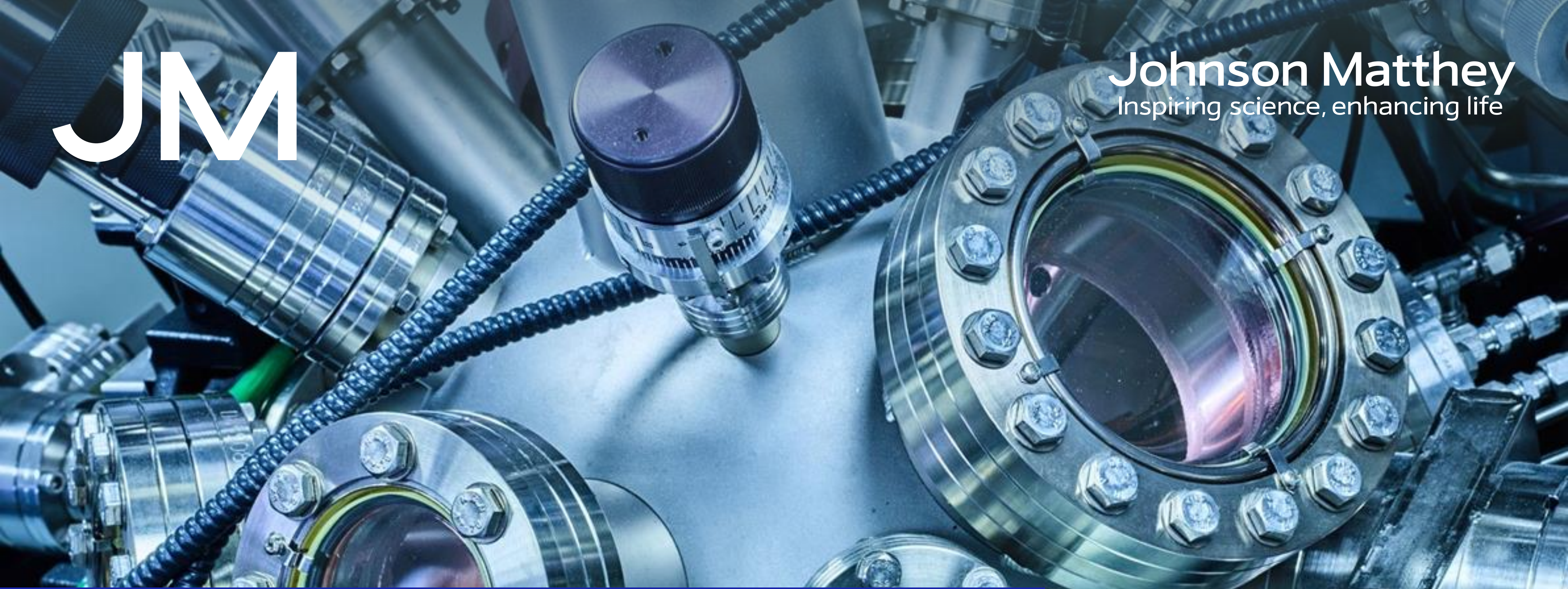


Johnson Matthey
Inspiring science, enhancing life

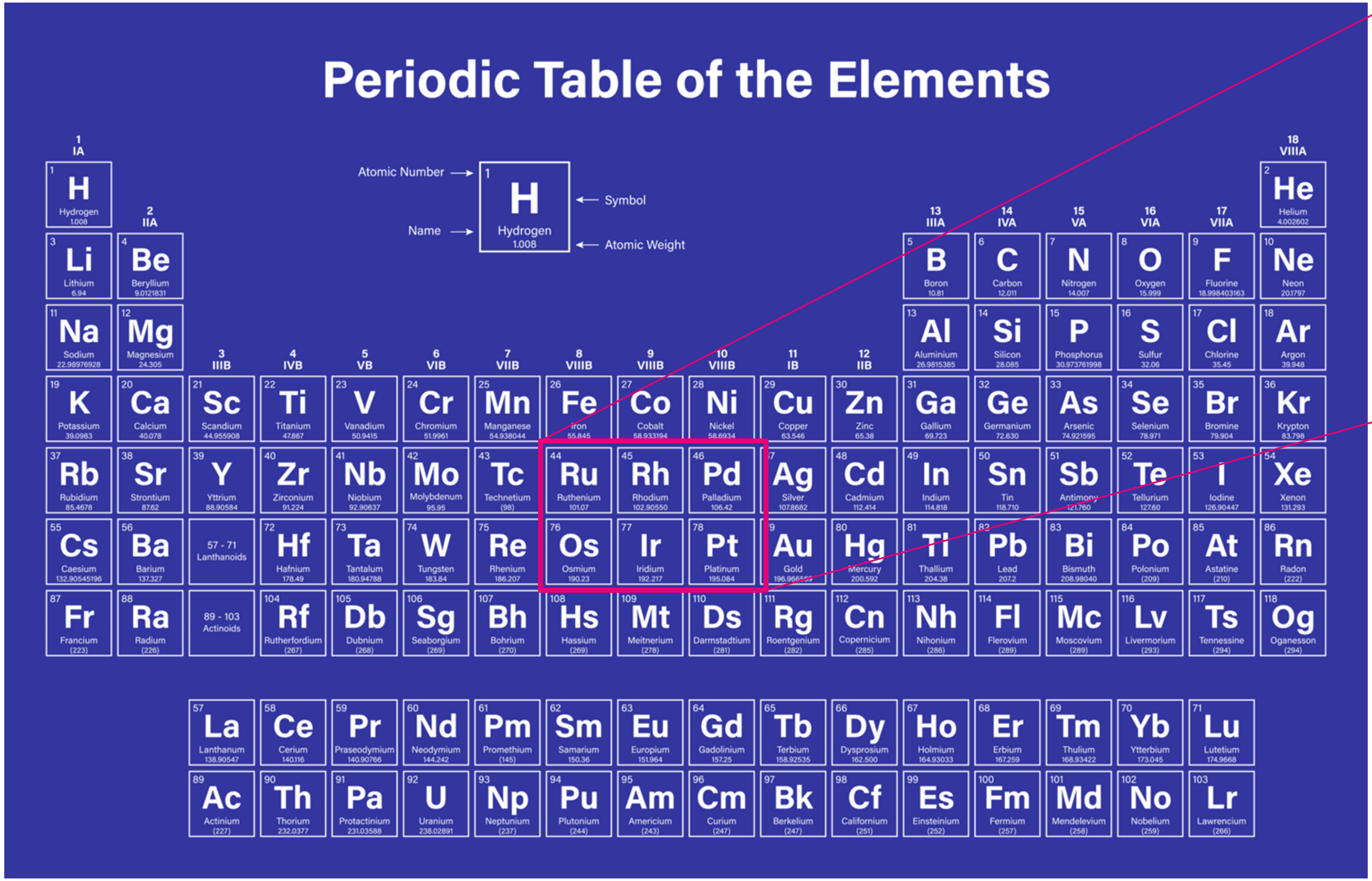
Challenges in (homogeneous) catalysis with precious metal catalysts

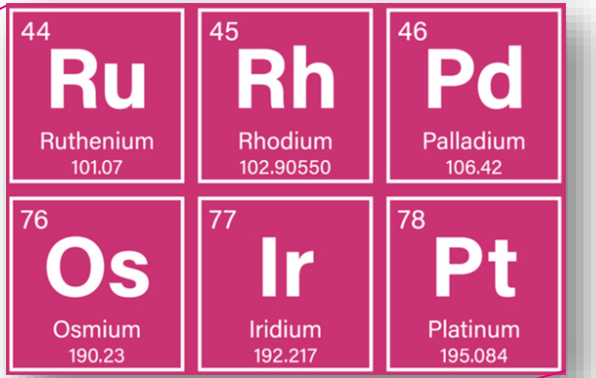
5 November 2024

Antonio Zanotti, Jane Patrick, Sarah Facchetti

About Platinum Group Metals

The platinum group metals (PGMs)





Platinum

Palladium

Rhodium

Ruthenium

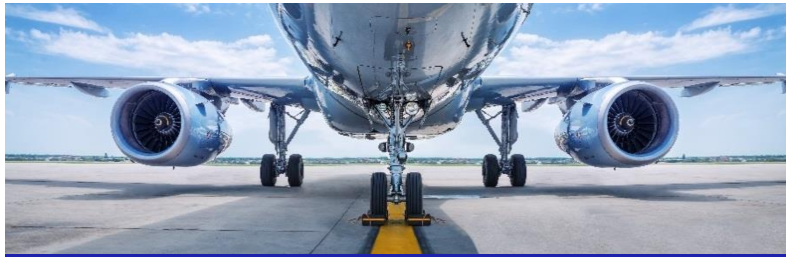
Iridium

Osmium

JM

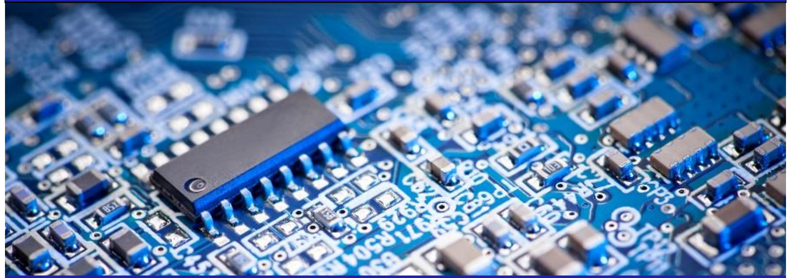
Global markets for PGMs

Automotive



Aerospace

Glass



Electronics/Sensors

Crystal growth

Jewellery

Pharma

Agro

Chemical

Introducing Johnson Matthey in the PGM landscape

PGMs are high demand precious metals …

- Palladium
- Platinum
- Rhodium
- Iridium
- Ruthenium

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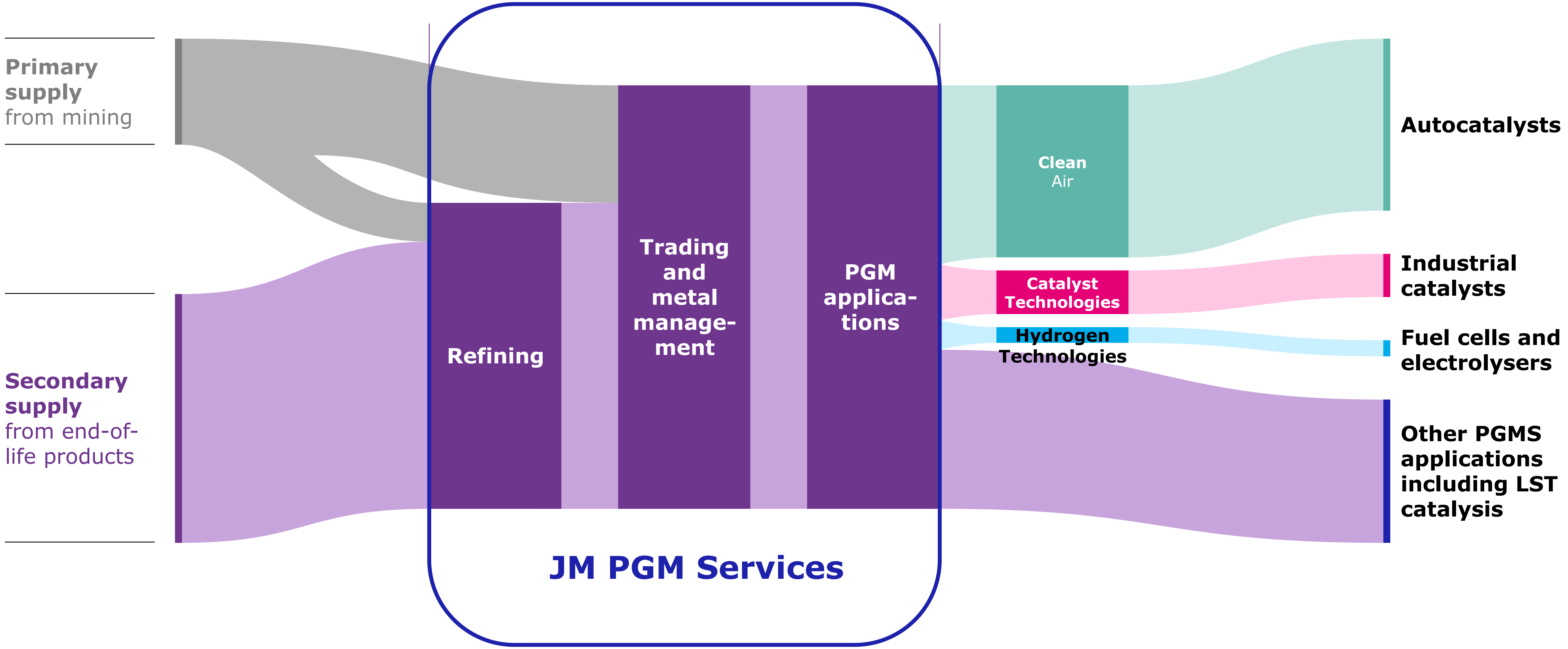
At the heart of the PGM market

