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# Platinum, palladium and rhodium complexes as volatile precursors for depositing materials

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## Abstract

This article reviews the transition-metal complexes of rhodium, palladium and platinum which were described in the literature as volatile. A classification has been adopted according to the ligands borne by each metal center, and the preparation procedures have been given. As the general aim of the review is to use the most convenient complexes for chemical vapor deposition, the yields of the syntheses and the stability and/or sensitivity of the complexes have been emphasized. When appropriate, their use in CVD and a detailed description of the resulting deposits have been reported. Challenges for researchers in the field are discussed.

*Keywords:* Chemical vapor deposition; MOCVD; Palladium; Platinum; Rhodium; Volatile complexes

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## 1. Introduction

Since the first deposition of highly pure nickel described by Mond in 1890 [1], the chemical vapor deposition (CVD) process to obtain films of various metals has become an expanding area of intense research. Of course, many efforts have been devoted to the synthesis of suitable precursors to fulfil the CVD requirements. In the course of our own CVD studies, we have shown that it is possible to use the CVD technique to prepare highly dispersed particles of metal supported on porous materials as an active catalyst from various metal–organic precursors [2].

Several comprehensive texts have recently been published concerning various volatile compounds and their applications in chemical vapor deposition [3–6]. Some reviews have been principally devoted to the different materials obtained, including pure metals, alloys, metal carbides, metal borides, metal nitrides, metal silicides, metal oxides and fluorides [3,4]: the precursors used were classified and listed for a great number of elements (Fe, Co, Ni, Pd, Pt, Ti, Cu, Si, Zr, Hf, Ga, etc.). Other reviews were more general, dealing with the reactivity and mechanisms in the CVD of late transition metals [5], or even with an overview of the processes in the chemical vapor deposition of metals [6]. These excellent articles give complementary information, since a number of various compounds from several elements are described and mechanisms of the CVD steps are examined.

The present report has a different and more specific purpose. We review here all the rhodium, palladium, and platinum complexes which are described as sufficiently volatile to be good candidates for CVD applications. For each complex we describe the synthesis, focusing particularly on the yields and the easiness of handling, and comment on the quality of the deposits obtained for a given substrate.

CVD of noble metals is achieved almost exclusively from metal–organic complexes. The main requirements that an ideal precursor should met can be determined from the present background on the CVD mechanisms. According to Maury [7], the precursors should show: (1) good volatility, more particularly a vapor pressure ≥0.1 Torr at 100 °C; (2) an adequate thermal stability, especially during the vaporization and the gas-phase transport steps; (3) a high level of purity; and (4) a clean decomposition, avoiding the contamination of the resulting material. In addition, they should preferably be: (5) non-toxic, as should their decomposition products; (6) easy to prepare in a good yield; and (7) adequately stable during storage. According to the expected use of such complexes, several criteria can be added or some of them become more important. Concerning the use of MOCVD to prepare catalysts, the three most important criteria are: (1) high volatility; (2) a very clean decomposition, providing no contamination of chlorine- or sulfur-containing fragments or giving rise to any catalyst poison; and finally (3) easy access with high yields.

To assess in advance whether a given compound will be volatile or not is a difficult task, although several factors which reduce this property have been recognized. Thus, very polar species or those carrying an anionic or cationic charge are generally not volatile due to strong molecular interactions in the solid. Polymers, adducts or compounds having hydrogen bonds also have a reduced volatility. In contrast, the volatility of several complexes was shown empirically to be increased by the presence of various ligands such as allyl or acetylacetonato ligands. For each metal the volatile complexes described are reviewed according to the nature of the ligands. Most of the complexes which we present have sublimation or boiling points lower than 100 °C under reduced pressure.

## 2. Platinum complexes

The first CVD experiments concerning platinum were carried out in the 1930s from $PtCl_2(CO)_2$ [8–10] or $[PtMe_3(acac)]_2$ (acac is the acetylacetonato ligand) [11]. However, the studies of Rand in the 1970s on $PtCl_2(CO)_2$, $Pt(PF_3)_4$ and $Pt(acac)_2$ are the actual starting point for the research of volatile complexes for CVD applications [12–14]. The complexes we considered sufficiently volatile to be possibly used in CVD are listed in Table 1.

### 2.1. ($\eta^3$-Allyl) platinum complexes

Platinum complexes containing the $\eta^3$-allyl ligand constitute the first family of those volatile compounds developed. In 1961, Shaw and Sheppard described the synthesis of the first allylic platinum derivative, Pt(allyl)Cp, which was prepared by reacting NaCp and allyl magnesium chloride with $[PtCl_2(propene)]_2$ [15].

$Pt(\eta^3\text{-allyl})_2$ was briefly mentioned by Wilke et al. [36] in 1966 as a colorless volatile complex. It was fully characterized in 1967 by O'Brien and coworkers [16]. The synthesis can be carried out from $PtCl_2$ and (allyl)MgCl according to a general procedure which was later extended.

Thus, in 1969 Shaw and coworkers described the preparation of $Pt(\eta^3\text{-methyl-2-allyl})_2$ from $PtCl_2$ and (Me-2-allyl)MgCl [37]. This latter synthesis was reported by O'Brien (but without indication of the yield) and involves a final purification step by sublimation as for $Pt(\eta^3\text{-allyl})_2$ [18].

Shaw and coworkers reported the syntheses of the $Pt(\eta^3\text{-methyl-2-allyl})(acac)$ and $Pt(\eta^3\text{-methyl-2-allyl})Cp$ complexes, whose purification was also achieved by a

Table 1
Platinum complexes

| Platinum complexes | Synthesis references | Yield | Volatility | Deposit quality |
|---|---|---|---|---|
| Pt($\eta^3$-allyl)(Cp) | [15] | * | — | *** |
| Pt($\eta^3$-allyl)$_2$ | [16] | — | — | NRV [17] |
| Pt($\eta^3$-methyl-2-allyl)$_2$ | [18] | — | — | NRV [17] |
| Pt($\eta^3$-methyl-2-allyl)(acac) | [19] | *** | — | — |
| Pt($\eta^3$-methyl-2-allyl)(Cp) | [19] | * | — | — |
| Pt($\eta^3$-allyl)(Me)(COD) | [20] | *** | — | *** |
| Pt($\eta^3$-allyl)(Me)(MeNC)$_2$ | [20] | **** | — | *** |
| Pt(acac)$_2$ | [21,22] | **** | Sublim. 140 °C, vaccum | *** |
| Pt(Tfacac)$_2$ | [22] | ** | — | — |
| Pt(hfacac)$_2$ | [22] | *** | VP: 0.5 Torr, 100 °C | * |
| [Pt(Me)$_3$(acac)]$_2$ | [11] | *** | Sublim. 160 °C, vaccum | ** |
| Pt(Me)$_3$(Cp) | [23–25] | *** | VP: 18 Torr, 100 °C | **** |
| Pt(Me)$_3$(MeCp) | [26] | **** | VP: 22 Torr, 100 °C | **** |
| Pt(Me)(CO)(Cp) | [27] | **** | — | *** |
| Pt(Me)(Cp)(COD) | [27] | **** | — | *** |
| Pt($\eta^3$-C$_9$F$_6$H$_5$)(Cp) | [27] | *** | — | — |
| Pt(Me)$_2$(acyl)(Cp) | [28] | *** | — | — |
| Pt(Me)(Et)(acyl)(Cp) | [28] | **** | — | — |
| Pt(Me)(Et)$_2$(Cp) | [28] | **** | — | — |
| Pt(Me)$_2$(Et)(Cp) | [28] | * | — | — |
| Pt(Me)$_2$(COD) | [29] | **** | VP: 0.1 Torr, 100 °C | *** |
| Pt(Me)Cl(COD) | [29] | **** | — | ** |
| Pt(COD)$_2$ | [30] | ** | — | — |
| Pt(Me)$_2$(MeNC)$_2$ | [31] | **** | VP: $3.3 \times 10^{-6}$ Torr, 25 °C | *** |
| Pt(vinyl)(Me)(MeNC)$_2$ | [20] | ** | — | ** |
| Pt(C≡C$^t$Bu)(Me)(MeNC)$_2$ | [20] | ** | — | * |
| Pt(CO)$_2$Cl$_2$ | [32,33] | *** | Sublim. 150 °C, vaccum | Wrinkled deposits |
| Pt(PF$_3$)$_4$ | [34] | **** | VP: 15 Torr, 0 °C | **** |
| Pt(C$_2$H$_4$)$_3$ | [30] | *** | — | — |
| Pt($\eta^1$-pentenyl)$_2$ | [35] | **** | — | ** |

NRV = no reported value.
VP = vapor pressure.
Evapor. = evaporate.
Sublim. = sublimate.
For yield ranging from: 0 to 25% low *; 25 to 50% medium **; 50 to 75% good ***; 75 to 100% excellent ****.
For the quality of the deposits, an amount of impurities: ≥20 at% low purity *; between 10 and 20 at% medium **; between 1 and 10 at% good ***; ≤1 at% excellent ****.

sublimation step [19]. It is worth mentioning that for the allyl ligand, the corresponding complex is a dimeric one with bridging allylic groups: [Pt($\eta^3$-allyl)(acac)]$_2$ is not a volatile complex, unlike the previous ones [37,38].

