APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 6, 609–617 (1992)

REVIEW

Organometallic chemical vapor deposition using allyl precursors

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Homoleptic allyl derivatives of many Main-Group and transition metals, $M(C_3H_5)_n$, are readily available through one-pot syntheses using metal halides and allyl Grignard reagents or by alkylation of alkali-metal salts. The relatively low molecular weight of a C_3H_5 ligand contributes to high vapor pressures whilst the stability of the allyl radical is predicted to reduce decomposition temperatures. These compounds represent a class of volatile precursors for organometallic chemical vapor deposition (OMCVD) of thin films. Film growth studies using iridium, molybdenum, palladium, platinum, rhodium, selenium, tellurium and tungsten compounds are reviewed and the relationships between pyrolysis pathways and film purity are discussed.

Keywords: Organometallic, vapor deposition, allyl, thin films

INTRODUCTION

The deposition of metals from gas-phase pyrolytic decomposition of molecular precursors has a long history dating as far back as the Mond process for purification of nickel.[1] The era of widespread application of organometallic chemical vapor deposition (OMCVD) to microelectronics is more recent, originating with the pioneering work of Manasavit on the deposition of gallium arsenide from trimethylgallium and arsine.[2] The intervening years have seen a dramatic surge in the range of elements and alloys deposited by OMVCVD as well as the applications of OMCVD-prepared materials (for a recent review, see Ref. 3). The present paper focuses on the utility of homoleptic allyl complexes for OMCVD, starting with a brief review and subsequently focusing on the details of using allyl precursors for the preparation of two selected materials; Group II–VI semiconductors and Group VI refractory metal films.

In the present paper, the term 'homoleptic allyl complexes' is used in reference to compounds in which all of the ligands are C_3H_5. An extremely large class of organometallic complexes bearing other ligands in addition to allyl group exists; however, these are largely excluded from the present discussion. The word 'chalcogenide' refers to the Group VIA elements oxygen, sulfur, selenium and tellurium.

ADVANTAGES OF ALLYL LIGANDS

The selection of the allyl group as the ligand of choice in designing precursors for OMCVD is driven by the need for high vapor pressure combined with low decomposition (growth) temperature. The relatively low molecular weight of a C_3H_5 ligand contributes to acceptable vapor pressures in Main-Group compounds (Table 1). For transition-metal complexes, homoleptic allyl complexes are among the most volatile organometallic derivatives of the second- and third-row elements (Table 2). The ability of allyl anions to behave as four-electron donors (η^3 coordination)[4] reduces the number of ligands in the coordination sphere of the metal and contributes to the volatility of the compounds by reducing their overall molecular weight. For transition-metal derivatives, the allyl ligand provides a further advantage in being stable with respect to kinetically favorable β-hydride elimination pathways which often prevent synthesis and isolation of alkyl complexes bearing ethyl, propyl or isopropyl ligands.[4] Allyl ligands are also an attractive alternative to alkyl ligands in forming significantly more stable carbon-centered radicals upon homolysis of metal–carbon bonds.[5,6] Radical stability has been observed to be inversely proportional to decomposition temperature, a second key consideration in the selection of a precursor for OMCVD.