… critical enablers for current and emerging applications

- Autocatalysts
- Industrial applications
- Fuel cells
- **Life Sciences Technologies**

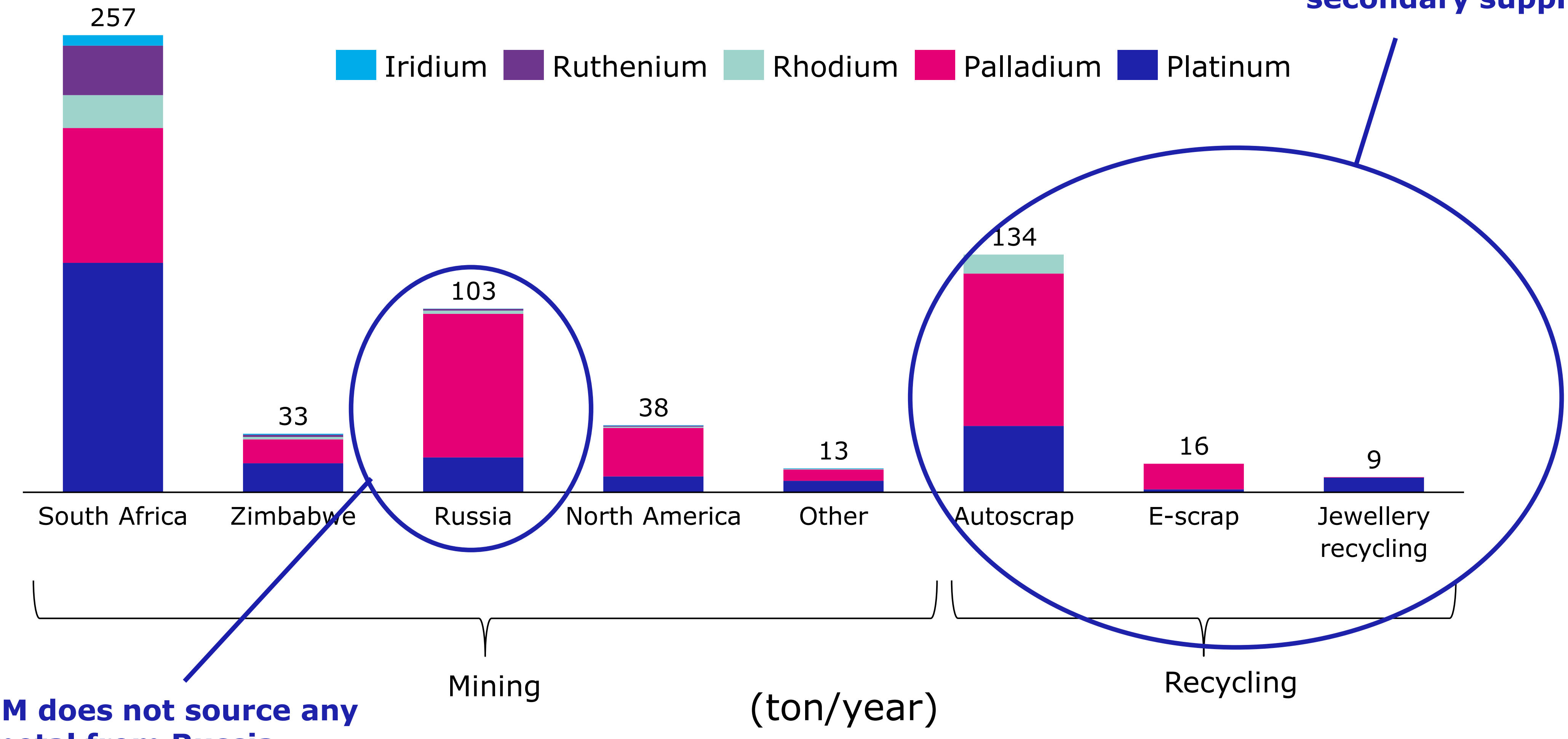
Introducing Johnson Matthey in the PGM landscape



Snapshot of PGM supply

Sources of PGM supply in 2023 (excluding closed-loop recycling)

~ 70% PGM used in JM products is from secondary supply

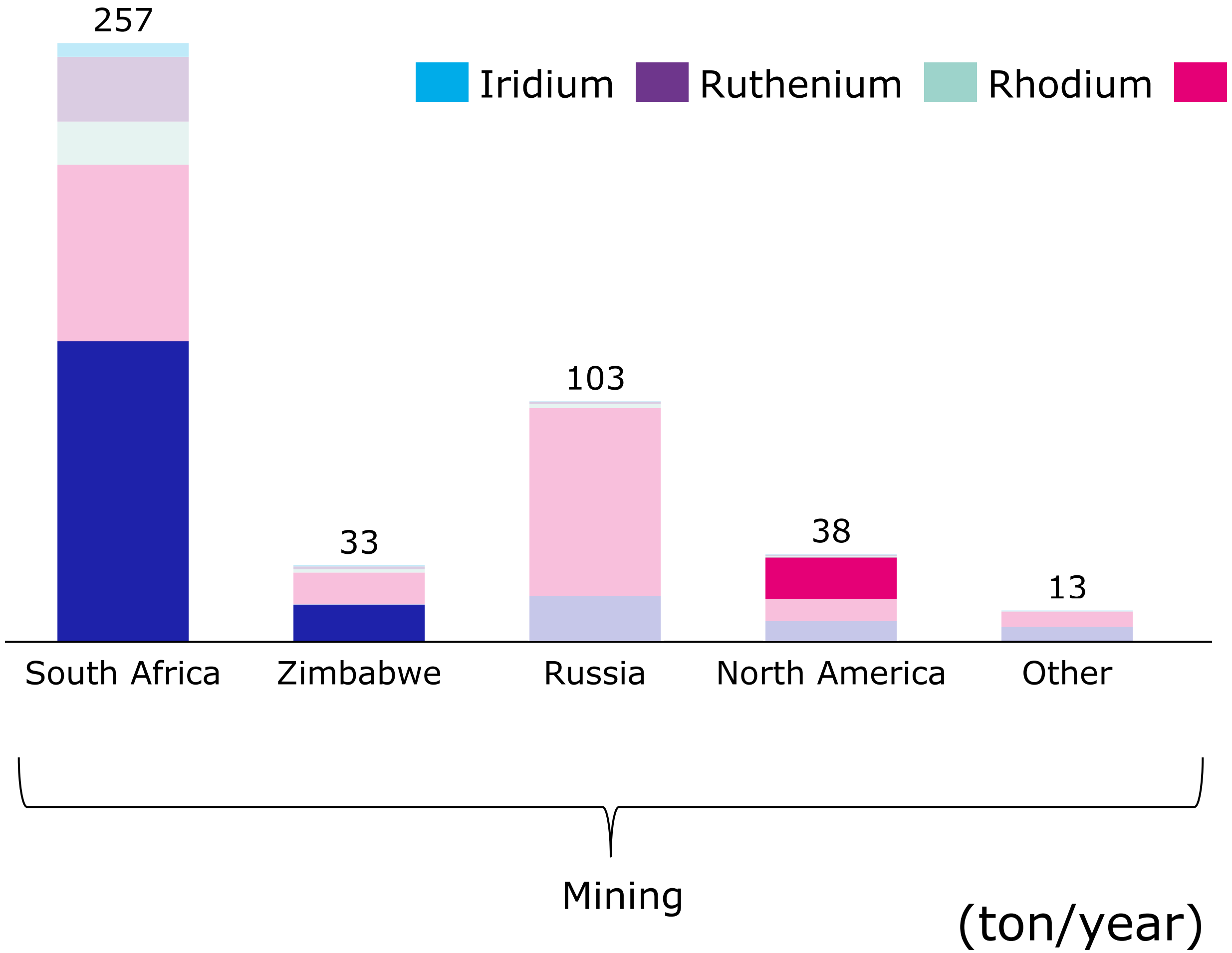


JM does not source any metal from Russia

JM

Snapshot of PGM supply

Sources of mined PGM supply in 2023



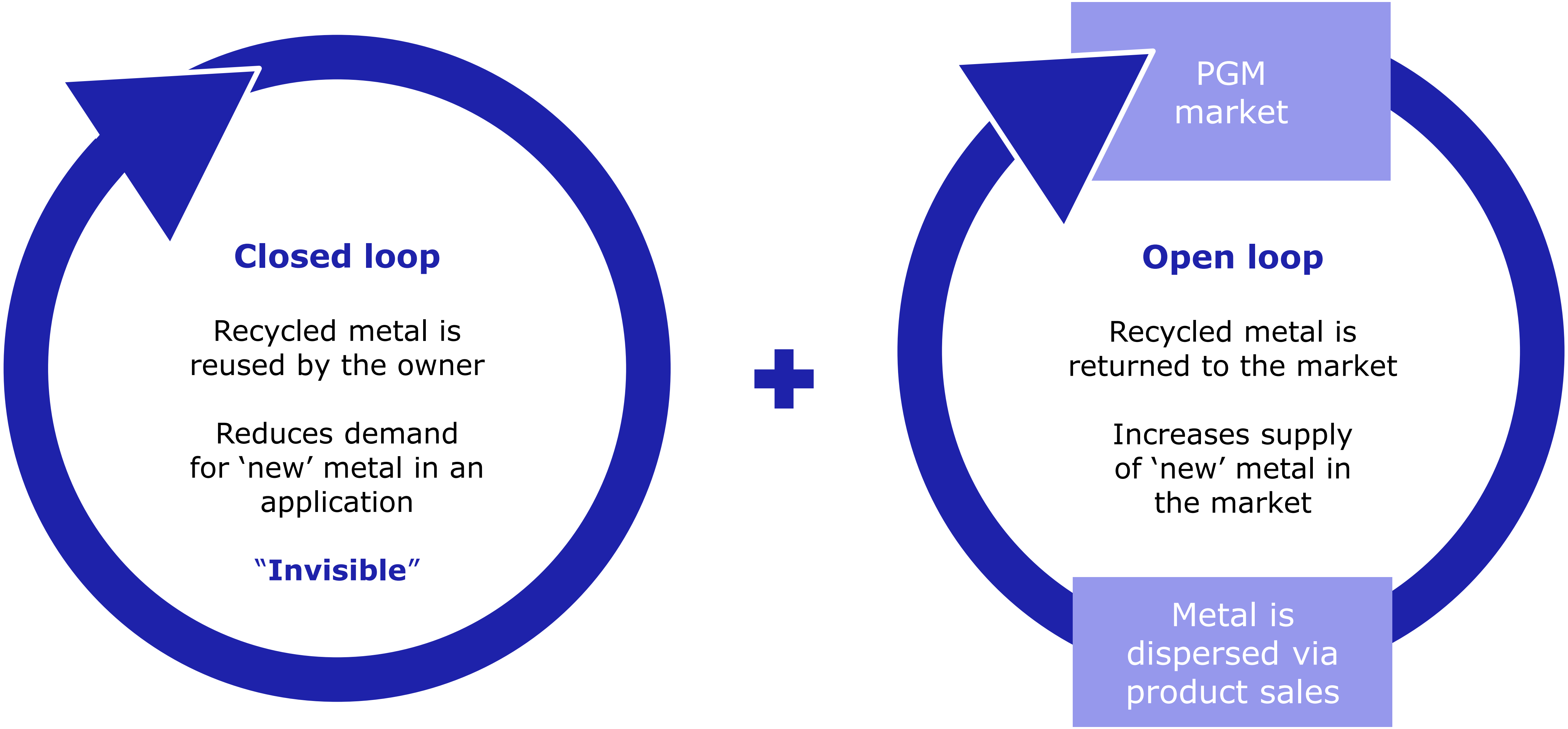
PGM supply is not elastic: the metals are mined in association with each other