We can note that the complex Pt($\eta^3$-allyl)(hfacac) (hfacac is the hexafluoroacetylacetonato ligand) was obtained by Hughes and Powell as a crystalline stable solid

[39,40]. Its synthesis was not described but, due to the presence of the $\eta^3$-allyl and hexafluoroacetylacetonato ligands, this complex should be volatile.

The preparations of Pt($\eta^3$-allyl)(Me)(COD) and Pt($\eta^3$-allyl)(Me)(MeCN)$_2$, reported in 1991 by Puddephatt and coworkers, are detailed in Sections 2.4 and 2.5.

No CVD study was reported for this family of complexes, except for that of Girolami and coworkers, who mentioned the formation of metallic films of high quality starting from Pt($\eta^3$-allyl)$_2$ at $10^{-4}$ Torr and 250 °C [17]. Also, Puddephatt and coworkers have briefly described platinum films obtained from Pt($\eta^3$-allyl)(Cp), whose carbon contamination can be reduced from 38 at% [41] to 5 at% provided some hydrogen is introduced [20].

It seems that the main reason for the small number of reports on complexes containing the Pt($\eta^3$-allyl) framework is the tedious syntheses involved, and especially the low yields observed. Indeed, the yields in isolated product were reported by Shaw and coworkers to be 15% for Pt($\eta^3$-allyl)Cp and 18% for Pt($\eta^3$-methyl-2-allyl)Cp [19]. Nevertheless, with a 54% yield, Pt($\eta^3$-methyl-2-allyl)(acac) could be used as a suitable precursor for platinum deposition.

### 2.2. *β-Diketonato platinum complexes*

Complexes containing the (β-diketonato)platinum framework belong to a second important grouping. The three complexes [Pt($\eta^3$-allyl)(acac)]$_2$, Pt($\eta^3$-methyl-2-allyl)(acac) and Pt($\eta^3$-allyl)(hfacac) were described in the previous section.

Pt(acac)$_2$ was the first (β-diketonato)platinum complex to be described in 1901 by Werner [42]. It was prepared with only a 35% yield by reacting $K_2PtCl_4$ and acetylacetone in strongly basic aqueous solutions [21]. However, a 75% yield was obtained in 1980 by Okeya and Kawaguchi, who formed the intermediate species $[Pt(H_2O)_4]^{2+}$ by adding $Hg^{2+}$ or $Ag^+$ ions during the dissolution of $K_2PtCl_4$ in water [22]: the simple addition of acetylacetone in basic medium afforded the complex Pt(acac)$_2$.

The same procedure using trifluoroacetylacetone or hexafluoroacetylacetone led to the complexes Pt(Tfacac)$_2$ (Tfacac is the trifluororacetylacetonato ligand) and Pt(hfacac)$_2$ with yields of 30 and 60%, respectively.

[PtMe$_3$(acac)]$_2$ was described in 1928 by Menzies as a volatile platinum complex [11]. Its preparation was carried out by reaction of Tl(acac) with [PtMe$_3$I]$_4$ with a 70% yield. The dimeric nature of [PtMe$_3$(acac)]$_2$ was shown later by Swallow and Truter [43].

Finally, it is worth mentioning the studies by Jin and Cavell which describe the preparation and characterization of several complexes [Pt(β-diketonato)(Me)(PPh$_3$)], some of which might be volatile [44].

Pt(acac)$_2$ has been extensively used in CVD due to its air- and moisture-insensitivity. Moreover, this complex is commercially available at a reasonable cost.

In 1947, Marboe patented the deposition of platinum from Pt(acac)$_2$ [45]. After that, in 1975, Rand obtained deposits between 500 and 600 °C under a $10^{-4}$ Torr pressure which suffered a high carbon contamination (50 at% C). The complex was reduced before sublimation when hydrogen was used as carrier gas. Pure deposits were shown to be obtained when oxygen was added during the decomposition of Pt(acac)$_2$ at 500 °C under pressures ranging from 1 to 10 Torr [46,47]. Kinetics and thermal decomposition studies carried out between 250 and 460 °C under a pressure between 2 and 8 Torr were reported [47]. Platinum mirrors were obtained at 190–200 °C starting from [Pt(Me)$_3$(acac)]$_2$ sublimated at 160 °C under reduced pressure [11]. More recently, Puddephatt and coworkers mentioned that the use of [Pt(Me)$_3$(acac)]$_2$ led to an extensive contamination in the absence of any reactive gas (C: 30 at%; O: 4 at%), while addition of hydrogen reduced the carbon contamination (C: 6 at%; O: 5 at%) [20].

Laser-assisted CVD from Pt(hfacac)$_2$ was studied in detail by van den Berg and coworkers, with the aim of developing micro- or optoelectronic devices [48–55]. This precursor was used in the preparation of metallic platinum powders as catalytic materials by laser photolysis under ambient conditions [56]. However, a high contamination in heteroelements was detected (F: 24 at%; O: 8 at%; C: 61 at%). Such contamination was reduced by the introduction of hydrogen and oxygen during photolysis [56]. Platinum-containing zeolites were prepared by Dossi et al. in a two-step method which involved an impregnation step followed by decomposition under $H_2$ [57–59]. Finally, we observed during our own studies on the CVD of platinum on planar substrates that Pt(hfacac)$_2$ begins to decompose in a 380–420 °C temperature range under reduced helium pressure, the decomposition ratio being only 25%. When hydrogen was added to the carrier gas the deposition temperature decreased to 140 °C: here also decomposition was largely incomplete. Under both experimental conditions, a high level of contamination was determined: without $H_2$, C: 48 at%; O: 2 at%; F: 12 at%; with $H_2$, C: 35–45 at% [7]. To the best of our knowledge, no CVD studies have been reported on Pt(tfacac)$_2$.

These studies clearly show that (β-diketonato)platinum complexes afford deposits suffering high levels of contamination when the decomposition is carried out without any reactive gas. The addition of oxygen to the carrier gas or the exclusive use of hydrogen improves the purity of the deposit, especially in the former case.

### 2.3. ($\eta^1$- or $\eta^5$-Cyclopentadienyl)platinum complexes

A lot of complexes belong to this class. The first to be synthesized was Pt(allyl)(Cp) (see Section 2.1).

In 1963 Robinson and Shaw obtained Pt(Me)$_3$Cp by reacting NaCp with [Pt(Me)$_3$I]$_4$: the 32% yield [23,24] was improved to 52% by performing the substitution at low temperature [25]. This complex is a white, crystalline, air-stable and volatile solid (vapor pressure = 0.05 Torr at 25 °C) [25].

Using the same procedure, Fritz and Schwarzhans prepared Pt(Me)$_3$(MeCp) with an 80% yield. This compound is a liquid above 30 °C (vapor pressure = 0.4 Torr at 50 °C) [26,60].

In 1975 Clark and Shaver reported the synthesis of three volatile complexes: Pt(Me)(Cp)(COD) (where COD is the cyclooctadienyl ligand), Pt(Me)(CO)(Cp) and Pt($\eta^3$-$C_9F_6H_5$)(Cp), as well as ten other Pt(Cp) compounds whose volatility was not mentioned [27]. Pt(Me)(Cp)(COD) was obtained with an 80% yield from PtCl(Me)(COD) and TlCp. Displacing the COD by bubbling CO afforded Pt(Me)(CO)(Cp) with an 85% yield. Pt($\eta^3$-$C_9F_6H_5$)(Cp) was prepared by treating Pt$(Cp)_2$(COD) (see Section 2.4) with 4 equiv. hexafluorobutyne (61% yield).

