KU LEUVEN

C-PlaNeT
CIRCULAR PLASTICS NETWORK FOR TRAINING

Production of sustainable and recyclable phosphorus flame retardant additives

Alejandro Fonseca

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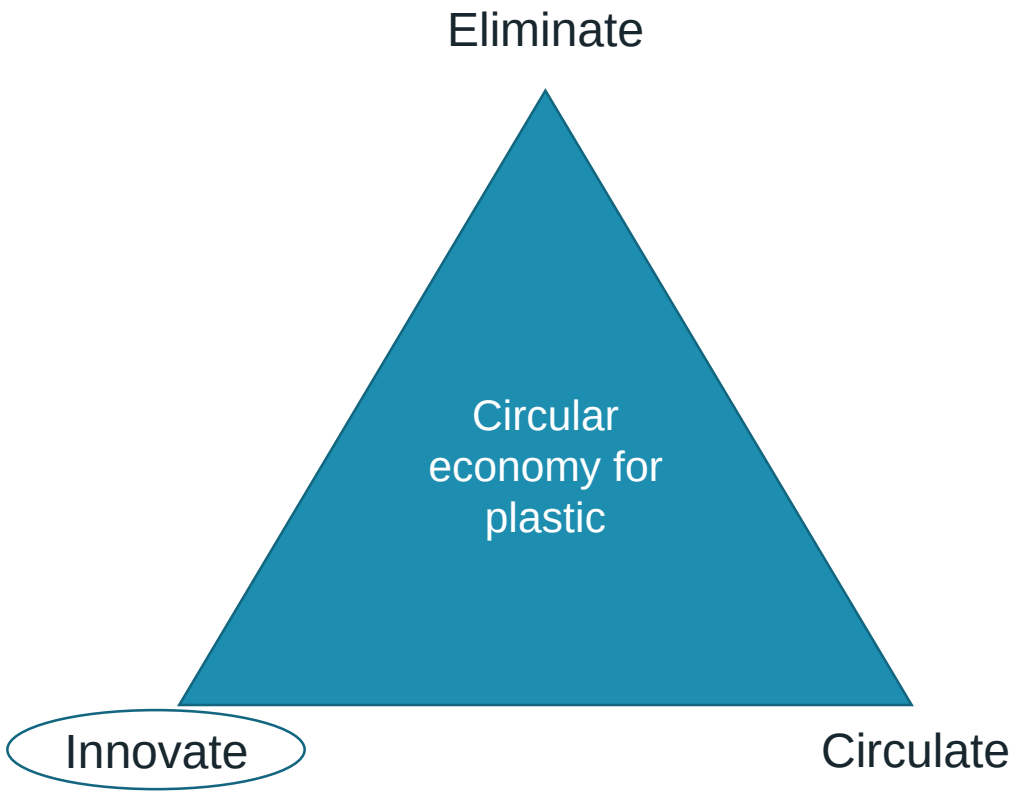
A little bit of context: Plastics in a circular economy

"We must change how we design, use, and reuse plastics. We cannot simply recycle or reduce our way out of the plastic pollution crisis. If we don't act now, by 2050 there could be more plastic than fish in the oceans"

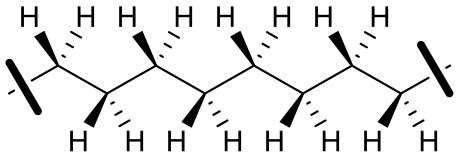
Ellen MacArthur Foundation

Plastics must be designed for circularity!

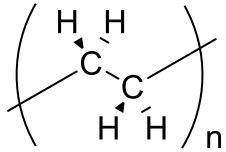


A little bit of context: Plastics chemical composition

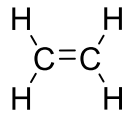
Polymer



or



Polyethylene



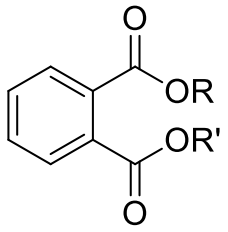
Ethylene (Monomer)

Substances composed of macromolecules

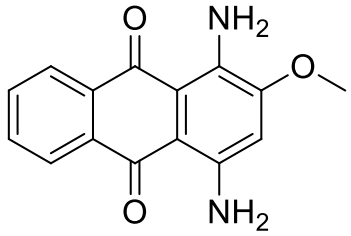
Formed by repetition of molecular units

\+

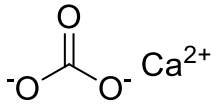
Additives



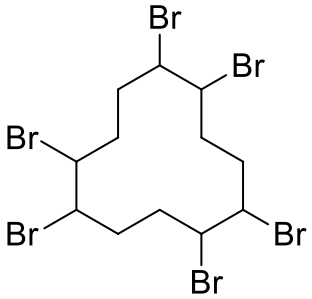
Plasticizers



Colorants

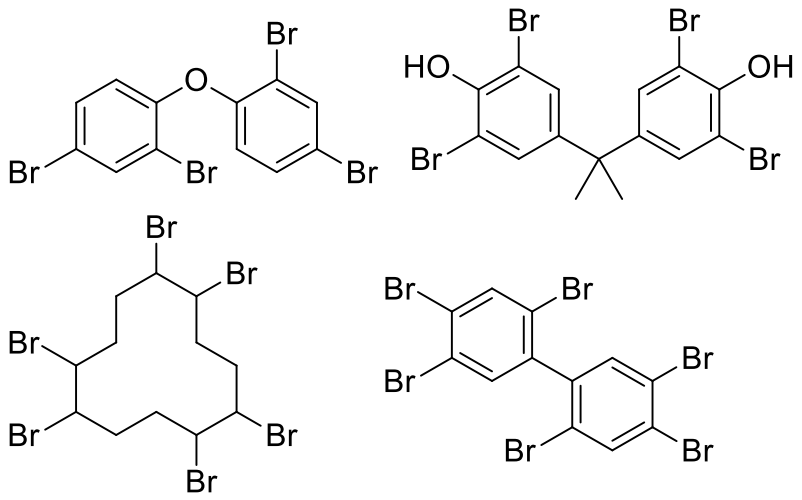


Fillers



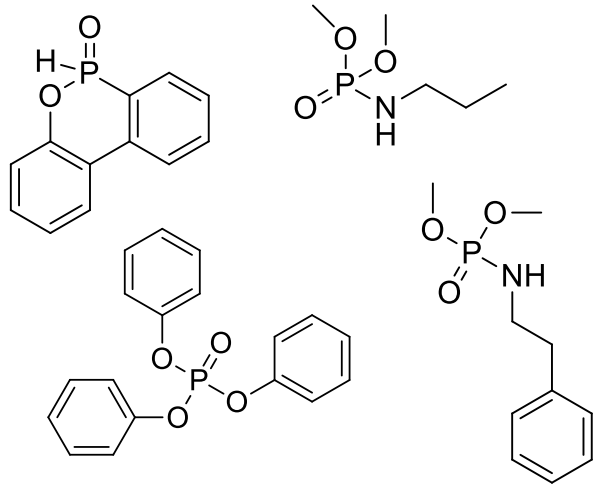
Flame retardants

A little bit of context: Phosphorus as an alternative



15
P
Phosphorus
30,974

as an alternative



- Recognized global contaminants
- Associated with adverse health effects
- Use of highly toxic reagents during synthesis

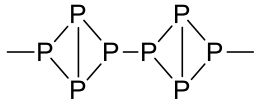
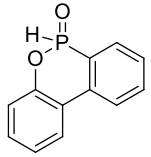
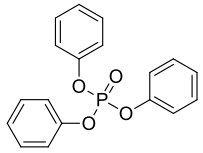
- Non-toxic
- Biodegradable/Recyclable
- Very efficient

Rev Environ Health. 2010 Oct-Dec;25(4):261-305.
Angew. Chem. Int. Ed. 2018, 57, 10450 – 10467

A little bit of context: Phosphorus based flame retardants

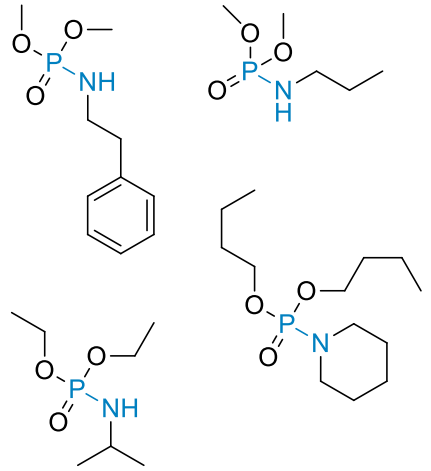
‘Molecules that incorporate phosphorus in their structure’

Their structure can vary greatly:

	P oxidation state		
	0	+3	+5
Inorganic		M_2HPO_3	$[NH_4PO_4]_n$
Organic			

Among them there's a very interesting kind of P-FR!

