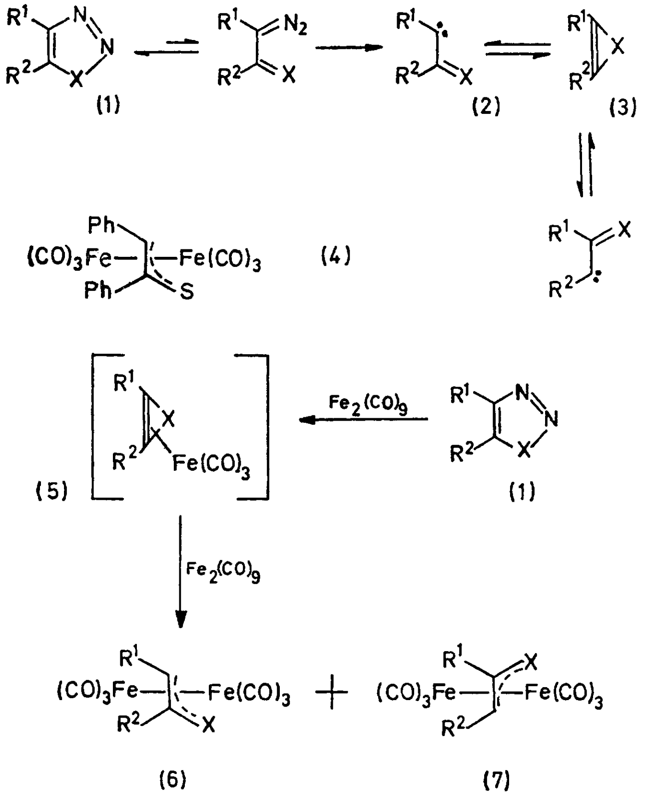
Symmetrical Intermediates in the Synthesis of Carbene–Metal Complexes from 1,2,3-Thiadiazoles and Selenadiazoles

By P. G. Mente and C. W. Rees*

(*The Robert Robinson Laboratories, University of Liverpool, P.O. Box* 147, *Liverpool* L69 3BX)

Summary Treatment of 1,2,3-thiadiazoles and selenadiazoles (**1**) with di-iron nonacarbonyl gives thioxo- and selenoxo-carbene complexes [*e.g.* (**4**)]; formation of cross-over products, (**6**) and (**7**), from 4,5-disubstituted diazoles implicates thiiren and seleniren derivatives as symmetrical intermediates.

When 1,2,3-triazoles are pyrolysed,[1] and 1,2,3-thiadiazoles are photolysed,[2] nitrogen is extruded and iminocarbenes and thioxocarbenes are produced. Furthermore, various heterocyclic 1,2-diaza-systems form complexes with di-iron nonacarbonyl,[3] which also catalyses the decomposition of organic azides.[4] We therefore expected that the thiadiazoles and selenadiazoles (**1**) would react with di-iron nonacarbonyl to undergo catalysed elimination of nitrogen and possible formation of iron complexes of the carbenes (**2**). Moreover, by starting with isomeric 4,5-disubstituted diazoles (**1**), any 'symmetrical' intermediates (**3**) could be detected and (by analogy with the isoelectronic carbocyclic system, cyclobutadiene) possibly preserved intact as a ligand on the metal. Heterocyclic compounds of this structure such as 1*H*-azirines (X = NR),[5] oxirens (X = O),[6] and thiirens (X = S),[7] are known only as transient intermediates, presumably because of their antiaromatic nature.



a; X=S, $R^1=R^2=$Ph
b; X=S, $R^1=$Ph, $R^2=p$-Bu^{t}C$_6$H$_4$
c; X=S, $R^1=p$-Bu^{t}C$_6$H$_4$, $R^2=$Ph
d; X=Se, $R^1=R^2=$Ph
e; X=Se, $R^1=$Ph, $R^2=p$-Bu^{t}C$_6$H$_4$
f; X=Se, $R^1=p$-Bu^{t}C$_6$H$_4$, $R^2=$Ph

The required diazoles (**1a**)–(**1f**) were obtained by adapting known synthetic procedures.[8] When treated with di-iron nonacarbonyl in tetrahydrofuran at room temperature (selenadiazoles) or under reflux (thiadiazoles), nitrogen was evolved and the remaining structural fragment, L, a diarylthioxo- or selenoxo-carbene isomeric with (**3**), was indeed incorporated into a metal complex of the form L·Fe$_2$(CO)$_6$, in up to 40% yield. 4,5-Diphenylthiadiazole (**1a**) gave a complex (**4**) identical with that prepared in an entirely different way by Schrauzer and his co-workers and shown to be a π-complex of 1,2-diphenylthioxocarbene (**2a**) by *X*-ray crystallography.[9] An analogous selenium complex was obtained, much more rapidly, from diphenylselenadiazole (**1d**); the structure of this, and the other complexes below, rests on analytical and spectroscopic characterisation and on analogy with Schrauzer's complex.

When the unsymmetrically disubstituted thia- (**1b**) and (**1c**) and selena-diazoles (**1e**) and (**1f**) were treated with di-iron nonacarbonyl, mixtures of two similar isomeric complexes (**6**) and (**7**) were formed in each case. The major isomer could be isolated pure by crystallisation from methanol. The n.m.r. spectrum showed the presence of the 'cross-over' product in which the sulphur or selenium has migrated from the carbon to which it was originally attached to the adjacent carbon. In each case the minor, cross-over product was identical (n.m.r.) with the major, unrearranged product obtained from the isomeric starting material with R¹ and R² reversed. The approximate extent of rearrangement was measured graphically from the n.m.r. spectra of the isomeric mixture of products and is shown in the Table; substantial, but not complete, scrambling of the aryl groups has occurred.

TABLE

Starting material	% Rearranged : % unrearranged product in the isomeric mixture	
(**1b**)	30:70	(**6b**:**7b**)
(**1c**)	30:70	(**7b**:**6b**)
(**1e**)	25:75	(**6e**:**7e**)
(**1f**)	25:75	(**7e**:**6e**)

Neither the starting materials nor the iron complexes show any change in their n.m.r. spectra on prolonged heating in tetrahydrofuran. Hence these results require the intervention of a symmetrical intermediate on the reaction pathway to at least half of the products and are most simply explained by a reaction scheme involving the complexed thiirens and selenirens (**5**). These mono-iron complexes could not be isolated, however, and their apparent instability is in striking contrast with the stability of cyclobutadieneiron tricarbonyl.

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