Insertion of X=C=Y heteroallenes into unsupported Zr–M bonds (M = Fe, Ru)

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The unsupported early–late heterobimetallics $HC(SiMe_2NC_6H_4F\text{-}2)_3Zr\text{–}M(CO)_2(\eta\text{-}C_5H_5)$ (M = Fe 1, Ru 2) undergo highly selective reactions with X=C=Y heteroallenes to yield the insertion products $HC(SiMe_2NC_6H_4F\text{-}2)_3Zr(XYC)M(CO)_2(\eta\text{-}C_5H_5)$ (X = O, S; Y = O, S, NR); single-crystal X-ray structure analyses of $HC(SiMe_2NC_6H_4F\text{-}2)_3Zr(S_2C)Fe(CO)_2(\eta\text{-}C_5H_5)$ 4 and $HC(SiMe_2NC_6H_4F\text{-}2)_3Zr(SCNPh)Fe(CO)_2(\eta\text{-}C_5H_5)$ 10 establish the mode of coordination of the substrates to the two metal centres.

Heterodinuclear complexes containing a polar metal–metal bond between an early and a late transition-metal element may display cooperative reactivity of the electrophilic and nucleophilic metal centres,[1] although direct experimental evidence is still rare.[2] Their interaction with polar, unsaturated organic substrates may, in principle, occur in a highly specific manner and induce patterns of reactivity which are not observed for the individual mononuclear or homodinuclear complexes. Direct evidence for this has yet to be obtained although recent work by Cutler and coworkers[3] has shown that Casey's Zr–M heterobimetallics[4] may insert CO_2 into their metal–metal bond (although being inert towards CS_2) while Bergman and coworkers reported the reactions of an imido-bridged Ir–Zr complex with CO_2, CS_2 and MeNCS, with the latter two undergoing fragmentation in the course of the reaction.[5] Our recent synthesis of unsupported Zr–M (M = Fe, Ru) heterobimetallics stabilized by tripodal amido ligands at the early transition-metal centre[6] afforded a unique opportunity for a systematic study of the interactions of early–late transition-metal heterobimetallics with X=C=Y heteroallenes.

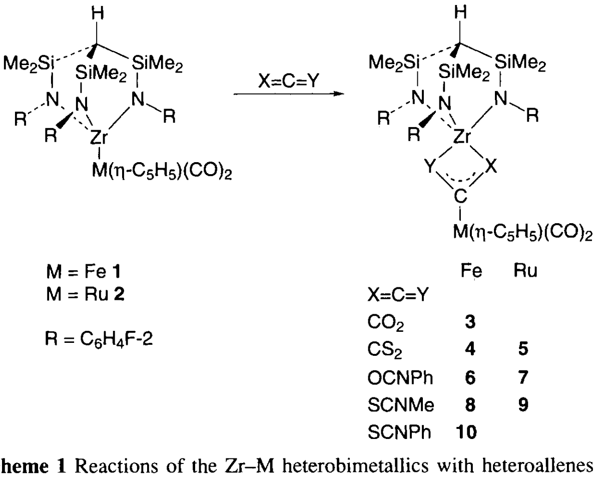
The system chosen in this study are Zr–M heterobimetallics in which the Zr fragment is coordinated by a tripodal amido ligand containing 2-fluorophenyl groups bonded to the amido nitrogen atoms.[7] The potential of the fluorine donors to coordinate weakly to the Zr centre in the course of the reactions and in the reaction product, thus playing the role of an 'active' ligand periphery, was of particular interest in the investigation of these systems.

Reaction of the Zr–M heterobimetallics $HC(SiMe_2NC_6H_4F\text{-}2)_3\text{-}Zr\text{–}M(CO)_2(\eta\text{-}C_5H_5)$ (M = Fe **1**, Ru **2**) with 1 equiv. of CO_2, CS_2, phenyl isocyanate, phenyl isothiocyanate or methyl isothiocyanate yields the insertion products **3**–**10** (Scheme 1). The formulations and structural proposals of the reaction products are supported by adequate spectroscopic and analytical data. Their most remarkable spectroscopic feature is the ^{13}C NMR chemical shifts of the heteroallene carbon resonances [$\delta(^{13}C)$ **3** 240.7, **4** 345.0, **5** 320.6, **6** 236.1, **7** 221.0, **8** 241.4, **9** 226.5, **10** 248.9]. Of these the position of the signal attributable to the $^{13}CS_2$ carbon in **4** and **5** is observed at remarkably low field (δ 345.0, 320.6, respectively), a situation which indicates a partially carbenoid character of the inserted carbon disulfide (best represented by a zwitterionic resonance structure of the dinuclear complex with the negative charge at Zr and the positive charge at M).

