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Attachment of Trinuclear Osmium and Ruthenium Carbonyl Clusters onto Thiol Functionalized Silica

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Molecular clusters have been used as homogeneous catalysts for a variety of reactions, namely carbon monoxide hydrogenation to produce alcohols, alkanes and other products [1, 2]. Because of the possibilities of cluster degradation and metal aggregation, and because of the technological problems of a homogeneous catalytic system, namely the difficulty of noble metal recovery, several attempts have recently been undertaken to attach molecular cluster compounds onto chemically functionalized supports, such as polymers and silica. In a recent review Lieto and Gates [3] discussed the potential use of attached cluster catalysts. Reported successful cluster attachments have almost exclusively used phosphinated polystyrene matrices and phosphinated silicas [3–8]. Among other mono- and bimetallic clusters, analogues of $[Os_3(CO)_{11}(PPh_3)]$, $[H_2Os_3(CO)_9(PPh_3)]$ [6, 7] and of $[H_4Ru_4(CO)_{12-x}(PPh_3)_x]$ [8] have been attached onto phosphinated supports. Since the nature of the substituent on the cluster framework may modify the chemical and catalytic properties (*e.g.* ligand dissociation), we have now synthesized trinuclear osmium and ruthenium clusters attached to thiol modified silica supports.

The silica used was an AEROSIL 380 from Degussa which had a BET surface area of 340 m^2/g. This material was evacuated ($<10^{-1}$ Nm^{-2}) at 570 K to remove molecularly adsorbed water. It was then refluxed in dry methanol under dry nitrogen for 4 hr. This procedure essentially removes strained siloxane bridges and reduces the residual hydroxyl group density on the surface. The modification was then carried out by refluxing the silica in a benzene/$(CH_3)_2(CH_3O)Si(CH_2)_3SH$ solution under dry nitrogen for 18 hr, which leads to the formation of pendent thiol ligands being anchored to the surface by Si–O–Si bridges. Elemental analysis gave the following results: 1.68% C; 0.88% H; 0.925% S, the theoretical value for the pendent ligand$\sim\!\sim\!\sim Si(CH_3)_2(CH_2)_3SH$ being 1.74% C for the experimentally determined sulfur content. This latter value corresponds to 0.51 pendent thiol ligands per nm^2.

The attachment of the triosmium cluster was caries out via two routes, either by reaction of the diene substituted cluster $[Os_3(CO)_{10}(C_6H_8)]$ with the pendent thiol ligands (route I) or by reaction of the substituted cluster $[HOs_3(CO)_{10}S(CH_2)_3Si(OCH_3)(CH_3)_2]$ with the methanol treated silica (route II). The diene compound was synthesized according to reported procedures [9]. The thiol derivative of the triosmium cluster [10] was prepared by refluxing $(CH_3)_2(CH_3O)Si(CH_2)_3SH$ and $[Os_3(CO)_{10}\text{-}C_6H_8)]$ in dry cyclohexane solution under nitrogen for 15 minutes. A yellow solution was obtained which gave the characteristic carbonyl stretching bands summarized in Table I. These infrared bands match very well those reported in the literature for well characterized thiol derivatives of triosmium clusters. For the attachment via route I the thiol modified silica was analogously refluxed together with a slight excess of $[Os_3(CO)_{10}(C_6H_8)]$ in dry cyclo-

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TABLE I. Infrared Characterization of Molecular and Surface-bound Thiol Derivatives of Triosmium Clusters.

Compound	$\nu_{CO}{}^a$ (cm^{-1})	Ref.
$HOs_3(CO)_{10}SH^b$	2108 m, 2066 vs, 2057 s, 2022 vs, 2018 sh, 1998 m, 1987 m, 1976 w	[9]
$HOs_3(CO)_{10}SPr^{i\ b}$	2108 m, 2065 vs, 2057 s, 2021 vs, 2017 sh, 1995 m, 1986 m, 1979 w	[9]
$HOs_3(CO)_{10}S(C_6H_6)^b$	2106 m, 2067 vs, 2057 s, 2024 vs, 2018 m, 2000 s, 1980 m	[10]
$HOs_3(CO)_{10}S(CH_2)_3Si(OCH_3)(CH_3)_2{}^b$	2107 m, 2065 vs, 2058 s, 2020 vs, 1996 m, 1987 w	this work
$HOs_3(CO)_{10}S(CH_2)_3Si(CH_3)_2O$ (anchored)	2110 m, 2070 vs, 2061 s, 2027 vs, 2003 m	this work

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [b] In cyclohexane solution.

TABLE II. Infrared Characterization of Molecular and Surface-bound Thiol Derivatives of Triruthenium Clusters.

