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SPIE.

Platinum and palladium oxalates: positive-tone extreme ultraviolet resists

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Abstract. Here, we present platinum and palladium mononuclear complexes with EUV photosensitivity and lithographic performance. Many platinum and palladium complexes show little or no EUV sensitivity; however, we have found that metal carbonates and metal oxalates ($L_2M(CO_3)$ and $L_2M(C_2O_4)$; $M = Pt$ or Pd) are sensitive to EUV. The metal carbonates give negative-tone behavior. The most interesting result is that the metal oxalates give the first positive-tone EUV resists based on mononuclear organometallic compounds. In particular, $(dppm)Pd(C_2O_4)$ ($dppm = 1,1$ -bis(diphenylphosphino)methane) (**23**) prints 30-nm dense lines with E_{size} of 50 mJ/cm². Derivatives of (**23**) were synthesized to explore the relationship between the core metal and the resist sensitivity. The study showed that palladium-based resists are more sensitive than platinum-based resists. The photoreaction has been investigated for two of our most promising resists, $(dppm)Pd(C_2O_4)$ (**23**) and $(Ph_2EtP)_2PdC_2O_4$ (**27**). Our experiments suggest the loss of CO₂ and the formation of a zerovalent L_4Pd complex upon exposure to light. We have identified $dppm_2Pd(\delta(P)23.6)$ as the main photoproduct for (**23**) and $(Ph_2EtP)_4Pd(\delta(P)32.7)$ as the main photoproduct for (**27**). © 2015 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.JMM.14.4.043511]

Keywords: platinum; palladium; oxalate; photoresist; extreme ultraviolet; positive-tone.

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1 Introduction

Extreme ultraviolet lithography (EUVL) is anticipated to succeed 193-nm immersion lithography to meet the demands of the future semiconductor nodes.¹ Unfortunately EUVL continues to face major challenges, which are still preventing it from being implemented in manufacturing. The challenges include, but are not limited to, light source power, resist performance, and mask defects. Mask defects have major consequences for production throughput and cost. A mask defect occurs, e.g., when a minuscule particle falls on the mask, potentially causing dark spots. Additionally, tiny bumps can be hidden underneath the thin reflective coatings, creating phase shifts.² Dark field masks, used for contact hole manufacturing, are usually easier to correct than bright field masks as the defect can be covered with absorber pattern.¹ Dark field masks are generally used with positive-tone photoresists.

The challenges associated with the resist performance at EUV are being addressed in innovative ways, e.g., by introducing metals to the resists. Inpria has shown excellent resist resolution with their hafnium oxide based resist,³ while Cornell University has shown an excellent sensitivity using hafnium oxide nanoparticles.^{4–6} The MORE project at the College of Nanoscale Science and Engineering has presented molecular organometallic resists with either good sensitivity^{7,8} or with outstanding line edge roughness (LER).⁹

Here, we continue to look at molecular organometallic resists. We hope to answer the challenges associated with

mask defects by introducing the first positive-tone molecular organometallic resist. Figure 1 shows the periodic table with shading to symbolize the EUV optical density of the elements, and by utilizing darker elements in our resists, we hope to improve the photon statistics. We will present the synthesis and lithographic evaluation of compounds containing platinum or palladium.

The photochemistry of platinum and palladium oxalates in solution at longer wavelengths is well documented.^{10–14} For example, Paonessa et al.¹⁰ identified the formation of two equivalents of CO₂ as $(L_2PtC_2O_4)$ is exposed to light. This produces a highly reactive intermediate (L_2Pt) which then reacts with itself to yield L_3Pt and platinum metal. Blake and Nyman¹² and Pan et al.¹⁴ identified the formation of an L_4Pt_2 dimer when $L_2PtC_2O_4$ is irradiated at UV. Here, we present similar photochemistry performed at EUV.

In the literature, the photomechanistic studies are mainly carried out in solution, while our lithographic evaluation of these resists is performed in the solid state on 4-in. wafers. In order for our material to work as a photoresist, a solubility switch must occur upon exposure. As we will show in Sec. 2.2.5, our proposed photomechanism supports a solubility switch in the resist, creating a photoproduct more soluble in the developer, thus producing a positive-tone resist. All resist systems have been evaluated lithographically at the Berkeley micro exposure tool (BMET) and at the Paul Scherrer Institute (PSI) in Villigen, Switzerland. The photoresists presented here will be reported and compared using E_0 (mJ/cm²), indicating the dose for minimum thickness.

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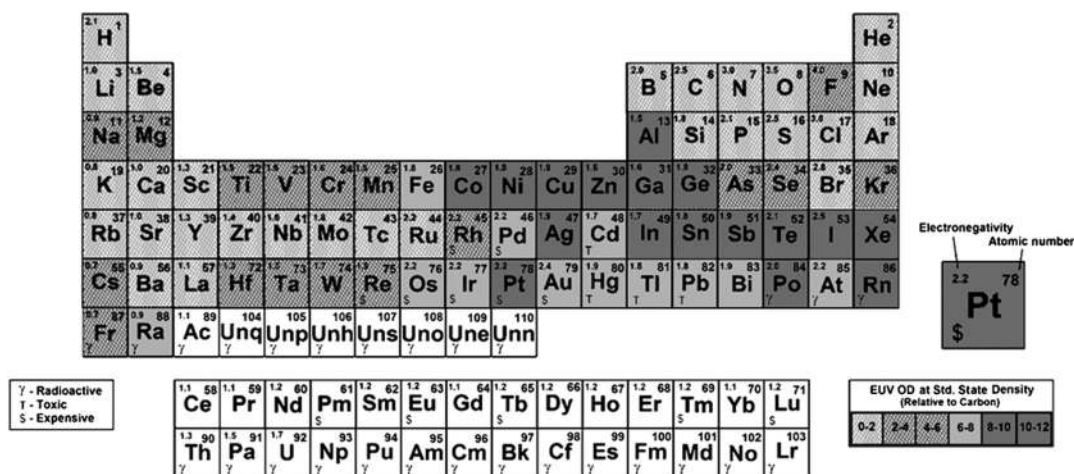


Fig. 1 The periodic table with respect to optical density.

2 Results and Discussion

2.1 Preliminary Studies

In early work done by other students in our group, we found organometallic complexes that are sensitive to EUV light despite no previously published photosensitivity at longer wavelengths.¹⁵ Specifically, Cardineau et al.¹⁵ showed that tin oxoclusters undergo reaction upon exposure to EUV light by mechanisms most likely involving the homolytic cleavage of tin-carbon bonds. Based on this knowledge, we began the research in platinum and palladium chemistry by testing the EUV lithographic performance of a wide range of synthetically accessible complexes (Fig. 2). Whether or not they had known photoreactivity at longer wavelengths was less important at this exploration stage.

The complexes tested for EUV sensitivity have good solubility and spin-coating properties. They are high in metal content, and contained the ligand *cis,cis*-1,5-cyclooctadiene (COD). We suspected that COD would β -hydride eliminate, which could possibly create a photoresponse in the resist upon exposure. The compounds were spin-coated in either acetone nitrile/propylene glycol monomethyl ether acetate (PMA) or toluene and tested for lithographic performance at BMET. Unfortunately, no latent image or pattern formation was visibly detected, but a chemical change did happen

in the resist film upon exposure which could be seen when breathing on the exposed wafer. The moisture made the exposed areas appear clear, while the unexposed areas looked foggy. As a result, the latent image became easier to see. Our hypothesis is that a low level of decomposition happened in the exposed areas, leaving residue on the surface. This decomposition might have caused a polarity change in the undeveloped resist film, causing the exposed areas to be hydrophilic and the unexposed areas to be hydrophobic.