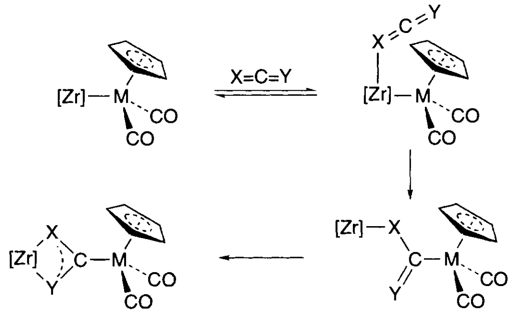
A preliminary kinetic study of the formation of compound **4** in toluene has established a rate law which is first order with respect to both the heterobimetallic complex and the substrate. This is consistent with a mechanistic proposal in which the rate-determining step, the cleavage of the Zr–Fe bond and insertion of CS_2, is preceded by a rapidly reversible Lewis acid–base interaction of the carbon disulfide with the Zr centre of the Zr–Fe complex (Scheme 2). That a potential heterolytic dissociation of the Zr–Fe complex is not the first (and rate determining) step in this reaction may be inferred from a significant decrease of the reaction rate in polar donor solvents such as thf which compete with the substrate in the preceding Lewis acid–base equilibrium. This observation is consistent with the results of Cutler's investigation of the mechanism of CO_2 insertion into Zr–M bonds.[3]

In order to establish the coordination mode of the XCY ligand (X = O, S; Y = O, S, NR) to the early and late transition-metal centres as a result of an *insertion* reaction, single-crystal X-ray structure analyses of **4** and **10** were carried out. Despite weak diffraction from available samples the principal structural features of both **4** and **10** were established (Fig. 1).†

The central structural unit in **4** [Fig. 1(*a*)] is the bent CS_2 fragment [S(1)–C(41)–S(2) 116.0(8)°] which links the two metal centres. Both of the S atoms bond directly to the zirconium [Zr–S(1) 2.628(4) Å, Zr–S(2) 2.648(4) Å]. The three nitrogen and one of the fluorine atoms of the tripodal ligand



Scheme 1 Reactions of the Zr–M heterobimetallics with heteroallenes to produce the insertion products **3**–**10**



Scheme 2 Proposed mechanism for the insertion reactions; [Zr] = $Zr[CH(SiMe_2NC_6H_4F\text{-}2)_3]$

complete the six-coordinate Zr sphere. The Zr–F distance is relatively large [Zr–F(1) 2.563(8) Å], presumably reflecting a principally electrostatic metal–donor interaction, but is of particular interest as it demonstrates the participation of the 'active' ligand periphery in the M–M′ insertion product. In contrast, the peripheral F atoms of the tripodal ligand in **10** [Fig. 1(*b*)] play a rather less significant role in the coordination of the early transition-metal centre although the shortest Zr···F contact [Zr–F(3) 2.70(1) Å] may indicate some metal–fluorine interaction. It is significant that the other 2-fluorophenyl rings in the structure show disorder corresponding to an interchange of the fluorine positions between the two *ortho* sites on the rings.

