Produktionsverfahren für Essigsäure

- **Fermentation von Ethanol** (→ 4 – 12 % Essigsäure)
- **Acetaldehyd-Oxidation** (im Zuge des Wacker-Hoechst-Verfahrens)
- **Oxidation von Butan** (früher Hauptmethode, heute < 10 %)

- **Carbonylierung von Methanol**

  i) $CH_3OH + HI \rightarrow CH_3I + H_2O$

  ii) $CH_3I + CO \rightarrow CH_3COI$

  iii) $CH_3COI + H_2O \rightarrow CH_3COOH + HI$

BASF-Prozess
(Co-Katalysator, 90 % MeOH-Selektivität, 250 °C, 600 bar)

Monsanto-Verfahren
(Rh-Katalysator, > 99 % MeOH-Selektivität, 150 – 200 °C, 30 – 60 bar)

Cativa-Verfahren
(Ir-Katalysator, > 99 % MeOH-Selektivität, 150 – 200 °C, 30 – 50 bar)

Monsanto-Prozess – Rhodium

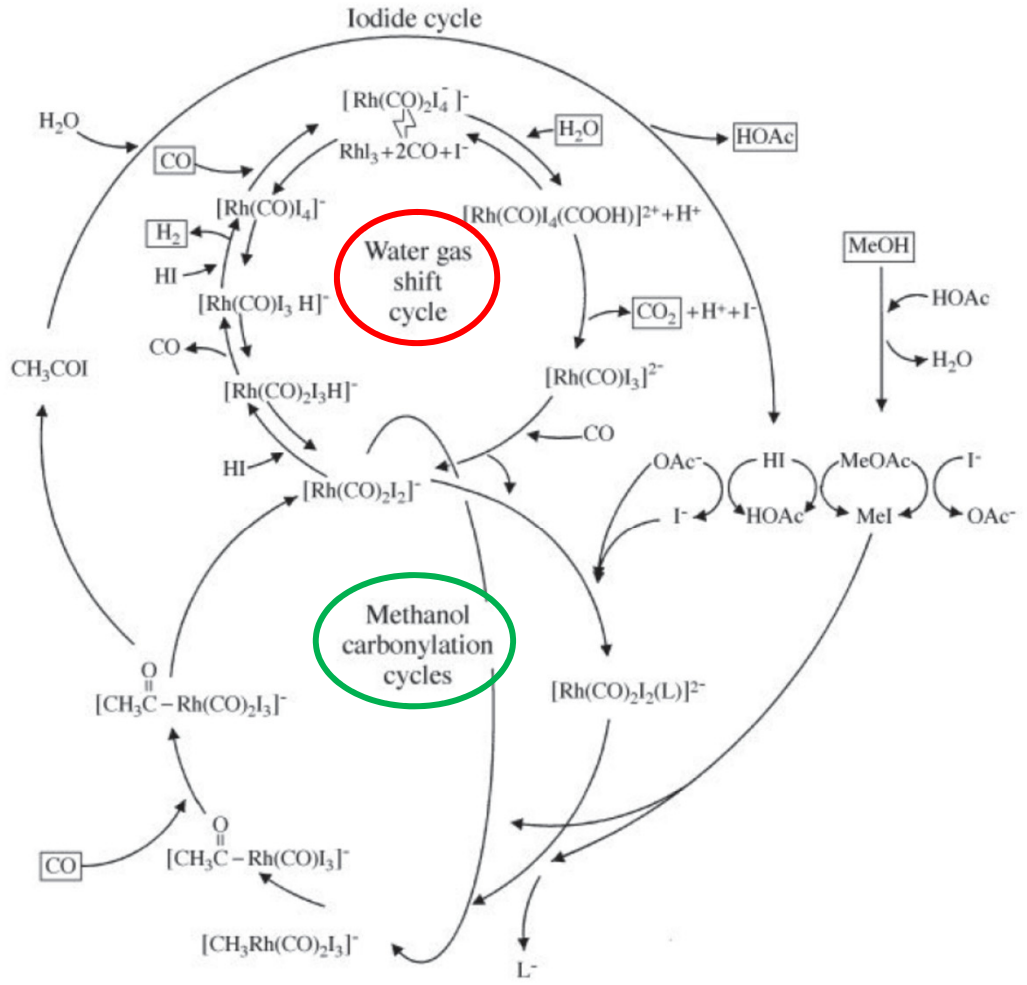
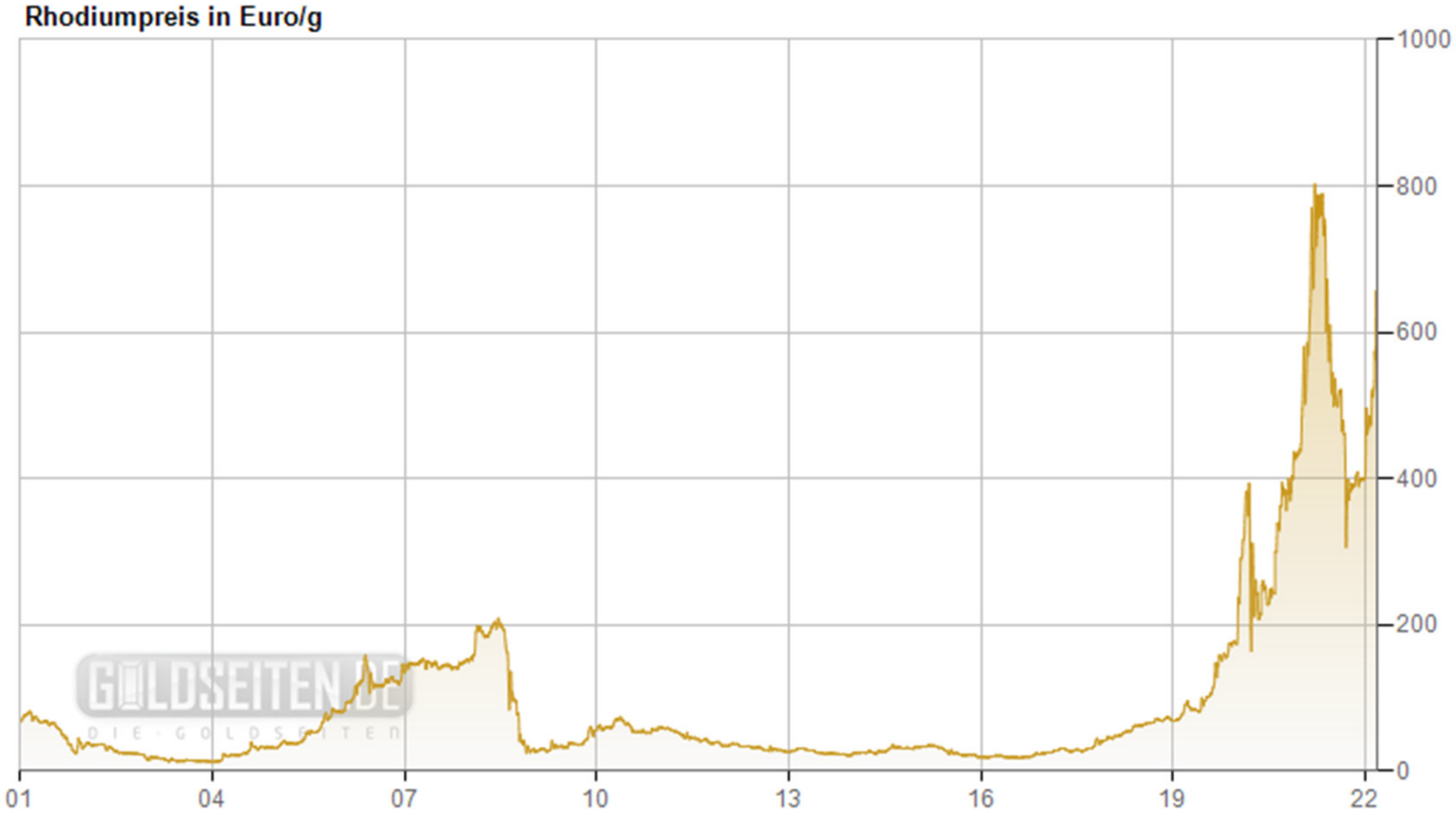


