Inorganic Tapas and Undergraduate Research

Linda H. Doerrer
Chemistry Department

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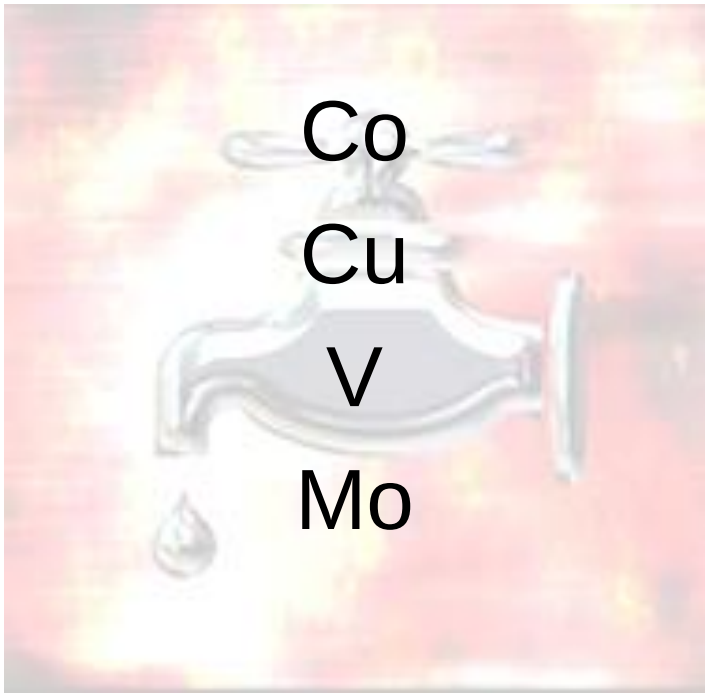
Inorganic Tapas Menu

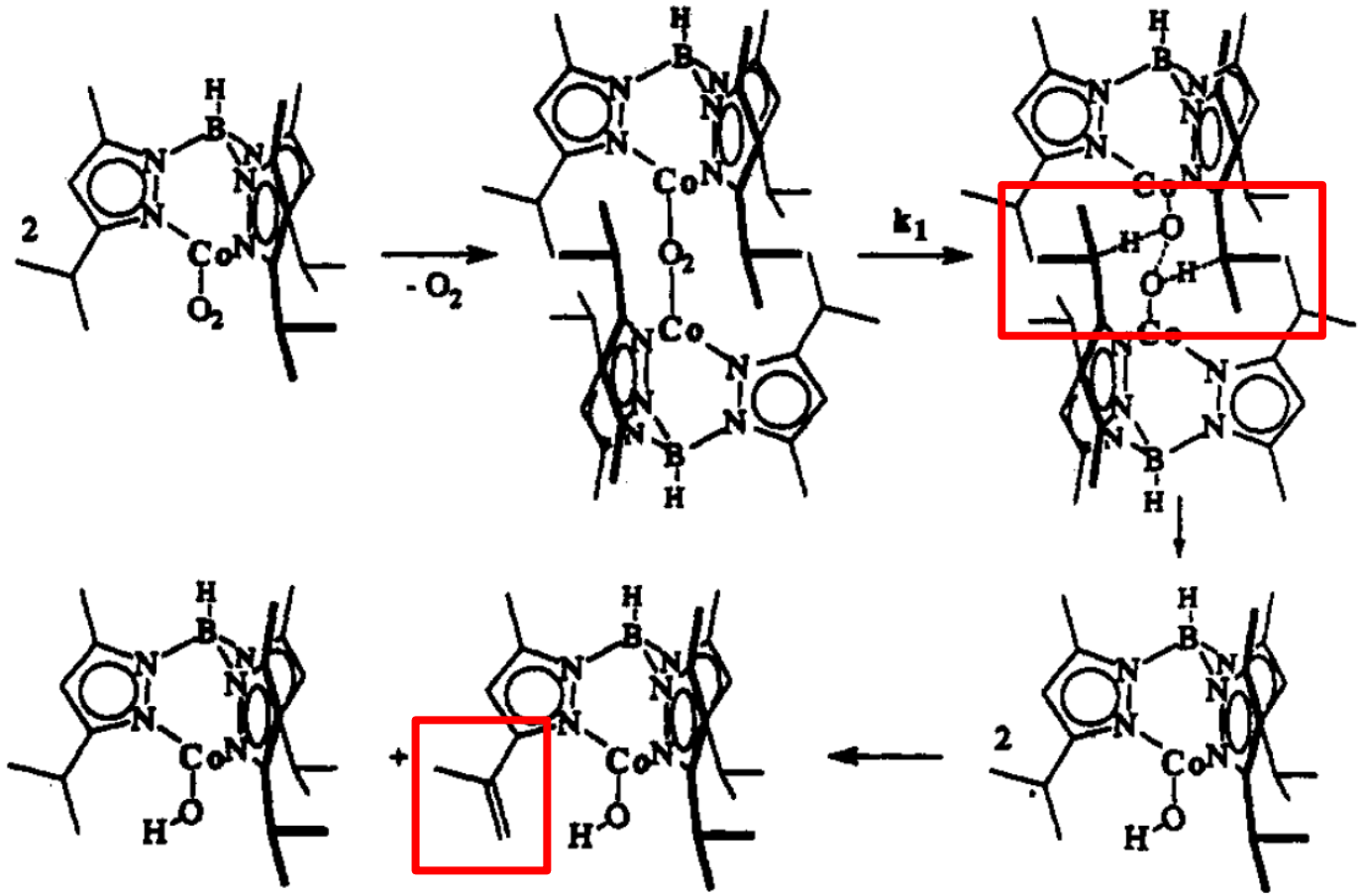
Fluorinated Alkoxide Complexes



Heterobimetallic Lantern Complexes

A New Family of Ligands

Why Fluorinated Alkoxides?



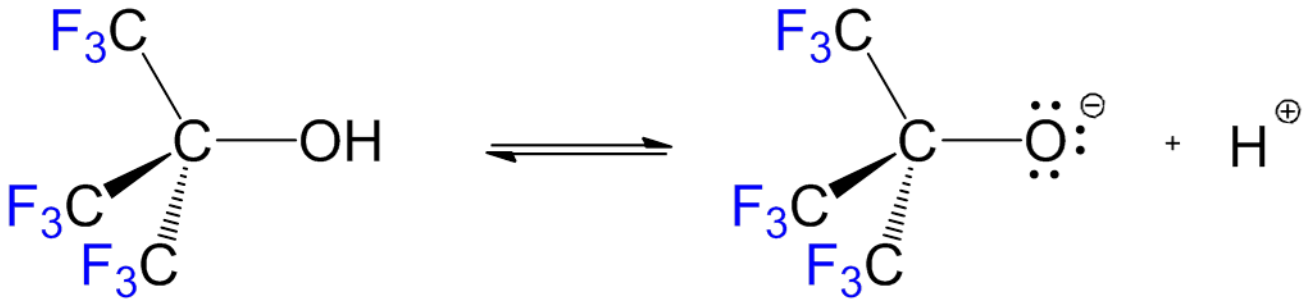
K. H. Theopold *et al., J. Am. Chem. Soc.*, **1994**, 6979

Less Basic Lessons from Fluorinated Aryloxides and Alkoxides

Published
Unpublished

								B	C
								Al	Si
V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb

LHD, *et al. Inorg Chem,* **2004**, *43*, 7709 - 7724
LHD, *et al. Polyhedron*, **2005**, *24*, 1803 - 1812
LHD, *et al. Inorg Chem,* **2006**, *45*, 3864-3877
LHD, *et al. Inorg Chem,* **2009**, *48*, 4274-4276
LHD, *et al. Dalton Trans.*, **2010**, *39*, 373-384
LHD, *et al. Inorg Chem,* **2011**, *50*, 6584-6596
LHD, *et al. Angew Chem Int Ed,* **2012**, *51*, 1000-1005
LHD, *et al. Inorg Chem,* **2013**, *52*, 14050-14063
LHD, *et al. Chem Commun,* **2018**, *54*, 12045 - 12048
LHD, *et al. Dalton Trans.*, **2019**, *48*, 4759 - 4768
LHD, *et al. Dalton Trans.*, **2019**, *48*, 6899 - 6909
LHD, *et al. Polyhedron*, **2020**, *186*, 114609
LHD, *et al. Dalton Trans.*, **2020**, *49*, 13773 - 13785
LHD, *et al. Inorg Chem,* **2020**, *59*, 9807 – 9823
LHD, *et al. Inorg Chem,* **2020**, *59*, 16500 – 16513

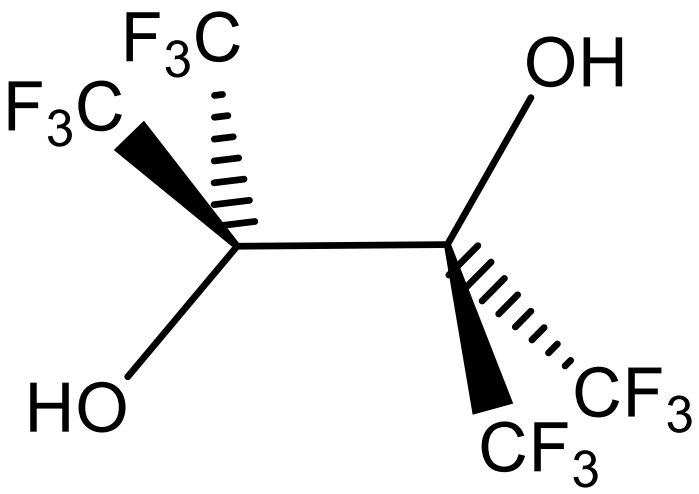


$pK_a = 9.6$

- Fewer μ-OR
- Less easily protonated in H_2O
- Weaker π-donor

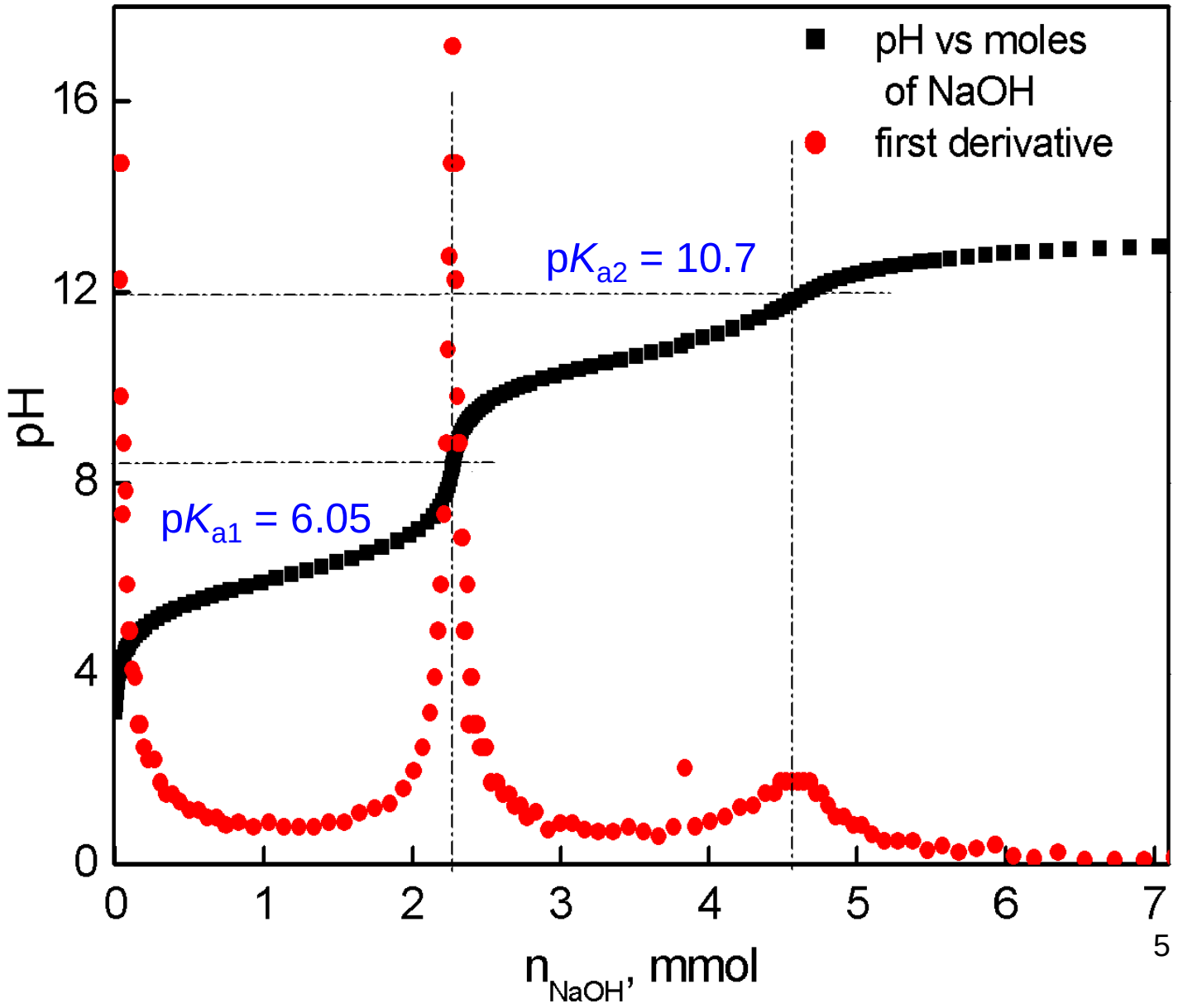
J. K. Elinburg, LHD, *Polyhedron*, **2020**, *190*, 114765

Perfluoropinacol

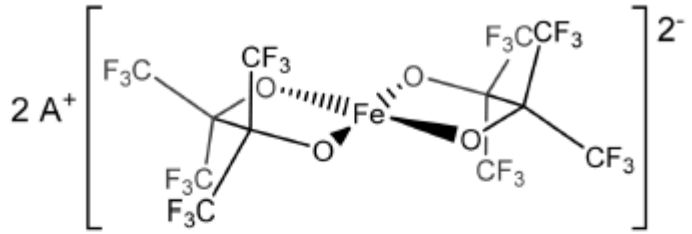


H_2pin^F = perfluoropinacol

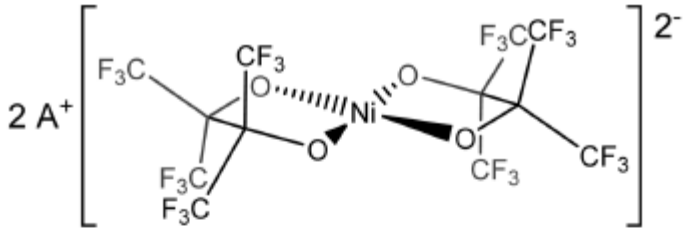
(pinacol pK_{a1} ~ 18)



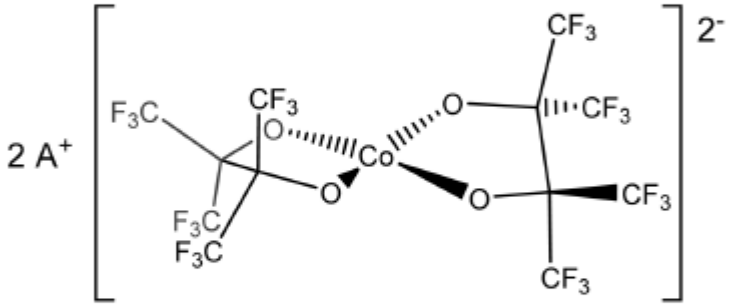
3*d* $[M(pin^F)_2]^{2-}$



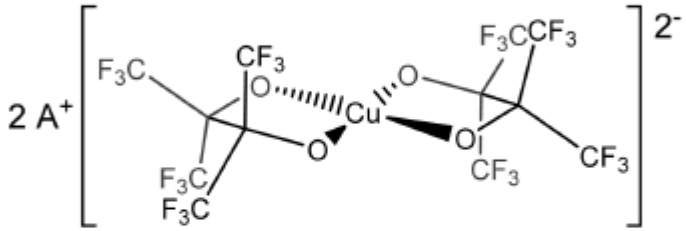
A = Me_4N



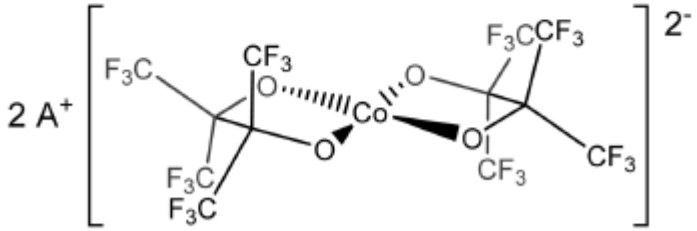
A = $K(DME)_2$, Me_4N



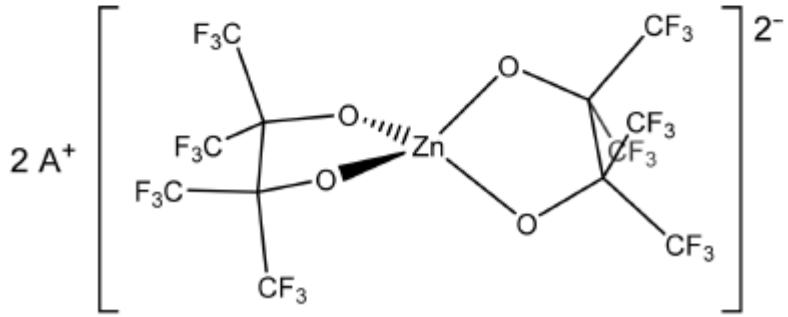
A = Me_4N



A = K, $K(DME)_2$, Me_4N



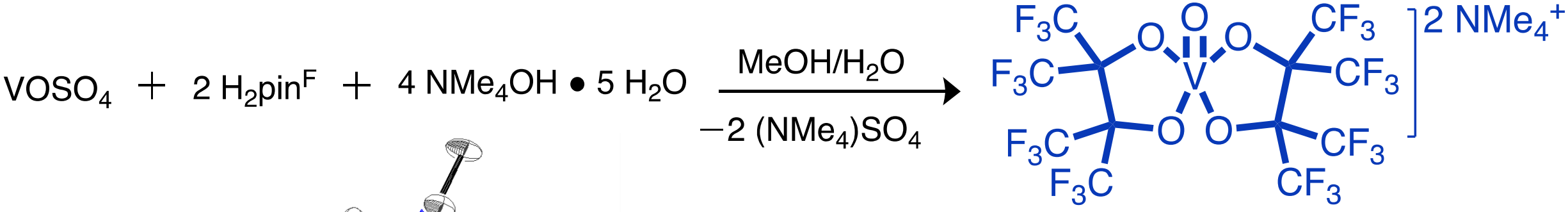
A = $^nBu_4N$

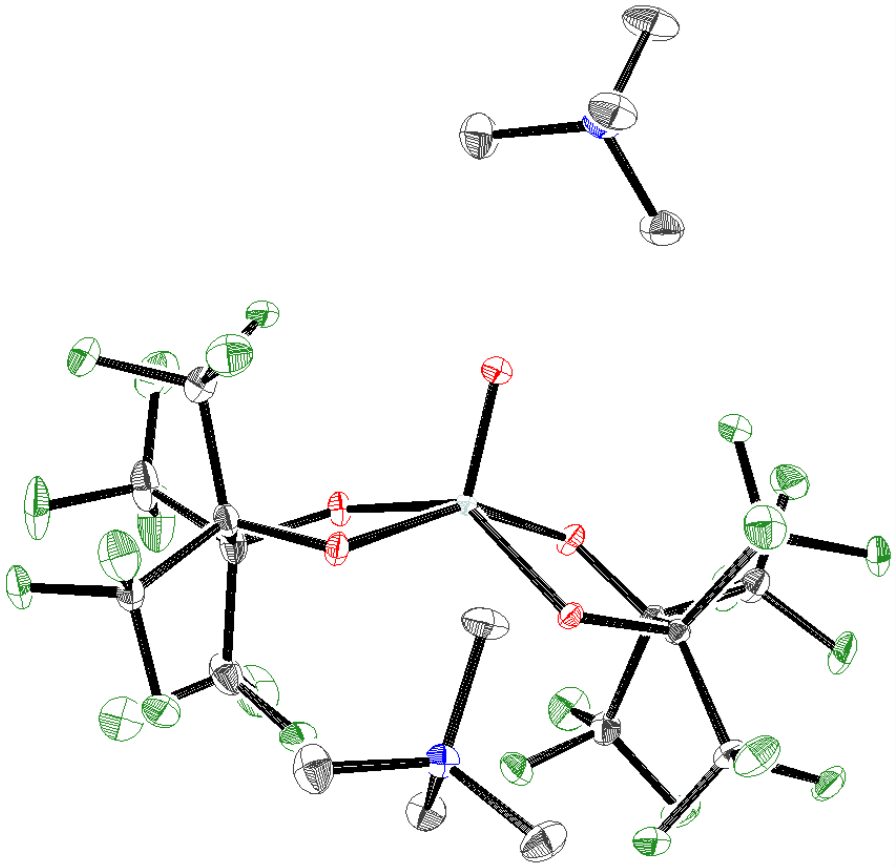


A = K

L. Tahsini, S.E. Specht, J.S. Lum, J.J.M. Nelson, A.F. Long, J.A. Golen, A.L. Rheingold, LHD, *Inorg. Chem.*, **2013**, *52*, 14050-14063

