Atom-transfer within the coordination sphere of early–late heterobimetallic complexes: rapid deoxygenation of sulfoxides at low temperatures

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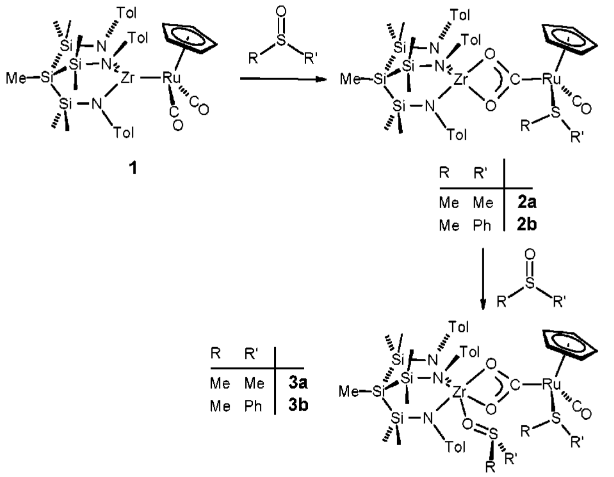
Extremely rapid oxygen transfer from sulfoxides to a carbonyl ligand to give the corresponding thioether and coordinated CO$_2$ is observed in the reactions of unsupported Zr–Ru heterodimetallic complexes with sulfoxides; this is interpreted to arise from the cooperative reactivity of the two complementary metal complex fragments bound to each other through a highly polar metal–metal bond.

The exploitation of the cooperative reactivity of different metal complex fragments is the underlying aim of the study of di- or tri-nuclear complexes containing highly polar metal–metal bonds between early and late transition metals.[1,2] The heteropolar addition of a metal nucleophile and electrophile to an organic substrate is the simplest manifestation of such reactivity,[3] the insertion (and subsequent cleavage) of carbonyl derivatives, which we reported recently, providing an example for this basic pattern.[4] Here we report the extremely rapid oxygen transfer from sulfoxides to coordinated CO to give CO$_2$ in the coordination sphere of Zr–Ru heterodi- and tri-nuclear complexes.

Metal ion mediated oxygen transfer reactions involving sulfoxides have been known for some time,[5] the most thoroughly studied systems effecting this transformation being Pt(II) complexes in acidic solution[6] and low valent Group VI complexes which are transformed to the corresponding oxo-species.[7] Deoxygenation of sulfoxides may also be achieved by some metal carbonyl derivatives under forcing conditions generating CO$_2$ derived from metal bound CO.[8] An important step in the labilization of the strong S–O bond is the addition of an electrophile to the oxygen atom. In reactions with early–late heterobimetallic complexes containing CO-ligands coordinated to the late transition metal *both* the electrophilic activation of the substrate and the transfer to an oxygen acceptor ligand (CO) were thought to be possible within the coordination sphere of *one* molecule.

Upon reaction of one molar equivalent of Me$_2$SO and Ph(Me)SO with the Zr–Ru heterodinuclear complex [MeSi(SiMe$_2$NTol)$_3$ZrRuCp(CO)$_2$] (**1**)[2b] at −40 °C in toluene an immediate transformation occurred yielding products which could be isolated as yellow solids by evaporation of the solvent *in vacuo*. On the basis of their analytical and ^{1}H, ^{13}C NMR as well as IR spectroscopic properties these were formulated as [MeSi(SiMe$_2$NTol)$_3$Zr(μ-O$_2$C)RuCp(CO){S(R)R′}] (R = R′ = Me: **2a**, R = Me, R′ = Ph: **2b**) (Scheme 1). Products of higher crystallinity were obtained upon addition of a second equivalent of sulfoxide giving μ-CO$_2$-linked dinuclear compounds containing an O-bonded sulfoxide ligand at the zirconium centre but being otherwise of analogous composition and spectroscopic properties: [MeSi(SiMe$_2$NTol)$_3$Zr{OS(R)R′-κO}(μ-O$_2$C)RuCp(CO){S(R)R′}] (R = R′ = Me: **3a**, R = Me, R′ = Ph: **3b**).

In order to establish the structure of the reaction products unambiguously a single crystal X-ray structure analysis of **3a** was carried out.† The centre piece of the molecular structure displayed in Fig. 1 is the Zr(μ-O$_2$C)Ru unit in which the CO$_2$ formed in the reaction links the two metal centres. The geometrical characteristics of the carboxylato-bridge [d{C(71)–O(61)} 1.276(11), d{C(71)–O(71)} 1.297(11) Å, d{Ru–C(71)} 2.082(9), θ{O(61)–C(71)–O(71)} 115.9(8)°] are similar to those found in a previously characterized CO$_2$-linked Zr–Ru



Scheme 1 Oxygen transfer upon reaction of the Zr–Ru heterodinuclear complexes with sulfoxides.

