A 'passe-partout' for the stabilization of highly polar unsupported M–M′ bonds (M = Ti, Zr, Hf; M′ = Fe, Ru) and α-addition of the metal nucleophile–electrophile pairs to an isocyanide

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The coordination of a novel type of tripodal amido ligand provides the key to the synthesis of stable M–M′ (M = Ti, Zr, Hf; M′ = Fe, Ru) heterobimetallic complexes, [MeSi{SiMe$_2$N(C$_6$H$_4$Me-4)}$_3$M–M′(η^5-C$_5$H$_5$)(CO)$_2$] 4–9, with unsupported metal–metal bonds and thus enables systematic studies of these complexes; the crystal structures of the Ti–Fe (4) and Zr–Fe (6) complexes are reported, the latter being the first X-ray structure of a compound containing a Zr–Fe bond; reaction of the M–M′ complexes with methyl isocyanide leads to the immediate insertion into the metal–metal bond, a reaction which is analogous to α-additions to isocyanides.

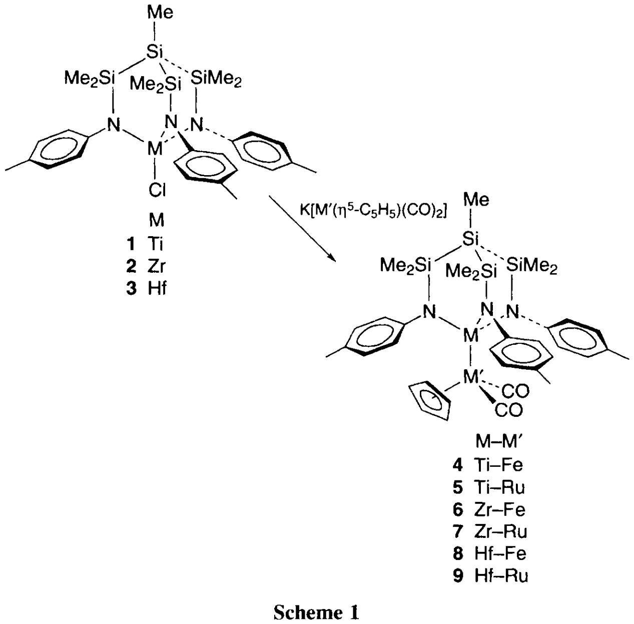
A systematic study of the properties of highly polar metal–metal bonds between the metals of the Ti-triad and late transition metals has been hampered by the intrinsic instability of most of the systems which have been prepared to date.[1] Of the few stable species almost each has a different set of ligands which impedes comparative studies of their structural characteristics as well as their chemical reactivity.[2] In order to overcome this situation, we have recently developed several new types of tripodal amido ligands[3] which were designed not only to meet the electronic demands of a high-valent early transition metal but, additionally, effectively shield a large part of its coordination sphere leaving an 'active site' for the coupling with a late transition-metal complex fragment.[4] This strategy has been successfully implemented in the case of several Ti–M′ (M′ = Fe, Ru) heterobimetallics,[5] however, the ligands employed proved to be unsuitable for the extension of the concept to the whole Ti-triad.

The fact that a tripodal amido ligand containing a trisilylsilane backbone serves equally well in the synthesis of Ti, Zr and, as shown here, Hf complexes offered the opportunity to generate a set of stable M–M′ (M = Ti, Zr, Hf, M′ = Fe, Ru) binuclear compounds. The reaction of [MeSi{SiMe$_2$N(C$_6$H$_4$Me-4)}$_3$MCl] (M = Ti **1**,[6] Zr **2**,[6] Hf **3**) with K[(η^5-C$_5$H$_5$)M′(CO)$_2$] afforded the metal–metal bonded complexes [MeSi{SiMe$_2$N(C$_6$H$_4$Me-4)}$_3$M–M′(η^5-C$_5$H$_5$)(CO)$_2$] **4–9** (Scheme 1) all of which are thermally stable in the solid state and in solution.

In order to confirm the proposed structural arrangement in **4–9** and for the first time establish an unsupported Zr–Fe bond in a molecule by X-ray crystallography, single-crystal X-ray structure analyses of **4** and **6** were carried out.† The molecular structure of **6** depicted in Fig. 1, which is very similar to that of **4**, illustrates the conceptual approach delineated above. The ligand framework and the peripheral tolyl groups of the amido ligand shield the coordination sphere of the tetravalent zirconium, which is part of a molecular cage thus formed, and leaving a cone-shaped binding site which accommodates the iron complex fragment. It may be appreciated that the size of the cavity is mainly dictated by two parameters: Firstly, the interatomic distances within the ligand framework [d_{av}(Si–Si) 2.340 Å] relative to the Zr–N (Ti–N) distances [d_{av}(Zr–N) 2.08 Å, d_{av}(Ti–N) 1.93 Å] dictates the degree to which the peripheral tolyl groups are tilted towards the second metal complex fragment. The second determining factor is the orientation of the tolyl groups which in compound **6** have an average torsion angle with respect to the Si–N vectors of 87.9° (**4**: 84.5°).

