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Synthesis of tricarbonyl(*N*-methylisatin)chromium(0) and an unanticipated transformation of a *N*-MEM to a *N*-MOM group

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Abstract

The synthesis of tricarbonyl(*N*-methylisatin)chromium(0) (**6**) was achieved by protection of the keto functionality of the ligand as an acetal followed by complexation with tricarbonyl(naphthalene)chromium(0) and subsequent deprotection with formic acid. In order to obtain a removable substituent at nitrogen, *N*-methoxyethoxymethyl (*N*-MEM) substituted isatin **12** was prepared. Upon acetalization with trimethylformiate in methanol under acidic reaction conditions the corresponding methoxymethyl (*N*-MOM) derivative was unexpectedly obtained. This substitution was highly accelerated by microwave irradiation. Complexation of the *N*-MEM and *N*-MOM substituted isatin afforded only poor yields. The addition of vinylmagnesium bromide at **6** takes place not only at the keto group but also at the lactam carbonyl group. Divinylation at either one of the carbonyl functions was also achieved with the product distribution being highly dependent on the reaction time.

Keywords: Chromium complexes; Isatin; MEM; MOM

1. Introduction

Arene tricarbonylchromium complexes with functionalized anellated rings deserve interest mainly for two reasons: the electron withdrawing tricarbonylchromium group, which in contrast to usual electron withdrawing arene substituents is easily removable, activates the anellated ring for nucleophilic attack. The steric shielding of one of the two arene faces facilitates stereoselective transformations as most reactions proceed by attack from the face opposite to the tricarbonylchromium group. In addition, some arene tricarbonylchromium complexes are planar chiral with the option of a transfer of the chiral information from the complex to the ligand [1–18]. We have studied the tricarbonylchromium complexes **1**–**5**, which bear anellated four- and five-membered carbocycles with one or more carbonyl functions, for some time. Compound **1** is reduced under exceptionally mild reaction conditions to the corresponding alcohol, which undergoes an anionic ring opening to the corresponding *ortho*-quinodimethane complex [19–22]. Compound **2** under equally mild reaction conditions undergoes alkenyllithium diaddition reactions followed by dianionic oxy-Cope rearrangements [23–26]. Complexes **3** and **4** of 1,2-indandione and 1,3-indandione also undergo nucleophilic attack from the face opposite to the tricarbonylchromium group [27,28]. In contrast to **2** and in contrast to uncoordinated 1,2-indandione the 1,2-indandione complex **3** so far did not undergo a dianionic oxy-Cope rearrangement, presumably because of the facile enolate formation [27]. Indantrione complex **5** undergoes hetero Diels–Alder cycloaddition at the central carbonyl group with attack of the diene from the face opposite to the tricarbonylchromium group [28].

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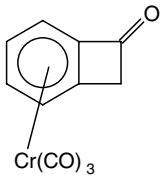

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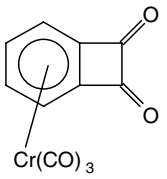

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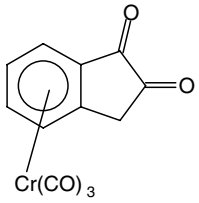

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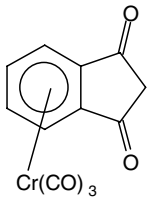

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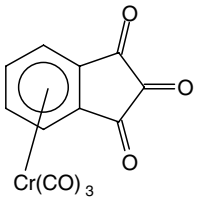
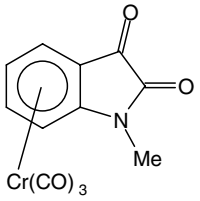


5

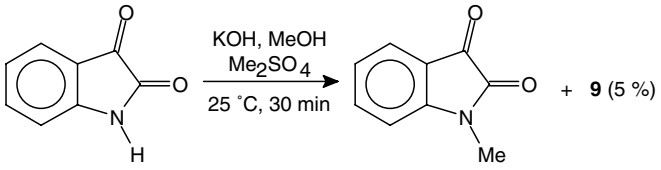
In order to avoid the enolate formation, we became interested in the synthesis of non-enolizable analogues of **3**, which might serve as substrates in these reactions. Isatin was regarded as a possible heterocyclic ligand, provided the acidic amide proton were replaced by a substituent. Here, we describe the synthesis of *rac*-tricarbonyl(*N*-methylisatin)chromium(0) (**6**) and some related complexes. In the course of our investigations we observed an unusual transformation of a methoxyethoxymethyl (MEM) group into a methoxymethyl (MOM) group.



