Precursors for Focused Electron Beam Induced Deposition (FEBID) of Nanostructures

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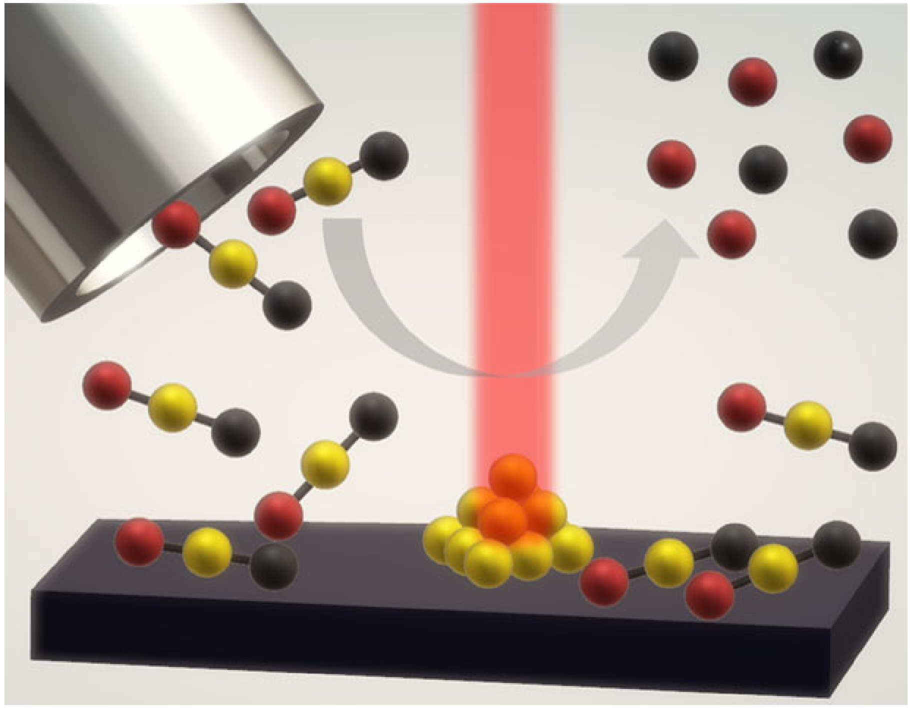
FEBID* of Metal Nanostructures

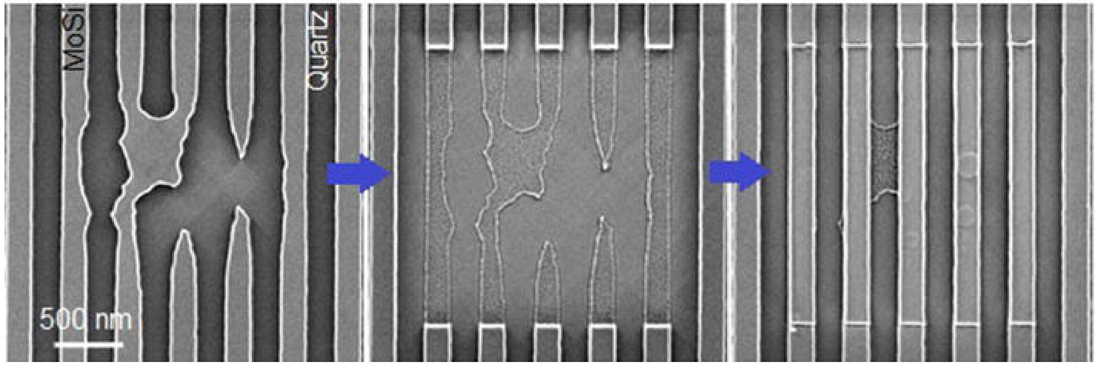
***Focused Electron Beam Induced Deposition**



Precursor design for FEBID: Spencer, Rosenberg, Barclay, Wu, McElwee-White, Fairbrother, *Appl. Phys. A.*, **2014**, *117*, 163
Carden, Lu, Spencer, Fairbrother, McElwee-White, *MRS Commun.*, **2018**, *8*, 343

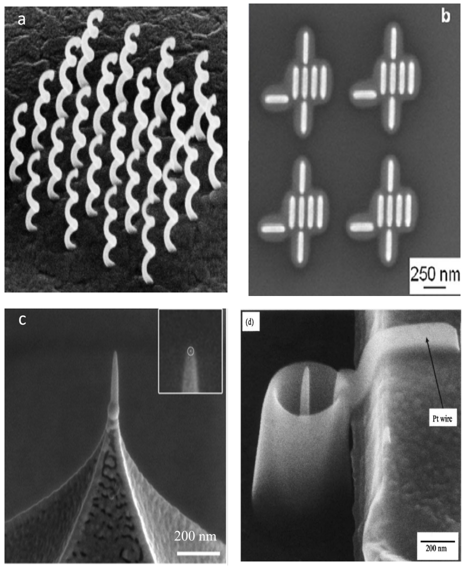
FEBID Applications

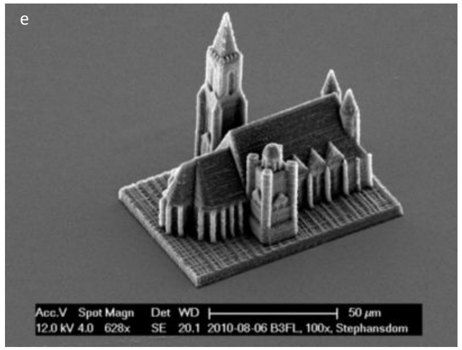
Industrial Applications
- Photomask repair
- Circuit edit

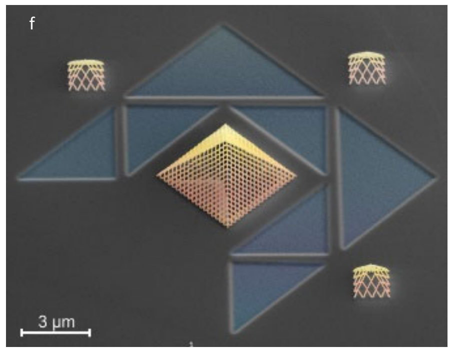


Bret, *Appl. Phys. A: Mater. Sci. Process.* **2014**, *117*, 1607

Academic Research
- Diodes
- Photonic crystals
- Probes
- Electron sources
- Conducting wires
- Seeds for nanotube growth
- Nanosoldering







(a) Silica/Au nanoplasmonic array
(b) Fe nanowires
(c) Pt AFM tip
(d) Pt source for I-V measurements
(e) Stephansdom model
(f) Louvre pyramid model

Images from the work of Acar, Wanzenboeck, Brown, Murakami, Plank, Winkler

FEBID of Metal Nanostructures – What's Important

Precursor decomposition: electron bombardment
thermal (surface)

Important considerations:

1. Composition of deposited material
   - Clean ligand loss upon e^- attachment or surface binding
2. Precursor volatility
   - Required for gas phase delivery
3. Thermal stability
   - Precursor decomposition temperature must be high to avoid CVD

Precursor design for FEBID: Spencer, Rosenberg, Barclay, Wu, McElwee-White, Fairbrother, *Appl. Phys. A.*, **2014**, *117*, 163
Carden, Lu, Spencer, Fairbrother, McElwee-White, *MRS Commun.*, **2018**, *8*, 343

Why Use CVD Precursors for FEBID?

1. They are commercially available

2. They are volatile

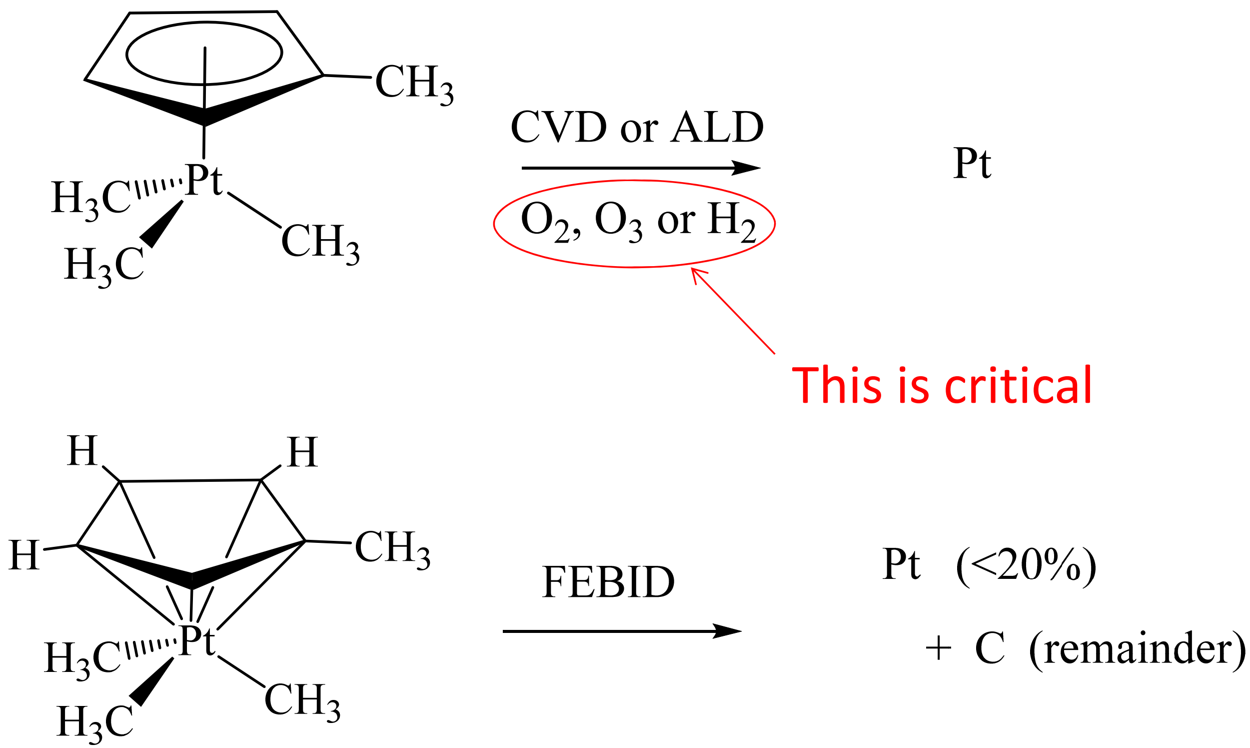
3. They have been demonstrated to decompose to some desired material…

