Chem. Mater. 1993, 5, 891-897

A New Cross-Linkable Palladium(0) Complex and Its Use for Electroless Metalization of Epoxy Resins

Bernd Tieke† and Sheik A. Zahir*

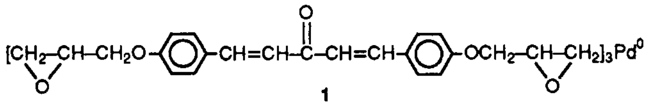
CIBA, Polymers Division PO 7.5, CH-4002 Basle, Switzerland

Received November 24, 1992. Revised Manuscript Received February 23, 1993

A new cross-linkable palladium complex, tris(4,4′-(2,3-epoxypropoxy)dibenzylideneacetone)-palladium(0) (1), has been prepared. Complex 1 is stable under ambient conditions but is rapidly decomposed at temperatures above 150 °C with formation of free ligand molecules and small palladium particles. Mixtures of 1 with the diglycidyl ether of bisphenol A (DGEBA) can be cured with various epoxy hardeners such as hexahydrophthalic anhydride (HHPA) of 4,4′-diaminodiphenylmethane (MDA) to yield three-dimensional polymer networks. Cured resins containing up to about 25 wt % of 1 have been prepared. Presence of 1 in the resins has no effect on mechanical strength, electrical, and thermal conductivity, but thermal stability and chemical properties are strongly changed. Upon annealing above 150 °C, the complex is decomposed and a fine dispersion of zerovalent palladium microparticles of 5–20-nm diameter is obtained in the resin matrix. The microparticles show a high catalytic activity. They catalyze, for example, the electroless nickel and copper plating of the resin surface. Dipping of the thermally activated resins into a commercial plating bath leads to rapid growth of a well adhering nickel or copper coating. Prolonged annealing of HHPA-cured resins in air at high temperatures (i.e., above 200 °C) leads to formation of a 100 nm thick, electrically conducting (>10 S cm^{-1}) palladium deposit on the resin surface and finally to a very rough surface containing large isolated palladium particles. Thermal effects are due to a palladium catalyzed decomposition of the organic matrix at the air-exposed surface.

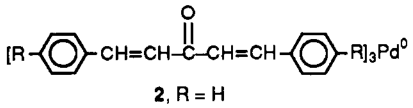
1. Introduction

The formation of finely dispersed metallic microparticles in a host matrix has recently become of great interest because of unusual physical properties and high catalytic activity. Most methods of production involve a chemical or electrochemical reduction of a metal salt in aqueous solution.[1] However, also high-energy radiation of metal salts was used[2] or photochemical,[3,4] photothermal,[3] and thermal decomposition of metal complexes.[5] In our paper we report on the preparation of finely dispersed metallic microparticles in a three-dimensional polymer network by thermal decomposition of the novel tris(4,4′-(2,3-epoxypropoxy)dibenzylideneacetone)palladium(0) complex (1). This complex represents a hexafunctional monomer, which can be cross-linked with various epoxide curing agents and thereby becomes a part of the resulting three-dimensional network.



1

From previous studies it is known that dibenzylideneacetone and some of its derivatives are able to form complexes with palladium and platinum in different stoichiometries,[6] as for example complex 2 with R being H.[7] These complexes have found considerable attraction, e.g. as homogeneous catalysts for hydrogenation[8] and cyclic oligomerization of organic compounds,[9] or production of hydrogen peroxide from the elements.[10] In addition, they are known as carriers for zerovalent palladium, which can be easily set free from the complex by thermal treatment at elevated temperatures.[11] As recently demonstrated,[12]



2, R = H
3, R = i-Pr

---

† New address: Universität zu Köln, Institut für Physikalische Chemie, Luxemburger Str. 116, D-5000 Köln 41, FRG.

* To whom correspondence should be addressed.

(1) (a) Harrison, D. J.; Wrighton, M. S. *J. Phys. Chem.* **1984**, *88*, 3932. (b) Mittal, K. L. *J. Vac. Sci. Technol.* **1976**, *13*, 19. (c) Newkome, G. R.; Yoneda, A. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 77. (d) Hamaya, T.; Kumagai, Y.; Koshizaki, N.; Kanbe, T. *Chem. Lett.* **1989**, 1461. (e) Tour, J. M.; Pendalwar, S. L.; Cooper, J. P. *Chem. Mater.* **1990**, *2*, 647. (f) De Oliveira, I. M. F.; Moutet, J.-C.; Hamar-Thibault, S. *J. Mater. Chem.* **1992**, *2*, 167.

(2) Henglein, A. *Pure Appl. Chem.* **1984**, *56*, 1215.

(3) Krasnansky, R.; Yamamura, S.; Thomas, J. K.; Dellaguardia, R. *Langmuir* **1991**, *7*, 2881.

(4) Eisch, J. J.; Boleslawski, M. P. U.S. Patent 5,063,083 (1991).

(5) (a) Cardenas-Trivino, G.; Klabunde, K. J.; Brock Dale, E. *Langmuir* **1987**, *3*, 986. (b) Rancourt, J. D.; Parta, G. M.; Moyer, E. S.; Madeleine, D. G.; Taylor, L. T. *J. Mater. Res.* **1988**, *3*, 996. (c) Furtsch, T. A.; Taylor, L. T.; Fritz, T. W.; Fortner, G.; Khor, E. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1287. (d) Furtsch, T. A.; Finklea, H. O.; Taylor, L. T. In *Polyimides*; Mittal, K. L., Ed.; Plenum Press: New York, 1984; Vol. 2, pp 1157ff.