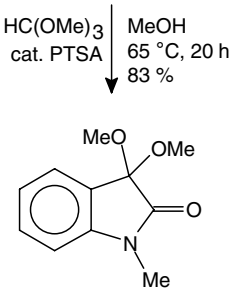
6

2. Results and discussion

For the synthesis of **6** we envisaged a route similar to those leading to complexes **1**–**5**, which made use of an acetal protection of the keto function. Therefore, isatin (**7**) was methylated by treatment with dimethyl sulfate under basic reaction conditions to give *N*-methylisatin (**8**) in 82% yield along with 5% of 3,3-dimethoxy-*N*-methylisatin (**9**) [29]. Subsequent acetalization of **8** with 2,2-dimethoxypropane in methanol with a catalytic amount of *para*-toluenesulfonic acid (PTSA) in methanol afforded **9** in 73% yield. The acetalization was improved by replacement of the 2,2-dimethoxypropane by trimethylorthoformiate giving a 83% yield of **9**.

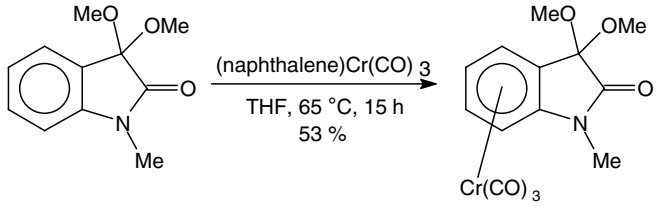


7 **8** (82 %)

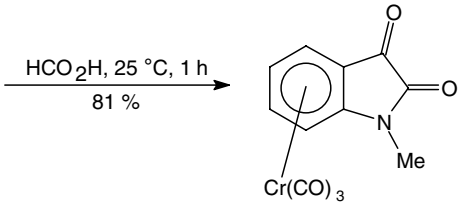


9

Complexation of **9** was achieved by the standard procedure with hexacarbonylchromium in boiling dibutyl ether/THF (10:1) over 20 h and gave complex *rac*-**10** in only 18% yield. Tricarbonyl(naphthalene)chromium(0) is a more reactive complexation reagent, which allows complexation reactions under much milder reaction conditions [30]. Complexation of the acetal **9** with this reagent afforded complex *rac*-**10** in 53% yield. For the following acetal hydrolysis we resorted to the protocol using formic acid, which had recently been successfully applied in the synthesis of tricarbonyl(1,2-indandione)chromium(0) (**3**) [27]. Treatment of *rac*-**10** with formic acid at 25 °C for 1 h afforded tricarbonyl(*N*-methylisatin)chromium(0) (*rac*-**6**) in 81% yield.



9 *rac*-**10**

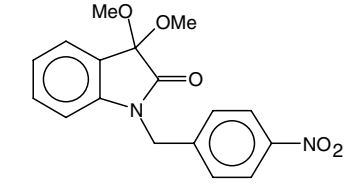


rac-**6**

In this context we note a recent report of Santra et al., who prepared the tricarbonylchromium complex of

5-chloroisatin by direct complexation with hexacarbonylchromium in decalin at 190 °C over 3 h [31]. This result is remarkable, because the ligand is unsubstituted at nitrogen and because temperatures as high as 190 °C usually cause – often autocatalytic – decomposition of (arene)tricarbonylchromium complexes [13]. Attempts to use this method for the preparation of *rac*-**6** or of the tricarbonylchromium complex of unsubstituted isatin failed in our hands and resulted in decomposed material only.

Having established a route to complex *rac*-**6** we became interested in systems allowing for a removal of the substituent at nitrogen [32]. In this context we first envisaged the attachment of a *para*-nitrobenzyl group with an electron poor aromatic system not prone for complexation at tricarbonylchromium. Acetal **11** was obtained by treatment of *N*-(*para*-nitrobenzyl)isatin [33] with trimethylorthoformiate and a catalytic amount of PTSA. Unfortunately, all attempts to obtain a tricarbonylchromium complex of **11** failed. Next, the MEM group was tried. Treatment of isatin (**7**) with methoxyethoxymethyl chloride (MEMCl) in the presence of ethyldiisopropylamine gave the MEM substituted isatin **12** in 83% yield. Acetalization with trimethylorthoformiate under standard conditions, however, unexpectedly resulted in a mixture of the MEM-substituted acetal **13** and the MOM-substituted derivative **14**.