The orientation of the carbonyl ligands at the iron centre is such that their interpretation as potentially semi-bridging may be ruled out [C(8)–Fe–M 83.9(2) (**4**), 83.9(5)° (**6**), C(9)–Fe–M 88.1(2) (**4**), 88.9(5)° (**6**), C(8)–M 2.86 Å (**4**), 2.98 Å (**6**), C(9)–M 2.97 Å (**4**), 3.11 Å (**6**)], and the metal–metal bond is therefore truly unsupported. The relatively short Zr–Fe distance of 2.605(2) Å in the crystal structure of **6**, as well as the even shorter Ti–Fe distance of 2.460(1) Å in **4** indicate that there is no significant repulsive interaction between the two complex fragments joined by the Zr–Fe and Ti–Fe bonds. On the other hand, due to the steric demand of the ligands at both metal centres which adopt a staggered arrangement in the crystal structures the free rotation about the metal–metal vector observed at temperatures above 330 K (spectral patterns indicating threefold symmetry of the Zr-complex fragment) may be frozen out on the NMR timescale upon cooling to 245 K; the effective symmetry of the molecule is thus reduced to C_s.

Since **4–9** are the first examples of M–M′ complexes containing an identical set of ligands, a meaningful comparison of the effect the metal–metal bonding has upon the electron density at the late transition-metal centre is possible by comparing the ν(CO) IR frequencies. The effect of replacing Ti by Zr (Hf) is evident in the comparison of **4** and **5** with **6** and **7** (**8** and **9**), the increased ionic character of **6–9** being reflected in a shift of the ν(CO) bands (recorded in toluene) from 1978,



Scheme 1

1931 cm^{-1} in **4** and 1991, 1937 cm^{-1} in **5** to 1961, 1910 cm^{-1} in **6** (1969, 1915 cm^{-1} in **8**) and 1986, 1932 cm^{-1} in **7** (1987, 1933 cm^{-1} in **9**). The reason for this trend may be related to the fact that, as previous theoretical studies of early–late heterobimetallics have shown, there is significant π-donor–acceptor interaction apart from the dominating σ bonding between the metals.[7] The Ti-fragment may be the better π acceptor and thus allow a greater degree of charge redistribution from the late transition metal to the early transition metal.

Upon reaction of **4–9** with 1 mol equiv. of methyl isocyanide immediate insertion into the polar metal–metal bond takes place generating [MeSi{SiMe$_2$N(C$_6$H$_4$Me-4)}$_3$M(η^2-C=NMe)M′(η^5-C$_5$H$_5$)(CO)$_2$] **10–15** (Scheme 2). This may be viewed as the first example of a true metal analogue of the well established α-addition reaction of an electrophile and a nucleophile to the carbon atom in isocyanide chemistry,[8] a type of reactivity also observed in reactions of early transition-metal alkyl compounds with isocyanides.[9] The only previous example of such an insertion into a (halide-supported) formal metal–metal bond is the reaction of fulvalene-bridged complex [(C$_{10}$H$_8$)Zr$_2$(η^5-C$_5$H$_5$)$_2$Cl$_2$] with Bu^{t}NC reported by Herrmann *et al.*[10] which, in view of the lack of M–M bond polarity in that system cannot be related to the α-addition pattern.

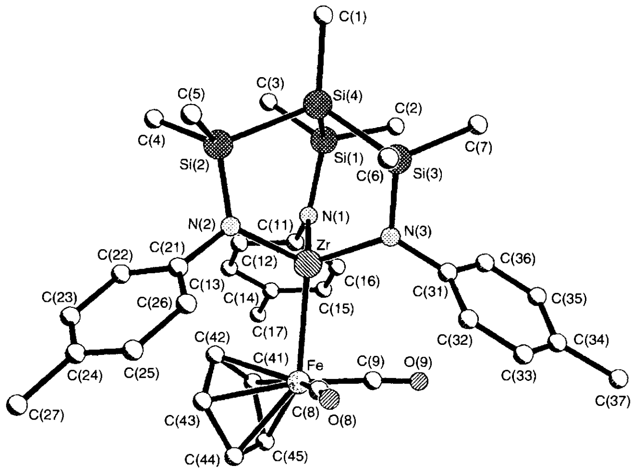
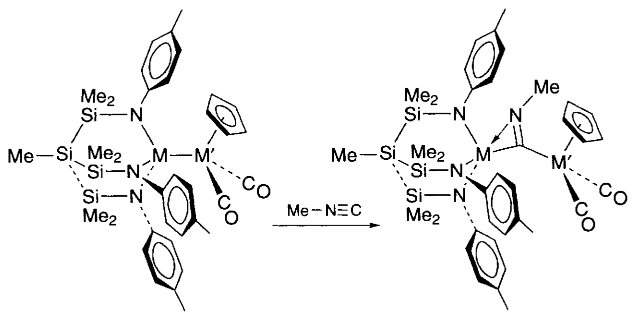