(6) (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065. (b) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 982.

(7) Mazza, M. C.; Pierpont, C. G. *Inorg. Chem.* **1973**, *12*, 2955.

(8) Laurer, P. R.; Schulz, G.; Wunsch, G.; Müller, F.-J.; Steck, W.; Irgang, M. Ger. Offen. 2,426,879, 1976; BASF AG; *Chem. Abstr.* **1976**, *84*, 112305.

(9) (a) Binger, P.; Biedenbach, B. *Chem. Ber.* **1987**, *120*, 601. (b) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1604.

(10) Michaelson, R. C. U.S. Patent 4,347,232, 1982; FMC Corp.; *Chem. Abstr.* **1982**, *97*, 165497.

(11) (a) Wunsch, G.; Deigner, P.; Falk, R.; Mahler, K.; Loeser, W.; Domas, F.; Felleisen, P.; Steck, W. U.S. Patent 4,128,672, 1978; BASF AG; *Chem. Abstr.* **1979**, *90*, 80083. (b) Stabenow, J.; Wunsch, G.; Deigner, P.; Müller, F.-J.; Loeser, W.; Steck, W. Ger. Offen. 2,451,217, 1976; BASF AG; *Chem. Abstr.* **1976**, *85*, 111893. (c) B. Tieke, S. A. Zahir, J. Finter, U.S. Patent 4,756,848, 1988, CIBA.

0897-4756/93/2805-0891$04.00/0

palladium(0) complex **3**, with R being isopropyl, can be deposited on substrates by the Langmuir–Blodgett (LB) technique. Thermal annealing of the resulting LB films allows us to set free precisely controlled amounts of catalytically active, zerovalent palladium, which are able to catalyze electroless nickel plating of the substrate.

Our present paper is concerned with the cross-linkable complex **1** and epoxy resins prepared thereof. After briefly describing some characteristic properties of the complex such as solubility and thermal stability, we report on curing experiments with hexahydrophthalic anhydride (HHPA) and 4,4'-diaminodiphenylmethane (MDA) as hardeners and on mechanical and thermal properties of the resulting cured resins.

Moreover, the catalytic activity will be described. Upon annealing of the resins at temperatures above 150 °C, small metallic palladium particles are formed which catalyze electroless copper and nickel plating of the resin surface. If kept in air at sufficiently high temperatures (i.e., above 200 °C), they also catalyze the oxidative decomposition of the polymer network. Our studies were carried out using thermogravimetric analysis, electron microscopy and UV–visible spectroscopy. In addition, mechanical and electrical properties were determined. The effect of incorporated metal particles was studied in a comparative investigation of metal-containing and corresponding metal-free resins.

2. Experimental Part

Materials. Diglycidyl ether of bisphenol A (DGEBA), hexahydrophthalic anhydride (HHPA), and 4,4'-diaminodiphenylmethane (MDA) are commercial products from Ciba Geigy AG, Switzerland. The diglycidyl ether of 4,4'-dihydroxydibenzylideneacetone (DGDBA) was prepared in analogy to a procedure reported for the diglycidyl ether of 4,4'-dihydroxychalcone.[13,14] Benzyldimethylamine (BDMA) and palladium chloride were purchased from Fluka and used without further purification. Complexes **2** and **3** were prepared according to the literature.[6,7,10]

Preparation of Complex 1. With vigorous stirring, 15 g of $PdCl_2$ is boiled in a solution of 10.7 g of NaCl in 65 mL of water until the palladium chloride is completely dissolved. The water is then distilled off. The residue is taken up in 200 mL of methanol, and the solution is heated to 60 °C. DGDBA (105.9 g) and sodium acetate·$3H_2O$ (42.8 g) are added, followed by the addition of another 175 mL of methanol. After a further 15 min at 60 °C, the mixture is cooled. A precipitate forms which is isolated by filtration under argon and washed successively with 100 mL of methanol, three 100-mL portions of water, and two more 100-mL portions of methanol. The product is subsequently dried in vacuo at 50 °C. For the complete removal of the residual DGDBA, the crystals are suspended in 700 mL of methanol and then isolated by filtration under argon. Subsequent drying in vacuo affords violet crystals: yield 100.7 g (97.4%). The crystals decompose in the temperature range between 120 and 160 °C with a rate peak at 140 °C. Elemental analysis calcd for $C_{69}H_{66}O_{15}Pd$: C 66.75%, H 5.32%, Pd 8.58%. Found: C 66.06%, H 5.41%, Pd 7.90%.

Curing of Epoxy Resins: *Epoxy Resin 1* (*R-1*) composed of Pd complex **1**, DGEBA, and HHPA: With stirring, 18.6 g (25.1 wt %) of **1**, 25.7 g (34.8 wt %) of DGEBA, and 29.4 g (39.8 wt %) of HHPA are mixed in vacuo for 1 h at 90 °C. Then 0.22 g (0.3 wt %) of benzyl dimethylamine are added. After stirring for a further 5 min at 90 °C, the mixture is poured into a mould (size 150 × 150 × 2 mm) which has been preheated to 100 °C. The mixture is then cured for 4 h at 100 °C and for 4 h at 120 °C.