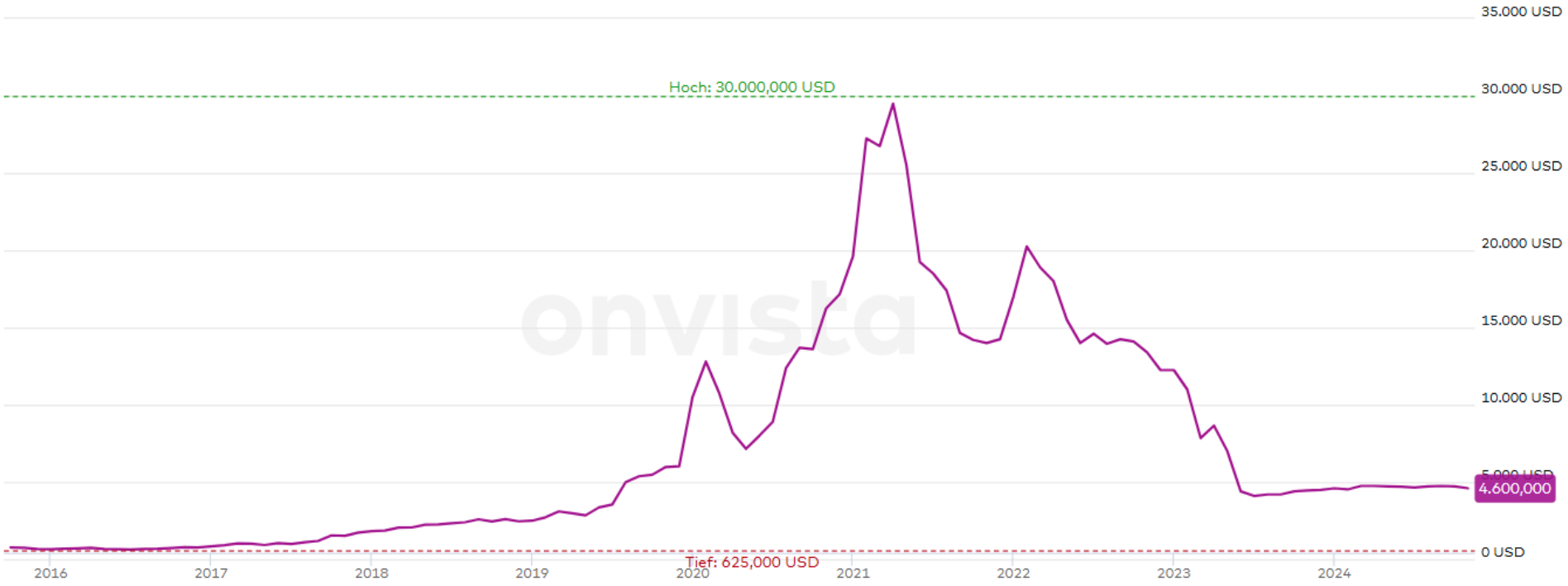
Figure 2. Reaction cycle proposed for the rhodium-catalyzed methanol carbonylation reaction (Monsanto process) and with inorganic iodide co-promotion (Celanese process)

[5] *Ullmann's Encyclopedia of Industrial Chemistry*

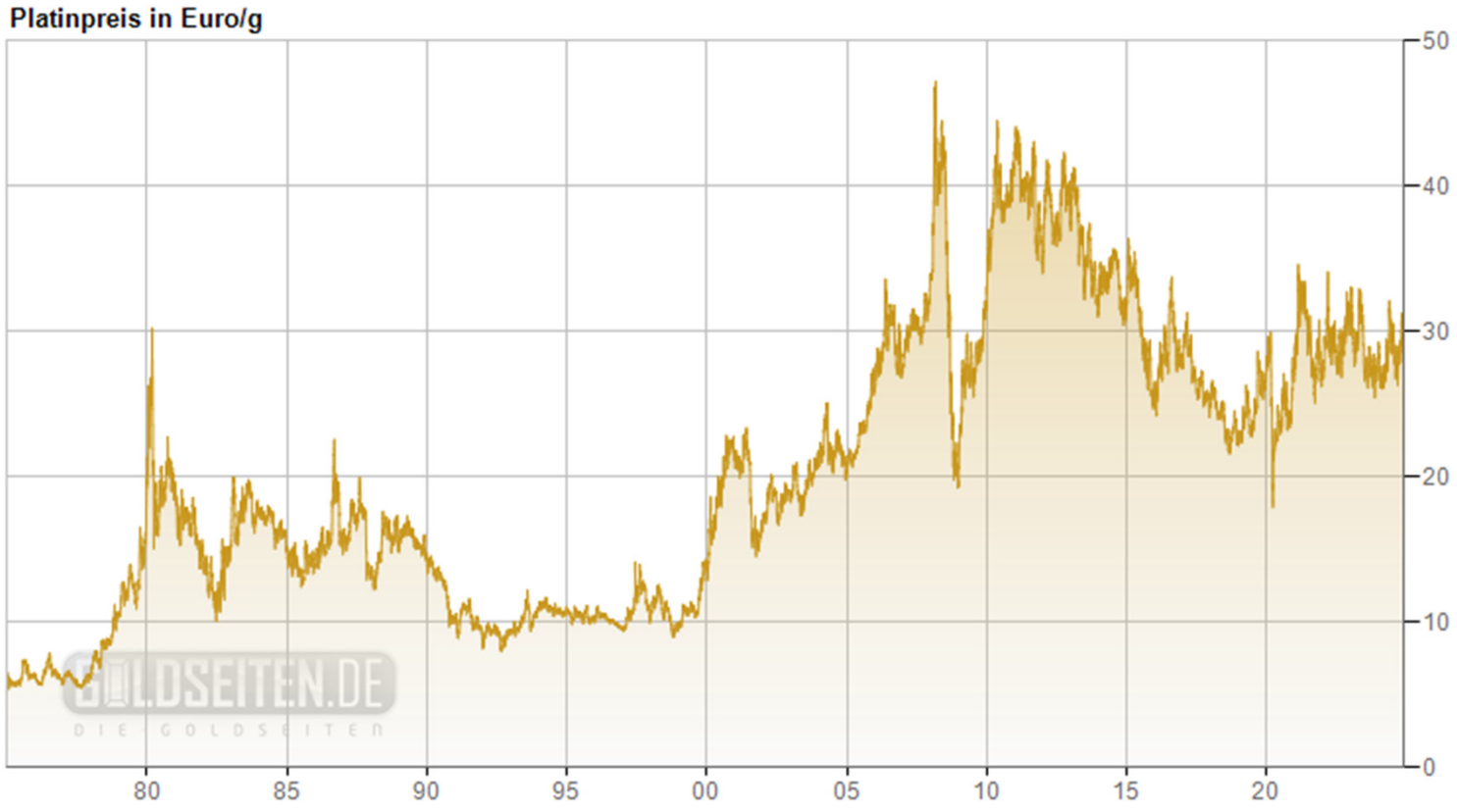
Edelmetallpreise – Rhodium (bis 2022)



