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A Novel Metal-Assisted [3 + 3] Cycloaddition Reaction of Ligated η^1-Allyl

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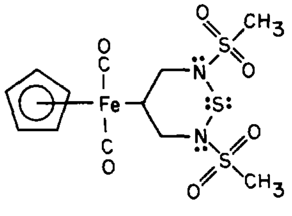
Cycloaddition reactions of transition metal–η^1-allyl complexes with unsaturated electrophilic reagents afford almost invariably [3 + 2] products [1, 2]. The lone exception is the reaction of a few metal–η^1-allyl complexes with SO_2, which yields what appear to be [3 + 1] cycloadducts of low stability [3]. We now report the first example of [3 + 3] cycloaddition to a transition metal–attached η^1-allyl ligand.

The complex η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ reacts with one equivalent of $S[NS(O)_2CH_3]_2$ in CH_2Cl_2 solution over 30 min at 25 °C to afford, after filtration through Florisil and crystallization from CH_2Cl_2–pentane, a 75% yield of *1* as a yellow solid, m.p. (dec.) 130 °C. Elemental analysis** shows *1* to be a 1:1 adduct of the reactants. The IR spectrum exhibits two strong $\nu(CO)$ absorptions at 1995 and 1920 cm^{-1} ($CHCl_3$ solution) and only two $\nu(SO_2)$ bands, at 1320 and 1155 cm^{-1} (Nujol mull), suggesting the absence of $S{=}NS(O)_2CH_3$ [4]. The ^1H NMR spectrum of *1* in $CDCl_3$ solution shows signals at δ 4.80 (singlet, 5H), 4.4–3.5 complex multiplet, 4H), 3.03 (singlet, 3H), and 2.85 ppm (center of multiplet, 1H). The multiplet at δ 4.4–3.5 ppm collapses to an AB pattern (δ 4.25 and 3.83 ppm, J_{AB} = 14 Hz) on irradiation at the frequency of the CH proton at δ 2.85 ppm. These experiments establish that the two $NS(O)_2CH_3$ groups and the two CH_2 groups are equivalent. The ^{13}C NMR spectrum, also in $CDCl_3$ solution, displays resonances at δ 215.6 (CO), 84.5 (C_5H_5), 62.2 (CH_2), 40.8 (CH_3), and 19.5 ppm (CH) to corroborate the aforementioned conclusions and indicate a six-membered, symmetrical [3 + 3] cycloadduct structure for the newly-formed heterocyclic ring.



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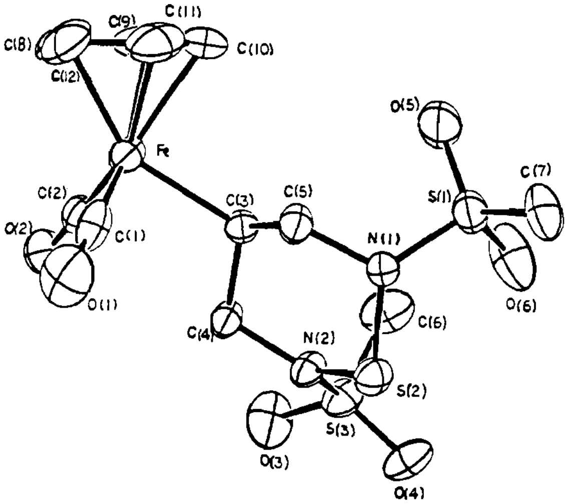

Fig. 1. The molecular structure of *1*, with hydrogen atoms omitted. Selected bond distances (Å) are: Fe–C(3), 2.090(3); C(5)–N(1), 1.497(4); C(4)–N(2), 1.486(4); N(1)–S(1), 1.659(1); N(2)–S(3), 1.641(3); N(1)–S(2), 1.681(2); N(2)–S(2), 1.692(3). Selected bond angles (deg.) are: C(5)–N(1)–S(1), 119.9(1); C(5)–N(1)–S(2), 113.0(1); N(1)–S(2)–N(2), 100.6(1); C(4)–N(2)–S(3), 122.2(2); C(4)–N(2)–S(2), 115.1(2).

Unambiguous structural characterization of *1* is based on a single crystal X-ray study. The crystals are monoclinic, space group $P2_1/c$ with a = 10.380(7), b = 19.565(15), c = 12.437(8) Å, β = 137.446(4)°, V = 1716.4(2) Å^3, and Z = 4. The structure solution by direct methods was based on 2225 observed independent reflections with $I > 3\sigma(I)$ collected at ambient temperature using Mo-Kα radiation. Refinement was accomplished to R = 0.050. The structure of *1*, Fig. 1 contains a six-membered $\overline{C(3)CNSNC}$ ring, in a chair conformation, linked to Fe through C(3). The geometry around each nitrogen is essentially planar.