Palladium is typically mined as a co-product – except in North America.

The minor metals are only ever mined as by-products

JM

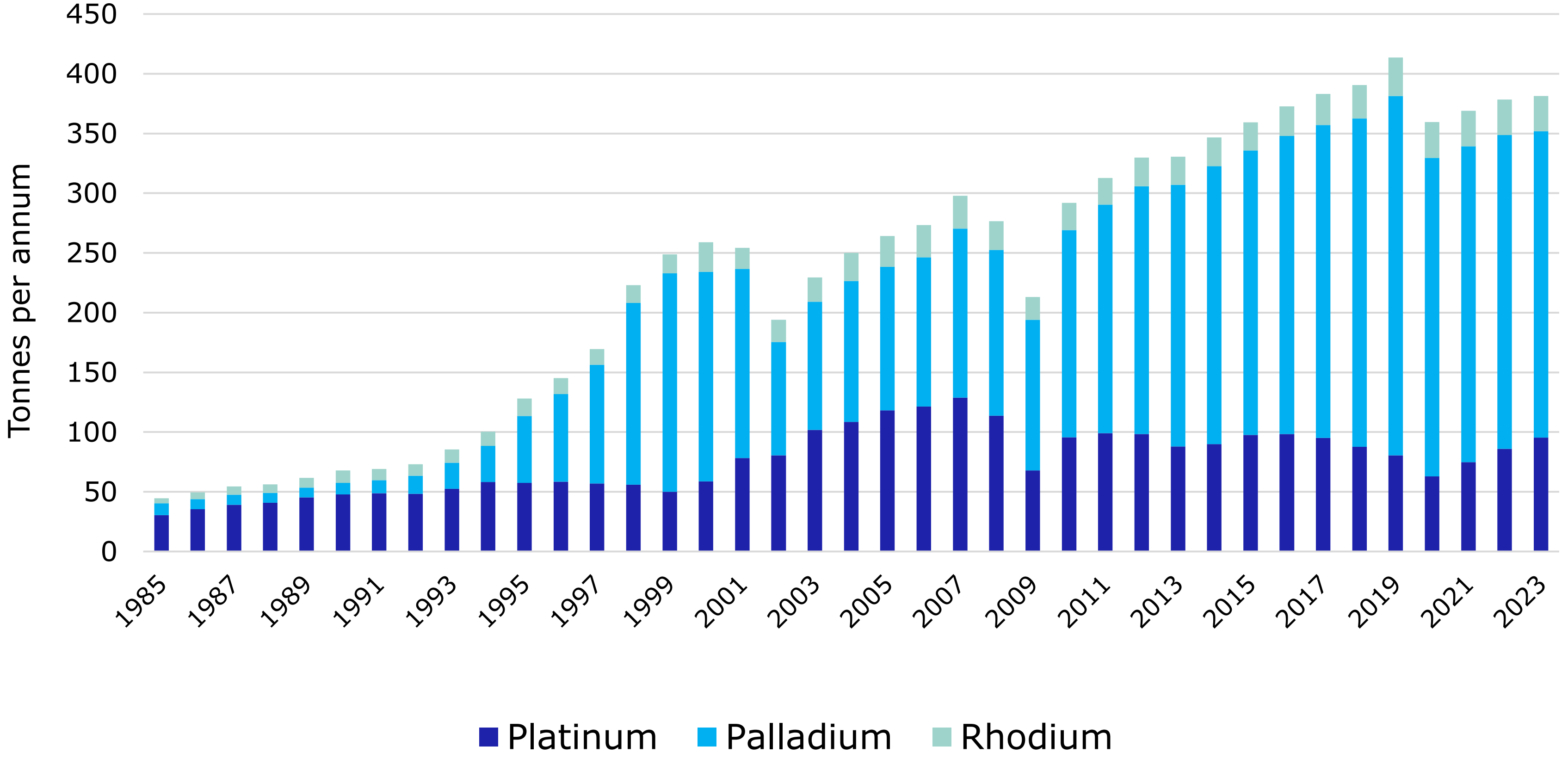
The different recycling loops



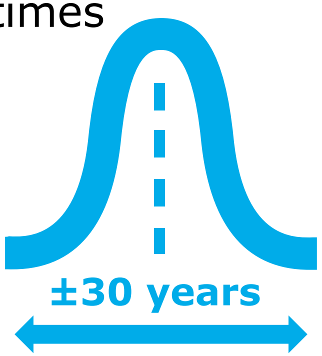
The urban mine

A source of low-carbon metal that can continue for decades

PGM used on new catalytic converters since 1985



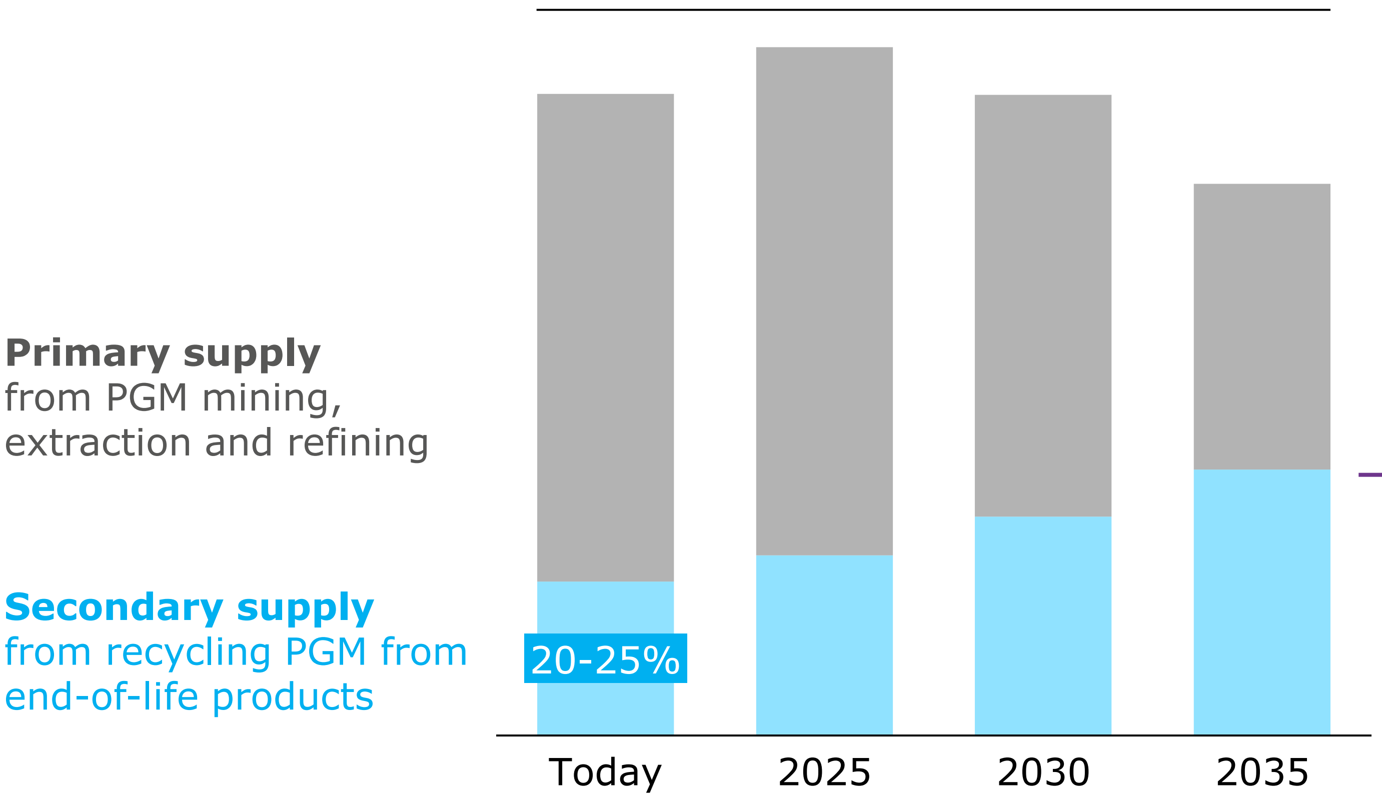
Available for recovery at end of vehicle lifetimes



JM

Recycled metals: critical raw materials management

Market supply of PGM volumes excluding closed loop supply



The world will continue to require PGMs

Decarbonisation trends make the recycling model even more relevant in the future due to:

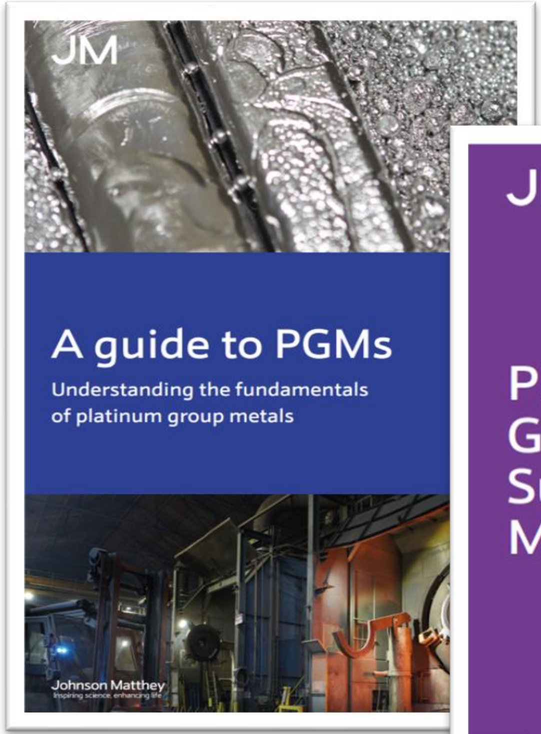
- Cost advantage
- Lower carbon content
- Circularity
- Supply security

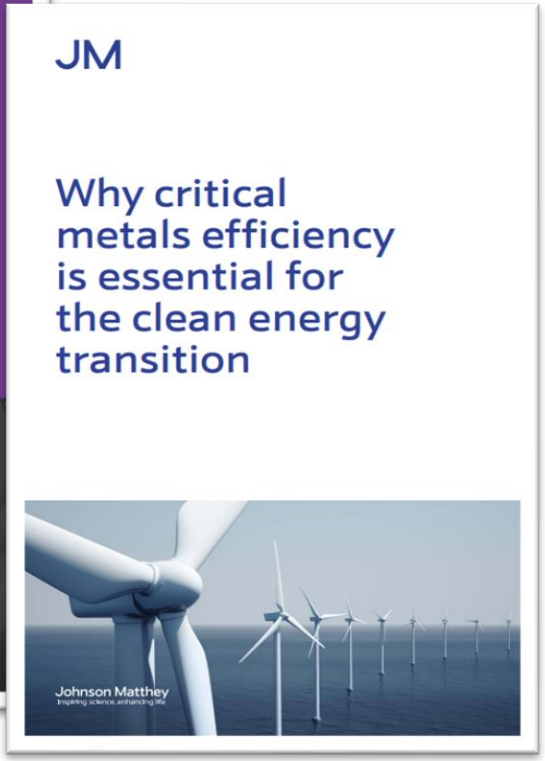
1. Platinum and palladium (which account for >85% of total pgm supplies annually).

