# Ionic cleavage of Ti–Co and Zr–Co bonds: the role of the nucleophilicity of the late transition metal in the reactive behaviour of early–late heterobimetallics

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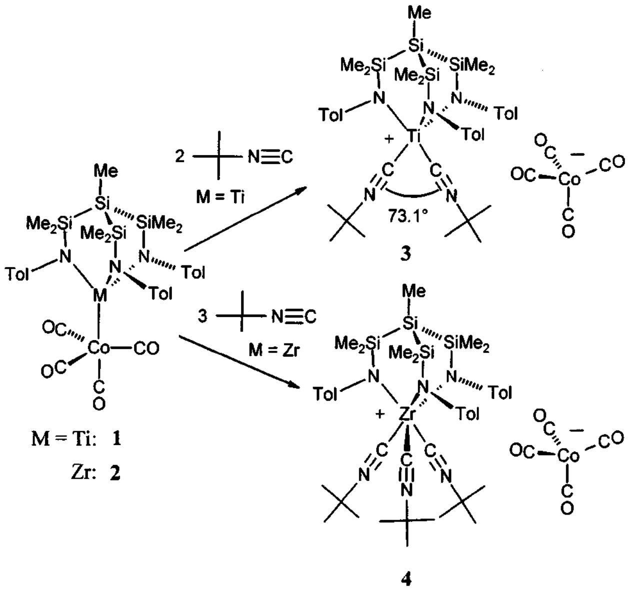
**The ionic cleavage of Ti–Co and Zr–Co bonds occurs upon reaction with Bu$^t$NC and the products [MeSi{SiMe$_2$N(*p*-Tol)}$_3$Ti(CNBu$^t$)$_2$][Co(CO)$_4$] 3 and[MeSi{SiMe$_2$N(*p*-Tol)}$_3$Zr(CNBu$^t$)$_3$][Co(CO)$_4$] 4 were characterized by single crystal X-ray diffraction; the importance of the nucleophilicity of the late transition metal fragment in reactions of the unsupported early–late heterobimetallics is demonstrated.**

In many cases, early–late heterobimetallic complexes display the reactive behaviour of pairs of metal nucleophiles and electrophiles which are 'masked' by the existence of a metal–metal bond and which is cleaved during the course of the reaction.[1–5]

In order to assess the validity of the concept of combining metal nucleophilicity and electrophilicity we decided to reduce the basicity of the late transition metal fragment to the degree at which polar additions to suitable unsaturated substrates no longer take place.[6] Instead, the heterolytic cleavage of the metal–metal bond and 'solvation' of the Ti-group fragment by the substrate was thought to be a possible reaction pathway yielding the *extremely rare* case of an ionic dissociation of the metal–metal bond between transition elements *without* concomitant redox reaction.[7] Redox disproportionation is observed in the well known reaction of $Co_2(CO)_8$ with donor ligands.[8] Here, we wish to give a first account of these investigations which led to the conversion of metal–metal bonded dinuclear complexes to fairly stable organometallic salts. More importantly, we could demonstrate that subsequent addition of a stronger metal nucleophile led to the re-formation of the polar metal–metal bond.

The objects of study were the heterobimetallic complexes [MeSi{SiMe$_2$N(*p*-Tol)}$_3$M-Co(CO)$_4$] (M = Ti **1**, Zr **2**)[9] in which the late transition metal fragment is characterized by low nucleophilicity.[6] Reaction of **1** and **2** with Bu$^t$NC in toluene led to the clean conversion to products which contain two and three molecules of isocyanide associated with every Ti and Zr centre, respectively, as established by elemental analysis. The formation of both compounds **3** and **4** occurred cooperatively, *i.e.* without detection of intermediates, and the products crystallized directly from the reaction mixture in yields of 75 and 77%, respectively. A single *ν*(CO) band at 1875 cm$^{-1}$ in the IR spectra of both compounds indicated the presence of the tetracarbonyl cobaltate anion[10] and their low solubility in the aromatic reaction medium indicated an ionic species. In both cases it proved to be possible to obtain single crystals of the apparently salt-like compounds directly from the reaction mixture. It was therefore possible to establish their structure by X-ray crystallography and to confirm their formulation as [MeSi{SiMe$_2$N(*p*-Tol)}$_3$Ti(CNBu$^t$)$_2$][Co(CO)$_4$] **3** and [MeSi{SiMe$_2$N(*p*-Tol)}$_3$Zr(CNBu$^t$)$_3$][Co(CO)$_4$] **4** (Scheme 1).†