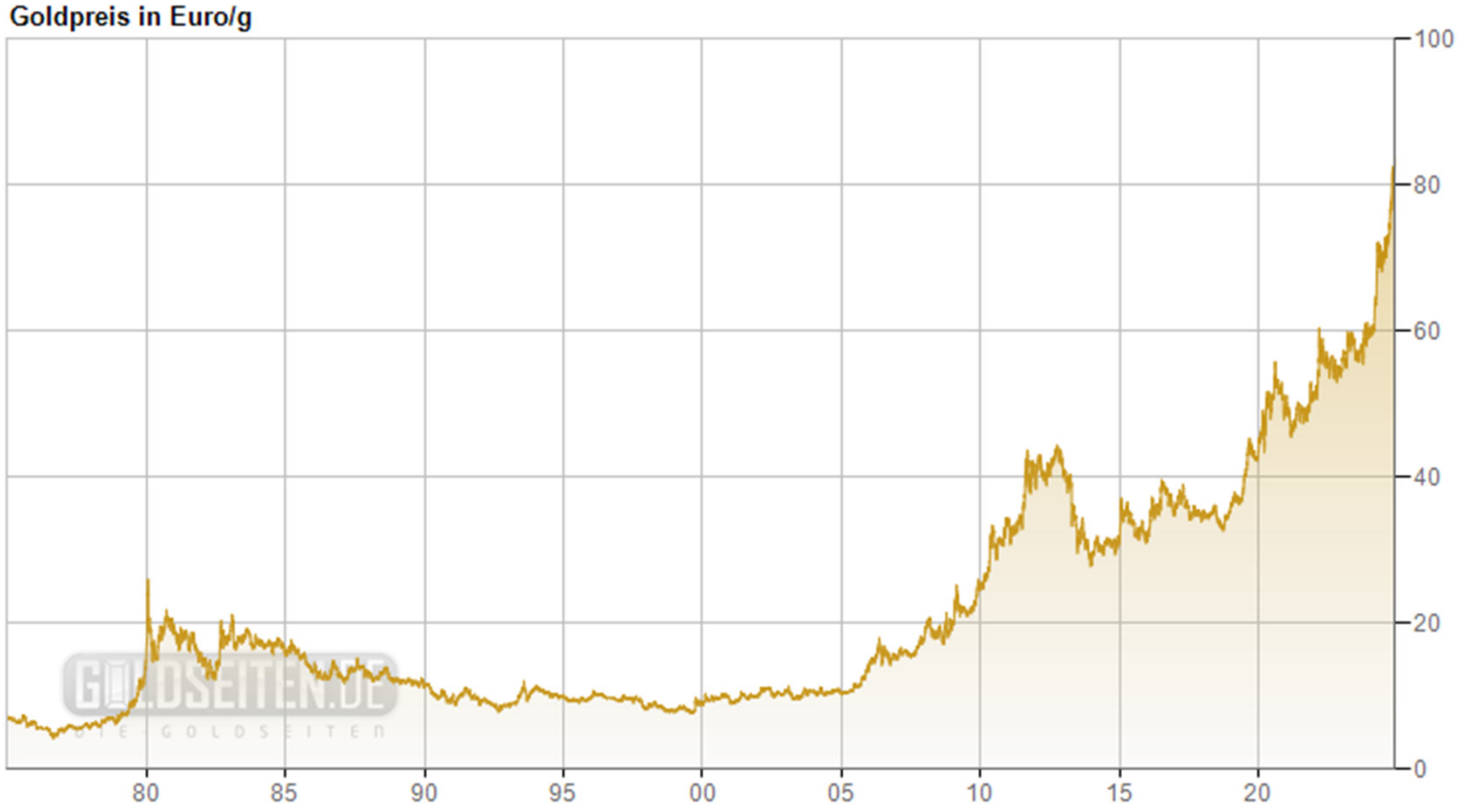
Edelmetallpreise – Rhodium



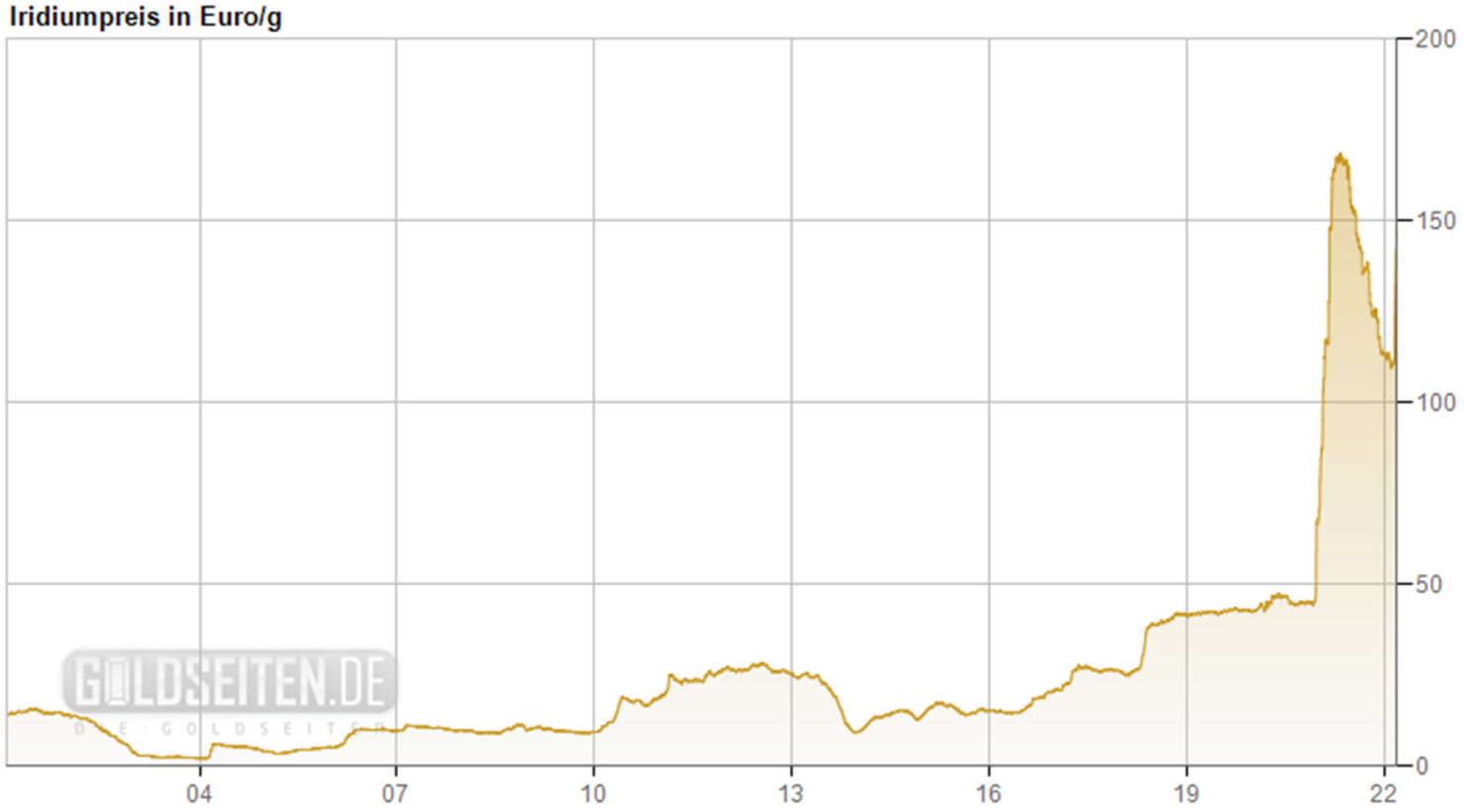
Edelmetallpreise – Platin