The synthesis of several volatile complexes which present the Pt$(alkyl)_3$(Cp) formula was described by Shaver in 1978: Pt$(Me)_2$(acyl)(Cp) (55% yield), Pt(Me)(Et)(acyl)(Cp) (88%), Pt(Me)$(Et)_2$(Cp) (83%), Pt$(Me)_2$(Et)(Cp) (18%) and Pt$(Et_2)$(acyl)(Cp) [28].

In 1970 Egger initiated studies on the gas-phase reactivity of Pt$(Me)_3$(Cp). Its mass spectra and vapor-pressure curve as a function of the temperature, $\log P = f(1/T)$, were reported [61]. Later, Kaesz and coworkers studied in more detail the use in CVD of the two precursors Pt$(Me)_3$(Cp) and Pt$(Me)_3$(MeCp). These authors were able to obtain polycrystalline films at 180 °C which show a good adhesion on silica or glass and contain less than 1 at% carbon and oxygen [25,62,63]. The deposition was achieved at atmospheric pressure in the presence of hydrogen. Mechanistic and kinetic studies showed the complex gives methane and cyclopentane (or methylcyclopentane) quantitatively by hydrogenation of the ligands [64]. The complex Pt$(Me)_3$(Cp) was also used as a precursor in LACVD under ambient conditions, but the carbon contamination reached 20 at% in the absence of $H_2$, as opposed to 4% when it is present [65]. A focused ion-beam induced deposition of platinum was carried out from Pt$(Me)_3$(Cp), but regardless of the presence or otherwise of hydrogen, the carbon contamination was 24%, that of oxygen being only 2% [60].

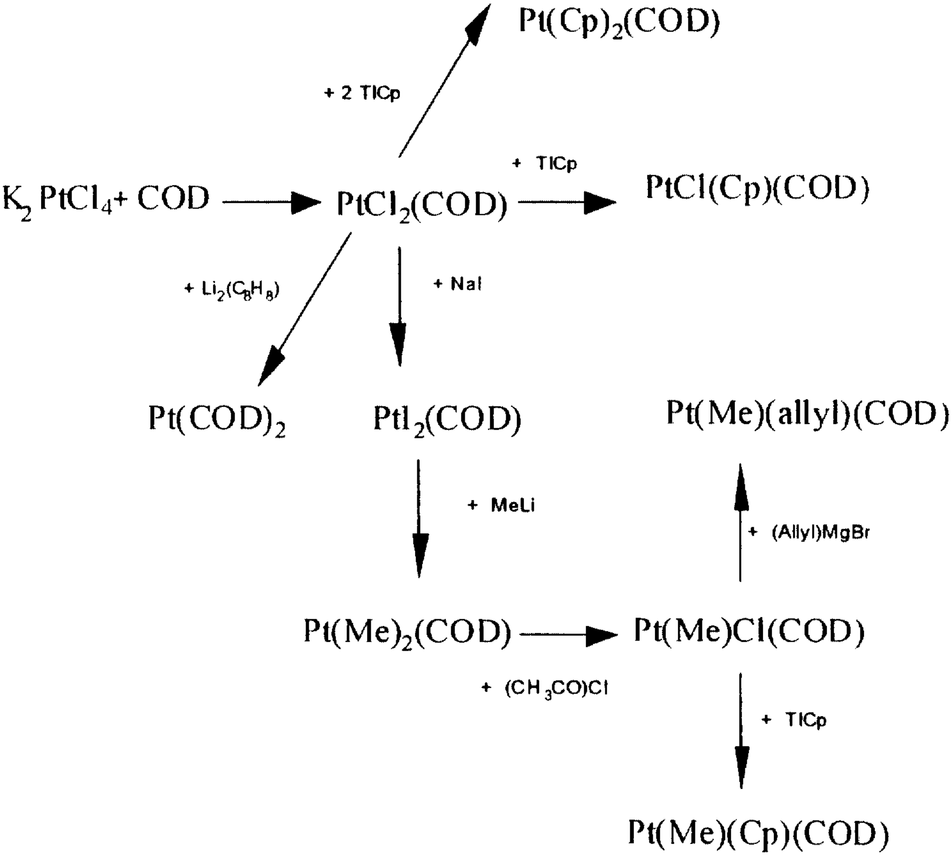
Deposits obtained from Pt(Me)(CO)(Cp) and Pt(Me)(Cp)(COD) have been briefly reported [20,41]. The introduction of hydrogen allowed a decrease in the decomposition temperature from 250 to 135 °C. This also reduced the surface contamination by carbon from 27 to 4 at% in the case of the carbonyl precursor and from 19 to 5 at% in the case of the cyclooctadiene precursor.

Many studies have been carried out on Pt$(Me)_3$(Cp) and Pt$(Me)_3$(MeCp). Their use as precursors in CVD was a great advance since, in the presence of hydrogen, remarkably pure platinum deposits are obtained. The other complexes belonging to this group, and particularly Pt$(alkyl)_3$(Cp), have not been studied for CVD. Like Pt$(Me)_3$(Cp), they may be good candidates, leading to highly pure deposits through catalytic hydrogenation of the ligands. However, these compounds seem to be less volatile and less stable than their methyl homologues [66].

### 2.4. Platinum complexes containing the cyclooctadienyl ligand

All the $\eta^4$-cyclooctadiene ligand-containing complexes result from the substitution of the chloro ligands in $PtCl_2$(COD), as summarized in Scheme 1. The preparation of Pt(Me)(Cp)(COD) was described in Section 2.3.

Clark and Manzer reported the synthesis of Pt$(Me)_2$(COD) from $PtCl_2$(COD) in a two-step process with an 83% yield from the starting salt $K_2PtCl_4$ [29]. From Pt$(Me)_2$(COD), Pt(Me)Cl(COD) was easily obtained by direct addition of acetylchloride in 97% yield [29]. This latter complex was shown by Clark and Shaver in



Scheme 1.

1976 to give Pt(Me)(Cp)(COD) by reaction with cyclopentadienyl thallium [27]. In the same paper, the preparation of Pt(Cp)$_2$(COD) and PtCl(Cp)(COD) was described: although no such indication was given by the authors, the simultaneous presence of the cyclopentadienyl and cylooctadienyl ligands could confer a degree of volatility to these complexes. Treatment of PtCl$_2$(COD) with 2 equiv. TlCp afforded Pt(Cp)$_2$(COD) with a 76% yield, whereas with 1 equiv. TlCp, PtCl(Cp)(COD) was obtained with only a 46% yield [27].

Green et al. described the synthesis of Pt(COD)$_2$ (yield 50%) by reacting PtCl$_2$(COD) with the lithium salt of the cyclooctatetraene dianion. The resulting complex was purified by sublimation [30]. The synthesis of Pt($\eta^3$-allyl)(Me)(COD) was described in 1991 by Puddephatt and coworkers from PtCl(Me)(COD) and allyl magnesium bromide with a 56% yield [20].

Puddephatt and coworkers used this group of complexes in CVD studies, and several decomposition mechanisms were reported [20,67]. Platinum films with surface contaminations of carbon (10 at%) and oxygen (4 at%) were obtained at 250 °C under a pressure of $10^{-2}$ Torr. The presence of hydrogen improved the purity of the films (4 at% C, 2 at% O). Our group has recently shown that platinum deposits with less than 1 wt% C are obtained from the decomposition of $Pt(Me)_2(COD)$ at 120 °C in the presence of hydrogen [68]. Analysis of the gas phase during the deposition process allowed the detection of cyclooctane and methane arising from hydrogenation of the ligands, while cyclooctadiene and cyclooctene were formed during deposition carried out in the absence of reactive gas [20,68]. We also reported the Clausius–Clapeyron equation $\log P = f(1/T)$ for $Pt(Me)_2(COD)$: this complex displays a relatively low volatility (0.1 Torr at 100 °C) [68].

Deposition carried out at 250 °C under a pressure of 0.1 Torr starting from PtCl(Me)(COD) without reactive gas suffered a contamination of 25 at% carbon and 5 at% oxygen. Upon the addition of hydrogen during the deposition, these atomic ratios decreased to 9% and 3%, respectively. Chlorine was not detected in the films [20,41].

$Pt(\eta^3\text{-allyl})(Me)(COD)$ has been briefly reported to be a CVD precursor leading to platinum films with a purity of 61% without reactive gas and 94% in the presence of hydrogen [20].

Thus, this family of platinum complexes can lead to relatively pure films in the presence of hydrogen as a reactive gas during deposition. This purity is due to the formation of cyclooctane from (COD) and methane from (Me), which circumvents the decomposition of the ligands by internal C–C bond breaking.