The [Co(CO)$_4$]$^-$ anion in the crystal structure of **3** was found to be highly disordered which precluded the complete refinement of the structural data. However, the presence of the pentacoordinate titanium complex cation [MeSi{SiMe$_2$N(*p*-Tol)}$_3$Ti(CNBu$^t$)$_2$]$^+$ could be established unambiguously. In contrast, the X-ray diffraction experiment performed on a single crystal of compound **4** yielded a data set of good quality and permitted full refinement of the structure which is depicted in Fig. 1.‡



Scheme 1 Ionic cleavage of the Ti–Co and Zr–Co bonds.

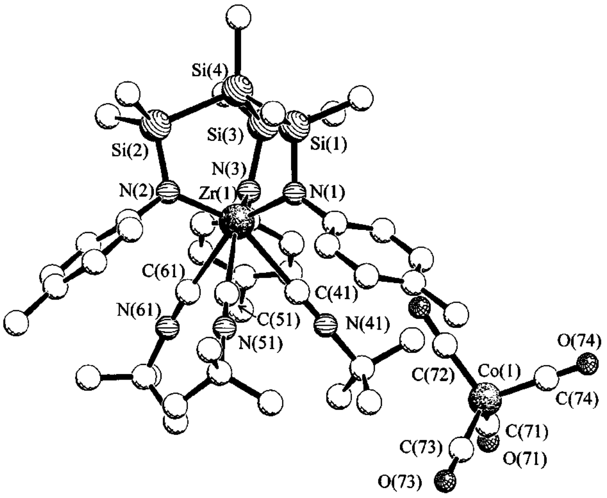
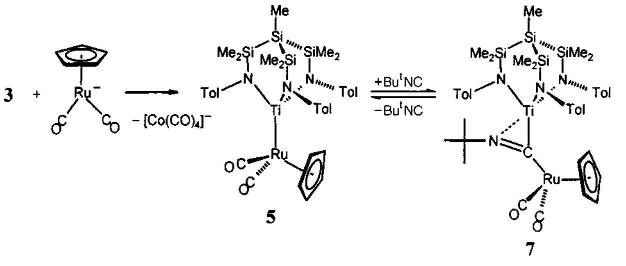


**Fig. 1** Molecular structure of **4** in the crystal. Principal bond lengths (Å) and interbond angles (°): Zr(1)–N(1) 2.074(4), Zr(1)–N(2) 2.076(5), Zr(1)–N(3) 2.082(5), Zr(1)–C(41) 2.431(7), Zr(1)–C(51) 2.448(7), Zr(1)–C(61) 2.440(7), Co(1)–C(71) 1.7332(9), Co(1)–C(72) 1.722(8), Co(1)–C(73) 1.769(8), Co(1)–C(74) 1.741(8); N(1)–Zr(1)–N(2) 105.8(2), N(1)–Zr(1)–N(3) 108.0(2), N(2)–Zr(1)–N(3) 108.9(2), C(41)–Zr(1)–C(51) 70.6(2), C(41)–Zr(1)–C(61) 72.1(2), C(51)–Zr(1)–C(61) 71.4(2).

