Synthesis of chromium(III) acetylacetonate – Protocol C

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$
$$CrCl_3 + 3(Hacac) + 3NH_3 \rightarrow [Cr(acac)_3] + 3NH_4Cl$$

Reaction. Weigh into a 100 mL Erlenmeyer flask 1.4 g (5 mmol) of chromium(III) chloride hexahydrate and dissolve it in 50 mL distilled water. Weigh out 6 g urea and add it in 3 or 4 portions to the deep green chromium solution, stirring well after each addition. Then add 3.5 mL (34 mmol) of acetylacetone (about 127% excess) dropwise, using a pipette. Clamp the flask in a boiling water bath and heat the mixture while stirring for approximately 1 hour. The solution should initially be very dark and almost black in appearance, but as the reaction proceeds, deep maroon plate-like crystals form as a crust on the surface of the reaction mixture.

Isolation. Cool the reaction mixture and vacuum-filter the product. Do not wash the product, dry it in air.

Purification. Not prescribed.

Safety. See hazards associated with the reagents in Table 1.

Greenness Assessment. The evaluation was performed using the Green Star (GS) and the results are shown in Figure 1.

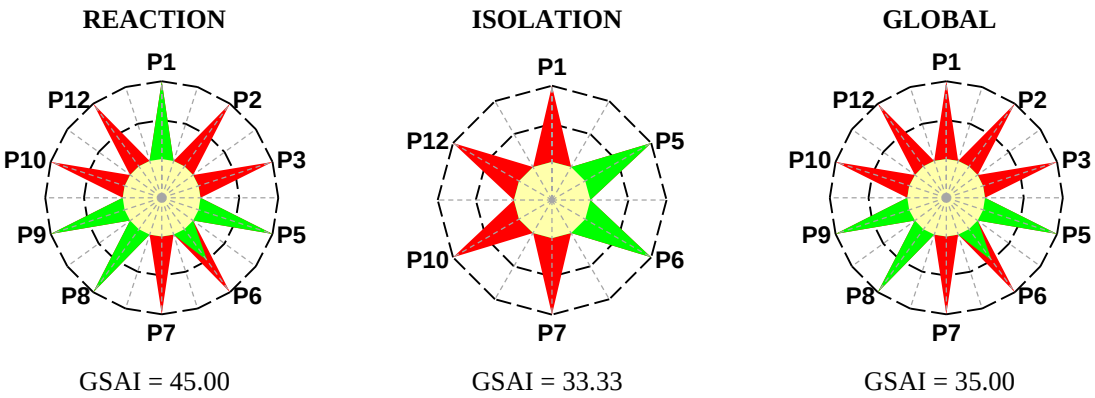

Figure 1. Greenness assessment (GS) for the synthesis of chromium(III) acetylacetonate

Construction of the GS

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

$$CrCl_3 + 3(Hacac) + 3NH_3 \rightarrow [Cr(acac)_3] + 3NH_4Cl$$

Table 1 presents the hazards and scores associated with the substances involved and Table 2 presents the scores used to construct the green stars.

Table 1. Hazards for the synthesis of chromium(III) acetylacetonate, protocol C[α]

Substances involved	Step			Hazard code	Score: hazards to...		
	R	I	Pu		HH	E	P
Stoichiometric reagents							
Acetylacetone[c] (CAS 123-54-6)	✓			H226, H302	2	1	2
Chromium(III) chloride hexahydrate (CAS 10060-12-5)	✓			H302	2	1	1
Auxiliary substances							
Solvents							
Water[a,b]	✓			-	1	1	1
Other auxiliary substances							
Urea (CAS 57-13-6)	✓			-	1	1	1
Product							
Chromium(III) acetylacetonate (21679-31-2)	✓	✓		H315, H319, H335	2	1	1
Waste							
Acetylacetone (excess)		✓		H226, H302	2	1	2
Ammonium chloride (aqueous solution)		✓		-	1	1	1
Ammonium hydroxide (excess, solution)		✓		H315, H318, H400	3	3	1
Carbon dioxide	✓			H280	1	1	2
Water[a,b]		✓		-	1	1	1

[α] R – Reaction; I – Isolation; Pu – Purification; HH – Human Health; E – Environment; P – Physical
[a] Renewable; [b] Degradable to innocuous products; [c] Degradable

Table 2. Scores used to construct the green star for the synthesis of chromium(III) acetylacetonate, protocol C[α]

Green Chemistry Principle	Reaction		Isolation		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	3	Carbon dioxide	1	Excess of ammonium hydroxide, H318, H400	1	Excess of ammonium hydroxide, H318, H400
P2 Atom Economy	1	Excess of acetylacetone and ammonium hydroxide > 10%, formation of by-products		NA	1	Excess of acetylacetone and ammonium hydroxide > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Excess of ammonium hydroxide, H318, H400		NA	1	Excess of ammonium hydroxide, H318, H400
P5 Safer solvents and auxiliary substances	3	Solvents and auxiliary substances are innocuous	3	Solvents and auxiliary substances are not used	3	Solvents and auxiliary substances are innocuous
P6 Increase energy efficiency	2	0 ºC ≤ T ≤ 100 ºC	3	Room temperature	2	0 ºC ≤ T ≤ 100 ºC
P7 Use renewable feedstocks	1	Substances not renewable	1	Substances not renewable	1	Substances not renewable
P8 Reduce derivatives	3	One stage		NA	3	One stage
P9 Catalysts	3	Without catalysts		NA	3	Without catalysts
P10 Design for degradation	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable
P12 Safer chemistry for accident prevention	1	Excess of ammonium hydroxide, H318	1	Excess of ammonium hydroxide, H318	1	Excess of ammonium hydroxide, H318

[α]s – Score; NA – Not applicable

References

Glidewell, C.; "Metal Acetylacetonate Complexes: Preparation and Characterization" in Woollins, J., Ed.; *Inorganic Experiments*, 2nd ed., Wiley-VCH, Weinheim, 2003; Exp. 3.16.