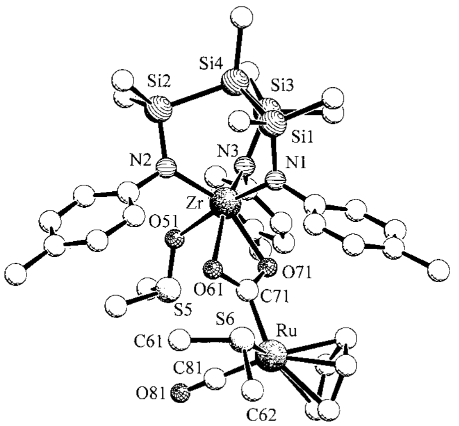


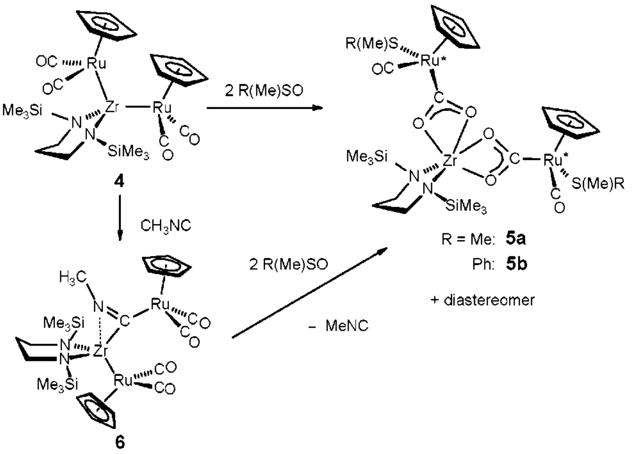
Fig. 1 Molecular structure of **3a** in the solid state. Principal bond lengths (Å) and angles (°): Ru–C(81) 1.883(14), Ru–C(71) 2.082(9), Ru–S(6) 2.364(3), Zr–N(1) 2.100(8), Zr–N(2) 2.119(8), Zr–N(3) 2.121(7), Zr–O(71) 2.221(6), Zr–O(61) 2.255(7), Zr–O(51) 2.261(7), S(5)–O(51) 1.520(7), O(61)–C(71) 1.276(11), O(71)–C(71) 1.297(11), O(81)–C(81) 1.128(13), C(81)–Ru–C(71) 87.8(4), N(1)–Zr–N(2) 99.5(3), N(1)–Zr–N(3) 101.7(3), N(2)–Zr–N(3) 104.9(3), N(1)–Zr–O(71) 90.2(3), N(2)–Zr–O(71) 152.6(3), N(3)–Zr–O(71) 97.9(3), N(1)–Zr–O(61) 92.6(3), N(2)–Zr–O(61) 95.5(3), N(3)–Zr–O(61) 152.6(3), O(71)–Zr–O(61) 58.3(2), O(61)–C(71)–O(71) 115.9(8)

heterodinuclear complex, [$Cp_2Zr(Cl)(\mu\text{-}O_2C)Ru(Cp^*)(CO)$], reported by Gibson *et al.*[9] The metallacarboxylato unit in **3a** is almost symmetrically coordinated to the zirconium centre [*d*{Zr–O(61)} 2.255(7), *d*{Zr–O(71)} 2.221(6) Å] and together with the Me_2SO ligand [*d*{Zr–O(51)} 2.261(7)] generates the hexacoordinate zirconium complex fragment the coordination geometry of which may be viewed as being highly distorted octahedral. The dimethyl sulfide molecule formed as a consequence of the sulfoxide deoxygenation is coordinated to the Ru atom making this a chiral centre (Fig. 1).

The complexes **2a**,**b** and **3a**,**b** have several very characteristic spectroscopic properties which aid the structural assignment. As a consequence of the generation of a chiral centre at the late transition metal fragment the ^1H and ^{13}C NMR resonances of the $Si(CH_3)_2$ groups in the tripod ligand are diastereotopically split. The coordination of the soft donor ligand RR′S at the Ru-centres is the reason for the observation of the single ν(CO) infrared band at faily low frequency (1924–1947 cm^{-1}). The chemical shifts of the ^{13}C NMR signals assigned to the $\mu\text{-}CO_2$ units depend quite sensitively upon the presence or absence of the additional RR′SO-donor at the Zr-centre. For **2a**,**b** they are observed at, respectively, δ 235.4 and 232.0, while the electronic readjustment within the molecule following the sulfoxide coordination at Zr leads to a significant shift of this signal to higher field [$\delta(^{13}C)$ **3a**: 225.1, **3b**: 225]. A study of this reaction employing compound **1** which was ^{13}C-labeled at the CO ligands provided support for the assumption of the role of these ligands as O-acceptors and their transformation to the bridging CO_2-unit.

