Anchoring Selenido-Carbonyl Ruthenium Clusters to Functionalised Silica Xerogels

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Silica Xerogels containing carbonyl Ru₃Se₂ nido clusters were prepared in three different ways. The simple dispersion of [Ru₃(µ₃-Se)(CO)₇(PPh₃)₂] via sol gel process produces an inhomogeneous material; by contrast, homogeneous xerogels were obtained by reaction of [Ru₃(µ₃-Se)(CO)₈(PPh₃)] with functionalised xerogels containing grafted diphenylphosphine moieties and by reaction of [Ru₃(CO)₁₂] with a xerogel containing grafted phosphine-selenide groups. The reaction between [Ru₃(CO)₁₂] and dodecylphenylphosphine selenide led to the formation of four selenido carbonyl clusters, which are soluble in hydrocarbon solvents and can be deposited as thin films from their solution by slow evaporation.

Keywords: selenium, ruthenium, carbonyl clusters, sol-gel, anchored clusters

Introduction

Transition metal species may combine with main group elements or related molecular fragments affording a variety of interesting cluster compounds. Apart from their fundamental significance as a class of complexes owning peculiar chemical and structural properties, the growing interest for these species derives from their potential applications as catalysts, electrocatalysts and precursors for semiconductors.¹⁻³ Very recently chalcogenide ruthenium derivatives have shown interesting catalytic activity in oxygen reduction reactions in polymer electrolyte fuel cells suggesting their application as cathode for these devices.⁴⁻⁷ The availability of substituted chalcogenido metal clusters, such as [M₂(µ-Se)(CO)₆(PR₃)₂], offers the opportunity to obtain, by stoichiometrically and kinetically controlled processes, extended inorganic solids like MₓEᵧ in the form of pure phases or microinhomogeneous materials (nanocomposites).⁸

In order to prepare transition-metal selenido clusters, different synthetic routes are presently available, such as those involving, as starting materials, diphenyl diselenide,⁹,¹⁰ phenylselenyl chloride,¹¹ selenophene,¹² trialkylsilyl selenides,¹³⁻¹⁵ polyselenide anions¹⁶,¹⁷ and phosphine selenides.¹⁸⁻²¹ Furthermore small selenido clusters, such as [M₂(µ-Se)(CO)₆] and [M₃(µ₃-Se)(CO)₉], can be conveniently used to prepare larger mono- and bimetallic species.²²,²³

The reactions of tertiary phosphine selenides with metal carbonyl species provide simple synthetic procedures to form selenido clusters through transfer of selenium atoms to low-valent metal centres, taking advantage of the frailty of the P = Se bond. Despite to its synthetic potentiality, this method has been explored only to a limited extent before the last years. For this reason, we started to study the reactions of tertiary phosphine and diophosphate selenides with [M₃(CO)₁₂] (M = Fe or Ru) with the aim to obtain new phosphine-substituted selenido-carbonyl iron and ruthenium clusters.²⁴

These reactions give a variety of such selenido carbonyl clusters, whose structural frameworks are shown in Scheme...
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1. The open-triangular, variously substituted, nido-clusters with the M3Se2 core are the major products for both metals, but significant amounts of clusters with dinuclear M2Se2, trinuclear M3Se and tetranuclear M4Se2 cores are also obtained. The product distribution is strongly dependent on the reaction conditions, on the nature of the phosphine and on the cluster/phosphine molar ratio. In the case of [Ru3(CO)12], the reactions with R3PSe proceed through two consecutive steps, the monoselenido clusters [Ru3(µ3-Se)(µ3-CO)(CO)8(PR3)] undergoing the second attack by R3PSe to form the corresponding diselenido derivatives [Ru3(µ3-Se)2(CO)7(PR3)2].