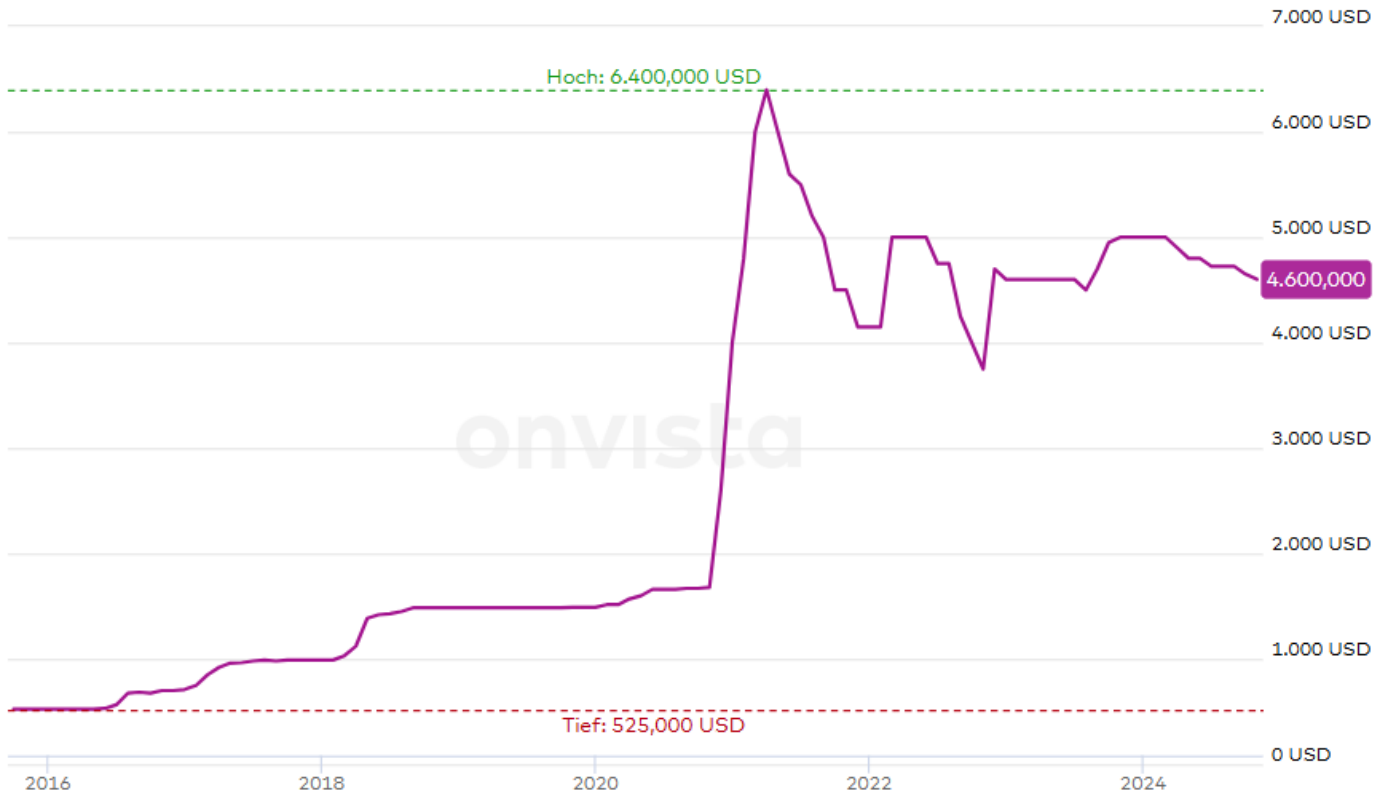
Edelmetallpreise – Gold



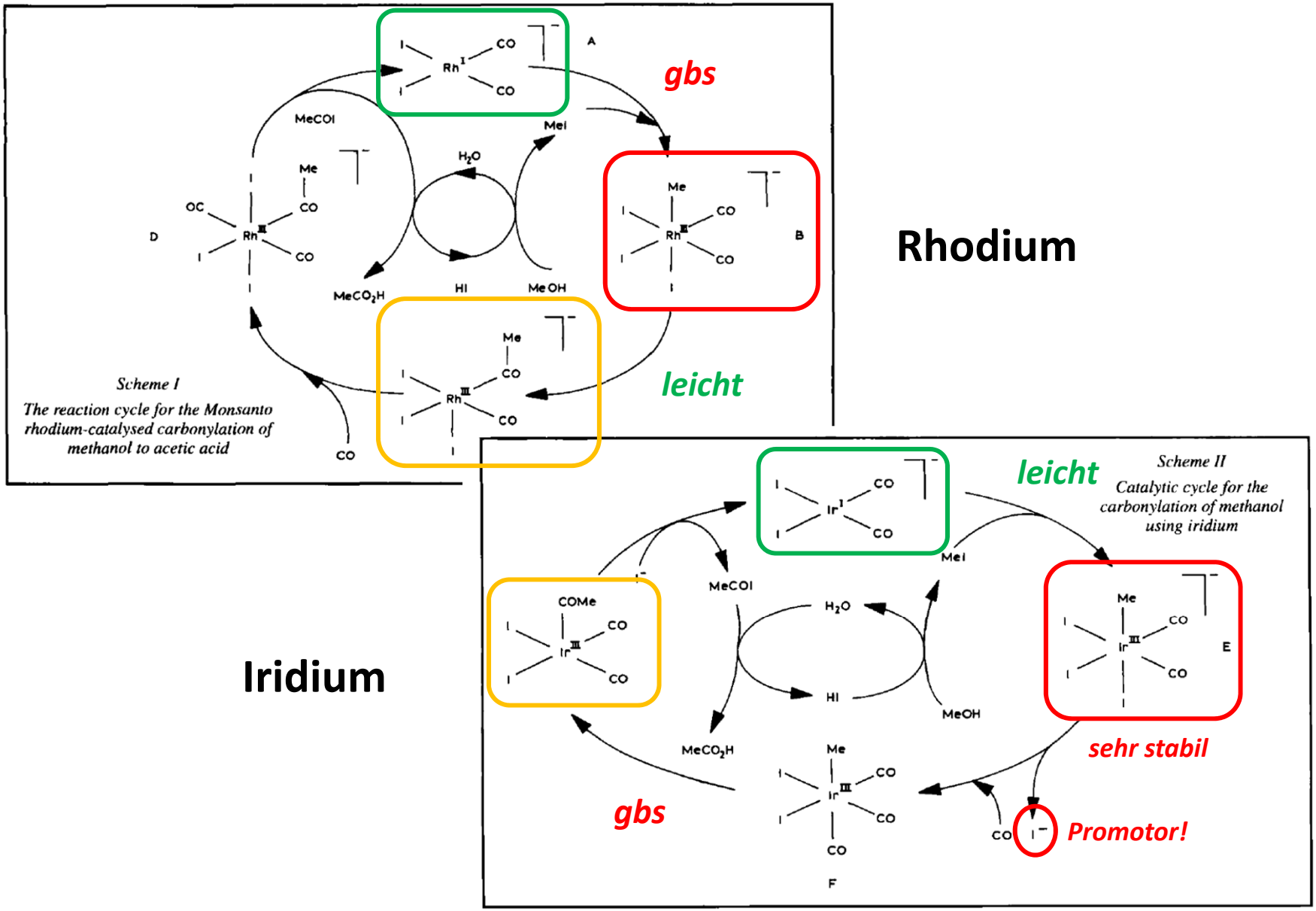
Edelmetallpreise – Iridium (bis 2022)