Vanadium in H_2O



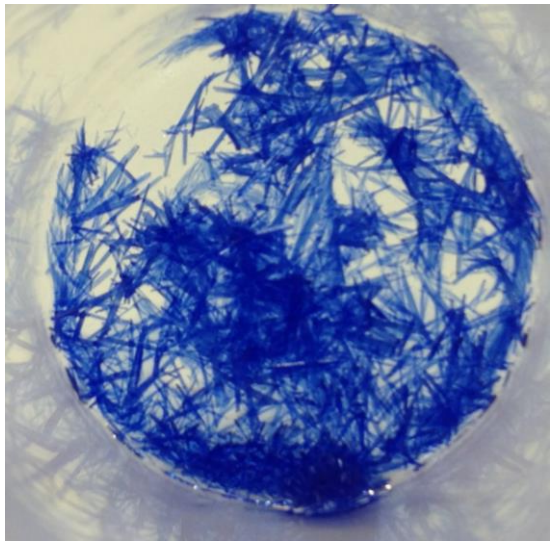


V=O 1.6089 Å

V-O (avg) 1.9620 Å

$\tau_5 = 0.22$

$\upsilon_{V=O} = 967\ cm^{-1}$



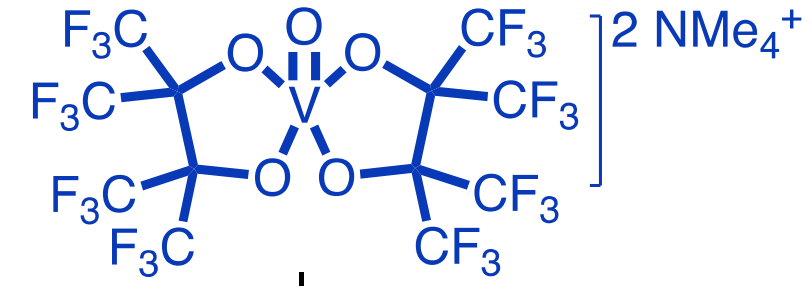
~ 80% yield

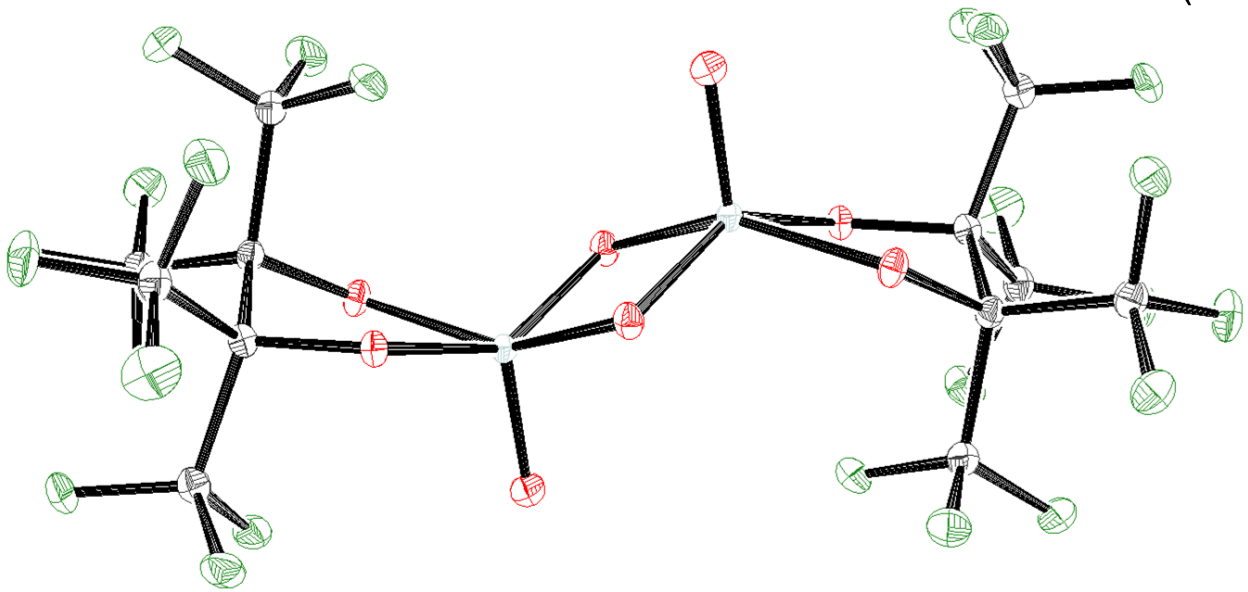
$\lambda_{max} = 361, 564, 624\ nm$

Elinburg, J. K.; Carter, S. L.; Nelson, J. J. M.; Fraser, D. G.; Crockett, M. P.; Beeler, A. B.; Nordlander, E.; Rheingold, A. L.; Doerrer, L. H. *Inorg. Chem*., **2020**, *59*, 16500-16513.

Oxidation of V(IV) Monomer in Air

$VOSO_4 + 2\ H_2pin^F + 4\ NMe_4OH \bullet 5\ H_2O \xrightarrow[2\ (NMe_4)SO_4]{MeOH/H_2O}$



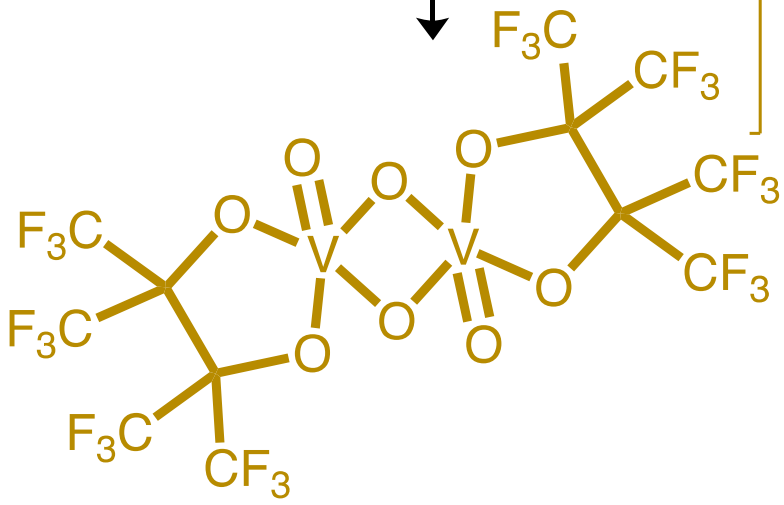


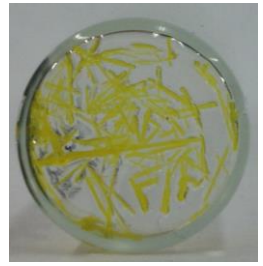
$\upsilon_{V=O} = 981\ cm^{-1}$

O_2, days
(minor product)

H_2O_2
(major product)

MeCN/H_2O





$\tau_5 = 0.12$

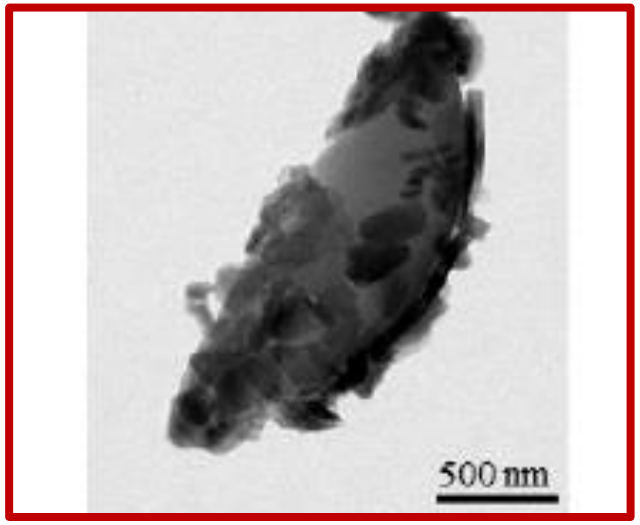
V=O	1.5943(12) Å
V-O(pin^F) (avg)	1.8225(12) Å
V-(μ_2-O) (avg)	1.9270(12) Å

Elinburg, J. K.; Carter, S. L.; Nelson, J. J. M.; Fraser, D. G.; Crockett, M. P.; Beeler, A. B.; Nordlander, E.; Rheingold, A. L.; Doerrer, L. H. *Inorg. Chem.*, **2020**, *59*, 16500-16513.

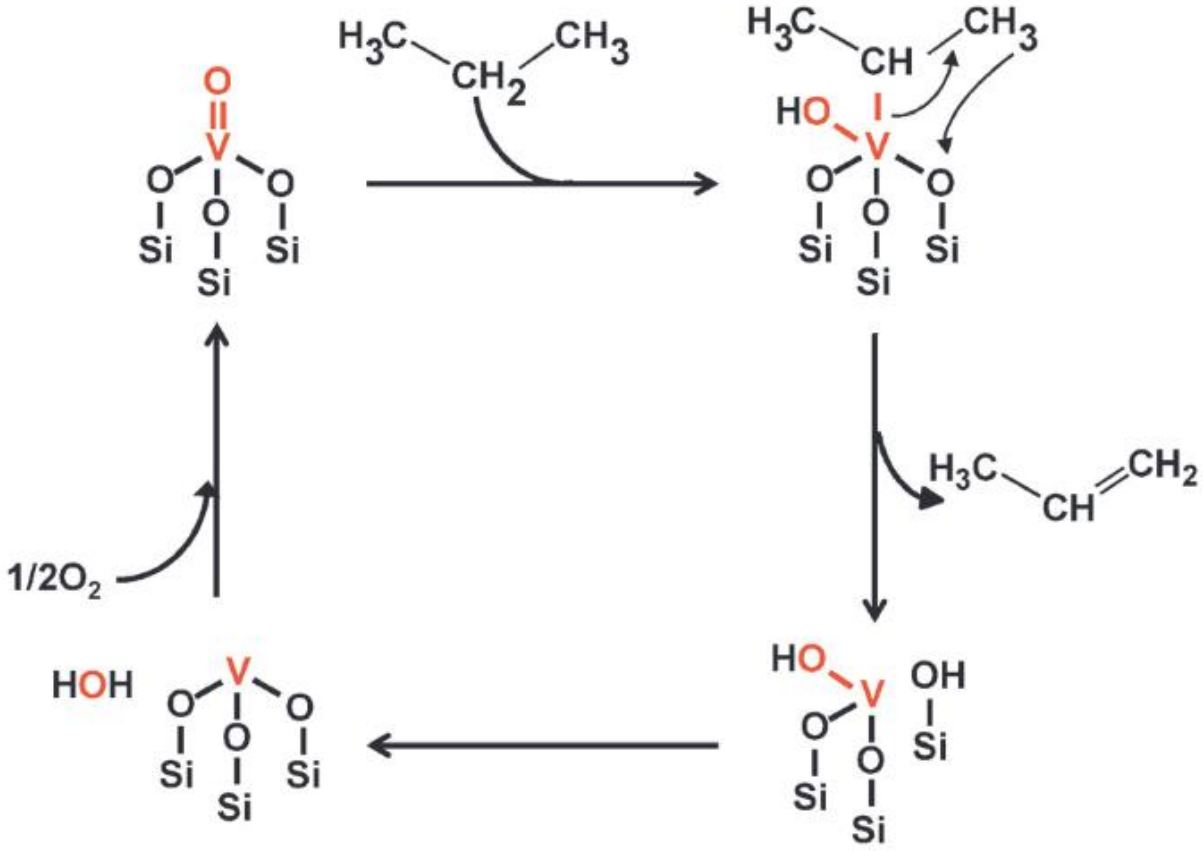
Supported VO_X for Oxidative Dehydrogenation

Oxidative dehydrogenation of alkanes & alcohols

Known for surface-supported vanadium oxides



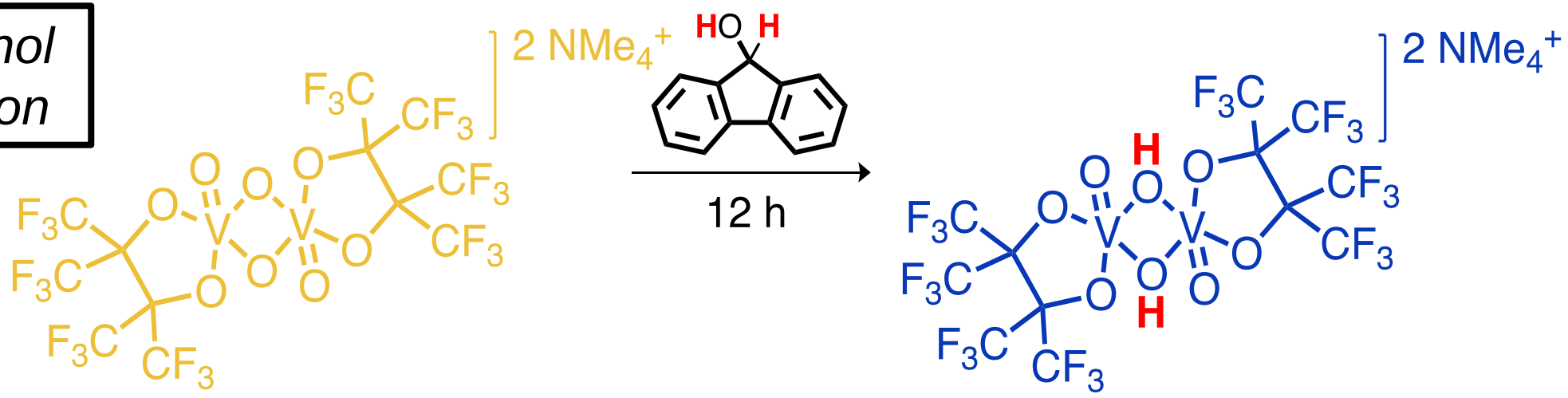
STEM image of V_2O_5 on SiO_2



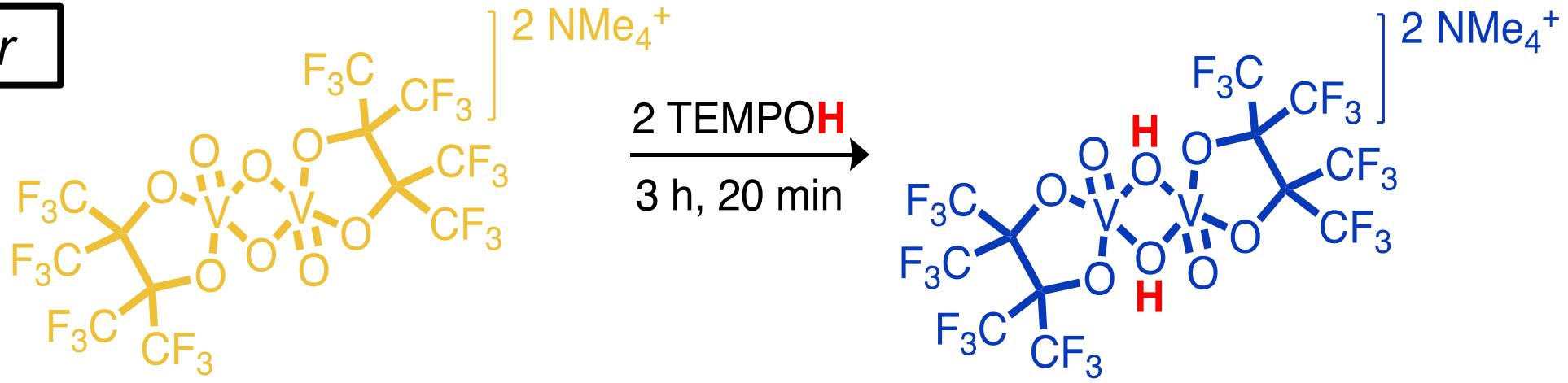
Niina Koivikko, Tiina Laitinen, Anass Mouammine, Satu Ojala, Riitta L. Keiski, *Catalysts* **2018**, *8* (2), 56.
Kenta Fukudome, Na-oki Ikenaga, Takanori Miyakea, Toshimitsu Suzuki, *Catal. Sci. Technol.*, **2011**, 987-998.

Two H Atom Sources

Oxidative alcohol dehydrogenation



H• atom transfer



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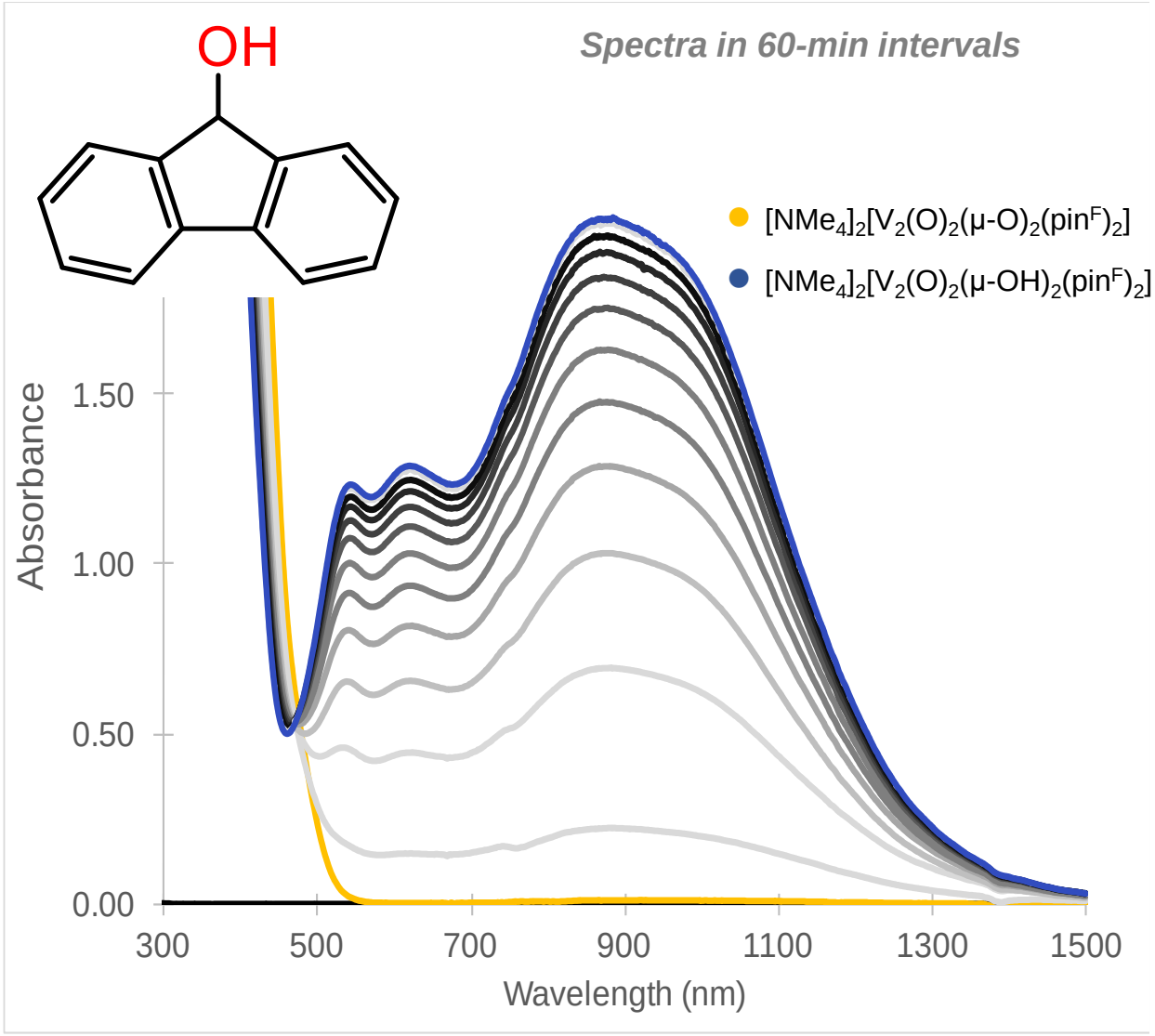
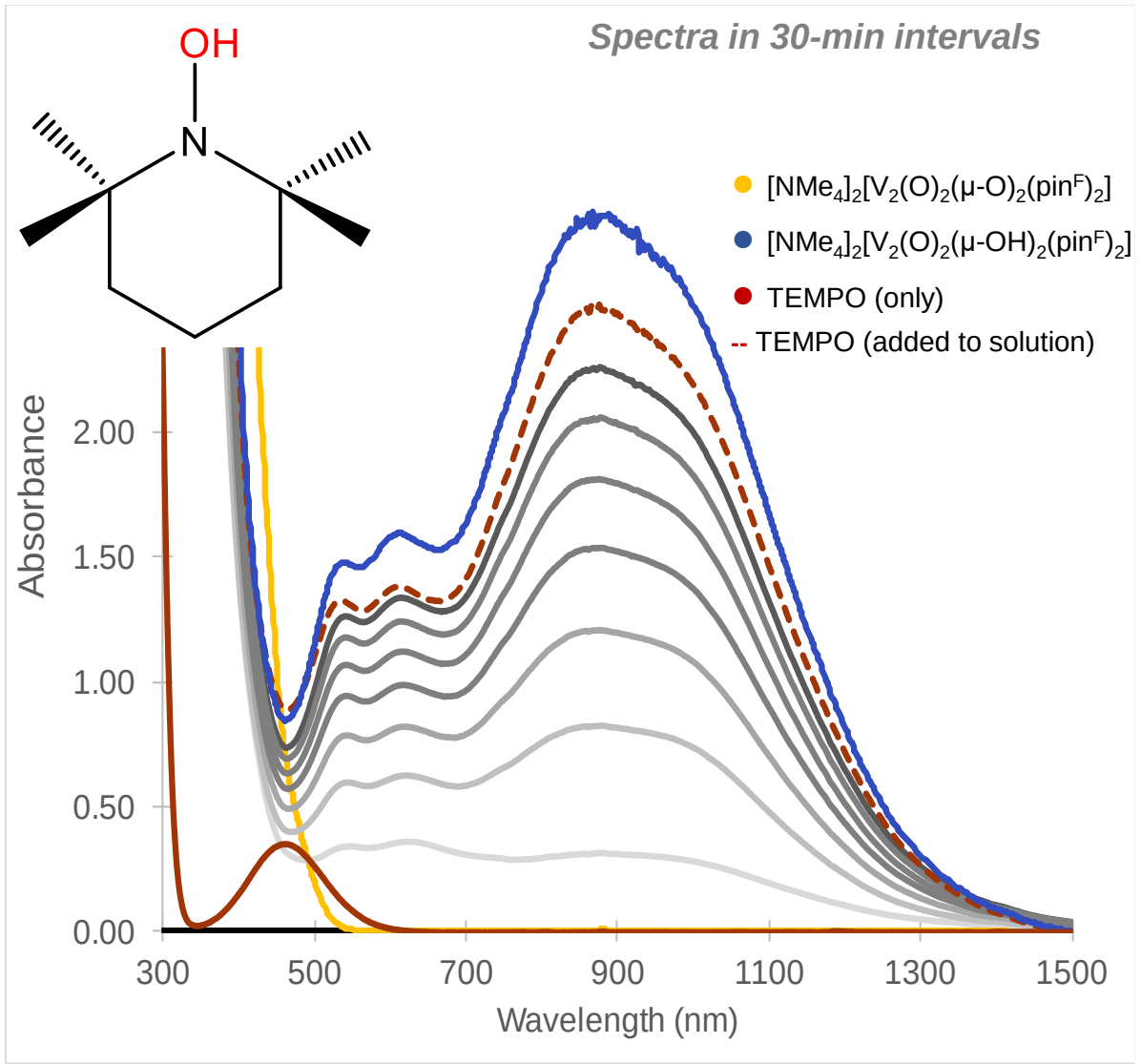
Reduction of V(V) to V(IV)





