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Synthesis and Characterization of Methylcyclopentadienyl-(η^3-allyl)platinum and its use as a Metallo-organic Chemical Vapour Deposition Precursor of Platinum

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This communication reports on rapid, efficient synthesis of the metal-organic chemical vapor deposition (MOCVD) precursor (methylcyclopentadienyl)allylplatinum. The compound is shown to be an effective precursor for the deposition of platinum thin films giving deposits of high quality and purity, probably due to the nature of ligands which seems to be good leaving groups as confirmed by mass spectrometric pathway. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

The deposition of metallic platinum thin films via MOCVD (metal organic chemical vapour deposition) has attracted interest for more than two decades for its applications in several fields, mainly in electronics.[1–5] However the films are generally affected by significant contamination, not only from adventitious impurities (e.g. oxygen) but also from intrinsic ones, i.e. atoms present in the precursor molecule which cannot be completely removed as part of easily eliminable gaseous side products. Thus in addition to the ubiquitous presence of carbon, phosphorus and oxygen have also been detected in the films when $Pt(PF_3)_4$ and $[C_3H_7O_2PtMe_3]_2$ have been used as precursors.[6,7] For the MOCVD growth of pure deposits of platinum, good leaving groups, lower deposition temperatures and the presence of hydrogen as reactant gas, appear to be favourable conditions. Examples are platinum complexes containing simple or substituted allyl and cyclopentadienyl ligands.[4,6] Here we report the synthesis, characterization and behaviour of methyl-substituted cyclopentadienylallylplatinum $[(C_5H_4CH_3)Pt(\eta^3\text{-}C_3H_5)]$ as a new precursor in platinum thin-film deposition.

EXPERIMENTAL

All manipulations were carried out using high-vacuum line and Schlenk techniques or dry-boxes filled with purified nitrogen. Methylcyclopentadienylthallium was prepared by adding freshly distilled methylcyclopentadiene (0.5 ml, 9.37 mmol) to a suspension of TlOEt (1.4 ml, 9.37 mmol) in 50 ml of purified n-hexane. A beige precipitate formed immediately. After 1 h of stirring it was filtered and washed with n-hexane. Methylcyclopentadienylthallium was identified by elemental analysis. Allylplatinum chloride was synthesized according to the literature procedure.[8]

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The solvents used (n-hexane and diethyl ether) were distilled under nitrogen from a potassium-benzophenone mixture. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 instrument, using anhydrous C_7D_8 as solvent.

Electron ionization (EI) (70 eV, 200 μA) mass spectra were obtained using a VG (Manchester, UK) ZAB 2F[9] mass spectrometer. The sample was introduced directly into the ion source, which was heated to 180 °C. The probe temperature was 50 °C. High-energy collision mass-analysed ion kinetic energy of (MIKE)[10] spectra were obtained by colliding the preselected species with nitrogen in the second field-free region. The pressure in the collision chamber was such as to reduce the main beam intensity to 60% of its usual value.

The small-area X-ray photoelectron spectroscopy (SA-XPS) study was carried out on an Escalab MkII spectrometer using Al $K_{1,2}$ radiation as excitation source ($h\nu = 1486.6$ eV). The hemispherical electron analyser was operating in fixed analyser transmission mode (FAT) by selecting a constant pass energy of 20 eV throughout all measurements. Under these conditions, the full width at half maximum (FWHM) of argon-ion-cleaned Ag $3d_{5/2}$ and Au $4f_{7/2}$ lines was 1.0 eV. The analysis area was about 1 mm in diameter. All measurements were performed at pressures of 5×10^{-10} mbar in the analysis chamber. Binding energies (BE) were referenced to the Fermi level of the analyser and confidence in the linearity of BE scale was based upon setting the position of Au $4f_{7/2}$, Cu $L_3M_{45}M_{45}$ and Cu $2p_{3/2}$ peaks at 83.8 eV, 567.8 eV and 932.5 eV, respectively. Corrections for the energy shift, due to the steady-state charging effect, were accomplished by assuming the C 1*s* line, resulting from the ubiquitous surface layer of adsorbed hydrocarbons, to lie at 284.6 eV. Reproducibility in the results was ± 0.15 eV. This value was also the estimated uncertainty in BE locations.

Elemental concentration depth profiles were obtained by alternating 25 sequences of SA-XPS measurements with argon-ion etching. Argon-ion sputtering was performed using a scanning argon-ion gun operated at a pressure of 5×10^{-6} mbar and at 2 keV, thus producing an ion current density of about 50 μA cm^{-2} as measured using a Faraday cup near the target surface. The ion incidence angle was 30 ° from the normal to the sample surface. Scanning electron microscopy (SEM) characterization was performed with a Cambridge 360 scanning electron microscope equipped with a LaB_6 filament.

