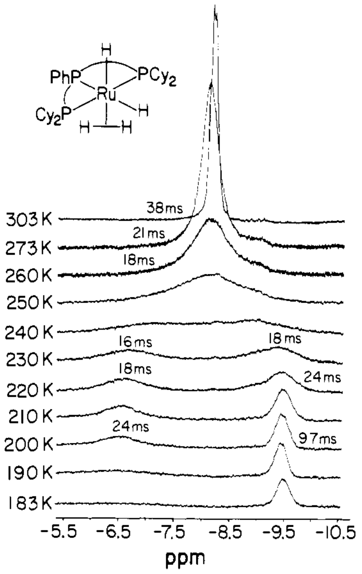

Figure 1. Variable temperature proton NMR spectra in the metal-hydride region. The calculated T_1 values are written on the −6.5 and −9.5 ppm peaks, which are assigned to the nonclassical Ru(η^2-H_2) and classical Ru–H units, respectively.

in [$MH(H_2)(dppe)_2$]BF_4 (M = Fe, Ru) was suggested for the broadening lines of the M(H_2) resonances at lower temperatures.[8b] A changeover of the rotational behavior of the molecule from the extreme narrowing to the slow-motion regimes has also been suggested as a possible origin for the line broadening in the spectra of M(H_2) complexes at low temperature.[4b] It is also possible that the line broadening in our system is caused by the exchange process involving rotation of the η^2-H_2 ligand beginning to freeze out, as suggested by one referee.

Like $RuH_4(PPh_3)_3$[3a,c] and $RuH_4(PCy_3)_3$,[8g] a broad band at ca. 1950 cm^{-1} was observed in the infrared spectrum of $RuH_2(\eta^2$-$H_2)$(Cyttp), which we attribute to the classical Ru–H bonds. We did not observe infrared bands that could be assigned to the nonclassical Ru(H_2) unit.

We tried to determine the $^1J_{HD}$ coupling constant by use of the partially deuterated compound RuH_xD_{4-x}(Cyttp) ($x \cong 2$), which was prepared in situ by bubbling deuterium gas into a toluene solution of RuH_4(Cyttp).[11] However, no $^1J_{HD}$ coupling was resolved in the temperature range 323–200 K. Other investigators have also failed to observe $^1J_{HD}$ in highly fluxional complexes that contain molecular dihydrogen (e.g., in [$FeH(H_2)(dppe)_2$]$^{+}$ [8b] and [$IrH_2(H_2)_2(PCy_3)_2$]$^{+}$ [4c,d]).

The hydride complex reacts with other ligands as if it were "RuH_2(Cyttp)". It inserts CO_2 to form a bidentate formate ligand in the resulting RuH(HCO_2)(Cyttp), and it adds CO, $P(OMe)_3$, and $P(OPh)_3$ instantly and irreversibly to form six-coordinate *cis-mer*-RuH_2L(Cyttp) complexes. It also reacts with N_2 reversibly to form *cis-mer*-$RuH_2(N_2)$(Cyttp). The N≡N stretching frequency of the N_2 compound was observed at 2100 cm^{-1}, which is consistent with Morris' proposal that when the $\nu_{N\equiv N}$ of the dinitrogen ligand is greater than 2060 cm^{-1} in a d^6 metal complex, then the nonclassical form, M(H_2), is favored over the corresponding classical dihydride, MH_2.[8a] An X-ray structure determination of $RuH_2(N_2)$(Cyttp) shows that the N_2 ligand is trans to one of the hydrides and attached "end-on" to form a nearly linear Ru-N-N linkage.[12] These reactions and structures will be reported soon.

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[11] If one bubbles D_2 gas into a solution of RuH_4(Cyttp) in benzene-d_6 or toluene-d_8, the intensity of the hydride resonance decreases and eventually almost disappears, presumably due to formation of RuD_4(Cyttp), as indicated by the ^{31}P NMR spectrum of the solution. The ^{31}P NMR parameters are almost identical with those of RuH_4(Cyttp), and the lines become wider compared to RuH_4(Cyttp).