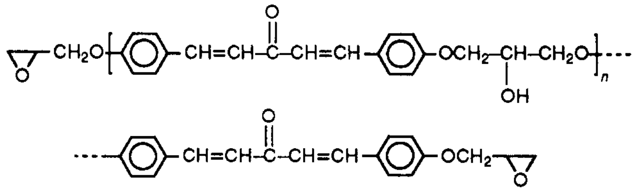
Epoxy resin 2 (*R-2*) composed of Pd complex **1**, DGEBA and MDA: With stirring, 20.7 g (25.2 wt %) of **1** and 44.8 g (54.6 wt %) of DGEBA are mixed in vacuo for 30 min at 90 °C. Then 16.6 g (20.2 wt %) of MDA are added and the mixture is stirred in vacuo for a further 10 min at 90 °C. The mixture is subsequently poured into a mould (size 150 × 150 × 2 mm) which has been preheated to 100 °C. The mixture is then cured for 4 h at 100 °C and 4 h at 120 °C.

Palladium-free epoxy resin 3 and 4 (*R-3 and R-4*) composed of DGDBA, DGEBA, and HHPA or DGDBA, DGEBA, and MDA, respectively, were prepared accordingly, except that the palladium complex **1** was replaced by an equivalent amount of DGDBA.

Methods. Differential scanning calorimetry (DSC) was carried out using a Mettler DSC-30 apparatus. The heating rate was 10 °C/min. Thermogravimetric analysis (TGA) was carried out using a Mettler TGA-50 apparatus. For isothermal weight loss measurements, 10-mg samples of powdered cured resin were heated to a chosen temperature at a rate of 10 K/min and then kept constant for 8 h. The film morphology was studied by transmission electron microscopy (TEM; Philips EM 300) and scanning electron microscopy (SEM; Cambridge Stereoscan S4-10). Cross sections were cut using an LKB Ultramicrotome III. UV–visible spectra were recorded using a Perkin-Elmer Lambda 7 spectrometer.

3. Results and Discussion

3.1. Characteristic Properties of Palladium Complex 1. Palladium complex **1** represents a hexafunctional monomer, which was prepared from the diglycidyl ether of 4,4'-dihydroxydibenzylideneacetone (DGDBA) and palladium chloride in analogy to a procedure previously reported for complex **3**.[10,12] From the elemental analysis the ligand-to-metal ratio could be determined to be approximately 3:1. Slight deviations from this ratio observed occasionally are probably due to the fact that the ligand compound actually represents a mixture of monomer, dimer, and trimer species, which are best represented by the common formula **4**, where *n* is 0, 1, or 2, respectively. This mixture could hardly be separated even after repeated recrystallization.[14] Previous studies on dibenzylideneacetone palladium complexes concentrated on a characterization of structure and electrochemistry using NMR spectroscopy,[15,16] cyclic voltammetry,[17] and X-ray scattering.[7,16,18] In the following, optical absorption and thermal properties of complex **1** and its nonpolymerizing analogues **2** and **3** are described more in detail.


4

Complexes **1** and **3** are well soluble in organic solvents such as benzene, toluene, tetrahydrofuran, or chlorinated hydrocarbons, whereas they are rapidly decomposed in strongly polar solvents such as alcohols or dimethylformamide. Complex **2** is only slightly soluble in most solvents. UV absorption spectra of **1**, **2**, and **3** are nearly identical.

---

[12] Tieke, B.; Zahir, S. A.; Mathieu, H. J. *Adv. Mater.* **1991**, *3*, 96.

[13] Panda, S. P. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1757.

[14] Zahir, S. A. *J. Appl. Polym. Sci.* **1979**, *23*, 1355.

[15] Keasey, A.; Mann, B. E.; Yates, A.; Maitlis, P. M. *J. Organomet. Chem.* **1978**, *152*, 117.

[16] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

[17] (a) Ito, N.; Aoyagui, S.; Saji, T. *J. Electroanal. Chem.* **1981**, *130*, 357. (b) Ito, N.; Saji, T.; Aoyagui, S. *J. Electroanal. Chem.* **1983**, *144*, 153.

[18] Pierpont, C. G.; Mazza, M. C. *Inorg. Chem.* **1974**, *13*, 1891.

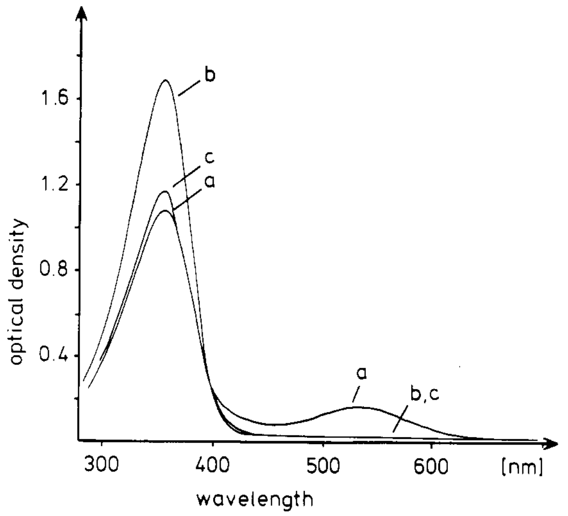


Figure 1. UV–visible absorption spectra of complex 1. 20 mg of the complex were annealed at different temperatures and subsequently the soluble part was extracted in toluene (1 L): (a) no heat treatment; (b) 2 h, 150 °C; (c) 2 h, 180 °C.

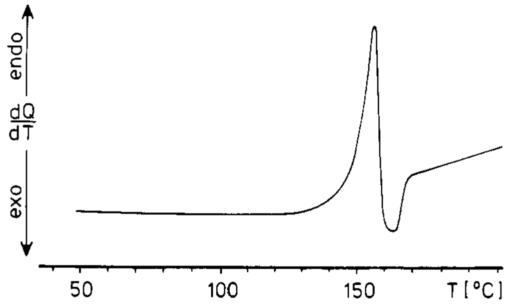


Figure 2. DSC diagram of complex 2 (heating rate 10 K/min).