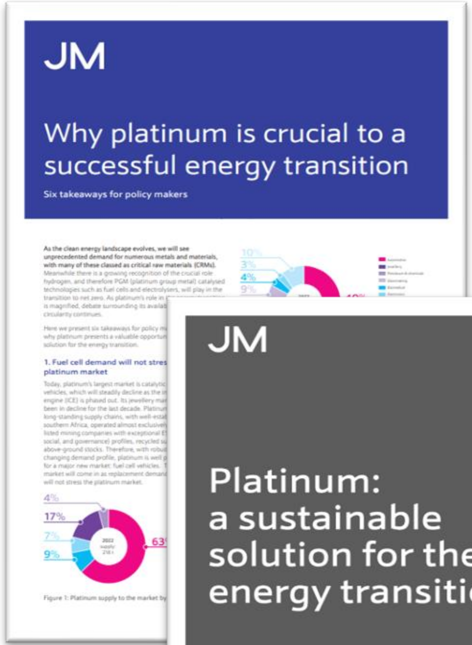
Source: Refinitiv GFMS, S&P Market Intelligence, Analyst Reports.

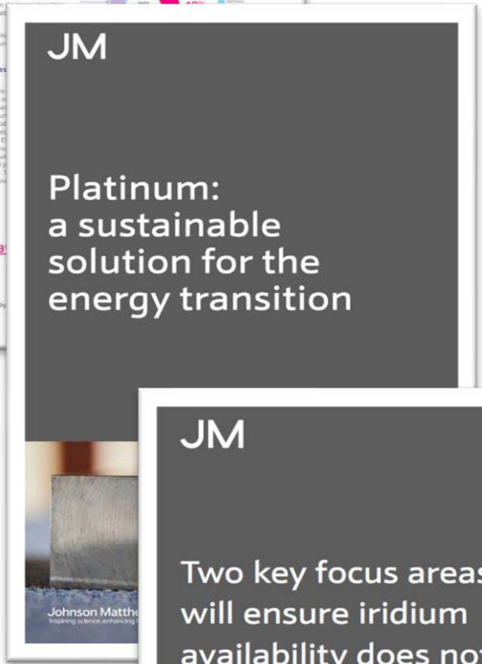
Lots of information on our website

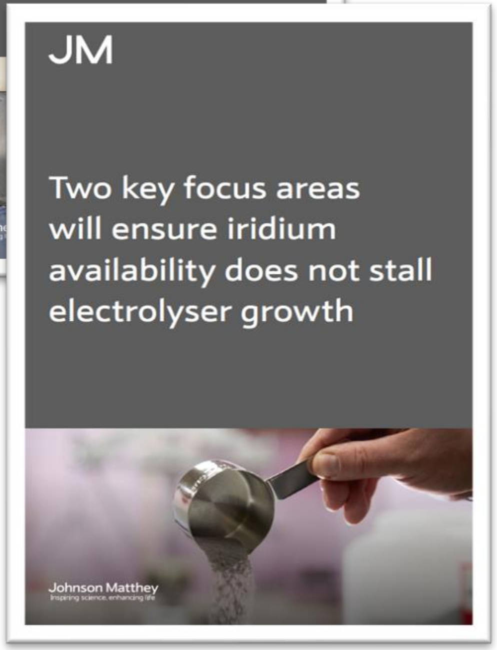
https://matthey.com/pgm-markets









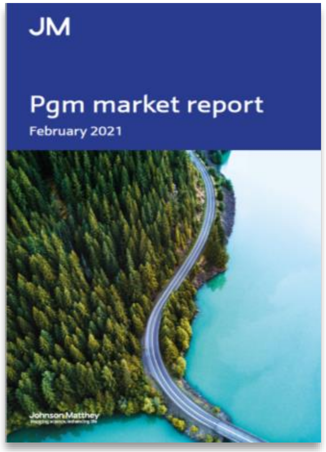


PGMS Market Research

- Team of analysts dedicated to analysis of the platinum group metals markets
- Principal authority on the pgm markets globally
- Deep insight into end-use product applications and markets, primary supply and recycling
- Short and long-term analysis for internal and customer strategic planning

Public domain resources

PGM Market Report



The PGM supply/demand equilibrium
https://www.youtube.com/watch?v=n7BjuMqTADg

PGM refining
https://www.youtube.com/watch?v=Vn4wnz5KSAM

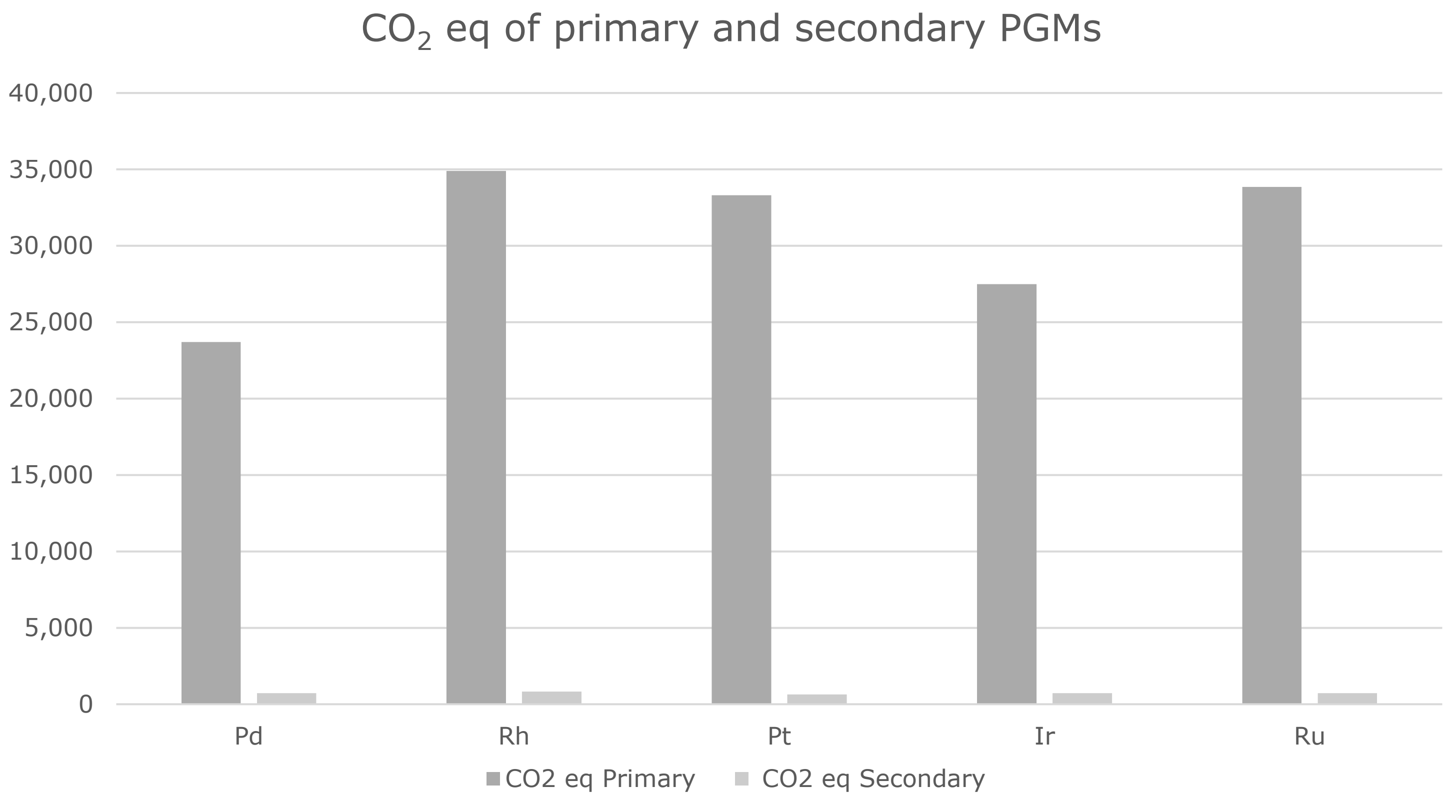
Fundamentals of PGMs
https://www.youtube.com/watch?v=QV0Ehx-MjJg

Platinum group metals: a circular solution for a net zero future
https://youtu.be/TeCvxN2Qo4U?si=htjGBZB-32PaEmrp