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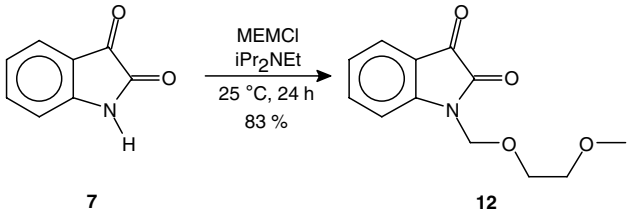
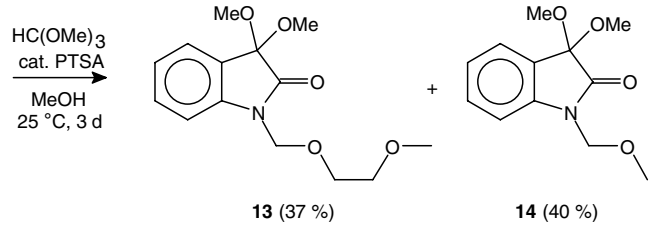
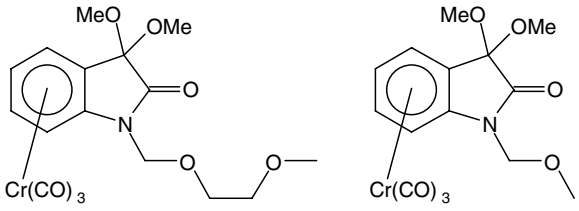


7 **12**



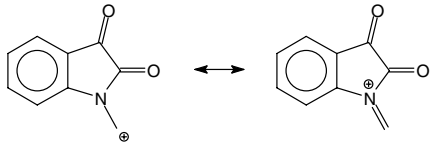
13 (37 %) **14** (40 %)

After chromatographic separation acetals **13** and **14** were coordinated at chromium by ligand exchange with tricarbonyl(naphthalene)chromium. Complexes *rac*-**15** and *rac*-**16**, were, however, formed only in poor yields of 19% and 15%, respectively. Although these yields caused this route to be abandoned at this point, the observation of the transformation of the MEM to the MOM substituent is unusual and deserves some comment.



rac-**15** (19 %) *rac*-**16** (15 %)

According to our knowledge a cleavage of a methoxyethoxymethyl group with formation of a methoxymethyl group has not been reported so far. Presumably the reaction proceeds via a protonation at the oxygen atom next to nitrogen followed by nucleophilic attack of the solvent methanol and dissociation of 2-methoxyethanol. This accounts for the reduced basicity of the lactam nitrogen atom in **12** as a consequence of its amide nature as compared to that in hemiaminals derived from amines. Assuming the S_N1 conditions given, the process might be facilitated by the intermediacy of an iminium ion like **17**. The key role of the solvent in the transformation is confirmed by a control experiment in ethanol under otherwise unchanged reaction conditions, which gave **18** and **19** in 28% and 43% yield, respectively. The inverse procedure, that is using triethylformiate in methanol, gave a mixture of **13** (38%), **14** (35%), **18** (5%), and **19** (4%).



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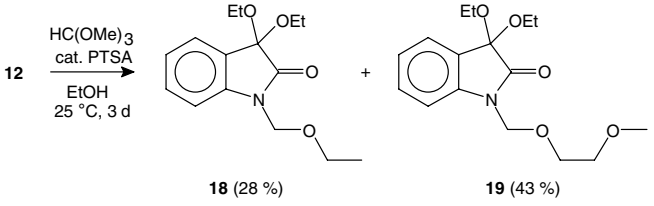


18 (28 %) **19** (43 %)

Interestingly, the reaction from **12** to **14** could be accelerated by microwave irradiation. While stirring the reaction mixture at 20 °C for 48 h resulted in **14** (40%) and

13 (37%), microwave irradiation (150 W, ramp time 2 min, then 5 min at 110 °C) resulted in a duplicated yield of **14** of 81%.