Phosphoramidates



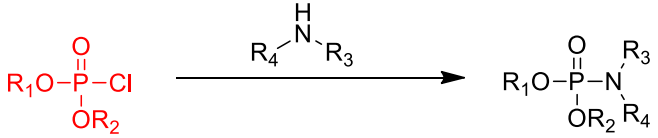
Multiple flame retardancy mechanisms due to P+N synergistic effects!

Fire Mater.2013;37:259–279
ACS Appl. Polym. Mater. 2019, 1, 1118−1128

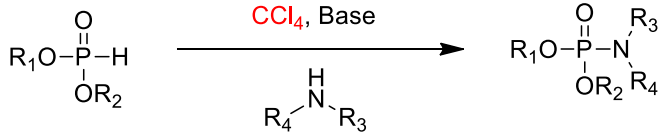
My research: Obtention of phosphoramidates

Synthetic approaches in literature:

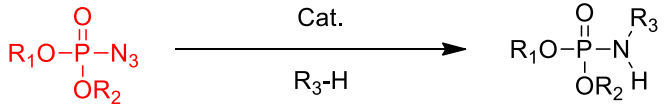
a Direct nucleophilic substitution



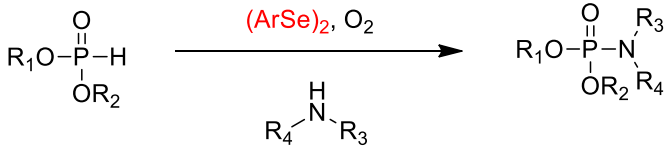
b Atherton Todd Reaction



c Phoshoryl Azide precursor



d Selenide catalyst



Phosphoramidates are common and widespread backbones for a great variety of chemicals!

Non-desired precursors/reagents, poor atom or unpractical reaction conditions

What if…

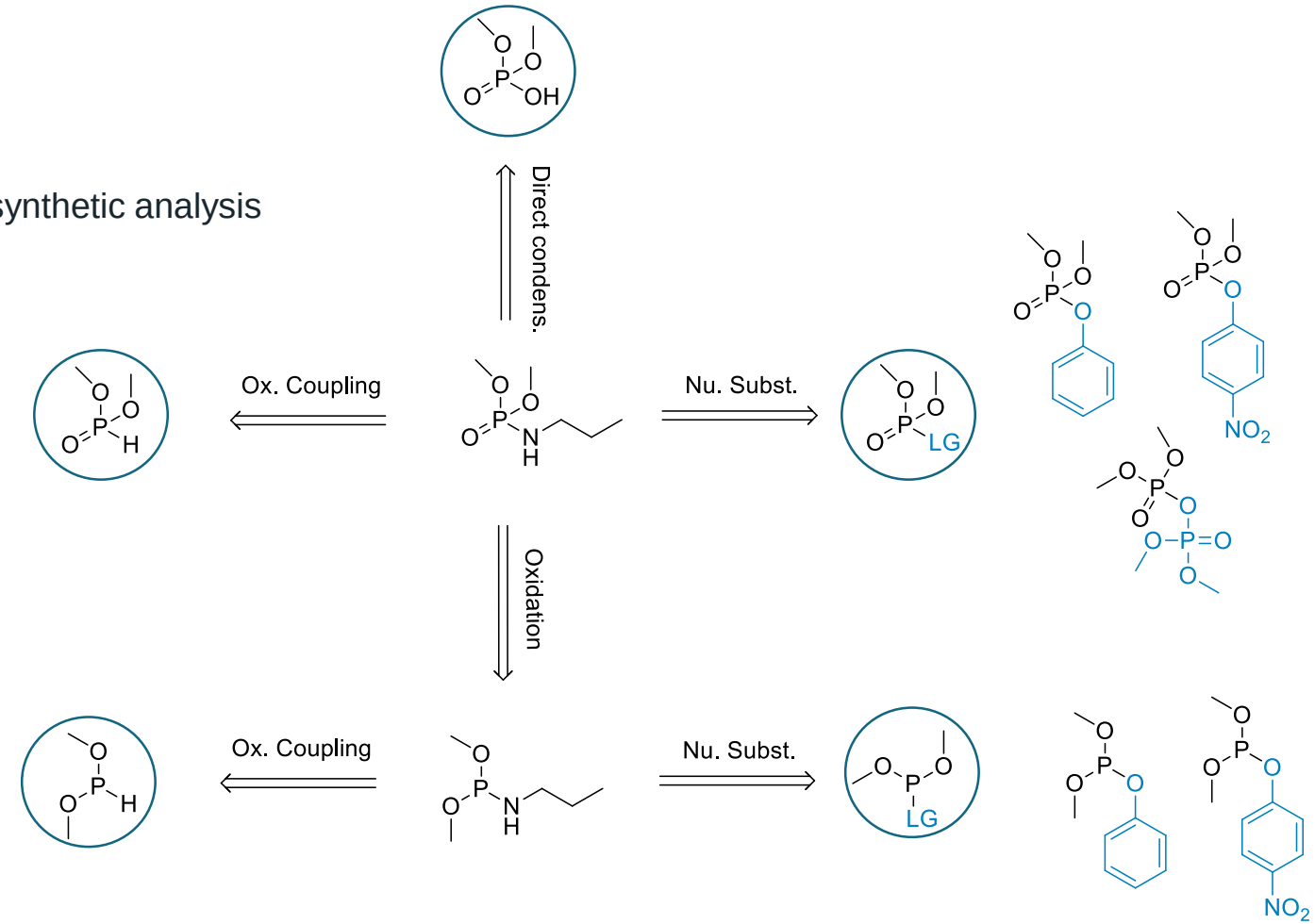
- Non-toxic reagents/precursors
- Good atom economy
- Mild reaction conditions

Where do we start from?

We want:

- Metal catalyzed reaction
- Non-toxic, non-expensive starting material
- One step reaction

Retrosynthetic analysis



Nucleophilic substitution route

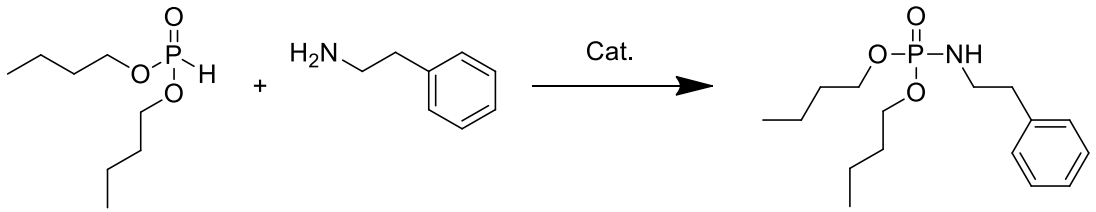
Direct condensation route

Oxidative coupling route

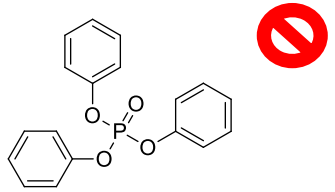
Oxidation route Two steps!

Preliminary experiments results

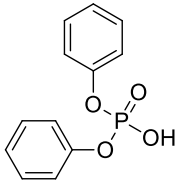
Route	Results
Nucleophilic substitution	Discarded
Direct condensation	Discarded
Oxidative coupling	It may work!



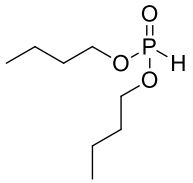
Observations



- Phosphate esters were inert to the tested reaction conditions



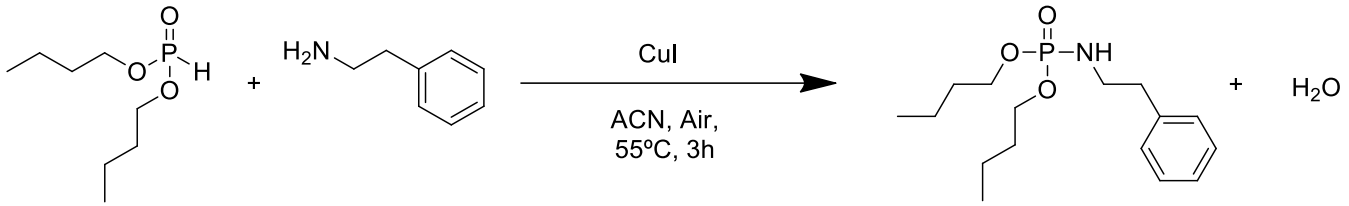
- Phosphoric acids were not able to couple with amines (formation of salt)



- Phosphites coupled well with amines in the presence of a Cu catalyst!