Edelmetallpreise – Iridium



heute:	**Rh:**	**141,93 €/g**	→	**14 604 €/mol**
	Ir:	**141,96 €/g**	→	**27 287 €/mol**
1990:	Rh:	142 €/g	→	14 600 €/mol
	Ir:	8 €/g	→	1 600 €/mol



[3] *Platinum Metals Rev.* **2000**, *44*, 94

Cativa-Prozess – Additive

Table II

Effect of Various Additives on the Rate for the Iridium-Catalysed Carbonylation of Methanol[a] from Batch Autoclave Data

Experimental run	Additive	Additive:iridium, molar ratio	Carbonylation rate, mol dm^{-3} h^{-1}
1	None	–	8.2
2	LiI	1:1	4.3
3	Bu_4NI	1:1	2.7
4	$Ru(CO)_4I_2$	5:1	21.6
5	$Os(CO)_4I_2$	5:1	18.6
6	$Re(CO)_5Cl$	5:1	9.7
7	$W(CO)_6$	5:1	9.0
8	ZnI_2	5:1	11.5
9	CdI_2	5:1	14.7
10	HgI_2	5:1	11.8
11	GaI_3	5:1	12.7
12	InI_3	5:1	14.8
13	$InI_3/Ru(CO)_4I_2$	5:1:1	19.4
14	$ZnI_2/Ru(CO)_4I_2$	5:1:1	13.1
15	$Ru(CO)_4I_2$	Control: no iridium[b]	0[c]

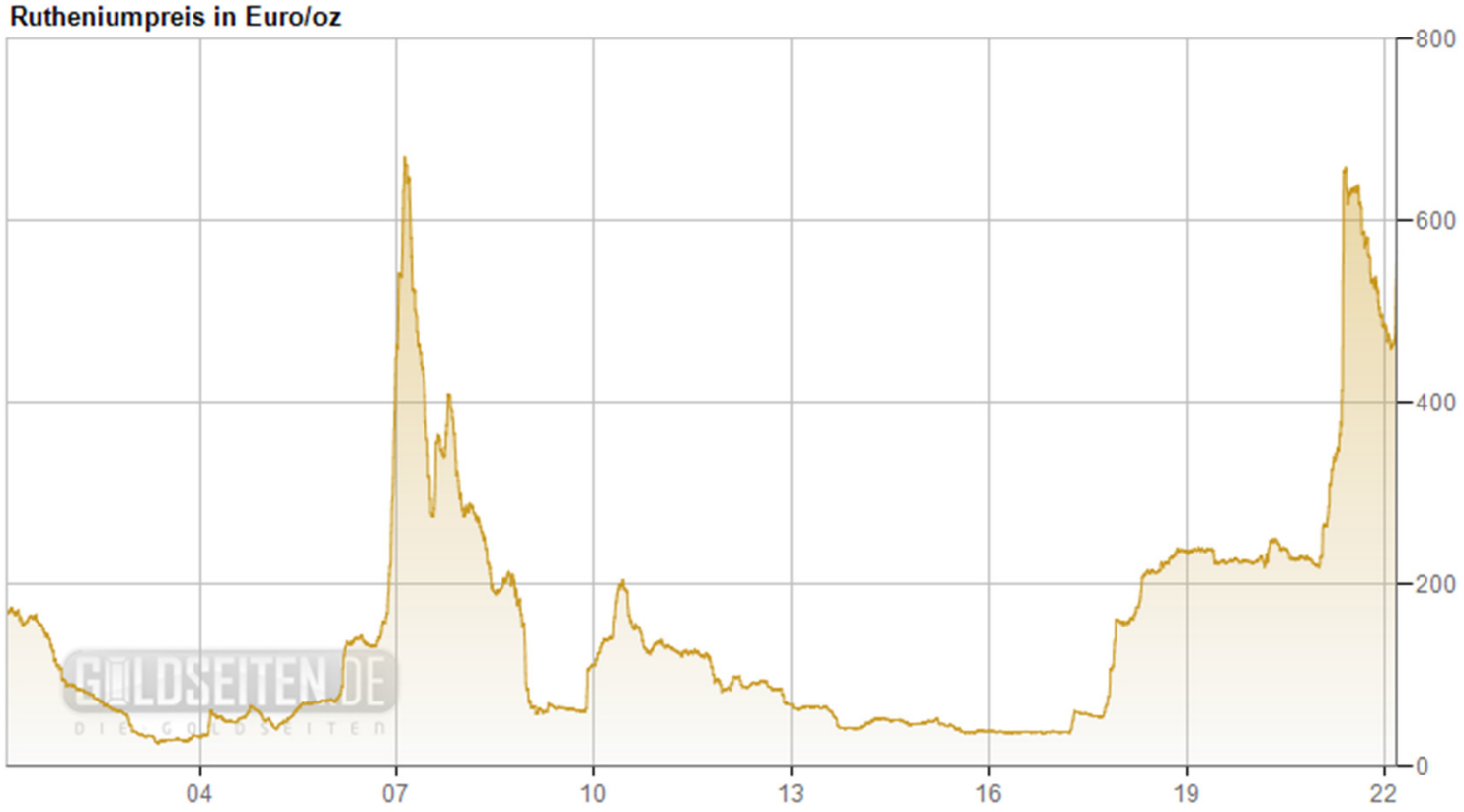
[a] *Reaction conditions: 190°C, 22 barg, and 1500 rpm. Autoclave charge: methyl acetate (648 mmol), water (943 mmol), acetic acid (1258 mmol), methyl iodide (62 mmol), and H_2IrCl_6 (1.56 mmol) plus additive as required. Carbonylation rate, in mol dm^{-3} h^{-1}, measured at 50 per cent conversion of methyl acetate.*

[b] *Control experiment conducted in the absence of iridium. Amount of the ruthenium complex used is the same as in run 4.*