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Thermal Evolution of an Oxide-Bound Organometallic Complex in Ultrahigh Vacuum: Stepwise Conversion of Tris(allyl)rhodium to Rhodium Metal on $TiO_2(001)$

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Chemical vapor deposition of an organometallic complex onto the surface of an oxide followed by mild thermal degradation is of demonstrated importance to "heterogeneous" catalysis[1] and modern materials synthesis.[2] We have described the chemistry of bulk oxide supported organorhodium compounds[3] and the hydrogenolysis of bis(allyl)rhodium on $TiO_2(001)$ prepared and modified in ultrahigh vacuum (UHV).[4] We now report the stepwise thermal evolution of TiO_2-bound bis(allyl)rhodium studied in UHV by photoelectron spectroscopy and on powdered supports by infrared methods. Thermolysis of the oxide-bound organometallic to the metal occurs *in stages* involving hydride complex intermediates, and our data strongly support the notion of covalency between the oxide and the organometallic and several of its derivatives.

The preparation of single crystal $TiO_2(001)$ for subsequent vapor phase deposition of tris(allyl)rhodium has been described,[4,5] as have experiments for studying deposition of the organometallic in UHV. He(I) radiation (21.2 eV) and Mg Kα radiation were used for ultraviolet and X-ray photoelectron spectroscopy respectively, with data collected in a pulse counting mode. X-ray photoelectron spectra were referenced to the Ti $2p_{3/2}$ peak at 458.5 eV. Samples prepared on bulk TiO_2 were made by depositing $Rh(allyl)_3$ on Degussa P-25 at a loading of 0.16 wt % rhodium. Infrared spectra were obtained by using a Perkin-Elmer Model 1710 Fourier transform infrared spectrometer.

Three peaks below the Fermi level are observed in the O(2p) UPS spectra for clean $TiO_2(001)$ (Figure 1A). The assignment of these peaks has been discussed.[4,6] After exposure of the TiO_2 surface to $Rh(allyl)_3$ (2000 L), the oxygen 2p binding energy maximum shifts from 7.1 to 8.1 eV (Figure 1B).[4] This indicates formation of a bond between the rhodium and the surface oxygens. The oxygen 2p binding energy maximum at 5.2 eV was barely affected by this deposition reaction showing that the rhodium complex interacts with only certain surface states of the oxide. The binding energy of Rh($3d_{5/2}$) electrons (309.0 eV)[7] was measured by XPS (Figure 2B) concommitantly with UPS determinations. Thermolysis of the supported bis(allyl) compound by resistive heating up to 150 °C was performed in 2-h stages, and both UPS and XPS determinations were made following each increase in annealing temperature. Two distinct plateaus were observed in both spectra, one in the region 60–100 °C and the other from 120 °C to 150 °C. These two regions correspond to

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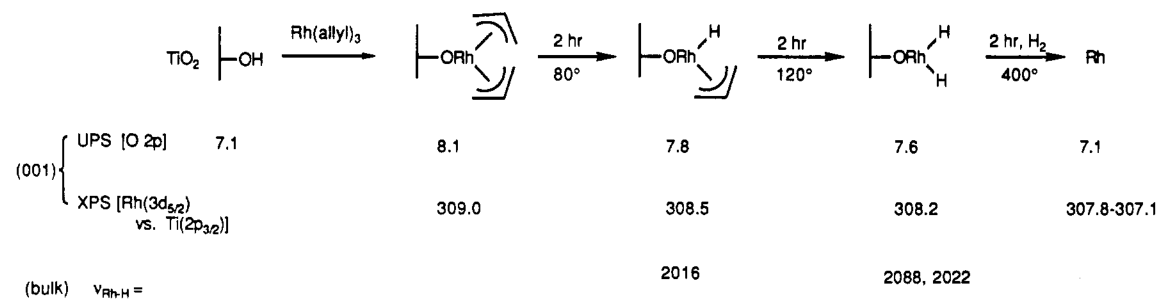
Scheme I. UPS-XPS-IR Correlations