Reaction optimization

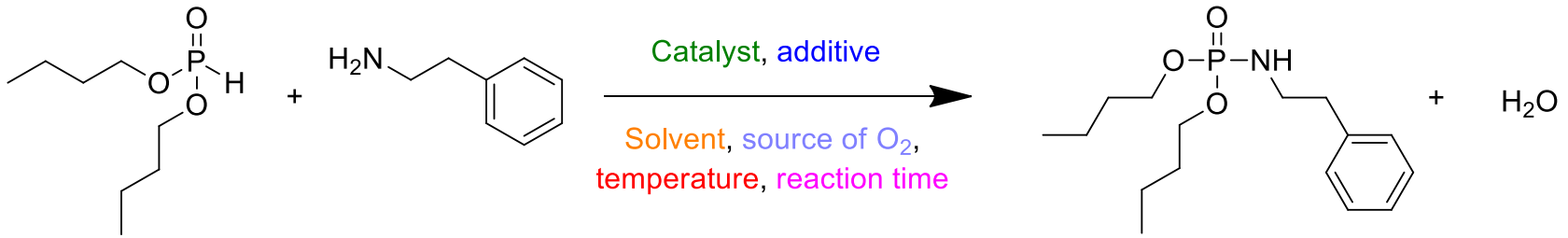
Fraser et. al.



73% yield

Improvement points

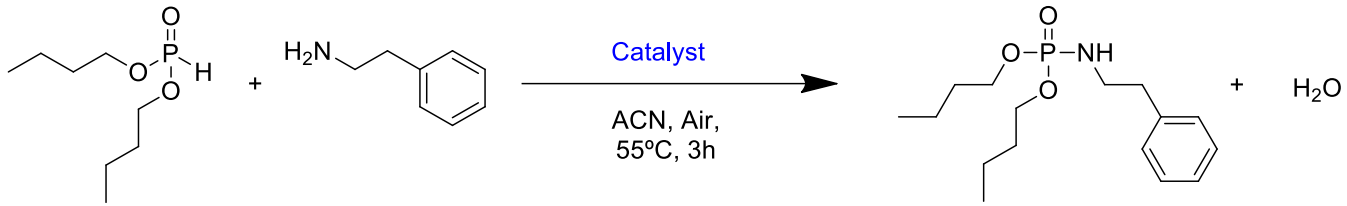
- Higher yield
- Lower reaction time
- Recyclable catalyst



We can play with the variables of the reaction!

Chem. Commun., 2013,49, 8919

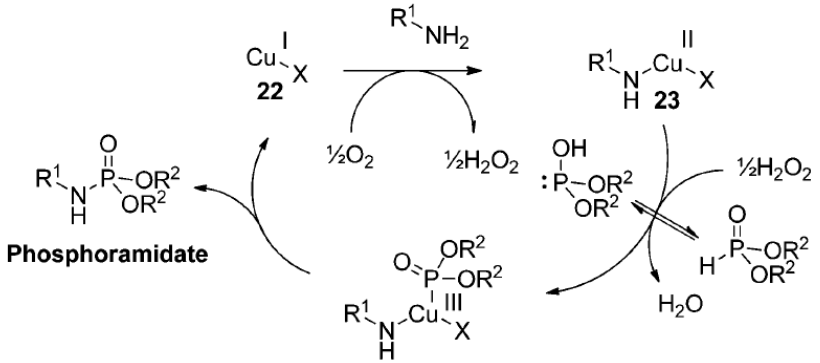
Reaction optimization: Catalyst



Catalyst	Yield
None	>1%
CuI	73%
$FeCl_2$	>1%
$AlCl_3$	>1%
$ZnCl_2$	>1%
$Zr(acac)_2$	>1%
TiO_2	>1%
CuO	>1%
$Cu(OAc)_2$	4%
Cu-Co DMC	6%
Cu-BTC	2%
Cu/SiO_2	>1%
$Cu_{0.33}Mg_{0.33}Al_{0.33}CO_3$	11%
Many more…	Not so good… :C

What makes **CuI** such a good catalyst?

Fraser et. al.

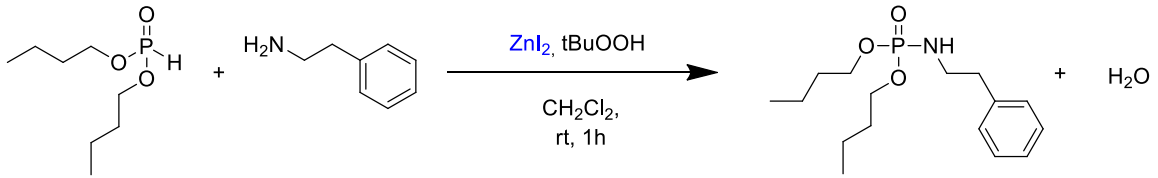


According to the mechanism, Cu should be able to promote the reaction

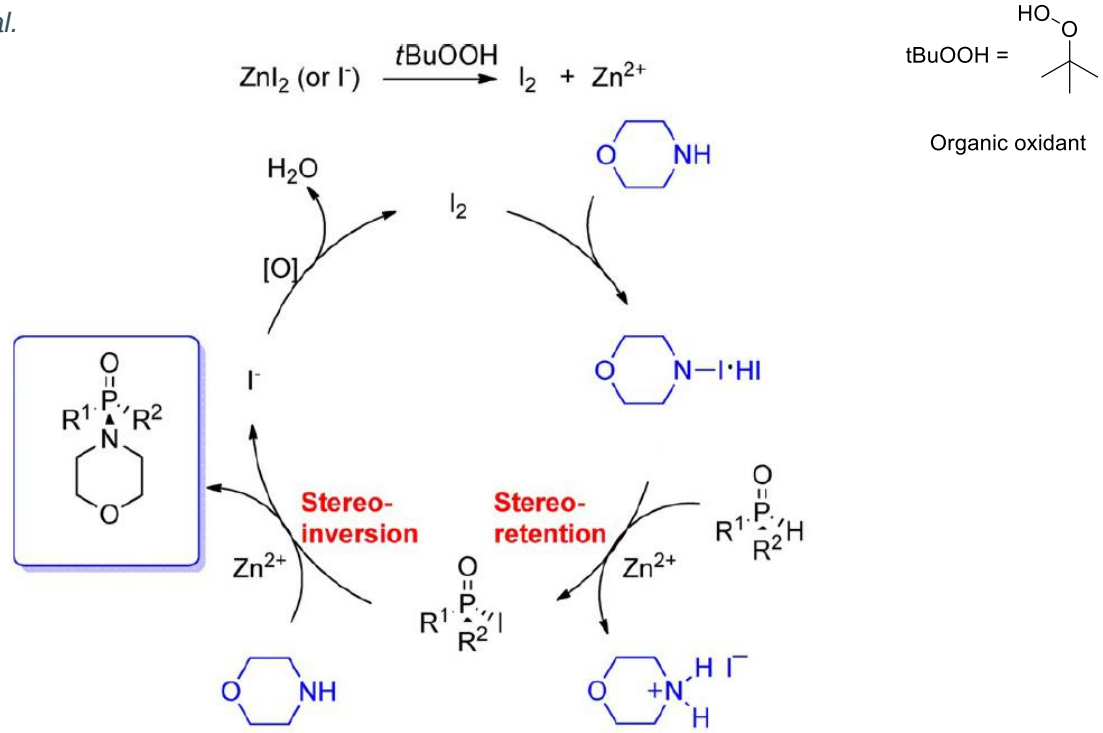
But why other Cu-based catalyst yield so little product?

Chem. Commun., 2013,49, 8919

Reaction optimization: Catalyst

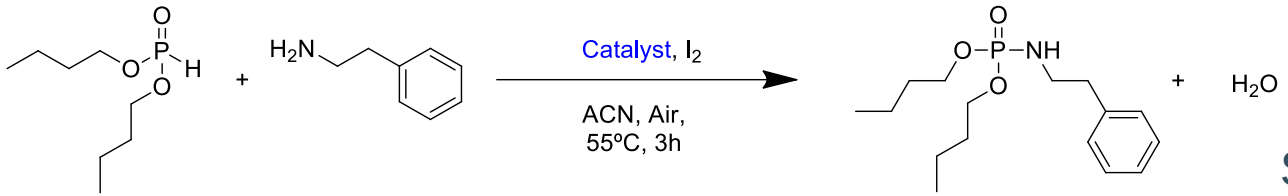


Chen et. al.



According to Chen et. al. an **Iodide** species is needed to promote the reaction!

Reaction optimization: Catalyst



Catalyst (10 mol %)	Yield (adding 15 mol % of I_2)
None	15%
$FeCl_2$	12%
$AlCl_3$	13%
$ZnCl_2$	13%
$Zr(acac)_2$	5%
TiO_2	14%
CuO	20%
$Cu(OAc)_2$	**86%**
Cu-Co DMC	**40%**
Cu-BTC	**96%**
Cu/SiO_2	10%
$Cu_{0.33}Mg_{0.33}Al_{0.33}CO_3$	27%

Some interesting results showed up!