…under some set of deposition conditions

Precursor design for CVD: McElwee-White, *Dalton Trans.* **2006**, 5327
McElwee-White, Koller, Kim, Anderson, *ECS Transactions,* **2009**, *25,* 161

Precursor design for FEBID: Spencer, Rosenberg, Barclay, Wu, McElwee-White, Fairbrother, *Appl. Phys. A.*, **2014**, *117*, 1631
Carden, Lu, Spencer, Fairbrother, McElwee-White, *MRS Commun.*, **2018**, *8*, 343

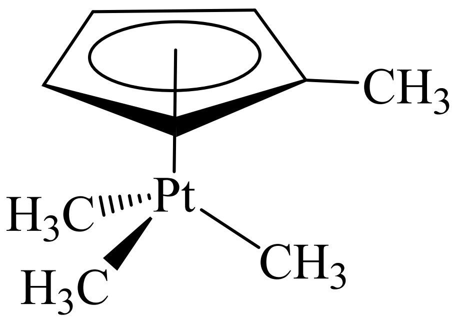
Why Not Use CVD Precursors for FEBID?

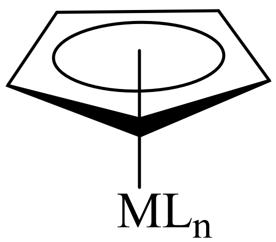


Xue, Strouse, Shuh, Knobler, Kaesz, Hicks, Williams, *J. Am. Chem. Soc.*, **1989**, *111*, 8779
Botman, Hesselberth, Mulders, *Microelectron. Eng.* **2008**, *85*, 1139

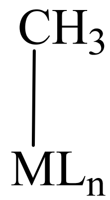
Thinking About Ligands

Design: What do we learn from Cp’PtMe$_3$?

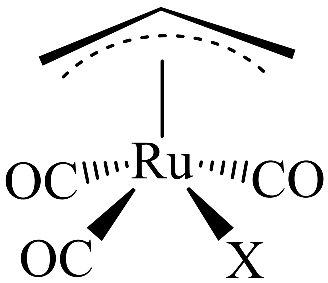




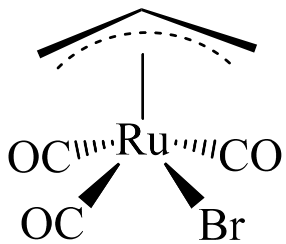
η^5–Cp

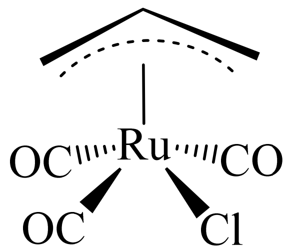


κ^1–alkyl



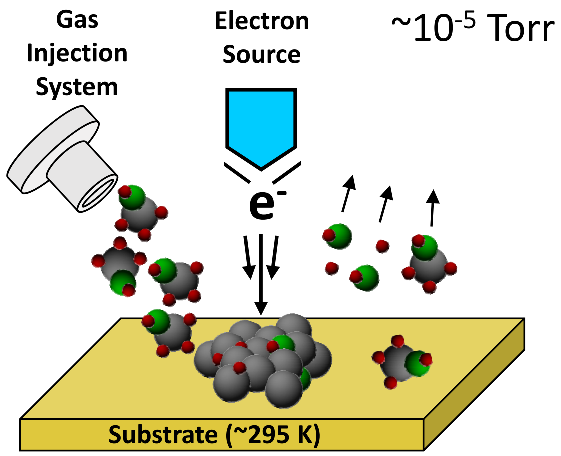
Test Precursors:



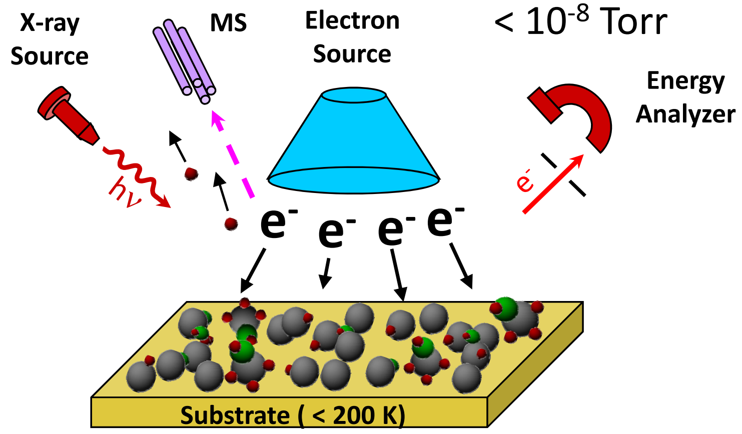


Applying a UHV Surface Science Approach

Typical FEBID Experiment



UHV Surface Science Approach

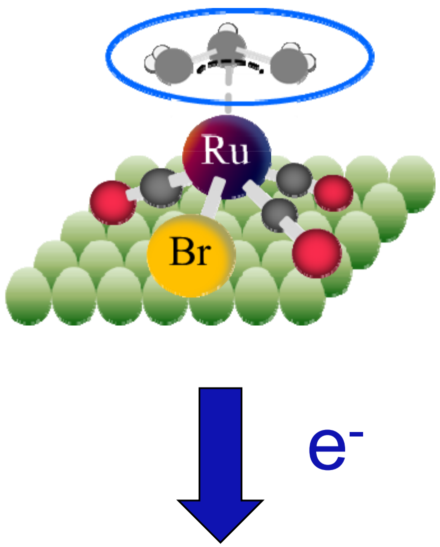


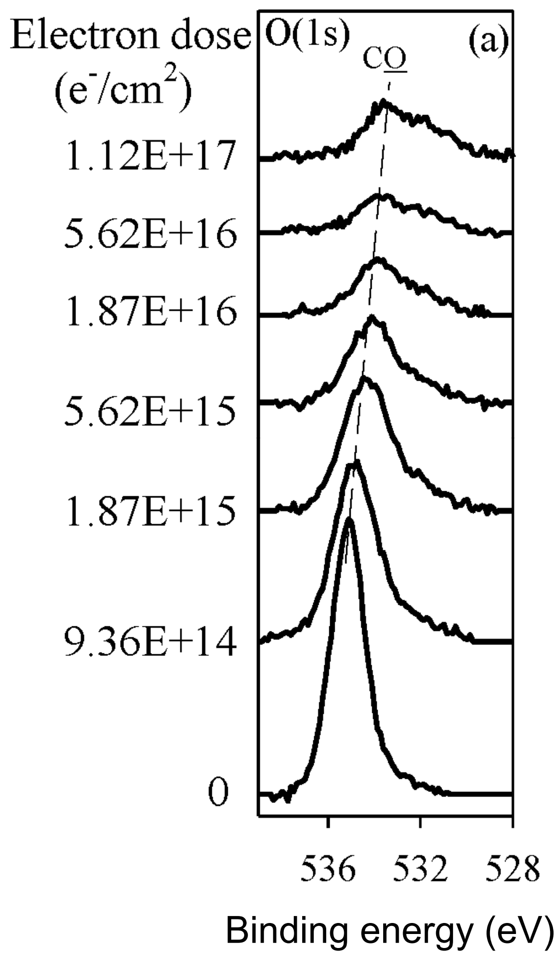
Graphic (and Experiments): Howard Fairbrother

- Constant partial pressure of precursor
- Substrate at room temperature
- Focused electron beam (20 – 200 KeV)
- Size scale: ~ nm^3
- Analytical techniques: SEM, EDX
- Information obtained: composition and dimensions of deposited structure