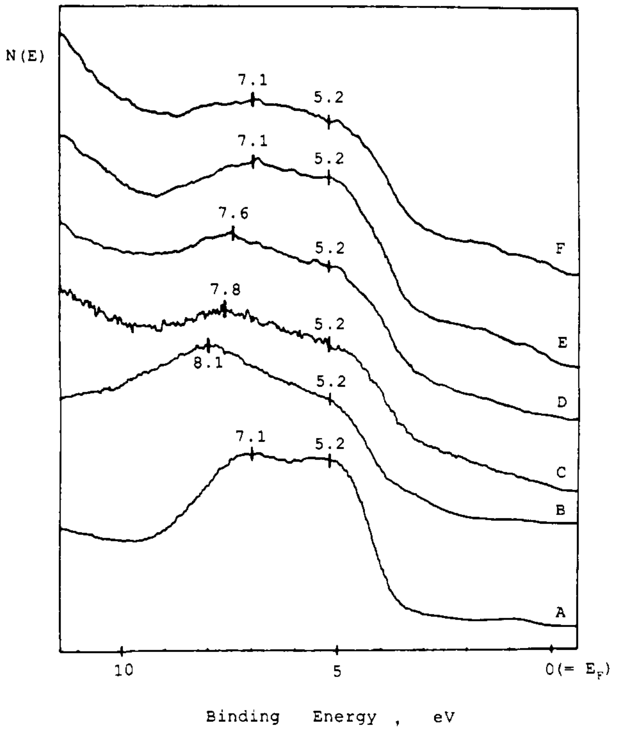


Figure 1. UP spectra of -O*-Rh(allyl)$_2$ and its thermal derivatives: (A) TiO$_2$(001) exposed to 200 L of H_2O; (B) following 2000 L of tris(allyl)rhodium exposure; (C) 80 °C heat treatment of (B) for 2 h; (D) 120 °C heat treatment of (C) for 2 h; (E) 400 °C heat treatment of (D) under H_2 for 2 h; (F) after a 5-day aging period at room temperature.

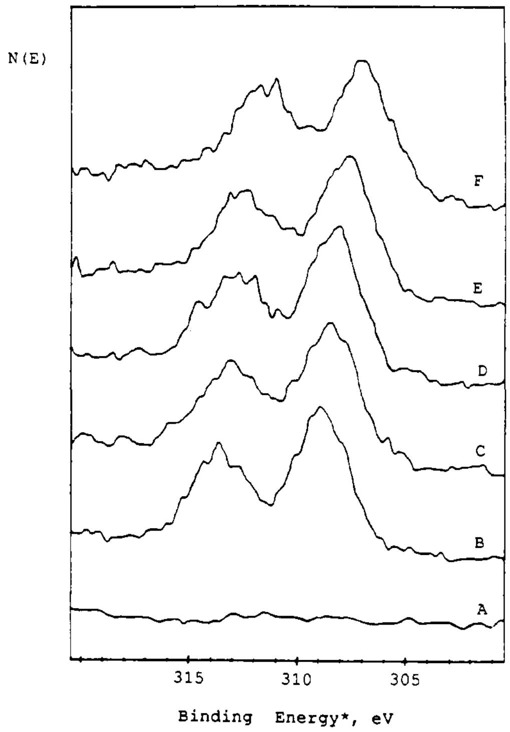


Figure 2. XP spectra of -O*-Rh(allyl)$_2$ and its thermal derivatives: (A) prior to tris(allyl)rhodium deposition; (B) following 2000 L tris(allyl)rhodium exposure; (C) 80 °C heat treatment of (B) for 2 h; (D) 120 °C heat treatment of (C) for 2 h; (E) 400 °C heat treatment of (D) under H_2 for 2 h; (F) after a 5-day aging period at room temperature. *Binding energies are referenced to Ti 2p$_{3/2}$ at 458.5 eV.