About a catalyst’s footprint in a catalytic step

JM

The carbon footprint of PGMs



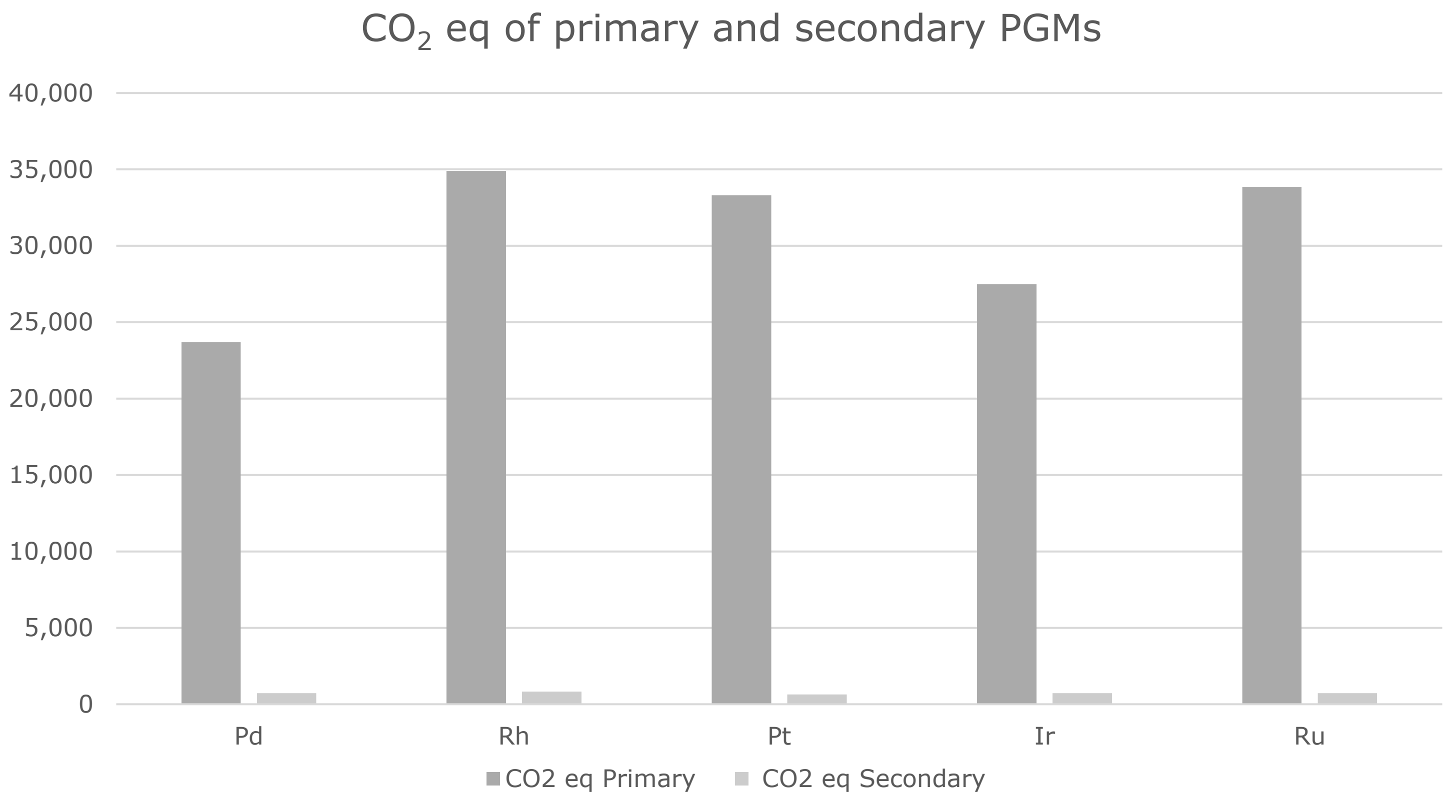
Recycled PGMs have a global warming contribution (CO_2 eq) 30/50 times lower than mined PGMs

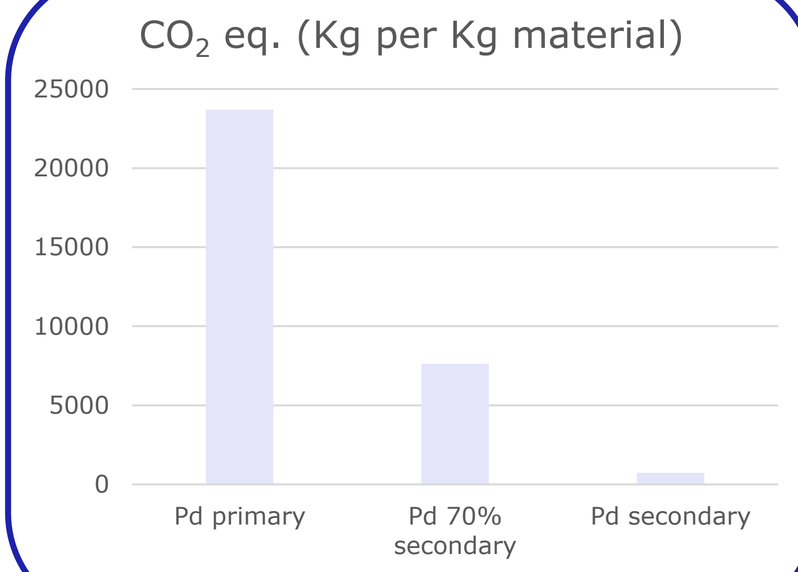
	CO_2 eq Primary	CO_2 eq Secondary
Pd	23,700	732
Rh	34,900	819
Pt	33,300	639
Ir	27,500	730
Ru	33,864	730

Source: 'Life Cycle Assessment of Global Platinum Group Metals Production' created by Sphera on behalf of The International Platinum Group Metals Association (IPA), v1.9, 20/10/2020 - Shannon Boonzaier, Christoph Hoppe, Johannes Gediga.
https://www.ipa-news.com/index/sustainability/lca-data-access.html

JM

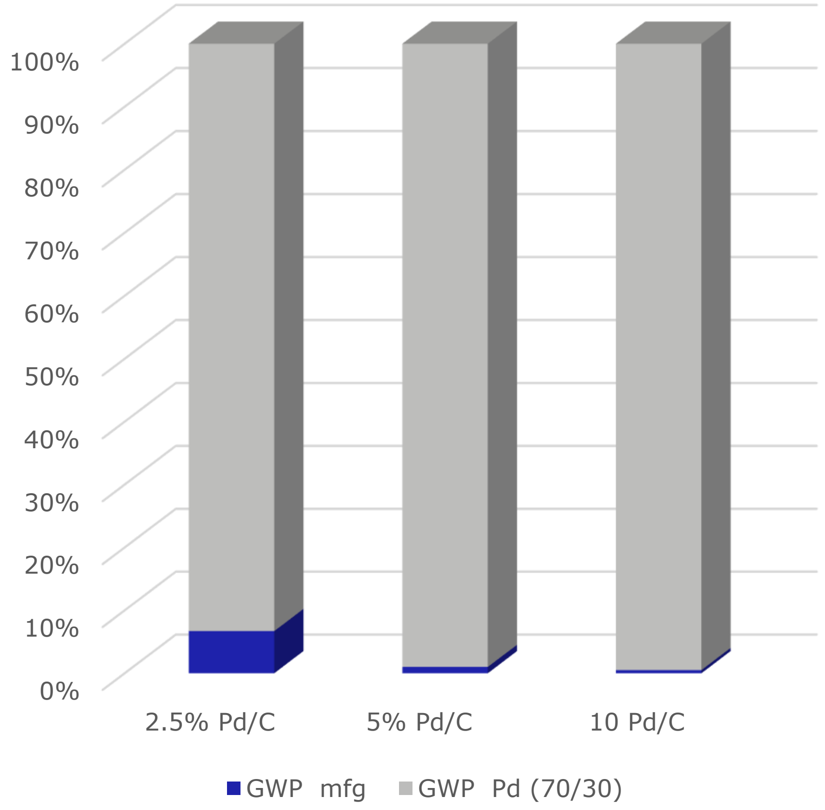
The carbon footprint of PGMs



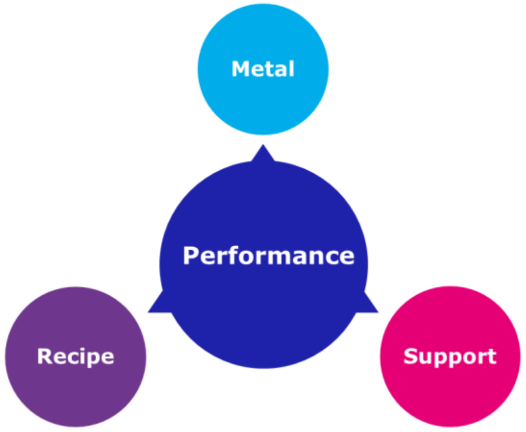


Certified 100% secondary metal is available

Heterogeneous catalysts



Manufacturing footprint of Pd/C is mostly negligible vs metal footprint



	Pd(Pb)/CaCO3	Pd,Pt(Bi)/C	Pd/Al2O3	Pd/BaSO4	Pd/C	Pd/CaCO3	Pt(Bi)/C	Pt(S)/C	Pt/C	Pt/Graphite	Rh/Al2O3	Rh/C	Ru/Al2O3	Ru/C
Alcohol Oxidation														
Carbocycles														
Heterocycles														
Alkyne & Alkenes to Alkanes														
Alkyne to Alkenes														
Alkyl Aldehydes & Ketones														
Aromatic Aldehydes & Ketones														
Unsaturated Aldehydes & Ketones														
Dehydrogenation														
Hydrodehalogenations														
Nitrogen Deprotection														
Oxygen Deprotection														
Ring Opening														
Imines & Oximes														
Nitriles														
Nitro, Nitroso & Halonitroaromatic														
Red Aminations & Alkylations														
Transfer Hydrogenation														

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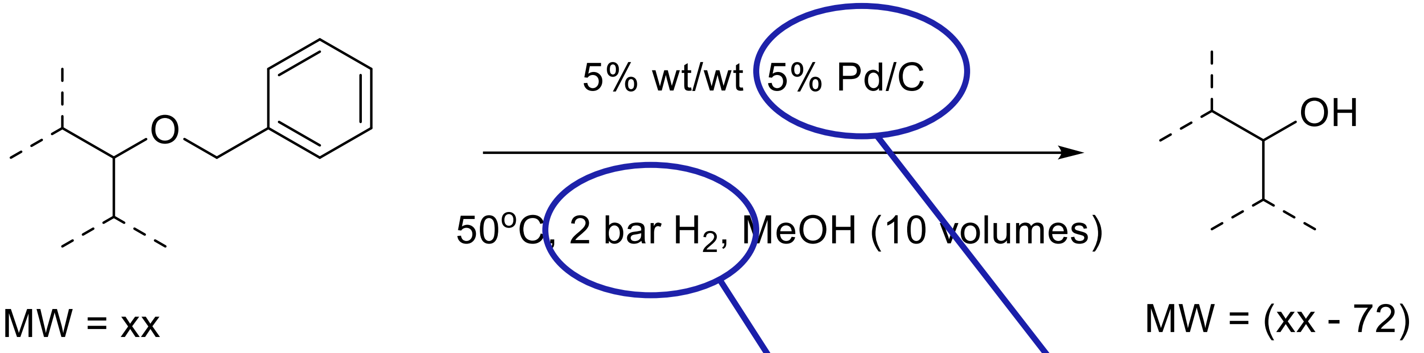
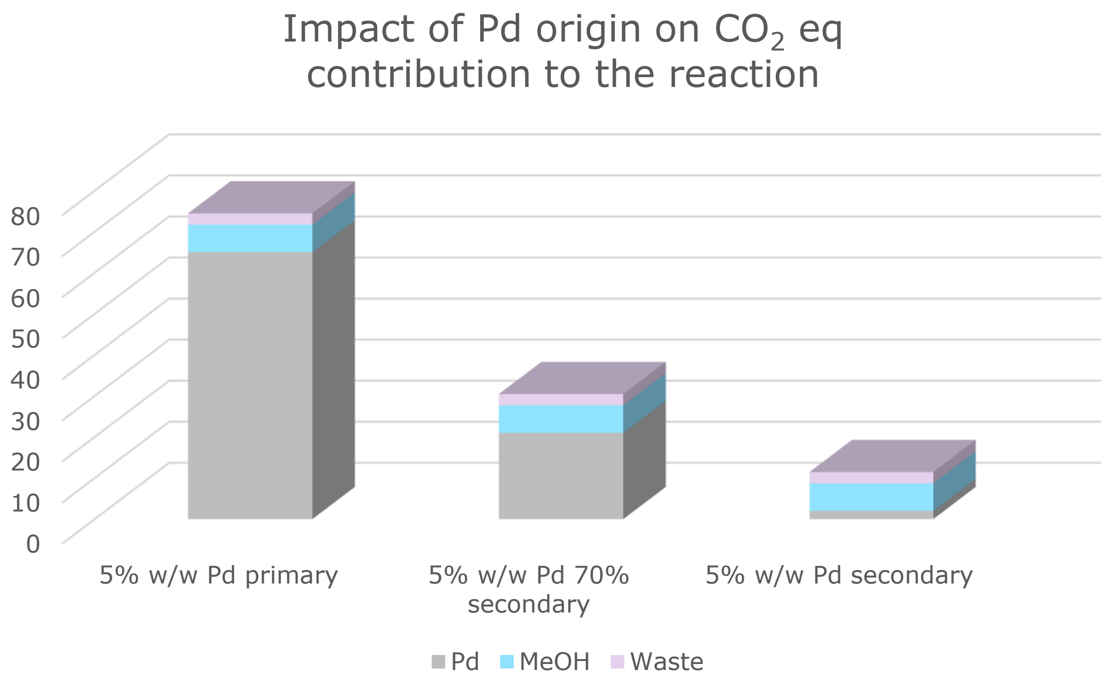
The carbon footprint of a Pd/C hydrogenation step