- Fixed initial coverage of precursor molecules
- Substrate cooled to < 200K
- Defocused low energy electron beam (0.5 KeV)
- Size scale: ~ cm^2
- Analytical techniques: XPS, MS
- Information obtained: kinetic and mechanistic details of precursor decomposition

Experiment: Fate of CO

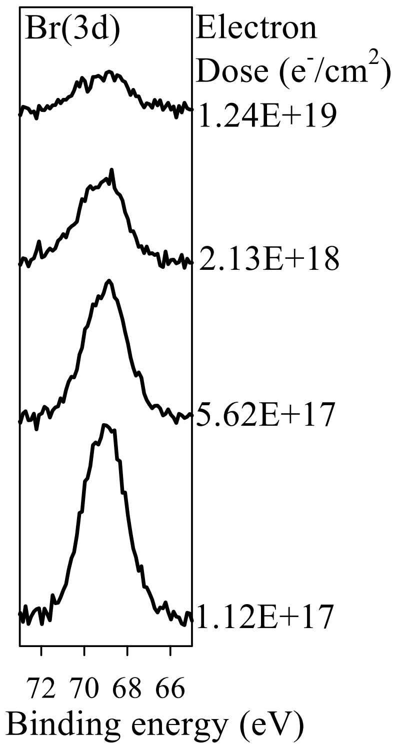


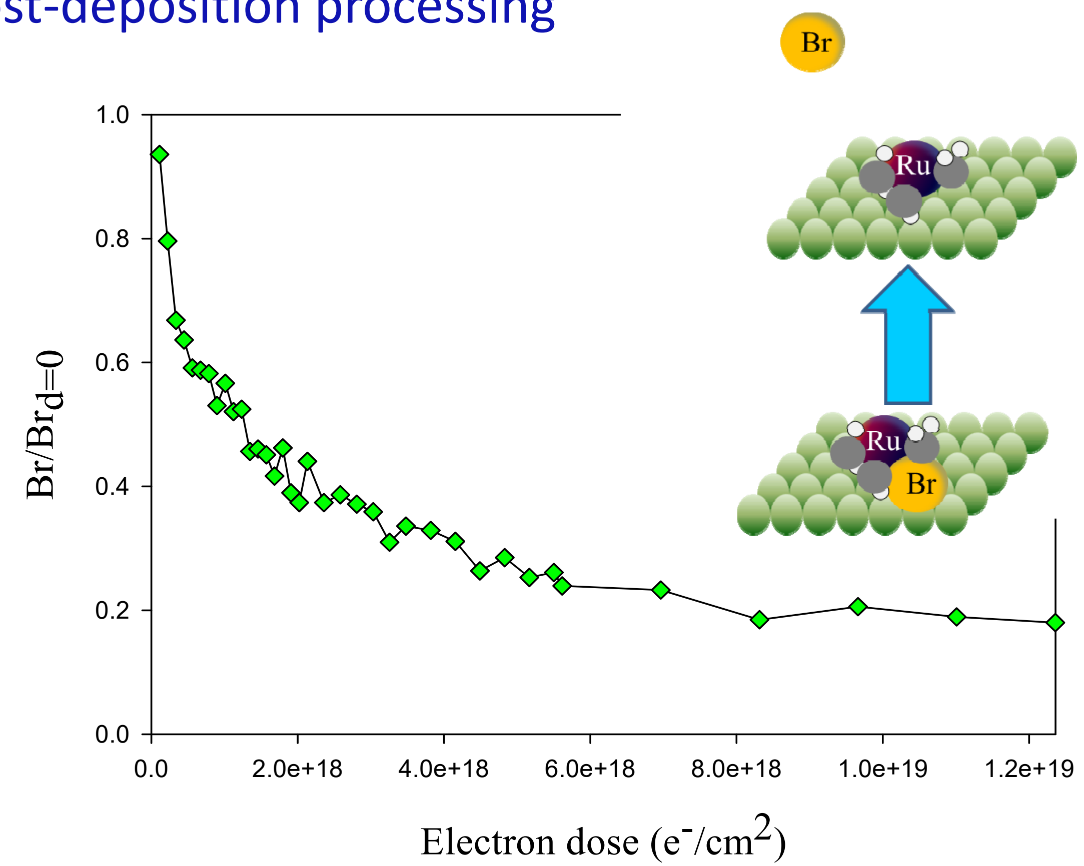


Spencer, Brannaka, Barclay, McElwee-White, Fairbrother, *J. Phys. Chem C.,* **2015**, *119*, 15349

But…

…halogens can be removed by post-deposition processing



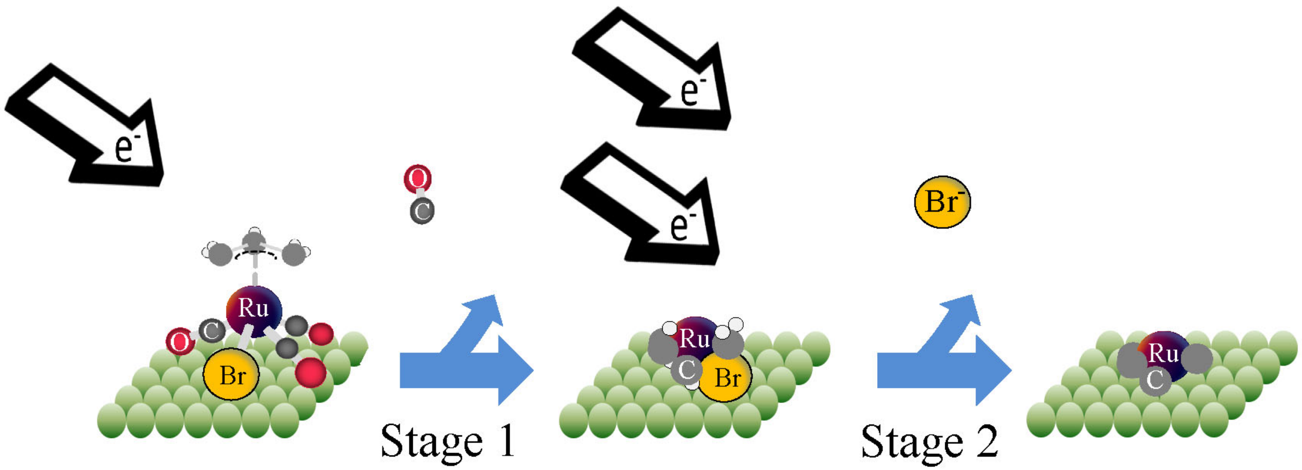


Spencer, Brannaka, Barclay, McElwee-White, Fairbrother, *J. Phys. Chem C.,* **2015**, *119*, 15349

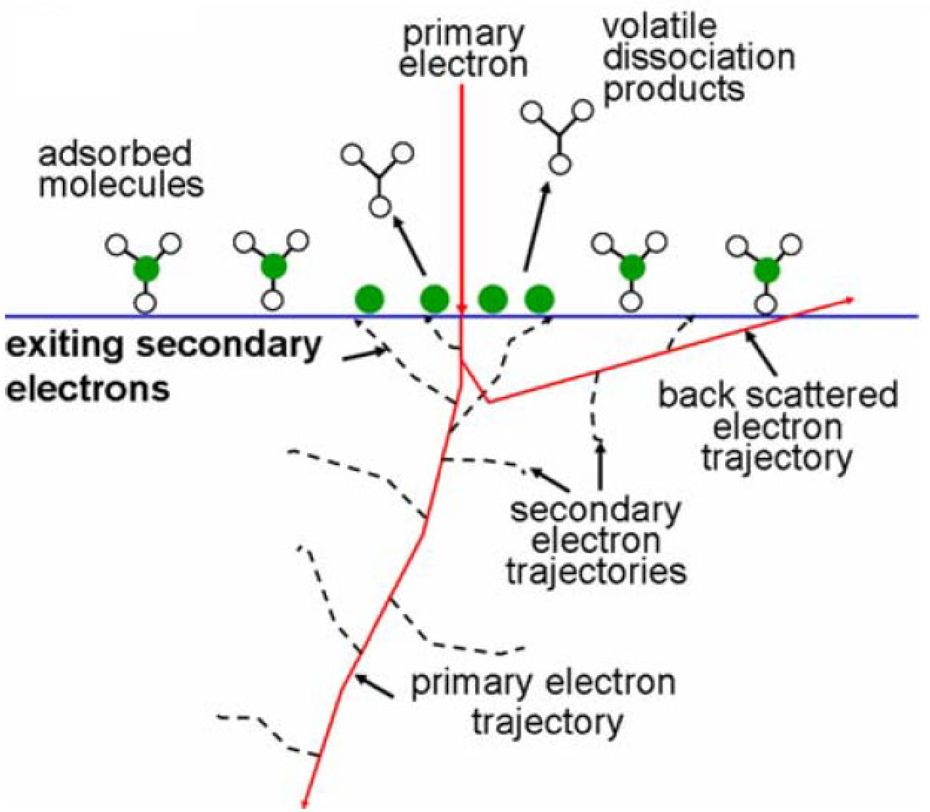
And the carbon?