two relatively stable intermediates, each of which still possesses covalent bonding interactions between oxygen surface states and the metal center, even though in the course of these conversions the rhodium complex becomes less oxidized (as indicated by XPS) and, therefore, less electrophilic (as seen in the O(2p) binding energies).[5] Finally, the material was heat-treated at 400 °C under H_2 for a total of 2 h, which slowly produced rhodium metal.[8-10] After this heat treatment, binding energies for oxygen and rhodium were measured at 7.1 and 307.8 eV, respectively (Figures 1E and 2E). When this metal was aged for 5 days at room temperature in UHV, a slow shift in the Rh(3d$_{5/2}$) binding energy was observed, eventually moving to 307.1 eV. The binding energy for O(2p) did not change, and this is attributed to weak (or no) covalent interaction between the rhodium metal and the oxide surface. The shift in rhodium 3d$_{5/2}$ binding energies is interpreted in terms of a particle size effect:[10] as the metal particle grows by aggregation, binding energies fall. Our values for Rh(3d$_{5/2}$) (307.8–307.1 eV) compare well with those reported by Prins[9] for Rh metal of varying particle sizes on TiO$_2$. It is important to note that our initial value for "freshly prepared metal", 307.8 eV, is relatively high compared with that noted for rhodium metal prepared by conventional deposition procedures. We believe, therefore, that this initially produced rhodium metal is very highly dispersed.

A correlation was made between organometallic complexes deposited in UHV and those prepared under "normal" laboratory conditions on powdered oxides. Tris(allyl)rhodium was deposited[3,11] onto powdered TiO$_2$ suspended in octane, and the resulting material was thermalized as a pressed pellet in stages according to those reported above. The material prepared at 60 °C displays a peak at 2016 cm^{-1}, assigned[3b,12] to (TiO$_2$)-Rh(allyl)H. When the temperature was increased to 120 °C, a new spectrum was obtained showing two peaks of equal intensity at 2088 and 2022 cm^{-1}, assigned[3b] to (TiO$_2$)-RhH$_2$. After 2 h under H_2 (1 atm) at 400 °C, IR analysis showed no peaks in this region. Structures of materials prepared in UHV were assigned accordingly (Scheme I). It is interesting to note that thermolysis provides a means to prepare either the (allyl)hydride or dihydride complexes cleanly; hydrogenolysis[13] of the supported bis(allyl)rhodium compound

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produced only mixtures of these hydride species, even under several different conditions.

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Registry No. Rh(allyl)$_3$, 12082-48-3; TiO$_2$, 13463-67-7; Rh, 7440-16-6.

Supplementary Material Available: Figures 1 and 2 containing binding energy changes of O(2p) and Rh(3d$_{5/2}$) electrons and IR spectra of -O*-Rh(allyl)$_2$ and its thermal derivatives, respectively, and Table I containing UPS, XPS, and IR data (3 pages). Ordering information is given on any current masthead page.

Synthesis of [(Ph$_4$P)AgSe$_4$]$_n$. A Novel One-Dimensional Inorganic Polymer

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Received July 18, 1988

The chemistry of soluble and solid-state metal chalcogenide materials is an area of intense investigation.[1] Interest in this large class of compounds is wide and it derives from their utility in diverse applications such as industrial catalysis,[2] modeling of metalloenzymes,[3] lubricants,[4] rechargeable batteries,[5] nonlinear optics,[6] and electronics.[7] The sulfides are relevant in all these areas, although the selenides and tellurides are more important in nonlinear optics[6] and electronics.[8] This is one of the reasons that the sulfides have been studied considerably more than the corresponding selenides and tellurides. Another important reason, at least in the case of soluble species, is that the corresponding synthetic procedure for Se and Te materials often cannot parallel that of the sulfides. Surprisingly, little transition-metal selenide chemistry has been reported although a few interesting reports have recently appeared in the literature.[9-12] Particularly interesting are the W$_2$Se$_{10}{}^{2-}$,[9a,c] W$_2$Se$_9{}^{2-}$,[9a,c] and V$_2$Se$_{13}{}^{2-}$ [9b] species reported by Ibers et al. for which no analogous sulfur chemistry, with respect to the size of Se$_x{}^{2-}$ ligands present, exists. For reasons that already have been noted,[9] selenide chemistry may not necessarily parallel that of sulfide.