2.2 Platinum and Palladium Complexes with Azide, Carbonate, and Oxalate

After determining that that the COD containing platinum and palladium complexes gave poor EUV sensitivity, we began an investigation into platinum and palladium complexes in combination with ligands with known photoreactivity at longer wavelengths. We prepared complexes containing azide (N_3), carbonate (CO_3), and oxalate (C_2O_4) ligands for a number of transition metal complexes.^{10-14,16-18}

2.2.1 Azides

The azide ligand has known photoreactivity at longer wavelengths,^{16,18} and we synthesized six azide complexes using both phosphines and amines as neutral ligands to investigate

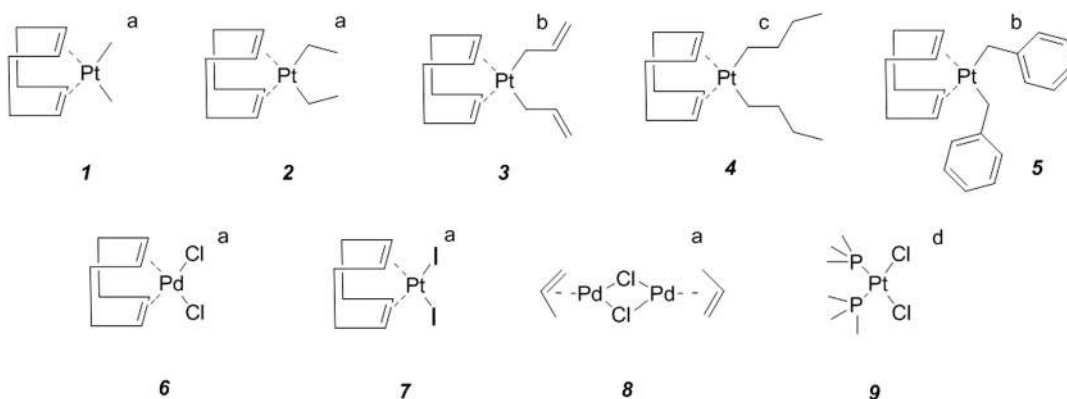


Fig. 2 Preliminary investigation of EUV reactivity of platinum and palladium. Results: (a) Latent image breath observable and image not visible. (b) Faint latent image but image not visible. (c) Latent image breath observable and image partly visible. (d) Breath observable latent image and image.

their reactivity to EUV (Fig. 3).^{11,16,19,20} These compounds were spin-coated from mixtures of methanol and ethyl lactate to form amorphous films, then evaluated lithographically at EUV using the interference lithographic tool at PSI. Unfortunately, the azide complexes showed very little sensitivity to EUV light and no lithographic performance. The latent image was barely visible and development produced no visible image.

2.2.2 Carbonates

Four $L_2M(CO_3)$ complexes were synthesized¹¹ since transition metal carbonates are known to show photoreactivity to UV light [Fig. 4(a)].^{11,17} Indeed, we found that three of these resists exhibited negative-tone behavior as EUV resists. However, we decided not to optimize these resists as they had poor sensitivity and were difficult to solubilize.

2.2.3 Oxalates

As mentioned previously, the photochemistry of platinum and palladium oxalates is well documented,^{10–14} and in our work, we found that oxalate complexes of first-row transition metals produce negative-tone EUV resists capable of 18-nm resolution with sizing doses of 30 mJ/cm^2 .⁷ To investigate the EUV photoreactivity of $L_2M(C_2O_4)$ ($M = \text{Pt}$ or Pd), four complexes were initially synthesized according to previously described methods [Fig. 4(b)].¹¹ These compounds were spin-coated in either 1:2 acetone nitrile/ethyl lactate or 1:2 methylene chloride/PMA and exposed to EUV at PSI. Up to this point of the MORE project, all of our resists have been negative-tone. Consequently, we expected the $L_2M(C_2O_4)$ to behave as negative-tone resists and developed them accordingly. However, when we developed $\text{dppmPdC}_2\text{O}_4$ (**23**) in a nonpolar developer, we

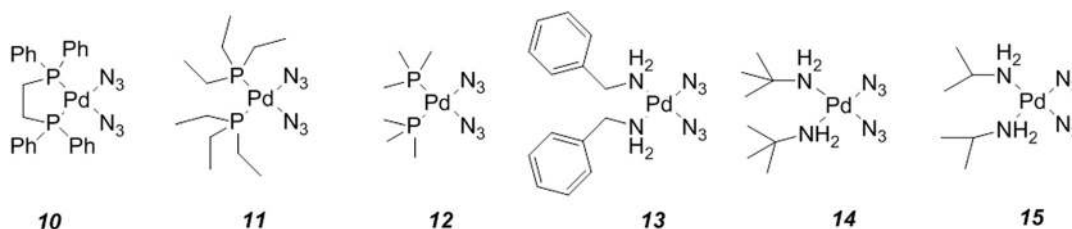


Fig. 3 $L_2\text{Pd}(\text{N}_3)_2$ complexes, where L = phosphines or amines.

Negative tone resists:				
(a)				
	E_{max} :	No data	282 mJ/cm^2	605 mJ/cm^2
		16	17	18
Positive tone resists:				
(b)				
	E_0 :	> 150 mJ/cm^2	247 mJ/cm^2	110 mJ/cm^2
		20	21	22

Fig. 4 $L_2M(C_2O_4)$ and $L_2M(CO_3)$ evaluated for EUV sensitivity. (a) Platinum and palladium carbonates showing negative-tone behavior. (b) Platinum and palladium oxalates showing positive-tone.

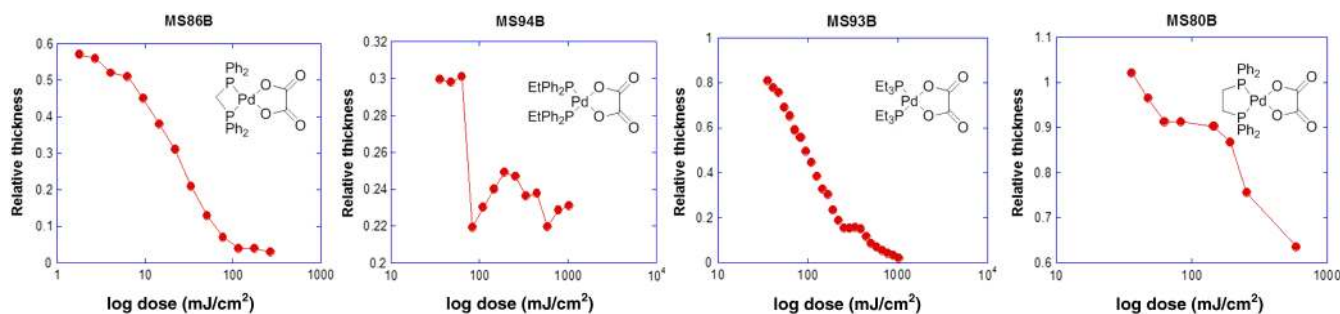


Fig. 5 Contrast curves of selected palladium oxalate resists, all showing a positive-tone photoresponse.

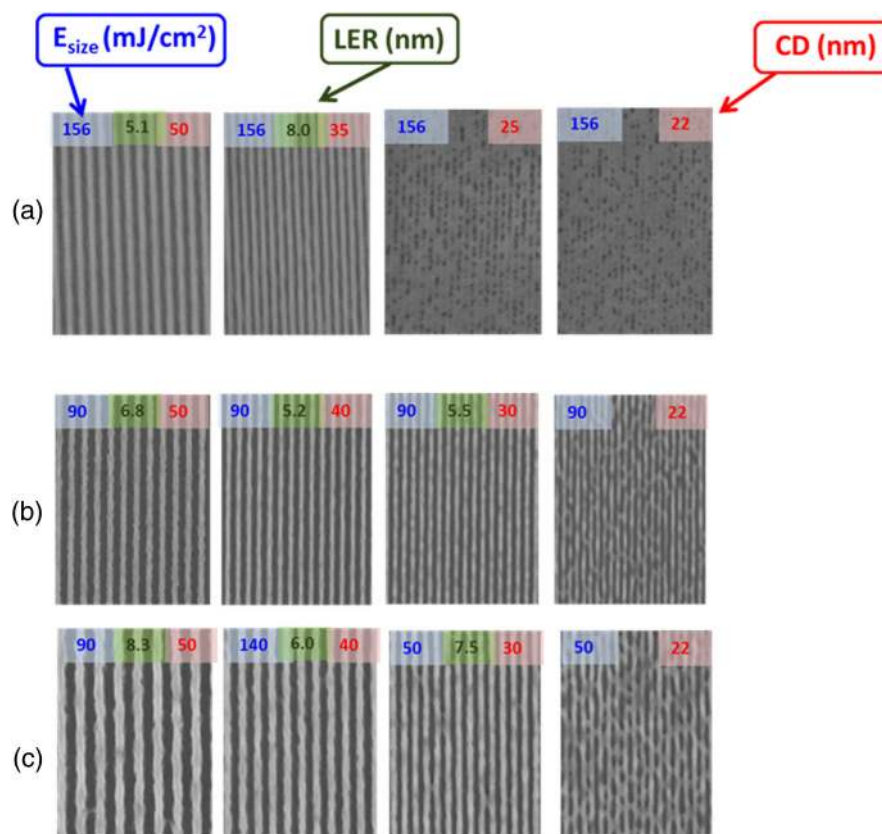


Fig. 6 First positive-tone MORE photoresist: (dppm)Pd(C₂O₄) (**23**) gives resolution down to 30-nm half pitch and modulations down to 22-nm half pitch. (a) Developer: 10% methyl isobutyl ketone (MIBK)/toluene, on underlayer. (b) Developer: 10% MIBK/toluene, no underlayer. (c) Developer: 20% MIBK/toluene, no underlayer.

discovered its positive-tone behavior. After that all the L₂M(C₂O₄) complexes were developed in a mixture of methyl isobutyl ketone (MIBK) and toluene which cleared the exposed areas, leaving the unexposed areas behind (Fig. 5). As seen in Fig. 4, (dppm)Pd(C₂O₄) (**23**) demonstrated the best sensitivity with an E_0 of 54 mJ/cm² and was able to print 30-nm dense lines at an E_{size} of 50 mJ/cm² [Fig. 6(c)].