As an extension of these investigations, we have tried to produce homogeneous dispersions of selenido-carbonyl clusters into inorganic or hybrid inorganic-organic matrices through the sol-gel process. This paper deals with the description of these materials aimed to act as precursors for finely dispersed chalcogenido nanoparticles. In this regard, this is the first time that chalcogenido-carbonyl molecular clusters are dispersed into solid matrices through anchoring with grafted phosphine ligands. Previous studies on cluster anchoring via phosphorus ligands concerned only carbonyl mono- and bimetallic clusters.

**Experimental**

**General procedures**

The starting reagents [Ru3(CO)12], KSeCN, elemental selenium, Ph2PCH2CH2Si(OEt)3, tetramethyl orthosilicate (TMOS), NH4F, n-dodecyl bromide, metallic Mg and Ph2PCl were pure commercial products (Aldrich and Fluka) and were used as received. [Ru3(µ3-Se)2(CO)8(PPh3)] and [Ru3(µ3-Se)2(CO)8(PPh3)] were prepared by reaction of [Ru3(CO)12] with Ph3PSe as reported in the literature. The solvents (Carlo Erba) were dried and distilled by standard techniques before use. All manipulations were carried out under dry nitrogen by means of standard Schlenk-tube techniques. TLC was carried out on 20x20 silica (Merck 60 PF254) plates. Elemental analyses (C, H) were performed with a Carlo Erba EA 1108 automated analyser. FTIR spectra (KBr discs and CH2Cl2 solutions) were recorded on a Nicolet Nexus FT spectrometer. 1H and 31P NMR spectra were recorded on AC300 (1H) and CXP200 (31P) Bruker spectrometers.

**Dispersion of Ru3(µ3-Se)2(CO)7(PPh3)2 in silica gel by sol-gel process**

300 mg of [Ru3(µ3-Se)2(CO)7(PPh3)] (0.25 mmol) were dissolved in 5 mL of a 1:1 CH2Cl2/MeOH mixture and added to 270.28 mg of TMOS (1.77 mmol). 128 µL of a 0.55 mol L⁻¹ solution of NH4F in water were added to the first solution under stirring. After 15 min the gelation process was complete. 24 h after the gelation, due to the evaporation of CH2Cl2, the gel became inhomogeneous and orange crystalline formations were observed. FTIR νCO/cm⁻¹: 2042s, 2009s, 1996s, 1980s, 1961s, 1948s (KBr).

**Preparation of the functionalized xerogel Xgp1**

A mixture of Ph2PCH2CH2Si(OEt)3 (590 mg, 1.57 mmol) and TMOS (1187 mg, 7.80 mmol) was dissolved in 5 mL of MeOH. A solution of 14 mg of NH4F (0.38 mmol) in 325 µL of distilled water was added to the mixture under stirring. The gelation process was complete in a few seconds. The white product was filtered, washed twice with MeOH and dried under vacuum. The xerogel was characterised by FTIR spectroscopy (CH2CH2PPh2 group). FTIR νCO/cm⁻¹: 592s, 740m, 793w, 952s, 1409w, 1436s, 1483w (KBr). Found: C, 28.8%; H, 2.35%. Anal. Calc. for 5SiO2.SiO3(CH2)2PPh2: C, 29.72%; H, 2.49 %.

**Selenuration of Xgp1**

500 mg of KSeCN (3.47 mmol) were added to a suspension of Xgp1 (1.5 g) in 50 mL of MeCN. The mixture was stirred for 5 h, the solvent was removed by filtration and the white solid obtained (Xgp2) was washed with amounts of MeCN and distilled water. FTIR spectra in KBr disc confirmed the selenuration: FTIR νPSe/cm⁻¹: 532 (KBr). Found: C, 26.2%; H, 2.28%. Anal. Calc. for 5SiO2.SiO32(CH2)2P(Se)Ph2: C, 26.08 %; H, 2.18 %.
Reaction [Ru(μ₃-Se)₂(CO)₆(PPh₃)] with Xgp1

225.2 mg of Xgp1 were added to a solution of [Ru(μ₃-Se)₂(CO)₆(PPh₃)] (300 mg, 0.30 mmol) in 100 mL of toluene. The suspension was stirred at 60 °C for 1 h and filtered. The pink-red solid (Xgp1) obtained was washed with CH₂Cl₂.

