Detection of a novel intermediate in the addition of thiols to osmium carbonyl clusters

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Spectroscopic studies of the reaction of [$Os_3(CO)_{11}$MeCN)] with *para*-thiocresol to form [$Os_3(\mu$-H)$(CO)_{10}(\mu$-SC_6H_4Me-*p*)] indicate that the reaction proceeds *via* a two-step consecutive process involving the intermediate [$Os_3(CO)_{11}$-(MeC_6H_4SH-*p*)], in which there is an agostic Os–H–S interaction.

Hydrodesulfurization (HDS) processes are used to remove sulfur from organosulfur compounds in fossil fuels.[1] These catalytic processes are subject to intensive investigation because of the widespread use of HDS and its economic and environmental importance. Although structures of the active components of HDS catalysts have been proposed,[1] the exact nature of the interaction between sulfur-containing hydrocarbons and the catalyst(s), and the mechanism of the catalytic reaction(s), have not been elucidated.

Friend *et al.*[2] have studied the adsorption and desulfurization of thiols on Mo(110) surfaces. The cleavage of the sulfur–hydrogen bond to form a metal-bound thiolate has been found to be rapid whereas the cleavage of the carbon–sulfur bond appears to be the rate-limiting step. Several metal complexes containing sulfur ligands have been synthesized as both structural and functional models for HDS processes.[3] We are currently studying whether it is possible to monitor the initial coordination of thiols to polynuclear metal complexes and to relate these phenomena to HDS processes.[4] Here we wish to describe how the reaction between [$Os_3(CO)_{11}$(MeCN)] **1** and *para*-thiocresol proceeds *via* the intermediate [$Os_3(CO)_{11}$-(MeC_6H_4SH-*p*)] **2** to form the final product [$Os_3(\mu$-H)$(CO)_{10}(\mu$-SC_6H_4Me-*p*)] **3**. The intermediate (**2**) is proposed to contain an agostic Os–H–S interaction; to our knowledge, this is the first example of an agostic interaction involving a thiol hydrogen.

Two resonances could be detected at high field when the reaction of stoichiometric equivalents of **1** and *para*-thiocresol was monitored by ^{1}H NMR at ambient temperature. Fig. 1(a) shows the variation of the intensities of the two signals with time. There is a relatively rapid build-up of the resonance at δ -4.81 followed by a slower decay of the intensity of this signal, while there is a gradual build-up of the signal at higher field. This implies that the resonance at lower field is due to an intermediate which is gradually converted to the final product with a resonance at δ -17.00. The high-field resonance may be ascribed to the bridging hydride of the final product **3**† by comparison to previously known [$Os_3(\mu$-H)$(CO)_{10}(\mu$-SR)] clusters.[4,5] The shift of the second resonance occurs at lower field than may be expected for a hydride coordinated to a triosmium cluster;[6] the signal is assigned to the thiol hydrogen and it is suggested that the shift arises from an agostic interaction of this hydrogen with one of the osmium atoms. The T_1 relaxation times for the two signals are similar, although not identical, being 2.08 s for the intermediate **2** and 4.37 s for the final species **3**. Greater discrepancies in relaxation times for the two signals have been observed for the same type of reaction involving other thiols.[7]

It was possible to slow down the above reaction so that the intermediate was the predominant species by mixing the reactants and rapidly cooling the solution to -60 °C; at this temperature, **2** was found to be stable for several hours. A ^{13}C NMR spectrum‡ of a carbon-13 enriched sample of **2** at -60 °C showed that the intermediate possesses eleven carbonyls, consistent with the proposed formula [$Os_3(CO)_{11}$(MeC_6H_4SH-*p*)]. On the basis of the ^{13}C–^{13}C and ^{13}C–^{1}H coupling pattern, several ^{13}CO resonances have been assigned. Moreover, a 2D-EXSY experiment showed that all CO ligands (except one at δ 171.54) exchange pair-wise, suggesting the possible occurrence

