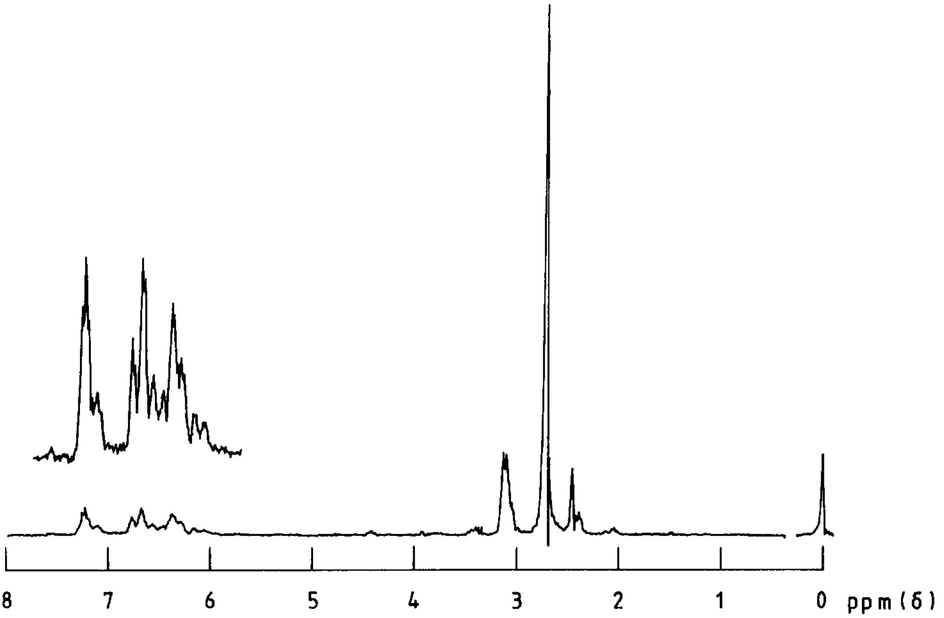


Fig. 1. PMR spectrum of Me_2Scp (0.2 M) in CF_3CO_2H.

7.17 ppm (1H) is assigned to H_2. In addition, this peak appears as a well-defined triplet, with $J = 1.8$ Hz being within the usually observed range for allylic coupling constants.

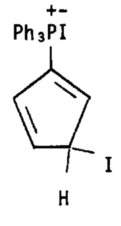
The splitting of the CH_2 signal thus results in part from this coupling process but additional coupling must occur with H_3.* On closer inspection, the six proton singlet was found to comprise two signals at 2.69 and 2.67 in the ratio of 1:1.7. This strongly suggests the presence of another isomer V. Support for this comes from the observation of a small multiplet just upfield from the H_2 triplet in approximately the same ratio as the methyl signals. The small singlet at 2.42 could well be due to a small amount of isomer VI since the S^+Me_2 group would lie above the plane of the cyclopentadiene ring and in the shielding zone of the cisoid diene. Thus it would appear that all three isomers occur (VI 56 %, V 33 %, VI 11 %). Since steric effects for CF_3CO_2H acting as an electrophile will be small and since this reactivity is high, then the selectivity of the reaction is likely to be correspondingly low.

A similar reaction was observed in acetic acid, the NMR spectrum showing signals at 7.2, 1H (tr $J \sim 1.5$ Hz); 6.67, 1H (tr $J = 5$ Hz), 6.37, 1H on 3.25 m (2H), 2.8 s (6H). The spectrum appeared to show principally isomer IV. This is in keeping with the greater selectivity of the weaker reagent.

Ph_3Pcp (I) reacted in a similar fashion with CF_3CO_2H, the NMR spectrum showing a very complex multiplet containing both aromatic and diene protons at 6–8 ppm (18H) and a somewhat broad singlet at 3.17 ppm (2H) due to the CH_2 signals. Owing to the complexity of the spectrum it is not possible to determine the isomeric composition. When the reaction was performed in deuteriated acid, little or no exchange was observed indicating that the protonation was essentially irreversible. This is a surprising result, particularly in view of the report of quantitative exchange observed when a chloroform solution of I was shaken with D_2O.[3] One can only assume that the exchange process requires the presence of a basic species in the medium. Interestingly, a brown solid was isolated from the reaction of I with CF_3CO_2H which analysed as $Ph_3Pcp.2CF_3CO_2H$. The exact structure of this species is unknown.