0268–2605/92/080609–09 $09.50

Received 12 February 1992
Accepted 7 April 1992

Table 1 Properties of known homoleptic main-group metal allyl compounds

Compound	Preparative method[a]	Isolated yield (%)	Boiling point (°C)	Reference
$Mg(\eta^1\text{-}C_3H_5)_2$	I	n.r.[b]	n.r.	26
$B(\eta^1-C_3H_5)_3$	I	63	52	26
$Al(\eta^1\text{-}C_3H_5)_3$	?	n.r.	n.r.	27[c]
$Si(\eta^1\text{-}C_3H_5)_4$	I	35	215–216, 85/10 Torr	28, 29
$Ge(\eta^1\text{-}C_3H_5)_4$	I	45	105/10 Torr	28, 29
$Sn(\eta^1\text{-}C_3H_5)_4$	I	53	69–70/1.5 Torr	30
$N(\eta^1\text{-}C_3H_5)_3$	V	57	155–156	31
$P(\eta^1\text{-}C_3H_5)_3$	I	n.r.	69/13 Torr	32
$As(\eta^1\text{-}C_3H_5)_3$	I	n.r.	111/50 Torr	32, 33
$O(\eta^1\text{-}C_3H_5)_2$	IV	46	94	34
$S(\eta^1\text{-}C_3H_5)_2$	II	71	35/5–7 Torr	35
$Se(\eta^1\text{-}C_3H_5)_2$	II	80	65/15 Torr	—[d]
	I	n.r.		—[e]
	III	n.r.		—[e]
$Te(\eta^1\text{-}C_3H_5)_2$	II	70	40–42/0.1 Torr	20, 36
	I	51		7
	III	n.r.		—[e]

[a] Methods I–VI are described by reactions [1]–[6], respectively in the text. [b] n.r., not reported. [c] In the author's opinion, the existence of $Al(allyl)_3$ is not clearly established in this reference. [d] Kosar, W. and Brown, D. W., unpublished results. [e] Gedridge, R. W., private communication.

Table 2 Properties of known homoleptic transition-metal allyl compounds

Compound	Method[a]	Isolated yield (%)	Sublimation temp. (°C/Torr)	Decomp. Temp. (°C)	Reference
$Ti(\eta^3\text{-}C_3H_5)_4$	I	n.r.[b]	n.r.	−80	37
$Zr(\eta^3\text{-}C_3H_5)_4$	I	46	$25/10^{-4}$	0	38
$Hf(\eta^3\text{-}C_3H_5)_4$	I	66	$25/10^{-4}$	0	38
$V(\eta^3\text{-}C_3H_5)_3$	I	n.r.	n.r.	−30	39
$Nb(\eta^3\text{-}C_3H_5)_4$	I	38	n.r.	0	38
$Ta(\eta^3\text{-}C_3H_5)_4$	I	n.r.	n.r.	0	38, 40
$Cr(\eta^3\text{-}C_3H_5)_3$	I	69–79	$60/10^{-2}$	60	41
$Mo(\eta^3\text{-}C_3H_5)_4$	I	25	$80/10^{-2}$	60	15, 42
$W(\eta^3\text{-}C_3H_5)_4$	I	60	$80/10^{-2}$	60	15, 43
$Fe(\eta^3\text{-}C_3H_5)_3$	I	n.r.	n.r.	−40	39
$Co(\eta^3\text{-}C_3H_5)_3$	I	n.r.	n.r.	−40	39
$Rh(\eta^3\text{-}C_3H_5)_3$	I	51	$25/10^{-2}$	<130	44, 45
$Ir(\eta^3\text{-}C_3H_5)_3$	I	20	$25/10^{-2}$	65	46
$Ni(\eta^3\text{-}C_3H_5)_2$	I	80	$0/10^{-1}$	20	47
$Pd(\eta^3\text{-}C_3H_5)_2$	I	69	$25/10^{-4}$	20	38
$Pt(\eta^3\text{-}C_3H_5)_2$	I	69	$25/10^{-4}$	20	38
$Zn(\eta^1\text{-}C_3H_5)_2$	I, VI	30	Sublimes	84	48
$Cd(\eta^1\text{-}C_3H_5)_2$	VI	99	n.r.	>0	49
$Hg(\eta^1\text{-}C_3H_5)_2$	I	73	b.p. 58	Unstable	50
$Th(\eta^3\text{-}C_3H_5)_4$	I	n.r.	n.r.	0	39

[a] Methods I–VI are described by reactions [1]–[6], respectively, in the text. [b] n.r., not reported.