2.2.4 Effect of metal and phosphine ligands

Seven platinum and palladium oxalates were synthesized with different phosphine ligands (Fig. 7).¹¹ These complexes were coated on silicon wafers and exposed to EUV using the interference lithography tool at PSI. In general, palladium complexes produced faster EUV resists than do platinum complexes. Direct comparisons can be made for complexes **21** versus **23** and for **24** versus **25**.

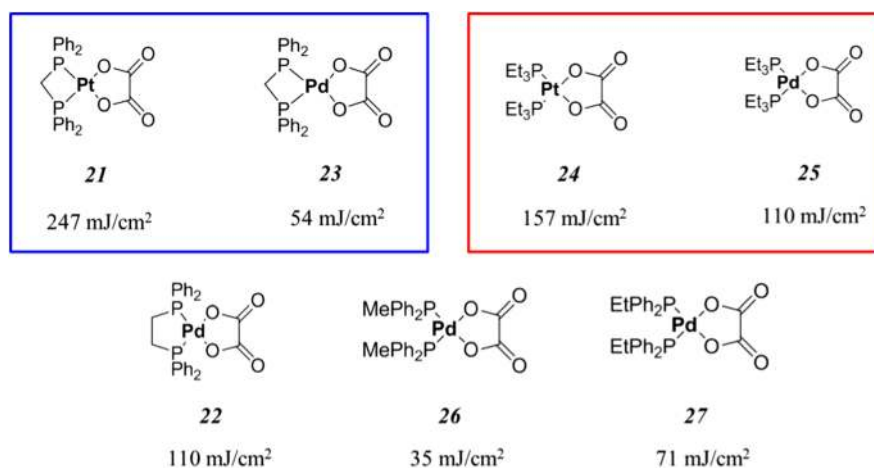


Fig. 7 E_0 for different platinum and palladium phosphine oxalates.

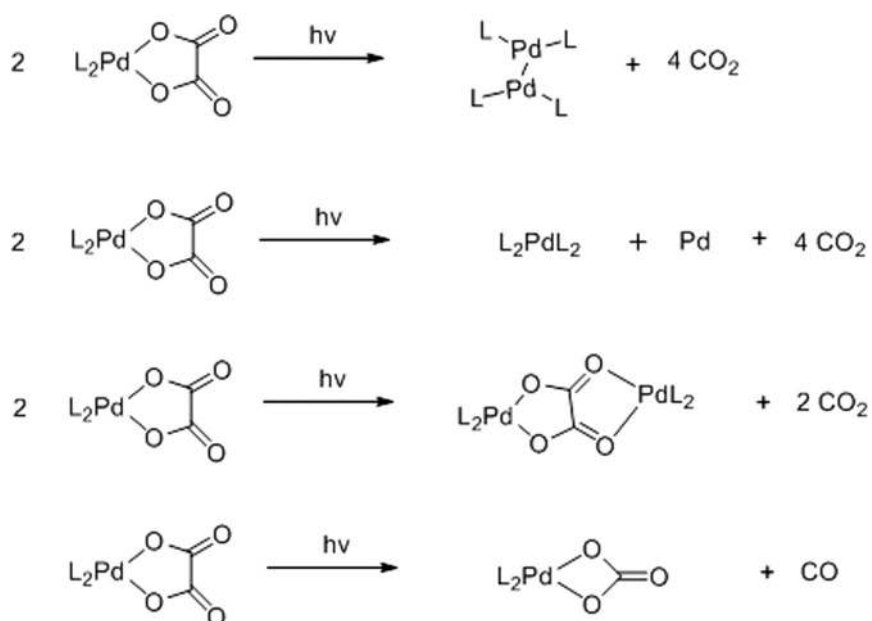


Fig. 8 Possible photoproducts based on literature reviews.

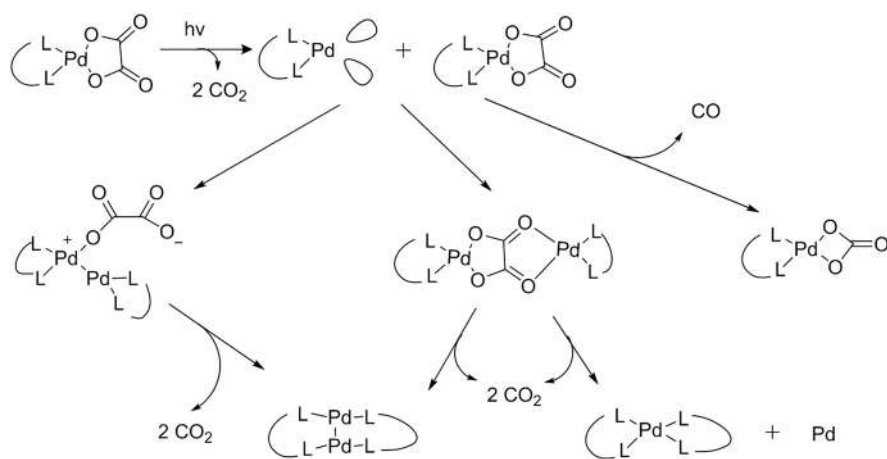
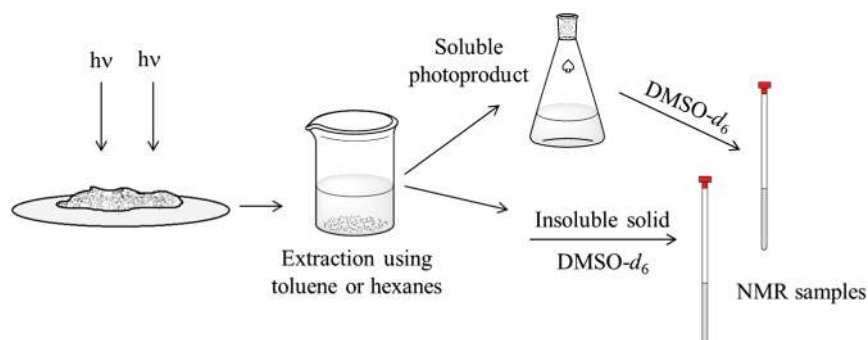
Fig. 9 Proposed photomechanisms for $\text{L}_2\text{PdC}_2\text{O}_4$.

Fig. 10 Powder of $\text{dppmPdC}_2\text{O}_4$ (**23**) and $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) was irradiated with i-line. The exposed solid was then stirred in the appropriate developer. The insoluble solid was filtered off and analyzed by nuclear magnetic resonance (NMR). The filtrate, which is the soluble photoproduct, was also analyzed by NMR.

2.2.5 Photomechanistic studies

As the resist system with the most potential, the $L_2PdC_2O_4$ platform was further investigated with the objective of improving the lithographic performance. We sought to better understand the underlying photomechanism of this system as this could potentially help us to improve the lithographic performance. The photomechanistic studies of $L_2M(C_2O_4)$ as presented in the literature show experiments performed at longer wavelengths, in solution and usually in the absence

of air.^{11–15} Though our photochemistry is done at EUV and in the solid state, we propose four possible photoproducts for the EUV exposure of $L_2PdC_2O_4$ based on the literature and based on educated guesses (Fig. 8). Figure 9 shows potential mechanistic pathways leading to the formation of the photoproducts.