- Indeed, the addition of Iodine to the reaction greatly improved the overall yield
- In general, stoichiometric amounts of phosphoramidate were formed compared to the amount of I_2 added
- Only in three cases the yield was abnormally high:
  - Homogeneous Cu salt, **$Cu(OAc)_2$**
  - Heterogeneous Cu based catalyst, **Cu-Co DMC**
  - Heterogeneous Cu based catalyst **Cu-BTC**

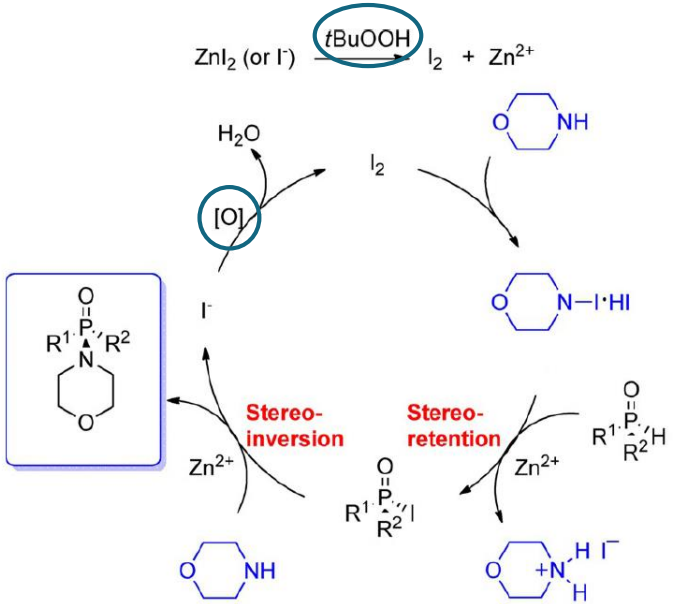
Reaction optimization: Catalyst and additive

Why only these three catalysts worked we

- Homogeneous Cu salt, **$Cu(OAc)_2$**
- Heterogeneous Cu based catalyst, **Cu-Co DMC**
- Heterogeneous Cu based catalyst **Cu-BTC**

Both reactions shared two common things:

- An Iodine species
- An oxidant



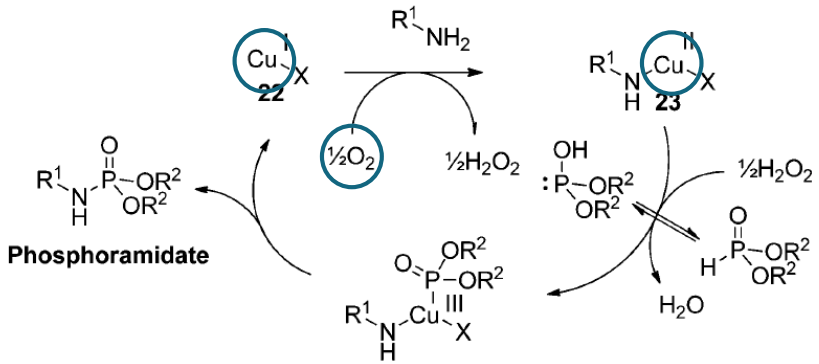
- CuO
- Cu/SiO_2
- $Cu_{0.33}Mg_{0.33}Al_{0.33}CO_3$

?

Cu is not able to easily change oxidation states !

That's why CuI was such a good catalyst!

- I^- as Iodine species
- $Cu\text{-}O_2$ as oxidant



Reaction optimization: Catalyst and additive

Our focus went to both heterogeneous catalyst:

- Cu-Co DMC
- **Cu-BTC**

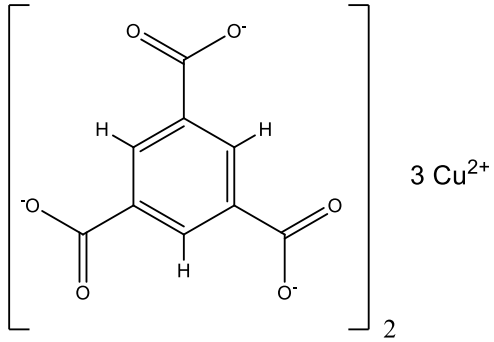
Catalyst	Yield
Cu-BTC	**96%**

!

However, analysis showed the catalyst was not stable and therefore not recoverable … (ICP-OES, Hot filtration test, XRD)

Even after changing some reaction conditions …

Cu-BTC

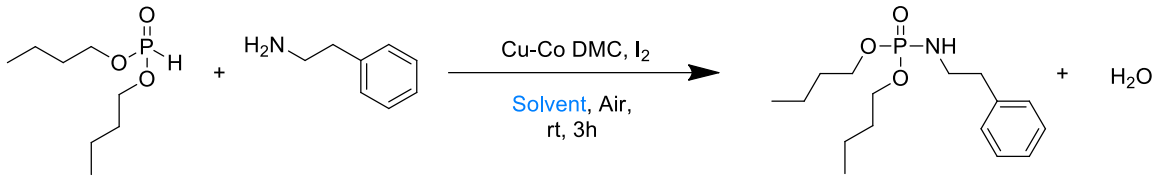


Metal **O**rganic **F**ramework

What about Cu-Co DMC?

Catalyst	Yield (adding 15 mol % of I_2)
Cu-Co DMC	**40%**

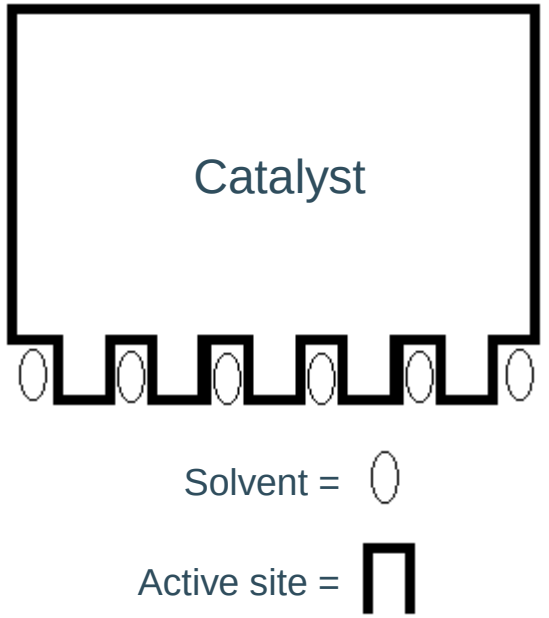
Reaction optimization: Solvent



Solvent	Yield
Acetonitrile	**40%**
Tetrahydrofurane	**90%**
Dichloromethane	**98%**
Toluene	**84%**
2-Methyl Tetrahydrofurane	**90%**
Dioxane	**89%**

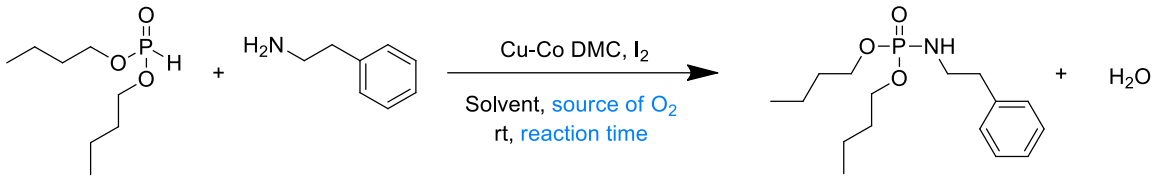
!

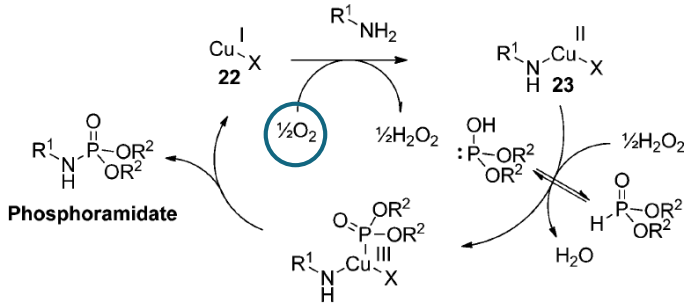
Simply using a less polar solvent greatly improved the yield!
And catalyst was stable!



Acetonitrile is a polar solvent and can block the catalyst sites, where the catalysis happens!