Reactions with halogens

Reactions of Ph_3Pcp (I) with *N*-halosuccinimides have been reported to yield exclusively tetrahalo derivatives.[3] When a solution of I was treated with an equimolar quantity of iodine, a brilliant green fluorescence occurred. The NMR spectrum of the solution showed a broad multiplet at 6.5–8.5 ppm (18H) and a somewhat broad singlet at 3.77 ppm (1H). On evaporation a black solid was obtained which analysed as $Ph_3Pcp.I_2$. In view of the previously reported attack at C_3 by HgI_2,[9] an electrophile of similar bulk to I_2, the structure of the *adduct* is likely to be



VII

Bromination gave a similar result, the methine appearing at 3.83 ppm. The iodination of Me_2Scp gave a complex mixture of products. Addition reactions predominate. It seems that a basic species must be present to generate the substitution product.

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* The CH_2 signal for 1-trimethylsilylcyclopentadience appeared at $\delta = 2.97$ and showed a very similar splitting pattern.[10]

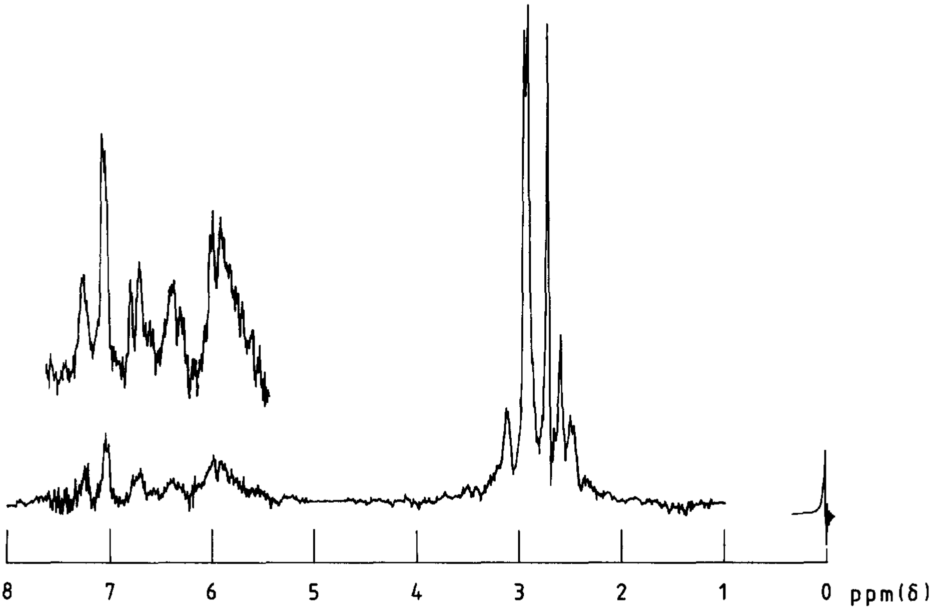
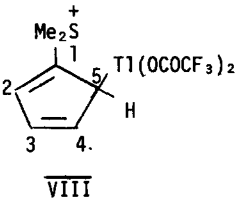


Fig. 2. PMR spectrum of reaction mixture ((0.2 M) in each reagent) of Me_2Scp and Tl $(OCOCF_3)_3$ after 20 h at 18° in solvent CF_3CO_2H.