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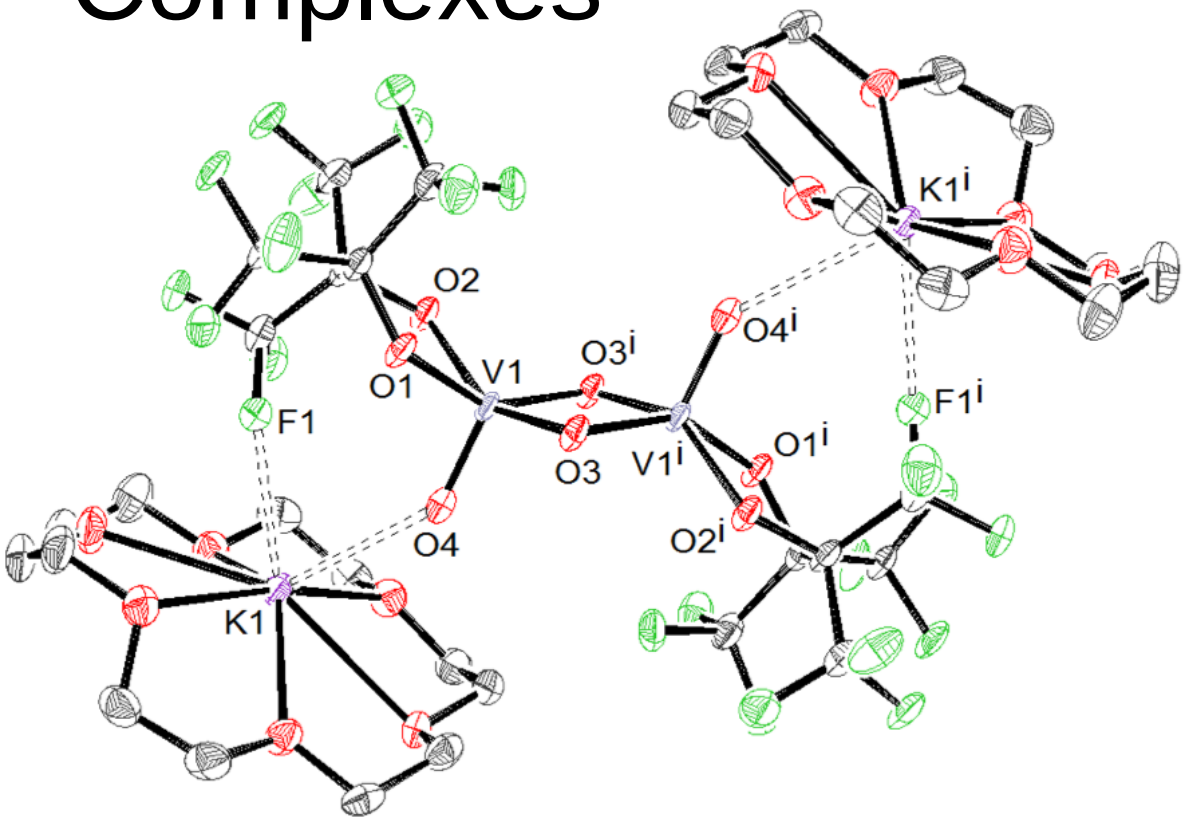
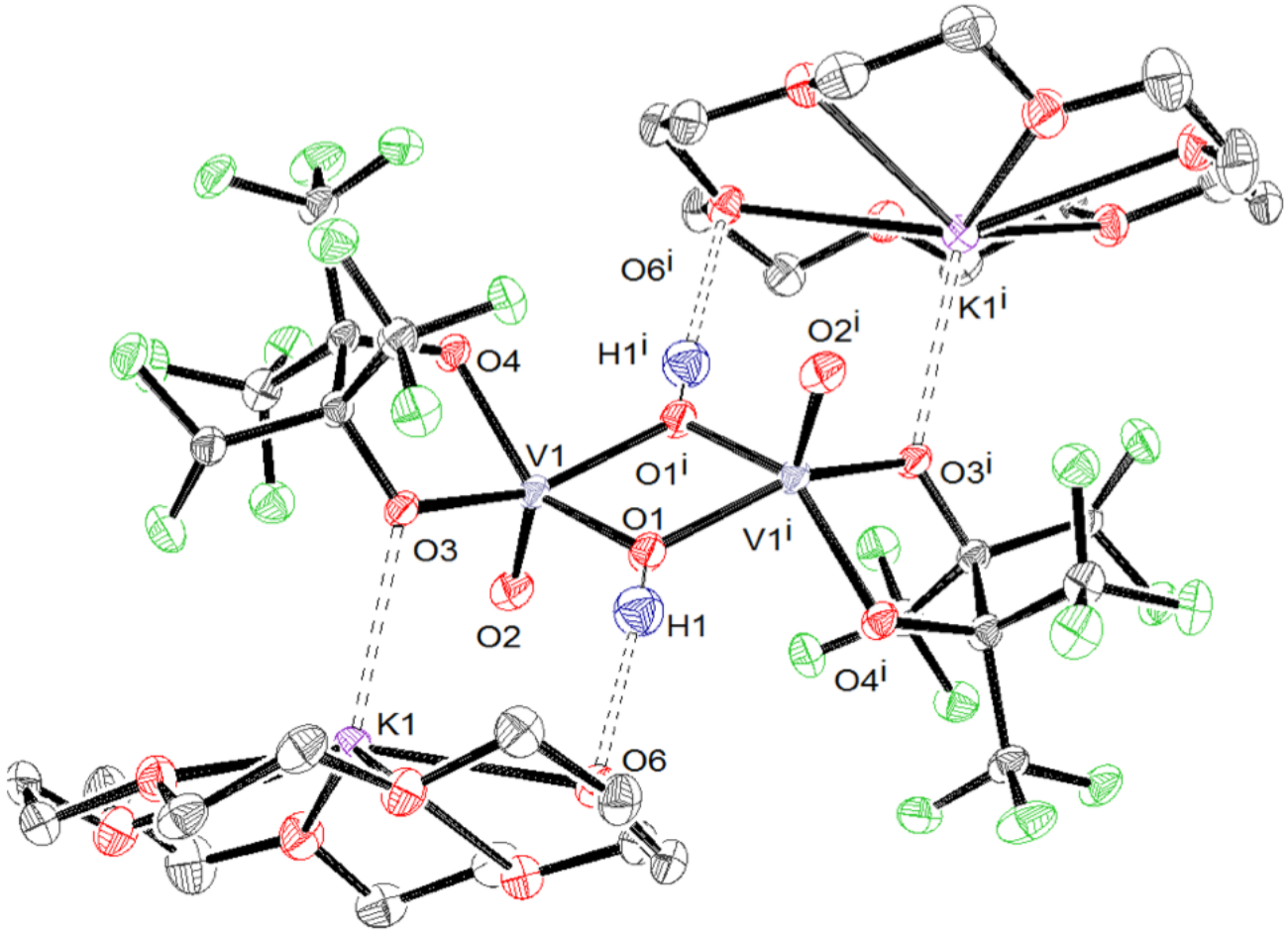
Dimeric (V=O)-pin^F Complexes



{K(18C6)}$_2$[V(V)(O)$_2$(μ-O)$_2$(pin^F)$_2$]



{K(18C6)}$_2$[V(IV)(O)$_2$(μ-OH)$_2$(pin^F)$_2$]

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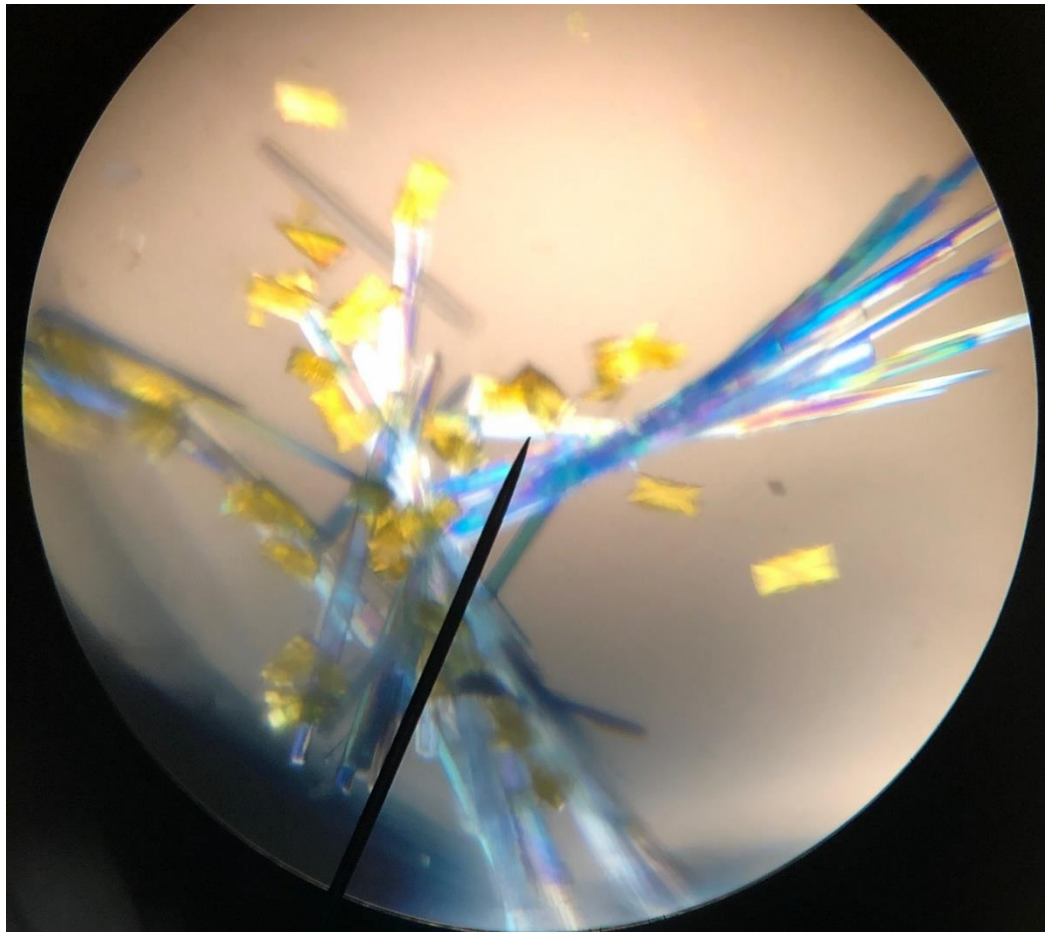
Formal Loss of H_2



Crystalline $[NMe_4]_2[V_2(O)_2(\mu\text{-}OH)_2(pin^F)_2]$ in air after approx. 8 h.

Upon exposure to air

$[NMe_4]_2[V_2(O)_2(\mu\text{-}OH)_2(pin^F)_2]$

converts to

$[NMe_4]_2[V_2(O)_2(\mu\text{-}O)_2(pin^F)_2]$

confirmed via X-ray analysis

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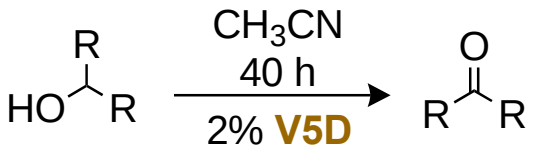
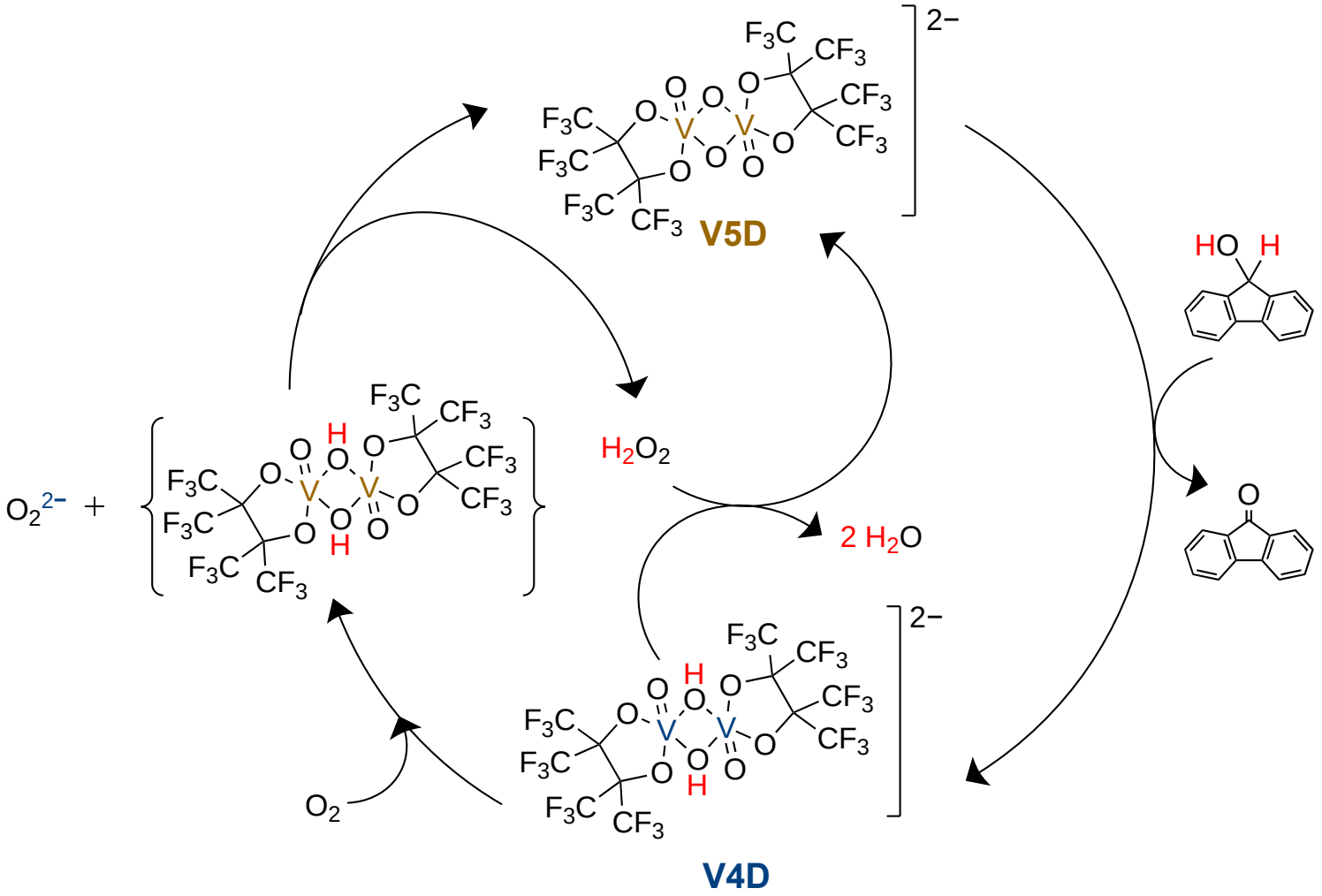
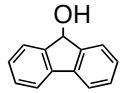
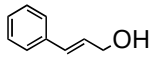
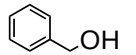
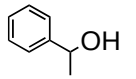
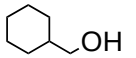
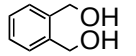
Catalytic Alcohol Oxidation by $\{V(V)_2\}$





Substrate	Conversion by ^{1}H NMR
 fluorenol	82% 54%[a]
 cinnamyl alcohol	40% 35%[a]
 benzyl alcohol	7%
 α-methylbenzyl alcohol	3%
 cyclohexanemethanol	0%
 1,2-benzenedimethanol	0%
[a]Isolated yield.	