FTIR νCO/cm⁻¹: 2046m, 2010s, 1998vs 1960sh (KBr).

Reaction of [Ru₃(CO)₁₂] with Xgp2

1.5 g of Xgp2 was added to a solution of 500 mg of [Ru₃(CO)₁₂]. The suspension was stirred at 90 °C for 2 h. After filtration, a reddish brown solid (Xgp2) was isolated and washed with CH₂Cl₂. FTIR spectra of the red solid shows CO stretching bands due to anchored carbonyl groups.

Preparation of dodecyldiphenylphosphine selenide (dodpSe)

1.85 g of KSeCN (12.8 mmol) were added to a solution of CH₂Cl₂/MeCN (20/80 mL) solution of dodp (2.3 g, 6 mmol). The mixture was stirred at room temperature for 2 h; the solvent was removed in vacuum and the white solid obtained was washed with water, filtered and dried under vacuum (yield 84%).

FTIR νSe/cm⁻¹: 531 (KBr). 31P{¹H} NMR (CDCl₃): δ 34.1 ¹J(P,Se) 721 Hz, ¹H NMR (CDCl₃): δ 0.85 (t, 3 H, CH₃ dd), ¹J(H,H) 6.9 Hz, 1.35 (m, 20 H, CH₂ dd) 2.50 (br, 2 H, P-CH₂ dd), 7.4-7.9 (m, 12 H, Ph).

Reaction of [Ru₃(CO)₁₂] with dodpSe

Treatment of a toluene solution of [Ru₃(CO)₁₂] (300 mg, 0.47 mmol) with 406 mg of dodpSe (0.94 mmol) for 1.5 h in toluene at 90 °C gave a deep red solution, which was evaporated to dryness. The residue was redissolved in a small amount of CH₂Cl₂. Four products were isolated by TLC using a mixture of CH₂Cl₂/hexane (1:1) as eluent: a red-orange band containing the nido cluster [Ru₃(μ₃-Se)₂(CO)₆(dodp)] (1) (yield 20%), a red band containing the nido cluster [Ru₃(μ₃-Se)₂(CO)₆(dodp)] (2) (yield 35%), a purple band containing the nido cluster [Ru₃(μ₃-Se)₂(CO)₆(dodp)] (3) (yield 10%) and a brown band containing the closo cluster [Ru₃(μ₄-Se)₈(CO)₉(dodp)] (4) (yield 15%). All products were identified by comparison of their spectroscopic data with those reported in the literature.

Clusters 1 FTIR νCO/cm⁻¹: 2077m, 2044s, 2022s, 1977s (CH₂Cl₂). Found: C, 37.1%; H 3.4%. Anal. Calc. for Ru₃Se₄P₈C₂₈O₇H₇0: C, 36.95%; H, 3.36%. 31P{¹H} NMR (CDCl₃): δ 46 br; ¹H NMR (CDCl₃): δ 0.88 (t, 3 H, CH₃ dd), ¹J(H,H) 6.9 Hz, 1.26 (m, 20 H, CH₂ dd), 2.61 (br, 2 H, PCH₂ dd), 7.5-7.8 (m, 12 H, Ph).

Cluster 2 FTIR νCO/cm⁻¹: 2045s, 2006vs, 1976s, 1944m (CH₂Cl₂). Found: C, 49.2%; H 5.2%. Anal. Calc. for Ru₃Se₄P₈C₂₈O₇H₇0: C, 48.35%; H, 5.16%. ¹H NMR (CDCl₃): δ 0.91 (t, 6 H, CH₂ dd), ¹J(H,H) 6.9 Hz, 1.28 (m, 40 H, CH₂ dd), δ 1.66 (br, 4 H, PCH₂ dd), 7.4-7.7 (m, 24 H, Ph).