SYNTHESIS OF HOMOLEPTIC ALLYL METAL COMPLEXES

The relative ease of preparation of homoleptic allyl metal complexes from commercially available starting materials is a particular advantage to the film grower; some homoleptic allyl compounds are now available commercially. Tables 1 and 2 summarize the preferred synthetic procedure for specific complexes. The most general procedure (Method I) is illustrated in reaction [1]. Metal halides are reacted with allyl Grignard reagents in ether solvents at temperatures ranging from below room temperature to reflux, producing the desired homoleptic allyl derivatives and magnesium salts. Evaporation of the reaction solvent followed by extraction with hydrocarbons is the most common procedure for separation of the desired product from the co-product of magnesium salts. Yields are variable, ranging from 10 to 90%, decreasing for second- and third-row elements. The product can be readily purified by crystallization, distillation or sublimation. Often, an excess of the Grignard reagent is used to reduce the metal halides to a final, lower oxidation state of the product, yielding hexadienes as the other reaction product. Transition-metal alkoxides and aryloxides have also been successfully employed in place of halide salts. With the exception of bis(allyl)cadmium, homoleptic transition-metal allyl derivatives have been prepared exclusively by reaction [1].

$$MX_n + nC_3H_5MgX' \rightarrow M(C_3H_5)_n + nMgXX' \quad [1]$$

$$(X, X' = Cl, Br, I)$$

Alternatively, S_N2 displacement of halide from allyl halides by metal anions (Method II; reaction [2]) has been employed for those elements (e.g. sulfur, selenium, tellurium) which can be readily reduced using chemical reducing agents (alkali metals, borohydride salts). Yields are quite high (up to 75% isolated yield) and the procedure is amenable to scale-up. An additional benefit is the ability to carry out the synthesis in aqueous solution with direct separation of the immiscible organometallic product or by a simple ether extraction. The products are readily purified by distillation under reduced pressure. Homoleptic allyl derivatives of selenium and tellurium have also been prepared by reaction of the metal powder with allyl Grignard followed by alkylation with allyl bromide (Method III; reaction [3]).[7]

$$[M^{n-}] + nC_3H_5X \rightarrow M(C_3H_5)_n + nX^- \quad [2]$$

$$(X = Cl, Br, I)$$

$$C_3H_5MgBr + M \rightarrow \{(C_3H_5)MMgBr\} \quad [3a]$$

$$\{(C_3H_5)MMgBr\} + C_3H_5X \rightarrow M(C_3H_5)_2 + MgBrX \quad [3b]$$

Bis(allyl)ether, tris(allyl)amine and bis(allyl)cadmium have been prepared by reactions [4]–[6] (Methods IV–VI), respectively, but do not represent general routes to the synthesis of *homoleptic* allyl derivatives. It is possible, however, that alkyl exchange reactions of the type indicated by Method VI (reaction [6]) may allow synthesis of the presently unknown homoleptic allyl derivatives of manganese, technetium, rhenium, ruthenium and osmium. Substituted allyl derivatives (e.g. $2\text{-}CH_3C_3H_4$ and crotyl) of selected metals have been prepared by substitution of the appropriate allyl reagent into reactions [1]–[6].

$$2\,C_3H_5OH \xrightarrow{Hg(OAc)_2} (C_3H_5)_2O + H_2O \quad [4]$$

$$3\,C_3H_5Br + 4\,NH_3 \rightarrow (C_3H_5)_3N + 3\,NH_4Br \quad [5]$$

$$3\,CdMe_2 + 2\,B(C_3H_5)_3 \rightarrow 3\,Cd(C_3H_5)_2 + 2\,BMe_3 \quad [6]$$

The thermal stability of homoleptic allyl complexes (Tables 1 and 2) varies from well below room temperature to above 100 °C. Whilst some of the precursors decompose at room temperature, the kinetics of decomposition do not preclude their application in OMCVD. With the exception of selected third-row transition-metal derivatives, $[Ir(\eta^3\text{-}C_3H_5)_3$ and $W(\eta\text{-}C_3H_5)_4]$, the majority of these allyl compounds are air-sensitive. Photolytic stability of the majority of these compounds is unknown, although photo-assisted CVD studies of rhodium allyls has been reported.[8] A single study on the intense UV photolysis of hafnium, tungsten and zirconium allyls has also been published.[9]