In Figure 1, a UV spectrum of 1 in toluene is shown. Two absorption maxima occuring at 535 and 335 nm can be tentatively assigned to a d-π^* (metal–olefin bonding) transition and a n-π^* transition of the ligand.[6b] Solutions are completely stable upon UV or visible light irradiation. Neither in solution nor in the solid state were any indications found for a (2+2) cycloaddition and/or trans–cis isomerization of the olefinic bonds of the ligand molecules.

In Figure 2, a DSC trace of complex 2 is shown. As can be seen, the complex exhibits a sharp melting endotherm around 145 °C. Melting is immediately followed by rapid exothermal decomposition. As will be shown, free ligand molecules and metallic palladium particles are formed according to eq 1.

$$[(\mathrm{dba})_3\mathrm{Pd}^0] \xrightarrow{T} 3\mathrm{dba} + \mathrm{Pd}^0\downarrow \qquad (1)$$

Table I. Weight Loss of Pure Pd Complexes 1 and 3 during Isothermal Heating at Different Temperatures

heating condition	weight loss of 1, %	weight loss of 3, %
2 h 150 °C in air	0.8	2.3
2 h 180 °C in air	2.3	12.0
2 h 230 °C in air	8.5	27.9
2 h 150 °C under N_2	0.4	1.0

Table II. Composition and Curing Conditions of resins R-1 to R-4

resin	composition[a]	curing conditions
R-1	25.1% complex 1 34.8% DGEBA 39.8% HHDA 0.3% BDMA	4 h 100 °C + 4 h 120 °C
R-2	25.2% complex 1 54.6% DGEBA 20.2% MDA	4 h 100 °C + 4 h 120 °C + 2 h 150 °C + 2 h 180 °C
R-3	24.2% DGDBA 35.2% DGEBA 40.3% HHDA 0.3% BDMA	4 h 100 °C + 4 h 120 °C
R-4	24.2% DGDBA 55.3% DGEBA 20.5% MDA	4 h 100 °C + 4 h 120 °C + 2 h 150 °C + 2 h 180 °C

[a] Percentage by weight.

In contrast to 2, 1 shows only a broad and weakly pronounced exothermal transition by DSC. It occurs between 120 and 160 °C and has a maximum around 150 °C. The lack of any sharp transition suggests that endothermal melting and exothermal decomposition overlap strongly with exothermal polymerization. Further information on the thermal behavior of 1 was obtained from thermogravimetric analysis. Complex 1 and its nonpolymerizing analogue 3 were annealed at different temperatures and then the weight loss was determined. As can be seen from Table I, the two complexes are more stable in nitrogen than in air. 3 exhibits a substantial weight loss at $T > 180$ °C, which is caused by sublimation of the ligand molecules and formation of other volatile decomposition products. The weight loss of 1 is much lower, which is evidence for a gradual thermal cross-linking of the ligand molecules.

The thermal stability of 1 was also studied by UV–visible absorption spectroscopy. Equal amounts (20 mg) of polycrystalline 1 were annealed at different temperatures for 2 h. Then the annealed samples were dissolved in toluene (1 L), and the spectra of the soluble part monitored in the UV spectrophotometer. After annealing for 2 h at 150 °C, 1 was completely soluble. The corresponding absorption spectrum is shown in Figure 1 (spectrum b). As can be seen, the 535 nm d-π^* transition of the complex has disappeared and the intensity of the 335 nm n-π^* transition of the ligand molecules has simultaneously increased. This indicates that the temperature of 150 °C is sufficient to cause a complete decomposition of the complex according to eq 1.

Spectrum (c) was taken from a sample annealed at 180 °C for 2 h. This sample was only partially soluble in

Table III. Characteristic Properties of Resins R-1 to R-4 after Moulding

resin	Pd conc (wt %)	T_g (°C)	flexural strength[a] (N mm^{-2})	ultimate strength[a] (kJ m^{-2})	thermal cond[b] (W K^{-1} m^{-1})	surface cond[b] (S cm^{-1})	spec vol resist[c] (Ω cm)	water absorption after 4 d at 20 °C (%)	after 1 h at 100 °C (%)
R-1	2.2	136	152.5 ± 3.3	9.3 ± 1.4	0.250	>100	3.6×10^{16}	0.33 ± 0.01	0.31 ± 0.01
R-3	0	126	151.9 ± 1.0	9.3 ± 1.4	0.223	$<10^{-12}$	8.1×10^{16}	0.33 ± 0.01	0.39 ± 0.02
R-2	2.2	181	135.9 ± 4.7	12.7 ± 1.9	0.291	>100	2.5×10^{15}	0.50 ± 0.04	0.50 ± 0.01
R-4	0	184	132.9 ± 5.4	13.2 ± 0.7	0.280	$<10^{-12}$	5.4×10^{14}	0.51 ± 0.02	0.53 ± 0.01

[a] According to DIN 53 435. [b] According to DIN 52612. [c] At room temperature.

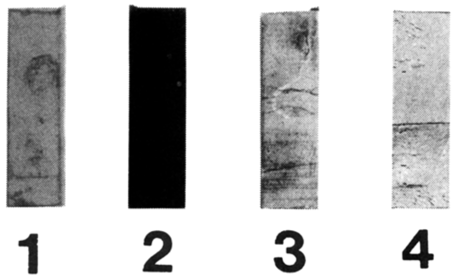


Figure 3. Epoxy resins after thermal curing: (1) metal-free resin R-3; (2) palladium-containing resin R-1; (3) R-1 after additional heat treatment at 220 °C leading to formation of a thin palladium film on the surface; (4) R-1 after electroless nickel plating.