Fig. 1 Molecular structure of **6**. Selected bond lengths (Å) and interbond angles (°): Zr–Fe 2.605(2), Zr–N(1) 2.080(9), Zr–N(2) 2.088(9), Zr–N(3) 2.065(9), Fe–C(8) 1.76(1), Fe–C(9) 1.74(1), Si(1)–Si(4) 2.354(5), Si(2)–Si(4) 2.340(6), Si(3)–Si(4) 2.326(6), C(8)–Fe–Zr 83.9(5), C(9)–Fe–Zr 88.9(5), C(8)–Fe–C(9) 96.6(6), N(1)–Zr–N(2) 105.1(4), N(2)–Zr–N(3) 106.7(4), N(1)–Zr–N(3) 104.4(4), tolyl–N–Si torsion angles: Si(1)–N(1)–C(11)–C(16) 93.1(4), Si(2)–N(2)–C(21)–C(22) 73.9(4), Si(3)–N(3)–C(31)–C(32) 96.7(4). The molecular arrangement of **4** is essentially similar to that of **6**. The corresponding bond lengths (Å) and interbond angles (°) are: Ti–Fe 2.460(1), Ti–N(1) 1.934(4), Ti–N(2) 1.941(4), Ti–N(3) 1.930(4), Fe–C(8) 1.735(6), Fe–C(9) 1.745(6), Si(1)–Si(4) 2.348(2), Si(2)–Si(4) 2.326(2), Si(3)–Si(4) 2.335(2), C(8)–Fe–Ti 83.9(2), C(9)–Fe–Ti 88.1(2), C(8)–Fe–C(9) 97.3(3), N(1)–Ti–N(2) 107.2(2), N(2)–Ti–N(3) 107.2(2), N(1)–Ti–N(3) 104.9(2), tolyl –N–Si torsion angles: Si(1)–N(1)–C(11)–C(16) 90.3(3), Si(2)–N(2)–C(21)–C(22) 71.5(3), Si(3)–N(3)–C(31)–C(32) 91.6(3).



	M	M′
10	Ti	Fe
11	Ti	Ru
12	Zr	Fe
13	Zr	Ru
14	Hf	Fe
15	Hf	Ru

Scheme 2

The considerable thermal stability of **4–9** indicates that the trisilylsilane-based tripodal amido ligand does indeed fulfil its expectations as a 'passe-partout' in the stabilization of highly polar metal–metal bonds. The reactivity of these compounds towards methyl isocyanide, a *general* pattern of reactivity of this type of metal–metal bonds, has established their nature as 'masked' electrophile–nucleophile pairs.

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Footnote

† *Crystal data*: C$_{35}$H$_{47}$FeN$_3$O$_2$Si$_4$Ti **4**, M = 757.87, monoclinic, space group $P2_1$/n, a = 12.290(3), b = 19.573(4), c = 16.418(4) Å, β = 93.73(3)°, Z = 4, U = 3941.03 Å^3, D_c = 1.281 g cm^{-3}, F(000) = 1592, μ(Mo-Kα) = 7.0 cm^{-1}, R = 0.050, R_w = 0.048 for 3933 absorbance corrected data with $I/\sigma(I) > 3$ and 418 parameters. C$_{35}$H$_{47}$FeN$_3$O$_2$Si$_4$FZr **6**, M = 801.19, monoclinic, space group $P2_1/n$, a = 12.577(3), b = 19.539(4), c = 16.349(4) Å, β = 95.63(3)°, Z = 4, U = 3998.26 Å^3, D_c = 1.331 g cm^{-3}, F(000) = 1664, μ(Mo-Kα) = 7.4 cm^{-1}, R = 0.054, R_W = 0.054 for 2177 absorbance corrected data with $I/\sigma(I) > 3$ and 240 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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