Manufacturing footprint negligible vs metal footprint

Hydrogen contribution negligible: 2g of H_2 per Kg of product

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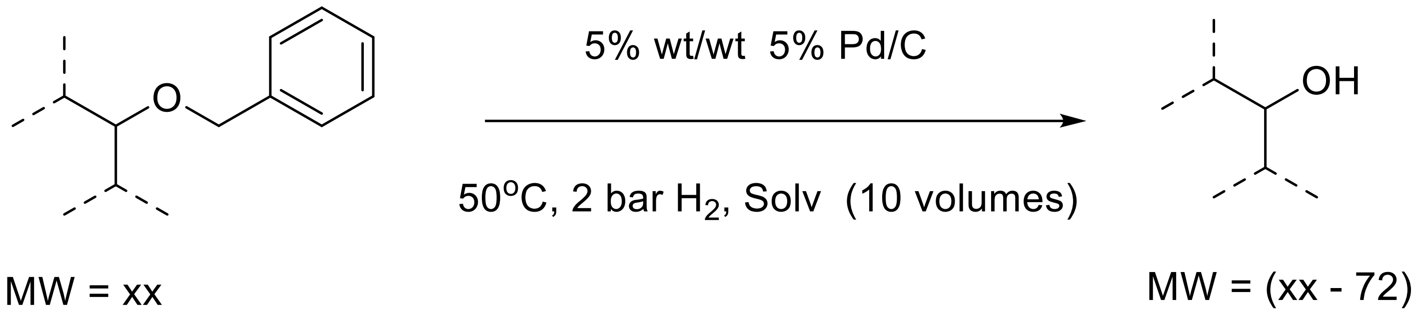
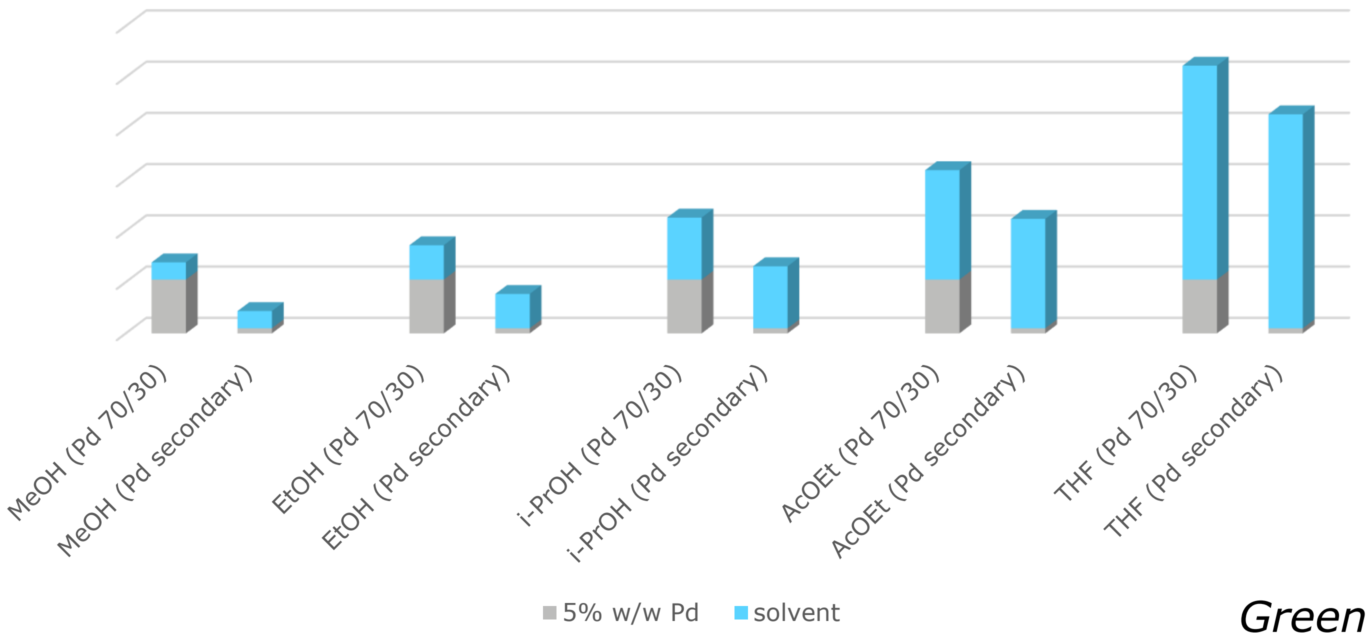
The carbon footprint of Pd/C hydrogenation step



Impact of solvents on GWP of catalytic step



The choice of solvent has a major impact on the catalyst step GWP

Note that selection purely based on GWP (CO_2 eq.) of solvents may differ from selection based on combined other metrics, e.g.:

Green Chem **2016**, *18*, 3879 (GSK)

Green Chem **2016**, *18*, 288 (GSK, Sanofi, Pfizer)

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About base metal catalysts *vs* PGM catalysts

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Growing interest for base metal catalysts

Recent advances in nonprecious metal catalysis
Ickes *et al. Org.Process.Res.Dev* **2023**, *27*, 423

Collaboration as a key to advance capabilities for earth abundant metal catalysis
Wisniewski *et al. Org.Process.Res.Dev* **2023**, *27*, 1160

Diversification of pharmaceutical manufacturing processes: taking the plung into the non-PGM catalyst pool
Engle, Seechurn *et al. ACS Catal.* **2024**, 9708

Advances in Earth abundant metal catalysis
Wheelhouse *et al. Org. Process Res. Dev.* **2023**, *27*, 1157

For a different point of view see:

B. Lipshutz *Johnson Matthey Technol. Rev.* **2023**, *67*, 278
E. Schofield *Johnson Matthey Technol. Rev.* **2023**, *67*, 285

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Sustainability of Ni and Pd coupling processes

	CO_2 eq catalyst preparation	CO_2 eq catalyst contribution in process	CO_2 eq entire process
Ni	**17.5**	**0.19**	**2326**
Pd	**11,289**	**2.37**	**1554**

Ni catalysis is not necessarily more sustainable than Pd catalysis, but it should be regarded as complementary

Look at the big picture!

From: M. U. Luescher, F. Gallou and B. H. Lipshutz, *Chem. Sci*., **2024**, DOI: 10.1039/D4SC00482E

Interactions of multiple metrics and environmental indicators to assess processes, detect environmental hotspots and guide future development
M.U. Luescher, F. Gallou *Green. Chem.* **2024**, *26*, 5239

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Sustainability of Ni and Pd coupling processes

More about cost:

An example of route comparisons in C-H activation:

Ni > Pd > no cat > Rh > Co > Ru

A.K. Komarova, D.S. Perekalin
Organometallics **2023**, *42*, 1433

More about toxicity:

Toxicity of metal compounds: knowledge and myths

K.S. Egorova, V.P. Ananikov
Organometallics **2017**, *36*, 4071

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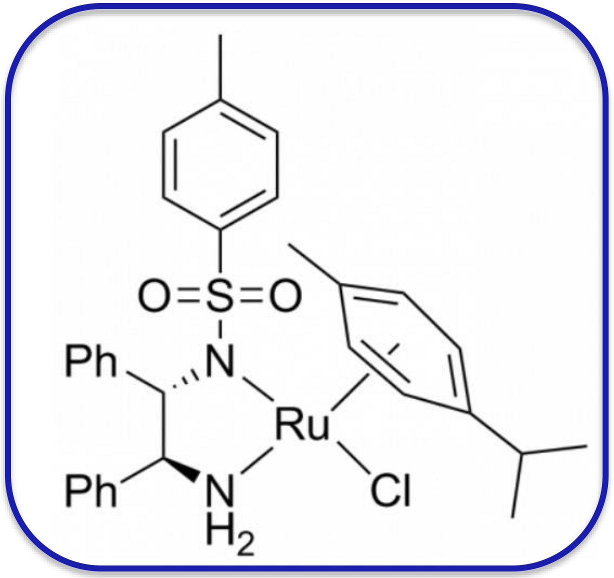
About the importance of process optimization

Asymmetric transfer hydrogenation

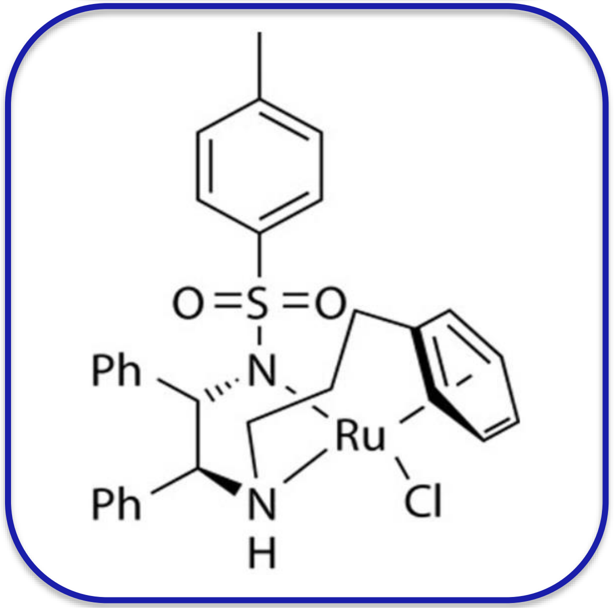
First Generation (Noyori)

- Reliable and flexible
- Well-understood scope
- Cost-effective



Second Generation (Wills)

- Special applications
- Enable the ‘impossible’



‘New transfer hydrogenation patents granted at a stable rate of around 50 per year’

Glorius, Leker *et al.*
Adv.Synth.Catal **2020**, *362*, 1258

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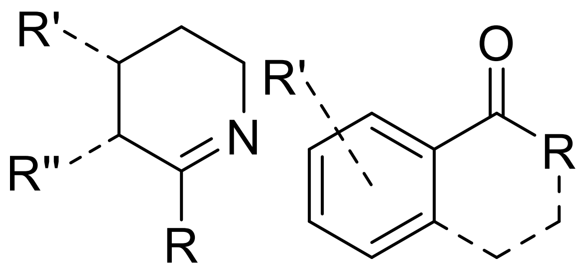
Catalyst loading in transfer hydrogenation

The 'simple' substrates

	Molar catalyst loading	Weight catalyst per ton substrate	ppm Ru (mg / Kg)
1st Gen (Noyori)	S/C 100– 2,000/1	20 - 1 Kg	3,000-150
2nd Gen (Wills)	S/C 1,000-20,000/1	2 Kg – 100 g	300-15



R', R'' = alkyl, aryl, halide, OR, NR_2

- First generation Noyori catalysts have well-understood scope
- Reliable and cost-effective on 'simpler' targets

Second generation Wills catalysts offer incremental advantages:

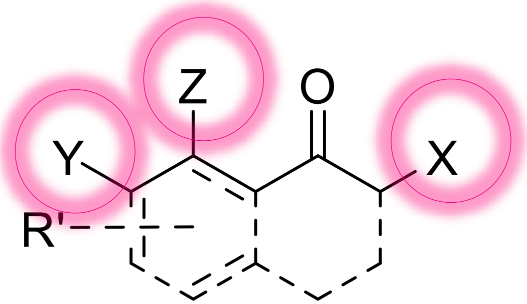
- Much lower loadings
- Easier product purification

*Assuming MW catalyst = 2 x MW substrate and Ru 1/6 of catalyst MW

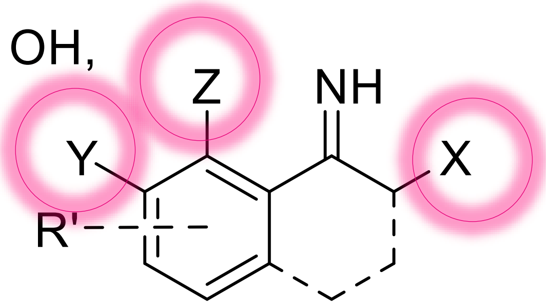
Catalyst loading in transfer hydrogenation

The complex substrates

	Molar catalyst loading	Weight catalyst per ton substrate	ppm Ru (mg / Kg)
1st Gen (Noyori)	S/C 20 - 100 (if possible at all…)	100 - 20 Kg	15,000-3,000
2nd Gen (Wills)	S/C 100– 1,000/1	20 – 2 Kg	3,000-300



X,Y,Z = NHR, NR_2, SR, OH, OR, COOR, $CONR_2$



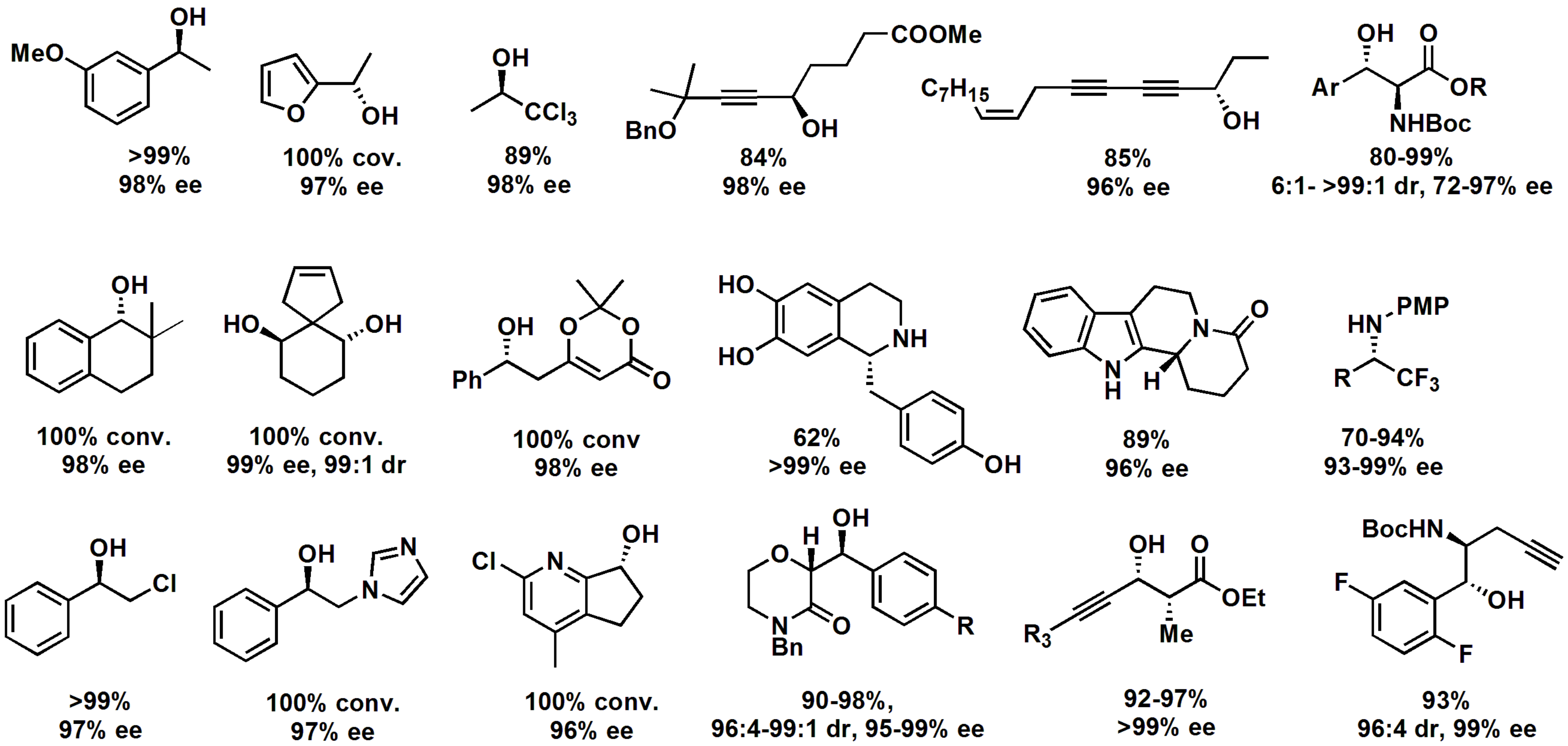
Second generation catalysts:

- provide more robust processes
- enable 'impossible' transformations
- Reduce catalyst loadings

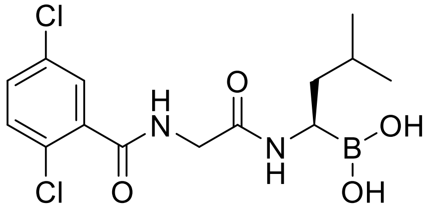
*Assuming MW catalyst = 2 x MW substrate and Ru 1/6 of catalyst MW

Transfer hydrogenation has a wide scope

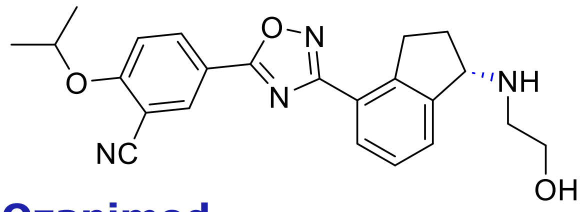
Second generation catalysts are effective on complex molecules



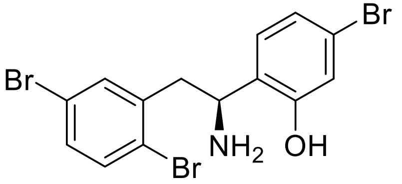
Review: Wills, Nedden, Zanotti *Chemical Records* **2016**, *16*, 2623



Ixazomib
Sandoz: *Chem. Sci.* **2022**, *13*, 2946–2953



Ozanimod
Chemessentia: *Eur. J. Org. Chem*. **2021**, 2021, 1924



98% ee, 96% yield

Elbasvir
Merck: *Org. Lett.* **2014**, *16*, 2310

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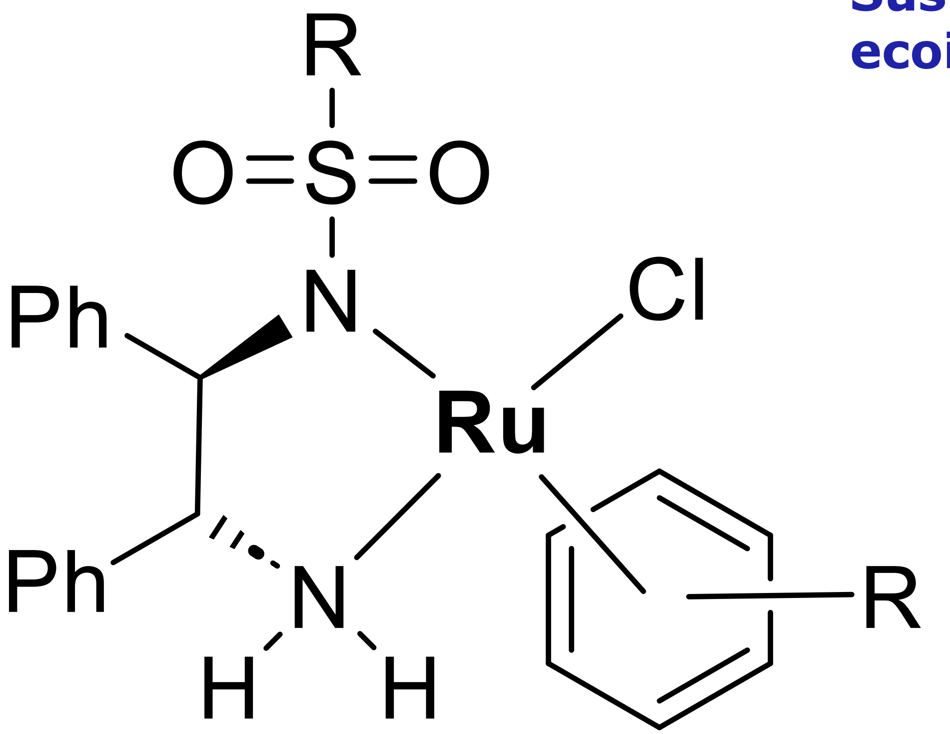
Carbon footprint of a first-generation TH catalyst



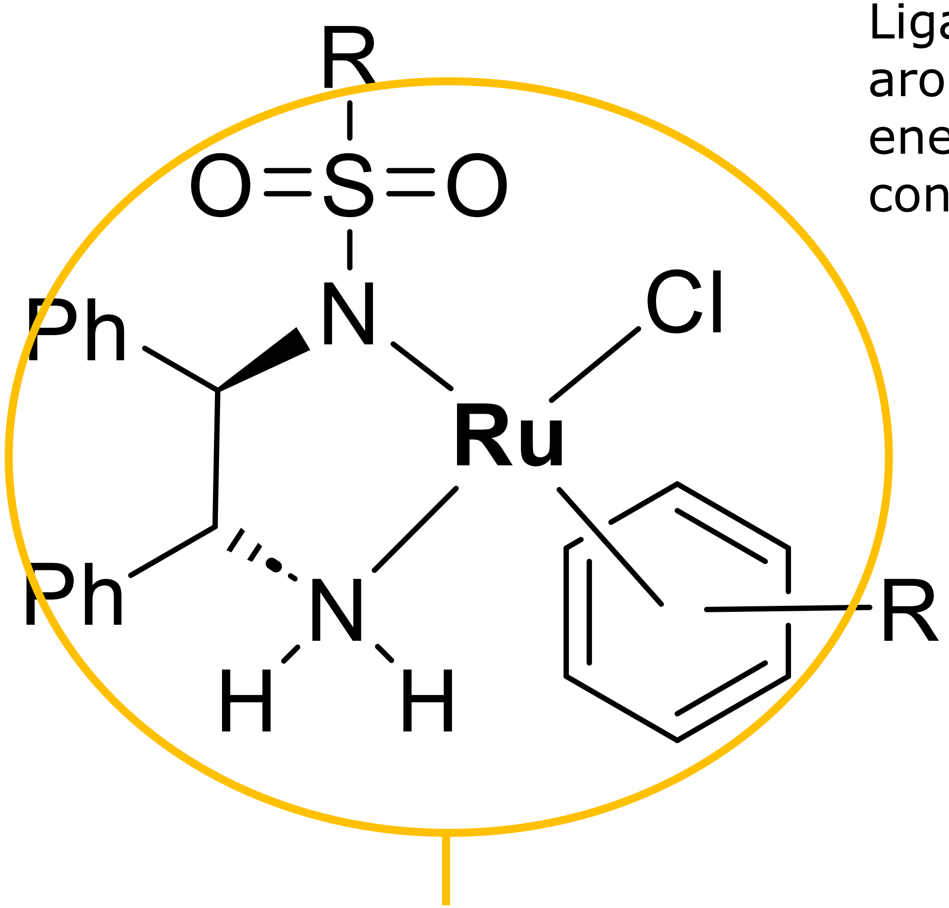
LCA Tools: SimaPro 9.6 (Pre-Sustainability, The Netherlands) with ecoinvent v3.10 (ecoinvent, Switzerland)

https://ecoinvent.org/database/
ecoinvent Version 3

Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., and Weidema, B., 2016. The ecoinvent database version 3 (part I): overview and methodology. The International Journal of Life Cycle Assessment, [online] 21(9), pp.1218–1230.