Reactions with metal salts

(a) *Thalliation.* In some ways a study of thalliation reactions is more instructive than that of the more commonly investigated mercuriation reactions. Thallium has two naturally occurring magnetic isotopes ^{205}Tl and ^{203}Tl (70.5 and 29.5 % abundance) both of spin $\frac{1}{2}$, and thus the nuclei can couple with neighbouring protons. Normally the ^{205}Tl-^{1}H and ^{203}Tl-^{1}H signals are not separable due to the almost identical gyromagnetic ratios. The latter except under conditions of very high resolution usually appear as a shoulder on the ^{205}Tl-H signal. The principal features of these interactions are the extremely large values of the Tl-H coupling constants (200–1000 Hz depending on the type of proton and the bonding involved). This often makes identification of products a much simpler task.[11] Such proved to be the case in the reaction of Ph_3Pcp(I) and Me_2Scp(III) with thallium(III) and tris(trifluoroacetate) at room temperature in CF_3CO_2H (0.2 M in each reagent). For III, reaction was much slower than the corresponding mercuriation *vide infra.* The six proton signal and the methylene resonance of IV gradually decreased and a sharp doublet ($J = 2$ Hz) appeared at 2.92 ppm, with corresponding changes in the diene multiplets, the broad product signals growing at ~5.8 ppm. The reaction appeared to come to equilibrium at 65 % conversion after 20 h. The final spectrum appears in Fig. (2). Close inspection revealed the presence of a small sharp doublet at 2.47 ppm ($J = 2$ Hz). A similar doublet was observed at 7.05 ppm ($J = 2$ Hz). The separation of the two doublets is thus 275 Hz which compares well with the corresponding Tl-H coupling constant in dicyclopentylthallium derivatives[11] (J Tl – αH ~ 214 Hz) particularly in view of the generally greater values of coupling constants for RTl^{2+} species compared with R_2Tl^+. The chemical shift of the methine in the product is therefore 4.76. This value compares with that observed for cyclopentadienylmercuric chloride at −113° (4.136),[12] the latter being a fluxional molecule with rapid 1–2 shifts.[13] The higher δ value for the thalliated species can be accounted for by the strong electron withdrawal of the Me_2S^+ substituent. The fact that the Tl-H signals appear as doublets suggest that the product has the structure VIII.



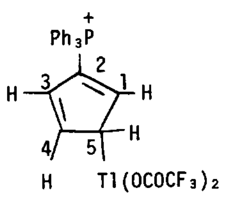
(counterion omitted)

VIII

The observed splitting of the methyl signal (2.92 ppm) is due to either restricted rotation about the Cl-sulphur bond, or long range Tl-CH coupling which is well documented in aromatic derivatives.[11]

The latter seems the more probable in view of the lack of such splitting in the case of mercuriation *vide infra.*

For Ph_3Pcp, the reaction is essentially complete after 48 h as judged from the disappearance of the $>CH_2$ signal at 3.10 ppm which is replaced by a *triplet* ($J = 5$ Hz) at 2.43 ppm. Close inspection of the aromatic multiplet revealed the presence of a triplet at 7.05 ppm giving a J Tl-H of again 275 Hz. The observation of triplets is consistent with the structure IX where the methine is adjacent to, and presumably equally coupled to protons at Cl and C4.



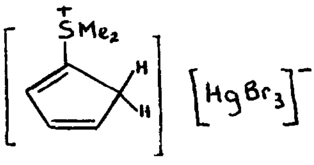
IX

This assignment is supported by X-ray analysis of the corresponding HgI_2 adduct in which the mercury attacked at C3 in Ph_3Pcp, instead of the usual C2 attack. This is probably due to the large steric compression between the incoming thallium salt and the Ph_3P group.[9] The chemical shift of the methine (C5) in IX is thus 4.74 ppm—very close to that observed for VIII.

The products do not seem to exhibit rapid fluxional behaviour. Rapid 1–2 shifts, such as those observed for the cyclopentadienyl mercurials, should result in a sharp singlet for the diene protons. The product signals are rather broad which suggests slower sigmatropic shifts in keeping with the presence of a positively charged substituent. As previously discussed,[14] satellite signals are observed even in rapidly exchanging systems provided that the processes are *intramolecular*.

(B) *Mercuriation*—(a) *in acidic media*. The reaction of Me_2Scp with $Hg(OCOCF_3)_2$ in CF_3CO_2H (0.2 M in each reagent) was much more rapid than the corresponding thalliations, and came to equilibrium in less than 10 min at room temperature at almost exactly 50% conversion. The Me_2S signal in the product appeared as a sharp singlet at 2.77 ppm. The diene portion of the product spectrum consisted of three rather broad peaks at 7.37, 6.83 and 5.83 ppm indicating that as for the thallium derivatives any fluxional processes must be rather slow. The downfield signal (1H) at 7.37 ppm is deshielded with respect to Me_2Scp itself (in $CDCl_3$) and close to the signal assigned to the hydrogen at C2 in IV (7.17 ppm). Thus attack at the 2-position in Me_2Scp is indicated.