Here, we present the mechanistic studies of two of our most promising palladium resist systems; $dppmPdC_2O_4$ (**23**) and $(Ph_2EtP)_2PdC_2O_4$ (**27**). The compound $dppmPdC_2O_4$

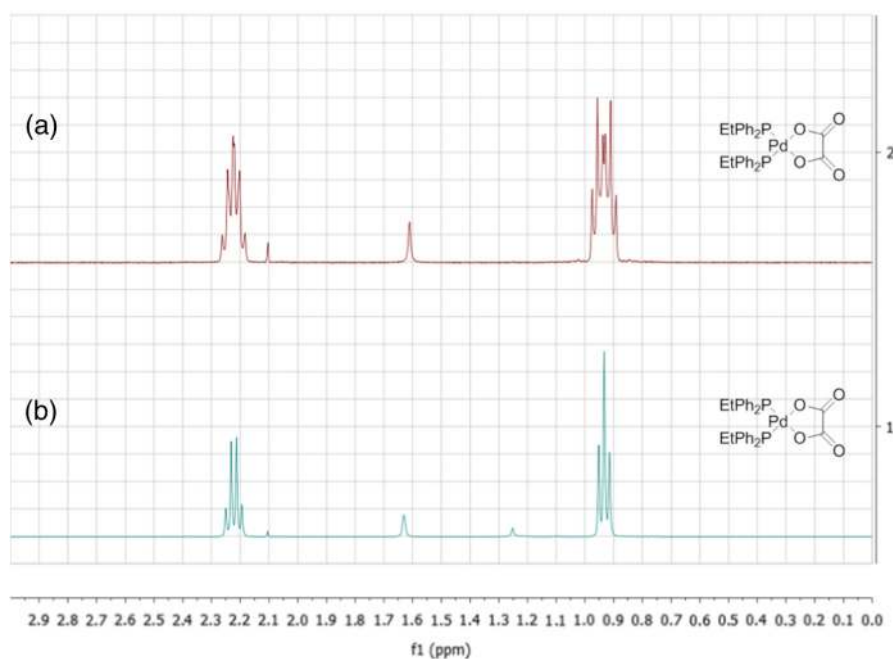


Fig. 11 (a) 1H NMR spectra of a portion of $(Ph_2EtP)_2PdC_2O_4$ (**27**). (b) ^{31}P decoupled 1H NMR of a portion of $(Ph_2EtP)_2PdC_2O_4$ (**27**).

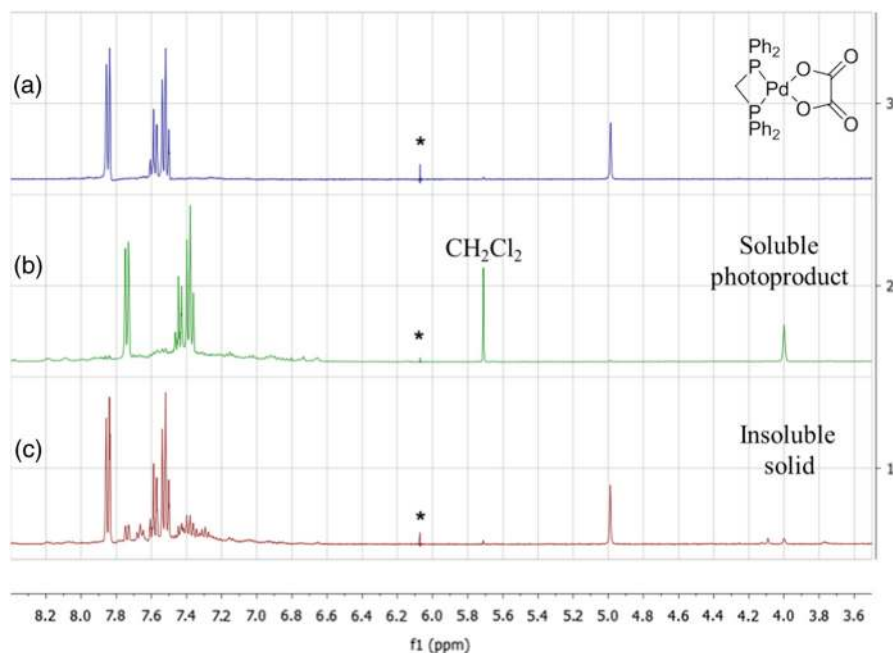


Fig. 12 ^{31}P decoupled 1H NMR: (a) $dppmPdC_2O_4$ (**23**) unexposed. (b) Soluble photoproduct from toluene extraction. (c) Insoluble solid from toluene extraction. *Known artifact.

(**23**) contains a bidentate phosphine ligand while $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) has two monodentate phosphine ligands. Bidentate ligands are known to produce more reactive intermediates,¹¹ and we wanted to investigate whether or not the nature of the ligand would have any effect on the photomechanism for the $\text{L}_2\text{PdC}_2\text{O}_4$ resist system.

Photomechanistic studies were performed with a near-UV 500 W exposure tool which produces 365, 405, and 436-nm light. Ideally, we would have used EUV light, but our main

characterization tool is nuclear magnetic resonance (NMR) spectroscopy which requires ~ 20 mg samples. If we were to expose 4-in. wafers to EUV, we would need to expose 40 wafers in order to prepare one NMR sample. Since this is both expensive and inefficient, we used i-line. For the same reasons as explained above, a powder of the material was exposed instead of wafers. The photoproduct was extracted from the starting material based on the solubility switch that happens in the resist upon exposure. As positive-tone

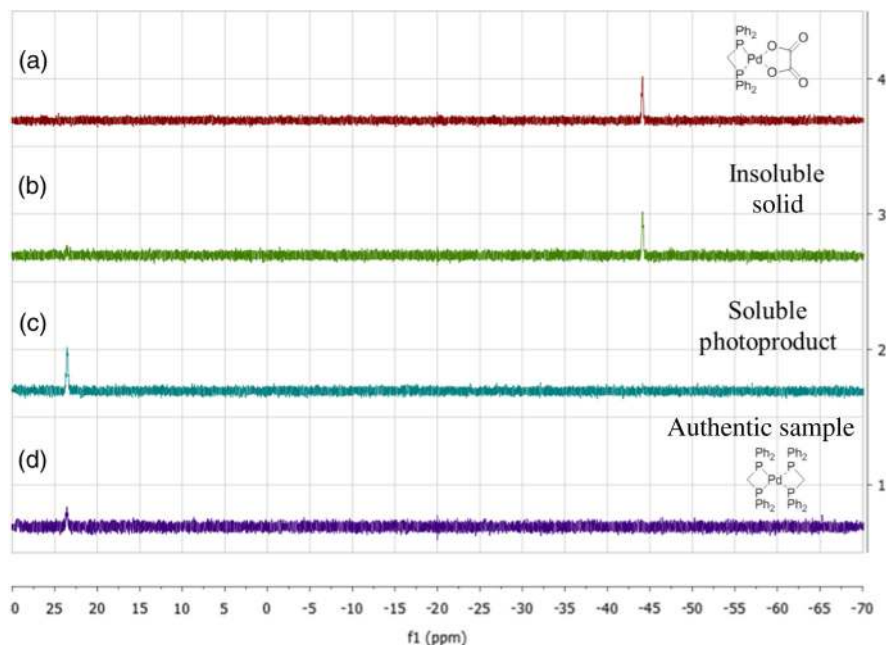


Fig. 13 ^{31}P NMR: (a) $\text{dppmPdC}_2\text{O}_4$ (**23**) unexposed. (b) Insoluble solid from toluene extraction. (c) Soluble photoproduct from toluene extraction. (d) Authentic sample of dppm_2Pd .

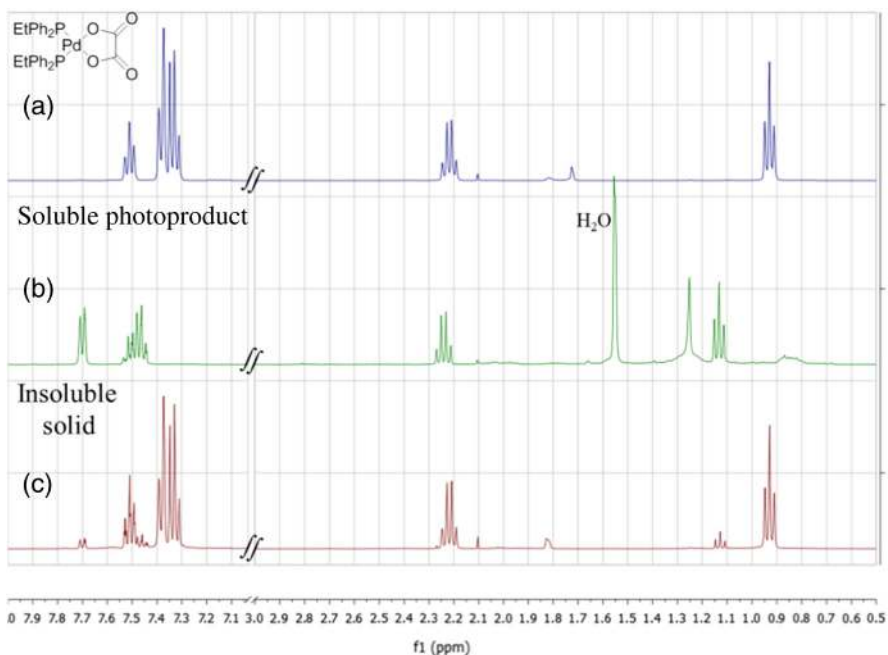


Fig. 14 ^{31}P decoupled ^1H NMR: (a) $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) unexposed. (b) Soluble photoproduct from hexanes extraction. (c) Insoluble solid from hexanes extraction.

photoresists, the photoproduct for both $\text{dppmPdC}_2\text{O}_4$ (**23**) and $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) is soluble in the developer, thus possible to solubilize and extract. Toluene was used to extract the photoproduct of $\text{dppmPdC}_2\text{O}_4$ (**23**) and hexanes for the photoproduct of $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) (Fig. 10).