Well, it's still there…

…but we learned something.



Secondary Electrons



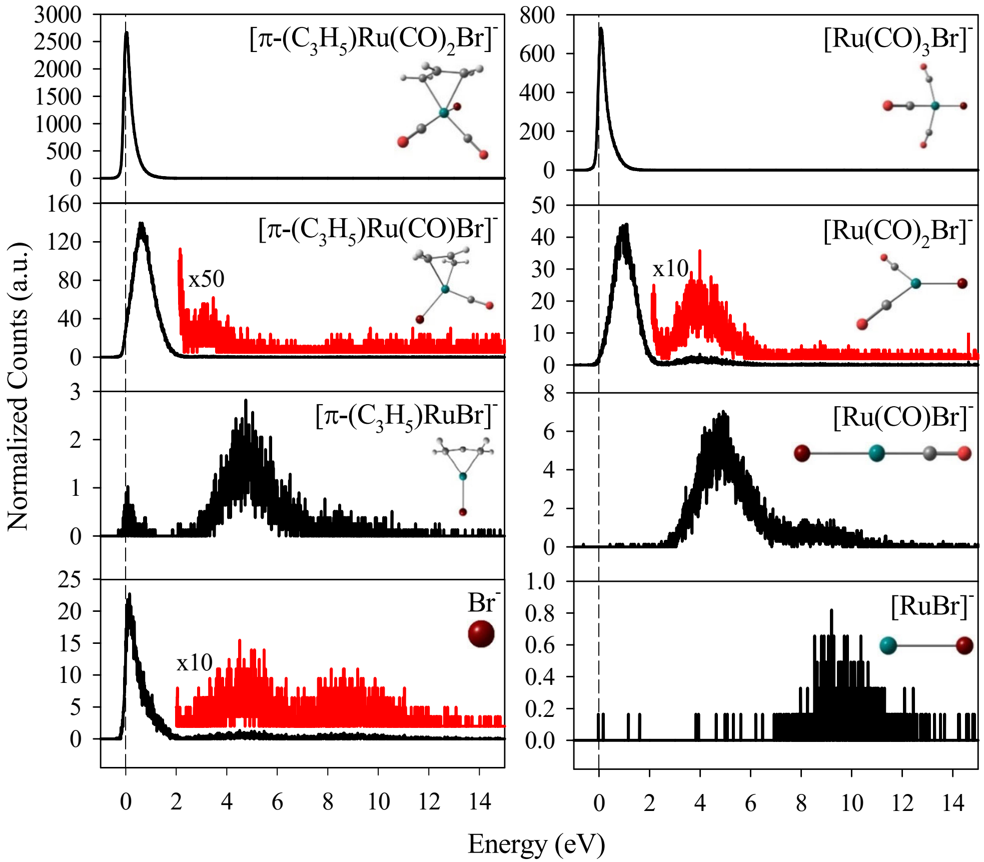
Utke, *J. Vac. Sci. Technol., B* **2008**, *26*, 1197

Gas Phase Electron-Molecule Interactions

Low energy electrons
→ dissociative electron attachment (DEA)

$AB + e^- \longrightarrow AB^{(\#)-}$

$AB^{(\#)-} \longrightarrow A^{(\#)-} + B^{(\#)}$



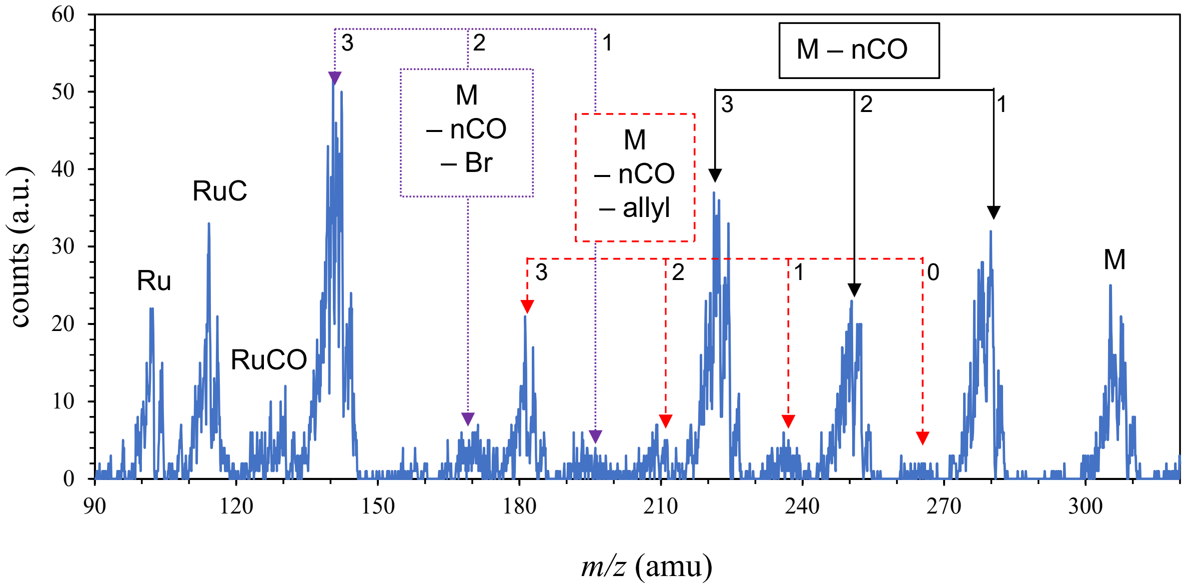
Thorman, Brannaka, McElwee-White, Ingólfsson, *Phys. Chem. Chem. Phys.*, **2017**, *19*, 13264

Gas Phase Electron-Molecule Interactions

High energy electrons (75 eV)
→ dissociative ionization (DI)

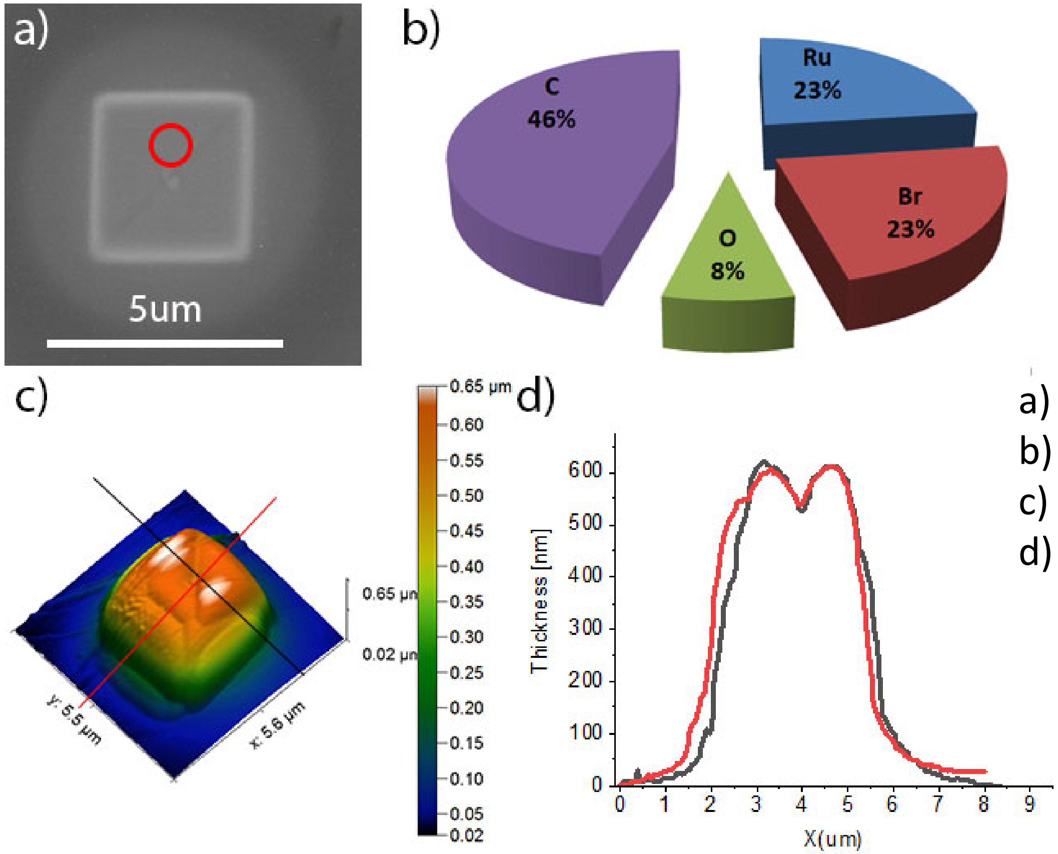
$$AB + e^- \longrightarrow AB^{(\#)+} + 2e^-$$

$$AB^{(\#)+} \longrightarrow A^{(\#)+} + B^{(\#)}$$



Cipriani, Thorman, Brewer, McElwee-White, Ingólfsson, *Eur. Phys. J. D*, under revision