OMCVD FROM HOMOLEPTIC ALLYL COMPLEXES

A number of homoleptic allyl complexes in Tables 1 and 2 have been included in film growth studies using OMCVD. The results are summar-

Table 3 Film growth using homoleptic allyl precursors

Element	Growth temp. (°C)	Principal impurities, concentration (atom %)	Reference
$Se(\eta^1\text{-}C_3H_5)_2$	400–450	C, <0.01	11
$Te(\eta^1\text{-}C_3H_5)_2$	250	Not reported	10
$Mo(\eta^3\text{-}C_3H_5)_4$	450	C, 49; O, 11	15
$W(\eta^3\text{-}C_3H_5)_4$	300	C, 39; O, 10	15
$Rh(\eta^3\text{-}C_3H_5)_3$	$120/H_2$	O, <2	13
	250	C, 70	14
$Ir(\eta^3\text{-}C_3H_5)_3$	$100/H_2$	O, <2	13
	250	C, 75	14
	450	C, 70	14
$Pd(\eta^3\text{-}C_3H_5)_2$	250	C, <1	12
$Pt(\eta^3\text{-}C_3H_5)_2$	250	C, <1	12

ized in Table 3. Although stable allyl derivatives are known for many Main-Group metals, allyl complexes of selenium and tellurium have received the greatest attention in OMCVD of thin films. There are no reports of semiconductor films grown using other homoleptic Main-Group metal precursors (boron, aluminum, silicon, germanium, tin, nitrogen, phosphorus or sulfur). Crystalline, high-purity HgTe and CdTe films were deposited on polished CdTe(111) using $Te(\eta^1\text{-}C_3H_5)_2$ at 240–290 °C (CdTe) and 180–290 °C (HgTe). Growth rates between 0.6 and 2.0 μm h^{-1} for CdTe and 1–22 μm h^{-1} for HgTe were reported.[10] ZnSe growth using $Se(\eta^1\text{-}C_3H_5)_2$ as a precursor for selenium at 400 °C produced smooth featureless films.[11] The growth rate became constant above 425 °C and a 40 μmol min^{-1} flow rate. The films were highly resistive but carbon contamination was comparable with that observed for films grown from hydrogen selenide (H_2Se) at a Se/Zn ratio of 1 : 1. As the Se/Zn ratio in the films increased, a corresponding increase in carbon contamination was observed relative to films grown from H_2Se.