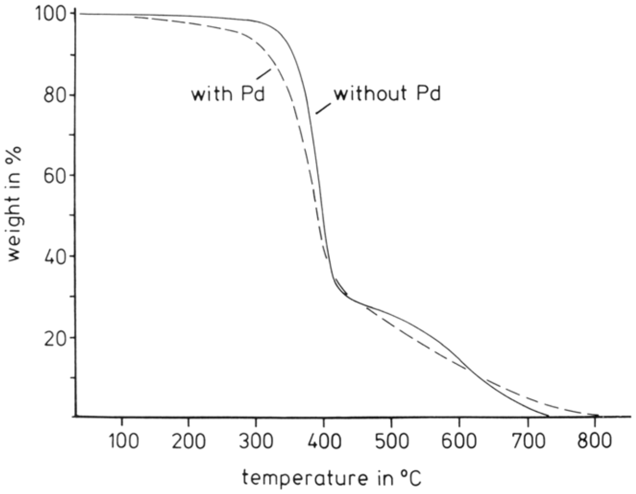


Figure 4. Weight loss vs temperature curves of cured resins R-1 and R-3 showing the enhanced thermal degradation of Pd containing resin R-1. Heating rate 10 K/min.

Table IV. Weight Loss of Moulded Resins R-1 to R-4 during Heating in Air (Heating Rate 10 K/min)

resin	Pd conc (wt %)	temp (°C) at which the weight loss amounts to 5%	10%	50%
R-1	2.2	290	325	390
R-3	0	330	350	400
R-2	2.2	310	315	480
R-4	0	320	335	500

toluene, due probably to a gradual thermal polymerization of the epoxy groups. Since only the nonpolymerized part of the ligand molecules is soluble, the optical density of the 335-nm transition is comparatively low. The third sample was annealed at 250 °C for 2 h. It was almost completely insoluble due to polymerization so that the toluene extract did not show any significant UV absorption.

In summary, the study of the thermal behavior shows that 1 decomposes at temperatures around 150 °C with formation of free ligand molecules and zerovalent palladium. Significant thermal polymerization sets in at temperatures above 150 °C but below 180 °C. Polymerization becomes rapid and essentially goes to completion at temperatures above 200 °C.

3.2. Curing of Epoxy Resins. The palladium complex 1 represents a hexafunctional monomer, which can be cross-linked with various curing agents with formation of three-dimensional polymer networks. Since the complex is a solid, it can be homogeneously distributed in the moulded article only when it is dissolved in a "reactive diluent" prior to curing. DGEBA was found to be excellently suited for this purpose. It was able to dissolve up to about 30 wt % of the complex.

Table V. Weight Loss of Moulded Resins R-1 to R-4 upon Isothermal Annealing at 240 °C in Air

resin	Pd conc (wt %)	weight loss (%) after 1 h	3 h	5 h
R-1	2.2	2.7	8.5	16.3
R-3	0	0.4	0.9	1.4
R-2	2.2	0.8	1.8	3.6
R-4	0	0.4	0.8	1.2

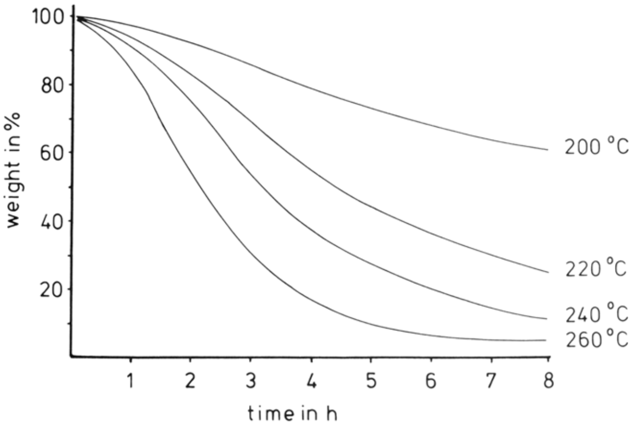


Figure 5. Weight loss vs time curves of cured resin R-1 at different temperatures. The curves show a rapid decomposition at temperatures above 200 °C.

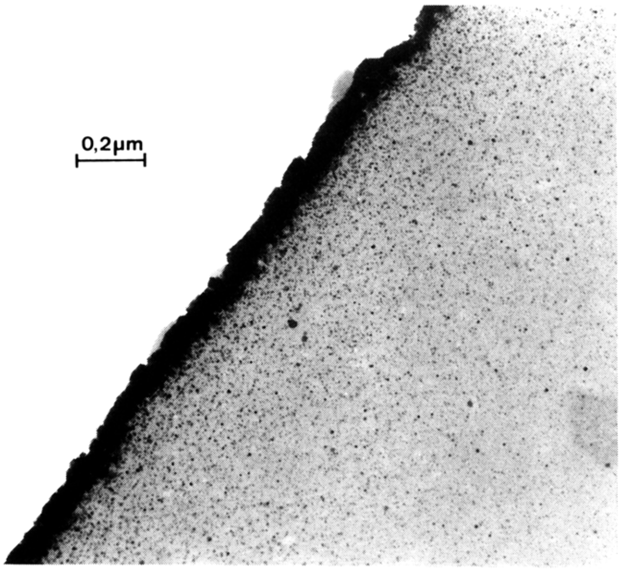


Figure 6. TEM picture of a cross-section of cured resin R-1. The cross section was prepared subsequent to annealing of the resin at 240 °C for 2 h. The picture shows a random distribution of palladium microparticles over the whole resin and a palladium enrichment ("film") on the surface of the resin.