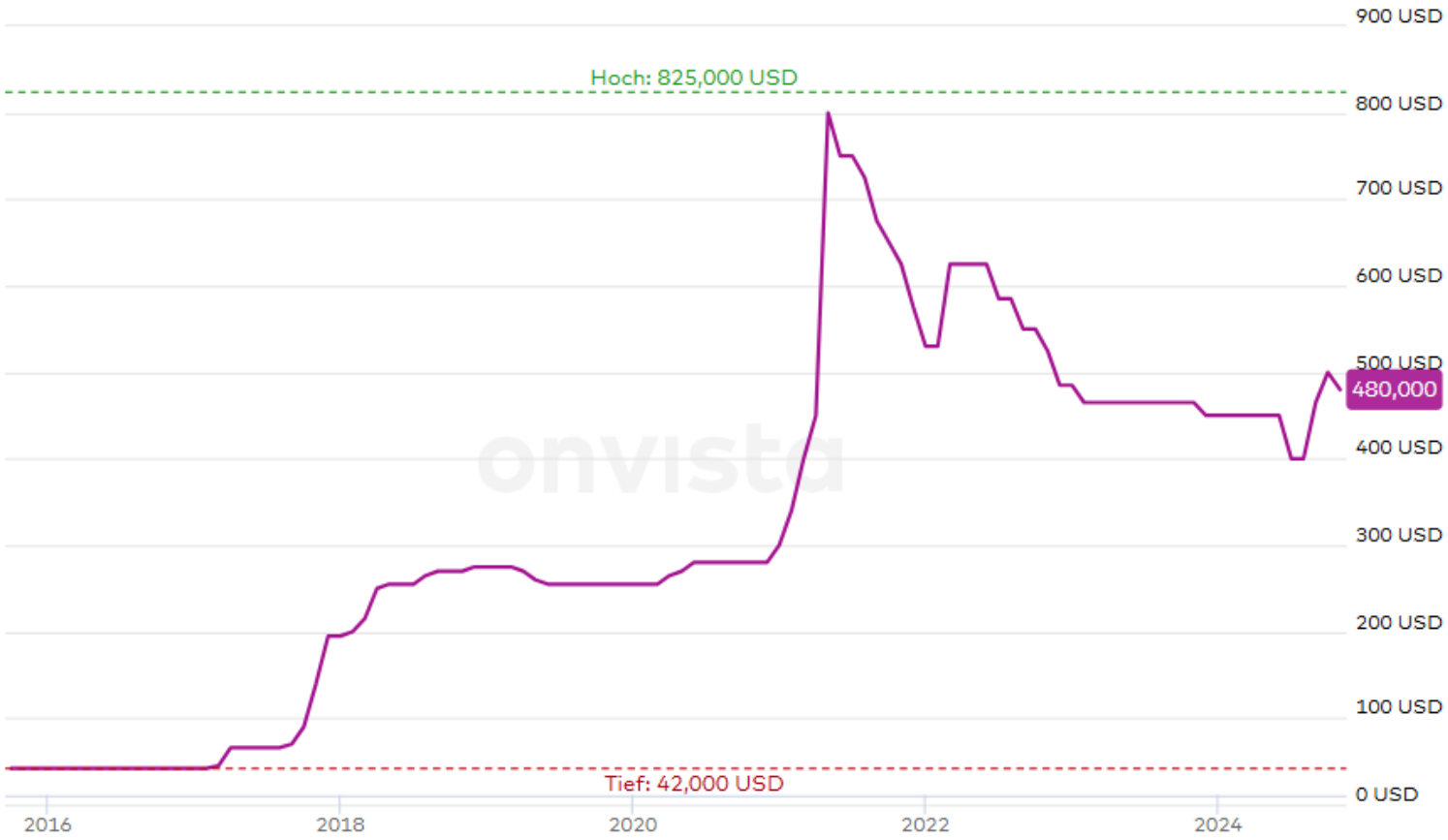
[c] *No CO uptake observed*

[3] *Platinum Metals Rev.* **2000**, *44*, 94

Edelmetallpreise – Ruthenium (bis 2022)

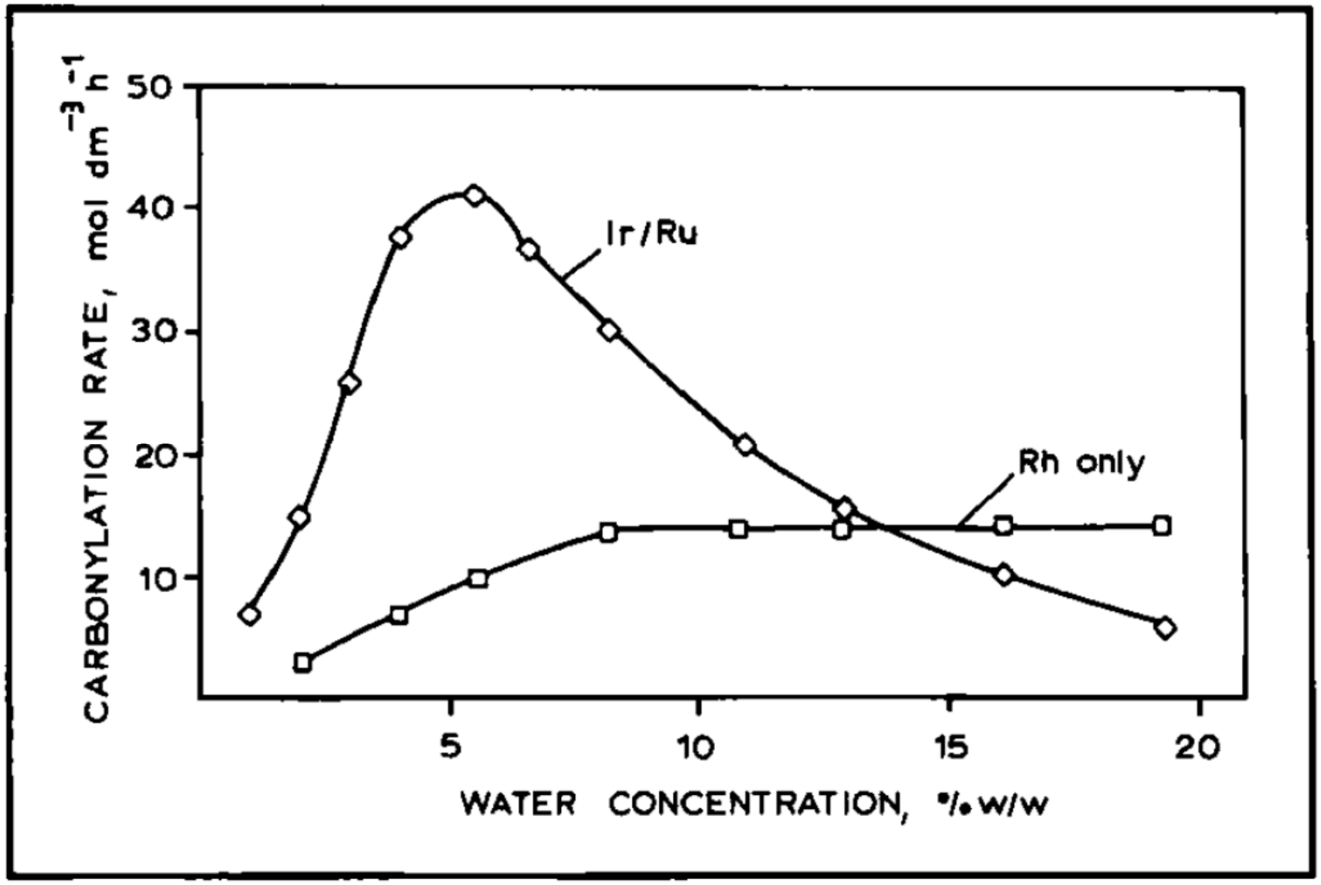


Edelmetallpreise – Ruthenium



Ru:	14,75 €/g	→	1 490 €/mol
Ir:	141,96 €/g	→	27 287 €/mol

Monsanto *vs.* Cativa



[3] *Platinum Metals Rev.* **2000**, *44*, 94

Vorteile des Cativa-Prozesses

- **geringere Wassermenge** („low-water conditions“, ca. 0.5 gew.-%)
  → weniger Wassergas-Shift-Reaktion (→ 94 % CO-Selektivität)
- **höhere Stabilität des Iridium-Katalysators**
  → weniger Metallabscheidung
- **bessere Löslichkeit der Iridiumkomplexe**
- mit Ru-Promotor **3-mal schneller als das Monsantoverfahren**
  → ca. 45 mol/(l · h) → bei einer 0.5 Mio-t-Anlage resultiert eine Reaktorgröße von 21 m^3
- **weniger Nebenprodukte** (v. a. Propionsäure und Acetaldehyd)
  → einfachere Aufarbeitung → **einfacherer Reaktor**

