# Structures and Elimination Reactions of the Trialkylamine Adducts Formed by Monosubstituted Tricarbonylhexadieniumiron Cations

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*Summary* The adducts of tertiary amines with tricarbonyl(hexa-1,3-dienium)iron hexafluorophosphates undergo elimination on heating to give triene complexes in good yields.

IT has been known for some time that $OH^-$ adds to the substituted end of the cation (I).[1] Primary and secondary amines also add in this manner to give compounds with structure (III).[2] It has been suggested on the basis of indirect evidence that tertiary amines add to give compounds having structure (IV).[3]

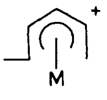
We now report that slow heating under reduced pressure of the trimethyl- and triethyl-amine adducts, (IVa) and (IVb), gives the triene complex (II) in almost quantitative yield. If the triene complex is distilled as it forms then the residue is found to contain only protonated amine. Rapid heating gives a non-volatile mixture.

The ease with which the elimination proceeds raises the

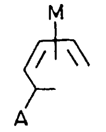
TABLE. $^{13}C$ N.m.r. spectra at 15·03 MHz (p.p.m. relative to $Me_4Si$).

| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | $(CO)_3$ |
|---|---|---|---|---|---|---|---|
| (IVb)[a] | 19·9 | 59·1[d] | 96·3 | 82·9 | 41·7 | 59·1 | 210·7 |
| (IVc)[a] | 19·8 | 60·8 | 96·5 | 82·0[d] | 43·0 (10)[e] | 25·0 (42)[e] | 210·9 |
| (IVc)[b,c] | 20·3 | 60·7 | 96·4 | 80·8 (2·9)[e] | 41·0 (9·8)[e] | 24·8 (42)[e] | 209·8 |
| | 19·0 | 59·3 | 86·8 | 83·6 (2·9)[e] | 43·6 (8·8)[e] | 28·4 (46)[e] | 210·6 |
| (IVd)[b] | 19·0 | 59·2 | 86·9 | 82·9 | 44·8 | 31·4 | 210·6 |

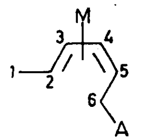
[a] MeCN solution. [b] $CDCl_3$ solution. [c] After 48 h. [d] Broad. [e] $J$ ($^{31}P$–$^{13}C$) in Hz in parentheses.



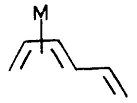
(I)



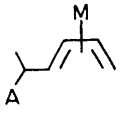
*anti*-(III)



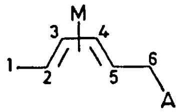
*syn, anti*-(IV)



(II)



*syn*-(III)



*syn,syn*-(IV)

M = $Fe(CO)_3$
(a), A = $Me_3N^+$; (b), A = $Et_3N^+$
(c), A = $Ph_3P^+$; (d), A = $Ph_3As^+$
All $PF_6^-$ salts

possibility that the iron is involved. Iron involvement would favour structure (IV). In an effort to eliminate any doubt about the structures adopted by the tertiary amine adducts[4] the phosphine and arsine adducts, (IVc) and (IVd), were prepared and their $^{13}C$ and $^1H$ n.m.r. spectra were examined. Important data from the $^{13}C$ n.m.r. spectra are given in the Table. It is possible to assign fully the spectrum of (IVc) with the aid of the three observed $^{31}P$–$^{13}C$ coupling constants. In spectra of (IVc), obtained with either off-resonance decoupling or no $^1H$ decoupling, the 25 p.p.m. resonance is observed as a triplet of doublets. This could only be explained in terms of structure (IV). The very close similarity between the spectra of (IVb) and (IVc) suggests that (IVb) also has the structure shown. After 48 h in $CDCl_3$ solution, (IVc) showed new absorptions the intensities of which corresponded approximately with those of the starting peaks. The arsine compound (IVd) showed absorptions in similar positions to those of the new peaks. Musco *et al.* have shown that it is possible to distinguish between *syn–syn* and *syn–anti* configurations using $^1H$ n.m.r. spectroscopy.[5] We have found that (IVb) has the *syn–anti* structure; (IVc) the *syn–anti* and *syn–syn*; and (IVd) the *syn–syn* structure. The *syn–anti* structures of (IVb) and (IVc) probably result from attack on the *cis* form of (I). Presumably $Ph_3As$ also adds to *cis*-(I) but the reaction is slow and an isomerization similar to that observed for (IVc) could explain the *syn–syn* product.

Thus, it appears that steric factors play a dominant role in the reaction of tertiary amines with cations of type (I) and elimination of trialkylammonium ion from the adducts provides a general method for the synthesis of triene complexes in high yield.

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