Two different palladium containing resins (R-1 and R-2) were prepared using either hexahydrophthalic anhydride (HHPA) or 4,4′-diaminodiphenylmethane (MDA) as curing agent. For comparison, metal-free resins were also prepared (R-3 and R-4). These resins had the same composition as the palladium-containing resins except that the palladium complex was replaced by the corresponding amount of the ligand compound DGDBA. Resins were cured in a mould 150 × 150 × 2 mm in size. Curing with HHPA was always carried out in the presence of small amounts of benzyldimethylamine (BDMA) as accelerator. Composition and curing conditions of R-1 to R-4 are summarized in Table II.

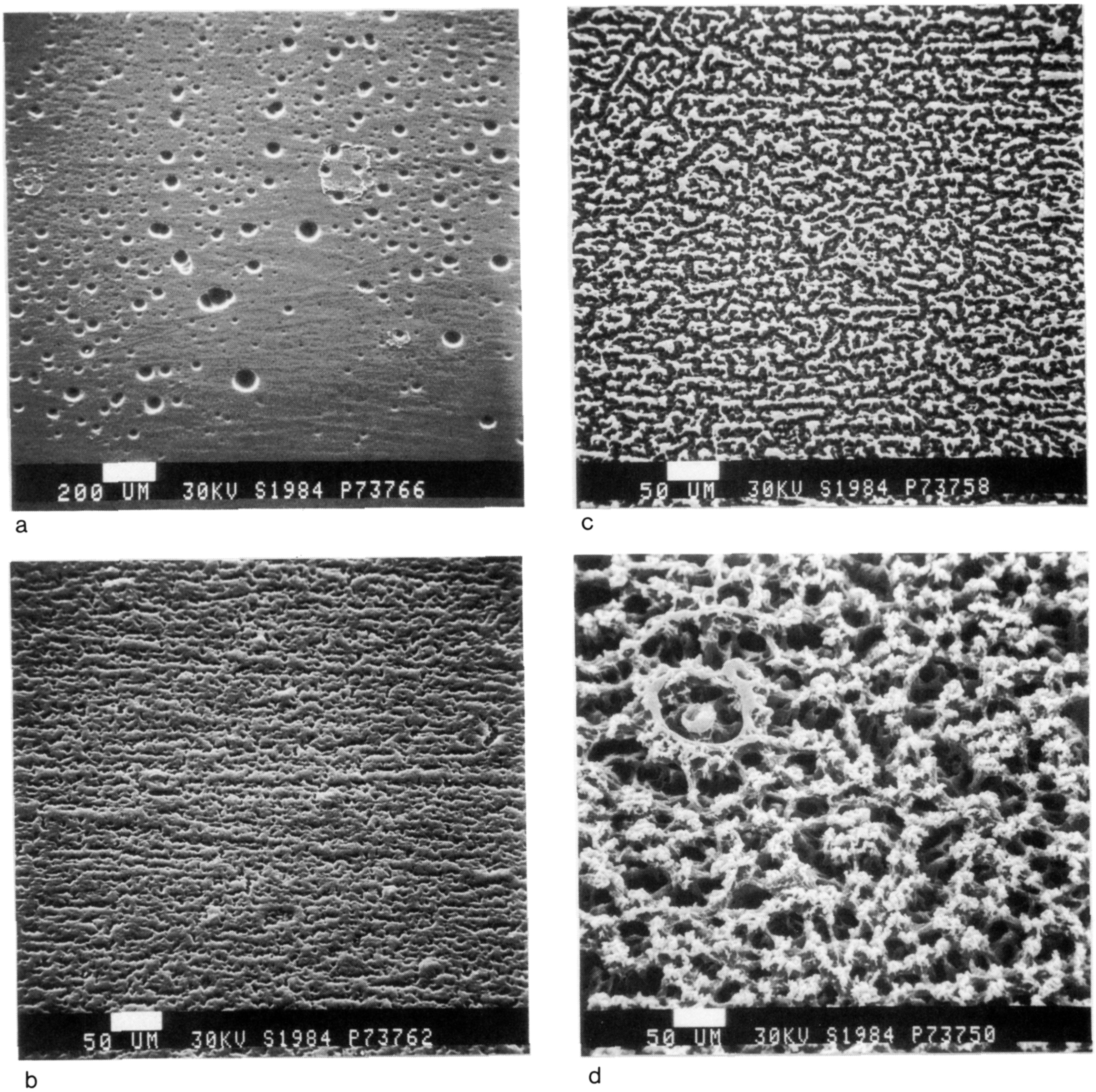


Figure 7. SEM picture of resins R-1 after heat treatment at 240 °C for (1) 1 h, (b) 2 h, (c) 3 h, and (d) 10 h.

3.3. Properties of Cured Resins. While thermal curing of metal-free resins R-3 and R-4 led to plates with brownish orange color originating from the dibenzylideneacetone chromophore, palladium-containing resins R-1 and R-2 were completely black after curing and did not reveal whether the complex was decomposed or not (Figure 3, samples 2 and 3). To obtain information on the complex stability, curing was therefore studied using thin transparent films of the resin. In these films the deeply wine-red color did not disappear upon curing. This clearly indicated that most of the complex was retained during the polymerization process. In Table III, some characteristic data of resins R-1 to R-4 are listed. Metal-containing and metal-free resins are nearly identical with regard to glass temperature, mechanical properties, thermal conductivity, specific volume resistance and water uptake, whereas the nature of the curing agent has some effect on the ultimate and flexural strength. Resins cured with HHPA were always less flexible than those cured with MDA.