The crystal structure of **4** clearly establishes the ionic cleavage of the metal–metal bond by which the slightly distorted tetrahedral $[Co(CO)_4]^-$ anion [OC–Co–CO′ 107.2–110.5°] and the trigonally distorted octahedral cation $[MeSi\{SiMe_2N(p\text{-}Tol)\}_3Zr(CNBu^t)_3]^+$ were generated. Owing to the sixfold coordination at the Zr-centre the Zr–N distances [2.073(4), 2.077(5), 2.082(5) Å] are somewhat greater than those found in previously reported four-coordinate tripodal amidozirconium complexes, in particular, the Zr–Co dinuclear complex **2** [2.037(5), 2.044(5), 2.032(5) Å].[9] Remarkably, the Zr–C bond lengths of the coordinated isocyanide ligands [2.439(7), 2.448(7), 2.430(7) Å] are significantly greater than those found in all known structurally characterized isocyanide–zirconium species [Zr–C 2.31–2.37 Å].[11]

In view of the previously observed insertions of isocyanides into the highly polar metal–metal bonds of unsupported early–late heterobimetallics[3] it was of particular interest to explore how the complex salts **3** and **4** would react with the strong metal nucleophile $[RuCp(CO)_2]^-$. In principle, two reaction pathways were conceivable, the direct nucleophilic attack at the C-atom of a coordinated, and thus activated, isocyanide ligand generating the metallaiminoacyl complexes. Alternatively, rapid nucleophilic substitution of the isocyanide ligands could intially lead to the M–Ru heterodinuclear complexes **5** and **6** which would over a period of several hours insert the displaced isocyanide. The latter was established by NMR and IR spectroscopy in the reaction of **3** with $K[RuCp(CO)_2]$ in $C_6D_6$. Almost instantaneous formation of the M–Ru complex **5** was observed[3] which, subsequently, was partially converted to the insertion product **7** (Scheme 2).‡ This result is pertinent to the previously proposed mechanism of the insertion of unsaturted polar substrates into the metal–metal bonds, which we derived from a kinetic study, and supports the notion that predissociation of the heterodinuclear complex and addition of the ionic fragments to the substrate does not appear to be the decisive step.[4] Rather, as proposed by us, the substrate coordinates to the early transition metal centre in the dinuclear complex, thus lablizing and polarizing the metal–metal bond which is cleaved in the subsequent rearrangement of the nucleophilic metal fragment to give the insertion product.



**Scheme 2** Reaction of **3** with $K[RuCp(CO)_2]$, initially yielding the Ti–Ru complex **5** which subsequently reversibly inserts $Bu^tNC$.

In view of the incomplete insertion of $Bu^tNC$ into the metal–metal bonds we studied the reaction leading to **7** in more detail by reacting **5** with varying amounts of isocyanide and determining the conversion of **5** to **7** by $^1H$ NMR spectrocopy as well as the reverse reaction taking place upon dissolution of isolated solid **7**. The insertion/de-insertion equilibrium depicted in Scheme 2 could thus be established for **5** and **7** with an equilibrium constant $K = [\mathbf{7}]/[\mathbf{5}][Bu^tNC] = 0.91\ dm^3\ mol^{-1}$ in toluene at 298 K.