Synthesis of (methylcyclopentadienyl) (η^3-allyl)platinum complex

[($C_5H_4CH_3Pt$ (η^3-C_3H_5)] can be obtained easily by the reaction represented by Eqn 1.

$$\frac{1}{4}[(CH_2CHCH_2)PtCl]_4 + (C_5H_4CH_3)Tl \longrightarrow$$
$$[(C_5H_4CH_3)Pt(\eta^3 - C_3H_5)] + TlCl$$

Methylcyclopentadienylthallium (0.26 g, 0.92 mmol) was added to a stirred solution of allylplatinum chloride (1.0 g, 3.68 mmol) in diethyl ether. After 20 h of stirring at room temperature, the brown solution was filtered and the solvent was removed under vacuum giving a dark red oily liquid product. ^1H NMR at 0 °C: $\delta = 2.11$ (d, 2H, $^3J_{H_aH_c} = 9.54$ Hz), 2.16 (s, 3 H), 3.56 (d, 2H, $^3J_{H_sH_c} = 10.0$ Hz), 3.98 (m, ^1H, $^2J_{HPt} = 52.03$ Hz), 5.55 (m, 2H), 5.65 ppm (m, 2H). ^{13}C NMR: $\delta = 15.1$, 27.7, 71.4, 88.9, 93.6, 109.5 ppm. IR (KBr discs): 2940 (s), 2920 (vs), 2852 (s), 1683 (w), 1615 (w), 1455 (m), 1376 (w), 1260 (w), 1020 (s), 793 (*s*) cm^{-1}.

MOCVD procedure

The reactor was composed of a glass tube 100 cm long (i.d. = 3 cm) disposed inside a furnace. The precursor was put in a small crucible which was located at the entrance of the reactor and heated at 30 °C by a heating tape, controlling its temperature with a thermocouple. The reactor worked up under a low-pressure regime and used a closed-end stipe. The reaction chamber was connected, through a liquid-nitrogen trap, with a vacuum pump. The carrier gas (nitrogen) flux was measured and controlled with a mass flow controller and the pressure was measured with a capacitance manometer. The

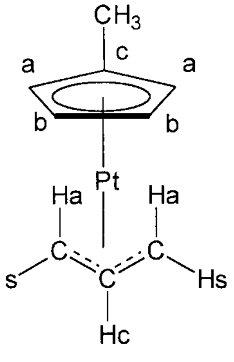
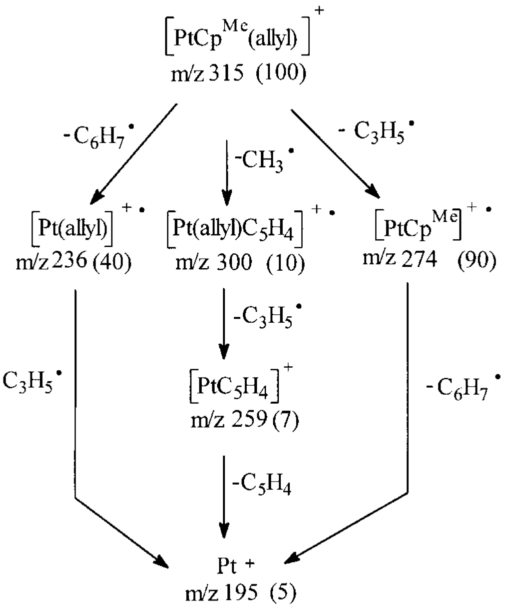


Figure 1 Methylcyclopentadienylallylplatinum complex.



Scheme 1 Fragmentation pattern of EI-induced M^+ species of the methylcyclopentadienylallylplatinum compound; *m/z* (relative abundance) values correspond to ionic species containing ^{195}Pt.

liquid-nitrogen-cooled trap attached to the reactor exhaust condensed by-products of the deposition. The surface of the glass substrates was cleaned by washing with hot dichloromethane and rinsed, several times, with distilled water. At the end of each deposition experiment, heating of the crucible containing the precursor was stopped, and the temperature of the substrate was decreased gradually with the nitrogen flow rate mantained until the substrate had reached room temperature.