3.4. Catalytic Activity. If annealed at high temperature, i.e., above the decomposition temperature of the complex at about 150 °C, the palladium-containing resins show some remarkable changes in their chemical and thermal properties. Dipping into a commercial plating bath for electroless metallization leads to rapid growth of a well adhering nickel or copper film on their surface. Also, they show an enhanced tendency to decompose at high temperatures (i.e., above 200 °C) in air, which is especially pronounced for the HHPA-cured resins and eventually leads to formation of a thin palladium film on the resin surface. The processes are described below in more detail.

3.4.1. Thermal Decomposition. In Table IV, weight loss data of the cured resins R-1 to R-4 are listed. The data were obtained from TGA measurements at constant heating rate of 10 K/min. They indicate that the HHPA-cured resins R-1 and R-3 are substantially less stable than the MDA-cured resins R-2 and R-4. Also, they show that the palladium containing resins R-1 and R-2 are decomposed more rapidly than their metal-free counterparts. Full TGA curves of resins R-1 and R-3 are shown in Figure 4, which again indicate the lower thermal stability of the metal-containing resin.

Further information on the thermal stability of the cured resins was obtained from isothermal weight loss measurements. In Table V, weight loss data are listed, which were obtained at 240 °C in air after different time periods. Again, it appears that the HHPA-cured resins are decomposed much faster than the resins cured with MDA, and that the corresponding palladium-containing resins are less stable than the metal-free resins. In Figure 5, weight loss isotherms of powdered samples of R-1 are shown, which indicate a strong effect of the annealing temperature on the decomposition rate. Since the powdered samples exhibit a much larger surface than bulk samples, the decomposition is substantially accelerated. As shown by the curves, rapid decomposition in particular occurs at temperatures above 220 °C. The rapid oxidative decomposition can be impressively demonstrated, for example, when the cured and powderized resin R-1 is heated on a hot plate in air. Soon after the temperature starts rising, the resin is spontaneously decomposed in a large blast of flame.

The rapid thermal decomposition of R-1 is mainly caused by the formation of catalytically active palladium particles which—when in contact with air—are able to catalyze the oxidative degradation of the resin. In addition, rapid decomposition of the HHDA-cured resin is favoured by the cycloaliphatic structure of HHPA, which is oxidized more easily than the aromatic MDA. The higher stability of MDA-cured resins may also originate from the higher network density which renders the diffusion of palladium atoms more difficult and thus delays the formation of catalytically active metal clusters.

3.4.2. Thermal Palladium Film Formation. Due to thermal degradation at high temperatures, the surface structure of the palladium containing resins is strongly changed. The loss of organic material from the surface of the resin leads to an enrichment of metallic palladium recognizable by the appearance of a metallic lustre (Figure 3, sample 3) and a high surface conductivity. For a sample of R-1 annealed at 220 °C for 2 h, the surface conductivity increases from insulating ($<10^{-12}$ S cm^{-1}) to values higher than 10 S cm^{-1}, while simultaneously the specific volume resistance remains unchanged (see Table III). The thickness of the metal deposit ("film") reaches values up to 100 nm. It can be easily controlled by time and temperature of annealing and by the palladium concentration of the resin. In Figure 6, the ultramicrotomed cross section of a heat-treated resin is shown. The transmission electron micrograph indicates an approximately 100-nm-thick metal film on the resin surface as well as small metallic microparticles, which are randomly distributed in the bulk resin. Their average diameter is in the range 5–20 nm. Formation of these microparticles must be due to cluster formation of the palladium atoms set free from the complex. This process will be subject to a more detailed investigation in the near future.

Prolonged exposure to air at very high temperatures leads to cavities in the resin surface (Figure 7a), which continuously increase in size and quantity (Figure 7b,c). Finally, isolated palladium particles several micrometers in diameter are formed and the resin surface becomes very rough (Figure 7d).

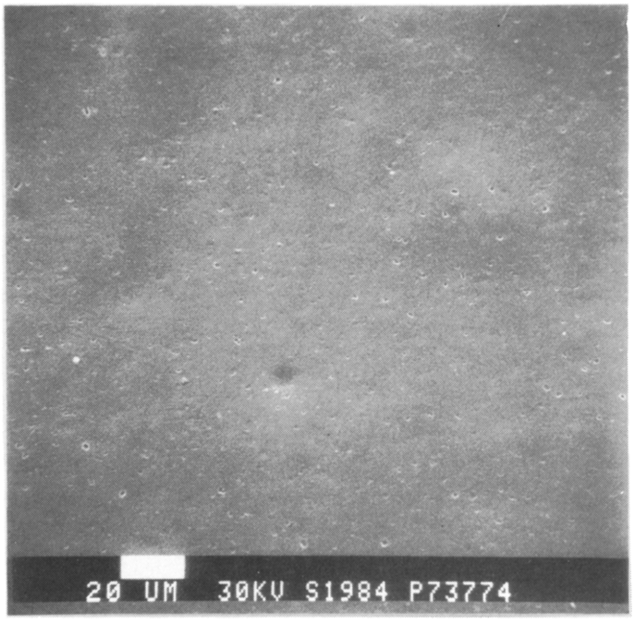


Figure 8. SEM picture of resin R-2 after heat treatment at 220 °C for 10 h.