Historically, the first transition-element films to be grown using homoleptic alklyl reagents were amorphous, smooth, low-resistivity ($\rho = 15 \pm 5\ \mu\Omega$ cm), carbon-free (<1 atom %) palladium films grown at 250 °C and 10^{-4} Torr from $Pd(\eta^3\text{-}C_3H_5)_2$ and the related $Pd(\eta^3\text{-}2\text{-}CH_3C_3H_4)_2$ precursors.[12] Platinum films with similar properties were reported using $Pt(\eta^3\text{-}C_3H_5)_2$ as the precursor.[13] Two separate studies on the preparation of rhodium and iridium films from homoleptic allyl metal precursors have been reported. Bright, amorphous rhodium and iridium films were deposited on silicon and Pyrex glass substrates at 120 and 100 °C, respectively, at atmospheric pressure using a horizontal cold-wall reactor and employing an argon carrier gas. Hydrogen gas was introduced separately, immediately above the heated substrate.[8, 13] Under these conditions, the amorphous films contained less than 2 atom % oxygen and no detectable carbon by XPS. The role of hydrogen in producing carbon-free films of rhodium and iridium from homoleptic allyl complexes appeared to be critical, as increased levels of carbon contamination were observed under a pure argon carrier gas. Photochemically assisted CVD at 23 °C using $Rh(\eta^3\text{-}C_3H_5)_3$ or $Ir(\eta^3\text{-}C_3H_5)_3$ produced amorphous films with greater concentrations of impurities than under thermal CVD conditions. In the second study, highly reflective, silvery films were observed when the deposition on glass was carried out under reduced pressure in both the presence [growth rate 2 nm h^{-1}, $(350\text{–}450) \times 10^{-3}$ Torr H_2, base pressure 15×10^{-3} Torr] and absence of hydrogen [growth rate 100–200 nm h^{-1}, base pressure $(3\text{–}10) \times 10^{-3}$ Torr] over a temperature range of 250–450 °C in a horizontal hot-wall reactor. Significant carbon contamination (13–17 wt %, 70–75 atom %) was observed by Auger electron spectroscopy.[15] A significant decrease in the level of carbon contamination (2 wt %) was achieved by hydrogen plasma ($H^{\bullet}$) processing. Smooth *crystalline* films with fine grain structure were observed under the latter conditions. Resistivity data for the rhodium and iridium films have not been reported. The nature of the carbon impurity, graphitic versus metal-bound, was not investigated in any of these studies.

Tungsten- and molybdenum-containing films deposited from $Mo(\eta^3\text{-}C_3H_5)_4$ and $W(\eta^3\text{-}C_3H_5)_4$ under vacuum [$(35–100)\times10^{-3}$ Torr base pressure, growth rate 60–180 nm h^{-1}, growth temperature 300–400 °C] in a horizontal hot-wall reactor were found to be smooth, featureless, and amorphous by scanning electron microscopy and X-ray diffraction, respectively.[15] Auger electron spectroscopy of the tungsten films revealed 44 atom % tungsten, 39 atom % carbon, 10 atom % oxygen and 7 atom % silicon after sputtering through the surface layers. Four-point sheet resistivity measurements of the tungsten-containing films indicated that they were insulating. Slightly better success was achieved in the deposition of molybdenum-containing films from $(\eta^3\text{-}C_3H_5)_4Mo$ on Pyrex and silicon substrates, although higher pyrolysis temperatures [350–450 °C, $(35–100)\times10^{-3}$ Torr base pressure, growth rate 60–180 nm h^{-1}] were required. Sheet resistance measurements were approximately three orders of magnitude greater than for pure molybdenum. Auger electron spectroscopy of the films (performed after exposure of the films to the atmosphere) revealed 35 atom % molybdenum, 49 atom % carbon, 11 atom % oxygen and 5 atom % calcium. These data should be treated with care, however, as difficulties in obtaining quantitative data from tungsten films contaminated with oxides and carbides have been described.[16] The carbon impurities in both tungsten- and molybdenum-containing films were identified as being a mixture of graphitic (285.0 eV, width 1.57 eV) and metal-bound carbon by ESCA suggesting that the films contained primarily refractory metal carbide phases. Electron binding energies of 31.69 eV (width 1.67 eV) and 33.78 eV (width 1.44 eV) were observed in the W(4*f*) region after sputtering with Ar^+. Reported binding energies for tungsten metal are 31.2 and 33.4 eV, respectively for the $W(4f_{7/2})$ and $W(4f_{5/2})$ electrons.[17] Binding energies of 31.77 and 33.91 were reported for tungsten carbide (WC) prepared by CVD from $(Me_3CCH_2)_3W{=}CSiMe_3$ and 31.7 and 33.9 eV for sputtered WC.[18] An electron binding energy of 228.7 eV (width 1.60 eV) was observed in the Mo(3*d*) region after sputtering with AR^+. Electron binding energies for molybdenum metal (Mo $3d_{5/2}$) were reported as 227.6 eV[19] while an electron binding energy of 228.3 eV (width 1.60 eV) was observed in the Mo(3*d*) region for molybdenum carbides. The observed C_{1s} binding energies of 283.9 (width 1.54 eV) and 283.6 eV (width 1.77 eV) for tungsten and molybdenum films, respectively, were consistent with the presence of metal-bound carbon (283.7 eV from the CVD of WC, 283.6 eV for molybdenum carbide).[17]

