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Desymmetrization of a *meso*-diol complex derived from [Cr(CO)$_3$(η^6-5,8-naphthoquinone)]: use of new diamine acylation catalysts†

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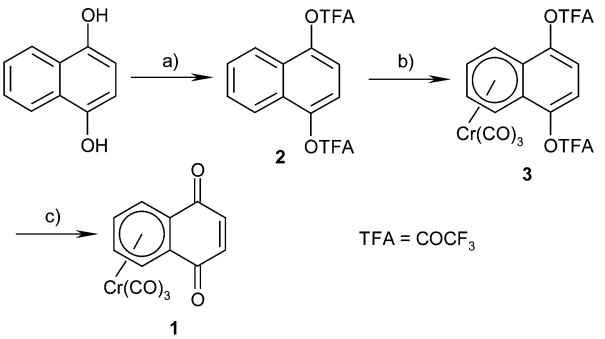
[Cr(CO)$_3$(naphthoquinone)] (1), prepared in a three-step sequence starting from 1,4-dihydroxynaphthalene, was reduced to the corresponding *meso*-dihydronaphthalene *syn*-diol complex and the latter was desymmetrized to give the mono-acyl complex with 99% ee *via* asymmetric acylation catalyzed by the two new and easily accessed chiral diamines 7 and 8.

Non-racemic planar chiral arene Cr(CO)$_3$ complexes increasingly find applications as chiral building blocks in highly diastereoselective transformations and as ligands in catalytic reactions.[1] Desymmetrization of *meso*-compounds is an elegant method for the preparation of highly enantiomerically enriched compounds and it has found wide application in organic synthesis.[2] Its application, with retention of metal coordination, to organometallic *meso* π-complexes is far less developed, however,[3] and access to planar chiral complexes has relied instead more on other asymmetric methodologies.

The present article focuses on the synthesis of the new complex [Cr(CO)$_3$(η^6-5,8-naphthoquinone)] (**1**) and its desymmetrization *via* a reduction–asymmetric acylation sequence. In the course of this work, we found a new efficient chiral diamine catalyst for the asymmetric acyl transfer reaction.

While **1** has not been previously reported, 6,7-dialkylated analogues have been obtained in low to moderate yield from a chromium carbene precursor *via* Dötz-benzannulation.[4] The synthesis of **1** by direct complexation of the free ligand in the presence of suitable Cr(CO)$_3$ sources is not feasible because of the sensitivity of Cr(0) complexes (*e.g.* [Cr(CO)$_6$], [Cr(CO)$_3$(CH$_3$CN)$_3$], [Cr(CO)$_3$(NH$_3$)$_3$], [Cr(CO)$_3$(naphthalene)]) to oxidation by the quinone. After some experimentation, we achieved the synthesis of **1** *via* the rt reaction of 1,4-bis(trifluoroacetoxy)naphthalene (**2**) with [Cr(CO)$_3$(NH$_3$)$_3$] in the presence of BF$_3$·Et$_2$O (3 equiv.) (Scheme 1).[5,6] Hydrolysis of the trifluroroacetate groups in **3** with triethylamine in the presence of silica,[7] followed by oxidation with 2,3-dichloro-5,6-dicyano-quinone (DDQ)[8] afforded **1** in good yield. On addition of DDQ, the orange solution of **3** turned instantly to deep violet, the colour of Cr(CO)$_3$(naphthoquinone) complexes.[4] The naphthoquinone complex **1** showed good stability towards oxidation and no special precautions were required for its purification by flash chromatography on silica.



a) $(CF_3CO)_2O$, Et_2O, rt, 2 days, 80%. b) [Cr(CO)$_3$(NH$_3$)$_3$], BF$_3$·Et$_2$O, Et$_2$O, rt, 5 days, 70%. c) 1) Silica, Et$_3$N, Et$_2$O, 0°C, 5 min; 2) DDQ, rt, 5 min, 82%.

Scheme 1 Synthesis of [Cr(CO)$_3$(5,8-naphthoquinone)] (**1**).

The structure of **1** was unambiguously determined by X-ray diffraction analysis‡ (Fig. 1).[9] The ring slippage parameter Δ[10] has a value of 0.044 Å toward the C(1)–C(6) bond. This shift is opposite to that found as a common feature in complexes of condensed arene ligands with group 6 metals.[1e,11]

Reduction of **1** under Luche's conditions[12] afforded the *cis*-diol **4** which was obtained in 82% yield as a single diastereoisomer (Scheme 2).[13] Attesting to the activation of the two carbonyl groups by the Cr(CO)$_3$ fragment, free naphthoquinone was not reduced under these conditions.[14]