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## Notes and references

† *Selected spectroscopic and analytical data*: **3**: $^1H$ NMR ($C_6D_6$) $\delta$ 0.22 (s, $CH_3Si$), 0.42 [s, $Si(CH_3)_2$], 1.21 [s, $CNC(CH_3)_3$], 2.24 [s, $CH_3C_6H_4$], 6.88–7.09 (m, Tol). $^{13}C\ \{^1H\}$ NMR ($C_6D_6$) $\delta$ −14.1 ($CH_3Si$), 2.4 [$Si(CH_3C_6H_4)$, 30.2 [$CNC(CH_3)_3$], 57.7 [$CNC(CH_3)_3$], 125.5 (Tol, $C^2$), 129.3 (Tol, $C^3$), 129.8 (Tol, $C^4$), 149.3 (C NR), 150.0 (Tol, $C^1$), IR (benzene): 2140, 2107 [m, $\nu$(NC)], 1875 [$\nu$(CO)] $cm^{-1}$. **4**: $^1H$ NMR ($C_6D_6$) $\delta$ 0.25 (s, $CH_3Si$), 0.38 [s, $Si(CH_3)_2$], 1.07 [s, $CNC(CH_3)_3$], 2.29 [s, $CH_3C_6H_4$], 6.79 [d, $^3J$(HH) 8.0 Hz, Tol], 7.03 (d, Tol). $^{13}C\ \{^1H\}$ NMR ($C_6D_6$) $\delta$ −16.8 ($CH_3Si$), 1.8 [$Si(CH_3)_2$], 20.8 ($CH_3C_6H_4$), 29.0 [$CNC(CH_3)_3$], 57.7 [$CNC(CH_3)_3$], 125.9 (Tol, $C^2$), 129.3 (Tol, $C^3$), 132.3 (Tol, $C^4$), 147.6 (C NR), 149.4 (Tol, $C^1$). IR (benzene): 2145s, 2120m [$\nu$(NC)], 1875 ($\nu$(CO)] $cm^{-1}$. **7**: $^1H$ NMR ($C_6D_6$) $\delta$ 0.34 (s, $CH_3Si$), 0.58 [s, $Si(CH_3)_2$], 1.00 [s, $CNC(CH_3)_3$], 2.18 [s, $CH_3C_6H_4$], 4.55 (s, $C_5H_5$), 6.90 [d, $^3J$(HH) 8.4 Hz, tol], 7.01 (d, Tol). $^{13}C\ \{^1H\}$ NMR ($C_6D_6$) $\delta$ −14.3 ($CH_3Si$), 2.9 [$Si(CH_3)_2$], 20.8 ($CH_3C_6H_4$), 28.3 [$CNC(CH_3)_3$], 62.4 [$CNC(CH_3)_3$], 89.9 ($C_5H_5$), 125.6 (Tol, $C^2$), 129.3 (Tol, $C^3$), 130.0 (Tol, $C^4$), 14.1 (Tol, $C^1$), 200.5 (CO), 266.1 (TiC=N). IR (benzene): 2043s, 1985s [s, $\nu$(CO)] $cm^{-1}$.

‡ *Crystal data*: for **3**: $C_{42}H_{60}CoN_5O_4Si_4Ti$, monoclinic, space group *Cc*, $a = 20.8267(15)$, $b = 14.1970(13)$, $c = 17.590(3)$ Å $\beta = 90.481(10)°$ $V$ 5167.8(10) $A^3$, $Z = 4$, $D_c = 1.180\ g\ cm^{-3}$ $T = 291(2)$ K, $\mu = 0.608\ cm^{-1}$; Siemens P4 diffractometer, 3396 measured data ($1.74 < \theta < 21.00°$), semi-empirical absorption corrections ($\psi$-scans, relative $T_{max} = 0.89039$, $T_{min} = 0.83523$), 3075 independent reflections, $R_{int} = 0.0373$, $R_1$ 0.0748, $wR_2 = 0.1748$ [$I > 2\sigma(I)$], $S = 0.959$ for 422 parameters.

For **4**: $C_{61}H_{85}CoN_6O_4Si_4Zr$, monoclinic, space group $P2_1/c$, $a = 24.622(5)$, $b = 14.092(3)$, $c = 21.316(4)$ Å, $\beta = 109.97(3)°$ $V = 6952(2)$ $A^3$, $Z = 4$, $D_c = 1.174\ g\ cm^{-3}$, $T = 183(2)$K, $\mu = 0.502\ mm^{-1}$; Siemens P4 diffractometer, 12997 measured data ($3.01 < \theta < 23.63°$), semi-empirical absorption corrections ($\psi$-scans, relative $T_{max} = 0.36434$, $T_{min} = 0.33836$), 9816 independent reflections, $R_{int} = 0.0650$, $R_1$ 0.0676, $wR_2 = 0.0799$ [$I > 2\sigma(I)$], $S = 1.010$ for 697 parameters. Programs: SHELXTL 5.03, Siemens Analytical X-Ray Instruments Inc., 1994, Madison WI, CCDC 182/1124.

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