Carbon footprint of a first-generation TH catalyst

DISCLAIMER: this is work in progress !



Ligand TsDpen based on *Org. Synth.* **1998**, *9*, 387: around ~1,000Kg CO_2 /Kg ; waste included, and energy not included (solvents biggest contributors).

Estimation based on model Birch reduction : *OPRD* **2024**, *28*, 2168 ~100Kg CO_2 /Kg (largely solvent dependent!), waste included, energy not included

Estimated total: ~3,500 Kg CO_2/Kg product, waste included, and energy not included. Metal contribution approx. 70% (assuming Ru 70% from secondary sources)

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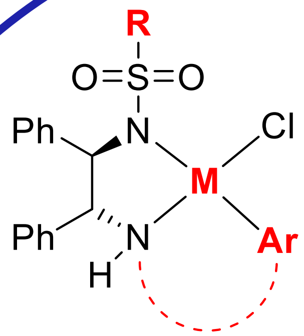
Reaction variables

Catalyst



Sulphonyl
Arene
Metal
1^{st} vs 2^{nd} gen
(tether)

Optimal process

Solvent

MeOH, EtOH, i-PrOH,
AcOEt, THF, MeTHF,
MeCN, DCM, etc.

Hydride source

HCO_2H/Et_3N
HCO_2H/HCO_2Na

pH 5 to 10

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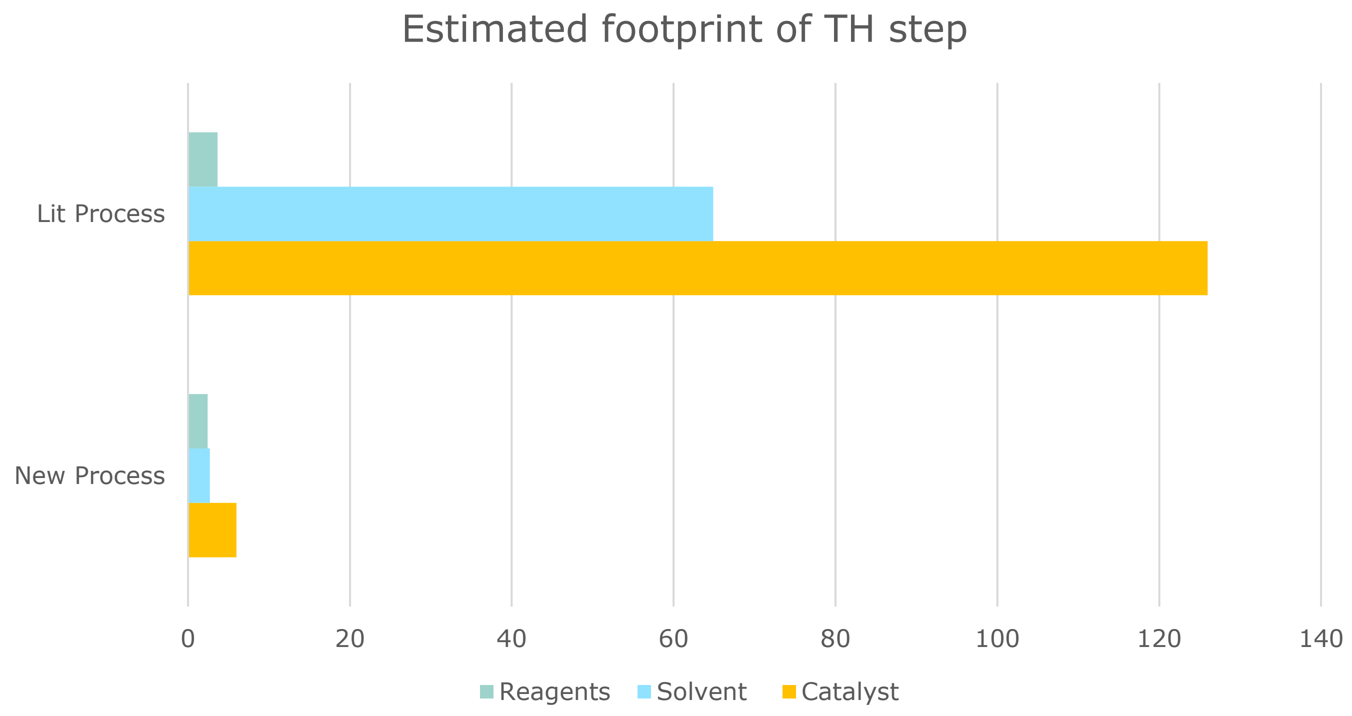
Optimisation case studies with TH catalysts

From literature conditions to scalable process

S/C 50/1,
$HCOOH/Et_3N$ 5/2, CH_3CN

1[st] Gen catalyst,
MeOH/water, 10 eq. NaOOCH

S/C 1,500/1



Catalyst GWP remains major contributor to step but is reduced by 30 times

Optimization enables reduction of solvent/reagents impact by a factor of 14 times

No isolation included
No waste disposal included

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Optimisation case studies with TH catalysts

From initial conditions to scalable process

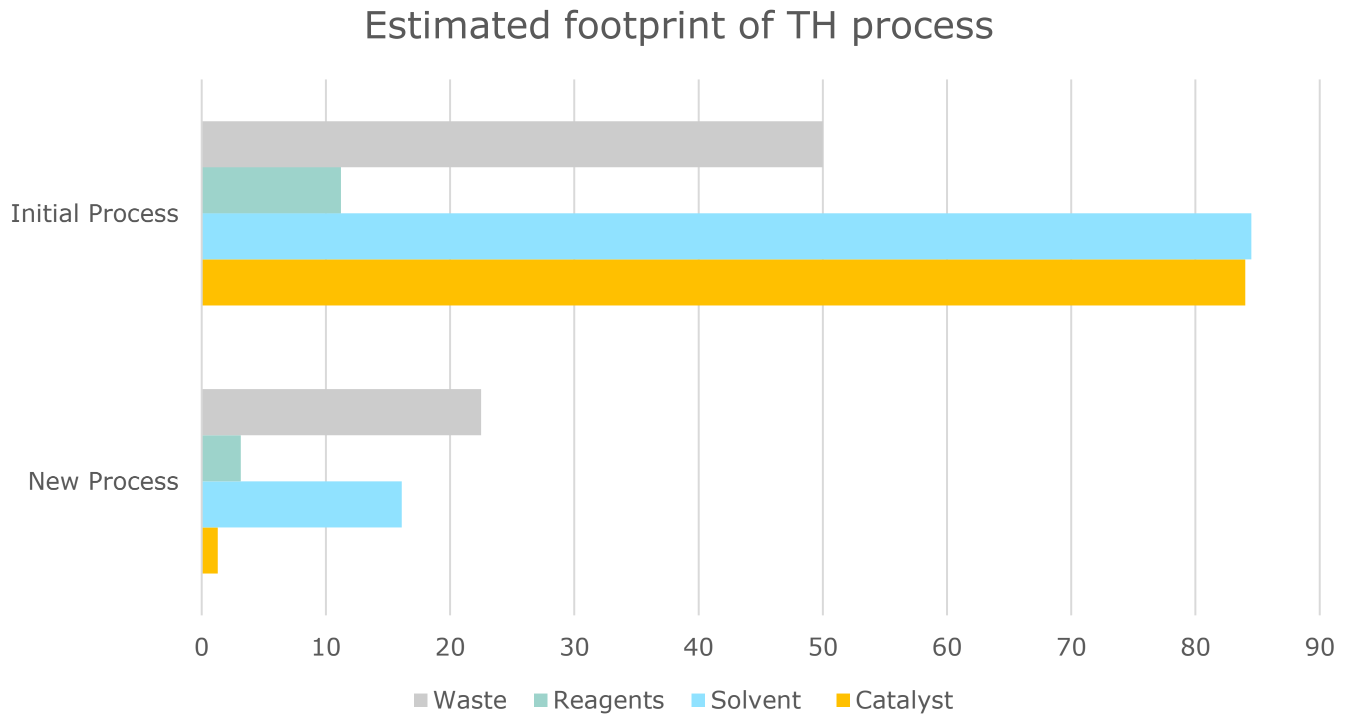
S/C 50/1

$HCOOH/Et_3N$ 1/1, THF

1[st] Gen catalyst, IPA,

0.1 eq. base, 1.1 eq. HOOCH,

S/C 3,000/1



Semi-optimized isolation and waste disposal included

Catalyst GWP similar to solvent in initial process and negligible in optimized process

Optimization reduced impact of catalyst by a factor of 60 and of combined solvent/reagent/waste by a factor of 3.5

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About design for refining

Challenges in closing the metal loop

Process optimization improves costs and sustainability, but metal recovery can be challenging

Low metal concentration

Nature of liquid waste (hazard, toxicity…)

Pretreatments requirements

Representative sampling

Understanding the mass balance – where does the metal escape?

Trade in and out of countries – regulations

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Design the process for refining

A closed-loop approach will reduce carbon emission and capital expenditure

It is important to:

- Understand metal balance
- Understand waste pre-treatment

D. Arnold *et al*.

‘Designing for refining’ submitted to *Chemistry Today*, **2024**

There are solutions to maximise value recovery from liquid waste:

See, for example:

https://www.mastermeltgroup.com/catalyst-webinar

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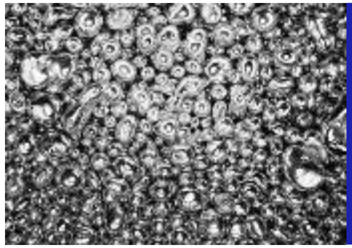
Conclusions

PGMs: challenging the myths



They are expensive, it would be better to switch to cheaper alternatives

They are used in small quantities: expensive on a per-gram basis, not on a **total cost contribution** basis. Because of efficiency of use and recycling, using PGMs is often cheaper than alternatives

They are difficult to recycle effectively

Recycling of all PGMs happens routinely & cost-effectively today. If retained in a closed loop, PGM value is retained and can be endlessly reused.

Mining is subject to geopolitical risk & ESG concerns

Mined PGMs from southern African is typically from **highly regulated companies** that report on ESG performance, support local communities and are investing to reduce environmental footprint.

They are scarce metals and there is not enough available

Hydrogen is a replacement market for the PGMs as catalytic converter use declines. JM's PGM market research experts project that hydrogen and fuel cell **market growth can be from existing supplies**.

And my own conclusions…

What matters is not the headline price / carbon footprint but the **economic**/**sustainability value** that PGMs create

Process optimization unlocks the value of catalysts, enables better use of resources, minimizes contribution of **catalyst cost**/**footprint**

PGMs are an example of functioning **circular economy** and their future availability is sustainable

(…and I have ignored the comparison with biocatalysis – for discussion another day!...)

JM

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