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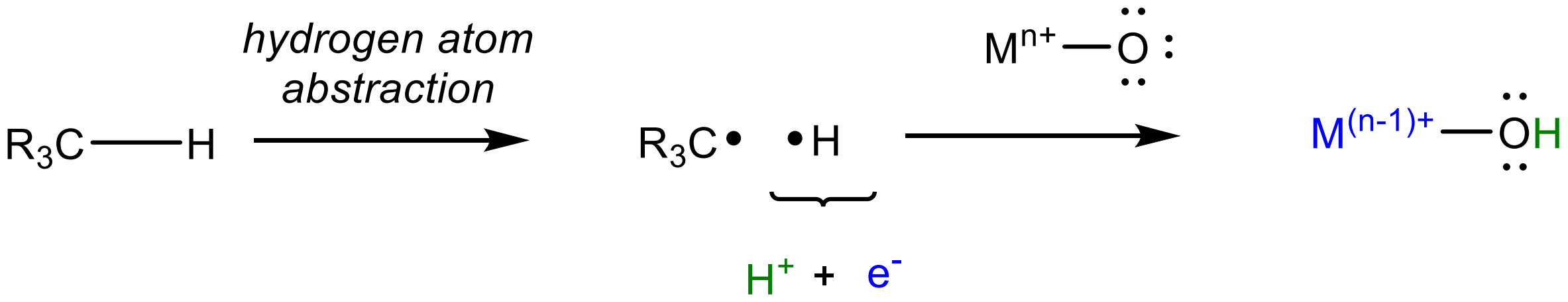
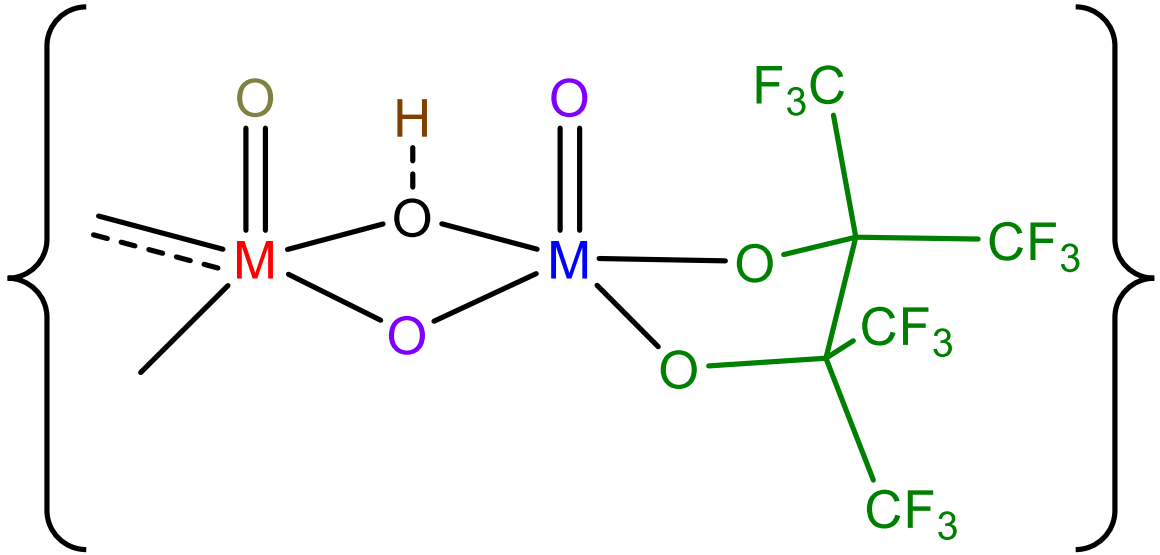
Metal Oxides for Oxidative Dehydrogenation



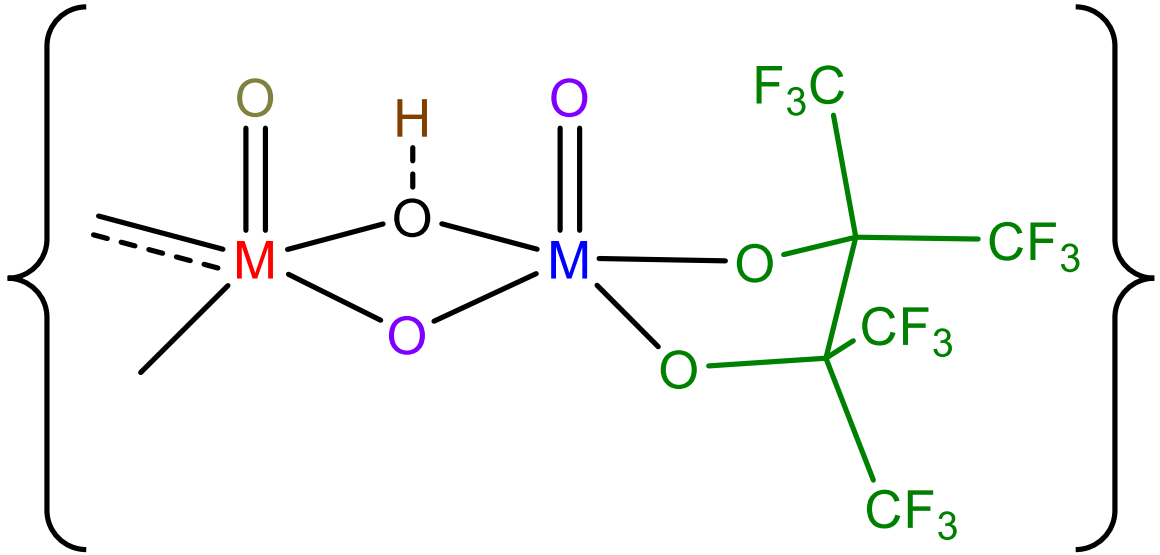
Knobs to Tune

metal oxidation state



https://www.musicmusingsandsuch.com/

Knobs to Tune

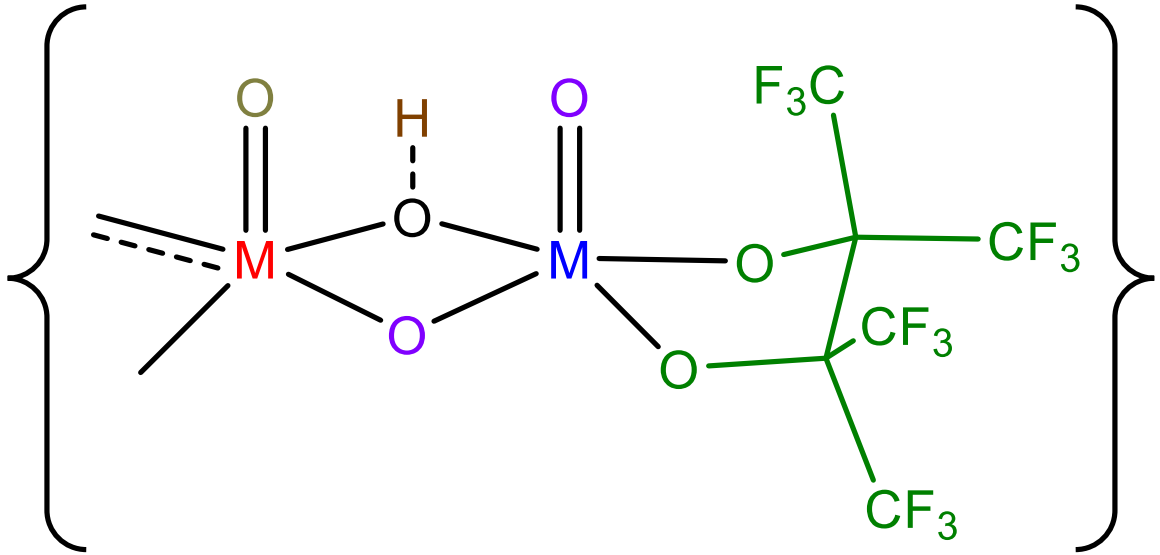


metal oxidation state

metal nuclearity (monomer vs dimer)

https://www.musicmusingsandsuch.com/

Knobs to Tune



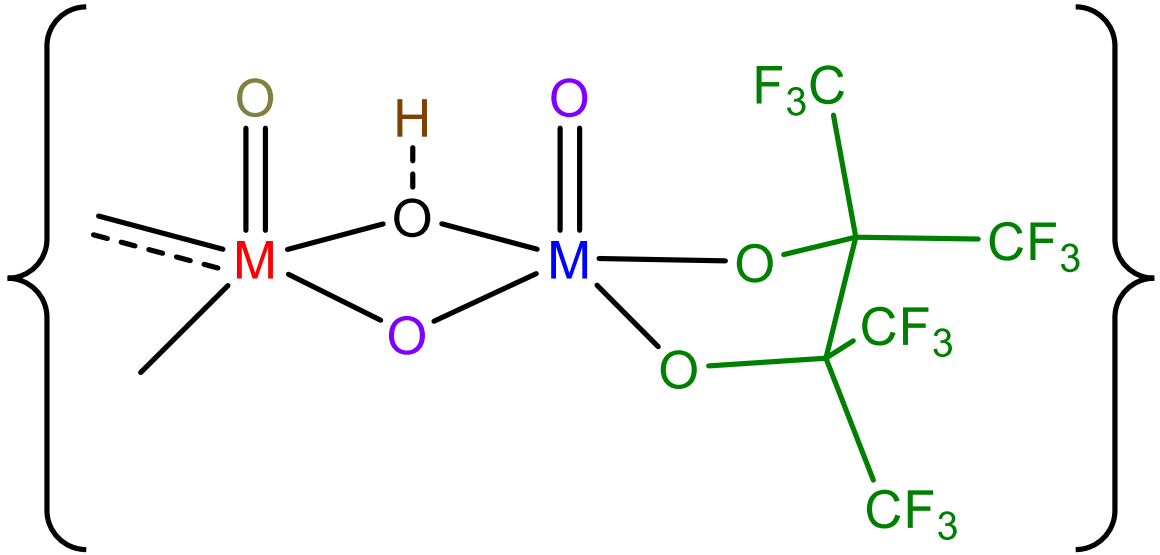
metal oxidation state

metal nuclearity (monomer vs dimer)

number of oxo groups

https://www.musicmusingsandsuch.com/

Knobs to Tune



metal oxidation state

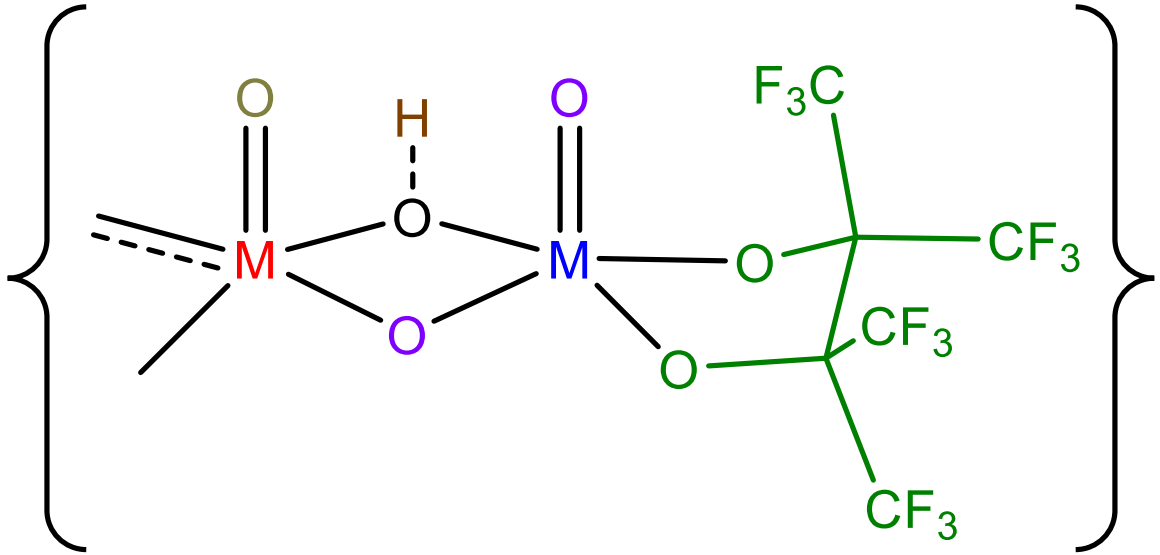
metal nuclearity (monomer vs dimer)

number of oxo groups

terminal vs bridging oxo

https://www.musicmusingsandsuch.com/

Knobs to Tune



metal oxidation state

metal nuclearity (monomer vs dimer)

number of oxo groups

terminal vs bridging oxo

oxo protonation state

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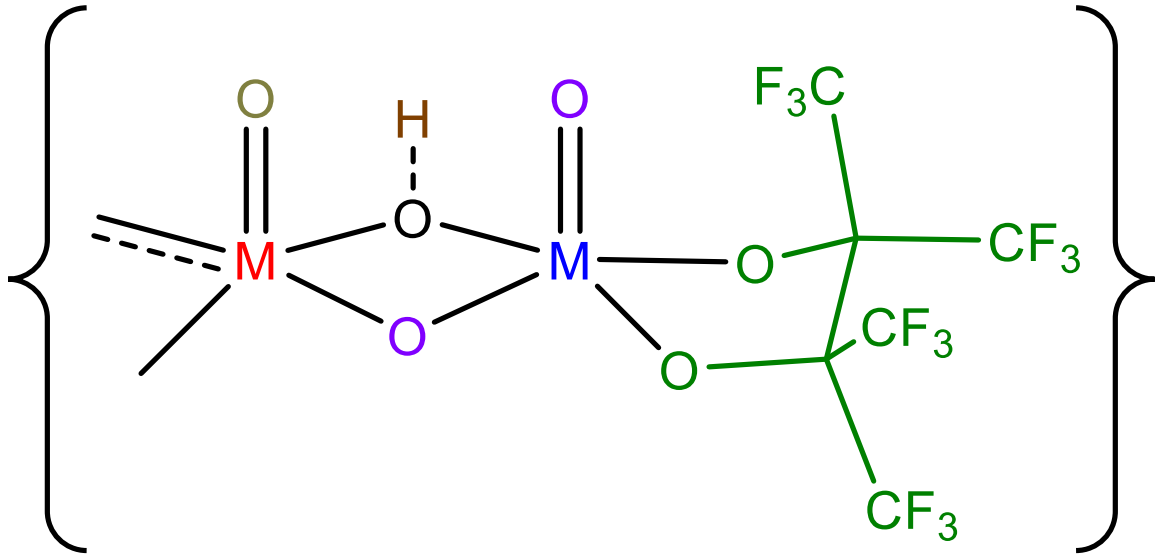
Knobs to Tune



metal oxidation state

metal nuclearity (monomer vs dimer)

number of oxo groups

terminal vs bridging oxo

oxo protonation state

number of pin^{F} ligands

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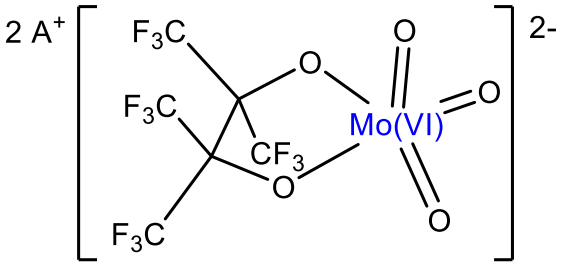
Mo Perfluoropinacolate Oxo Complexes

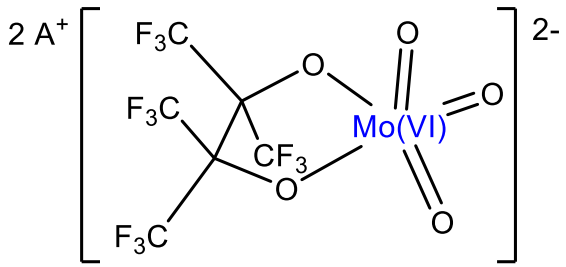


$[Mo(VI)(O)_3(pin^F)]^{2-}$

A = Et_3NH^+, Me_4N^+, $\{K(18C6)\}^+$

SCXRD data

Mo Perfluoropinacolate Oxo Complexes

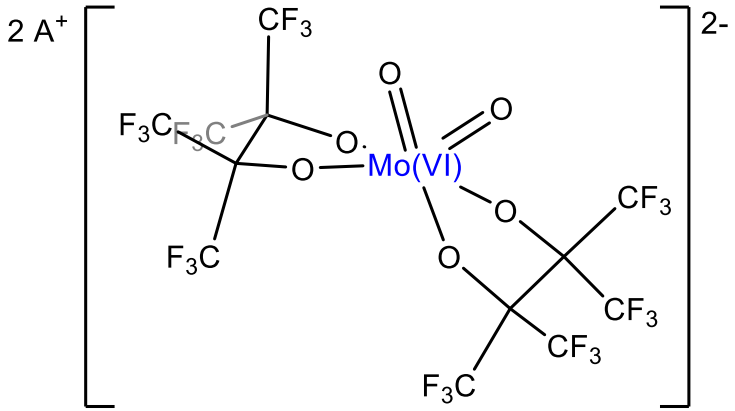


$[Mo(VI)(O)_3(pin^F)]^{2-}$

A = Et_3NH^+, Me_4N^+, $\{K(18C6)\}^+$

number of oxo groups

number of pin^F ligands

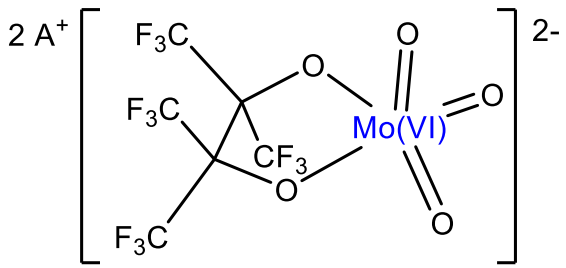


$[Mo(VI)(O)_2(pin^F)_2]^{2-}$

A = Et_3NH^+, Me_4N^+

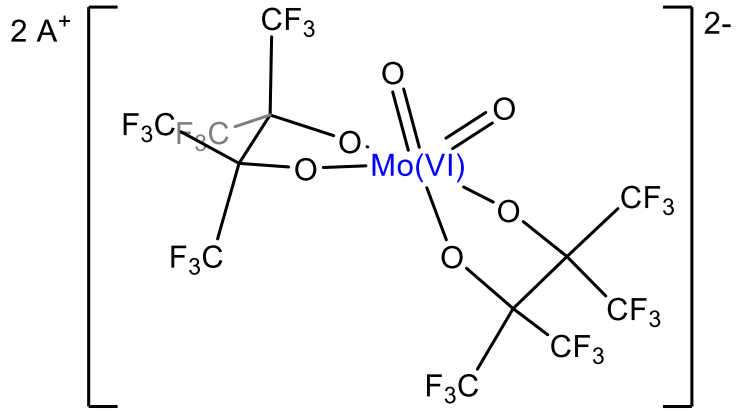
SCXRD data

Mo Perfluoropinacolate Oxo Complexes



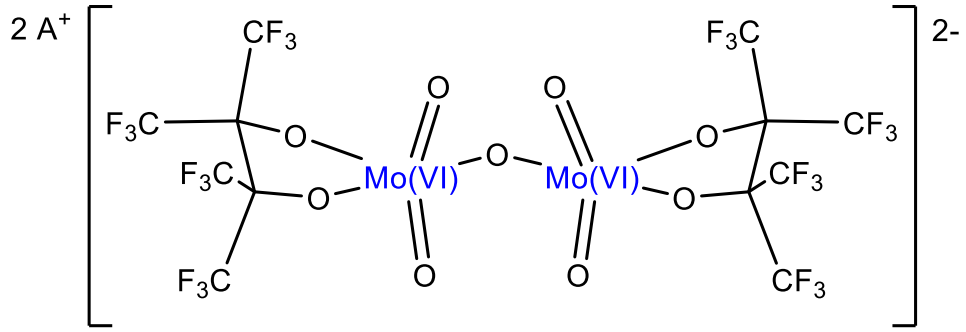
$[Mo(VI)(O)_3(pin^F)]^{2-}$

A = Et_3NH^+, Me_4N^+, $\{K(18C6)\}^+$



$[Mo(VI)(O)_2(pin^F)_2]^{2-}$

A = Et_3NH^+, Me_4N^+



$[Mo(VI)_2(O)_4(\mu\text{-}O)(pin^F)_2]^{2-}$

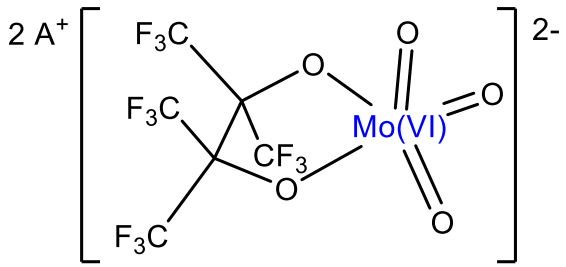
A = Et_3NH^+, Me_4N^+

metal nuclearity (monomer vs dimer)