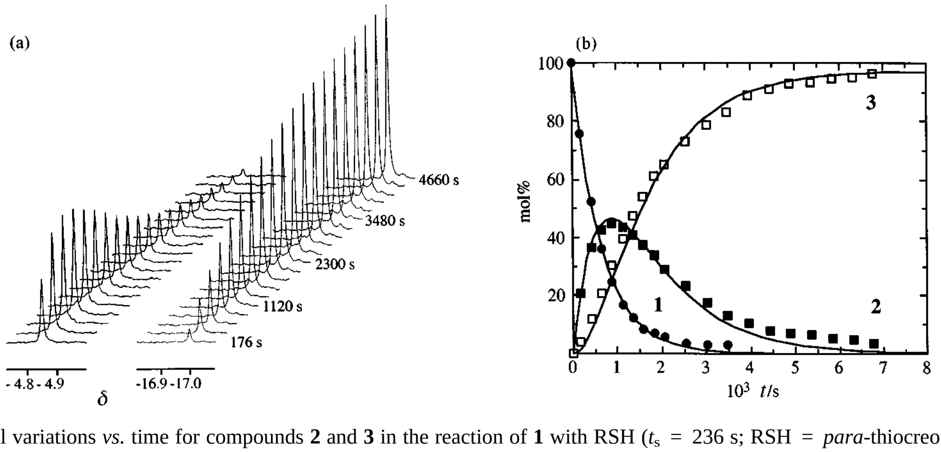
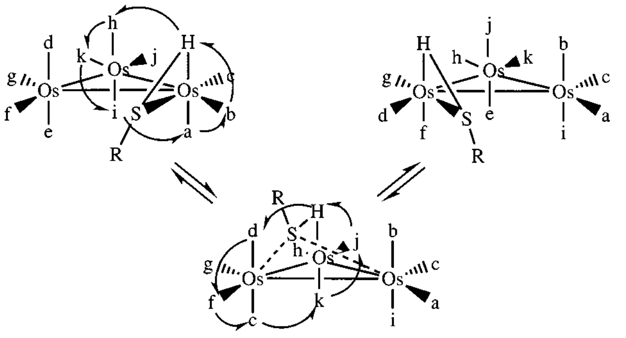


Fig. 1(a) ^{1}H NMR signal variations *vs.* time for compounds **2** and **3** in the reaction of **1** with RSH (t_s = 236 s; RSH = *para*-thiocreosol; [**1**] = 0.012 M; [RSH] = 0.053 M; [MeCN] = 0.054 M; solvent = $CDCl_3$; T = 295.2 K). (b) Time dependence of the concentrations of the species **1**–**3**.



Scheme 1 Proposed fluxional mechanism for ligand exchange in the intermediate $[Os_3(CO)_{11}(MeC_6H_4SH\text{-}p)]$ **2**. This mechanism is in agreement with the following pairwise exchange for all carbonyls except k, which stays in the same magnetic environment: a ↔ f, b ↔ d, c ↔ g, e ↔ i, h ↔ j.

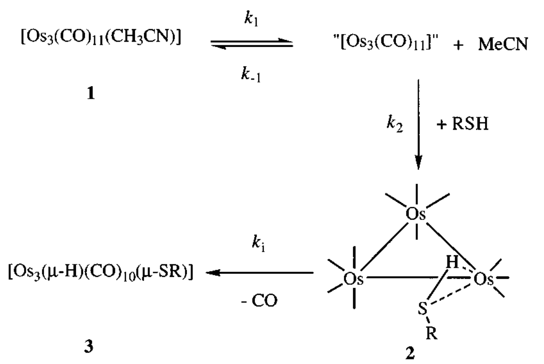
of a sliding motion of the thiol moiety on the surface of the cluster accompanied by two successive, one-step-only, merry-go-round processes as depicted in Scheme 1. This exchange process is reminiscent of that observed in the enantiomerization of $[Os_3H(\mu\text{-}H)(CO)_{11}]$.[6] Further (indirect) evidence for an agostic Os–H–S interaction could be derived from the reaction of **1** with PhSeH which proceeds *via* an intermediate with a characteristic ^1H NMR resonance at δ −5.4. This resonance contains satellites due to ^1H–^{77}Se coupling and the value of the coupling constant is unusually low ($^1J_{SeH}$ = 38.1 Hz), which is consistent with elongation of the Se–H bond.

The kinetics of the reaction of **1** with *para*-thiocresol were measured by UV–VIS, IR and NMR spectroscopy. Two consecutive reactions were observed in dichloromethane at 298.2 K. Analysis of the changes of the IR and ^1H NMR spectra during the course of the reaction showed that the processes under study involve fast thiol addition to **1** and subsequent slow cleavage of the S–H bond with concomitant dissociation of a carbonyl ligand to yield the final product [eqn. (1)].

$$\mathbf{1} + \mathrm{RSH} \xrightarrow[-\,\mathrm{MeCN}]{k_{\mathrm{obs1}}} \underset{\mathbf{2}}{[\mathrm{Os_3(CO)_{11}(RSH)}]} \xrightarrow[-\,\mathrm{CO}]{k_{\mathrm{obs2}}} \mathbf{3} \qquad (1)$$