### 2.5. *Platinum complexes containing the (Me) and $(MeNC)_2$ ligands*

The group of complexes containing both a methyl ligand and two methyl isonitrile ligands is the most recently developed. The synthesis of $Pt(Me)_2(MeNC)_2$ by the treatment of $[Pt_2(Me)_4(SMe_2)_2]$ with methyl isonitrile (MeNC) at 0 °C (yield 85%) was reported [31]. The authors later described the syntheses of $Pt(vinyl)(Me)(MeNC)_2$, $Pt(allyl)(Me)(MeNC)_2$, and $Pt(C{\equiv}C^tBu)(Me)(MeNC)_2$ [2]. $Pt(vinyl)(Me)(MeNC)_2$ was obtained in a yield of 40% by addition of MeNC to a solution of $Pt(Me)Cl(SMe_2)_2$ and vinyl magnesium bromide. A similar procedure using allyl magnesium bromide led to $Pt(allyl)(Me)(MeNC)_2$ in an 87% yield. Using (t-butylethynyl)lithium, $Pt(C{\equiv}C^tBu)(Me)(MeNC)_2$ was obtained (yield 49%).

$Pt(Me)_2(MeNC)_2$ pyrolysis occurred at a relatively high temperature (250 °C), without any reactive gas and with a contamination of 34 at% carbon [20]. This temperature was decreased to 180 °C in the presence of hydrogen. Detailed studies were reported for platinum deposition from this complex with different molar ratios of hydrogen. Thus, a purity superior to 99.5 at% was obtained by adjusting the $H_2$ flow. The vapor pressure of the compound was reported, showing its relatively low volatility ($3.3 \times 10^{-6}$ Torr at 25 °C). $CH_4$, $C_2H_6$ and MeNC were detected during thermolysis studies conducted under reduced pressure [20].

The decomposition of $Pt(allyl)(Me)(MeNC)_2$ occurred at lower temperature than that of $Pt(Me)_2(MeNC)_2$ (180 °C without any reactive gas). According to

Puddephatt and coworkers, this behavior could be due to the lower bond energy of Pt–allyl compared to Pt–Me [20].

Puddephatt obtained medium-purity metallic films starting from the complexes $Pt(C{\equiv}C^tBu)(Me)(MeNC_2)$ and $Pt(vinyl)(Me)(MeNC)_2$. However, no extensive CVD study was described.

In summary, good quality films can be obtained from this group of complexes, especially from $Pt(Me)_2(MeNC)_2$. Nevertheless, several drawbacks concerning the application to CVD may be noted, i.e. poor synthesis yields, low volatility of the compounds, and therefore a slow rate of growth of the metallic films.

### 2.6. *Other volatile platinum complexes*

$Pt(CO)_2Cl_2$, $Pt(PF_3)_4$ and $Pt(C_2H_4)_3$ cannot be classified into any of the groups described above.

$Pt(CO)_2Cl_2$ was prepared as early as 1868 by Schutzenberger [32,33]. In 1954, Lutton and Parry studied the equilibrium which controls the formation of the three known Pt–(chloro)–(carbonyl) complexes [69]. A synthesis of $Pt(CO)_2Cl_2$ from $PtCl_3$ at 125 °C under 40 bar CO was given (yield 75%).

Powell et al. recommended the use of Pt–(chloro)–(carbonyl) compounds in CVD, especially $Pt(CO)_2Cl_2$ [70]. However, a study by Rand pointed out several drawbacks shown by this precursor [12]. Indeed, $Pt(CO)_2Cl_2$ rapidly decomposed in the absence of a CO atmosphere, and led to wrinkled deposits.

$Pt(PF_3)_4$ was obtained by Kruck and Baur in 1965: the synthesis was carried out under a pressure of 100 bar $PF_3$ from $PtCl_2$ in the presence of copper powder [34]. The compound is a very volatile liquid under standard conditions (vapor pressure 15 Torr at 0 °C). It is air-stable and moisture-sensitive. This complex was studied for CVD by Rand, who obtained adherent deposits which were slightly contaminated by phosphorus [12]. $Pt(PF_3)_4$ was also used as a precursor for CVD assisted by laser photolysis [71,72].

Finally, $Pt(C_2H_4)_3$, which contains coordinated ethylene, was described as a volatile complex [30]. It was obtained as white crystals, only stable under an ethylene atmosphere, by substitution of cyclooctadiene in $Pt(COD)_2$ with an ethylene pressure of 1 bar in 60% yield [30]. The use of this complex as a CVD precursor was not reported, probably because of its low stability.

### 2.7. *More recently reported results on volatile platinum complexes*

In the last few years, Tagge et al. have published the synthesis and CVD studies of the platinum(II) complex $Pt(\eta^1,\eta^2\text{-}C_5H_9)_2$, which contains the $\eta^2,\eta^1$-pent-4-en-1-yl ligand [35]. This complex was prepared with an 85% yield by treating $PtCl_2(COD)$ with pentenylmagnesiumbromide in diethylether. It is stable towards air and moisture, but it is difficult to store at room temperature. The deposits obtained at 175 °C under argon were contaminated with 18 at% carbon. However, the introduction of hydrogen as a carrier gas led to the decomposition of the complex above 25 °C. Kinetic, deuterium labelling and chemical trapping experiments were carried out, and these indicated that a platinum hydride intermediate is formed during the thermal decomposition. The high volatility of this compound was attributed to the small compact shape and low molecular weight imparted by the two chelating pentenyl ligands. Unfortunately, the values of vapor pressure versus temperature were not reported.

## 3. Palladium complexes

Volatile compounds of palladium are slightly less numerous than those of platinum. Due to the importance of palladium films for microelectronic applications, there has been much interest in the design and study of palladium complexes for use as precursors for CVD over the past few years. The complexes considered to be sufficiently volatile to be used for CVD are given in Table 2.

### *3.1. ($\eta^3$-Allyl)palladium complexes*

This group of complexes was developed in parallel with the ($\eta^3$-allyl) platinum family. Thus, in 1960, Shaw first described the complex Pd($\eta^3$-allyl)(Cp) [91]. This synthesis was detailed in 1961 by McClellan et al. from [Pd($\eta^3$-allyl)Cl]$_2$ and LiCp (yield 83%) [73]. A complete synthesis including the preparation of [Pd($\eta^3$-allyl)Cl]$_2$ was proposed in 1979 by Tatsuno et al. [92].

Pd($\eta^3$-allyl)$_2$ was described as a pale yellow complex, less stable than Pt($\eta^3$-allyl)$_2$, by Wilke et al. in 1966. Becconsall et al. reported the detailed prepara-

Table 2
Palladium complexes

| Palladium complexes | Synthesis references | Yield | Volatility | Deposit quality |
|---|---|---|---|---|
| Pd($\eta^3$-allyl)(Cp) | [73] | **** | VP: 25 Torr, 100 °C | *** |
| Pd($\eta^3$-allyl)$_2$ | [16] | **** | — | **** |
| Pd($\eta^3$-methyl-2-allyl)$_2$ | [74] | **** | — | **** |
| Pd($\eta^3$-allyl)(acac) | [75,76] | *** | — | **** |
| Pd($\eta^3$-methyl-2-allyl)(acac) | [75,76] | *** | Sublim. 70 °C, $10^{-4}$ Torr | *** |
| Pd($\eta^3$-allyl)(hfacac) | [77,78] | **** | VP: 2.5 Torr, 100 °C | **** |
| Pd($\eta^3$-methyl-2-allyl)(hfacac) | [77] | — | — | **** |
| Pd(acac)$_2$ | [79,80] | — | Sublim. 300 °C, $10^{-4}$ Torr | Patented [81] |
| Pd(hfacac)$_2$ | [82,83] | *** | — | **** |
| Pd(tod)$_2$ | — | — | NRV [84] | — |
| Pd(Me)$_2$(PEt$_3$)$_2$ | [85] | **** | Sublim. 50 °C, $10^{-3}$ Torr | ** |
| Pd(Me)$_2$(PMe$_3$)$_2$ | [86] | *** | Sublim. 50 °C, $10^{-3}$ Torr | ** |
| Pd(Me)$_2$(tmeda) | [87] | *** | Sublim. 50 °C, $10^{-3}$ Torr | ** |
| Pd(Cp)($C_{10}H_{12}OCH_3$) | [88] | ** | — | — |
| Pd(PF$_3$)$_4$ | [34] | — | — | — |
| Pd($C_2H_4$)$_3$ | [30] | — | — | NRV [89] |
| Pd($S_2COCHMe_2$) | [90] | — | Sublim. 95 °C, $10^{-2}$ Torr | *** |

tion of the complex in 1967: it was obtained in a 70% yield from the treatment of $PdCl_2$ with allyl magnesium chloride at −80 °C [16].