The η^1-allyl complexes η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$, η^5-$C_5H_5Mo(CO)_3CH_2C(R){=}CH_2$ (R = H, CH_3), and $Mn(CO)_5CH_2CH{=}CH_2$ undergo similar reactions with $S[NS(O)_2CH_3]_2$ to afford analogous [3 + 3] cycloadducts. These complexes were characterized by comparison of their spectroscopic properties with those of *1*; they will be described fully later [5], along with details of the structure of *1*.

In contrast to the aforementioned [3 + 3] cycloaddition, reaction of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ with $CH_3S(O)_2NSO$ under comparable experimental

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**Anal. Calcd. for $C_{12}H_{16}FeN_2O_6S_3$: C, 33.03; H, 3.70; N, 6.42. Found C, 33.05; H, 3.74; N, 6.23.

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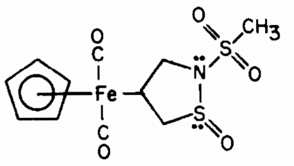
conditions affords a [3 + 2] cycloadduct*, *2*, as a yellow solid, m.p. (dec.) 143 °C, in 66% yield. The presence of a five-membered heterocyclic ring in *2* is indicated by the appearance of three IR S–O stretching absorptions at 1335, 1155 ($\nu(SO_2)$), and 1140–1060 (broad) cm^{-1} ($\nu(SO)$) (Nujol mull), and of a ^1H NMR CH_3 signal at δ 3.10 ppm ($CDCl_3$ solution), the position of which argues against the presence of $S{=}NS(O)_2CH_3$ [4]. The η^1-allyl complexes $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2CH{=}CH_2$ and $Mn(CO)_5\text{-}CH_2CH{=}CH_2$ yield analogous [3 + 2] cycloadducts with $CH_3S(O)_2NSO$.



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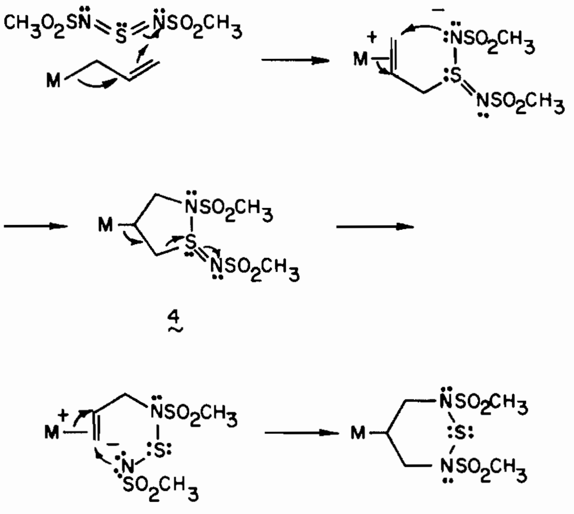
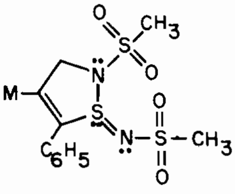
The formation of *1* and related [3 + 3] cycloadducts may proceed via initial formation of [3 + 2] cycloaddition derivatives followed by a rearrangement to stable products. This route is depicted in Scheme 1. A direct, two-step pathway for the formation of the [3 + 3] cycloadducts is improbable, since the nitrogen atoms of $S[NS(O)_2CH_3]_2$ lack the necessary electrophilic properties to initiate such a sequence. In this context it is noteworthy that the transition metal–propargyl complexes $MCH_2C{\equiv}CC_6H_5$ where $M = \eta^5\text{-}C_5H_5Fe(CO)_2$, $\eta^5\text{-}C_5H_5Mo(CO)_3$, and $Mn(CO)_5$ do afford expected [3 + 2] cycloaddition products, *3*, with $S[NS(O)_2CH_3]_2$ [6]. The much higher stability of *3* compared to the proposed intermediate [3 + 2] cycloadduct in Scheme 1 (*4*) may derive from a stabilization of the five-membered ring in the former by conjugation, C=C–S=N. And finally, the different stabilities of the [3 + 2] cycloadducts from metal–η^1-allyl complexes and each of $CH_3S(O)_2NSO$ and $S[NS(O)_2CH_3]_2$ suggest that steric effects associated with the $NS(O)_2CH_3$ group are important.



Scheme 1



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Acknowledgement

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**Anal.* Calcd. for $C_{11}H_{13}FeNO_5SO_2$: C, 36.78; H, 3.64. Found: C, 36.61; H, 3.61.