PYROLYSIS PATHWAYS

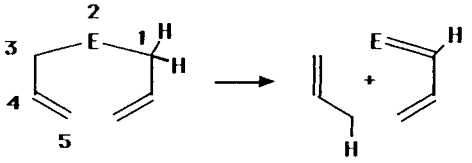
The differing results presented in the previous section for rhodium and iridium film growth emphasize the potential effects of reactor design, reactor pressures and surface treatment of substrates on the purity of films deposited from homoleptic allyl precursors. Homogeneous and heterogeneous decomposition pathways for metal allyl complexes during OMCVD conditions are equally, if not more, important in determining film purity and the nature of the product. Whilst high-purity selenium and tellurium films were prepared using the corresponding diallyl precursors, tetra-allyl tungsten and molybdenum compounds yielded metal carbide films. The role of homogeneous decomposition pathways in determining product purity can be probed by correlation of the volatile products from the OMCVD reaction with film properties. With the exception of studies on the pyrolytic decomposition of allyl Group VI (oxygen, sulfur, selenium, tellurium), tungsten and molybdenum derivatives, however, relatively little published data on pyrolytic decomposition pathways of allyl compounds are available.[15,20]

For the allyl chalcogenide compounds, there is strong evidence for a contribution from two decomposition pathways: a bond homolysis pathway (reaction [7]) and an 'ene' pathway (reaction [8]) involving a unimolecular six-member transition state. Pyrolysis of diallyltelluride or di(2-methylallyl)tellurium led to formation of 1,5-hexadiene (or 2,5-dimethyl-1,5-hexadiene) and propene (or isobutene) in a 97:3 ratio, consistent with a bond homolysis pathway and generation of allyl radicals.[20] These data were similar to the product ratios for gas-phase decomposition of the corresponding azo derivatives, $RC_3H_4N{=}NC_3H_4R$ (for R = H, Me). An intramolecular pathway (reaction [9]) for the decomposition of bis(2-methylallyl)tellurium was predicted to yield exclusively 2,5-dimethyl-1,5-hexadiene; however, three isomeric dienes (C_8H_{14}) were observed, consistent with a bond homolysis pathway.

Decomposition of diallylselenide, however, led

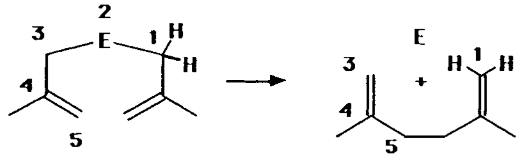
$$(C_3H_5)_2E \longrightarrow \{C_3H_5\bullet + \bullet EC_3H_5\} \longrightarrow C_6H_{10} + E \qquad [7]$$

E=N_2, Se, Te

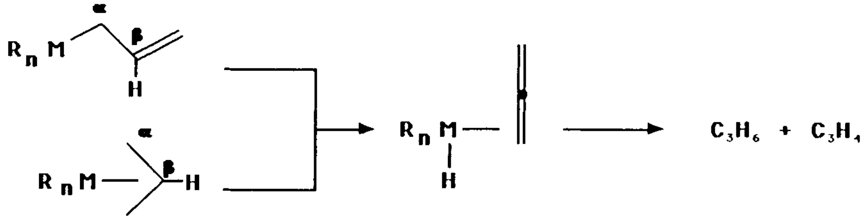


[8]

E=O, S, Se

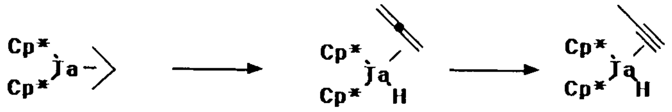


[9]