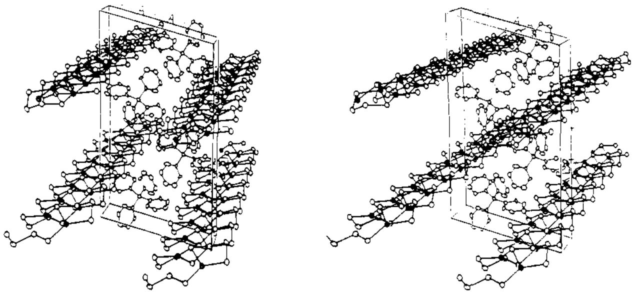

Figure 1. ORTEP representation (stereoview) of the packing arrangement of the [Ag(Se$_4$)]$_n{}^{n-}$ chains in the monoclinic lattice. Black circles represent Ag atoms.

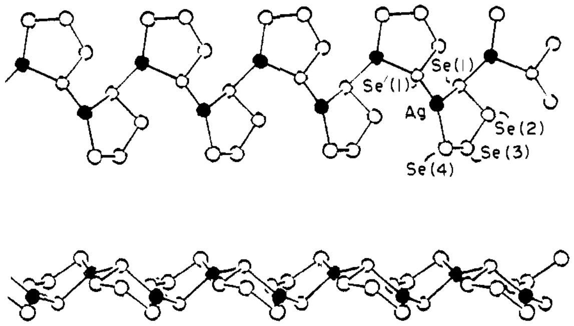

Figure 2. Two views of a [Ag(Se$_4$)]$_n{}^{n-}$ chain four unit cells long as drawn by ORTEP with labeling scheme. Black circles represent Ag atoms. Angles about the Ag atom are Se(1)-Ag-Se(1), 114.3 (1)°; Se(1)-Ag-Se(4), 106.6 (1)°; Se'(1)-Ag-Se(4), 138.8 (1)°.

Here we wish to report the synthesis and structural characterization of the new [Ag(Se$_4$)]$_n{}^{n-}$, which is the first silver polyselenide. It features an unprecedented low-dimensional polymer structure.

The reaction of AgNO$_3$ with 2 equiv of Na$_2$Se$_5$[13] in dimethyl formamide (DMF) solution in the presence of Ph$_4$PCl followed by filtration and dilution with diethyl ether affords large (up to 2 mm in length) red needles of [(Ph$_4$P)AgSe$_4$]$_n$,[14] (I) in 85% yield within several days. Smaller crystals can be obtained overnight with excess diethyl ether. A single-crystal X-ray diffraction analysis[15] reveals that I is composed of noninteracting Ph$_4$P$^+$ cations and [Ag(Se$_4$)]$_n{}^{n-}$ macroanions. The latter are infinite one-dimensional chains running parallel to the monoclinic *b*-axis. The basic repeating unit is a five-membered AgSe$_4$ ring containing the chelating Se$_4{}^{2-}$ ligand. Figure 1 represents the packing of the

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(13) Sodium pentaselenide was prepared by the reaction of elemental sodium and selenium in the appropriate ratio in an evacuated Pyrex tube at 450 °C.

(14) Elemental Anal. Calcd for C$_{24}$H$_{20}$PAgSe$_4$: C, 37.76; H, 2.62; Ag, 14.14; Se, 41.41. Found: C, 36.89; H, 2.60; Ag, 14.00; Se, 39.36.

(15) Crystal data for [(Ph$_4$P)AgSe$_4$]$_n$: monoclinic $P2_1/c$, $Z = 4$, $a = 14.145$ (3) Å, $b = 7.076$ (2) Å, $c = 24.939$ (5) Å, $\beta = 105.23$ (2)°, $V = 2408$ Å^3 at 25 °C. $2\theta_{max}$ (Cu Kα) = 110°. Number of data measured 3505. Number of data having $F_o^2 > 3\sigma(F_o^2)$: 2046. An empirical absorption correction was applied, $\mu = 147$ cm^{-1}. The minimum and maximum transmission was 0.66 and 0.99, respectively. The structure was solved with SHELXS-86 and was refined with the SDP package of crystallographic programs. Final $R = 0.075$ and $R_w = 0.076$.

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