

Preliminary communication

THE REACTION OF TETRACYANOETHYLENE WITH SUBSTITUTED 7-METHYLENE-CYCLOHEPTATRIENE COMPLEXES OF TRICARBONYLIRON

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Summary

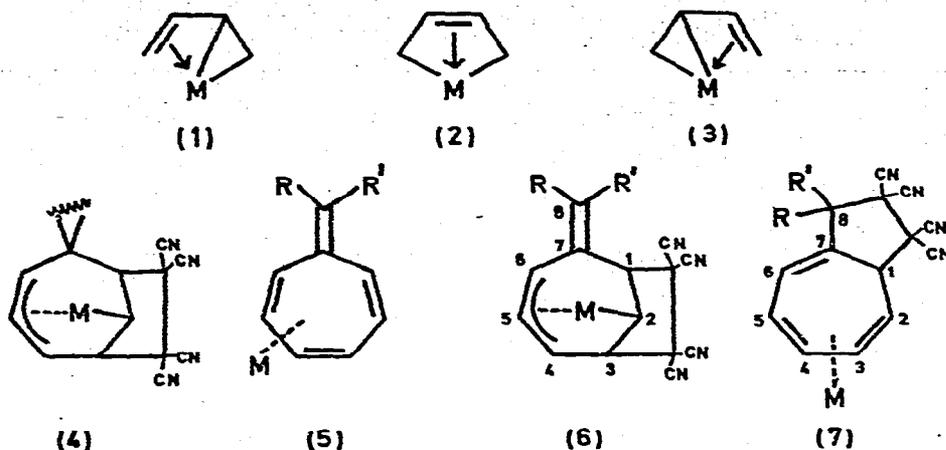
Mono and di-8-substituted derivatives of tricarbonyl(1-4-7-7-methylenecycloheptatriene)iron add tetracyanoethylene to give complexes containing an organic ligand which is derived from the azulene system. The application of orbital symmetry rules to this addition is discussed.

Recently Green et al. have reported experimental results which suggested that the 1,3-addition of tetracyanoethylene to $\text{Fe}(\text{CO})_3$ complexes of cycloheptatriene, tropone and other triene ligands proceeded by a concerted mechanism to give (4) [1]. It was also suggested that orbital symmetry rules could be used to rationalise the cycloaddition reactions if the canonical form (2) was used to describe the metal-1,3-diene bond.

It was decided to examine the cycloaddition reactions of the 7-methylenecycloheptatriene complexes (5) because these systems could undergo either 1,3-addition (on the ring) to give a structure similar to (4), i.e. (6), or 1,3-addition to give (7). The latter would be analogous to the well established allowed [8 + 2] cycloaddition of acetylenedimethyldicarboxylate to unco-ordinated 7-methylenecycloheptatriene [2],[3]. Unsubstituted (5), $\text{R} = \text{R}' = \text{H}$, has been reported to form an adduct of unknown structure with dimethylacetylenedicarboxylate [4]. This dieneophile however, did not form adducts with the substituted complexes.

In contrast tetracyanoethylene readily adds to (5a), (5b) and (5c). Hydrogen-1 n.m.r. spectra of the addition products

indicate structure (7). For example (7b) in $(\text{CD}_3)_2\text{CO}$ had; δ 2.72(m, 4 H, Aryl), 3.99(m, 2 H, H^3 and H^4), 4.28(m, 1 H, H^6), 5.01(t, J 2.5 Hz, 1 H, $\text{H}^8(\text{R}')$), 5.82(m, 1 H, H^1), 6.66(m, 1 H, H^2), 6.85(t, J 8 Hz, 1 H, H^5), 7.68(s, 3 H, Me).



$\text{M} = \text{Fe}(\text{CO})_3$; (a) $\text{R} = \text{Me}$, $\text{R}' = \text{H}$
 (b) $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$
 (c) $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$

Spin decoupling experiments revealed a 2.5 Hz coupling between H^1 and H^8 . This is probably due to the presence of a favourable W conformation in part of the molecule [5]. Structure (6b) was ruled out because neither the highfield resonance expected for H^2 nor the singlet expected for H^8 were observed [6], [7].

Since this result is analogous to the known [8 + 2] cycloaddition of 7-methylenecycloheptatriene it is not necessary in this case to use forms (1) - (3) to describe the metal-diene bond in order to classify the reaction allowed. If form (2) is used to describe the metal-diene bond in (5) and (2) or (1) used to describe the product then the reaction appears to be forbidden. The use of form (1) for both (5) and (7) renders the reaction allowed. The degree of selectivity required in the choice of a suitable resonance form for the metal-diene bond would seem to limit the predictive nature of orbital symmetry rules when applied to cycloadditions of tricarbonyl-iron complexes.

References

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