Compound	$\tilde{\nu}_{CO}$ (cm^{-1})	Ref.
$HRu_3(CO)_{10}SC_2H_5$[a]	2105 m, 2064 s, 2056 s, 2026 vs, 2012 m, 2008 s, 1994 m	[10]
$HRu_3(CO)_{10}SC_4H_9$[a]	2105 m, 2064 s, 2056 s, 2025 vs, 2012 m, 2007 s, 1994 m	[10]
$HRu_3(CO)_{10}S(CH_2)_3Si(OCH_3)(CH_3)_2$[a]	2103 m, 2063 s, 2054 s, 2022 s, 2006 s, 1993 m	this work
$HRu_3(CO)_{10}S(CH_2)_3S(CH_3)_2O\sim\sim$ (anchored)	2106 m, 2065 s, 2058 s, 2026 s, 2010 s, sh 1996 m, sh	this work

[a] In CCl_4 solution.

hexane under N_2 for 20 minutes, while methanol treated silica was refluxed under N_2 for 18 hr in benzene solution containing the substituted cluster compound $HOs_3(CO)_{10}S(CH_2)_3Si(OCH_3)(CH_3)_2$ when route II was chosen. Both routes yielded a pale yellow powder containing 0.16 wt.% Os after washing with hot cyclohexane and drying. The infrared carbonyl spectra of both products were identical and very closely resemble those of the thiol derivative of the cluster and of well characterized reference compounds (Table I). This strongly suggests the successful attachment of the trinuclear osmium cluster onto the thiol functionalized silica surface. The material prepared via route I shows a weak S–H stretching band at 2583 cm^{-1}, suggesting a certain number of ligands being unreacted. No free thiol ligands, however, can be detected when the attachment was carried out via route II.

Refluxing $Os_3(CO)_{12}$ in cyclohexane with the thiol modified silica for 3 hr also yielded a pale yellow powder which contained 0.26 wt.% Os. Infrared carbonyl bands of this material were found at 2112(m), 2071(s), 2059(s) and 2029(s) cm^{-1}. These bands coincide with the most intense bands of the molecular and surface-bound thiol derivates described above; the weaker bands, however, cannot be resolved. This might indicate the formation of analogous anchored products via this different route though the larger width of carbonyl stretching bands suggests more severe structural distortions.

The attachment of the triruthenium cluster was carried out by following the procedure described by Crooks *et al.* [10]. The thiol functionalized silica was refluxed in dry benzene which contained dissolved $Ru_3(CO)_{12}$ under N_2 for 30 minutes. A light yellow powder was obtained after washing with hot benzene and cyclohexane and drying. For reference purposes $Ru_3(CO)_{12}$ was also reacted with $HS(CH_2)_3Si(OCH_3)(CH_3)_2$ in the homogeneous phase by refluxing in dry benzene under N_2 for 15 minutes. A yellow solid could be isolated from the concentrated solution. The infrared carbonyl spectra of this compound and of the anchored cluster are compared with the corresponding spectra of the reported well characterized compounds $[HRu_3(CO)_{10}SR]$ ($R = C_2H_5$ or C_4H_9) in Table II. The spectra of both compounds, the homogeneous and the anchored cluster, very closely resemble those of the reference compounds. This strongly suggests the successful attachment of the trinuclear ruthenium cluster onto the thiol functionalized silica by formation of the thiol derivative $HRu_3(CO)_{10}\ S(CH_2)_3Si(CH_3)O\sim$. The Ru content of this material was 0.19 wt.%, which corresponds to a Ru_3/S ratio of 0.02. The S–H stretching vibration of unreacted thiol groups, however, was not detected in the infrared spectra.

The reaction between unmodified silica and $[HRu_3(CO)_{10}S(CH_2)_3Si(OCH_3)(CH_3)_2]$ (reflux in dry benzene under dry N_2 for 2 hr) did not yield the attached cluster although the corresponding reaction with the analogous triosmium compound was successful when methanol treated silica was used. The obtained red-brown powder showed infrared carbonyl bands at 2102(m), 2030(vs), and 1982(s) cm^{-1}. Still another preparation with methanol pretreated silica gave rise to infrared carbonyl bands at 2107(m), 2037(vs), 2009(s, sh) 1988(s, sh) cm^{-1}. The nature of these products is still unclear. The different infrared spectra of the two preparations using different silica surfaces, however, seems to suggest that the nature of the support surface (OH-density) may critically determine possible degradation reactions of cluster compounds.

In conclusion, analogues of $[HOs_3(CO)_{10}SR]$ and of $[HRu_3(CO)_{10}SR]$ can be anchored successfully onto thiol modified silica surfaces. The study of the thermal stability and catalytic properties of these materials is presently in progress.

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