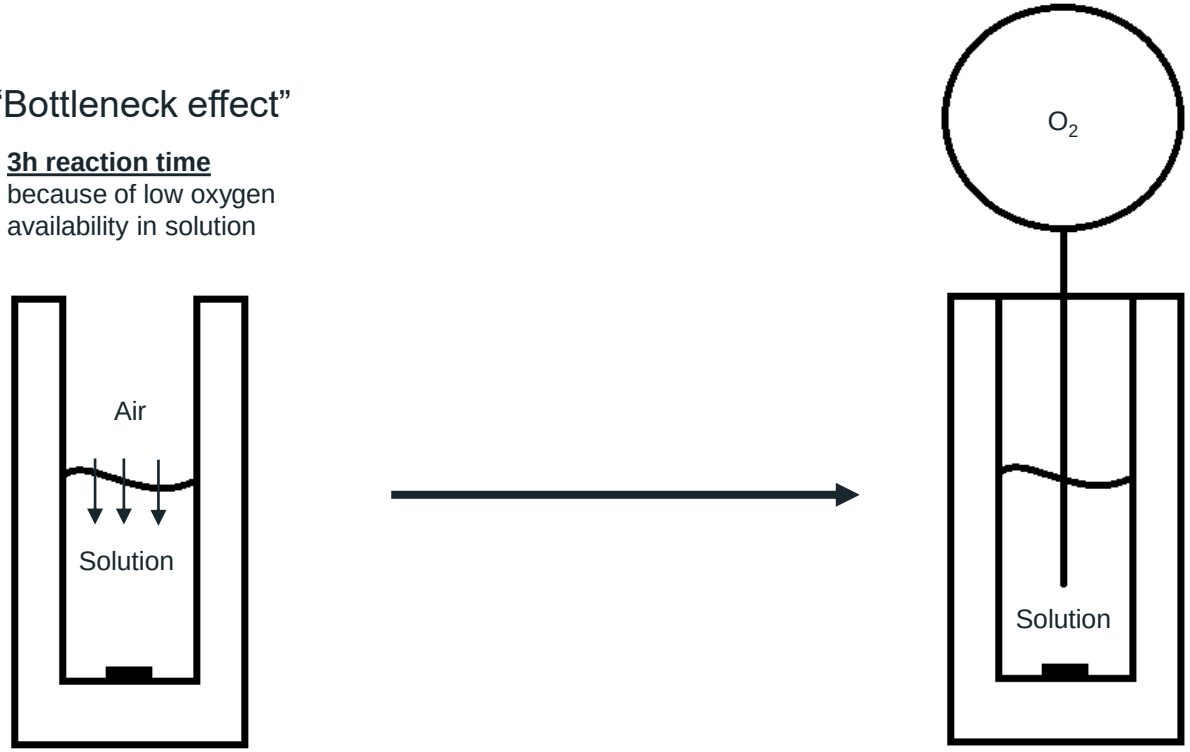
Reaction optimization: Source of O_2 and reaction time





"Bottleneck effect"

3h reaction time
because of low oxygen availability in solution



3h → 30 mins!!

No oxidative decomposition of reagents was observed

Reaction optimization: Final touches

Other parameters were refined

- Catalyst loading
- Amount of additive
- Reaction concentration
- Phopshite to amine ratio

Final reaction conditions!

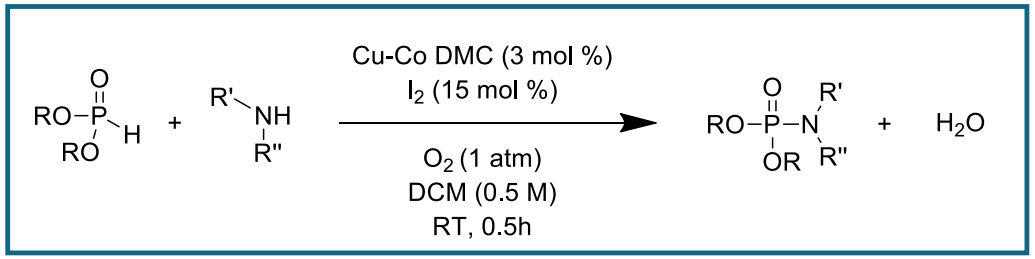
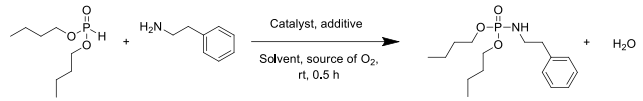


Table 1 Reaction optimization



Entry	Catalyst (mol%)	Solvent	Phosphite/Amine/I_2 (equivalents)	Source of O_2	Yield
1	No Cat.	ACN	1/2/0	Air	>1% [c]
2	CuI (20%)	ACN	1/2/0	Air	73% [c]
3	$Cu(OAc)_2$ (20%)	ACN	1/2/0	Air	4% [c]
4	CuO (20%)	ACN	1/2/0	Air	>1% [c]
5	Cu-Co-DMC (3%)	ACN	1/2/0	Air	6% [c]
6	Cu BTC (3%)	ACN	1/2/0	Air	2% [c]
7	Cu/SiO_2 (3%)	ACN	1/2/0	Air	>1% [c]
8	$Cu_{0.33}Mg_{0.33}Al_{0.33}CO_3$ (3%)	ACN	1/2/0	Air	11% [c]
9	$Cu(OAc)_2$ (20%)	ACN	1/2/0.20	Air	86% [c]
10	No Cat	ACN	1/2/0.20	Air	15% [c]
11	$Cu(OAc)_2$ (20%)	ACN	1/2/0.20	O_2 balloon	90%
12	Cu-Co-DMC (3%)	ACN	1/2/0.2	O_2 balloon	49%
13	Cu-Co-DMC (3%)	THF	1/2/0.2	O_2 balloon	90%
14	Cu-Co-DMC (3%)	Dioxane	1/2/0.2	O_2 balloon	89%
15	Cu-Co-DMC (3%)	DCM	1/2/0.2	O_2 balloon	98%
16	Cu-Co-DMC (3%)	Toluene	1/2/0.2	O_2 balloon	84%
17	Cu-Co-DMC (3%)	2-MeTHF	1/2/0.2	O_2 balloon	90%
18	Cu-Co-DMC (1%)	DCM	1/2/0.2	O_2 balloon	72%
19	Cu-Co-DMC (6%)	DCM	1/2/0.2	O_2 balloon	99%
20	Cu-Co-DMC (3%)	DCM	1/2/0.15	O_2 balloon	**99%**
21	Cu-Co-DMC (3%)	DCM	1/2/0.1	O_2 balloon	87%
22	Cu-Co-DMC (3%)	DCM	1/2/0.05	O_2 balloon	53%
23	Cu-Co-DMC (3%)	DCM	1/1/0.15	O_2 balloon	42%
24	Cu-Co-DMC (3%)	DCM	1/3/0.15	O_2 balloon	90%
25	Cu BTC (3%)	DCM	1/2/0.15	O_2 balloon	98%
26	CuO	DCM	1/2/0.15	O_2 balloon	20%
27	Cu/SiO_2 (3%)	DCM	1/2/0.15	O_2 balloon	12%
28	$Cu_{0.33}Mg_{0.33}Al_{0.33}CO_3$	DCM	1/2/0.15	O_2 balloon	35%

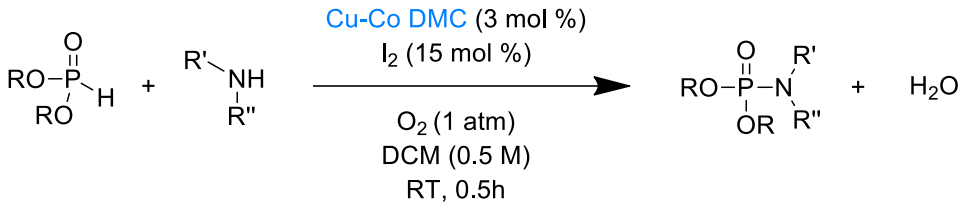
[a] All reactions were performed using a dibutyl phosphite as limiting reagent at a scale of 2 mmol, amine, catalyst, solvent (4 ml), Iodine and a source of oxygen at room temperature for half an hour. [b] Yields were determined on dibutyl phenylethyl phosphoramidates by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c] Reaction time 3 h

A. Fonseca et. al (to be published in ***Commun Chem***, *2022-23*)

Catalyst characterization: Cu-Co DMC

Cu-Co DMC = **Co**pper-**Co**balt **D**ouble **M**etal **C**yanide

- A class of molecular salts made up of a crystalline metal cyanide framework
- Theoretical formula: $Cu_3[Co(CN)_6]_2$
- Other DMC with different metal combination exist: $Zn_3[Co(CN)_6]_2$ structure is very similar



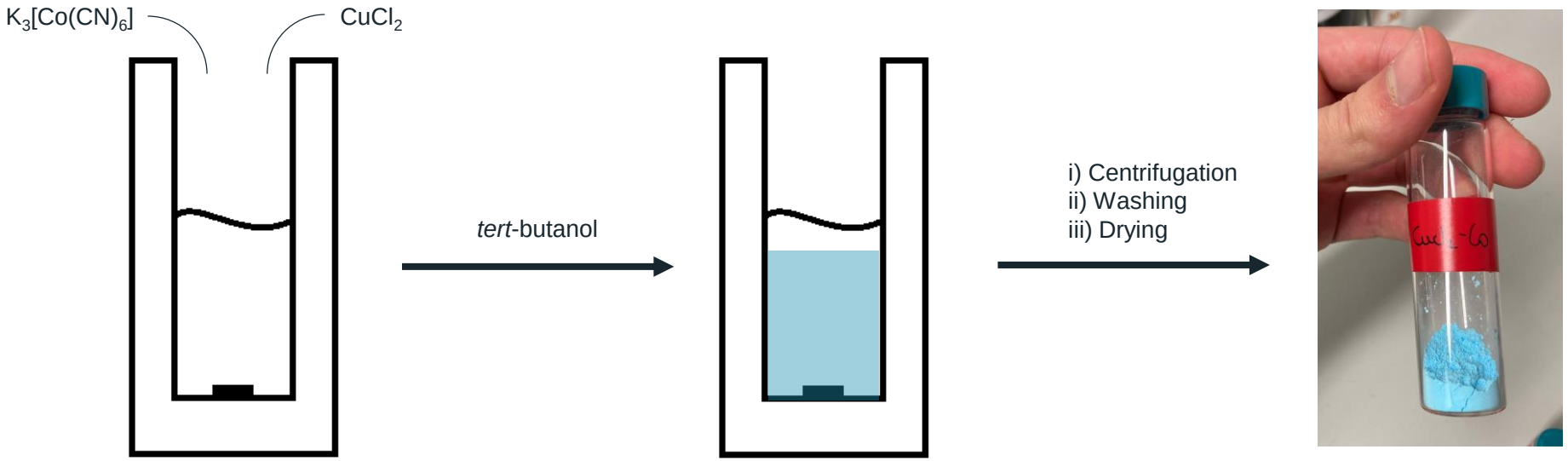
Was characterized by:

- Powder X-ray diffraction (PXRD)
- Inductively coupled plasma atomic emission spectroscopy (ICP-OES)
- N_2 physisorption
- Fourier-transform infrared spectroscopy (FTIR)
- X-ray absorption spectroscopy (XAS)

Catalyst characterization: Cu-Co DMC

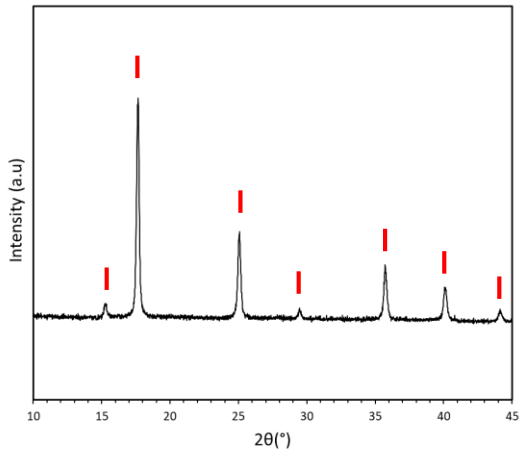
Cu-Co DMC synthesis: $Cu_3[Co(CN)_6]_2$

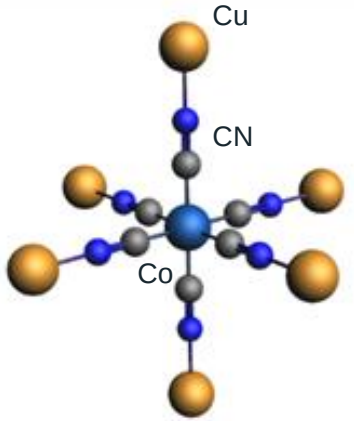
Very easy to prepare!



Catalyst characterization: Cu-Co DMC

PXRD

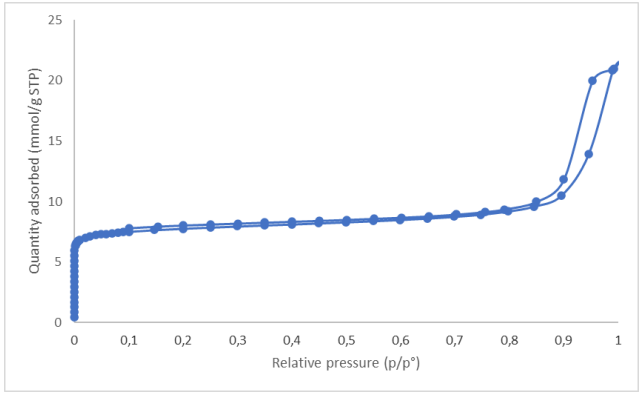




Typical pattern for $M_3[Co(CN_6)]_2$-type DMCs!

Suggest octahedral coordination!

N_2 Physisorption



Type 1 isotherm → Microporous material

- Surface area of 660 m^2/g
- Pore volume of 0,22 cm^3
- Pore diameter of 6,4 Å

Dalton Trans., 2019,48, 3946-3954
Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1978, 34, 3558–3561

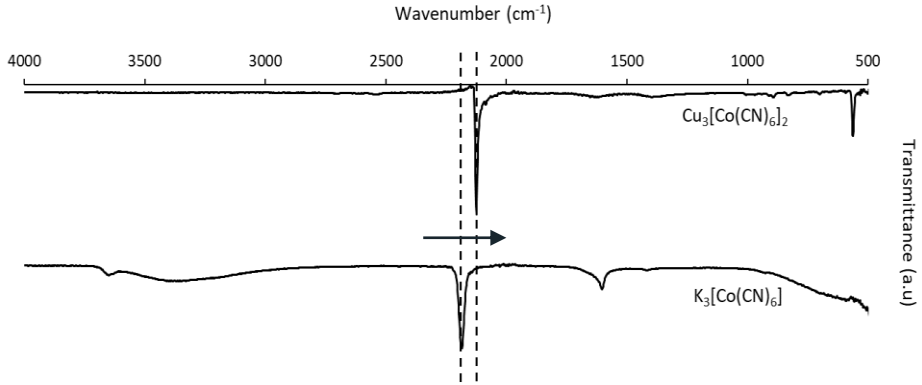
Catalyst characterization: Cu-Co DMC

ICP-OES → Cu:Co ratio of 1.7

But for $Cu_3[Co(CN)_6]_2$ ratio should be 3/2 = 1.5?

Little excess of Cu in the structure.

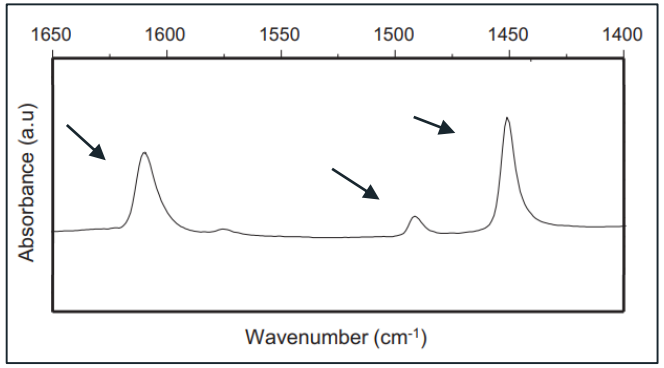
FTIR



Shift of the CN^- signal towards higher energy indicates Cu-CN-Co bond formation

If pyridine is adsorbed

Indicates the presence of Lewis acid catalytic sites!



Catalyst characterization: Cu-Co DMC

Heterogeneity of the reaction needed to be proved!

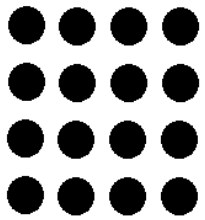
This was done by:

- ICP-OES of filtered solution after reaction → only **1.7%** of the total Copper in the catalyst was lost
- Reusing the catalyst for several iterations of the reaction → It was possible to **reuse it for at least 5 times**!