[10]

R=C_3H_5, M=transition metal



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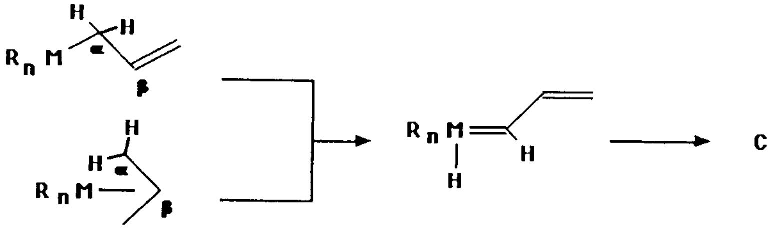
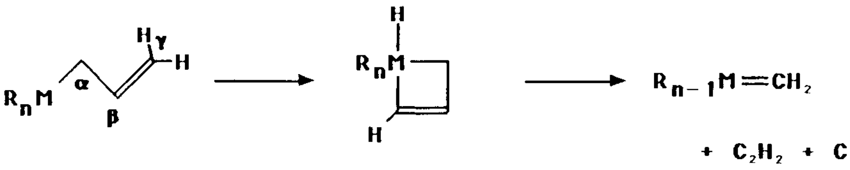


[12]

M=Mo, W; R=C_3H_5; n=3



[13]

M=Mo, W; R=C_3H_5; n=3

to propene as the major product rather than hexadiene as observed for diallyltelluride and azo bispropene under identical conditions.[20] A pathway related to the intramolecular decomposition in reaction [9] is the 'ene' pathway (reaction [8]) which accounts for the observation of propene during pyrolysis of diallylselenide without requiring the presence of allyl radicals. Comparing the pyrolysis products of the remaining bisallyl chalcogenide derivatives, diallyl ether yielded propene and acrolein[21] whilst pyrolysis of diallyl sulfide yielded a mixture of propene and a transient species $CH_2{=}CHC({=}S)H$, which subsequently dimerized. The latter was proposed to occur by the 'ene' pathway. The decreased thermal stability of $CH_2{=}CHC({=}E)H$ species ($E = O$, S, Se or Te), combined with a decreased element–carbon bond strength for the heavier chalcogenides, appears to correlate with the appearance of hexadiene (C_6) products and a greater contribution from a bond homolysis pathway for the heavier Group VIA allyl complexes. Zinc selenide film growth studies using both $CH_3Se(\eta^1\text{-}C_3H_5)$ and $Se(\eta^1\text{-}C_3H_5)_2$ have suggested that increased carbon contamination using the former precursor resulted from a greater contribution of the 'ene' pathway and correlated with an increased propene/diene ratio for the volatile products.[11,20]

MECHANISTIC SPECULATION

With the exception of $Pd(\eta^3\text{-}C_3H_5)_2$, pyrolysis of homoleptic transition-metal allyl complexes, $M(\eta^3\text{-}C_3H_5)_x$, ($M = Hf$, Mo, W, $x = 4$; $M = Rh$, Cr, $x = 3$), under vacuum yielded primarily C_3 products and carbon-rich films (Table 4). Even in the pyrolysis of $Pd(\eta^3\text{-}C_3H_5)_2$, the amount of hexadiene observed is much less than for diallyltellurium and similar to the product ratio for diallylselenium. Whilst the absence of C_6 hydrocarbon products argues against a bond homolysis pathway involving the intermediacy of allyl radicals, the pyrolysis pathways for transition-metal allyl compounds have received very little attention. In addition to an 'ene'-type mechanism, three alternative pathways, β-hydride elimination, α-hydride eliminations and activation of vinylic C–H bonds, might be considered to account for the observed distribution and nature of the volatile products in Table 4, as well as the elemental composition of the films. Whilst there is presently no evidence to favor one particular pathway, ongoing studies in our laboratory and by others (Girolami, G.S., private communication) using isotopically labelled allyl ligands are designed to elucidate the most likely decomposition pathways for transition-metal allyl complexes. Any proposed pathway, however, should be consistent with the formation of propene as the major volatile product and, in the case of molybdenum and tungsten allyl complexes, it should be consistent with the formation of solid, non-volatile, metal carbide products.