Using a fourfold excess of mercuric salt 80% conversion was observed together with some dimercuriation. The reaction of Ph_3Pcp followed a very similar pattern giving 55% conversion at equimolar concentrations. The signals of the diene protons were, in part, masked by the large aromatic multiplet, precluding any structural assignment, though it is assumed that due to steric effects attack now occurs in the 3-position.[9] Me_2Scp was also mercuriated by $Hg(oAc)_2$ in solvent acetic acid. When reaction mixtures were quenched in *dilute* aqueous KBr, a compound was isolated which analysed as $Me_2SC_5H_5 . HgBr_3$. The NMR spectrum in DMSO-d_6 comprised broad one-proton signals at 7.63, 7.05, and 6.83, a broad two-proton signal at 3.67, and a sharp singlet at 3.17 ppm (6H). On adding D_2O all signals except the latter underwent exchange. The structure of the complex is likely to be



X

This product results, very probably from bromide ion catalysed solvolysis of the C–Hg bond in the original adduct. Such reactions are well documented in organomercury chemistry.

Mercuric salts are known to react rapidly with simple ylenes,[15] the reaction being a simple addition

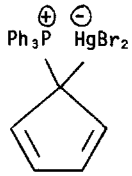
$$Ph_3P=CH_2 + HgCl_2 \rightarrow [Ph_3P-CH_2HgCl]^+ Cl^- \quad (1)$$

across the ylenic double bond. However more complicated processes[16] are sometimes observed

$$2Ph_3P{=}CH_2 + 3HgBr_2 \rightarrow [(Ph_3PCH_2)_2Hg]^{2+} 2HgBr_3^- \quad (2)$$

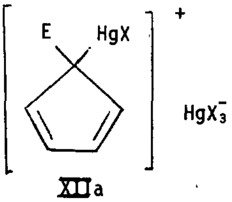
The structure of the latter complex is unknown, however in the presence of excess mercuric salt, complexes with the trihalomercurate anion are formed.[16,17] A complex of stoichiometry $Ph_3PC_5H_5 . HgBr_2$. KBr was obtained when reaction mixtures of I were quenched in *concentrated* KBr. The structure is probably a dicationic complex $K^+ [Ph_3PC_5H_5]^+ [HgBr_4]^{2-}$ whose organic cation has the structure as in *X*.

When exactly *two* equivalents of KBr in dilute solution were used a compound was obtained which was identical with that formed by PhP_3cp and $HgBr_2$ in acetone which, by analogy with the corresponding Me_2Scp derivative *vide infra*, is probably

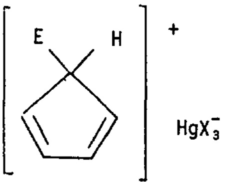


XI

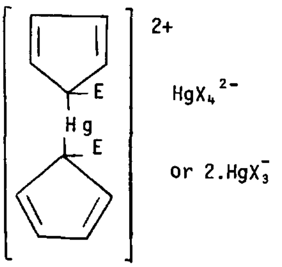
Clearly changes in solvent and acidity have a very marked effect on the type of product formed. The exact nature of these interesting species must however await detailed X-ray analysis.



XIIa



XIIb

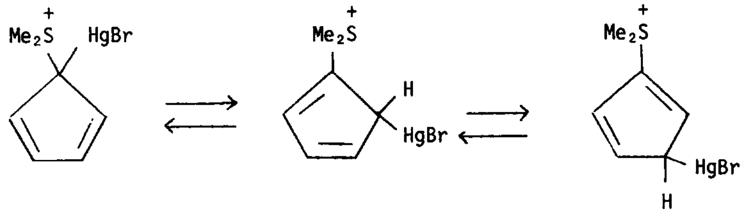


XIIc

Other possible structures of the halide complexes such as XII a–c are ruled out by elemental analysis and/or NMR spectra.

In view of the rapid nature of the addition of mercury salts to ylenes, the first step in the above reaction is also probably an addition followed by rearrangement and complexation with halide ion. Further support comes from the well established thermodynamic stability of 55′ cyclopentadienes *vide infra*.