The steric effects in the conformational equilibrium of $Pd(\eta^3\text{-methyl-2-allyl})_2$ and $Pd(\eta^3\text{-allyl})_2$ were studied by Faller and Incorvia in 1968 [93]. Nevertheless, the complete synthesis of $Pd(\eta^3\text{-methyl-2-allyl})_2$ was described only in 1980 by Henc et al. [74]. A yellow air-sensitive solid was obtained in a yield of 83%.

A general method for the preparation of $Pd(\eta^3\text{-allyl})(\beta\text{-diketonate})$ was reported in 1963 by Robinson and Shaw [75]. A solution of $[Pd(\eta^3\text{-allyl})Cl]_2$ in benzene was treated with Tl(acac) to give $Pd(\eta^3\text{-allyl})(acac)$ with a yield of 52%: this compound is air-sensitive. In the same way, $Pd(\eta^3\text{-methyl-2-allyl})(acac)$ was obtained from $[Pd(\eta^3\text{-methyl-2-allyl})Cl]_2$ with a yield of 62%. Later, Imamura et al. proposed an alternative synthesis: $Pd(\eta^3\text{-allyl})(acac)$ was obtained from a solution of $[Pd(\eta^3\text{-allyl})Cl]_2$ in ether treated with a basic solution of Na(acac) [76]. Using this procedure, Yuan and Puddephatt have prepared $Pd(\eta^3\text{-allyl})(hfacac)$ and $Pd(\eta^3\text{-methyl-2-allyl})(hfacac)$ [77].

$Pd(\eta^3\text{-allyl})(Cp)$ was extensively studied for palladium deposition because it is stable in moist air, volatile and prepared with a high yield [77]. Its use in CVD was initiated by Girolami and coworkers [17]: its decomposition at 250 °C, $10^{-4}$ Torr, and in the absence of carrier gas afforded palladium films with around 5 at% carbon. Our own investigations on the decomposition of $Pd(\eta^3\text{-allyl})(Cp)$, adding hydrogen to the carrier gas, showed that highly pure films of palladium can be obtained operating in the temperature range 30–60 °C at 60 Torr [78]. Analyses of the gas phase revealed that the allyl and cyclopentadienyl ligands were hydrogenated stepwise to give propane and cyclopentane as final products. Application of the CVD procedures to porous supports in a suitable apparatus led us to realise a one-step method for the preparation of heterogeneous catalysts [68]. Feurer and Suhr used an oxygen plasma to assist the CVD of $Pd(\eta^3\text{-allyl})(Cp)$. In a first step PdO was formed (16 at% oxygen), and then pure palladium films were obtained in a hydrogen plasma [94]. Stauf and Dowben were the first to report the CVD of $Pd(\eta^3\text{-allyl})(Cp)$ assisted by laser photolysis [95]. This complex was also decomposed photochemically through UV irradiation in the gas phase at $10^{-3}$ Torr [96]. As in this case no thermal source is present, depositions on sensitive supports like organic polymers can be carried out. Preparation of films which were catalytically active for non-electrolytic copper plating was achieved. Finally, Dossi et al. took advantage of the high volatility of $Pd(\eta^3\text{-allyl})(Cp)$ to deposit it inside various zeolites, and then to produce metallic palladium by reduction with hydrogen [57,58]. These materials were studied for the catalytic reforming of methylcyclopentane. The curve of vapor pressure versus temperature of Pd(allyl)(Cp) [68], as well as its mass spectrum [95], have been reported.

The two complexes $Pd(\eta^3\text{-allyl})_2$ and $Pd(\eta^3\text{-methyl-2-allyl})_2$ were also studied as precursors of thin films of palladium [17]. Whereas the use of $Pd(\eta^3\text{-allyl})(Cp)$ led to 5 at% carbon contamination, these two complexes allowed the production of films with minimal incorporation of carbon (<1 at%). The depositions were carried out at 250 °C under $10^{-4}$ Torr in the absence of carrier gas: analysis of the gas phase showed the presence of propene and also various hexadienes. However, the lack of vapor-pressure measurements and thermogravimetric and thermodifferential analyses is notable in the literature, especially as several authors have mentioned the instability of Pd($\eta^3$-allyl)$_2$ [66,77].

Pd($\eta^3$-allyl)(acac), Pd($\eta^3$-methyl-2-allyl)(acac), Pd($\eta^3$-allyl)(hfacac) and Pd($\eta^3$-methyl-2-allyl)(hfacac) were compared in CVD studies at various temperatures and using different reactive gases by Yuan and Puddephatt [77]. Pd($\eta^3$-allyl)(acac) decomposes under ambient conditions. However, thin films of high purity ($>99\%$ in Pd) were produced starting from the other three complexes at 330–370 °C, at $10^{-2}$ Torr, and in the presence of oxygen as a reactive gas. As the complex Pd($\eta^3$-methyl-2-allyl)(acac) is less volatile than those containing the hexafluoroacetylacetonato ligand, the growth rate of the films was five times slower under the same experimental conditions. The use of other reactive gases such as CO, $H_2$ or $H_2/H_2O$ led to deposits of palladium which were less pure than with oxygen.

We also mention our own results on the deposits obtained from Pd($\eta^3$-allyl)(hfacac) under unexpectedly mild conditions [78]. At 45–60 °C, at a pressure of 60 Torr, thin films of high purity ($<1$ wt% C) in palladium were obtained provided small quantities of hydrogen were added to the carrier gas ($H_2/He \approx 1\%$). As observed previously by Puddephatt and coworkers, we did not detect any contamination by fluorine or oxygen in the films. The Clausius–Clapeyron equation giving vapor pressure versus temperature was reported [68]. The formation of propene, propane and trifluoropropanone during the decomposition of the complex in the presence of hydrogen was detected by MS and GC/MS.

Out of this group of complexes we can conclude that Pd($\eta^3$-allyl)(Cp), Pd($\eta^3$-allyl)(hfacac) and Pd($\eta^3$-methyl-2-allyl)(hfacac) present good volatile properties and an adequate stability towards air and temperature. CVD from these complexes has led to high-quality films, and they are suitable candidates for further CVD applications.

### *3.2. Palladium complexes with β-diketonato ligands*

The Pd($\eta^3$-allyl)(β-diketonato) complexes were described in Section 3.1.

Pd(acac)$_2$ was synthesized by adding the acetylacetonate ion to $K_2PdCl_4$ in water [79,80].

Pd(hfacac)$_2$ was mentioned in 1980 by Siedle and Pignolet [97]. The synthesis, described in 1981, consists of the addition of an aqueous solution of hexafluoroacetylacetone and soda to an aqueous solution of $Na_2PdCl_4$: the yield in isolated product was 42% [82]. Later, using aqueous $PdCl_2$ suspensions led to an improvement of the yield to 72% [83].

Pd(tod)$_2$, where tod is the 2,2,7-trimethyl-3,5-octanedionato ligand, was described by Sievers and coworkers as being a volatile material [84].

More recently, a study on the thermal decomposition of vapors of two volatile Pd(β-diketonato) complexes, Pd(tfacac)$_2$ and Pd(dpm)$_2$ (dpm = dipivaloylmethanato ligand), has been reported [98].

In this group of complexes, Pd(hfacac)$_2$ has been the most studied [99–101]. Girolami and coworkers decomposed it between 200 and 425 °C under a pressure of $10^{-4}$ Torr in the presence of hydrogen. Deposits containing less than 1 at% carbon, oxygen or fluorine were obtained. In further studies, the authors deposited Pd from Pd(hfacac)$_2$ on a copper surface and analyzed the mechanism of the redox transmetallation reaction:

$$\mathrm{Pd(hfacac)_2 + Cu(0) \rightarrow Cu(hfacac)_2 + Pd(0)}$$

Very recently, Pd(hfacac)$_2$ has been used to deposit palladium films in the 80–200 °C temperature range in the presence of hydrogen [102]. Under reduced pressures, high growth rates were obtained (1000–4000 Å min$^{-1}$), which is interesting for the expected electronic applications. Willwohl et al., using laser photolysis in the gas phase, prepared metallic powders for catalyst preparation [56]. These powders contain high levels of carbon, oxygen and fluorine contaminations. However, they seem to be more active in ethane hydrogenolysis than catalysts prepared in a classical way [56].