The extracted material was analyzed with ^1H and ^{31}P NMR spectroscopy. Figure 11(a) shows a complex ^1H spectrum of a portion of $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) with phosphorous coupled to the proton. By decoupling the phosphorous, the spectrum only show proton splitting and is therefore easier to read [Fig. 11(b)]. All other ^1H NMR spectra presented in this paper will be ^{31}P decoupled.

The ^1H and ^{31}P NMR spectra (Figs. 12–15) show the difference between unexposed and exposed material. In the case

of both $\text{dppmPdC}_2\text{O}_4$ (**23**) and $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**), it seems to be mainly one photoproduct forming, $\delta(\text{P})23.5(\text{d}, J = 19.1 \text{ Hz})$ [Figs. 12(b) and 13(c) for (**23**)] and $\delta(\text{P}) 32.6$ [Figs. 14(b) and 15(c) for (**27**)]. Both photoproducts can be explained by the elimination of 2 equivalents of CO_2 from the starting material followed by the addition of ligands to the reactive dppmPd or $(\text{Ph}_2\text{EtP})_2\text{Pd}$ fragment. These photoproducts were identified as $(\text{dppm})_2\text{Pd}$ ($\delta(\text{P})23.6$) and $(\text{Ph}_2\text{EtP})_4\text{Pd}$ ($\delta(\text{P})32.7$) by comparing their NMR parameters to those of authentic samples [Figs. 13(d) for (**23**) and 15(d) for (**27**)]. The elimination of CO_2 is confirmed by outgassing data performed with a 2000 eV electron gun and a mass spectrometer (Fig. 16). The data show that both (**23**) and (**27**) mainly outgas CO_2 upon exposure to light.

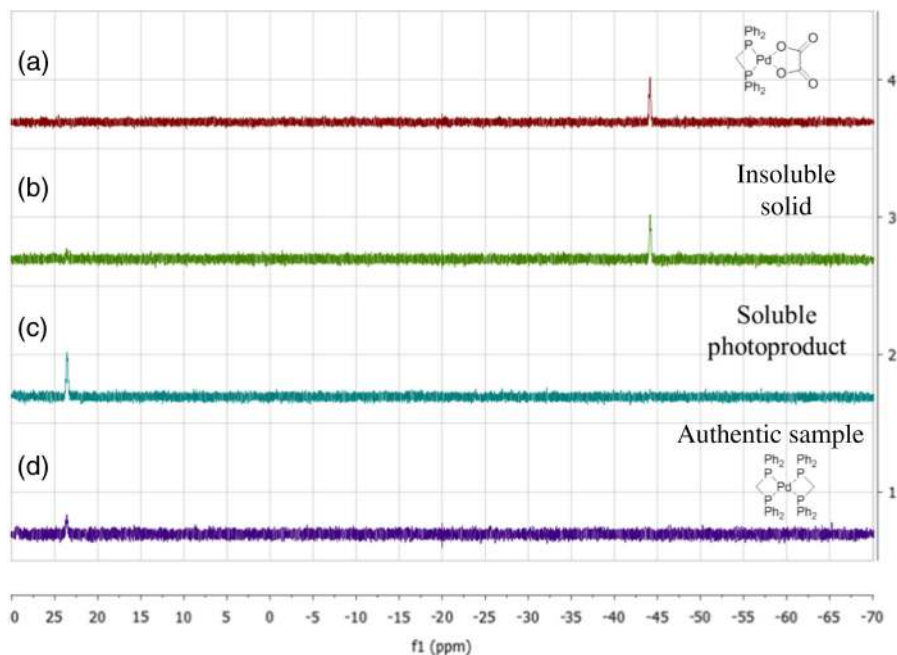


Fig. 15 ^{31}P NMR: (a) $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) unexposed. (b) Insoluble solid from hexanes extraction. (c) Soluble photoproduct from hexanes extraction. (d) Authentic sample of $(\text{Ph}_2\text{EtP})_4\text{Pd}$.

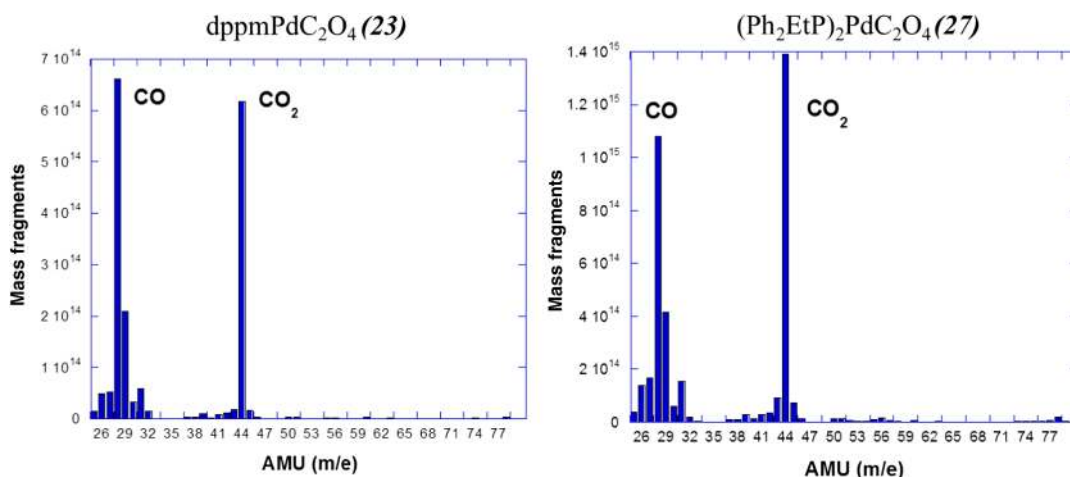


Fig. 16 Outgassing data using a 2000 eV electron gun and a mass spectrometer. Both $\text{dppmPdC}_2\text{O}_4$ (**23**) and $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) show outgassing of CO_2 .

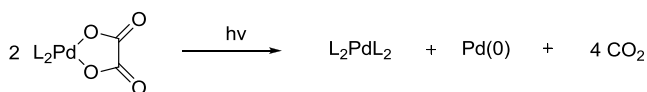


Fig. 17 Proposed photoreaction for $\text{dppmPdC}_2\text{O}_4$ (**23**) and $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**). The photoreaction is consistent with all experimental data.

Based on the experimental data, we propose the following photoreaction: irradiation of $\text{L}_2\text{PdC}_2\text{O}_4$ results in the reductive elimination of 2 equivalents of CO_2 and a reactive intermediate L_2Pd . The reactive intermediate readily reacts with another $\text{L}_2\text{PdC}_2\text{O}_4$ molecule and extract its ligands to form a zerovalent L_2PdL_2 complex, leaving behind a naked Pd(0) metal atom and 2 equivalents CO_2 (Figs. 9 and 17). This photoreaction is consistent with all experimental data and with the literature, which show similar results.^{10,11} It also explains the positive-tone behavior of this resist system as the nonpolar photoproduct would be very soluble in the nonpolar developer. No difference was found in the photomechanism when comparing the bidentate ligand in $\text{dppmPdC}_2\text{O}_4$ (**23**) versus the monodentate ligands in $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**). The creation of a bent, and thus more reactive, L_2Pd fragment in bidentate $\text{L}_2\text{MC}_2\text{O}_4$ complexes shows no correlation with sensitivity to EUV.

3 Conclusions

We have investigated the EUV photoreactivity of mononuclear platinum and palladium complexes. The preliminary results from COD platinum and palladium complexes showed the need for a photoactive ligand and lithographic performance was discovered for $\text{L}_2\text{M}(\text{CO}_3)$ and $\text{L}_2\text{M}(\text{C}_2\text{O}_4)$ resist systems. A series of $\text{L}_2\text{M}(\text{C}_2\text{O}_4)$ complexes were synthesized to investigate sensitivity with respect to molecular weight and to better understand the photomechanism. We used E_0 (mJ/cm^2) to compare the resist performance, and we demonstrated that using palladium as a core metal offers faster resists than when platinum is used. The $\text{L}_2\text{M}(\text{C}_2\text{O}_4)$ resist system shows no correlation between sensitivity and molecular weight. Seeking to improve the lithographic performance of the $\text{L}_2\text{Pd}(\text{C}_2\text{O}_4)$ resist system we sought to understand the underlying photomechanism. The photoproduct was isolated and identified for both $\text{dppmPdC}_2\text{O}_4$ (**23**) and $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) and a possible photoreaction was proposed for both compounds, consistent with all experimental data.

