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Preliminary communication

exo-endo-ISOMERS OF PHOSPHINE-SUBSTITUTED TRICARBONYL-(η-CYCLOHEPTA-1,3-DIENE)IRON COMPLEXES

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Summary

Nucleophilic addition to the tricarbonyl(1—5-η-cycloheptadienylium)iron cation by phosphines forms either the 5-*exo* or 5-*endo* isomer depending on reaction conditions and solvent used; in dichloromethane, direct attack at the ring gives the 5-*exo* phosphine substituted product whereas in acetonitrile, a red intermediate is observed and the 5-*endo* isomer is formed probably via a metal-assisted pathway.

Cyclic diene metal carbonyl complexes may undergo nucleophilic attack at either the dienyl ring [2], the metal [2] or the carbonyl group [3]. In the case of ring attack, the 5-*exo*-substituted product is normally obtained [2] and only very rarely is *endo* substitution observed [4]. However, initial attack if kinetically controlled may not lead directly to the thermodynamically stable product; for example, substitution of the tricarbonyl(1—5-η-cycloheptadienylium) iron cation (I) by ethoxide ions at low temperatures gives the carboethoxy derivative, $C_7H_9Fe(CO)_2(COOEt)$ which on raising the temperature rearranges by a dissociative mechanism to give the 5-*exo* ring substituted ethoxy compound, $C_7H_9OEtFe(CO)_3$ [5]. Recently, it has been shown for the analogous cyclohexadienyl complexes that the 5-*endo* isomer can also be obtained provided the formation of the *exo* isomer is reversible in the presence of acid and the *endo* form possesses sufficient thermodynamic stability [6].

We have suggested previously that for the above cycloheptadienylium iron complex, initial interaction may occur between the attacking nucleophile and the metal atom as evidenced by an intermediate red colour prior to either ring addition [1] or carbonyl substitution followed by ring substitution [5] but in all cases the 5-*exo* isomer is the final product. Our previous report of a

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red colour developing during phosphine substitution has been criticized [7]. In this note, we report that by careful choice of both phosphine (PEt_3, P-n-Pr_3, P-n-Bu_3 and PMe_2Ph) and solvent (CH_3CN and CH_2Cl_2), the 5-*endo* and 5-*exo* phosphine substituted isomers are formed, respectively.

The yellow 5-*exo* product was obtained by adding the corresponding phosphine (1/1 molar ratio) to a stirred suspension of I in CH_2Cl_2 which rapidly turned pale yellow. No red intermediate was observed in this solvent contrary to our previous report [1] where the quoted solvent should have been acetonitrile. Reduction in reaction volume and addition to pentane gave good yields of the 5-*exo* product. The brown 5-*endo* isomer was obtained by treating I with a slight excess of phosphine (1/1.2 molar ratio) and adding excess acetonitrile (e.g. 50 ml of CH_3CN for 3 mmol of I). On stirring, a red colour developed within 5 min and after reaction for 15—30 min, reduction of volume and addition to ether the brown 5-*endo* product was isolated. The concentrations of reactants are important in this case and, for example, if insufficient CH_3CN is used only the yellow *exo* isomer is formed. All products gave satisfactory analyses. Metal carbonyl IR data (in CH_2Cl_2) of a pair of isomers are very similar except that the highest frequency band is about 5 cm^{-1} lower for the *endo* isomer. However, the ^1H and ^{13}C NMR spectra are quite distinctive.

A detailed study of the *exo*- and *endo*-triethylphosphonium complexes was carried out in deuterochloroform and deuterated dichloromethane. The spectra were consistent with a 5 substituted system. In the *exo* case, H(5) is coupled to the H(6) *exo* and H(6) *endo* protons and an ABX system results. H(4) occurred at slightly higher field than H(5), resulting in overlapping. Decoupling experiments enabled H(5) to be observed as a double doublet and showed H(4,5) to be zero. In the *endo* case, H(4) was shown to be coupled to H(5), and the H(5) signal was considerably narrowed. This is analogous behaviour to that observed in *exo*- and *endo*-anilino derivatives [8] and shows the yellow and brown compounds to be 5-*exo* and 5-*endo*, respectively.

^{13}C studies supported the above results. In the *exo* case, C(4) occurred as a doublet, due to coupling with the phosphonium group (J(P—C) 4.9 Hz). C(5) was also a doublet, (J(P—C) 39.1 Hz). In the *endo* case, the corresponding values of J(P—C) were 7.3 and 36.6 Hz. Thus a change in orientation of the phosphonium group with respect to the ring system is clearly demonstrated.

A ring inversion at C(6) is excluded since H(1) occurs as a triplet in both isomers in the proton spectra, and C(6) and C(7) occur at almost the same values in both isomers in the ^{13}C spectra.

For a particular phosphine, both isomers are reasonably stable but treatment of the 5-*exo* isomer with excess phosphine in acetonitrile leads to its conversion to the 5-*endo* isomer with again development of a red colouration during reaction. However, in the case of phosphines with more than one phenyl substituent, only the 5-*exo* isomer can be prepared irrespective of reaction conditions.

These results show clearly that addition to the tricarbonyl (1—5-η-cycloheptadienylium) iron cation by phosphines yields both the 5-*exo* and 5-*endo* isomers depending on reaction conditions. The presence of a red colouration during reaction in acetonitrile and the subsequent formation of the 5-*endo* isomer is consistent with our previous suggestion of metal-assisted substitution

[1,5]. The inability of phenyl-substituted phosphines to form the 5-*endo* isomer is presumably due to steric inhibition of the metal-assisted pathway. In contrast, substitution in dichloromethane proceeds by direct attack at the ring to give the 5-*exo* product with no steric inhibition.

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