terminal vs bridging oxo

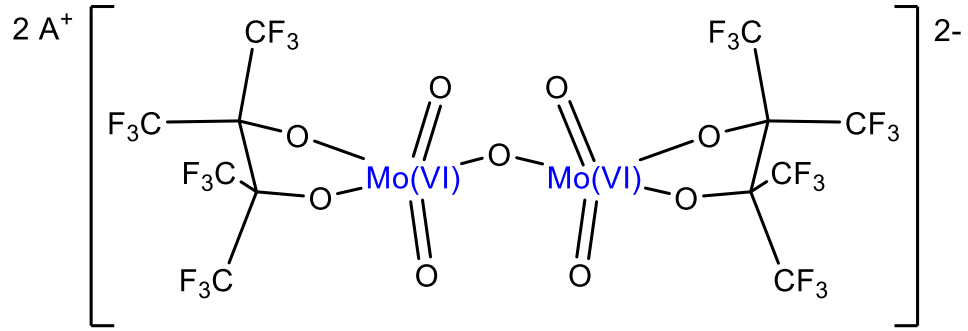
SCXRD data

Mo Perfluoropinacolate Oxo Complexes



$[Mo(VI)(O)_3(pin^F)]^{2-}$

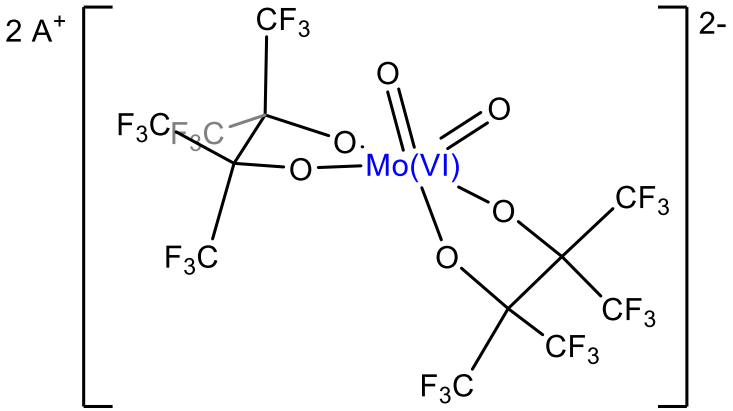
A = Et_3NH^+, Me_4N^+, $\{K(18C6)\}^+$



$[Mo(VI)_2(O)_4(\mu\text{-}O)(pin^F)_2]^{2-}$

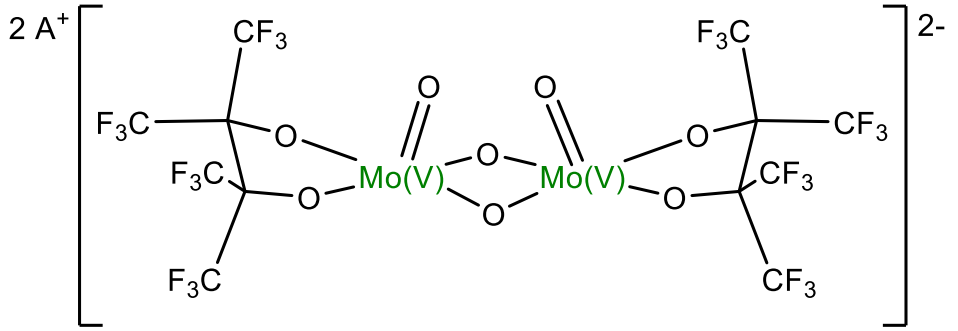
A = Et_3NH^+, Me_4N^+

metal oxidation state



$[Mo(VI)(O)_2(pin^F)_2]^{2-}$

A = Et_3NH^+, Me_4N^+

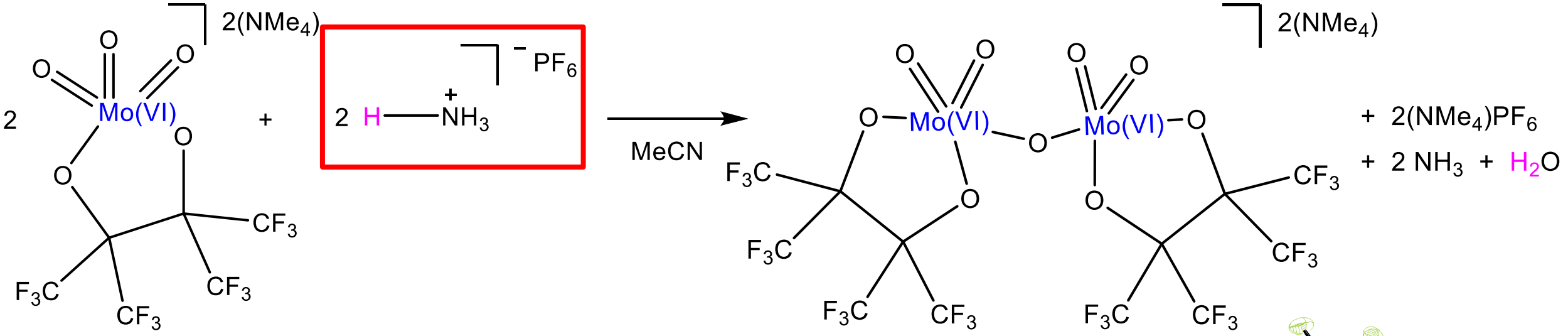


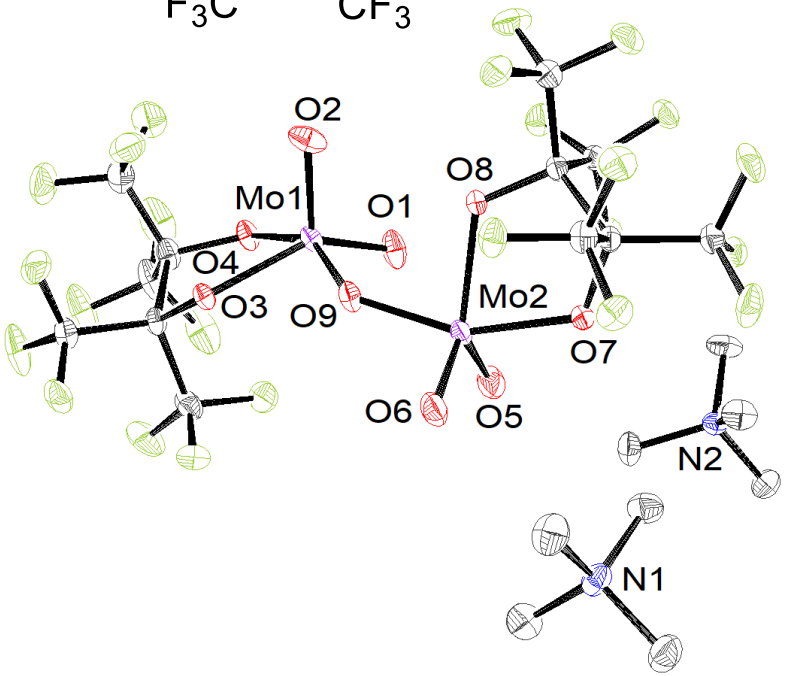
$[Mo(V)_2(O)_2(\mu\text{-}O)_2(pin^F)_2]^{2-}$

A = Et_3NH^+

SCXRD data

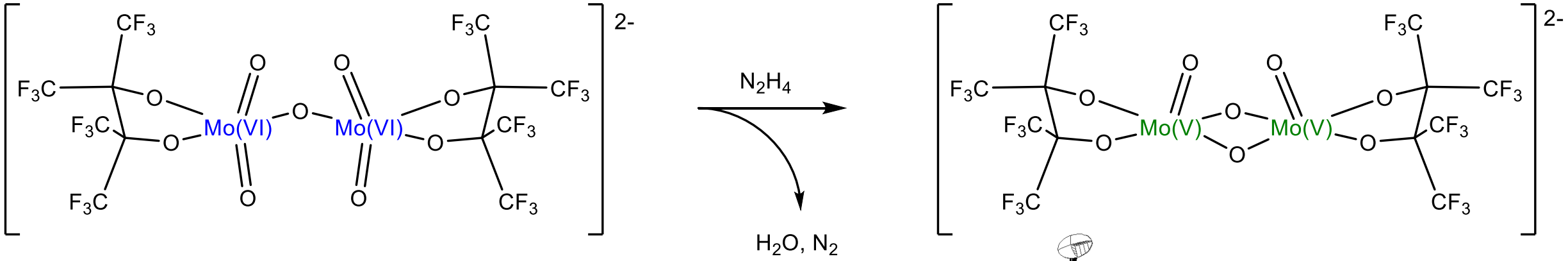
Monomer to Dimer Condensation with H^+

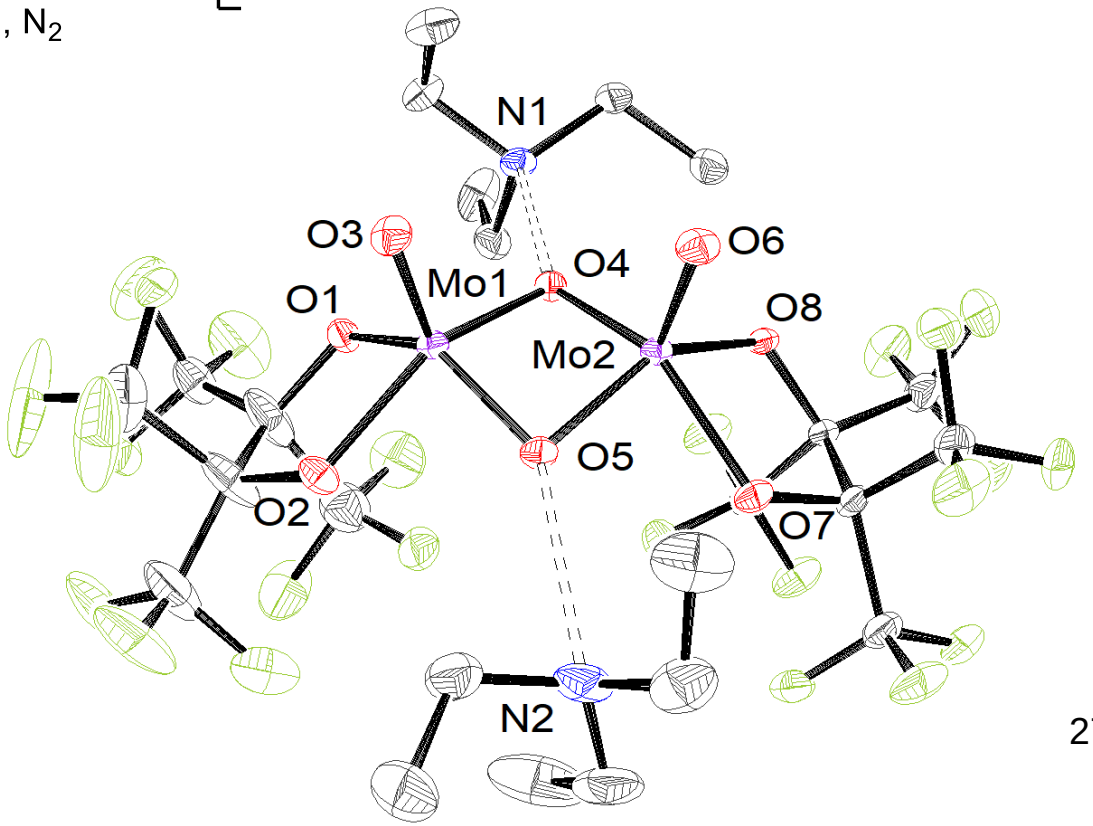




R. B. Abdu, T. B. Mdalel, L. H. Doerrer, *unpublished results*, **2021**

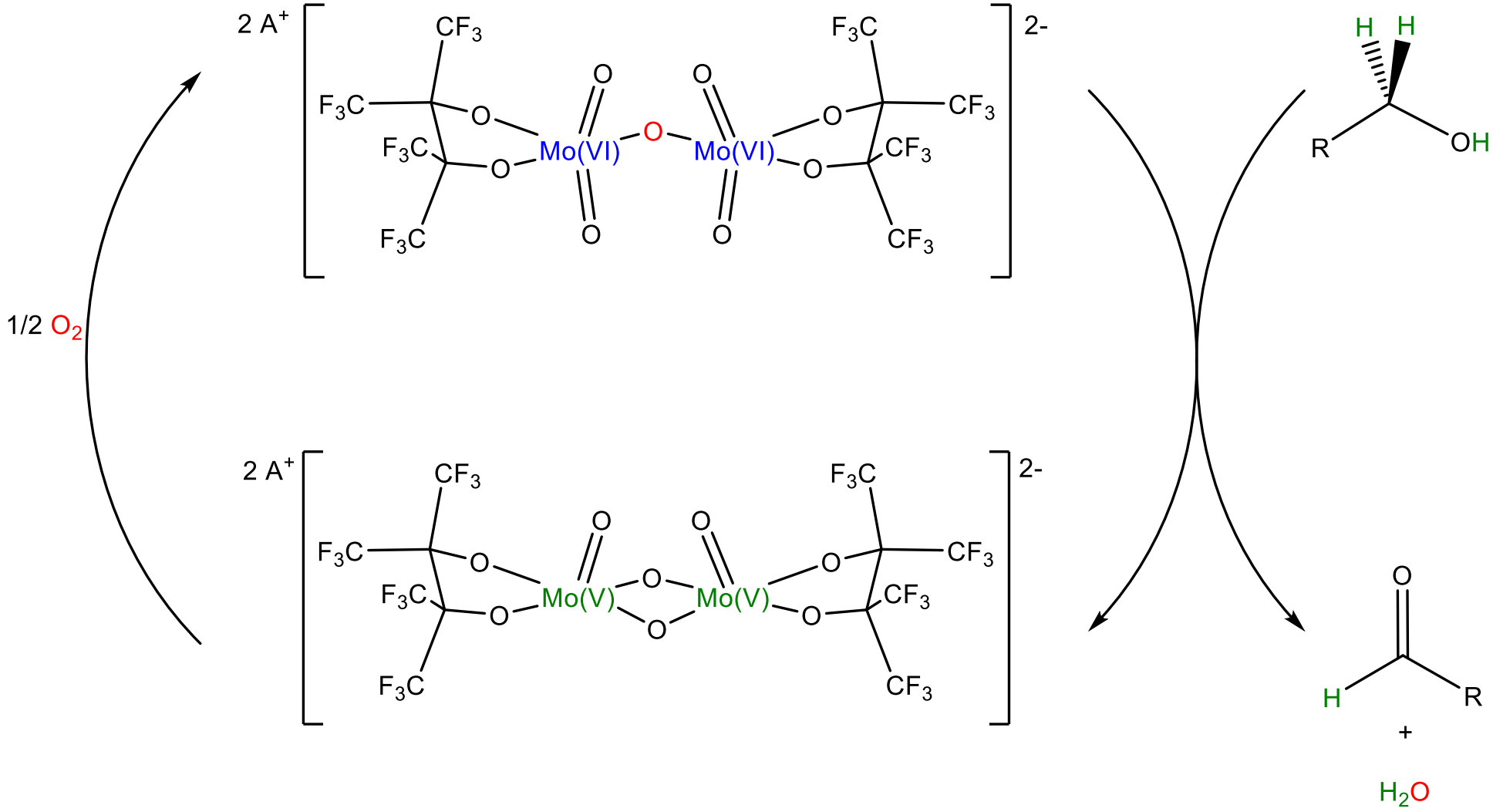
Reduction of Mo(VI) to Mo(V) via N_2H_4





S. Choi, L. H. Doerrer, *unpublished results*, **2021**

Possible {Mo(O)(pin^F)} Catalytic Reactivity



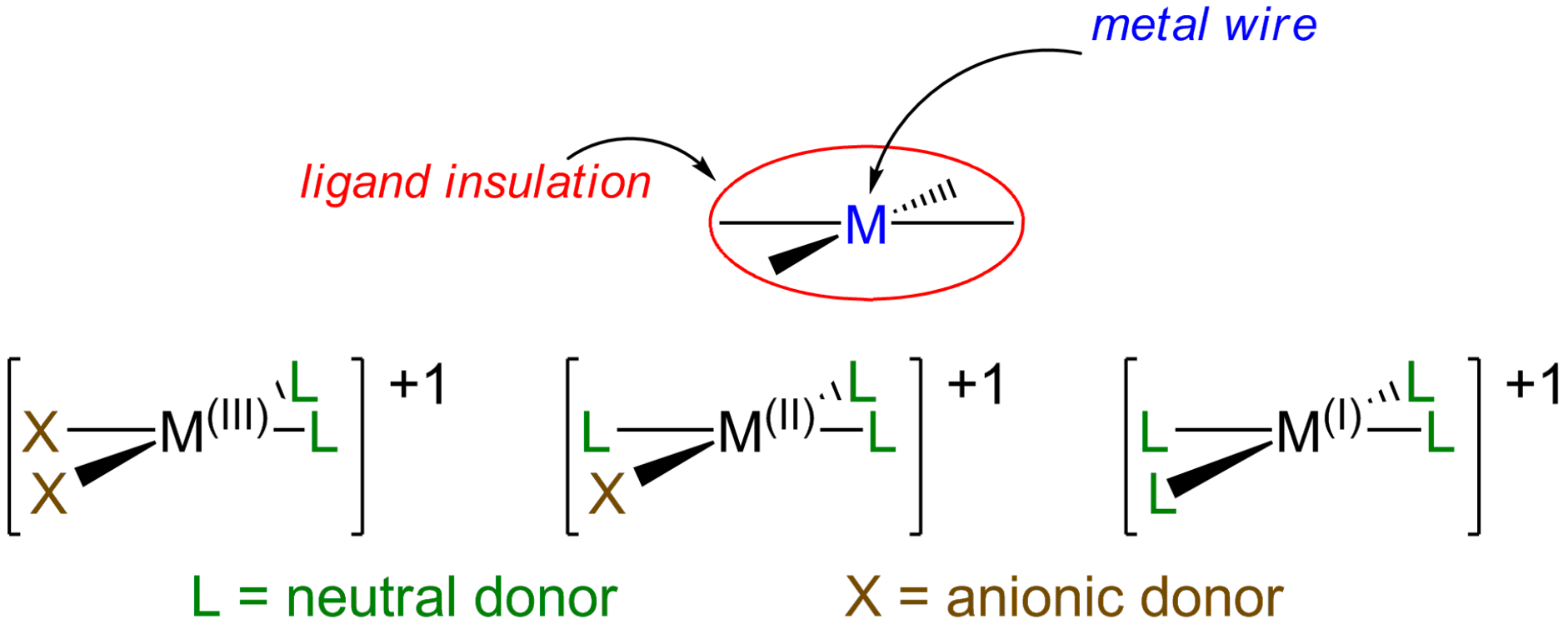
Inorganic Tapas Menu

Fluorinated Alkoxide Complexes

Heterobimetallic Lantern Complexes

A New Family of Ligands

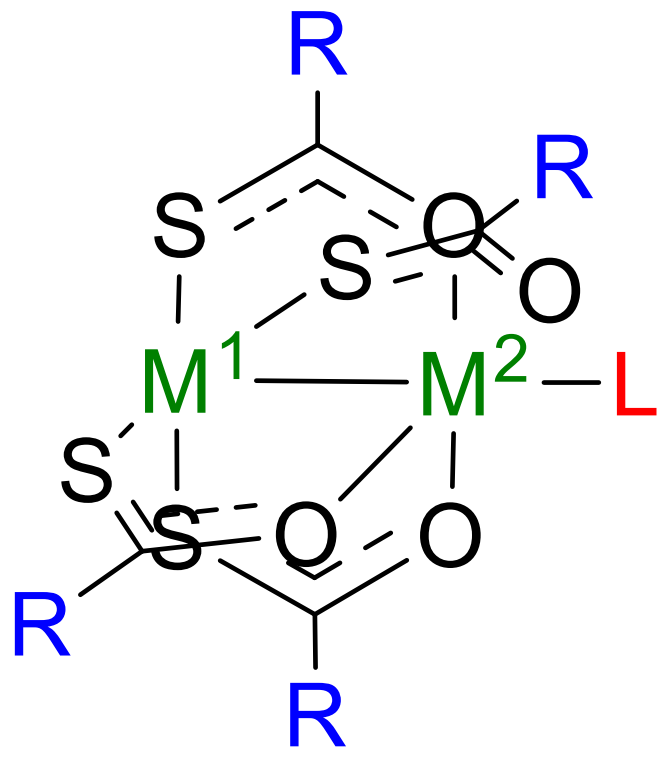
Quasi 1D from the Metal and Out



LHD, *Comments Inorg. Chem.*, **2008**, *29*, 93-127

LHD, *Dalton Trans.*, **2010**, *39*, 3543-3553

Variables in Lantern Compounds



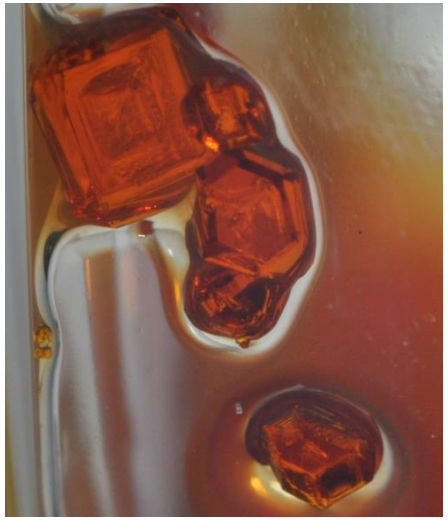
Incorporating New Metals

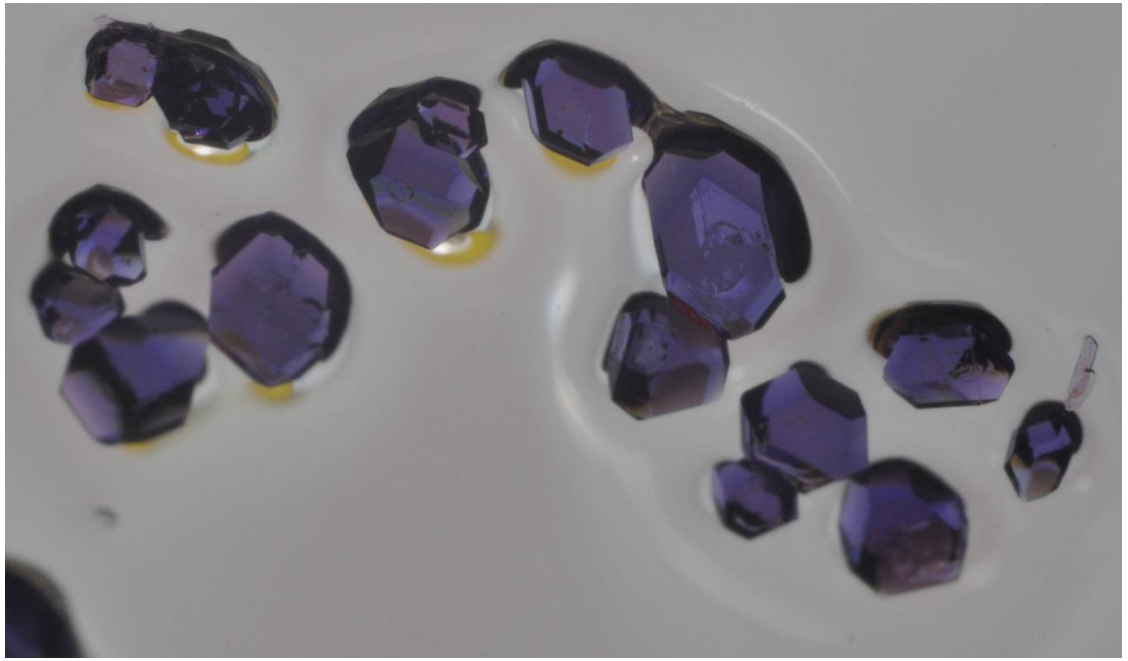
New Bridging or Terminal Ligands

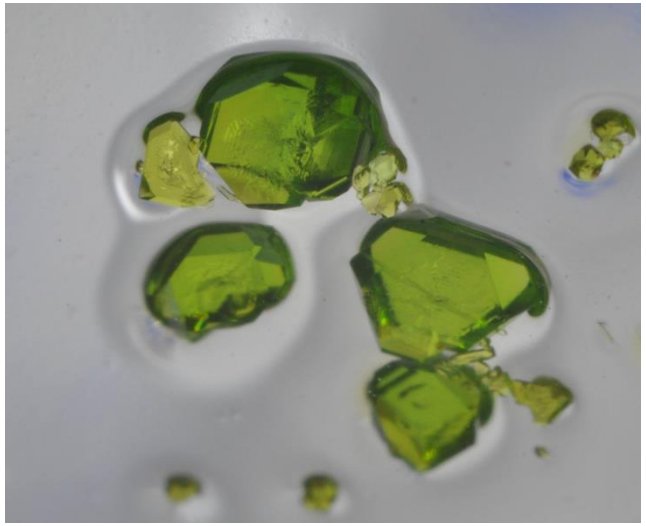
Modification of Thiocarboxylate Backbone