The CVD of Pd(acac)$_2$ has been patented. It was claimed that palladium deposits can be obtained below 300 °C and $10^{-4}$ Torr [81]. However, some authors have reported that the volatility of this complex is poor [77]. The mechanism of the decomposition of Pd(acac)$_2$ in the gas phase has been reported by Semyannikov et al. [98].

In conclusion, for this group of β-diketonato complexes, Pd(hfacac)$_2$ seems to be the most profitable complex to use, since highly pure films can be obtained provided that sufficient amounts of hydrogen are introduced during the deposition. Some authors suggest that the direct and full hydrogenation of the ligand occurs [99,102] to give hexafluoroacetylacetone and palladium(0), whereas others propose that various competing reactions can take place according to the experimental conditions: various organofluoro products may be generated [103], as has been demonstrated for the deposition of palladium on copper surfaces at high temperature [100,101].

### 3.3. Palladium complexes containing two methyl ligands

Numerous compounds where two methyl ligands are attached to palladium are known, but few of them have been described as being volatile.

Pd(Me)$_2$(PEt$_3$)$_2$ was prepared in 1960 by Calvin and Coates by the addition of methyllithium to PdBr$_2$(PEt$_3$)$_2$ in the presence of PEt$_3$, with a 90% yield [85].

A similar procedure was used by Yuan et al. to obtain Pd(Me)$_2$(PMe$_3$)$_2$ with a 62% yield [86].

Pd(Me)$_2$(tmeda)$_2$, where tmeda is the N,N,N′,N′-tetramethylethanediamine ligand, was described in 1989 by de Graaf et al. [87]. The addition of tmeda to PdCl$_2$(CH$_3$CN)$_2$, which was undoubtedly formed on dissolution of PdCl$_2$ in refluxing acetonitrile, led to PdCl$_2$(tmeda): the addition of methyllithium produced Pd(Me)$_2$(tmeda) with yields ranging from 55 to 75%.

Yuan et al. studied the three previously mentioned complexes for the deposition of palladium films by CVD [86]. The two phosphine-containing complexes afforded films at 200 °C and $10^{-3}$ Torr in the absence of any carrier gas, but these showed a significant carbon contamination (~10%). However, using hydrogen as the carrier gas led to the deposition of palladium at 150–200 °C with no carbon contamination, but with the incorporation of 10 at% phosphorus. $Pd(Me)_2(tmeda)$ was decomposed at 150 °C under vacuum, or at 130 °C with nitrogen as the carrier gas and the addition of hydrogen as the reactive gas. In any case, 10–20 at% contamination was observed. Analyses of the gas phase revealed the presence of methane, ethane and ethylene in addition to free phosphine or tmeda ligands.

Even if the presence of hydrogen led to great amounts of methane generated from these dimethylpalladium complexes, the amounts of contaminants remain at a high level in the palladium deposits, so that other reactive gases should be examined in order to improve the purity of the films.

### *3.4. Miscellaneous volatile palladium complexes*

A dicyclopentadiene palladium complex, having the formula $Pd(Cp)(C_{10}H_{12}OCH_3)$ and resulting from the coordination of a methoxylated dicyclopentadiene ligand, was described by King in 1963. This compound was purified by sublimation at 80 °C at 0.1 Torr with a 37% yield in isolated product [88].

$Pd(Cp)_2$ has been patented as a good precursor for CVD [81]. Previously, several authors have reported that they were unable to prepare this complex, possibly due to the low affinity of palladium(II) for an octahedral environment [104].

$Pd(PF_3)_4$ was synthesized by Kruck and Baur [34]. This compound is highly volatile but decomposes above −20 °C, so it is difficult to handle in a classical CVD process.

$Pd(C_2H_4)_3$ [30] was reported by Igumenov to be volatile, stable only under an ethylene atmosphere, and to lead to pure palladium films [89].

The isopropyldithiocarbonato complex $Pd(S_2COCHMe_2)_2$ was used by Zink and coworkers to produce palladium sulfide films by laser-assisted photolysis [90].

Attempts to prepare volatile complexes containing trimethylphosphine and hexafluoroacetylacetonate in fact led to an ionic palladium(I) species $[Pd_2(PMe_3)_6][hfacac]_2$, whose low volatility is a drawback for a potential CVD precursor. It can be partially sublimed at 100 °C and $10^{-3}$ Torr, but decomposition produced several compounds, among them $[Pd_2Me(PMe_3)_3][hfacac]$ resulting from a phosphorus–carbon bond cleavage. $Pd_2(PMe)_4Cl_2$ or $Pd_2(PMe_3)_4I_2$ were prepared, but, despite being non-ionic, they did not sublime at 120 °C and $10^{-3}$ Torr [105].

In a recent article, Igumenov mentioned several volatile palladium complexes containing dithiocarbonato, monothio-β-diketonato and ketiminato ligands, either fluorinated or not [89]. Due to the presence of these chelating ligands the complexes present a high thermal stability.

### *3.5. Latest advances concerning volatile palladium complexes*

Recently, Zhang and Puddephatt reported an interesting achievement: for the first time, liquid palladium complexes were prepared for CVD applications [106]. Indeed, Pd(allyl)(β-diketonate) where the disymmetrical β-diketonato ligand contains simultaneously the $C_3F_7$ and *t*-butyl substituants, led to very pure palladium films (>99%) at 260 °C in the presence of oxygen. The use of liquid precursors allowed a better control of the molar ratio of the complexes in the gas flow through a good control of the exchange area between the precursor and the carrier gas [7,107].

## 4. Rhodium complexes

The first rhodium complex bearing metal–carbon bonds to be synthesized was the dimeric species $Rh_2(\mu\text{-}Cl)_2(CO)_4$ in 1925 [108]. Since then, numerous rhodium complexes which could be suitable for CVD have been described. However, few in-depth studies have been carried out concerning their volatility and conditions of deposition. Table 3 displays the rhodium complexes which have been found to be sufficiently volatile to be potential precursors for CVD.

### 4.1. ($\eta^3$-Allyl) rhodium complexes

Most of the ($\eta^3$-allyl) rhodium compounds were obtained from $Rh_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_4$, which was itself prepared from $Rh_2(\mu\text{-}Cl)_2(CO)_4$ by addition

Table 3
Rhodium complexes

| Rhodium complexes | Synthesis references | Yield | Volatility | Deposit quality |
|---|---|---|---|---|
| $Rh(\eta^3\text{-allyl})_2(acac)$ | [109] | *** | — | — |
| $Rh(\eta^3\text{-methyl-2-allyl})_2(acac)$ | [109] | **** | — | — |
| $[Rh(\eta^1\text{-allyl})(\eta^3\text{-allyl})(Cp)]$ | [109] | *** | Evapor. 130 °C, $10^{-2}$ Torr | — |
| $Rh(\eta^3\text{-allyl})_3$ | [109] | **** | VP: 6 Torr, 100 °C | *** |
| $Rh(\text{methyl-2-allyl})_2(Cp)$ | [109] | *** | Evapor. 40 °C, $10^{-2}$ Torr | — |
| $Rh(\eta^3\text{-allyl})(CO)_2$ | [110] | — | Sublim. 50 °C, $10^{-2}$ Torr | *** |
| $Rh(acac)_3$ | [111] | **** | Sublim. 240 °C, 1 Torr | — |
| $Rh(acac)(CO)_2$ | [112] | **** | VP: 1.7 Torr, 100 °C | ** |
| $Rh(thd)(CO)_2$ | [112] | — | — | ** |
| $Rh(tfacac)(CO)_2$ | [112] | **** | — | NRV [113] |
| $Rh(hfacac)(CO)_2$ | [112] | — | — | *** |
| $Rh(acac)(COD)$ | [114] | — | — | — |
| $Rh(hfacac)(COD)$ | [112] | — | — | Patented [21] |
| $Rh(tfacac)_3$ | [115] | ** | | |
| $Rh(Cp)(COD)$ | [116] | — | — | *** |
| $Rh(Cp)(C_2H_4)_2$ | [88] | ** | Sublim. 50 °C, 1 Torr | **** LACVD |
| $Rh(Cp)(C_2H_4)(PMe_3)$ | [117] | *** | — | — |
| $Rh(Cp)(CO)_2$ | [118,119] | **** | — | ** |
| $Rh(Cp)(CCF_3)_6$ | [120] | ** | Sublim. 100 °C, vaccum | — |
| $Rh(Cp)(CO(CCF_3)_4)$ | [120] | ** | Sublim. 80 °C, vaccum | — |
| $Rh(Cp^*)(CO)_2$ | [121] | *** | Sublim. 40 °C, $10^{-3}$ Torr | — |
| $Rh(Cp)(PF_3)_2$ | [122] | *** | Sublim. 25 °C, $10^{-3}$ Torr | — |
| $[RhCl(CO)_2]_2$ | [123–125] | **** | VP: 2.7 Torr, 100 °C | *** |
| $[RhCl(PF_3)_2]_2$ | [122,126] | **** | VP: $5\times10^{-3}$ Torr, 100 °C | NRV [16] |