Monsanto-Prozess - Anlage

[3] *Platinum Metals Rev.* **2000**, *44*, 94

Monsanto-Prozess - Anlage

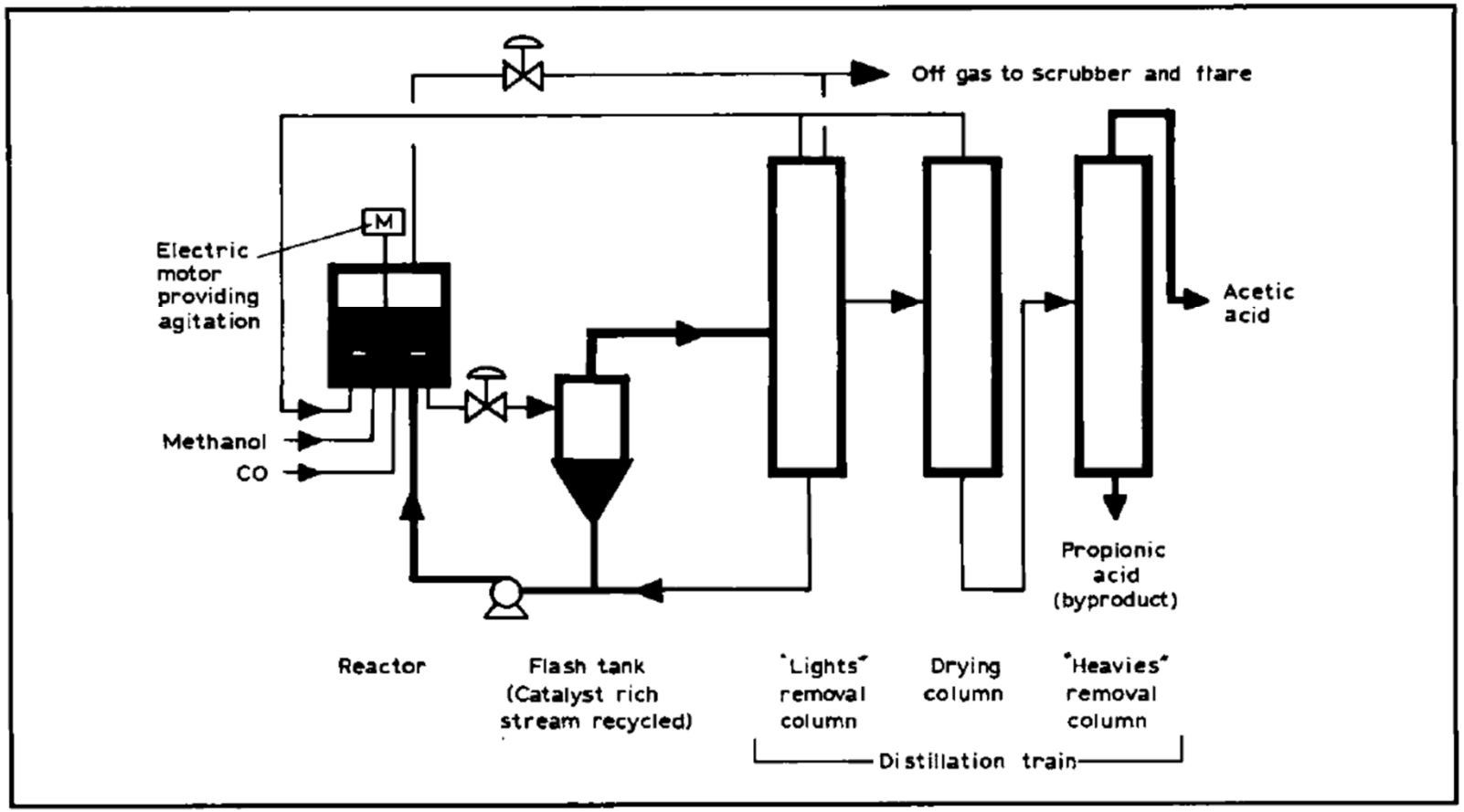


Fig. 2 The major units comprising a commercial-scale Monsanto methanol operating plant, which uses a rhodium-based catalyst. The technology uses three distillation columns to sequentially remove low boilers (methyl iodide and methyl acetate), water, and high boilers (propionic acid) and deliver high purity acetic acid product

[3] *Platinum Metals Rev.* **2000**, *44*, 94

Cativa-Prozess - Anlage

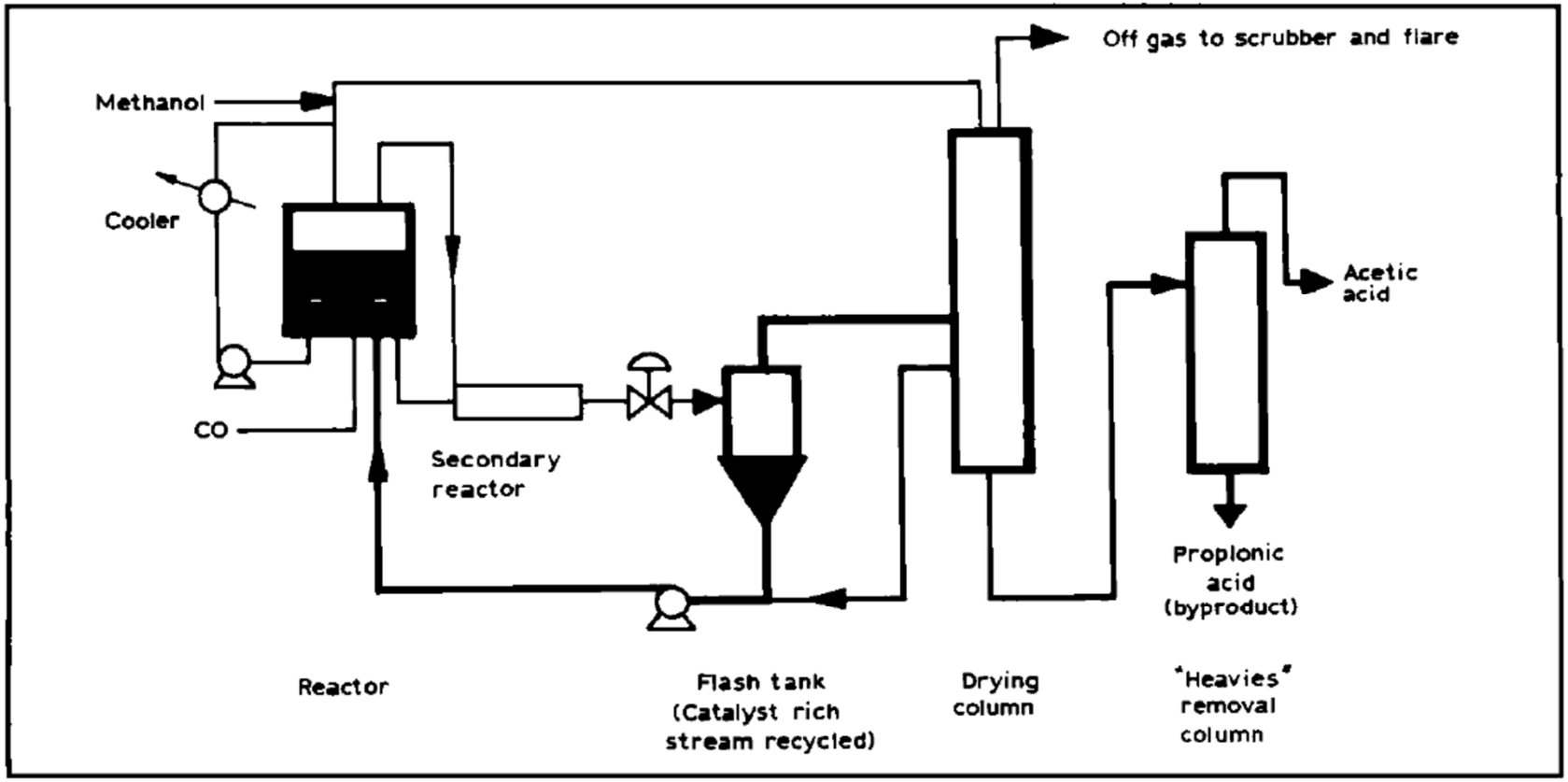


Fig. 6 Simplified process flowsheet for a commercial scale Cativa™ methanol carbonylation plant. The low boiler and water removal duties are combined into one, smaller, distillation column. The size of the high boiler removal column has also been reduced