RESULTS AND DISCUSSION

Methylcyclopentadienylallylplatinum is an oily substance at room temperature, moderately sensitive to the normal atmosphere. Its ^{1}H NMR spectra have been recorded in the −70 °C to 25 °C temperature range. At 0 °C the allyl group shows a multiplet centred at 3.98 ppm ($^2J_{H_cPt} = 52.03$ Hz) for the central proton Hc and a doublet at 2.11 ppm ($^3J_{H_aH_c} = 9.54$ Hz) flanked by ^{195}Pt satellites ($^2J_{H_aPt} = 108.5$ Hz) for the *anti* protons, while the signal for the *syn* protons appears as a doublet at 3.56 ppm ($^3J_{H_sH_c} = 10.0$ Hz) flanked by ^{195}Pt satellites ($^2J_{H_sPt} = 60.0$ Hz). The methylcyclopentadienyl system gives rise to two complex multiplets at 5.55 and 5.65 ppm which can be ascribed to the H_a and H_b protons of the ring. The protons of CH_3 appear as a singlet at 2.16 ppm with ^{195}Pt coupling ($J_{HPt} = 4.58$ Hz). The ^{1}H NMR spectrum does not vary in the −70 °C to 25 °C temperature range, thus

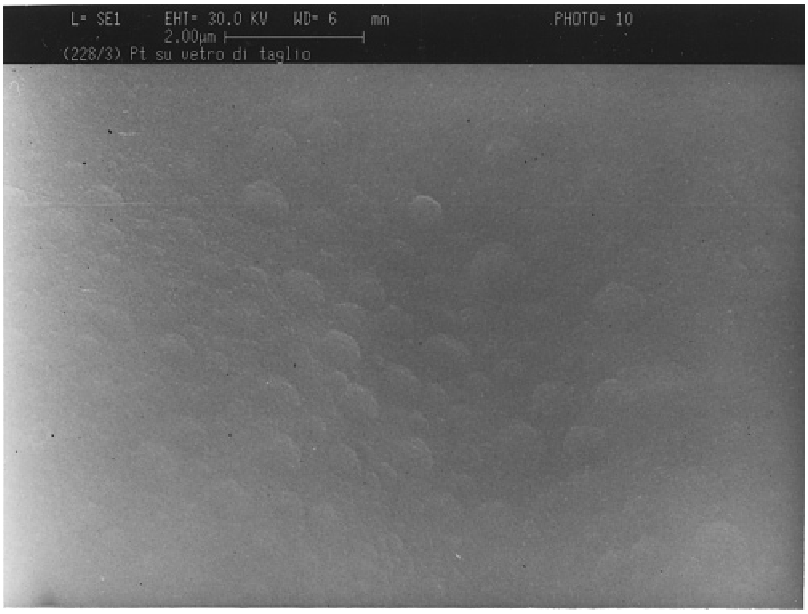


Figure 2 SEM micrograph of the morphology of platinum deposited on glass.

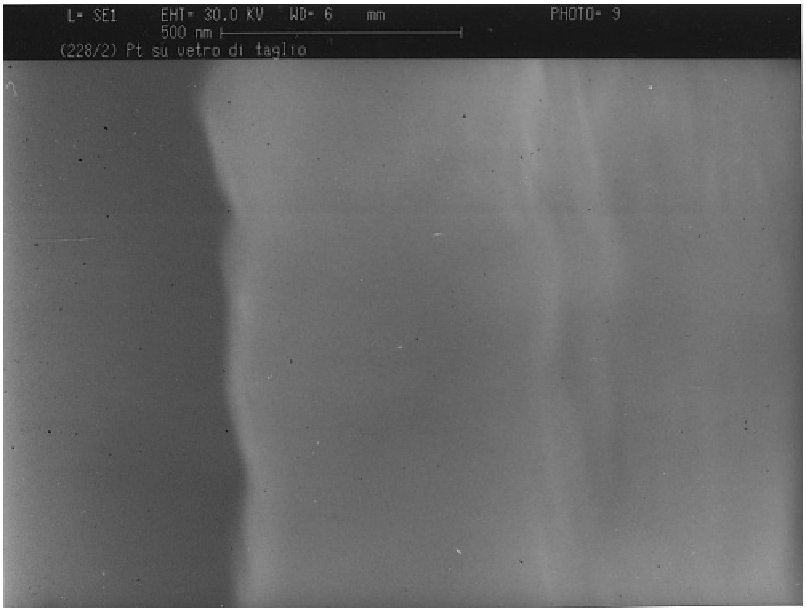


Figure 3 SEM micrograph of a cross-section of a platinum film on glass.