(b) *Reaction in neutral media*. Treatment of Me_2Scp with $HgBr_2$ in solvent acetone rapidly gave a 1:1 adduct. The NMR spectrum in DMSO-d_6 comprised a sharp singlet at 3.02 (6H) and two symmetrical triplets at 6.00 (2H) and 6.63 ppm (2H) [$J = 2.4$ Hz]. This compares with the symmetrical triplets observed at 5.7 and 6.6 ppm [$J = 3$ Hz] for Me_2Scp in this solvent. The triplets are probably due to deceptively simple AA′BB′ systems with coincident coupling constants. In addition the IR spectrum has bands typical of diene-like ligands.[18] Thus the product would appear to have the structure XIIIa



XIIIa XIIIb XIIIc (3)

which can in theory give rise to isomers b and c via sigmatropic shifts. Work on the corresponding uncharged disubstituted cyclopentadienes has shown conclusively that the 5,5′ isomer is the most thermodynamically stable form.[19] 5,5′ bis(trimethylstannyl) cyclopentadiene was found to undergo fairly rapid 1–3 metallotropic shifts but the equilibrium at room temperature strongly favoured the 5,5′ isomer.[20] The corresponding silicon analogue shows similar behaviour but the rate of rearrangement is much slower.[21] Thus structure XIIIa is likely to predominate particularly in view of the strong electron attraction by Me_2S^+ which would deactivate the ring towards sigmatropic shifts. The corresponding reaction with Ph_3Pcp gives an NMR spectrum showing two broad singlets (each 2H) at 6.05 and 6.33 ppm together with the aromatic multiplet (15H) at 7–8 ppm which again suggests a structure like XIIIa.

The question as to why attack should be at Cl in neutral solution and C2 in the presence of excess bromide ion is intriguing. A structure such as XI would undoubtedly be stabilised by a bromine bridge between phosphorus and mercury. Addition of a second bromide ion may be just sufficient to destabilise XI by steric interaction and produce attack at C2 or C3. Another unanswered question is why, in acetone solution, should attack be at Cl, whereas in THF the C3 adduct is formed?[9] It seems that there is a very delicate balance of polar, steric, and solvation effects which dictates the nature of the reaction products. It is also clear that the dominant reaction is one of *addition* rather than the hitherto reported substitution. The latter is only observed when a sufficiently strong base is present either in the reaction medium or in the work-up procedure.

EXPERIMENTAL

Me_2Scp[6] and Ph_3Pcp[22, 23] were prepared by standard lit methods. Iodine and bromine were of Analar quality. Thallium(III) tris(trifluoroacetate) was supplied by Aldrich Chemicals Ltd. Mercuric(II) bis(trifluoroacetate) was prepared by dissolving yellow mercuric oxide in excess CF_3CO_2H containing 10% $(CF_3CO)_2O$ and allowing to crystallise. Mercuric halides were recrystallised from acetone or methanol and mercuric acetate from glacial acetic acid. Trifluoroacetic acid was redistilled prior to use. The deuteriated acid was prepared by *carefully* adding D_2O (99.7 at %D) to a slight excess gently refluxing $(CF_3CO)_2O$ and fractionating the reaction mixture to give CF_3CO_2D (98 at %D) in 90% yield. Other deuteriated solvents were obtained commercially and used without further purification.

NMR spectra were run on a Varian EM 360 spectrometer housed in a constant temperature room (18°). Chemical shifts (δ) were measured in ppm from Me_4Si. The spectra obtained are discussed in the main text. Microanalyses were performed by Mr. M. Hart (University of Manchester).

(i) *Preparation of mercury compounds and complexes*

(a) *Neutral solution*. Ph_3Pcp (0.65 g 2 m mol) was dissolved in hot AR acetone (60 ml) and solid $HgCl_2$ (0.54 g 2 m mol) added. The resultant soln was cooled to 0° and crystallisation occurred. The light brown crystals were filtered to give 0.80 g (67%) MP 163–164. (Found: C, 46.6; H, 3.3; Cl, 11.2. Calc. for $(C_6H_5)_3PC_5H_4.HgCl_2$: C, 46.2; H, 3.2; Cl, 11.9%) The m.p. was 20° lower than that of the complex isolated by Holy *et al.* in THF.[9]

IR (Nujol and hexachlorobutadiene mulls) 3040 vw, 2810 vw, 1710 w, 1590 w, 1485 m, 1475 w, 1440 vs, 1415 vs, 1350 m, 1310 w, 1215 w, 1105 vs, 1080 m, 1030 w, 1000 s, 905 w, 850 s, 835 s, 810 s, 760 m, 745 m, 735 m, 720 vs, 690 vs.

The corresponding bromide (91% MP 176°) and iodide (68% MP 181°) were also obtained with almost identical IR spectra to that of the chloride.

