Synthesis of cobalt(III) acetylacetonate

$$2CoCO_3 + 6(Hacac) + H_2O_2 \rightarrow 2[Co(acac)_3] + 2CO_2 + 4H_2O$$

Greenness optimization

The greenest procedures for each step are $R_1^{1\text{-}6}$ for the reaction, $I_1^{1\text{-}3,6}$ and I_3^5 (showing different GS, but with the same GSAI) for the isolation, and Pu_1^1 or Pu_5^6 (showing the same GS) for the purification. Combining these procedures it is possible to obtain greener procedures than those of the original protocols.

In Table 1 are presented three combinations (1, 2 and 3) of procedures for the reaction, isolation and purification steps.

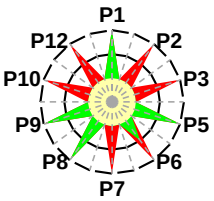
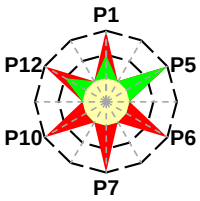
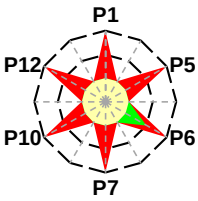
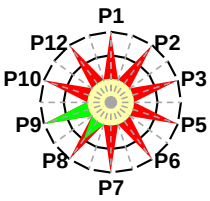
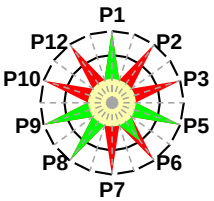
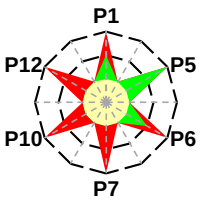
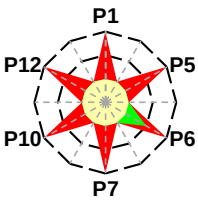
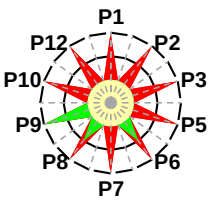
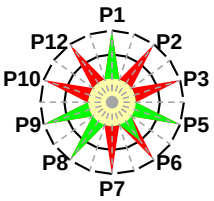
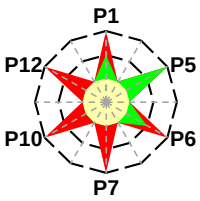
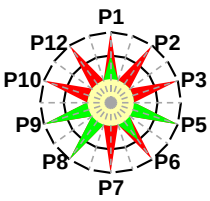
Combination 1 coincides with protocol A^1 (GSAI = 15.00).

Combination 2 is greener than combination 1 (GSAI = 20.00). Combination 2 uses procedure I_3 for isolation instead of I_1; as in this procedure principle P6 scores 2, equal to the respective scores for the other steps, the global score of this principle is not reduced.

Combination 3 is the greenest (GSAI = 40.00), because purification is not prescribed. This combination is greener than protocol C (GSAI = 35.00), where purification was, also, not prescribed.

Optimized protocols are described below.

Table 1. Green star obtained by combining the greenest procedures of each step

Combination	Reaction	Isolation	Purification	Global process
1 = Pr A	**R_1**  **GSAI = 45.00**	**I_1**  **GSAI = 33.33**	**Pu_1 or Pu_5**  **GSAI = 8.33**	 **GSAI = 15.00**
2	**R_1**  **GSAI = 45.00**	**I_3**  **GSAI = 33.33**	**Pu_1 or Pu_5**  **GSAI = 8.33**	 **GSAI = 20.00**
3	**R_1**  **GSAI = 45.00**	**I_3**  **GSAI = 33.33**	Without purification	 **GSAI = 40.00**

Optimized protocol 1

Reaction. Add 2.5 g (21 mmol) of cobalt(II) carbonate and 20 mL (194 mmol) of acetylacetone (about 208% excess) in a 100-mL flask. Heat the mixture to about 90 ºC, stirring and monitoring the temperature. Then add 30 mL (88 mmol) of 10% hydrogen peroxide solution (about 738% excess), dropwise (about 30 minutes). Cover the flask with a watch glass between additions. When all the hydrogen peroxide has been added, maintain the temperature and stirring for a further 30 minutes.

Isolation. Cool the solution in an ice-salt bath for 30 minutes. Filter the dark green product and dry it at 110 ºC.

Purification. Dissolve 300 mg of the product in hot toluene. Decant the dark solution using a glass funnel with a cotton plug. Heat the solution again and add petroleum ether. Cool first to room temperature and then cool it in an ice bath until the product crystallizes. Filter the product, wash it with cold petroleum ether and air dry it.

Optimized protocol 2

Reaction. Add 2.5 g (21 mmol) of cobalt(II) carbonate and 20 mL (194 mmol) of acetylacetone (about 208% excess) in a 100-mL flask. Heat the mixture to about 90 ºC, stirring and monitoring the temperature. Then add 30 mL (88 mmol) of 10% hydrogen peroxide solution (about 738% excess), dropwise (about 30 minutes). Cover the flask with a watch glass between additions. When all the hydrogen peroxide has been added, maintain the temperature and stirring for a further 30 minutes.

Isolation. The flask is chilled in an ice-salt bath and is vacuum filtered. The product is then washed with cold ethanol and then air-dried.

Purification. Dissolve 300 mg of the product in hot toluene. Decant the dark solution using a glass funnel with a cotton plug. Heat the solution again and add petroleum ether. Cool first to room temperature and then cool it in an ice bath until the product crystallizes. Filter the product, wash it with cold petroleum ether and air dry it.

Optimized protocol 3

Reaction. Add 2.5 g (21 mmol) of cobalt(II) carbonate and 20 mL (194 mmol) of acetylacetone (about 208% excess) in a 100-mL flask. Heat the mixture to about 90 ºC, stirring and monitoring the temperature. Then add 30 mL (88 mmol) of 10% hydrogen peroxide solution (about 738% excess), dropwise (about 30 minutes). Cover the flask with a watch glass between additions. When all the hydrogen peroxide has been added, maintain the temperature and stirring for a further 30 minutes.

Isolation. The flask is chilled in an ice-salt bath and is vacuum filtered. The product is then washed with cold ethanol and then air-dried.

Purification. Not prescribed.

References

(1) Faculdade de Ciências e Tecnologia da Universidade de Coimbra, *https://woc.**uc**.pt/**quimica**/getFile.do?tipo=2&id=1438* (accessed February 2011).

(2) University of Malaya, *http://www.kimia.um.edu.my/images/kimia/lab%20manual/level%202/Lab%20Manual%20Yr%202%20Inorganic.pdf* (accessed May 2011).

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

(4) Shalhoub, G.M. $Co(acac)_3$: Synthesis, Reactions and Spectra. *J. Chem. Educ.* **1980**, *57 (7)*, 525-526.

(5) Radboud University of Nijmegen, *www.orgchem.science.ru.nl/molmat/mm-web/srm4.doc* (accessed April 2011).
(6) Moeller, T. *et al*. *Inorganic Syntheses – Volume V*. McGraw-Hill Book Company, Inc: New York, 1957, pp. 188-189.