4 Experimental Methods

4.1 General

All reactions were carried out under an inert atmosphere. Platinum metal was purchased from Alfa Aesar and palladium(II) chloride were purchased from Sigma–Aldrich. *cis,cis*-1,5-COD was purchased from Sigma–Aldrich and the phosphine ligands were purchased from Strem and Sigma–Aldrich. All other reagents were purchased from Sigma–Aldrich. All reagents were used as received unless otherwise specified. Allylpalladium(II) chloride dimer (**8**) was purchased from Sigma–Aldrich.

4.2 Instruments

A Bruker 400 NMR spectrometer was used to measure ^1H and ^{31}P NMR spectra using tetramethyl silane and KH_2PO_4 as an internal reference, respectively. All chemical shifts are reported as parts per million.

4.3 Resist Formulation and Imaging

Resist formulations were made by dissolving solids in 1:2 acetonitrile/ethyl lactate or 1:2 methylene chloride/PMA and filtering through a $0.2 \mu\text{m}$ poly tetra fluoro ethylene (PTFE) filter. Unless otherwise specified, all formulations were spin-coated onto a custom underlayer (cross-linked hydroxyethyl methacrylate/methyl methacrylate copolymers) on 4-in. silicon wafers. About 40- to 60-nm thick resist films were made by adjusting spin-speed and formulation concentration. Resist films were then exposed with 13.5-nm radiation and developed with a mixture of MIBK and toluene, MIBK and hexanes, or dichloromethane and hexanes. Exposures were performed at PSI on the XIL-II beamline using interference lithography.

4.4 Scanning Electron Microscope Metrology

Scanning electron microscope (SEM) micrographs were collected at PSI on a Zeiss Supra VP55. Accelerating voltage was set between 1 and 2 KeV and the working distance was 4 mm. All images were at either 150,000 \times or 200,000 \times magnification.

4.5 Line Edge Roughness Analysis

All LER values were obtained from the analysis of the SEM micrographs in SuMMIT Lithography Image Analysis software.

4.6 Photomechanistic Studies

About 100-mg white solid of $\text{dppmPdC}_2\text{O}_4$ (**23**) or $(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**) was put on a watch glass and the solid was exposed using a OAI near-UV 500 W exposure tool, given a dose of $30 \text{ J}/\text{cm}^2$. The exposure was carried out in air. The copper-colored, exposed solid was then dissolved in 20-mL toluene ($\text{dppmPdC}_2\text{O}_4$ (**23**)) or 20-mL hexanes ($(\text{Ph}_2\text{EtP})_2\text{PdC}_2\text{O}_4$ (**27**)) and stirred for several hours at room temperature. The suspension was then filtered, and the filtrate concentrated to yield a solid. Both the filtered solid and filtrate were characterized by ^1H and ^{31}P NMR. In each case, the possibility of a hydride forming as a photoproduct was investigated. However, no peaks occurred in either the ^1H or ^{31}P NMR where hydride peaks usually appear.

$\text{Ag}_2\text{C}_2\text{O}_4$. AgNO_3 (11.2 g, 66 mmol) dissolved in distilled water. An aqueous solution of $\text{Na}_2\text{C}_2\text{O}_4$ (4 g, 30 mmol) was added to the solution. $\text{Ag}_2\text{C}_2\text{O}_4$ precipitates immediately from the solution and the solid is collected by filtration and washed with ethanol before it is dried in vacuum. [$\text{Ag}_2\text{C}_2\text{O}_4$] (8.92 g, 98%).

Dichloro(1,5-cyclooctadiene)platinum(II) ((COD) PtCl_2).²¹ Platinum metal (14.4 mmol) was dissolved in aqua regia (25 mL) at 60°C overnight. The clear, pink solution was then transferred to a beaker on a hot plate. An equal volume of HCl (25 mL) was added and NO_2 gas was monitored as the solution evaporated. More HCl can be added if necessary.

When no remaining NO₂ gas can be seen, the solution was evaporated almost to dryness. 40 mL distilled water and 30 mL 2-propanol was added to the now dark-red solution. COD (49 mmol) and SnCl₂ · H₂O (14.4 mmol) were then added and the solution was stirred at room temperature for 5 days. A yellow solid was filtered off and washed with H₂O and ethanol. The solid was dried in vacuum to yield [Pt(COD)Cl₂] (4.91 g, 91%). Recrystallization from dichloromethane. ¹H NMR (400 MHz, chloroform-*d*) δ 5.77 to 5.41 (t, *J*_{Pt} = 34.7, 32.3 Hz, 4H), 2.88 to 2.48 (m, 4H), 2.40 to 2.16 (m, 4H).

Dichloro(1,5-cyclooctadiene)palladium(II) ((COD)PdCl₂) (**6**).²² PdCl₂ (22.6 mmol) was suspended in methanol. COD (67.7 mmol) was added dropwise to the suspension. Suspension was stirred at room temperature for 48 h. A yellow solid was filtered off and washed with methanol to yield [Pd(COD)Cl₂] (6.25 g, 97%). The product is recrystallized from dichloromethane. ¹H NMR (400 MHz, chloroform-*d*) δ 6.38 to 6.21 (m, 4H), 2.89 (qd, *J* = 11.7, 11.0, 4.3 Hz, 4H), 2.55 (dd, *J* = 9.2, 7.6 Hz, 4H).

4.7 General Synthetic Procedure for Compounds 1 to 5

The general procedure was adapted from procedures found in the chemistry literature.²³ Copper(I) iodide (1.96 equiv) was suspended in dry diethyl ether and cooled to -20°C under nitrogen. The appropriate Grignard reagent (4.48 equiv) was added rapidly to give a yellow precipitate at first which turned into a clear, pale, and yellow solution. Pt(COD)Cl₂ (1 equiv) was then added to form a dark suspension, which was stirred at room temperature for 30 min. The mixture was then cooled to -20°C and hydrolyzed with a few drops of water. The mixture was allowed to warm up to room temperature before an equal volume of water and diethyl ether was added and the mixture stirred for further 15 min. After filtration, the diethyl ether layer was extracted and dried over Na₂O₃, before evaporated to dryness to yield a white solid. The product was used without any further purification. Yields improved greatly when dichloromethane was used as a solvent.

(COD)Pt(CH₃)₂ (**1**). MeLi (3.57 mL, 6 mmol) was used as the Grignard reagent. [(COD)Pt(CH₃)₂] (370 mg, 82%) collected as a white solid. ¹H NMR (400 MHz, chloroform-*d*) δ 4.91 to 4.69 (t, *J*_{Pt} = 19.3 Hz, 4H), 2.41 to 2.19 (m, 8H), 0.89 to 0.56 (t, *J*_{Pt} = 41.1 Hz, 6H).

(COD)Pt(CH₂CH₃)₂ (**2**). Ethylmagnesium bromide (1 mL, 3 mmol) was used as the Grignard reagent. [(COD)Pt(CH₂CH₃)₂] (110 mg, 45%) was obtained as a white solid. ¹H NMR (400 MHz, chloroform-*d*) δ 5.66 to 5.47 (m, 4H), 4.49 (dd, *J*_{Pt} = 5.1, 2.4 Hz, 4H), 2.40 (dt, *J*_{Pt} = 14.3, 7.8 Hz, 4H), 2.01 (dt, *J*_{Pt} = 14.8, 7.9 Hz, 4H), 1.16 (t, *J*_{Pt} = 7.6 Hz, 6H).

(COD)Pt(CH₂CH=CH₂)₂ (**3**). Allylmagnesium bromide (4.1 mL, 4.1 mmol) was used as the Grignard reagent. [(COD)Pt(CH₂CH=CH₂)₂] (290 mg, 56%) was obtained as a white solid. ¹H NMR (400 MHz, chloroform-*d*) δ 5.18 to 4.94 (m, 4H), 3.77 (d, *J* = 10.8 Hz, 2H), 2.34 (s, 8H), 2.17 to 2.06 (m, 4H), 1.22 (s, 4H).

(COD)Pt((CH₃)₃CH₂)₂ (**4**). Butylmagnesium bromide (2.5 mL, 6 mmol) was used as the Grignard reagent. [(COD)Pt((CH₃)₃CH₂)₂] (330 mg, 59%) was obtained as

a white solid. ¹H NMR (400 MHz, chloroform-*d*) δ 4.87 to 4.68 (m, 4H), 2.31 to 2.17 (m, 8H), 1.45 to 1.40 (m, 4H), 1.30 to 1.23 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 6H).

(COD)Pt(CH₂Ph)₂ (**5**). Benzylmagnesium chloride (1.8 mL, 1.8 mmol) was used as the Grignard reagent. [(COD)Pt(CH₂Ph)₂] (220 mg, 92%) was obtained as a white solid. ¹H NMR (400 MHz, chloroform-*d*) δ 7.18 to 6.89 (m, 10H), 4.74 to 4.42 (t, *J*_{Pt} = 20.2 Hz, 4H), 3.04 to 2.73 (t, *J*_{Pt} = 56.9 Hz, 4H), 2.26 to 2.05 (m, 8H).