of allyl chloride with small amounts of water [127]. In this paper, Powell and Shaw reported the synthesis of the two volatile complexes Rh($\eta^3$-allyl)$_2$(acac) and Rh($\eta^3$-methyl-2-allyl)$_2$(acac) by reacting Tl(acac) on Rh$_2$($\mu$-Cl)$_2$($\eta^3$-allyl)$_4$ and Rh$_2$($\mu$-Cl)$_2$($\eta^3$-methyl-2-allyl)$_4$, respectively [127]. The use of TlCp led to Rh($\eta^1$-allyl)($\eta^3$-allyl)(Cp).

The same authors described the preparation of Rh($\eta^3$-allyl)$_3$ as a volatile pale yellow solid by reacting Rh$_2$($\mu$-Cl)$_2$($\eta^3$-allyl)$_4$ with allyl magnesium chloride [128]. Full details of these syntheses were given in Ref. [109]. Thus, Rh($\eta^3$-allyl)$_2$(acac) was obtained with a 63% yield after sublimation at 35 °C and $10^{-2}$ Torr. The yield for Rh($\eta^3$-methyl-2-allyl)$_2$(acac) was 77%. Rh($\eta^3$-allyl)$_3$ was purified by sublimation at 40 °C and $10^{-2}$ Torr with an 85% yield. Concerning Rh($\eta^1$-allyl)($\eta^3$-allyl)(Cp), it is interesting to note that it is a liquid which vaporises at $10^{-2}$ Torr: its yield was 55%. Similarly, Rh($\eta^1$-methyl-2-allyl)($\eta^3$-methyl-2-allyl)(Cp) is a liquid whose boiling point at $10^{-2}$ Torr is 40 °C (yield 53%).

The direct addition of allyl magnesium chloride to Rh$_2$($\mu$-Cl)$_2$(CO)$_4$ was shown by O'Brien to lead to the air-sensitive volatile complex Rh($\eta^3$-allyl)$_3$(CO)$_2$ [110].

Many rhodium deposition studies were carried out from Rh(allyl)$_3$. Smith et al. adsorbed this complex onto a clean hydroxylated TiO$_2$ surface and showed that one allyl ligand was removed with a hydrogen atom of an OH group to anchor the rhodium complex to the surface. Addition of hydrogen led to Rh(H)($\eta^3$-allyl)(O–Ti surface) which exhibited a catalytic activity for hydrogenation of alkenes and arenes [129]. Pyrolysis of Rh($\eta^3$-allyl)$_3$ at 125 °C was shown by Kaesz et al. to produce rhodium films on glass beads of high quality, containing only 2% oxygen as impurity after elimination of the surface contaminants [63,130]. Rhodium films on glass substrates containing 14% residual carbon were obtained by decomposition of Rh($\eta^3$-allyl)$_3$ at 250 °C in vacuum [131,132]. The addition of hydrogen at the same temperature did not reduce this contamination. However, using a hydrogen plasma reduced the carbon incorporation to 2% (w/w). Similar results were obtained by Kumar and Puddephatt for deposition on silicon wafers carried out at 270 °C in the absence of hydrogen; nevertheless, with H$_2$ the purity of the deposit was significantly increased to 98% (w/w) at 270 °C [133]. Mild conditions were used by Kalck and coworkers to deposit rhodium on glass substrates at 60 °C, 100 Torr and with a carrier gas (10% H$_2$/He) [134]. The resulting rhodium films contained 7% (w/w) of carbon. Mass spectrometry analyses of the organic products in the gas phase revealed the presence of propane and propene. The curve of saturated vapor pressure of Rh($\eta^3$-allyl)$_3$ versus temperature has been published [68,134].

Rh($\eta^3$-allyl)(CO)$_2$ is the other compound of this group which has been studied for the CVD of rhodium. Whereas at 270 °C at $10^{-3}$ Torr a substantial contamination of the rhodium deposit was observed (C: 40%; O: 12%), the addition of hydrogen (270 °C and $10^{-3}$ Torr) reduced the contamination to only 4% in carbon [133].

In our opinion, the two complexes Rh($\eta^1$-allyl)($\eta^3$-allyl)(Cp) and Rh($\eta^1$-methyl-2-allyl)($\eta^3$-methyl-2-allyl)(Cp) have the potential to be good candidates for CVD since they are liquid under ambient conditions, but the yield in their syntheses is only moderate (~50%). Rh($\eta^3$-methyl-2-allyl)$_2$(acac) which can be prepared with high yields is also interesting to consider.

### 4.2. Rhodium complexes with β-diketonato ligands

The Rh($\eta^3$-allyl)(β-diketonato) complexes were described in the previous section. Rh(acac)$_3$, the first β-diketonato rhodium complex, was synthesized in 1953 [111]. It was obtained with a 75% yield by the reaction of acetylacetone on Rh(NO$_3$)$_3$ in an acidic medium. Its volatility is rather low (it sublimes at 240 °C under 1 Torr) and it was reported to decompose above 280 °C.

In 1964 Bonati and Wilkinson described the syntheses of four volatile complexes, i.e. Rh(acac)(CO)$_2$, Rh(Hfacac)(CO)$_2$, Rh(thd)(CO)$_2$ and Rh(hfacac)(COD), where the thd ligand is tetramethyl-3,5-heptanedionato [112].

Rh(acac)(CO)$_2$ was obtained in a yield better than 90% when Rh$_2$(μ-Cl)$_2$(CO)$_4$ was reacted for one week with acetylacetone in the presence of BaCO$_3$. The product was purified by sublimation under vacuum at 90 °C, although a slight decomposition occurred. With the same procedure the yield for Rh(tfacac)(CO)$_2$ was 94%, but no yield was quoted for Rh(hfacac)(CO)$_2$. These latter two complexes are more volatile than Rh(acac)(CO)$_2$ and were sublimed at 70 °C under vacuum.

Rh(acac)(COD) was prepared by Chatt and Venanzi [114], and was later reported to be a volatile compound by Igumenov [89].

A general pathway for the synthesis of the Rh(β-diketonato)(COD) complexes from Rh(β-diketonato)(CO)$_2$ complexes and cyclooctadiene was described by Bonati and Wilkinson [112].

The kinetics of such reactions have been studied by Grobler and coworkers [135]. The authors described the complexes Rh(tfacac)(COD), Rh(hfacac)(COD), Rh(DBM)(COD), Rh(TFBA)(COD) and Rh(BA)(COD) (where DBM is dibenzolylmethane, TFBA is trifluorobenzoylacetone, and BA is benzoylacetone) without any indication of their volatility, except for that of Rh(hfacac)(COD) [135].

Rh(tfacac)$_3$ was obtained in 1963 by Fay and Piper with a 50% yield from Rh(NO$_3$)$_3$ treated with trifluoroacetylacetone in acidic conditions [115].

Among the previously mentioned compounds, Rh(acac)(CO)$_2$ has been the most commonly used for CVD experiments. Rhodium deposits on TiO$_2$, realized by the pyrolysis of Rh(acac)(CO)$_2$ at temperatures between 200 and 500 °C in the absence of a reactive gas, were contaminated by carbon and oxygen [136]. Later, more detailed studies concerning this compound were conducted [137]. Under a pressure of 100 Torr, decomposition occurred at 100 °C in the presence of hydrogen, the resulting thin films containing carbon impurities (14 wt%). The Clausius–Clapeyron relationship of Rh(acac)(CO)$_2$ has been reported [68,137]. Rh(acac)(CO)$_2$ was also used by Etspuler and Suhr in plasma-assisted CVD to produce thin films of rhodium [138].