The corresponding complex for Me_2Scp with mercuric bromide was prepared in 74% yield, m.p. 140–141°. (Found: C, 18.0; H, 2.2. Calc. $(CH_3)_2SC_5H_4.HgBr_2$: C, 17.3; H, 2.1.) IR (nujol) 1335 w, 1210 vw, 1150 m, 1065 w, 1040 s, 1015 m, 1000 vs, 980 s, 975 s, 935 m, 870 vs, 830 m, 815 vs, 725 s, 675 m.

(b) *Acidic solution*. Ph_3Pcp (3.3 g 10.1 m mol) in glacial AcOH (50 ml) was treated dropwise with mercuric acetate (3.2 g, 10.0 m mol) in AcOH (100 mls) at room temp. The soln was left for 5 min then poured into KBr aq (11 g, 92 m mol in 250 ml). A flocculent white ppt occurred which was filtered off, washed with a little distilled water and dried at the pump. (6.5 g) The product was recrystallised from $CHCl_3$ (75 ml) to give white crystals, m.p. 163°. Flame tests showed the presence of K^+. (Found: C, 32.8; H, 2.4; P, 3.6; Br, 37.7. Calc. for

$(C_6H_5)_3PC_5H_5 . HgBr_3 . KBr$: C, 31.2; H, 2.27; P, 3.55; Br, 36.1 %.)

IR (nujol, hexachlorobutadiene) 3010 vw, 2930 vw, 2860 vw, 1585 w, 1570 vw, 1480 vs, 1435 vs, 1365 vw, 1350 s, 1335 m, 1310 w, 1260 vw, 1230 w, 1180 w, 1160 vw, 1110 vs, 1025 w, 1015 w, 1000 m, 960 w, 915 w, 880 m, 850 w, 820 w, 765 s, 745 s, 720 vs, 690 vs.

When the reaction was repeated and quenched with exactly *two* equivs of KBr, a product was obtained (72 %), m.p. 175°, whose IR and NMR spectra were identical to those of the $HgBr_2$ adduct in neutral soln.

When $Me_2Scp/Hg(oAc)_2$ mixtures were quenched in excess *dil.* KBr (no precipitation occurred in concentrated KBr) a white ppt occurred which after filtration was recrystallised from 95 % EtOH to give long white needles, m.p. 109. (Found: C, 14.8; H, 1.9; Br, 41.5. Calc. $(CH_3)_2SC_5H_5 . HgBr_3$: C, 14.8; H, 1.9; Br, 42.2 %.)

IR (nujol) 1430 m, 1350 s, 1100 w, 1090 m, 1035 w, 1000 s, 975 m, 955 m, 930 w, 900 m, 880 w, 860 vw, 810 w, 720 m, 680 s.

(ii) *Product of reaction of* Ph_3Pcp *with* CF_3CO_2H. Ph_3Pcp (1.0 g 3.0 m mol) was dissolved in CF_3CO_2H (10 mls) to give a colourless soln. Excess acid was removed by rotary evaporation to give a golden oil (2.3 g). This was dissolved in $CHCl_3$ and the soln allowed to stand for 24 hr over anhyd. Na_2CO_3. The mixture was filtered, warmed with a little charcoal, refiltered and evaporated to give a brown solid (1.0 g) which was insoluble in CCl_4. (Found: C, 58.8; H, 3.8. Calc. for $Ph_3Pcp . 2CF_3CO_2H$: C, 58.5; H, 3.8 %.) The IR spectrum showed a strong COl band at 1780 and an intense ν(C–F) band at 1150–1200 cm^{-1}.

(iii) *Product of reaction of* Ph_3Pcp *with iodine*. Ph_3Pcp (0.8 g 2.5 m mol) was dissolved in $CHCl_3$ (10 mls) and AR iodine (0.65 g 9.6 m mol) added portionwise. Immediately a brilliant green fluorescence occurred. The mixture was left for 24 hr at room temp., then evaporated to give a black solid (1.45 g, 100 %). (Found: C, 47.0; H, 3.2; I, 42.9. Calc. for $Ph_3Pcp . I_2$: C, 47.6; H, 3.3; I, 43.8 %.)

(iv) *Note on stability of* Me_2Scp. Me_2Scp slowly underwent decomposition in $CHCl_3$, the original Me resonance at 2.80 ppm being replaced by a signal at 2.18 ppm after a period of 7 days.

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