The first step could be observed by rapid-mixing UV–VIS spectroscopy in the range 300–480 nm and the kinetics of the two steps were studied spectrophotometrically at different ligand concentrations under pseudo-first-order conditions. The observed rate constants, $k_{obs1} = (1.52 \pm 0.1) \times 10^{-2}\ s^{-1}$ and $k_{obs2} = (1.09 \pm 0.08) \times 10^{-3}\ s^{-1}$, were found to be independent of ligand concentration. On the other hand, studies carried out in the presence of different concentrations of free acetonitrile indicated consecutive processes. Immediately after mixing the reactants, the ^1H NMR spectra showed the presence of resonances belonging to the starting cluster **1**, the intermediate **2** and the final product **3**. The concentrations of the three species were evaluated from the integrals of the signals at δ 2.72 for CH_3CN in **1** and of the agostic hydrogen (**2**) and hydride (**3**) resonances [*cf.* Fig 1(a)]. The time dependence of the concentrations for the three species is shown in Fig. 1(b).

The dissociative natures of the transition states for both steps are confirmed by the fact that (i) both rate constants are independent of ligand concentration, (ii) the activation parameters§ obtained from the temperature dependence of k_{obs1} and k_{obs2} [*cf.* eqn. (1)] are consistent with a dissociative process, and (iii) in the first step, the displacement of the acetonitrile by the sulfur donor ligands is retarded by the addition of the free leaving group; a plot of the rate constants for the *para*-thiocreosol at different acetonitrile concentrations shows saturation, with a curvilinear dependence on the concentration of the entering thiol. Scheme 2 shows the overall mechanism proposed for these reactions. The first step is a reversible dissociation of acetonitrile from **1**, to give a labile and coordinatively unsatured intermediate, '$[Os_3(CO)_{11}]$', which undergoes either acetonitrile addition to form the starting cluster or thiol addition to form the intermediate $[Os_3(CO)_{11}(RSH)]$ **2**. The latter loses carbon monoxide to form the final compound $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SC_6H_4Me\text{-}p)]$ **3**.¶ The mechanism depicted in Scheme 2 appears to be general. Thus far, similar kinetics and the same type of intermediate have been detected for all thiols that we have reacted with $[Os_3(CO)_{11}(NCMe)]$, including ethanethiol, *ortho*- and *meta*-thiocresol, 2-naphthalenethiol and *tert*-butylthiol.[7]



Scheme 2 Proposed mechanism for the formation of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SC_6H_4Me\text{-}p)]$ **3** *via* the intermediate $[Os_3(CO)_{11}(MeC_6H_4SH\text{-}p)]$ **2**.

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Notes and references

† *Selected spectroscopic data* for **3**: ^1H NMR (CD_2Cl_2, 300 MHz) δ 7.19–7.05 (m, 4H), 2.35 (s, 3H), −17.00 (s, 1H); IR (hexane) ν_{CO}/cm^{-1} 2108w, 2067s, 2057m, 2024s 2016m, 2002m, 1990w, 1983w; FABMS *m/z* 976 (M^+). The molecular structure of **3** has been determined by X-ray crystallography.[7]

‡ ^{13}C NMR ($CDCl_3$) δ 181.83 ($^2J_{CC}$ 37.2 Hz), 180.90 ($^2J_{CH}$ 27.5 Hz), 180.31 ($^2J_{CC}$ 35.1 Hz), 179.84 ($^2J_{CC}$ 37.2 Hz), 179.42 ($^2J_{CH}$ 6.5 Hz), 177.29 ($^2J_{CC}$ 35.1 Hz), 175.71, 171.54, 170.95, 169.96 ($^2J_{CH}$ 6.5 Hz), 159.99.

§ k_{obs1}: $\Delta H^{\ddagger} = 98 \pm 2\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = 48 \pm 7\ J\ K^{-1}\ mol^{-1}$; k_{obs2}: $\Delta H^{\ddagger} = 90 \pm 2\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = 2 \pm 8\ J\ K^{-1}\ mol^{-1}$.

¶ The experimental data were fitted by the following equation:

$$k_{obs1} = a[RSH]/(b[MeCN] + [RSH])$$

The rate laws for the two steps of the mechanism depicted in Scheme 2 are:

$$k_{obs1} = k_1[RSH]/(k_{-1}/k_2[MeCN] + [RSH]);\ k_{obs2} = k_i$$

The calculated parameters a and b can be related to the rate constants as $a = k_1 = (1.46 \pm 0.04) \times 10^{-2}\ s^{-1}$ and $b = k_{-1}/k_2 = (0.591 \pm 0.06)$.

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