Suhr and coworkers have studied the three precursors Rh(acac)(CO)$_2$, Rh(dpm)(CO)$_2$ and Rh(hfacac)(CO)$_2$ using the laser-induced CVD method [139]. The authors showed that the most volatile precursor, i.e. Rh(hfacac)(CO)$_2$, led to the most satisfactory results and, at room temperature, deposits of high quality were obtained [139,140].

The complex Rh(tfacac)$_3$ was shown by van Hemert et al. to sublime at 110 °C under atmospheric pressure and to be decomposed at 250 °C in the presence of hydrogen. Under these conditions, the trifluoroacetylacetonato ligands were hydrogenated to trifluoroacetylacetone [113].

Finally, the chemical deposition of rhodium from Rh(hfacac)(COD) was patented recently [141].

### 4.3. ($\eta^5$-Cyclopentadienyl) rhodium complexes

The complexes Rh($\eta^1$-allyl)($\eta^3$-allyl)(Cp) and [Rh($\eta^1$-methyl-2-allyl)($\eta^3$-methyl-2-allyl)(Cp)] were described in Section 4.1.

The first synthesized Rh(Cp) complex, Rh(Cp)(COD), was prepared by Chatt and Venanzi in 1956 by the direct reaction of sodium cyclopentadienide with $Rh_2(\mu\text{-Cl})_2(COD)_2$ [116].

A similar procedure was used by King in 1963 to obtain $Rh(Cp)(C_2H_4)_2$ from $Rh_2(\mu\text{-Cl})_2(C_2H_4)_4$ with a 45% yield [88]. The resulting compound sublimes above 50 °C at 1 Torr.

A general procedure to synthesize 16 new Rh(Cp)(diene) complexes was given in 1973 by Nelson et al., in which purification involved a sublimation or a distillation step at 100 °C and 0.2 Torr [142].

$Rh(Cp)(C_2H_4)(PMe_3)$ was obtained by Werner and Feser with a 70% yield by treatment of $Rh_2(\mu\text{-Cl})_2(C_2H_4)_4$ with TlCp and $PMe_3$ [117]. Its volatility was mentioned later by Igumenov [89].

The $Rh(Cp)(CO)_2$ complex was also prepared in 1961 by Fisher and coworkers, who reacted $Rh_2(\mu\text{-Cl})_2(CO)_4$ with NaCp [118,119]. This carbonyl compound is an orange liquid under ambient conditions and can be prepared in greater than 90% yield [143].

Two volatile complexes, $Rh(Cp)\{(CCF_3)_6\}$ and $Rh(Cp)\{CO(CCF_3)_4\}$ (yields 48 and 45%, respectively) were shown by Dickson and Wilkinson to result from the reaction of hexafluorobut-2-yne with $Rh(Cp)(CO)_2$ [120]. The first complex, containing the ligand hexakis(trifluoromethyl)hexadiene, is a yellow air-stable solid which sublimes under vacuum at around 100 °C. The second, which contains the ligand tetrakis(trifluoromethyl)cyclopentenone, is an orange air-stable solid which sublimes at 80 °C under vacuum.

Concerning the use of the pentamethylcyclopentadienyl ligand, Kang and Maitlis have prepared $Rh(Cp^*)(CO)_2$ in a 56% yield by bubbling carbon monoxide through a methanol solution of $[RhCl_2(Cp^*)]_2$ containing a suspension of zinc powder [121]. The resulting complex was purified by sublimation at 30–40 °C under $10^{-3}$ Torr.

Treatment of $Rh_2(\mu\text{-Cl})_2(PF_3)_4$ by TlCp led to the orange–red liquid complex $Rh(Cp)(PF_3)_2$ with a 58% yield as reported by Bennett and Patmore [122]. Its purification was carried out at 25 °C under $10^{-3}$ Torr on a $-80$ °C probe.

Kumar and Puddephatt studied the CVD of rhodium films from the two precursors Rh(Cp)(COD) and $Rh(Cp)(CO)_2$ [133]. The first complex decomposed at 270 °C under $10^{-3}$ Torr in the absence of reactive gas, but 20 at% contamination of carbon was observed. CVD experiments performed at 230 °C with hydrogen reduced this contamination to 3%. Studies of the gas phase during deposition did not allow a clear identification of the gaseous species resulting from the pyrolysis of the complexes [133]. Regardless of the presence or otherwise of hydrogen, $Rh(Cp)(CO)_2$ decomposed at 180 °C under $10^{-3}$ Torr, but contamination by heteroelements was substantial (5 at% oxygen in both cases, 20 at% C without hydrogen and 7% otherwise). Pyrolysis of $Rh(Cp)(CO)_2$ led to the loss of CO and the formation of dimeric and trimeric rhodium complexes.

$Rh(Cp)(C_2H_4)_2$ was examined by Zink and coworkers in laser-enhanced CVD experiments [144]. Particularly interesting is the observation of highly pure rhodium films ($<1$ at% C contamination) obtained under ambient conditions in the presence of hydrogen.

Surprisingly, most of the complexes of this group have not been studied for CVD applications. Many studies could be performed on these Rh(Cp) complexes to reach a level of knowledge similar to that of platinum or palladium chemical vapor deposition.

### 4.4. *Dimeric volatile rhodium complexes*

As a singular feature of rhodium chemistry, two binuclear complexes bridged by two chloro ligands present interesting properties of volatility: $Rh_2(\mu\text{-}Cl)_2(CO)_4$ and $Rh_2(\mu\text{-}Cl)_2(PF_3)_4$. In the earliest days of coordination chemistry in 1925, $Rh_2(\mu\text{-}Cl)_2(CO)_4$ was reported by Manchot and König [145]. McCleverty and Wilkinson described in detail the synthesis of this compound (yield 96%) from $RhCl_3.3H_2O$ which was treated with CO at around 100 °C [123]. Other preparative methods have also been reported [124,125]. Bubbling $PF_3$ into pentane solutions of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ led to the air-stable, volatile binuclear complex $Rh_2(\mu\text{-}Cl)_2(PF_3)_4$ with an 88% yield [122,126].

Deposition of rhodium films from $Rh_2(\mu\text{-}Cl)_2(CO)_4$ was first carried out by Kumar and Puddephatt at 180 °C with a substantial contamination by carbon and oxygen. Use of hydrogen as the carrier gas significantly reduced the contamination of the films (7 at% C and 2 at% O).

More recently, Kalck and coworkers showed that this tetracarbonyl complex was a good precursor for the preparation of heterogeneous catalysts by CVD in a fluidized bed. Indeed, under 50 Torr and at 100 °C in the presence of $H_2$ rhodium deposits were obtained containing only 1.5% Cl [146]. CO and HCl were shown to be the two species produced in the gas phase. In addition, the curve of vapor pressure versus temperature was reported [68].

The volatility and pyrolysis conditions of $Rh_2(\mu\text{-}Cl)_2(PF_3)_4$ suggest the possibility of CVD applications, since at 150 °C this complex begins to decompose with the release of $PF_3$. The vapor pressure of this compound has also been measured as a function of temperature. Nevertheless, no report has appeared to date on the deposits or the characterization of films resulting from the decomposition of the complex.

### 4.5. Conclusion on the rhodium complexes

From a general point of view, the classical deposition experiments carried out on rhodium complexes lead to deposits less pure than those obtained for palladium and platinum. Some promising results have been observed by chemical vapor deposition assisted by laser or by plasma, but it generally appears that it would be fruitful to explore the use of reactive gases, in order to cleanly remove the organic ligands attached to the metal.

## 5. General conclusion

Considering that the chemical vapor deposition method is a key process for many applications involving noble metal deposition on various substrates, the literature analysis reveals that, in fact, there are few rhodium, palladium or platinum complexes which meet the requirements of high volatility and easy and high-yield preparation, which could permit their industrial utilization. Moreover, the organic fragments or, generally speaking, the ligands need to be removed to ensure no contamination remains on the metal. All the published results show that it is convenient to assist the deposition by introducing a reactive gas or by the use of a laser beam or of a cold plasma, so that the deposits contain lower amounts of contaminants and the deposition temperature is also significantly decreased. To this end, the main goal to aim for is to avoid breaking the ligand internal bonds, which lead to pollutant incorporation in the deposit. Thus, in parallel with the synthesis of new precursors, the study of novel reactive gases (other than hydrogen, oxygen or water vapor) and even the conception of novel procedures (dismutation of complexes for instance) to compete with the ligand pyrolysis are important challenges for researchers in this field.

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