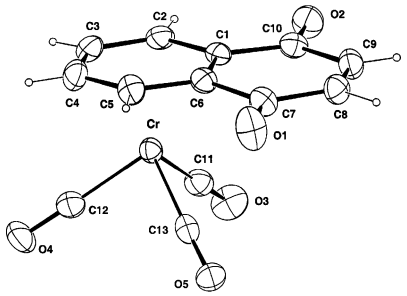
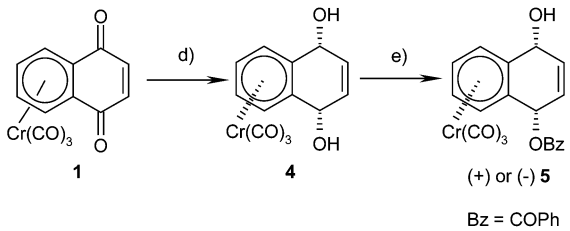
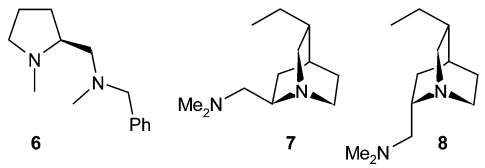


Fig. 1 ORTEP view of the crystal structure of **1**. Ellipsoids are represented at the 40% probability level.



d) NaBH$_4$, CeCl$_3$.7H$_2$O, MeOH, 0 °C, 5 min, 82%. e) BzCl 1.5 equiv, Et$_3$N 1 equiv, MS 4Å, CH_2Cl_2, diamine catalysts **6** - **8**.

Diamine catalysts:



Scheme 2 Reduction of **1** and efficient desymmetrization of the 5,8-dihydro-naphthalene-5,8-diol complex **4**.

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra for compounds **1–5**. See http://www.rsc.org/suppdata/cc/b4/b404006f/

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Table 1 Asymmetric benzoylations of *meso* complex **4** catalyzed by chiral diamines **6–8**

Entry	Diamine	Temp./time	Yield	ee[a] (enantiomer)
1	**6** (10 mol%)	−40 °C/22 h	71%	96% (−)
2	**6** (10 mol%)	−60 °C/23 h	74%	98% (−)
3	**7** (10 mol%)	−40 °C/23 h	80%	97% (+)
4	**8** (10 mol%)	−40 °C/21 h	89%	99% (−)
5	**8** (2 mol%)	−40 °C/23 h	83%	99% (−)

[a] The ee was determined by chiral HPLC (Chiralcel OJ). The absolute configuration has not yet been assigned.

For the desymmetrization of the *meso*-complex **4**, we focused on asymmetric acylation. Besides enzymatic methods for this transformation,[15] much progress has been recently made in this area using small molecule catalysts.[16] Impressed by the literature results, we first tested the (*S*)-proline-derived diamine **6**, a catalyst developped by Oriyama for the asymmetric acylation of 1,2-diols.[16e] Although being a 1,4-diol rather than a 1,2-diol, the reaction with **4** proceeded smoothly and provided the monobenzoate complex **5** with good isolated yields (71–74%) and good to excellent enantiomeric excess (96–98%) (Table 1, Entries 1–2). Small amounts (5–10%) of the very unstable dibenzoate complex were also formed in this reaction. (*R*)-proline, the starting material for *ent*-**6** is less accessible and we therefore looked for easily synthesized chiral diamines available in both enantiomeric forms that might provide efficient catalytic access to either (+)-**5** or (−)-**5**. We turned our attention to the two pseudo-enantiomeric quincorine- and quincoridine-derived diamines[17,18] **7** and **8**. Indeed, as shown in Table 1, the two diamines **7** and **8** outperformed catalyst **6** in the enantioselective monobenzoylation of **4**, and, as shown in entry 5, the amount of catalyst can be reduced to 2% without loss of asymmetric induction. Gratifyingly, the reaction stops after a first acyl transfer and no dibenzoate complex was formed.

In conclusion, the complex [$Cr(CO)_3$(η^6-5,8-naphthoquinone)] (**1**) will provide useful in synthesis. The reaction sequence reduction–desymmetrization gives access to new highly enantiomerically enriched planar chiral complexes that offer opportunities for further elaboration. Asymmetric Diels–Alder cycloadditions to **1** are another way to exploit the blocking of one face of the naphthoquinone and these reactions will receive attention. Finally, the new chiral diamines **7** and **8** hold much promise as readily accessible asymmetric acylation catalysts.

Notes and references

‡ CCDC 235092 (**1**). See http://www.rsc.org/suppdata/cc/b4/b404006f/ for crystallographic data in .cif or other electronic format.

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6 The bis-trifluoroacetate was chosen after finding the bis-acetate difficult to isolate and to handle.

7 Silica appears to act as a mild proton source during the reaction.

8 Preliminary studies with molecular oxygen as the oxidizing agent led to complex **1** with a lower yield (30–40%).

9 *Crystal data for* **1**‡: [$Cr(CO)_3(C_{10}H_6O_2)$], M = 294.2; triclinic, space group $P\bar{1}$, a = 7.1180(8), b = 7.6777(9), c = 10.9461(14) Å, α = 87.055(15), β = 73.479(14), γ = 86.175(14) °, V = 571.9(1) Å^3, Z = 2, d_x = 1.708 g·cm^{-3}, μ = 1.013 mm^{-1}, $T_{min,max}$ = 0.8447, 0.9436; T = 200 K, 7602 reflections collected, 2587 independent reflections (R_{int} = 0.041) of which 1788 were observables ($|Fo| > 4\sigma(Fo)$), R = 0.043, ωR = 0.041, S = 1.55(2).

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