indicating a rapid exchange of the environment of these groups under these conditions. The ^{13}C NMR (50.323 MHz) spectrum of the complex at 25 °C shows signals at 109.547 ppm for the C_c atom, and at 93.62 ppm (J_{PtC_a} = 33.0 Hz) and 88.99 ppm (J_{PtC_b} = 48.4 Hz) for the C_a and C_b atoms respectively. The carbon signal of the methyl group appears at 15.15 ppm. The allyl group gives rise to a singlet at 27.71 ppm (J_{C_aH} = 385.1 Hz) for the two lateral C_a atoms and at 71.36 ppm for the central C_b atom (J_{C_bPt} = 77.0 Hz). The above values compare well with those reported in the literature for related compounds.[2,8] Thus η^3 and η^5 modes of bonding for the allyl (CH_2CHCH_2) and methylcyclopentadienyl (MeCp) groups can be unequivocally proposed to be as shown in Figure 1.

The compound is characterized by an appreciable volatility and its EI mass spectrum shows the molecular species M^+ as the most abundant peak at *m*/*z* 315; MIKE experiments performed on the M^+ ion have allowed the identification of three fragmentation patterns as reported in scheme 1.

It is interesting that the various fragment ions are generated by ligand losses rather than by ligand fragmentation reactions; evidently, methylcyclopentadienyl and allyl act as easily as leaving groups they as do as radical species.

MOCVD experiments have been carried out at 300 °C under a low-pressure nitrogen regime (20 mbar). The material was deposited on Pyrex glass substrate by evaporating the precursor in a stream of nitrogen from a crucible maintained at 30 °C, with carrier gas flow of 50 ml min^{-1}. The films obtained were bright and reflective and the deposition rate was 0.8–1 μm h^{-1}.

The films studied by SEM presented smooth surfaces and even at high magnification (10000×) no defects or voids were observed. A SEM micrograph (Fig. 2) shows the typical micromor-

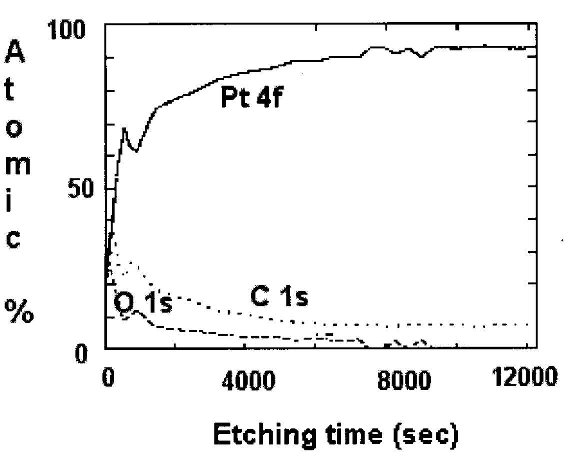


Figure 4 XPS depth profiles of a platinum deposit.

phology of the platinum deposits on glass. The film thickness is about 600 mm as shown in Fig. 3, where a section of a platinum film is shown in a SEM micrograph.

An X-ray powder diffraction spectrum of the deposits obtained had narrow peaks, probably as a consequence of high polycrystallinity of the material. The positions of the peaks corresponded to the Pt(111), Pt(200), Pt(220), Pt(311) and Pt(222) reflections. Their intensities were comparable, except that for Pt(222) which was far lower. Our films showed the same reflections observed by Kaesz *et al.*, [1b] except for the intensity of the (220) and (311) reflection patterns, which were lower. Thus it may be concluded that in our case also the films tended to be deposited without any preferred orientation and that the difference between our intensities and the intensities found by Kaesz *et al.* may depend on the different deposition mechanisms. The XPS spectrum shows the peaks of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ at 70.8 eV (±0.15) and 74.1 eV (±0.15) respectively, as expected for metallic platinum. The spectrum also shows the presence of carbon (30%) and oxygen (10%) as surface impurities, which probably arise from subsequent exposure of the film to the atmosphere rather than from the MOCVD process itself. Upon sintering, carbon and oxygen percentages decrease very rapidly with sputter depth (Fig. 4) and, at about 40 nm, oxygen disappears while carbon is reduced below 2%. Moreover, the peaks in the C1*s* binding energy region indicate that surface carbon is present as C═O and C—OH groups, whereas in the film it is present as C—C and C—H, presumably due to incomplete desorption of the ligands. No other impurities have been detected. In conclusion methylcyclopentadienylallylplatinum appears to be a suitable precursor for the deposition of good-quality platinum metal via MOCVD. In this context it must be pointed out that carbon contamination of our platinum deposited in a nitrogen atmosphere is comparable with or lower than previously deposited platinum using hydrogen carrier gas, this therefore represents a good improvement from the economic and safety point of view.

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