The remarkable reactivity of **1** towards sulfoxides and the selectivity of the reaction raised the question of the generality of this reactive pattern of metal–metal bonded early–late heterodinuclear {$CpRu(CO)_2$} derivatives. Reaction of the heterotrinuclear complex [$CH_2(CH_2NSiMe_3)_2Zr\{RuCp(CO)_2\}_2$] **4**[10] which contains two structurally equivalent {$CpRu(CO)_2$} units bonded to a Zr amido complex fragment with two molar equivalents of Me_2SO and Ph(Me)SO led to the immediate conversion to reaction products which were formulated on the basis of their analytical and spectroscopic properties as [$CH_2(CH_2NSiMe_3)_2Zr\{(\mu\text{-}O_2C)RuCp(CO)(SMeR)\}_2$] (R = Me: **5a**, Ph: **5b**) in which the Zr atom is coordinated by *two* metallacarboxy units and the thioethers derived from the sulfoxides are also bonded to the Ru centres (Scheme 2).

Remarkably, all attempts to isolate, or even unambiguously detect, intermediate species in which only one metal–metal bond is cleaved failed, an observation which implies that the conversion at one centre significantly enhances the reactivity of the other. This should be compared to the results from our previous studies of simple insertion reactions of unsaturated polar substrates into these metal–metal bonds in which the reaction involving the cleavage of only one Zr–Ru bond was observed exclusively.[10] We would like to point out in this context, that in contrast to the rapid deoxygenation reactions involving the Zr–Ir complex [$Cp_2Zr(\mu\text{-}NBu^t)IrCp^*$] studied in Bergman's group,[1c] the presence of carbonyl ligands in **1** and **4** leads to carboxy-linked species rather than oxo complexes. The formation of a C–O and two Zr–O bonds is the thermodynamic driving force in these conversions which is sufficiently strong even to effect the displacement of an inserted isonitrile molecule from the trinuclear complex [$CH_2(CH_2NSiMe_3)_2Zr\{\eta^2\text{-}C({=}NMe)M(CO)_2Cp\}\{M(CO)_2Cp\}$] **6** (Scheme 2).



Scheme 2 Oxygen transfer upon reaction of the $ZrRu_2$ heterotrinuclear complexes with sulfoxides yielding hexacoordinate zirconium complexes containing two ruthenacarboxylato 'ligands'.

In conclusion, the reactions reported represent the first examples of transformation involving amido ligand-stabilized unsupported early–late heterobimetallics (*i.e.* containing a M–M′ bond without a bridging ligand) in which not only both metal complex fragments interact with the substrate but involvement of a coordinated ligand in an atom transfer reaction occurs. This combined and complementary reactivity of the two metal centres enables the reduction of a sulfoxide by CO under extraordinarily mild conditions.

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Notes and references

† *Crystal data* for **3a**: [$MeSi\{SiMe_2N(p\text{-}Tol)\}_3Zr(OSMe_2\text{-}\kappa O)(\mu\text{-}O_2C)\text{-}RuCp(CO)(SMe_2)]\cdot 0.25MeC_6H_5$: $C_{40.75}H_{56}N_3O_4RuS_2Si_4Zr$, triclinic, space group $P\bar{1}$, a = 12.426(3), b = 14.510(3), c = 16.742(4) Å, α = 115.41(2), β = 96.302(13), γ = 96.682(15)°, V = 2665.0(10) Å^3, Z = 2, $F(000)$ 1051, D_c = 1.272 g cm^{-3}, T = 296(2) K, μ = 0.683 mm^{-1}; Siemens *P*4 diffractometer, 8600 measured data ($1.37 < \theta < 23.00°$), empirical absorption corrections (relative T_{max} 0.6108, T_{min} 0.4556), 7388 independent reflections, R_{int} = 0.0648, R_1 = 0.0709, wR_2 = 0.1523 [$I > 2\sigma(I)$], S = 0.958 for 503 parameters. Programs: SHELXTL 5.03, Siemens Analytical X-Ray Instruments Inc., 1994, Madison WI, USA and DIFABS, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158. CCDC 182/1167.

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