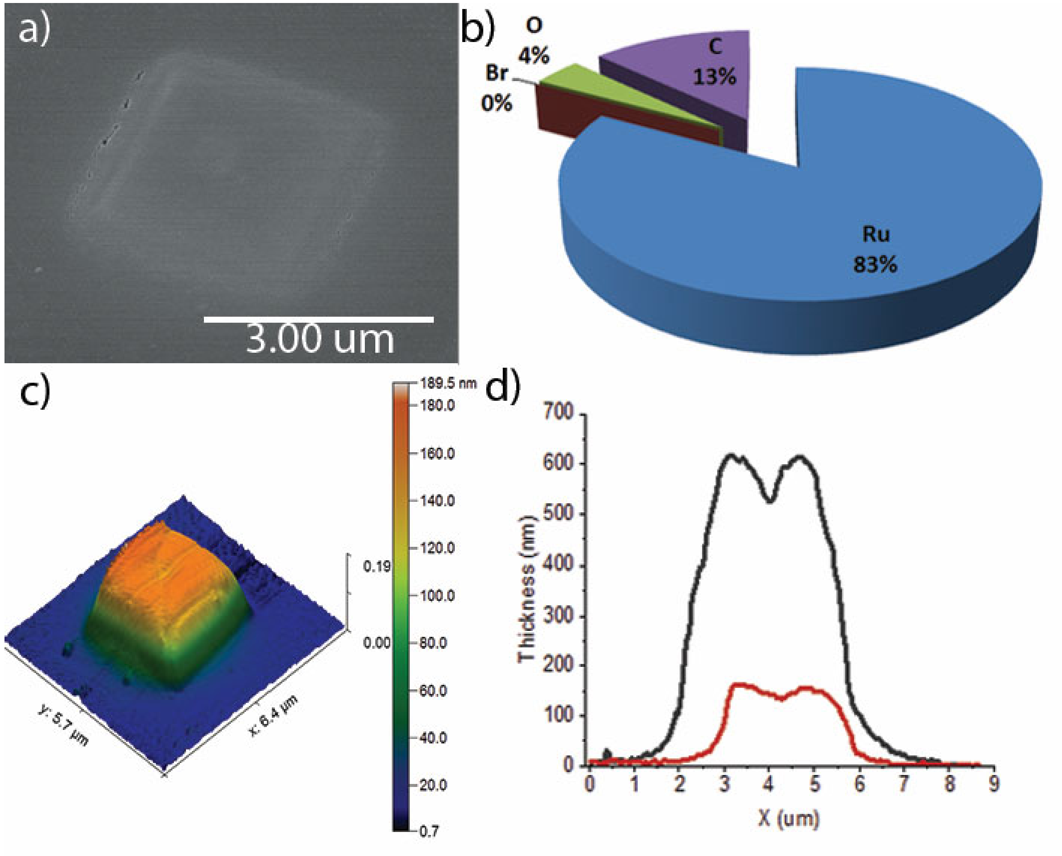
FEBID of Ru



a) SEM
b) Composition by EDX
c) AFM
d) AFM profiles through center

Jurczyk, Brewer, Hawkins, Polyakov, Kapusta, McElwee-White, Utke, submitted for publication

FEBID of Ru – With Purification

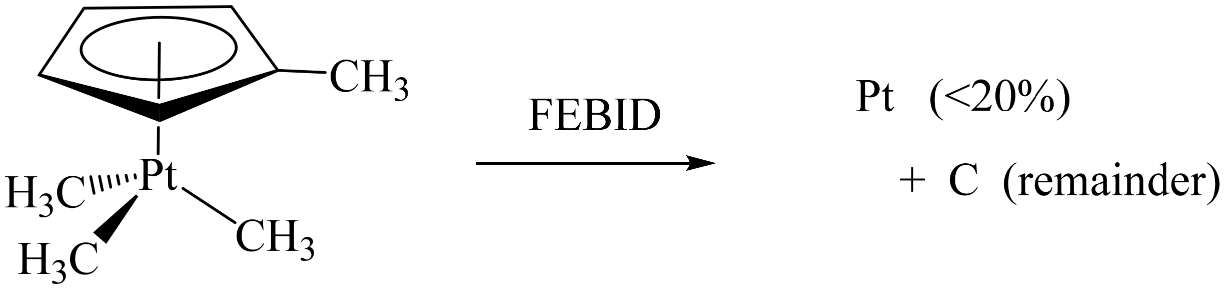


After heating in $2\% \ H_2/98\% \ N_2$ at 300 °C

a) SEM
b) Composition by EDX
c) AFM
d) AFM profile through center (before/after)

Jurczyk, Brewer, Hawkins, Polyakov, Kapusta, McElwee-White, Utke, submitted for publication

Revisiting the Pt problem…



Botman, Hesselberth, Mulders, *Microelectron. Eng.* **2008**, *85*, 1139

…with what we learned about design rules

- π-Facial carbon ligands don't dissociate well on the surface
- CO can dissociate readily in early stage e^- flux
- Halide ligands can be removed by continued e^- flux

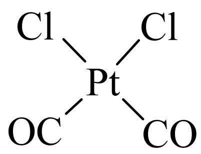
cis-$Pt(CO)_2Cl_2$

Synthesis

$$PtI_2 + SO_2Cl_2 \xrightarrow[\text{toluene}]{\text{CO}} cis\text{-}Pt(CO)_2Cl_2$$

Bagnoli *et al*, *J. Chem. Soc., Dalton Trans.*, **1996**, 4317

Characterization



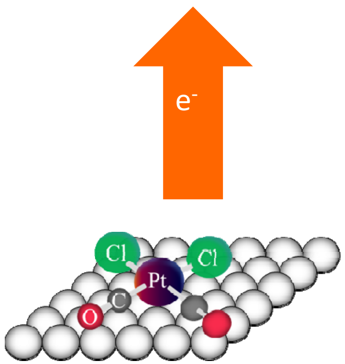
IR: ν_{CO} 2127, 2171 cm^{-1}
^{13}C NMR: δ 151.84

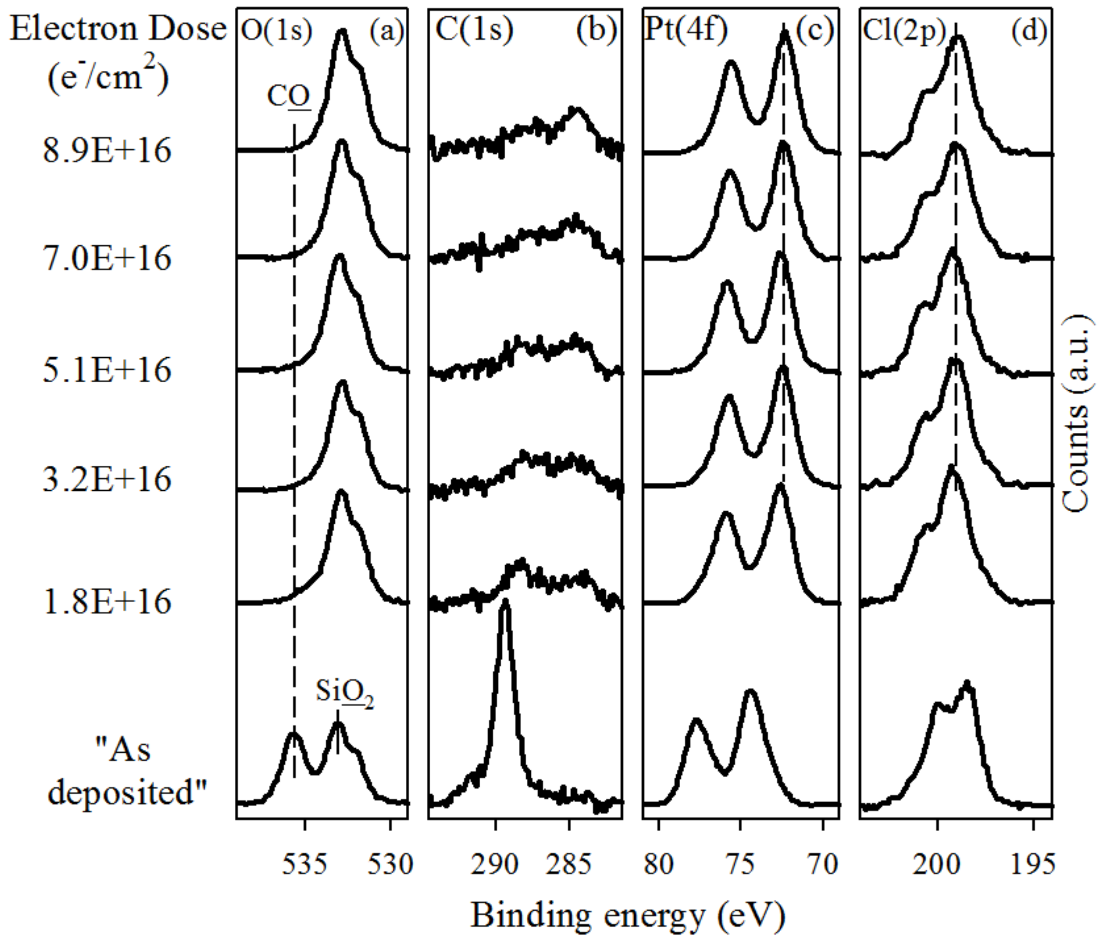
Properties

- White/light yellow needles
- Extreme sensitivity to moisture
- Stable under CO in the freezer for months
- Sublimes under vacuum