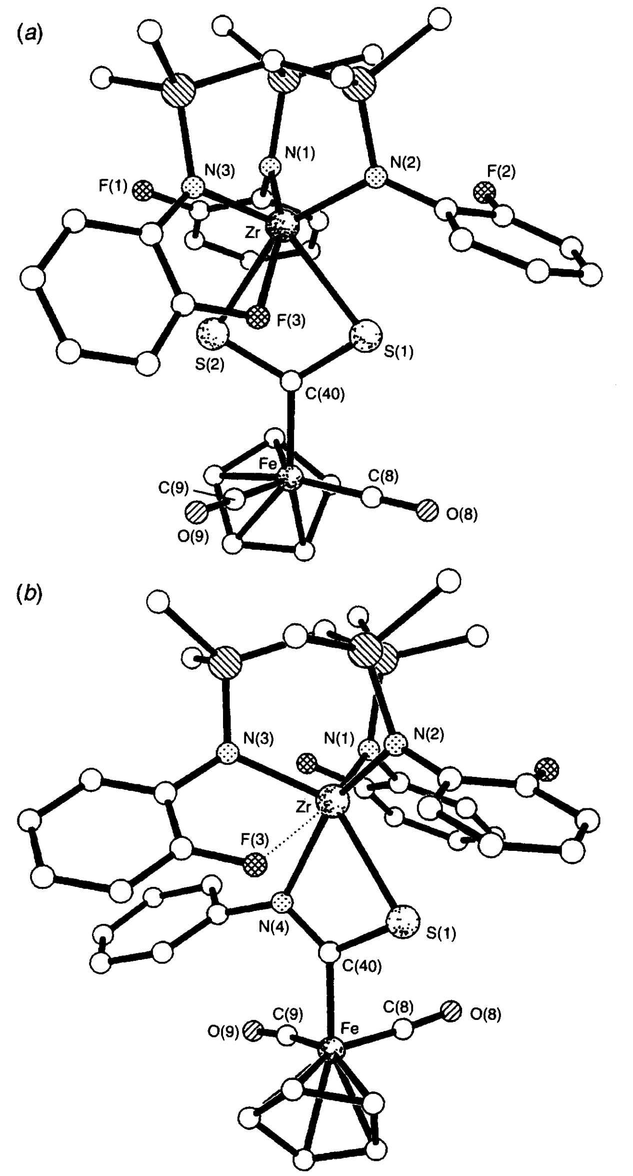


Fig. 1 (*a*) Molecular structure of **4**. Selected bond lengths (Å) and interbond angles (°): Zr–N(1) 2.053(11), Zr–N(2) 2.091(11), Zr–N(3) 2.133(10), Zr–F(3) 2.563(8), Zr–S(1) 2.628(4), Zr–S(2) 2.648(4), Fe–C(8) 1.77(2), Fe–C(9) 1.78(2), Fe–C(40) 1.935(14), C(8)–Fe–C(9) 94.4(7), S(2)–C(40)–S(1) 116.1(8). (*b*) Molecular structure of **10**. Selected bond lengths (Å) and interbond angles (°): Zr–S(1) 2.571(5), Zr–N(4) 2.282(13), Zr–N(1) 2.053(12), Zr–N(2) 2.093(13), Zr–N(3) 2.105(13), Zr–F(3) 2.70(1), Fe–C(8) 1.67(3), Fe–C(9) 1.72(3), Fe–C(40) 1.95(2) S(1)–C(40) 1.75(2), C(40)–N(4) 1.31(2), C(9)–Fe–C(8) 87(1), N(4)–C(40)–S(1) 112(1).

The NCS heteroallene, linear in the free isothiocyanate, is bent in **10** [N(4)–C(2)–S(1) 112(1)°] and bridges the metals in a manner similar to that found in the CS_2 analogue, **4**. Whereas the C–S distance of 1.75(2) Å lies in the range of a C–S single bond, the carbon–nitrogen bond [1.31(2) Å] retains considerable double-bond character.[8]

The reactivity of the heterobimetallic complexes towards X=C=Y has provided additional evidence for their reactive nature as being that of 'masked' electrophile–nucleophile pairs.

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Footnote

† *Crystal data*: **4**: $C_{33}H_{36}F_3FeN_3O_2S_2Si_3Zr$, M = 859.11, triclinic, space group $P\bar{1}$, a = 10.293(4), b = 12.538(3), c = 16.294(5) Å, α = 97.76(2), β = 90.80(2), γ = 111.53(3)°, Z = 2, U = 1933(1) Å^3, D_c = 1.476 g cm^{-3}, μ(Mo-Kα) = 0.893 mm^{-1}, $F(000)$ = 876. Data were collected on a Siemens P4 four-circle diffractometer and the structure was solved by direct methods and refined on F^2 (SHELXTL PC version 5.03, Siemens Analytical X-Ray, Madison, WI, 1995). Refinement converged at wR_2 = 0.171 (all data) [R_1 = 0.088 for 2136 data with $I > 2\sigma(I)$], GOF on F^2 = 0.97 for 4042 absorption corrected unique reflections an 433 parameters.

10: $C_{39}H_{41}F_3FeN_4O_2SSi_3Zr$, M = 918.16, monoclinic, space group $P2_1/n$, a = 19.388(3), b = 17.358(3), c = 12.642(2) Å, β = 90.72(2)°, Z = 8, U = 4254 Å^3, D_c = 1.434 g cm^{-3}, μ(Mo-Kα) = 0.73 mm^{-1}, $F(000)$ = 3200. Data were collected on a Philips PW1100 four-circle diffractometer and the structure was solved by the Patterson method and refined on F (SHELX76, G. M. Sheldrick, University of Cambridge, 1976). Refinement converged at R = 0.065, R_w = 0.066 for 1874 absorption corrected data with $I > 3\sigma(I)$ and 267 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/170.

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