(COD)PtI₂ (**7**).²⁴ CODPtCl₂ (120 mg, 0.32 mmol) is readily converted to CODPtI₂ by adding a slight excess KI (110 mg, 0.67 mmol) to the dichloride suspended in acetone. The solution immediately turned yellow and the solvent was removed by rotary evaporation. The residue was collected on a frit and washed three times with distilled water. [CODPtI₂] (0.17 g, 94%) was collected as a solid and dried in vacuum. ¹H NMR (400 MHz, chloroform-*d*) δ 5.91 to 5.56 (t, *J*_{Pt} = 33.0 Hz, 4H), 2.43 (dd, *J*_{Pt} = 9.7, 5.0 Hz, 4H), 2.06 to 1.73 (m, 4H).

(PMe₃)PtCl₂ (**9**). The general procedure was adapted from procedures found in the chemistry literature.²⁵ To a solution of CODPtCl₂ (1.34 mmol) in toluene (10 mL), trimethylphosphine (2.67 mmol) was added dropwise. Solution stirred at room temperature for 1 h. The solvent was removed by rotary evaporation. [(PMe₃)PtCl₂] (460 mg, 98%) was collected as a white solid. ¹H NMR (400 MHz, chloroform-*d*) δ 1.75 (m, 6H) (*d*²*J*_{(P-H)}} = 10.9 Hz, ³*J*_{(Pt-H)}} = 35.4 Hz).

4.8 Synthetic Procedure for Compounds 10 to 12

The general procedure was adapted from procedures found in the chemistry literature.^{12,20} (COD)PdCl₂ (1 equiv) was dissolved in dichloromethane. The appropriate phosphine (1 equiv) was dissolved in dichloromethane added dropwise to the solution. A color is observed in the solution after addition. The colors vary with the phosphine added. The solution was stirred for 1 h and NaN₃ (10 equiv) was then added. The solution was stirred overnight and the unreacted NaN₃ and NaCl was filtered off and washed with dichloromethane. The combined filtrates were carefully evaporated almost to dryness. Ethyl ether was added to precipitate out the product. The product was used without further purification.

dppmPd(N₃)₂ (**10**). 1,1-Bis(diphenylphosphino)methane was used as the phosphine ligand and dppmPdCl₂ (680 mg, 1.21 mmol) was reacted with NaN₃ (790 mg, 12.1 mmol) to yield [dppmPd(N₃)₂] (420 mg, 63%) as pink crystals. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.81 (s, 6H), 7.61 to 7.45 (m, 14H), 4.86 (s, 2H). *ν*(N₃)2024 cm⁻¹.

(PEt₃)₂Pd(N₃)₂ (**11**). Triethylphosphine (5.3 mL, 7 mmol) was used as the phosphine ligand. [(PEt₃)₂Pd(N₃)₂] (680 mg, 45%) was obtained as white crystals. ¹H NMR (400 MHz, DMSO-*d*₆) δ 1.81 (dq, *J* = 9.7, 7.6 Hz, 12H), 1.07 (dt, *J* = 17.5, 7.6 Hz, 18H). *ν*(N₃)2036 cm⁻¹.

(Me₃P)₂Pd(N₃)₂ (**12**). Trimethylphosphine was used as the phosphine ligand and (Me₃P)₂PdCl₂ (460 mg, 1.4 mmol) was reacted with NaN₃ (1.8 g, 28 mmol) to yield [(Me₃P)₂Pd(N₃)₂] (470 mg, 98%) as white solids. ¹H NMR (400 MHz, DMSO-*d*₆) δ 1.62 to 1.44 (t, *J* = 5.5 Hz, 18H). *ν*(N₃)2039 cm⁻¹.

4.9 Synthetic Procedure for Compounds 13 to 15

The general procedure was adapted from procedures found in the chemistry literature.^{16,19} To a suspension of PdCl₂ (1 equiv) in acetonitrile the appropriate ligand RNH₂ (2 equiv) was added dropwise. The mixture was refluxed for 3 h and the now clear solution was concentrated by rotary evaporation until crystals started to precipitate out. The crystals were filtered off and dried in vacuum. The yellow solids were used without any further purification. To a suspension of (RNH₂)₂PdCl₂ (1 equiv) in water, an aqueous solution of AgNO₃ was added dropwise. The suspension was stirred in darkness overnight. AgCl was filtered off and NaN₃ (20 equiv) was then added. The suspension was again stirred overnight. Excess NaN₃ was filtered off and the volume reduced. The product was filtered off and dried in vacuum. Unfortunately, all compounds were too insoluble to be analyzed by NMR and were unsuccessfully used as photoresists.

(PhCH₂NH₂)₂Pd(N₃)₂ (**13**). (PhCH₂NH₂)₂PdCl₂ (430 mg, 1 mmol) was reacted with AgNO₃ (370 mg, 2.2 mmol) and NaN₃ (1.8 g, 27 mmol) and [(PhCH₂NH₂)₂Pd(N₃)₂] (340 mg, 77%) was obtained as a white solid. $\nu(\text{N}_3)$ 2067 cm⁻¹.

((CH₃)₃CNH₂)₂Pd(N₃)₂ (**14**). ((CH₃)₃CNH₂)₂PdCl₂ (500 mg, 1.6 mmol) was reacted with AgNO₃ (530 mg, 3.1 mmol) and NaN₃ (2 g, 31 mmol) and [((CH₃)₃CNH₂)₂Pd(N₃)₂] (400 mg, 77%) was obtained as a white solid. $\nu(\text{N}_3)$ 2053 cm⁻¹.

((CH₃)₂CHNH₂)₂Pd(N₃)₂ (**15**). ((CH₃)₂CHNH₂)₂PdCl₂ (620 mg, 2 mmol) was reacted with AgNO₃ (710 mg, 4.2 mmol) and NaN₃ (2.7 g, 42 mmol) and [((CH₃)₂CHNH₂)₂Pd(N₃)₂] (640 mg, 98%) was obtained as a white solid. $\nu(\text{N}_3)$ 2031 cm⁻¹.

4.10 Synthetic Procedure for Compounds 16 to 19

All compounds were prepared according modified literature procedures.¹² (COD)PtCl₂ or (COD)PdCl₂ (1 equiv) was dissolved in dichloromethane. The appropriate phosphine (1 equiv) was dissolved in dichloromethane and added dropwise to the solution. A color change should be observed in the solution after addition. The colors vary with the phosphine added. Solution was stirred for 15 min before adding Ag₂CO₃ (2.2 equiv). The mixture was stirred at room temperature in darkness for 48 h. The mixture was then filtered and the filtrate concentrated. Addition of hexanes gave the product as a precipitate.

dppePtCO₃ (**16**). 1,2-Bis(diphenylphosphino)ethane (530 mg, 1.3 mmol) was used as the phosphine ligand. [dppePtCO₃] (310 mg, 35%) was obtained as beige solid. ¹H NMR (400 MHz, chloroform-*d*) δ 8.03 to 7.31 (m, 20H), 2.48 to 2.20 (dt, *J* = 7.0, 10.9, 18.5 Hz, 4H). $\nu(\text{CO})$ 1487, 1270, 982, and 830 cm⁻¹.

dppmPtCO₃ (**17**). 1,1-Bis(diphenylphosphino)methane (520 mg, 1.3 mmol) was used as the phosphine ligand. [dppmPtCO₃] (190 mg, 22%) was obtained as beige solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.02 to 7.40 (m, 20H), 5.33 (q, *J* = 12.6 Hz, 2H). $\nu(\text{CO})$ 1430, 1103, 995, and 893 cm⁻¹.

dppePdCO₃ (**18**). 1,2-Bis(diphenylphosphino)ethane (700 mg, 1.8 mmol) was used as the phosphine ligand. [dppePdCO₃] (190 mg, 19%) was obtained as beige solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.12 to 7.37 (m, 20H), 3.17 to 2.68 (t, *J* = 26.3, 52.8 Hz, 4H). $\nu(\text{CO})$ 1465, 1267, 999, and 817 cm⁻¹.

dppmPdCO₃ (**19**). 1,1-Bis(diphenylphosphino)methane (670 mg, 1.8 mmol) was used as the phosphine ligand. [dppmPdCO₃] (800 mg, 83%) was obtained as beige solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.06 to 7.41 (m, 20H), 4.92 (t, *J* = 11.5 Hz, 2H). $\nu(\text{CO})$ 1433, 1103, 995, and 840 cm⁻¹.