Spencer, Wu, McElwee-White, Fairbrother, *J. Am. Chem. Soc.*, **2016**, *138*, 9172

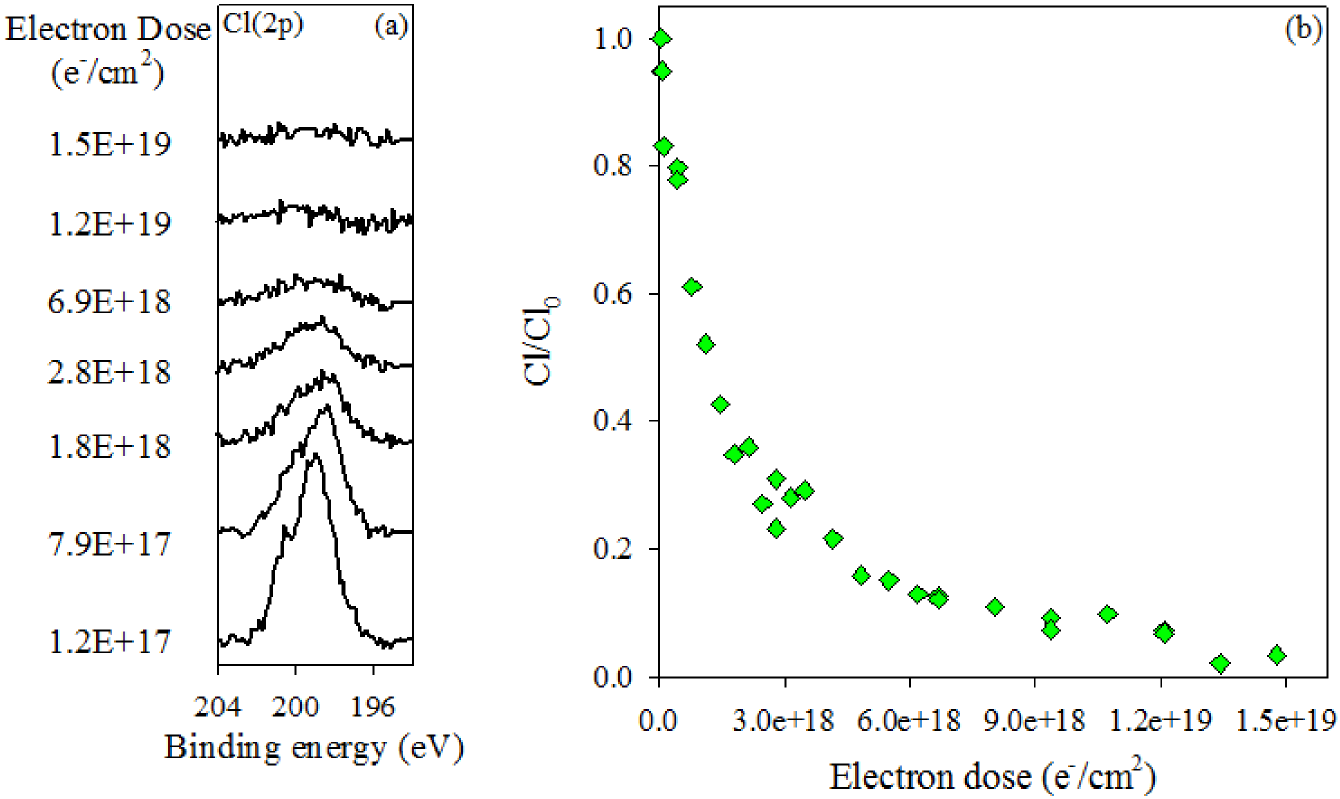
Electron Irradiation: *cis*-$PtCl_2(CO)_2$ on SiO_2





Spencer, Wu, McElwee-White, Fairbrother, *J. Am. Chem. Soc.*, **2016**, *138*, 9172

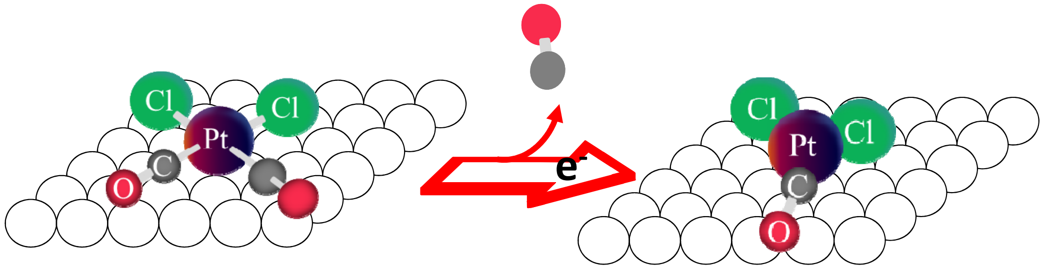
Removal of Halide



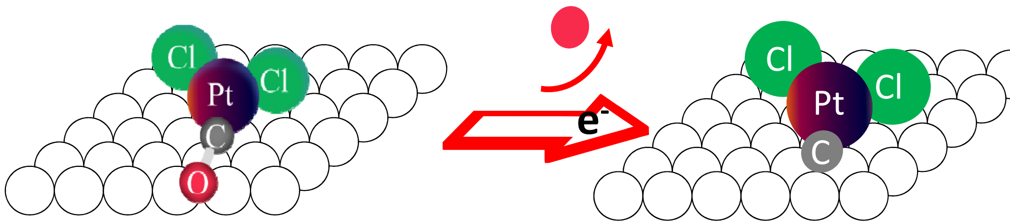
Spencer, Wu, McElwee-White, Fairbrother, *J. Am. Chem. Soc.*, **2016**, *138*, 9172