Something curious showed during this study…

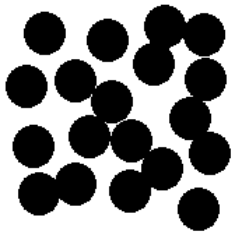
Pristine catalyst

Crystalline



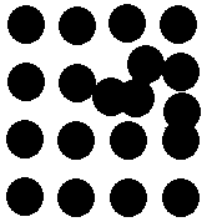
Catalyst after reaction

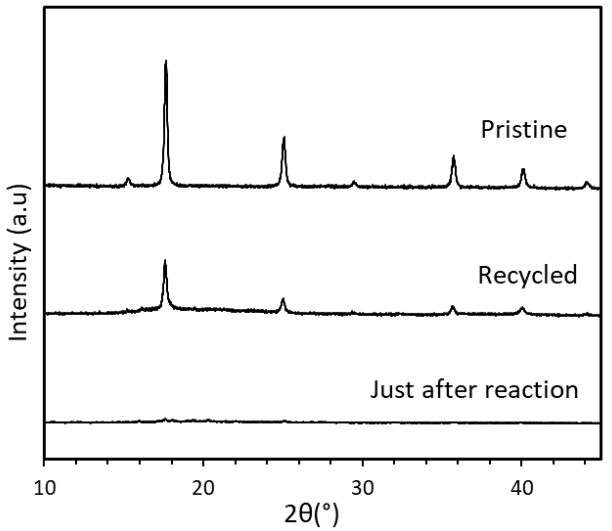
Amorphous



Recycled catalyst

Partial recovery of crystallinity

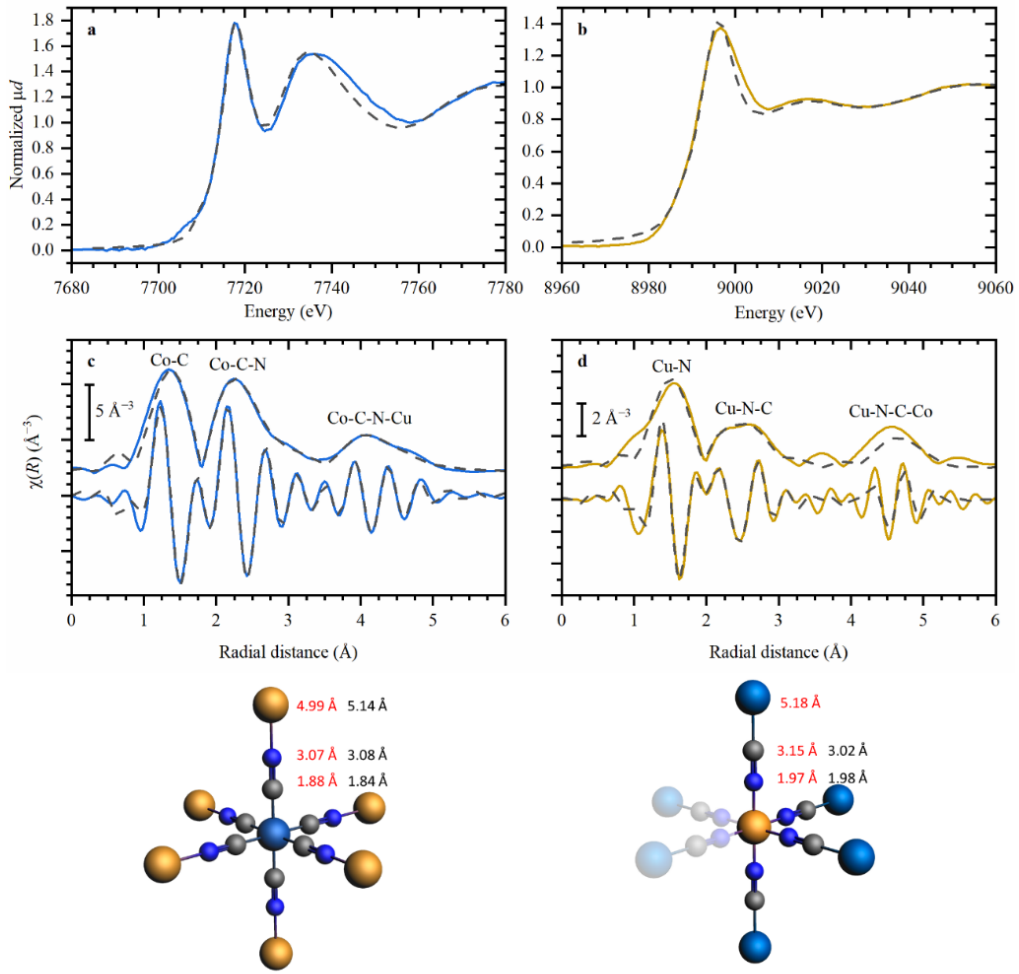




This didn't affect the catalytic activity!

Catalyst characterization: Cu-Co DMC

We wanted to know more!



Catalyst characterization: Cu-Co DMC

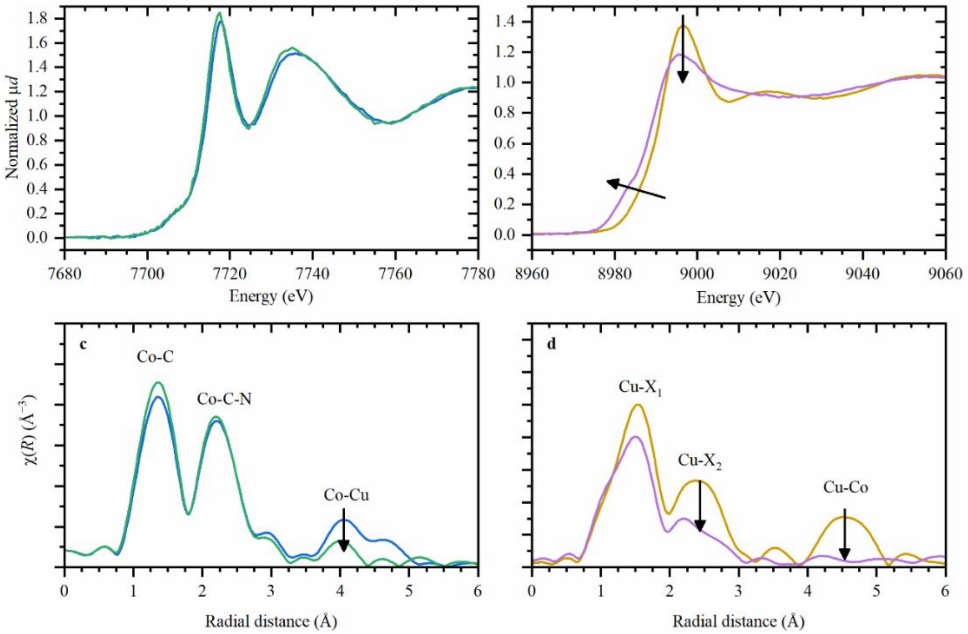
We wanted to know more about this structural change!

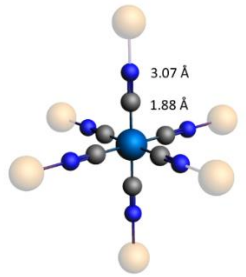
XAS spectroscopy → Allows us to know what atoms are near the metallic centers (Cu and Co) and their disposition in space

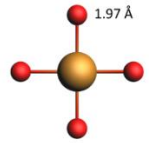
For the **spent** (just after reaction) Cu-Co DMC catalyst:

- Co atoms electronic and spatial structure was not changed
- However, Co-Cu long distance coordination was partially lost

- Cu appeared to exchange CN^- ligands for other ones
- Identifying this exact ligands is hard, but O and N atoms give a good fitting
- Cu adopts a newly square planar geometry







Catalyst characterization: Cu-Co DMC

Partial recovery of crystallinity

We wanted to know more about this structural change!

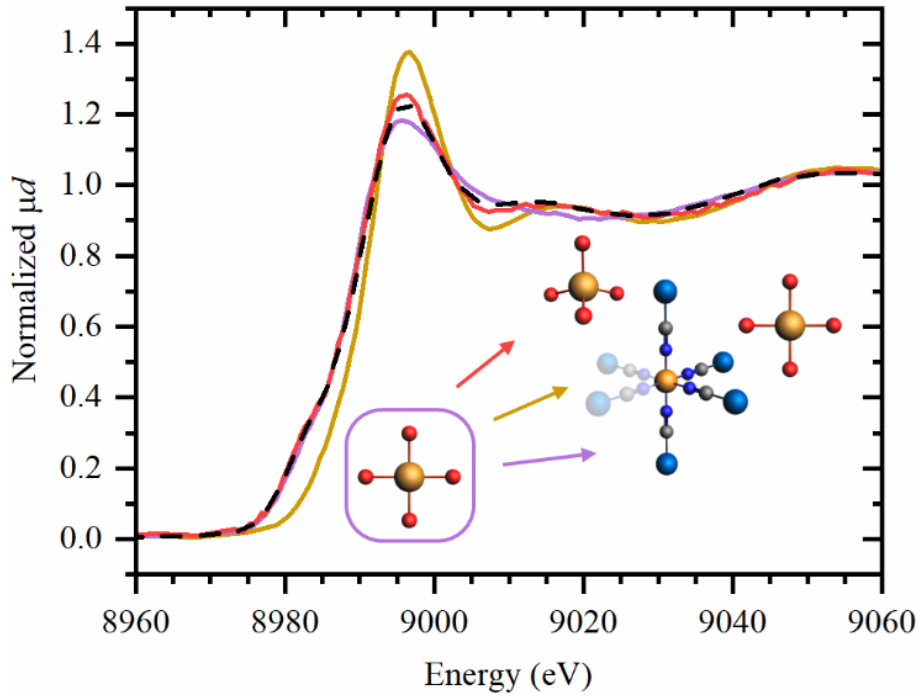
XAS spectroscopy → Allows us to know what atoms are near the metallic centers (Cu and Co) and their disposition in space

For the **recycled** Cu-Co DMC catalyst:

- Co atoms remain unchanged, but this time Co-Cu coordination was recovered

- Part of Cu atoms returned to their octahedral geometry
- Part of the Cu atoms stayed in the square planar geometry
- Part of the Cu atoms adopted a new tetrahedral geometry!

These findings explained what we saw in the PXRD!



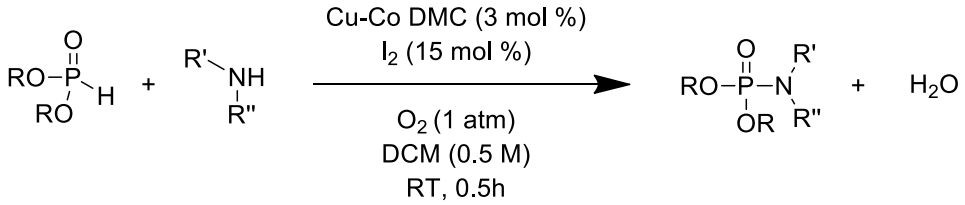
Reaction mechanism

How does the reaction work?