S. A. Beach, L. H. Doerrer, *Acc. Chem. Res.*, **2018**, *51*,1063-72

$[PtM(SAc)_4(OH_2)]$ from acetone



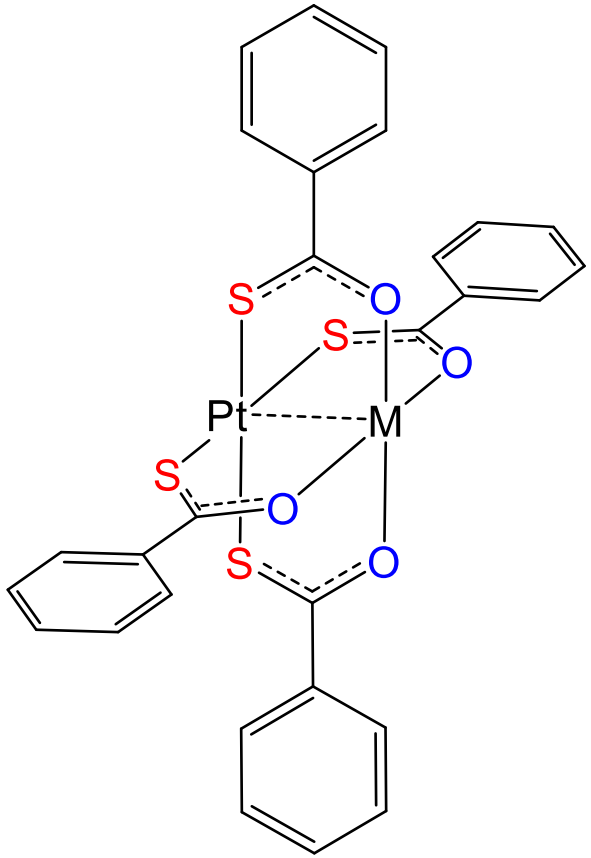


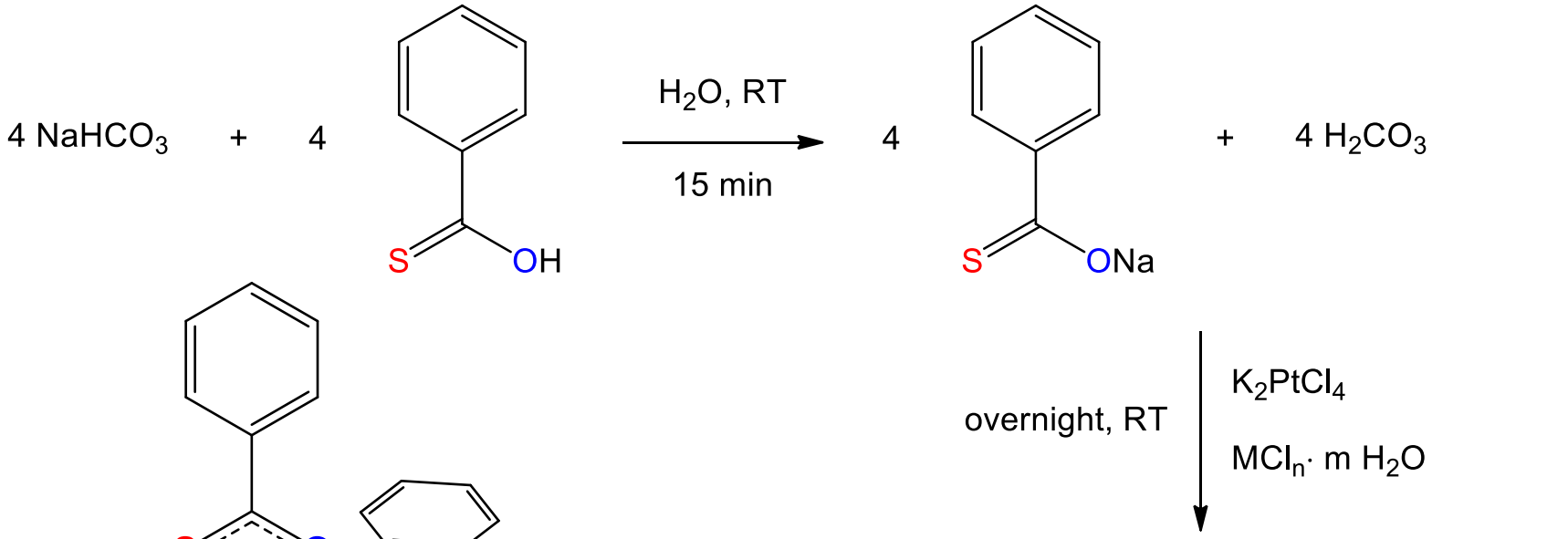


$[PtFe(SAc)_4(OH_2)]$ $[PtCo(SAc)_4(OH_2)]_2$ $[PtNi(SAc)_4(OH_2)]_2$

F. G. Baddour, S. R. Fielder, M. P. Shores, J. A. Golen, A. L. Rheingold, LHD*, Inorg. Chem.,* **2013**, *52*, 4926-4933

$[PtM(tba)_4]$ Synthesis

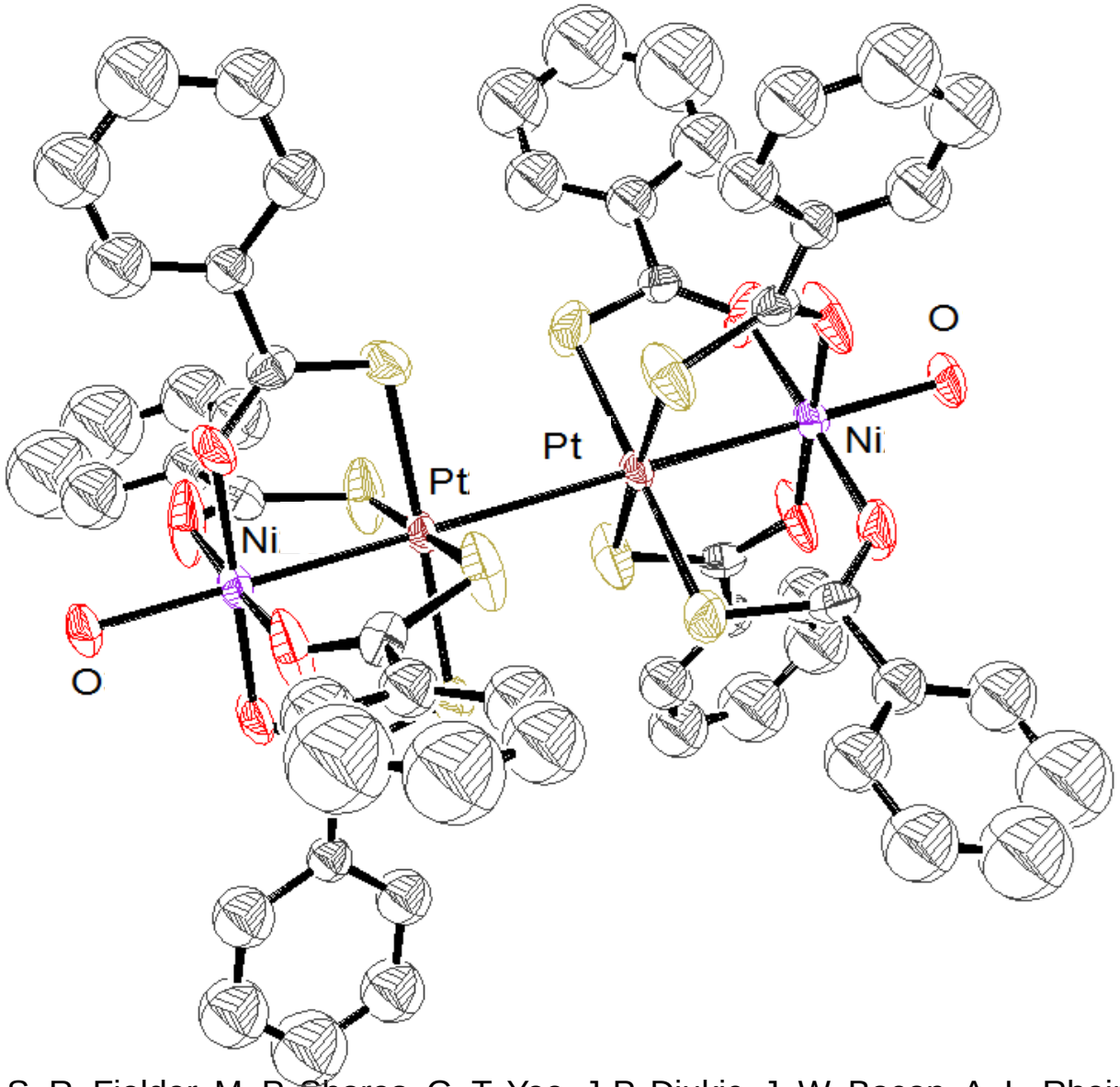




~60 - 70% Yield

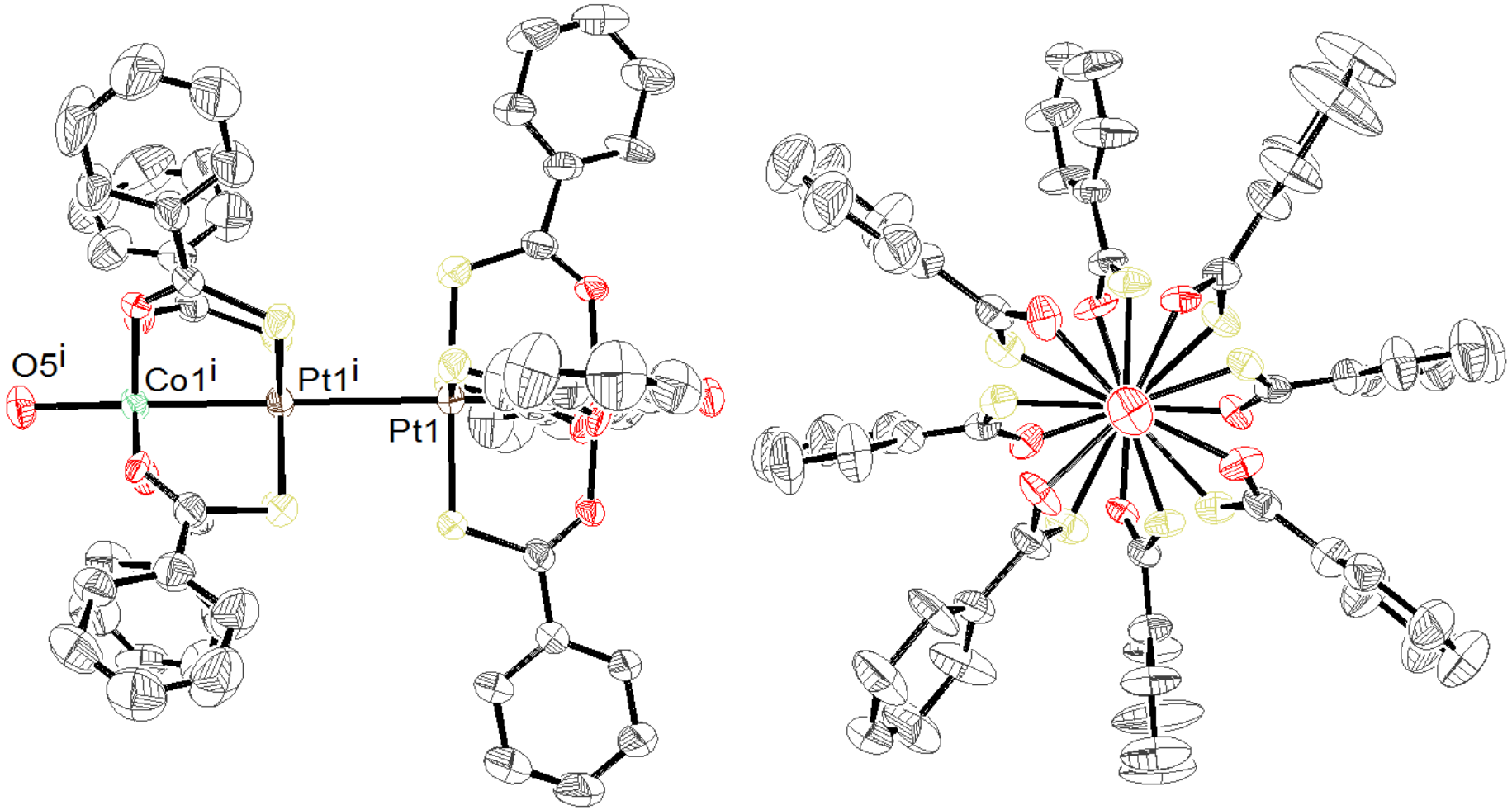
E. W. Dahl, F. G. Baddour, W. A. Hoffert, S. R. Fielder, M. P. Shores, G. T. Yee, J-P. Djukic, J. W. Bacon, A. L. Rheingold, LHD, *Chem. Sci.,* **2012**, *3*, 602-609

$[PtNi(tba)_4(OH_2)]_2$



E. W. Dahl, F. G. Baddour, W. A. Hoffert, S. R. Fielder, M. P. Shores, G. T. Yee, J-P. Djukic, J. W. Bacon, A. L. Rheingold, LHD, *Chem. Sci.,* **2012**, *3*, 602-609

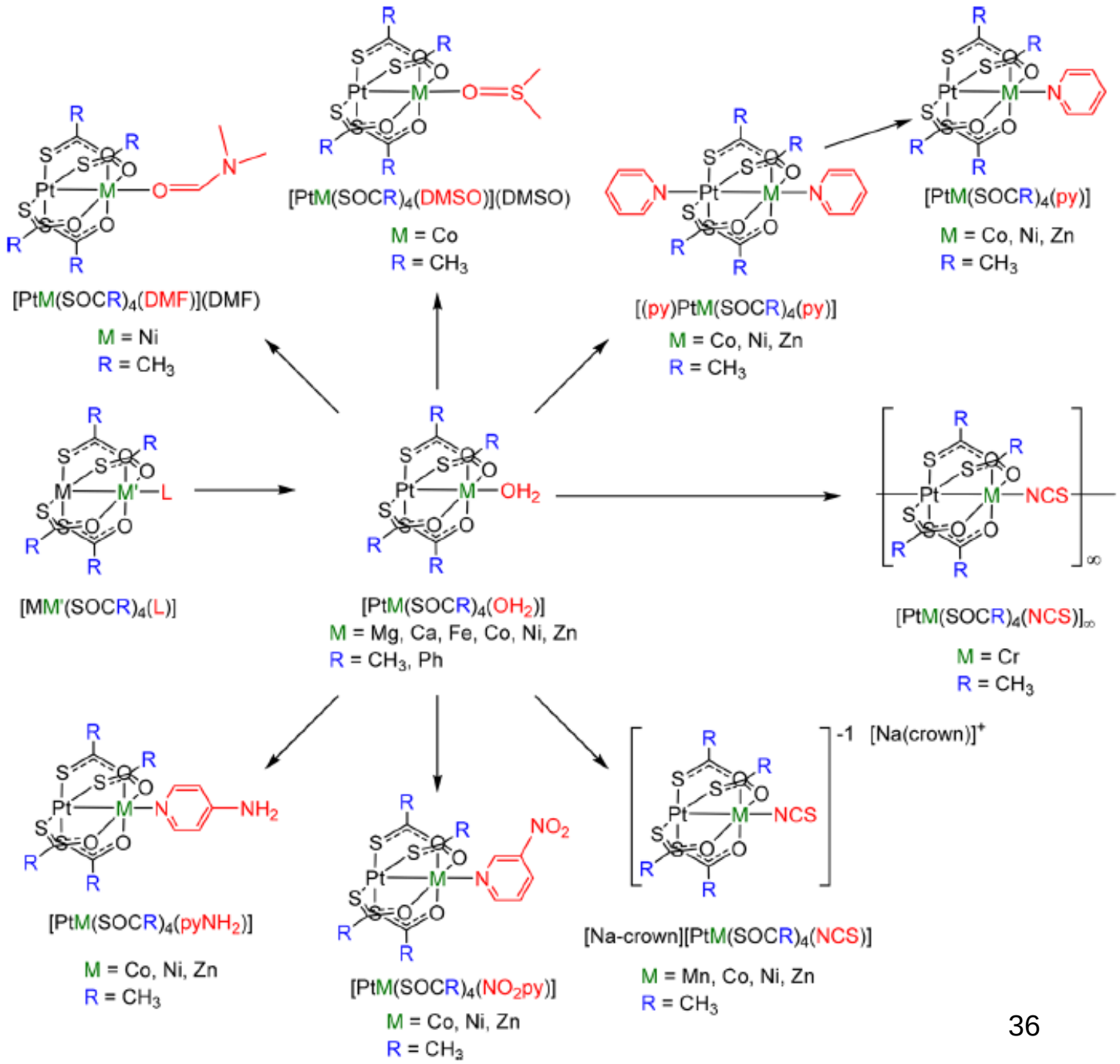
$[PtCo(tba)_4(OH_2)_2]$ – purple form



Staggered along Co…Co vector

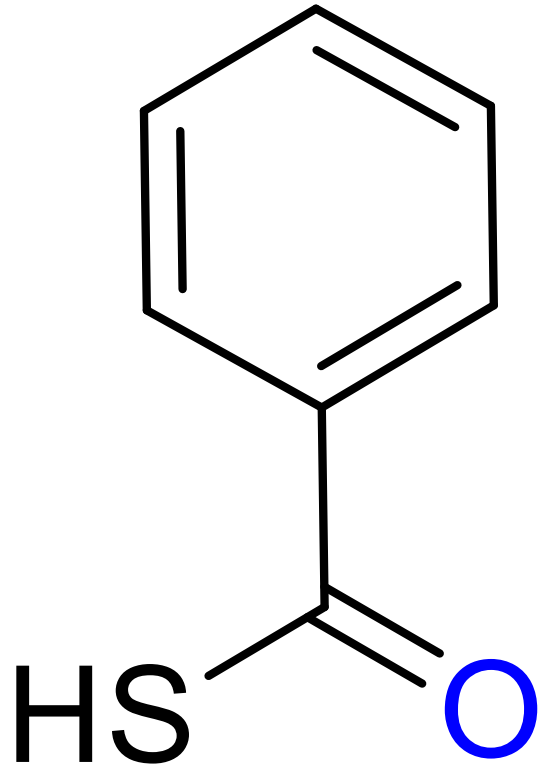
E. W. Dahl, F. G. Baddour, W. A. Hoffert, S. R. Fielder, M. P. Shores, G. T. Yee, J-P. Djukic, J. W. Bacon, A. L. Rheingold, LHD, *Chem. Sci.,* **2012**, *3*, 602-609

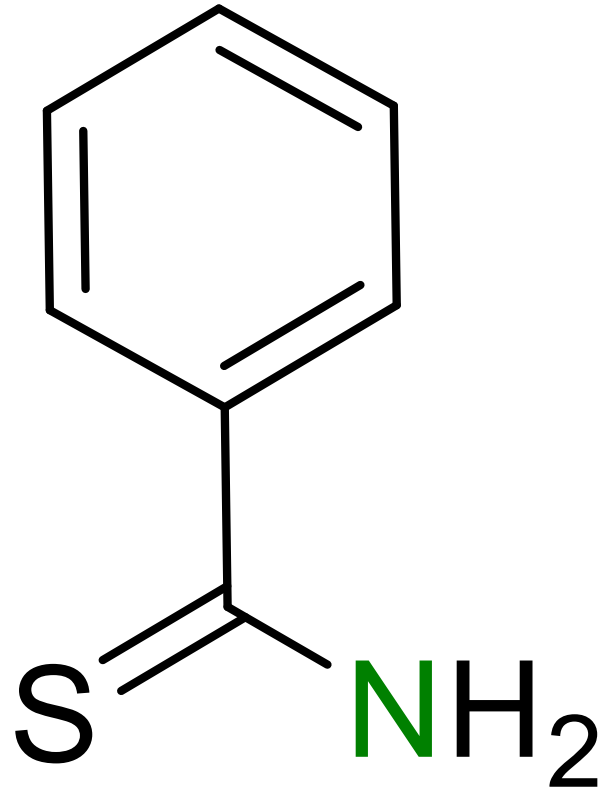
Many Thiocarboxylate Lantern Complexes



S. A. Beach, L. H. Doerrer, *Acc. Chem. Res.*, **2018**, *51*,1063-72

Change O to N ?