$Pt(CO)_2Cl_2$ – A Possible Route to Pt EBID

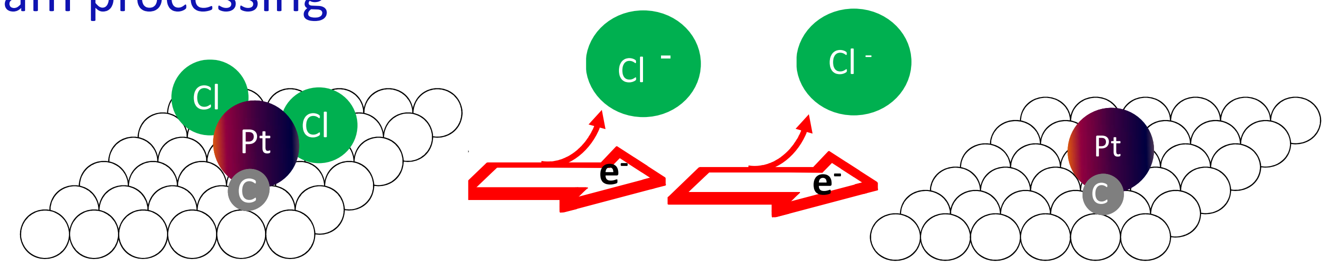
Ligand (CO) desorption



Ligand (CO) decomposition

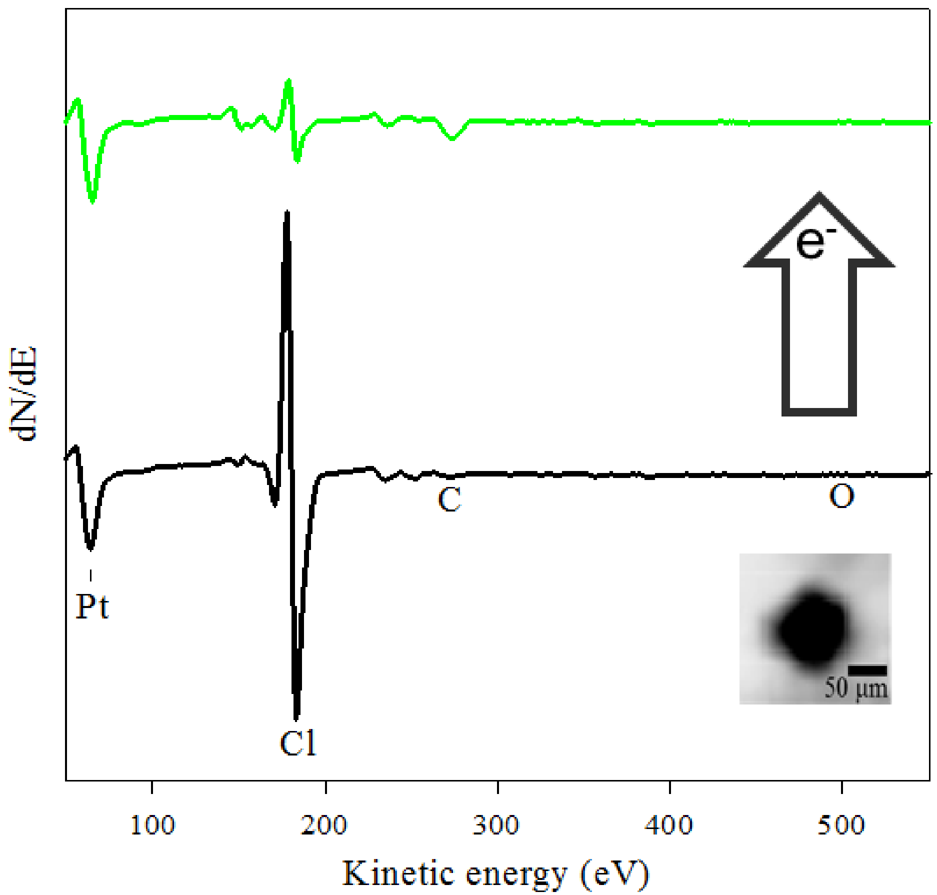


Post-deposition e-beam processing



Spencer, Wu, McElwee-White, Fairbrother, *J. Am. Chem. Soc.*, **2016**, *138*, 9172

EBID Structures from $Pt(CO)_2Cl_2$



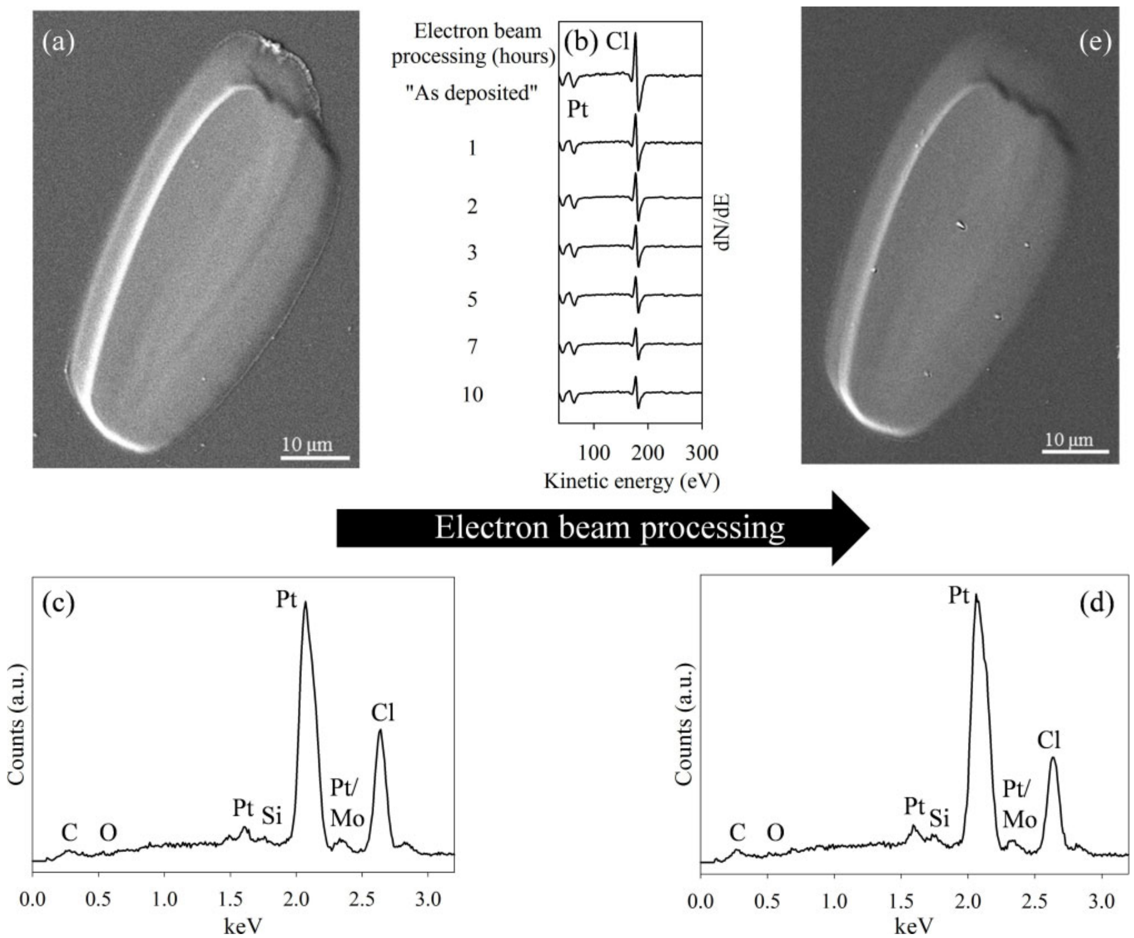
deposit after electron processing **(Cl removed)**

initial deposit **(carbon and oxygen free)**

Spencer, Wu, McElwee-White, Fairbrother, *J. Am. Chem. Soc.*, **2016**, *138*, 9172

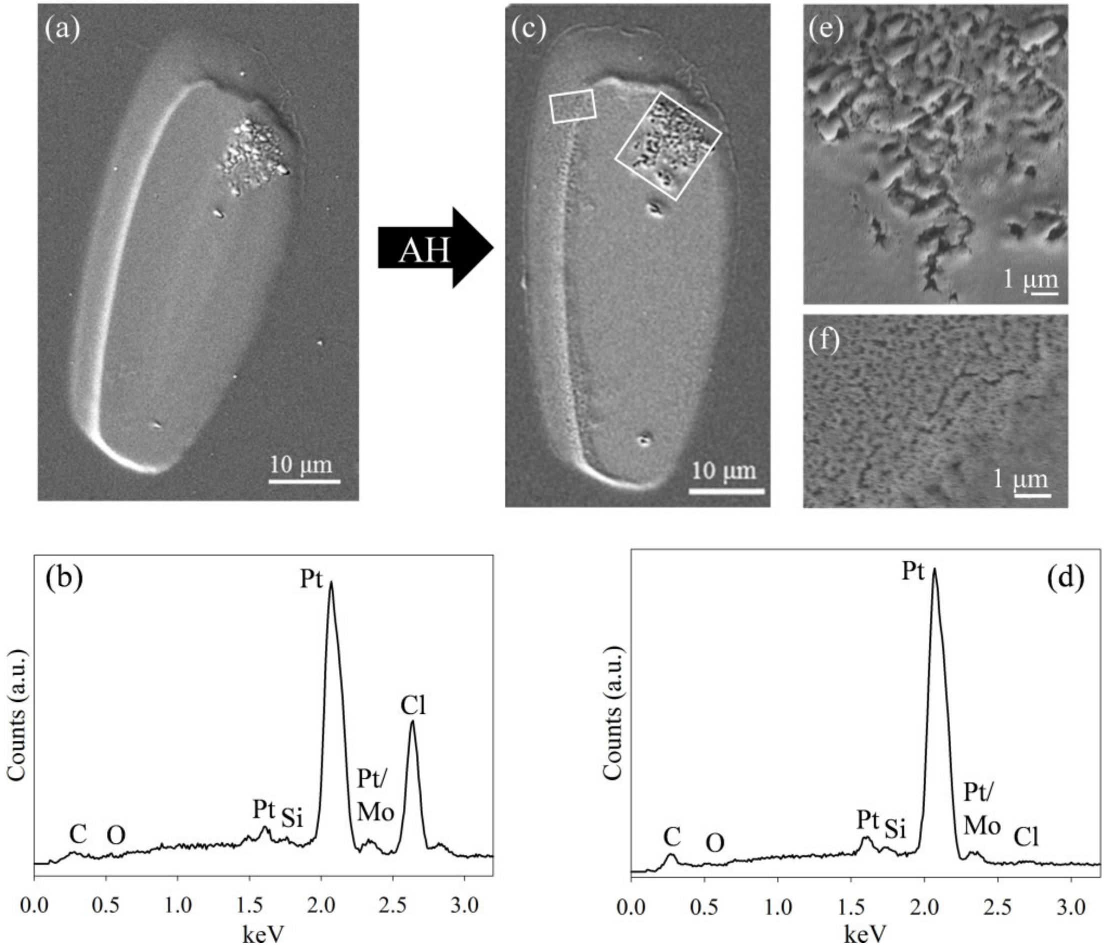
Spencer, Barclay, Gallagher, Winkler, Unlu, Wu, Plank, McElwee-White, Fairbrother, *Beilstein J. Nanotech.*, **2017**, *8*, 2410