Whilst the perceived stability of allyl ligands bound to transition metals with respect to thermal β-hydride elimination reactions (reaction [10]), was attractive in selecting potential precursors for MOCVD (*vide supra*), the role of β-hydride elimination pathways in homoleptic allyl complexes of the transition elements has recently been questioned. Upon heating a benzene solution of $Cp_2Ta(\eta^3\text{-}C_3H_5)$, the spectroscopic identification of allene and propyne complexes was consistent with a β-hydride elimination pathway (reaction [11]).[23] Nevertheless, the absence of allene or propyne among the volatile products in Table 4 argues against intramolecular β-hydride elimination pathways in the decomposition of $M(\eta^3\text{-}C_3H_5)_4$ ($M = Mo$, W). Furthermore, β-hydride elimination pathways do not readily account for the formation of strong metal–carbon bonds implied by the metal-bound carbon

Table 4 Volatile products from pyrolysis of allyl compounds

Compound	Temperature (°C)	Products[a] (%)			Reference
		Propene	Hexadiene	Others	
$Se(\eta^1\text{-}C_3H_5)_2$	400	67	33	0	20
$Te(\eta^1\text{-}C_3H_5)_2$	300	0	97	0	20
$Hf(\eta^3\text{-}C_3H_5)_4$	150	99	1	0	This work
$Cr(\eta^3\text{-}C_3H_5)_3$	150	99	1	0	This work
$Mo(\eta^3\text{-}C_3H_5)_4$	400	99	0	1[b]	15
$W(\eta^3\text{-}C_3H_5)_4$	400	94	0	6[c]	15
$Rh(\eta^3\text{-}C_3H_5)_3$	150	99	1	0	This work
$Pd(\eta^3\text{-}C_3H_5)_2$	250	67	33	0	12

[a] Determined by gas chromatography and/or NMR spectroscopy. [b] Propane. [c] Mixture of ethylene and propane.

detected in the molybdenum- and tungsten-containing films.

Pathways involving α-hydride elimination both increase the metal–carbon bond order (reaction [12]) and are consistent with the formation of propene as the exclusive volatile product. Stable tungsten alkylidene and propadienylidene complexes (e.g. $(CO)_5W{=}C{=}C{=}CR_2$ for R = iPr, tBu, Ph_2) are known.[24] Vinylic C–H activation generates a tungstenocyclobutene (reaction [13]) which could decompose to acetylene and a tungsten carbene by a retro (2 + 2) cycloaddition by analogy to well-documented tungsten metallocycles and alkylidene chemistry.[25]

CONCLUSIONS AND FUTURE PERSPECTIVES

Homoleptic allyl metal compounds represent a large class of volatile, potential precursors for OMCVD of thin films. Whilst selenium, tellurium and possibly palladium or platinum films prepared from the corresponding allyl precursors may prove useful in fabrication of electronic devices in the immediate future, the unacceptably high carbon impurities in OMCVD films currently prepared using rhodium, iridium, tungsten and molybdenum allyl compounds requires the introduction of hydrogen gas and/or deposition in the presence of $H^{\bullet}$ sources to obtain high-quality films. Optimization of these conditions will be necessary for widespread application of these precursors. Nevertheless, the role of homoleptic allyl compounds as precursors for ceramic remains unexplored. In addition, the relationships between reagent structure, pyrolysis pathways and film purity are likely to remain a fruitful area of research.

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Note added in proof: MOCVO using diallylzine has recently been reported[51].