L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

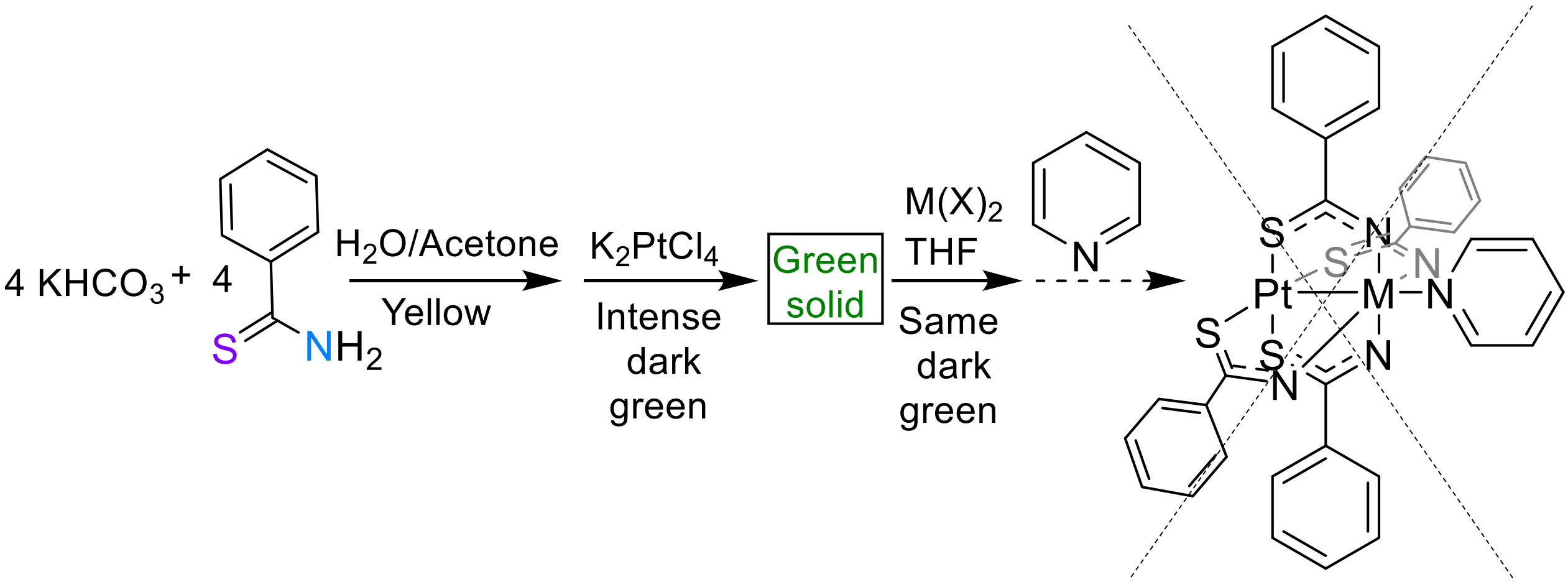
Inorganic Tapas Menu

Fluorinated Alkoxide Complexes

Heterobimetallic Lantern Complexes

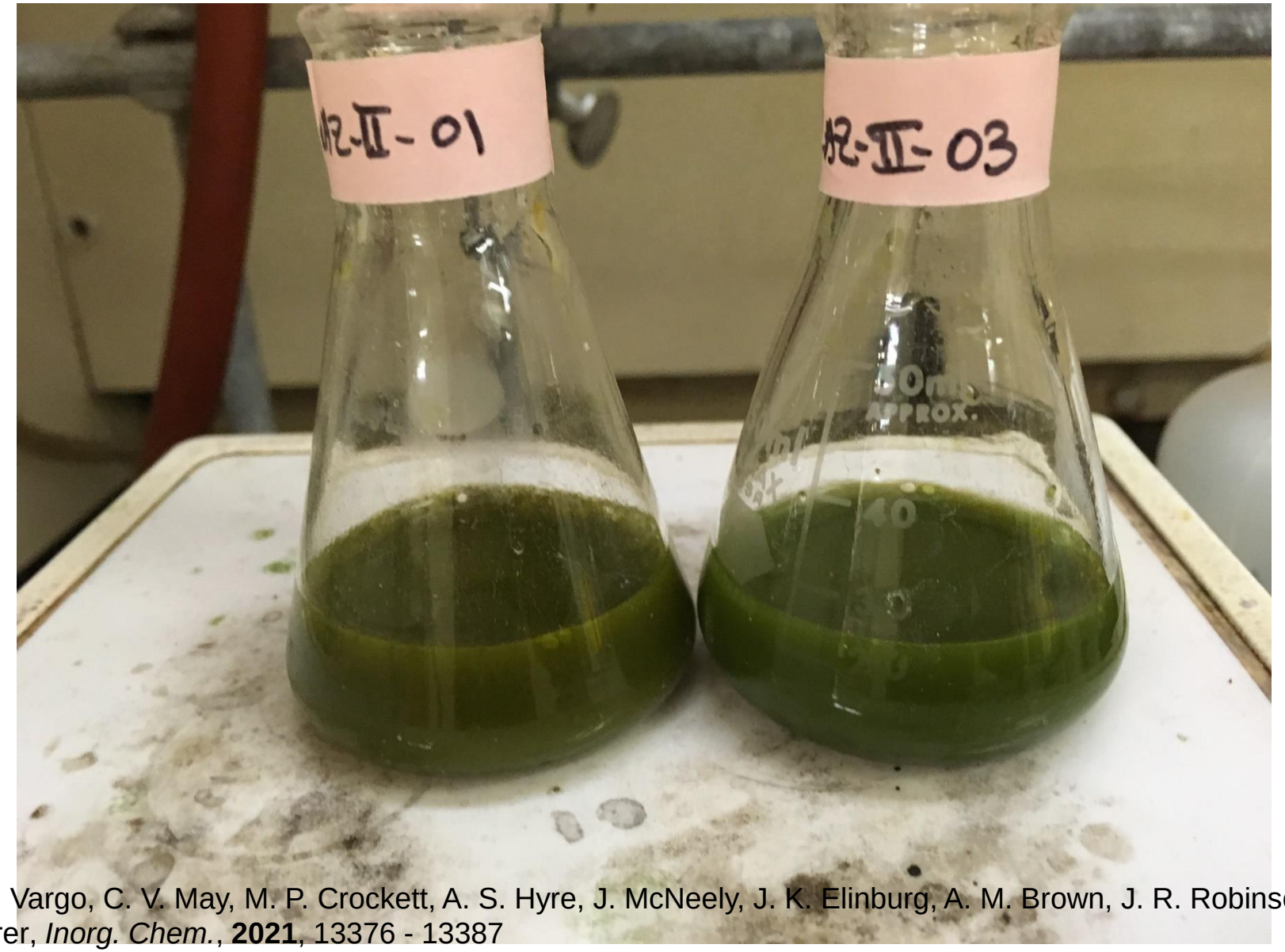
A New Family of Ligands

Planned Synthesis



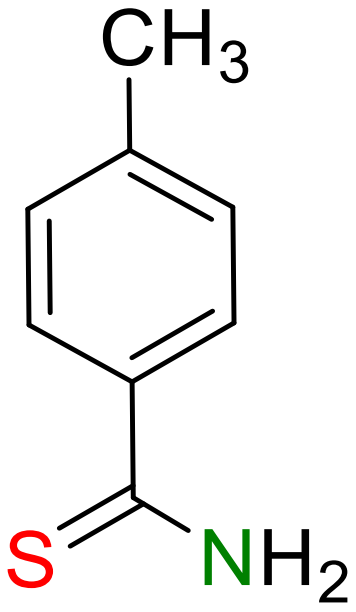
L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

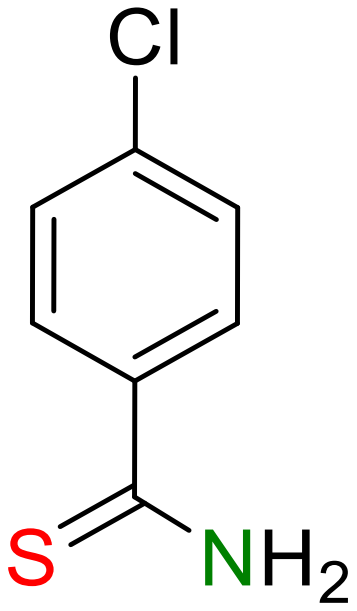
Dark Green Product

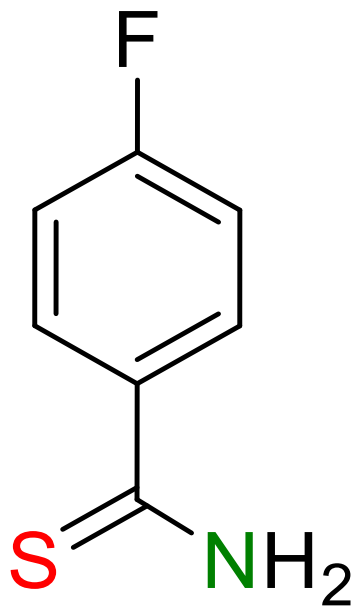


L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

Three Other Thiobenzamides

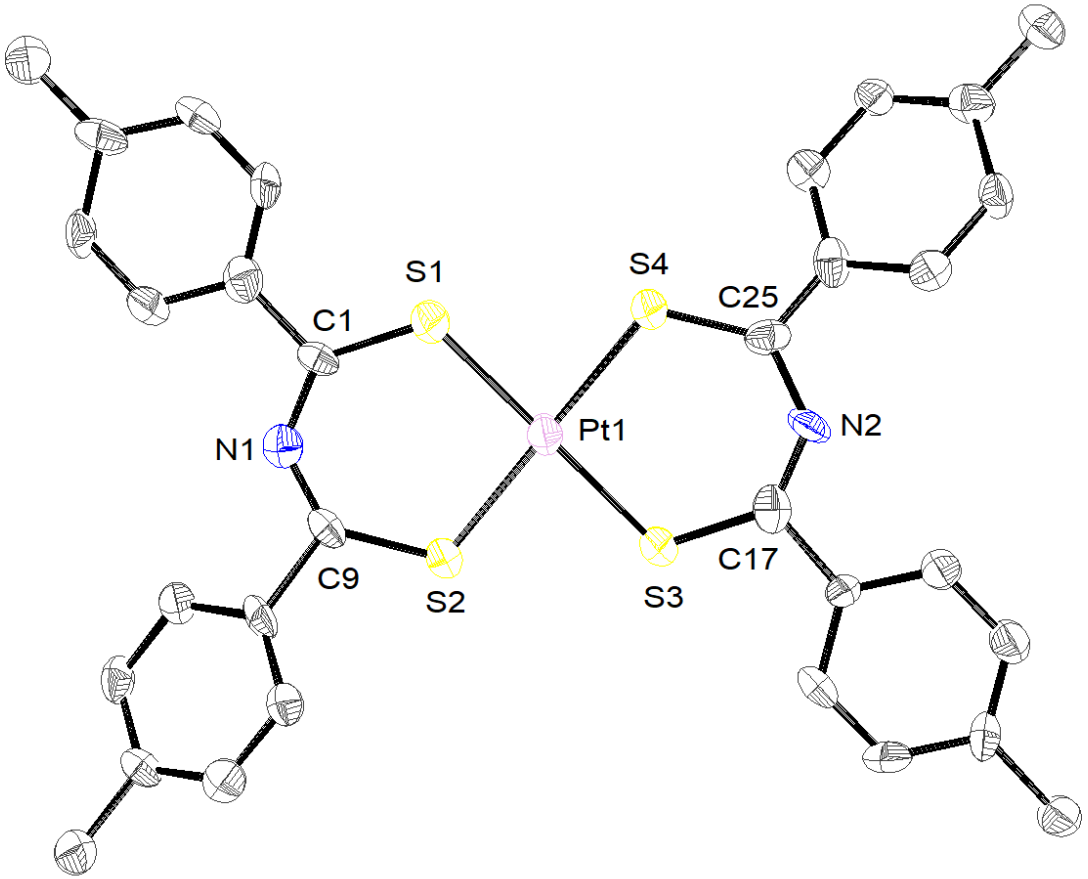


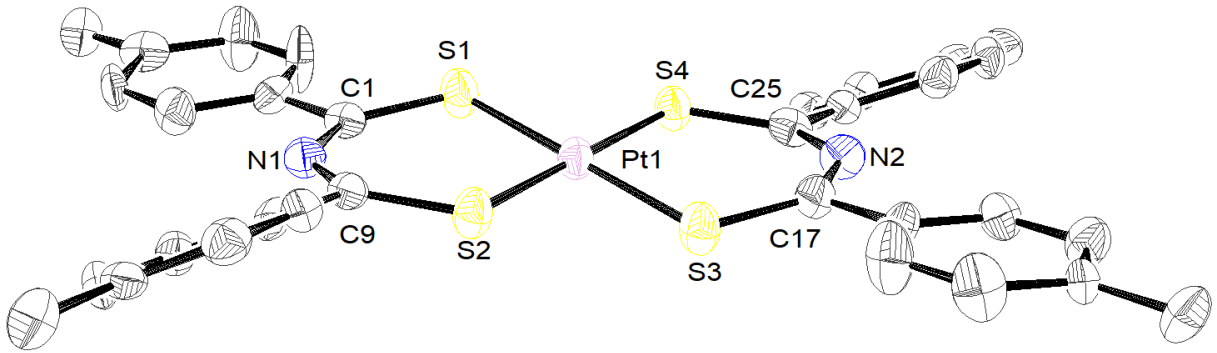




L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

A New Compound and a New Ligand !

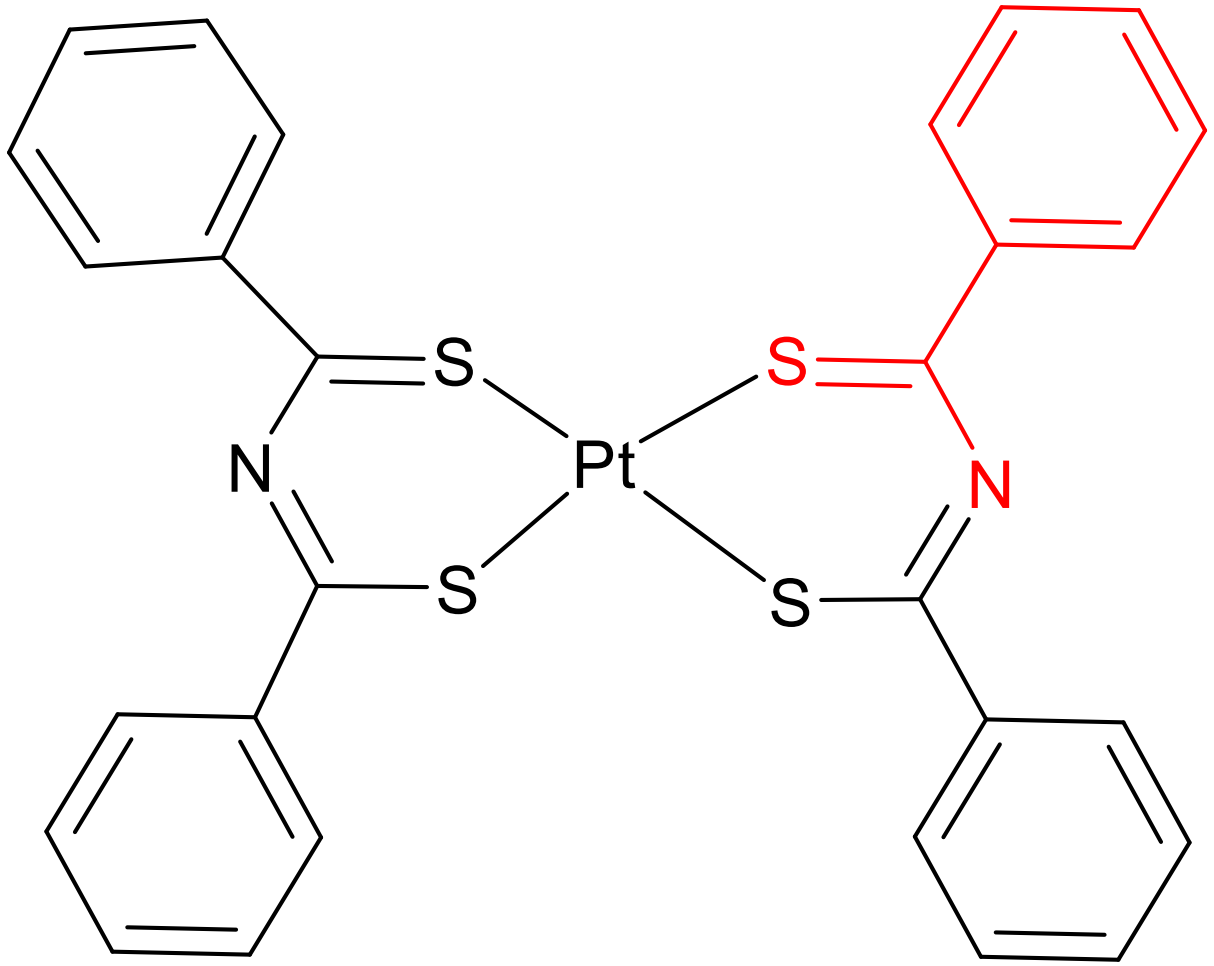




$[Pt(ctaPh^{Me})_2]$

L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

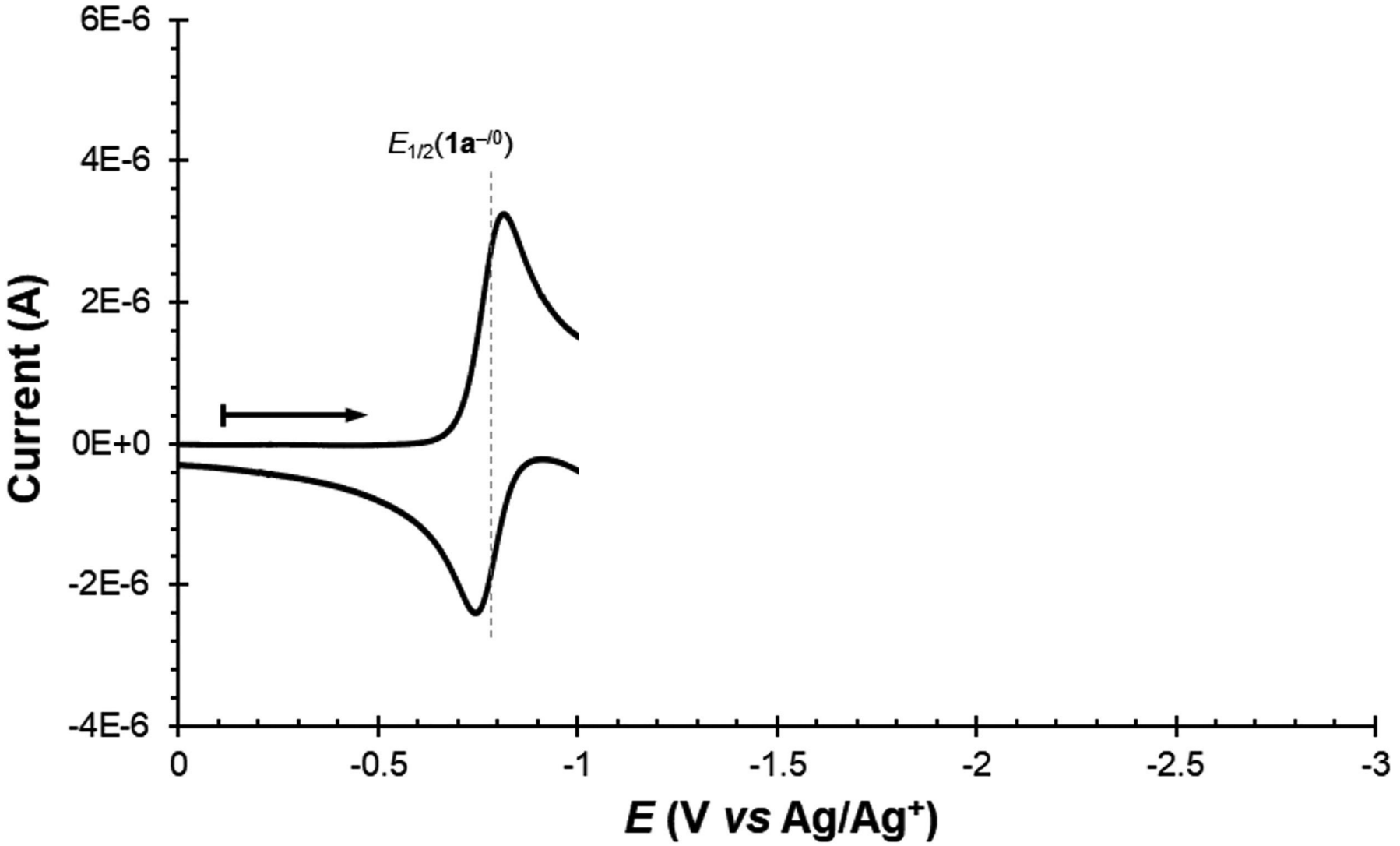
$[Pt(ctaPh)_2]$



cta = condensed thioamide

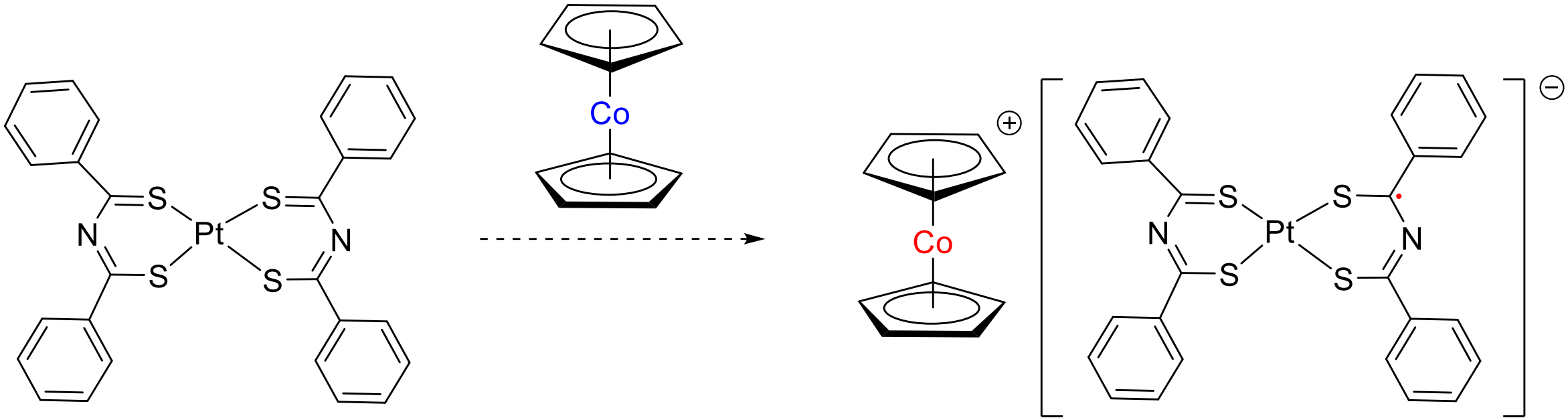
L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