Cluster 3 FTIR νCO/cm⁻¹: 2013m, 1965s, 1943sh (CH₂Cl₂). Found: C, 53.8%; H 5.9%. Anal. Calc. for Ru₃Se₄P₈C₂₈O₇H₇0: C, 55.34%; H, 5.67%. ³¹P{¹H} NMR (CDCl₃): δ 39.4, 39.5, 42.2; ¹H NMR (CDCl₃): δ 0.87 (t, 9 H, CH₃ dd), ¹J(H,H) 6.5 Hz, 1.24 (m, 60 H, CH₂ dd), 2.47 (br, 6 H, PCH₂ dd), 7.4-7.7 (m, 36 H, Ph).

Cluster 4 FTIR νCO/cm⁻¹: 2037w, 2010vs, 1955m, 1840w, 1799w (CH₂Cl₂). Found: C, 44.2%; H 4.6%. Anal. Calc. for Ru₃Se₄P₈C₂₈O₇H₇0: C, 44.94%; H, 4.63%. ³¹P{¹H} NMR (CDCl₃): δ 42.6 br; ¹H NMR (CDCl₃): δ 0.87 (t, 6 H, CH₂ dd), ¹J(H,H) 6.3 Hz, 1.24 (m, 40, CH₂ dd), 1.66 (br, 4 H, PCH₂ dd), 7.3-7.5 (m, 48 H, Ph).

Results and Discussion

Xerogels containing selenido carbonyl nido clusters of formula Ru₄Se₂ were prepared by three different ways: (i) by reaction of [Ru₃(CO)₁₂] with a functionalised xerogel
containing selenised CH$_2$CH$_2$PPh$_3$ groups; (ii) by reaction of [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] with phosphinated silica; (iii) by simple dispersion of [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] in silica by sol-gel process.

In the last case, a solution of [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] and TMOS (5:1 Ru/Si molar ratio) in a CH$_2$Cl$_2$/MeOH/H$_2$O mixture yielded, by hydrolysis and condensation reactions, an homogeneous ruby-red material. Nevertheless, subsequent solvent evaporation leads to the growth of [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] microcrystals (Figure 1) that gradually separate in the monolithic bulk.

The final material is inhomogeneous and completely releases the cluster by washing with organic solvent. This occurs also in the case of a lower Ru/Si ratio. The FTIR spectra shows strong CO stretching bands that perfectly superimpose the typical solid state [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] absorption pattern (Figure 2); these bands disappear after washing with CH$_2$Cl$_2$, indicating the total extraction of the carbonyl cluster from the gel.

Homogeneous xerogels containing dispersed selenido clusters can be prepared by the other two ways (i and ii, mentioned above), which lead to cluster-anchoring through phosphine ligands attached to the silica. Mode (ii) involves the reaction between the molecular selenido cluster [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] with the phosphine functionalized xerogel Xgp$_1$. This is prepared by sol-gel co-processing TMOS and (EtO)$_3$SiCH$_2$CH$_2$PPh$_3$ in a MeOH/H$_2$O mixture. The gelation process is fast and produces an air stable material which reacts with [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] at 60 °C, yielding a purple-red solid (Xgp$_3$). The FTIR spectrum shows strong carbonyl absorption bands in the typical range of the selenido carbonyl ruthenium clusters. A comparison of the pattern with those described in the literature shows clearly that two species are anchored to the silica matrix: the phospine di- and tri-substituted species with the Ru$_3$Se$_2$ core (Figure 3). As one of the phosphine ligands is the original PPh$_3$ (if we exclude its dissociation from the clusters), the di- and tri-substituted species are anchored to the gel through one and two phosphine ligands respectively.