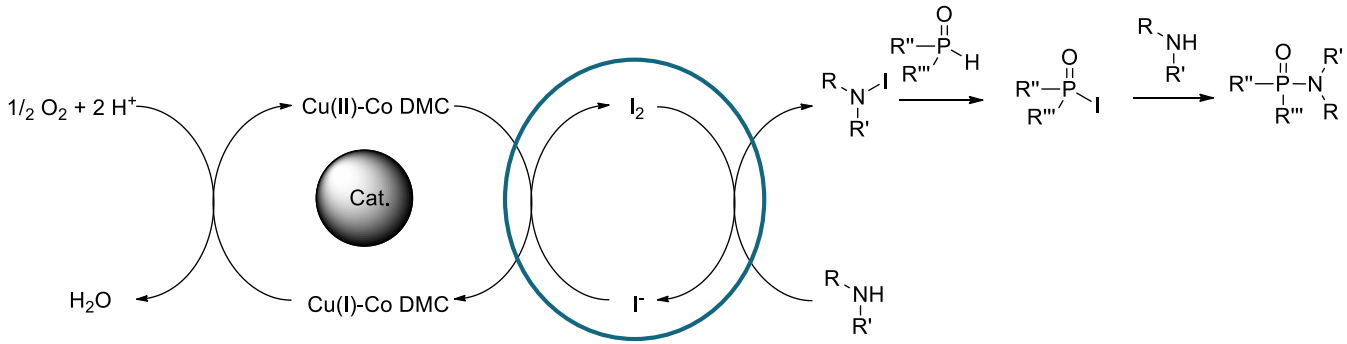
What we know so far:

- Face centered crystalline unit cell
- Cu and Co adopt an octahedral geometry
- Cu atoms have vacancies around them
- Co atoms remain in a single electronic and geometrical structure during the reaction
- Cu atoms geometry changes during the reaction

It's safe to assume that Cu atoms are responsible for the catalysis
(literature supports this hypothesis!)



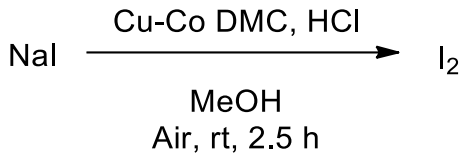
Proposed reaction mechanism

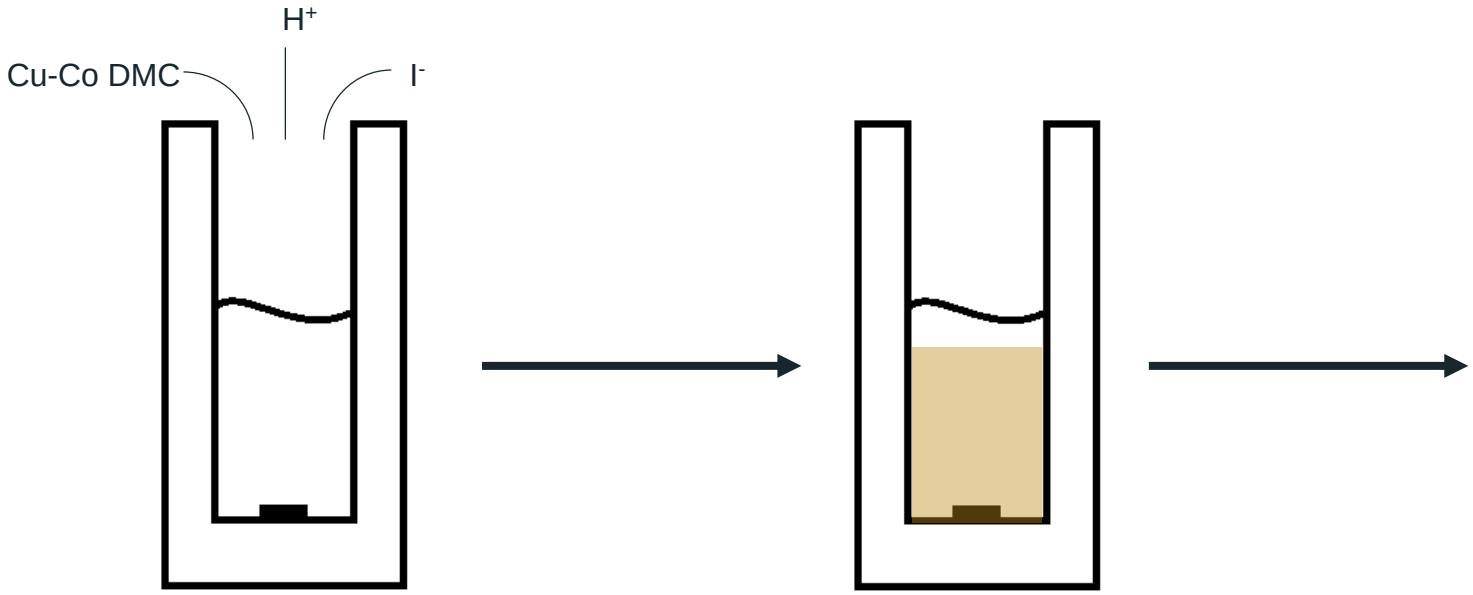


We can prove that Cu can oxidize I^- back to I_2!

Reaction mechanism

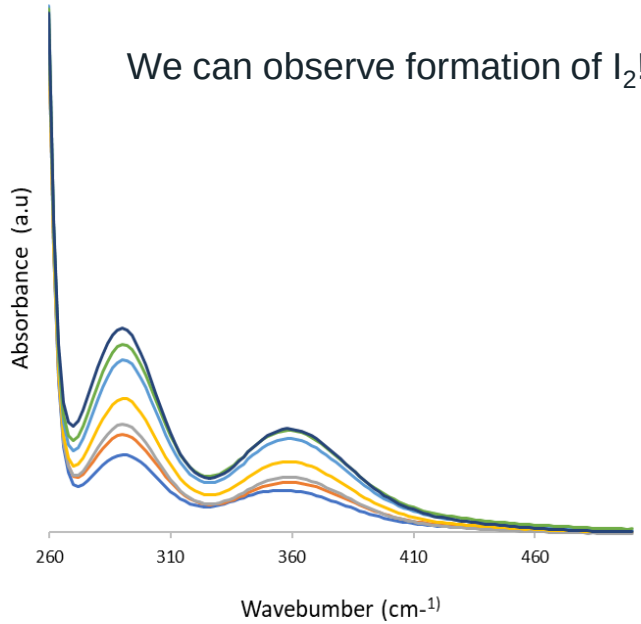
Cu-Co DMC can oxidize I^- back to I_2





UV-Vis Spectroscopy

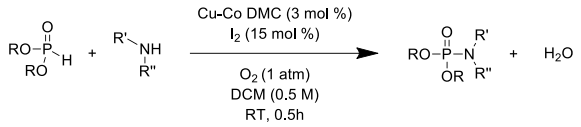
We can observe formation of I_2!

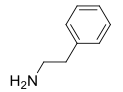
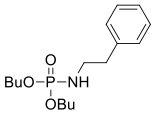
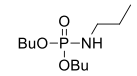
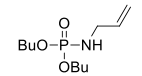
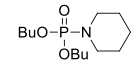
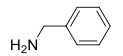
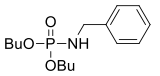
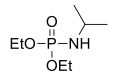
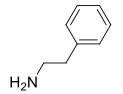
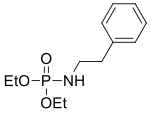
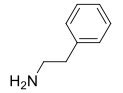
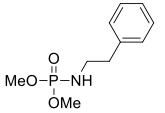
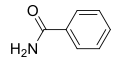
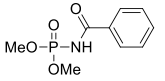


Reaction scope

Are we able to produce different phosphoramidates?

- Yes, we are!
- Different phosphoramidates could be synthetized with this method
- Yields are good!
- Clean reaction (little formation of side products)
- Catalyst can be easily recovered and reused!



Entry	Phosphite	Amine	Product	Yield[a]
1				99%
2				81%
3				21%
4				26%
5				89%
6				82%
7				94%
8				71%
9				61%

Future plans

- MUL secondment: Analyzing the fate of flame retardants during the processing and reprocessing of polymers

  - Physical and chemical behavior
  - Can it indeed be recycled?
  - How are the polymer properties affected
  - Do they really act as good flame retardancy agents?

Conclusions

- An insight on a chemical synthesis investigation
- Modern trends in flame retardant additives
- Creation of a new method of producing phosphoramidates

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C-PlaNeT
CIRCULAR PLASTICS NETWORK FOR TRAINING

Thank you!

Alejandro Fonseca
alejandro.fonseca@kuleuven.be

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