The MDA-cured palladium resin R-2 behaves similarly although at a much longer time scale. After annealing at 240 °C for 10 h, the surface is still lustrous and smooth (Figure 8). Oxidation is probably retarded by the presence of the aromatic amino groups in MDA and the higher network density of the cross-linked plastic.

3.4.3. Electroless Metalization. The high catalytic activity of the palladium microparticles can be used for electroless nickel or copper plating of the resin according to eq 2.[19] In a typical experiment, the cured resin is

$$2H_2PO_2^- + Ni^{2+} + 2H_2O \xrightarrow{Pd^0} 2H_3PO_3 + Ni^0\downarrow + H_2\uparrow \quad (2)$$

annealed at 240 °C in air for half an hour and subsequently immersed in an alkaline plating bath for electroless nickel decomposition. After 90 s, a lustrous metallic nickel film, which firmly adheres to the resin surface, has formed (Figure 3, sample 4). Resins cured with HHPA and MDA are both suited for metal plating. Systematic variation of the palladium content indicated that a minimum amount of one weight percent of metal is sufficient to cause the formation of a homogeneous, well adhering nickel deposit. A similar experiment carried out with a plating bath for copper deposition showed that a slightly higher palladium concentration is necessary to cause formation of a well-adhering copper film.

The disadvantage of the relatively high palladium concentration needed in bulk samples can be easily overcome, if the substrate to be activated is only surface-coated with a thin film of the palladium-containing epoxy resin. For electroless metallization of multilayer epoxy glass fibre laminates, for example, it is sufficient, when only the uppermost layer contains the palladium complex. A corresponding metallized sample is shown in Figure 9.

---

[19] (a) Gabrielli, C.; Raulin, F. *J. Appl. Electrochem.* **1974**, *1*, 167. (b) Flis, J.; Duquette, D. J. *J. Electrochem. Soc.* **1984**, *131*, 254. (c) Gutzeit, G. *Plating* **1959**, *46*, 1158; **1959**, *46*, 1275; **1960**, *47*, 63.

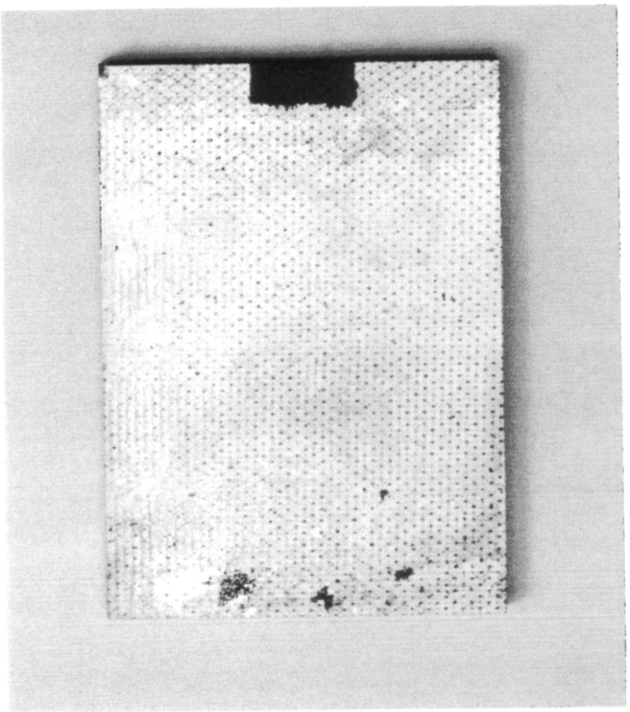


Figure 9. Multilayer epoxy glass fiber laminate after electroless metal plating. The laminate contains R-1 in the uppermost layer and R-3 in the 13 subsequent layers. For comparison, a small area on top of the laminate has not been plated.

4. Summary and Conclusions

In our paper, a new cross-linkable palladium(0) complex is described, which can be used for preparation of epoxy resins with unusual thermal and catalytic properties. The complex represents a carrier for zerovalent palladium, which can be homogeneously distributed in the resin matrix in a maximum concentration of about thirty weight percent of the resin. Thermal treatment at high temperatures ($T > 150$ °C) sets the metal atoms free, which immediately aggregate and form microparticles. The diameter of the particles is in the range 5–20 nm.

Metallic particles formed near the surface of the resin exhibit a high catalytic activity. If the resin is kept in air at high temperatures, i.e., above 200 °C, they catalyze the thermal degradation of the polymer network. The palladium particles also catalyze the electroless nickel and copper plating of the resin surface. Incorporation of complex **1** in epoxy resins followed by a distinct thermal treatment of the resin therefore represents a new and versatile method of surface activation, which makes the use of several activation baths usually needed for metal plating of plastics[20] unnecessary.

The palladium containing epoxy resins also allow a patternwise liberation of the metallic palladium on the surface. Preliminary studies indicate that the heat evolving from irradiation with a few laser pulses is sufficient to activate the surface of the resin for a patterned metallization. Finally, the palladium containing resins may also be useful for other catalytic reactions or sensor applications, e.g., for the detection of hydrogen.

Acknowledgment. The authors wish to thank Mr. M. O. Chard for valuable technical assistance in the preparation of the complexes and resins, as well as Mr. W. Gabriel for taking the electron micrographs and Mr. F. Perritaz for the TGA measurements.

---

[20] Krutik, G. A. *J. Chem. Educ.* **1978**, *55*, 361.