Purification of Pt FEBID Deposits - Electrons



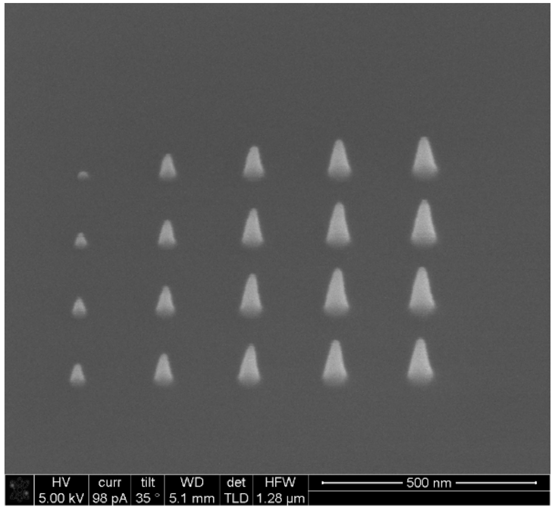
Spencer, Barclay, Gallagher, Winkler, Unlu, Wu, Plank, McElwee-White, Fairbrother, *Beilstein J. Nanotech.*, **2017**, *8*, 2410

Purification of Pt FEBID Deposits – Atomic H



Spencer, Barclay, Gallagher, Winkler, Unlu, Wu, Plank, McElwee-White, Fairbrother, *Beilstein J. Nanotech.*, **2017**, *8*, 2410

$Pt(CO)_2Cl_2$ – FEBID



- Deposited at: 18 KeV, 38pA
- Dwell time per pixel per pass: 0.5→ 20 ms
- Refresh time: 10 ms
- 100 Passes

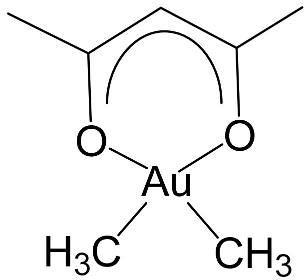
Results are highly dependent on reaction conditions!

	$PtCl_2(CO)_2$	
Element	**Before plasma**	**After plasma**
C	53,5	47,8
Pt	21,1	27
Si	5,7	5,7
O	7,4	6,6
N	4,5	4,9
Br	---	---
Cl	7,8	7,9

Mahgoub, Lu, McElwee-White, Hagen, manuscript in preparation

Au FEBID Precursors: A Partial History

The common commercial precursor is Au(acac)Me_2



Deposit Au but are too unstable: ClAuCO and $ClAuPF_3$
Also reported: $MeAuPMe_3$

- $ClAuPMe_3$ and ClAu(SMe_2) could not be delivered in the gas phase

Mulders, Veerhoek, Bosch, Trompenaars, *J. Phys. D-Appl. Phys.* **2012**, *45,* 475301
Utke, Hoffmann, Dwir, Leifer, Kapon, Doppelt, *J. Vac. Sci. Technol. B* **2000**, *18*, 3168
van Dorp, Wu, Mulders, Harder, Rudolf, De Hosson, *Langmuir* **2014**, *30*, 12097

Volatility of Au(I) Complexes

Compound	T_{sub} (°C)[a] 125 mTorr[b]	T_{dec} (°C) 760 Torr
$ClAuCN^tBu$	64	162
$BrAuCN^tBu$	53	147
$IAuCN^tBu$	51	96
ClAuCNMe	83	184
BrAuCNMe	79	204
IAuCNMe	65	174
$ClAuPMe_3$	78	231
$BrAuPMe_3$	83	231
$IAuPMe_3$	70	179
$ClAuP(NMe_2)_3$	69	183
$BrAuP(NMe_2)_3$	73	134
$IAuP(NMe_2)_3$	62	138
$ClAuP(OCH_2CF_3)_3$	55[c]	61
$BrAuP(OCH_2CF_3)_3$	73[c]	93
$IAuP(OCH_2CF_3)_3$	56[c]	67

[a] ± 0.5 °C
[b] ± 1 mTorr
[c] melting before sublimation

Carden, Pedziwiatr, Abboud, McElwee-White, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 40998

Refining the Precursor Design

Tunable X-Au-L scaffold

— Stability control
— Volatility control

Increase size → X—Au—L ← Increase σ donation

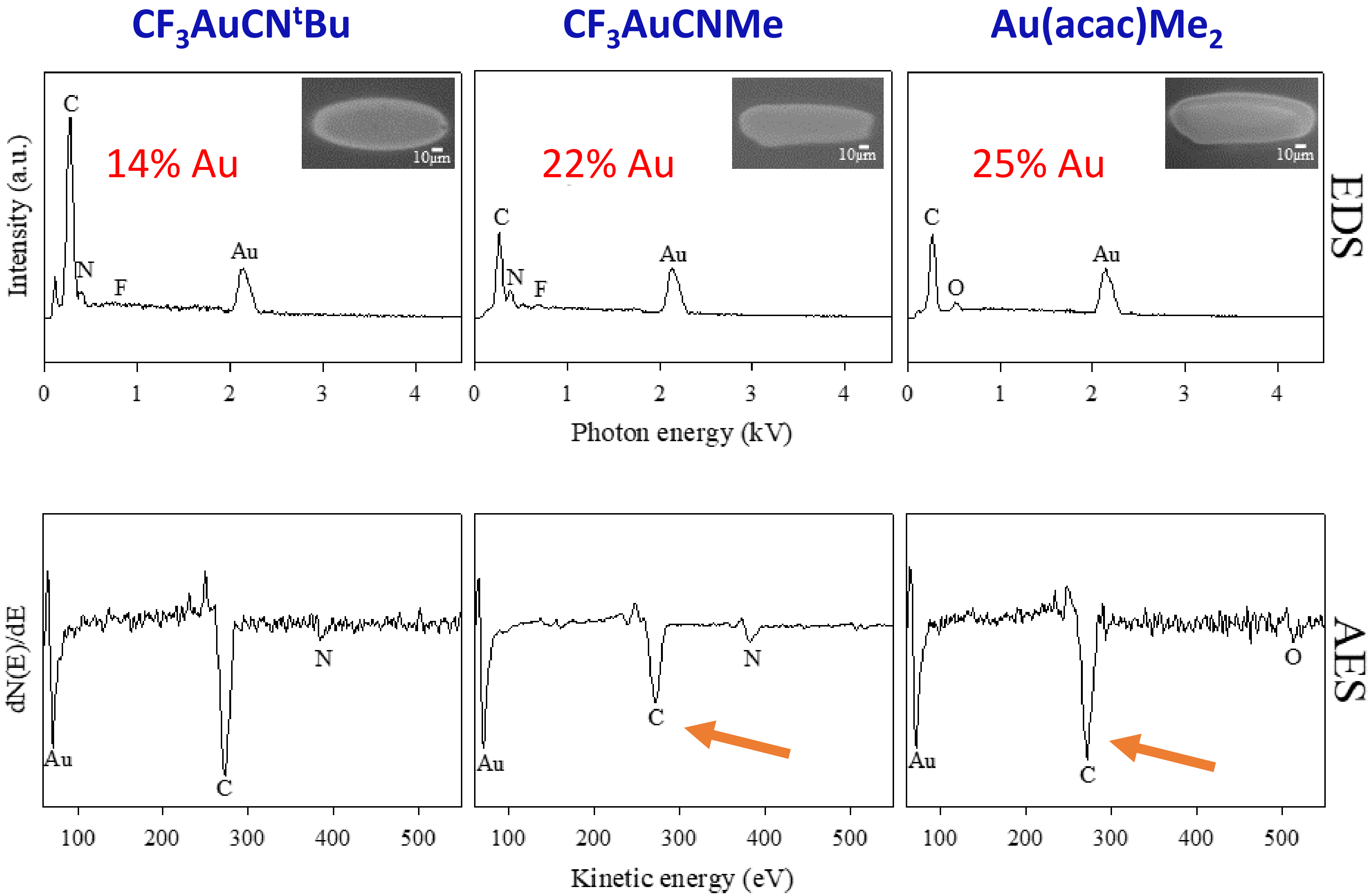
Carden, Thorman, Unlu, Abboud, Fairbrother, McElwee-White, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 11976

Volatility of Au(I) Complexes

ClAuCNMe	83 °C/125 mTorr	(onset)
ClAuCN^{t}Bu	64 °C/125 mTorr	(onset)
CF_3AuCN^{t}Bu	57 °C/115 mTorr	(prep)
CF_3AuCNMe	67 °C/115 mTorr	(prep)

Carden, Thorman, Unlu, Abboud, Fairbrother, McElwee-White, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 11976

FEBID Structures (Steady State Deposition)



Carden, Thorman, Unlu, Abboud, Fairbrother, McElwee-White, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 11976

What We Have Learned (So Far)

1. Anionic π-facial carbon ligands such as η^5-Cp and η^3-allyl are not a good idea.
2. CO ligands can be removed under e^- irradiation.
3. Halide ligands can also be removed but may require more e^- or other reductive coreactants.
4. Volatility can be controlled by halide substitution.

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Precursor Synthesis
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Jackie Cetola
Matthew Alderman
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