Cyclic Voltammetry of $[Pt(ctaPh^{Me})_2]$



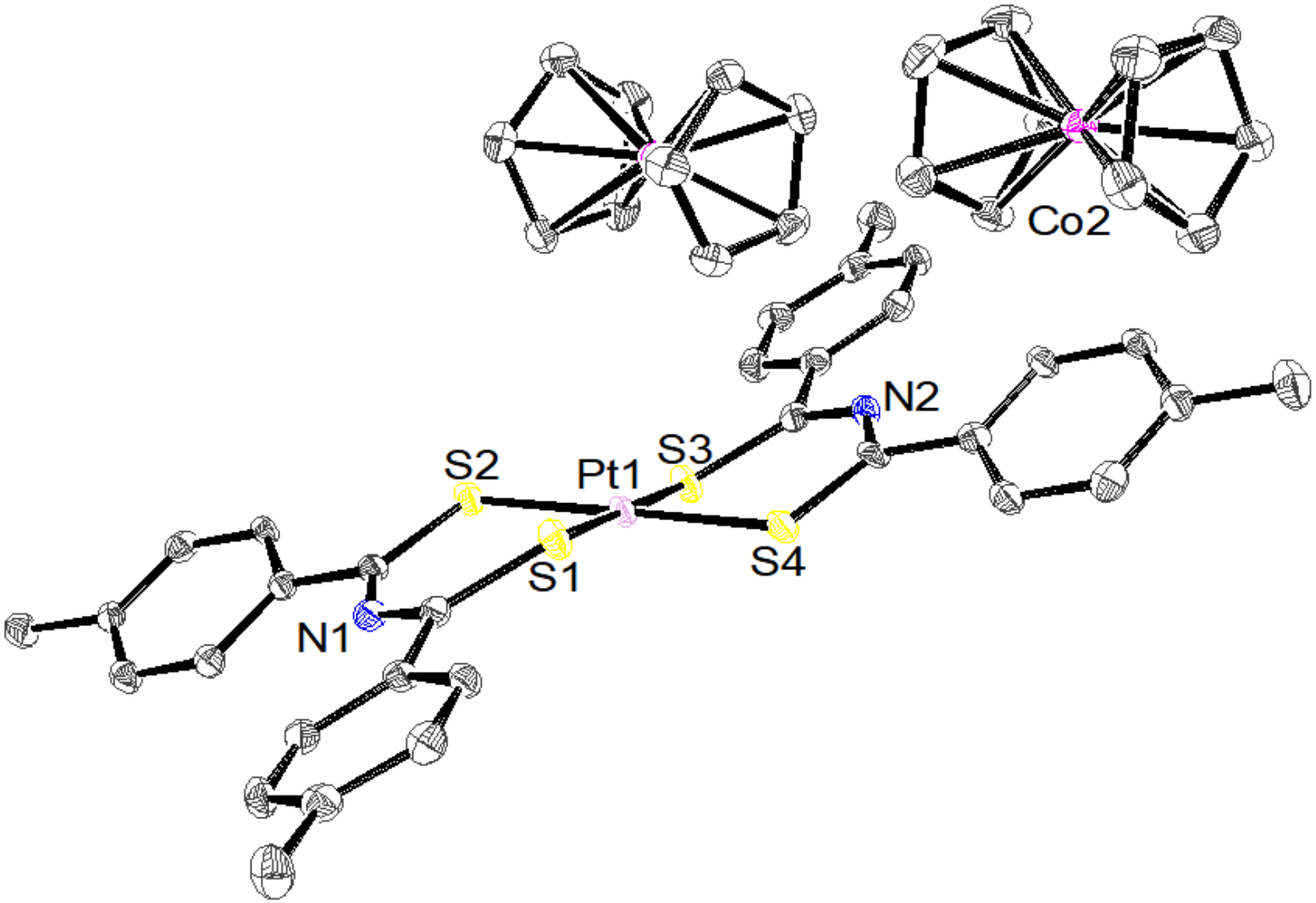
L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

One-electron Reduction to form $[Pt(ctaPh)_2]^-$



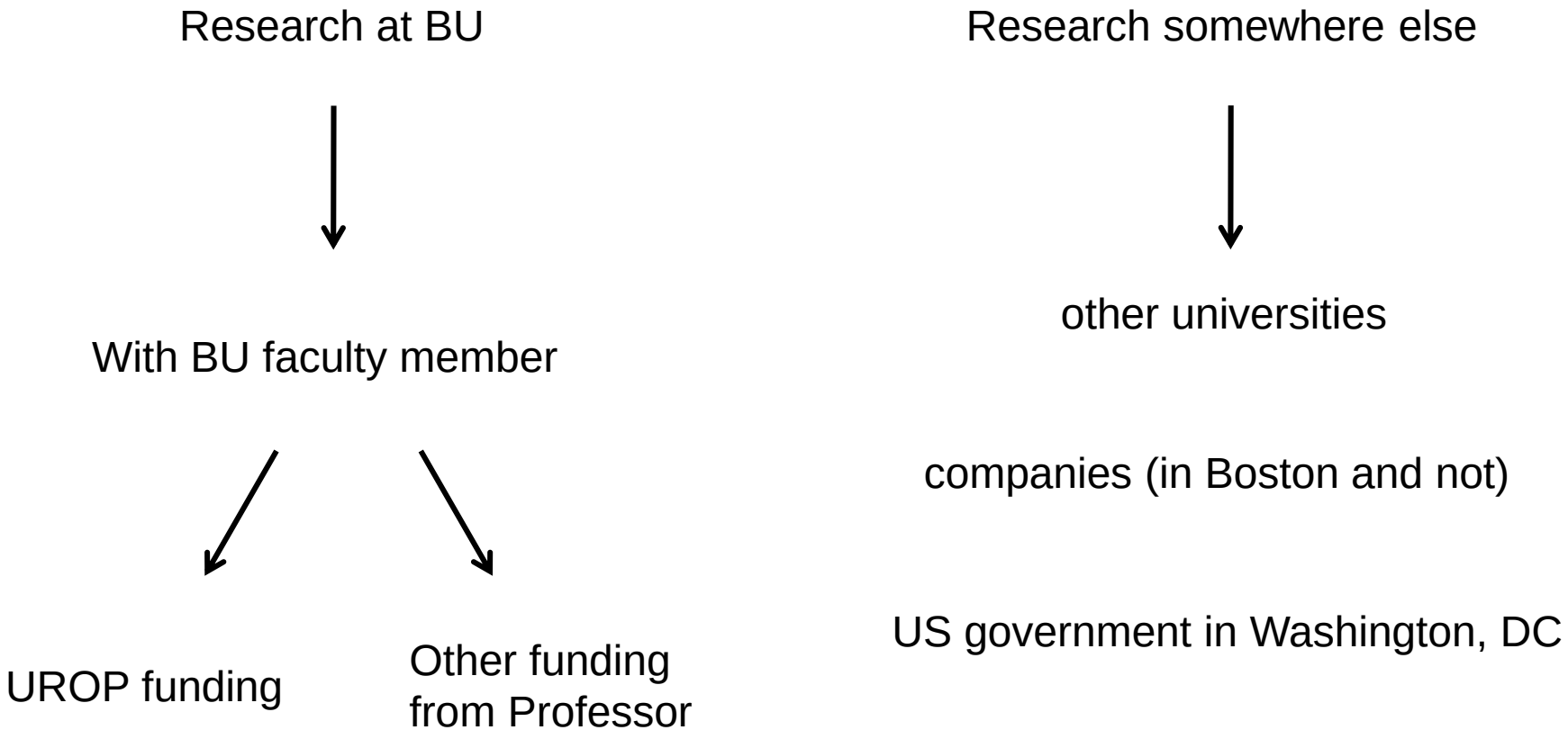
L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

Product has *two* $[Cp_2Co]^+$



L. A. Zuckerman, N. P. Vargo, C. V. May, M. P. Crockett, A. S. Hyre, J. McNeely, J. K. Elinburg, A. M. Brown, J. R. Robinson, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.*, **2021**, 13376 - 13387

Undergraduate Research



With BU faculty member

Step 1: Inform yourself about opportunities
- read website of department and faculty members
- ask your TFs, particularly graduate students
- ask your professors

Step 2: Find out about opportunities in a particular group
- email TFs or professors individually with your interest
- offer to send CV, transcript, and names of references

Step 3: If there is interest in you, offer to apply for UROP funding

http://www.bu.edu/urop/ (summer deadline already past)

Ask about other options for funding (will vary)

Research somewhere else

National Science Foundation –
Research Experiences for Undergraduates (REU)

http://www.nsf.gov/crssprgm/reu/reu_search.cfm

Astronomical Sciences
Atmospheric and Geospace Sciences
Biological Sciences
Chemistry
Computer and Information Science and Engineering
Cyberinfrastructure
Department of Defense (DoD)
Earth Sciences
Education and Human Resources
Engineering
Ethics and Values Studies
International Science and Engineering
Materials Research
Mathematical Sciences
Ocean Sciences
Physics
Polar Programs
Social, Behavioral, and Economic Sciences

- Check individual institutions for deadline dates
- Consider less “cool” places to go which will receive fewer applications

Research somewhere else (con'd)

National Institutes of Health

https://www.training.nih.gov/programs

OD	NIA	NIDDK	NLM
NCI = National Cancer Institute	NIAAA	NIDA	CIT
	NIAID	NIEHS	CSR
NEI	NIAMS	NIGMS	FIC
NHLBI = National Heart, Lung, and Blood Institute	NIBIB	NIMH	NCCAM
	NICHD	NIMHD	NCRR
	NIDCD	NINDS	CC
NHGRI	NIDCR	NINR	

Undergraduate Scholarship Program (UGSP)

Summer Internship Program (SIP)

http://www.ninds.nih.gov/jobs_and_training/summer/

Summer Program in the Neurological Sciences and Other Neuroscience Research Training and Funding Opportunities

Research somewhere else (con’d)

Other Summer Programs at the NIH

https://www.training.nih.gov/other_summer_programs_at_the_nih

Biomedical Engineering Summer Internship Program (BESIP)
Introduction to Cancer Research Careers (ICRC)
Werner H. Kirsten Student Intern Program (Frederick, MD)
Cancer Research Interns (CRI) Summer Program
Summer Internship Program in Biomedical Research for Veterinary Medical Students

Diversity in Vision Research & Opthalmology (DIVRO)
NIDDK Office of Minority Health Research Coordination (OMHRC) Summer Internship Program
NIDCR Summer Dental Student Award
Office of Research Facilities Summer Intern Program (opportunities in trades, architecture, and physical sciences)
Recruitment and Training for Under-represented Populations (RTURP) Program (NIDA, Baltimore, MD)

Research somewhere else (con’d)

Department of Defense REU – ASSURE
(Awards to Stimulate and Support
Undergraduate Research Education)

http://www.nsf.gov/crssprgm/reu/list_result.cfm?unitid=10023

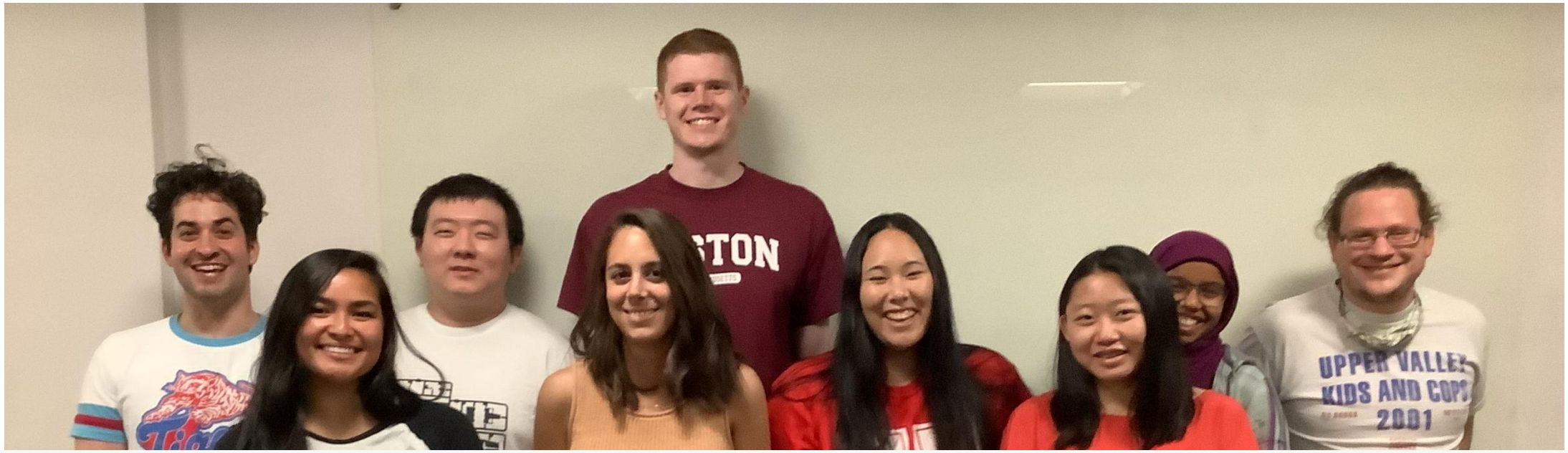
Ask around:

- more senior undergraduates, TFs and other graduate students
- family, friends who are PhD scientists employed somewhere
- Google search on “summer research internship”
- contact local Boston companies (find via LinkedIn)

General Points

- Rising juniors are most desirable, then seniors, then sophomores
- Don’t plan on taking a class and doing research, if at all possible
- This is a BIG opportunity for you so if you get a spot, throw yourself into it.
- Regardless of your grades, you are a newbie researcher and the more senior members in the lab deserve your respect.
- Do even the most menial tasks well and be a team player.
- Most undergraduates don’t get a publication in 10 weeks.
- Undergraduates can get publications in 1-2 years. The more you work like a graduate student, the more you will publish like a graduate student.
- Maintain good communication with the professor (PI = principal investigator) and don’t burn any bridges.

Acknowledgements



L to R : Thor Mdalel (G2), Cathlene DelRosario (G5), Lihao Feng (MS), Léa Toubiana (G4), Shawn Moore (G4), Caroline Sabanos (BU'23), Alice Fan (BU'24), Rana Abdu (REU), Dr. Jordan Aguirre

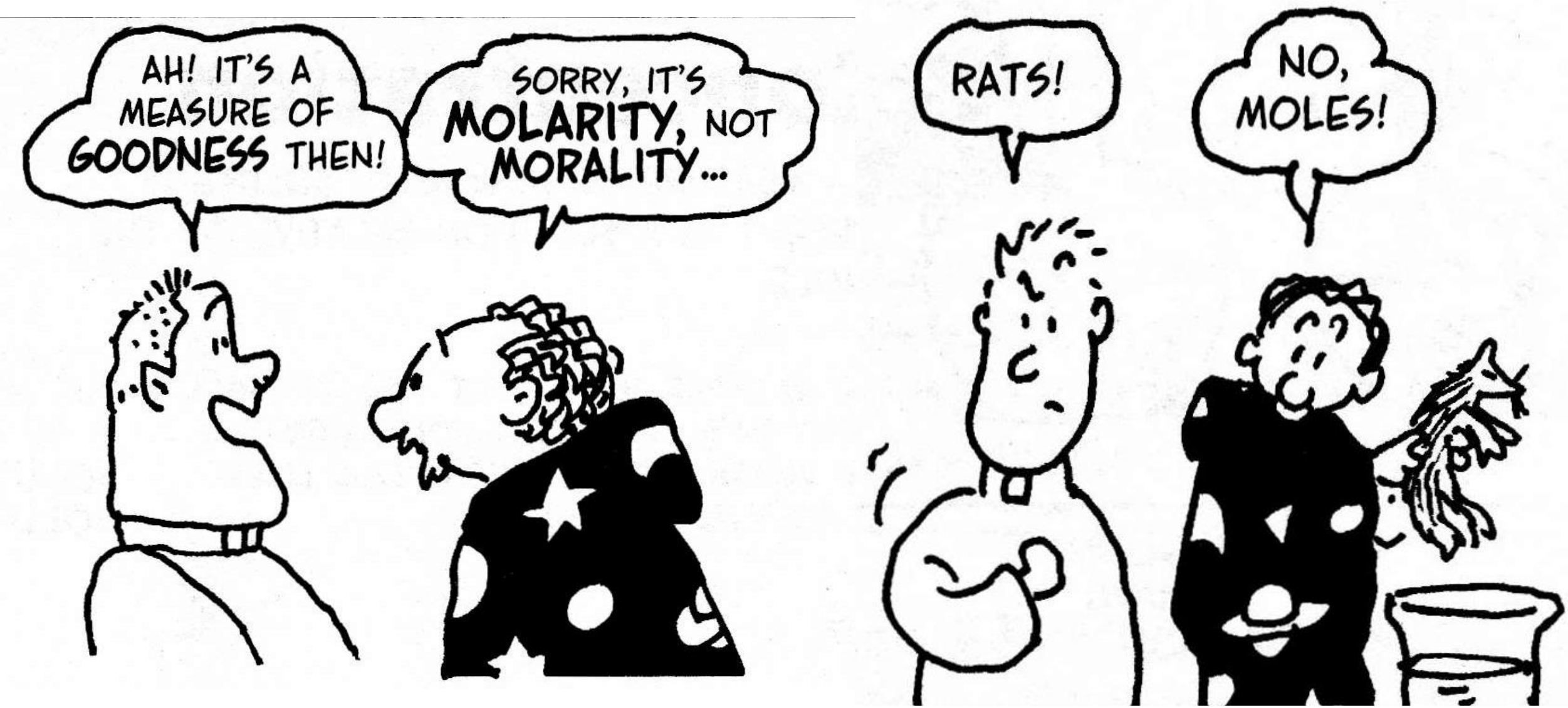
not shown: Hannah Skipper (G4), Ana Herning (BU'23)

ACS PRF

PRF 38007-GB3
PRF 48022-AC3
PRF 58601-ND3

NSF

CHE-1800313, CHE-2102532



The Cartoon Guide to Chemistry, (2005) L. Gonick, C. Criddle, pp. 249