[3] *Platinum Metals Rev.* **2000**, *44*, 94

Cativa-Anlagen
(bis 2003)

1995	Eastman (bis 2011 Sterling)	Texas City, USA	
1997	BP + Samsung	Ulsan, Südkorea	
1998	BP (heute Eastman)	Hull, UK	
1998	YARACO (BP + Sichuan Vinylon) (YARACO = Yangtze River Acetyls Co. Ltd)	Chongqing, China	200 000 t pro Jahr (150 000 t geplant)
1999	Eastman (bis 2011 Sterling)	Texas City, USA	
2000	BP + Petronas	Kertih, Malaysia	500 000 t pro Jahr
2003	YARACO (BP + Sichuan Vinylon) (YARACO = Yangtze River Acetyls Co. Ltd)	Chongqing, China	400 000 t pro Jahr

Cativa-Anlagen

BP + Samsung, Ulsan, Südkorea

Cativa-Anlagen

BP, Hull, UK

Cativa-Anlagen

1: Reaktor
2: Entfernung von MeOH, CO und H_2O

Cativa-Anlagen

BP + Petronas, Kertih, Malaysia

Cativa-Anlagen

However, the venture suffers from a frustrating **logistical handicap**: The **railroad track** from which YARACO can ship its products to various parts of China sits about **50 miles away from the plant site**. This is the one criteria that wasn't met on BP's list.

YARACO, Chongqing, China

„One is limited to walking or reading books for entertainment. **We get satellite TV but without the sound."**

A new highway has cut commuting time to the center of Chongqing from three hours to one hour though. The **commute was occasionally taking up to 10 hours** because of accidents blocking the flow of traffic.

Cativa-Anlagen

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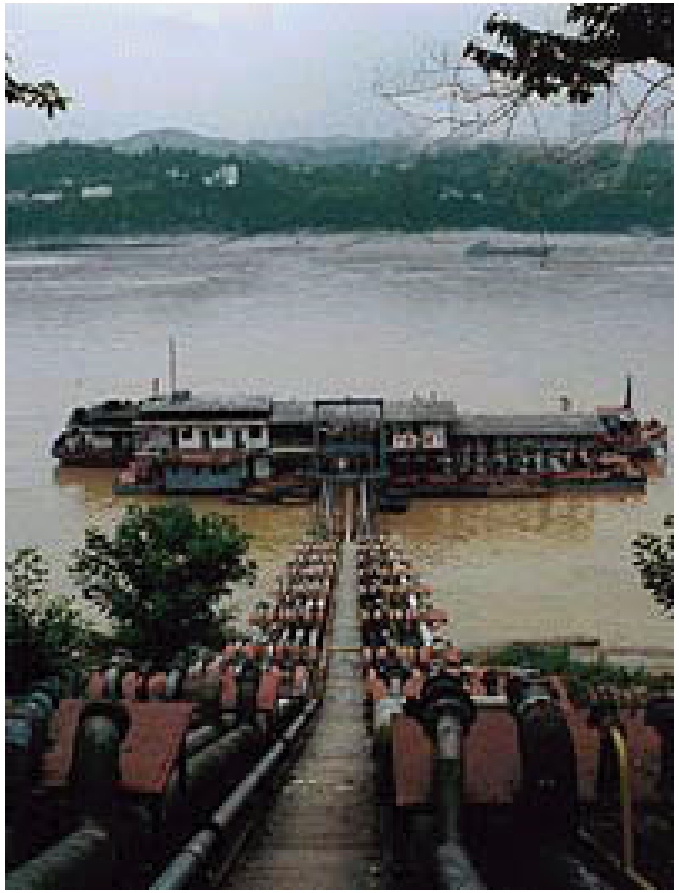

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Cativa-Anlagen

BP and ZPCC explore the creation of a world-scale acetic acid joint venture in China

Release date: 18 October 2019

Press release PDF / 85 KB

The proposed facility – in Zhoushan, Zhejiang Province – would deploy BP's CATIVA® XL technology to produce acetic acid, a versatile intermediate chemical used in a variety of products such as paints, adhesives and solvents. It is also used in the production of purified terephthalic acid (PTA) of which BP is a leading global manufacturer.

The potential new plant, which would be an addition to ZPCC's major integrated refining and petrochemical manufacturing complex at Zhoushan, would be BP's largest acetic acid producing site in the world.

BP and China's Zhejiang Petroleum and Chemical Corporation (ZPCC) have signed a memorandum of understanding (MOU) to explore the creation of a new equally-owned joint venture to build and operate a 1 million tonne per annum (tpa) acetic acid plant in eastern China.

Cativa-Anlagen

INEOS ÜBERNIMMT BP-GESCHÄFTSBEREICHE

1 min

2020

INEOS hat vereinbart, zusätzliche für BP nicht länger interess
globalen Geschäftsbereiche Aromatics und Acetyls von BP, di
bestehen.

INEOS-Gründer Sir Jim Ratcliffe sieht den fünf Milliarden Doll
bestehenden Produktionsanlagen passt. Im Rahmen des Absc
Präsenz von INEOS in Geel, Belgien, ausgeweitet. „Im Grun
petrochemischen Geschäfts", meint er.

Die BP-Anlage in Geel ist der wichtigste Produzent reiner Terephthalsäure in Europa. PTA, wie das Produkt abgekürzt heißt,
kommt bei der Herstellung von flexiblen PET-Trinkflaschen, Textilien, Folien, Kleidung aus Polyester sowie

Am 29. Juni 2020 übernahm Ineos das Petrochemie-Geschäft von BP für 5 Milliarden Dollar.

INEOS hat vereinbart, zusätzliche für BP nicht länger interessante Geschäftsbereiche zu übernehmen. Diesmal sind es die globalen Geschäftsbereiche Aromatics und Acetyls von BP, die aus 25 Anlagen und zehn führenden Joint Ventures weltweit bestehen.

INEOS-Gründer Sir Jim Ratcliffe sieht den fünf Milliarden Dollar-Deal als sinnvolle Investition für INEOS, die gut zu den bestehenden Produktionsanlagen passt. Im Rahmen des Abschlusses wird die Anlage in Hull wieder eingegliedert und die Präsenz von INEOS in Geel, Belgien, ausgeweitet. „Im Grunde ist dies die logische Weiterentwicklung unseres bestehenden petrochemischen Geschäfts", meint er.

Cativa-Anlagen

INEOS: Übernahme des globalen Aromatics & Acetyls-Geschäfts von BP abgeschlossen

Mittwoch, 6. Januar 2021 Köln

Cativa-Anlagen

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INEOS Acetyls Asia provides acetic acid and commercial services across the region. It is one of the largest acetic acid suppliers in Asia, with a strong reputation in the industry for following world-class standards of production and customer management.

We produce across five joint venture plants

Located in Mainland China, Taiwan, Malaysia and South Korea. We operate our production and commercial business on the principle of 'no accidents, no harm to people and no damage to the environment'.

Sites

- Yangtze River Acetyls Co. Ltd (YARACO): CHONGQING, CHINA
- INEOS YPC Acetyls Company (Nanjing) Ltd. (IYC): NANJING, CHINA
- Formosa INEOS Chemicals Corporation (FICC): MAILIAO, TAIWAN
- INEOS PCG Acetyls Sdn Bhd (IPASB): KERTIH, MALAYSIA
- Lotte INEOS Chemical (LIC): ULSAN, SOUTH KOREA