4.11 Synthetic Procedure for Compounds 20 to 27

All compounds were prepared according to modified literature procedures.¹² (COD)PtCl₂ or (COD)PdCl₂ (1 equiv) was dissolved in dichloromethane. The appropriate phosphine (1 equiv) was dissolved in dichloromethane and added dropwise to the solution. A color change should be observed in the solution after addition. The colors vary with the phosphine added. The solution was stirred for 15 min before adding Ag₂C₂O₄ (2.5 equiv). Additional Ag₂C₂O₄ was added then what is reported in the literature to insure higher yields. The mixture was stirred at room temperature, in darkness, for 4 to 7 days. The mixture was then filtered and the filtrate concentrated. Addition of ethyl ether gave the product as a precipitate.

dppePtC₂O₄ (**20**). 1,2-Bis(diphenylphosphino)ethane (190 mg, 0.5 mmol) was used as the phosphine ligand. [dppePtC₂O₄] (35 mg, 11%) was obtained as a white solid. ¹H NMR (400 MHz, methylene chloride-*d*₂) δ 8.00 to 7.40 (m, 20H), 2.5 to 2.21 (dt, *J* = 8.0, 11.0, and 18.6 Hz, 4H). $\nu(\text{CO})$ 1699, 1676, and 1354 cm⁻¹.

dppmPtC₂O₄ (**21**). 1,1-Bis(diphenylphosphino)methane (200 mg, 0.53 mmol) was used as the phosphine ligand. [dppmPtC₂O₄] (290 mg, 82%) was obtained as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.99 to 7.44 (m, 20H), 5.28 (t, *J* = 12.0 Hz, 2H). $\nu(\text{CO})$ 1696, 1676, 1661, and 1352 cm⁻¹.

dppePdC₂O₄ (**22**). 1,2-Bis(diphenylphosphino)ethane (280 mg, 0.7 mmol) was used as the phosphine ligand. [dppePdC₂O₄] (240 mg, 58%) was obtained as a white solid. ¹H NMR (400 MHz, chloroform-*d*) δ 7.90 to 7.36 (m, 20H), 2.65 (d, *J* = 20.7 Hz, 4H). $\nu(\text{CO})$ 1699, 1661, and 1369 cm⁻¹.

dppmPdC₂O₄ (**23**). As the most successful photoresist, the synthetic procedure of dppmPdC₂O₄ has been modified and improved extensively. The most important improvement made to the synthesis was to isolate and purify the intermediate dppmPdCl₂ and then redissolve this in dichloromethane before adding the Ag₂C₂O₄. This ensured higher purification of the product. To a solution of CODPdCl₂ (1 g, 3.5 mmol) in a minimum amount of dichloromethane (120 mL) was 1,1-bis(diphenylphosphino)methane (1.35 g, 3.5 mmol), also dissolved in a minimum amount of dichloromethane (5 mL), added dropwise. After 5 min of stirring, the solution became cloudy and [dppmPdCl₂] (1.4 g, 70%) could be filtered off after 30 min of stirring and dried in vacuum. Recrystallization from dichloromethane. To a solution of dppmPdCl₂ (510 mg, 0.9 mmol) in dichloromethane, Ag₂C₂O₄ (690 mg, 2.3 mmol) was added. Mixture stirred for 6 days at room temperature, filtered and the filtrate reduced and the product precipitated out by ethyl ether as described above. [dppmPdC₂O₄] (480 mg, 91%) was obtained as a white solid. Recrystallization from dichloromethane/acetone. Anal. Found: C, 55.79; H, 3.74; Pd, 18.8. C₂₇H₂₂O₄P₂Pd calc.: C, 56.03; H, 3.83; Pd, 18.39%. ³¹P NMR (162 MHz, DMSO) δ -44.12. ¹H NMR (400 MHz,

DMSO- d_6) δ 7.92 to 7.44 (m, 20H), 4.99 (t, $J = 12.0$ Hz, 2H). $\nu(\text{CO})$ 1696, 1664, 1643, and 1361 cm^{-1} .

$(\text{PEt}_3)_2\text{PtC}_2\text{O}_4$ (**24**). Triethylphosphine (0.82 mL, 1.1 mmol) was used as the phosphine ligand. $[(\text{PEt}_3)_2\text{PtC}_2\text{O}_4]$ (200 mg, 73%) was obtained as a white solid. ^1H NMR (400 MHz, chloroform- d) δ 1.89 (q, $J = 16.0, 11.7$ Hz, 12H), 1.17 (dtd, $J = 15.9, 7.6, 3.9$ Hz, 18H). $\nu(\text{CO})$ 1698, 1675, 1664, and 1356 cm^{-1} .

$(\text{PEt}_3)_2\text{PdC}_2\text{O}_4$ (**25**). Triethylphosphine was used as the phosphine ligand. $\text{Ag}_2\text{C}_2\text{O}_4$ (470 mg, 1.6 mmol) was added to $(\text{PEt}_3)_2\text{PdCl}_2$ (430 mg, 1 mmol) to yield $[(\text{PEt}_3)_2\text{PdC}_2\text{O}_4]$ (390 mg, 87%) as a white solid. ^1H NMR (400 MHz, chloroform- d) δ 1.88 (dq, $J = 9.7, 7.5$ Hz, 12H), 1.20 (dt, $J = 17.7, 7.6$ Hz, 18H). $\nu(\text{CO})$ 1699, 1664, 1647, and 1358 cm^{-1} .

$(\text{PMePh}_2)_2\text{PdC}_2\text{O}_4$ (**26**). Methylidiphenylphosphine (0.33 mL, 1.8 mmol) was used as the phosphine ligand. $[(\text{PMePh}_2)_2\text{PdC}_2\text{O}_4]$ (490 mg, 93%) was obtained as a white solid. ^1H NMR (400 MHz, DMSO- d_6) δ 7.60 to 7.22 (m, 20H), 1.97 to 1.78 (d, $J = 10.8$ Hz, 6H). $\nu(\text{CO})$ 1693, 1672, 1647, and 1359 cm^{-1} .

$(\text{PEtPh}_2)_2\text{PdC}_2\text{O}_4$ (**27**). Same synthetic procedure as applied for $\text{dppmPdC}_2\text{O}_4$ (**23**). Ethyldiphenylphosphine (1 mL, 4.9 mmol) used as the phosphine ligand. $[(\text{PEtPh}_2)_2\text{PdCl}_2]$ (1.43 g, 97%) was recrystallized from dichloromethane/acetone. $(\text{PEtPh}_2)_2\text{PdCl}_2$ (1 g, 1.65 mmol) was dissolved in a minimum amount of dichloromethane (180 mL) and $\text{Ag}_2\text{C}_2\text{O}_4$ (2.5 g, 8.3 mmol) was added and mixture stirred for 3 days. $[(\text{PEtPh}_2)_2\text{PdCl}_2]$ (970 mg, 94%) was obtained as a white solid. Recrystallization from dichloromethane/acetone. Anal. Found: C, 57.61; H, 4.85; Pd, 16.7. $\text{C}_{30}\text{H}_{30}\text{O}_4\text{P}_2\text{Pd}$ calc.: C, 57.84; H, 4.85; Pd, 17.08%. ^{31}P NMR (162 MHz, methylene chloride- d_2) δ 29.89. ^1H NMR (400 MHz, methylene chloride- d_2) δ 7.60 to 7.25 (m, 20H), 2.22 (dq, $J = 9.2, 7.3$ Hz, 4H), 0.93 (dt, $J = 18.2, 7.4$ Hz, 6H). $\nu(\text{CO})$ 1693, 1673, 1652, and 1349 cm^{-1} .

4.12 Synthesis of Authentic Photoproducts

These compounds are air and moisture sensitive and were difficult to synthesize without causing decomposition. This led to impurities in the ^{31}P NMR spectra for both dppm_2Pd and $(\text{Ph}_2\text{EtP})_4\text{Pd}$.

dppm_2Pd .²⁶ dppm (540 mg, 1.4 mmol) was added to a solution of dppmPdCl_2 (800 mg, 1.4 mmol) in ethanol. NaBH_4 (110 mg, 2.8 mmol) was added slowly, and the solution stirred for 30 min. The orange product was filtered off and washed with ethanol. $[\text{dppm}_2\text{Pd}]$ (350 mg, 28%). ^{31}P NMR (162 MHz, DMSO- d_6) δ 23.57.

$(\text{Ph}_2\text{EtP})_4\text{Pd}$.²⁷ CODPdCl_2 (600 mg, 2.10 mmol) was suspended in methanol (100 mL) and reacted with a methanol solution of KOH (240 mg, 4.2 mmol) and stirred for 30 min at room temperature. The slurry was then reacted with ethyldiphenylphosphine (0.87 mL, 4.2 mmol) and stirred for 1 h at room temperature. The product was filtered and washed with water and methanol to give product as a yellow solid. $[(\text{Ph}_2\text{EtP})_4\text{Pd}]$ (50 mg, 2.5%). ^{31}P NMR (162 MHz, methylene chloride- d_2) δ 32.68.

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