Actually, the P/Si molar ratio is high enough to permit that occasionally two anchored phosphine ligands coordinate two different ruthenium atoms yielding also the tri-substituted cluster, as observed for the analogous reaction between [Ru$_3$(µ$_3$-Se)$_2$(CO)$_4$(PPh$_3$)$_2$] and PPh$_3$ carried out in the liquid phase. The xerogel completely retains the cluster even if treated with CH$_2$Cl$_2$ or hot toluene.

The first route (i) to anchored selenido clusters requires the use of phosphine selenides grafted to silica. Therefore...
Xgp1 was treated with KSeCN at room temperature, resulting in the selenation of the grafted phosphine functions which was verified by the presence of the PSe stretching band at 532 cm\(^{-1}\) in the FTIR spectrum.

The selenised xerogel (Xgp2) reacts with \([\text{Ru}_3(\text{CO})_{12}]\) in hot toluene, yielding a brick-red solid Xgp4, whose FTIR spectrum shows strong carbonyl absorption as in the case of Xgp3. A comparison of the absorption pattern (see Figure 4) with those reported in literature for the selenido-carbonyl ruthenium clusters confirms that the major product is the Ru\(_3\)Se\(_2\)-core cluster, anchored to the gel via two phosphine ligands. Scheme 2 represents the idealized structural diagram of the Ru\(_3\)Se\(_2\) cluster anchored to silica in Xgp4.

![Scheme 2](image)

The formation of \([\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_7(L)]_2\) (L=≡SiCH\(_2\)CH\(_2\)PPh\(_3\)) species is more selective than in the case of Xgp3. Despite this high selectivity, it is probable that other selenido cluster species are anchored to the gel, similarly to what observed in the reaction of \([\text{Ru}_3(\text{CO})_{12}]\) with R,PSe in the liquid phase, which affords a variety of minor products.\(^{24}\) In this regard, the presence of the mono-substituted Ru\(_3\)Se\(_2\) clusters, whereas the band at 1830 cm\(^{-1}\) is attributed to the \((\mu_2\text{-CO})\) stretching in the Ru\(_3\)Se\(_2\)-core clusters.

It is interesting to observe the broadening effect of the anchorage on the carbonyl stretching bands which are solution-like, broader than those observed for Xgp3 and different to the \([\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_7(P\text{Ph}_3)_2]\) solid state pattern. The broadening effect is similar to that reported in the literature for various species anchored to silica gels. The xerogel does not release the cluster when treated with organic solvents and presents a high homogeneity, as in the case of Xgp3.

Furthermore, formation of small amounts of \([\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_6]\) in the reaction solvent should be noted from a side reaction during the anchoring process (i). This secondary reaction pattern was not observed in the case of the reaction of \([\text{Ru}_3(\text{CO})_{12}]\) with R3PSe in liquid phases. It could be the result of selenium transfer without ligand substitution due to leaching of selenido carbonyl ruthenium species.

Finally, the reaction between dodpSe and \([\text{Ru}_3(\text{CO})_{12}]\) leads to the formation of four products: \([\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_9(dodp)]_2\) (yield 20%), \([\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_7(dodp)_2]_2\) (yield 35%), \([\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_6(dodp)_3]}\) (yield 10%) and \([\text{Ru}_4(\mu_4\text{-Se})_2(\text{CO})_9(dodp)_2]\) (yield 15%). This distribution is similar to that observed in the analogous reaction with PPh\(_3\).\(^{24}\) Nido clusters 1, 2 and 3 contain the same square pyramidal Ru\(_3\)Se\(_2\) core, substituted, respectively, with one, two and three phosphine ligands. Two phosphines coordinate the octahedral Ru\(_4\)Se\(_2\) core of the closo cluster 4. These compounds, particularly derivatives 2 and 3, are deeply coloured species soluble in hydrocarbons and easily depositable as thin films on solid surfaces by slow evaporation of their solutions; they are potential candidates for optical (NLO) applications.\(^{27}\)

References


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