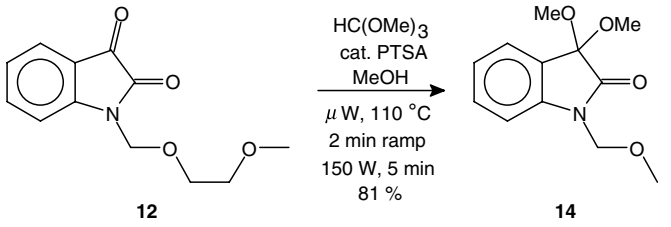
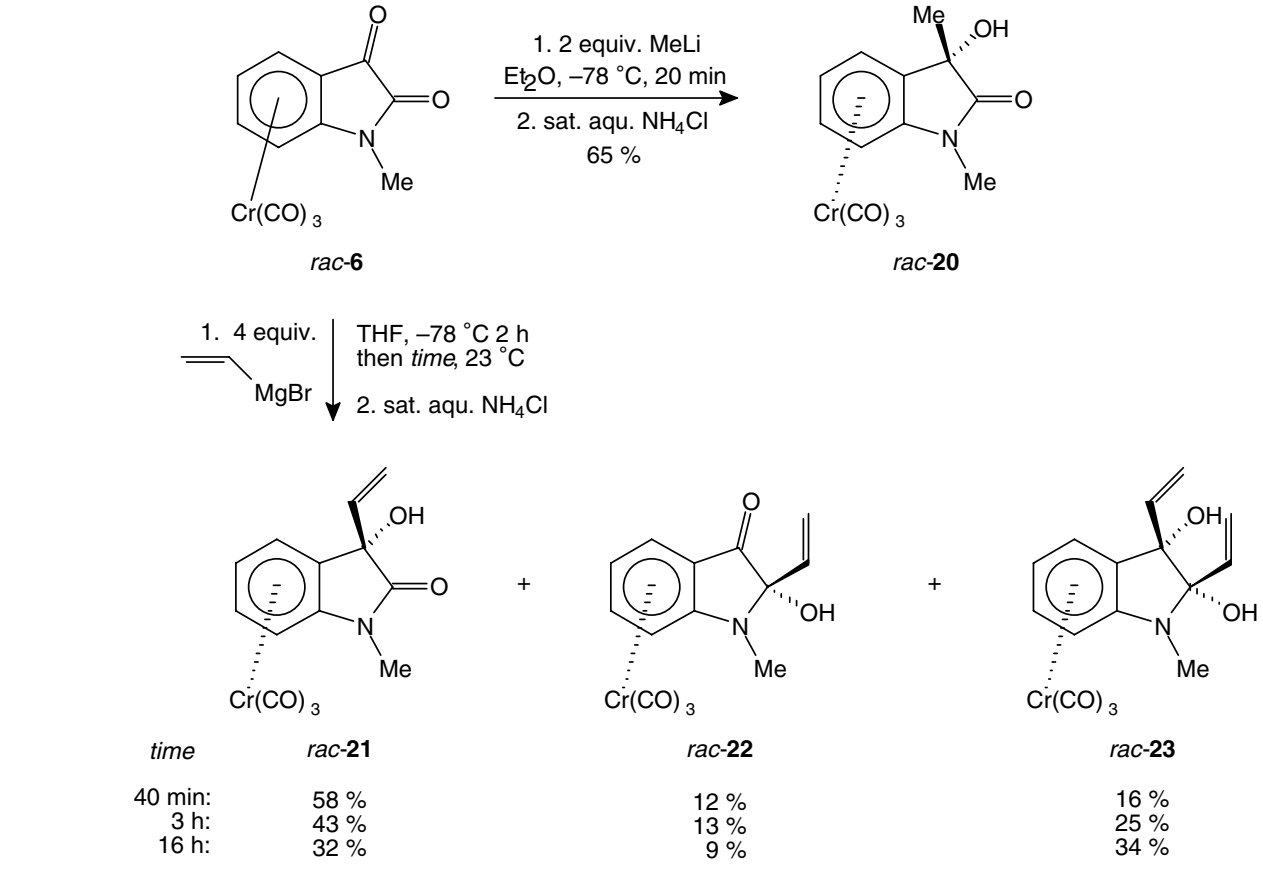


Table 1
Carbonyl IR absorptions of complexes

Compound	$\tilde{\nu}$ (Ketone)	$\tilde{\nu}$ (Lactam) (cm^{-1})
rac-**10**	–	1737
rac-**6**	1706	1737
rac-**15**	–	1744
rac-**16**	–	1739
rac-**20**	–	1712
rac-**21**	–	1724
rac-**22**	1697	–
rac-**23**		

Tricarbonyl(isatin)chromium(0) (*rac*-**6**) undergoes nucleophilic addition with organolithium and Grignard reagents. Treatment with methyllithium at −78 °C affords the methylated complex *rac*-**20** as a single diastereomer in 65% yield. In accord with all other nucleophilic additions at compounds **1**–**5** [10,12,34] we regard this as the *exo*-methyl diastereomer for obvious steric reasons. Next, addition of 4 equiv. of vinylmagnesium bromide was tried in order to obtain a diadduct prone for an anionic oxy-Cope rearrangement. The reaction resulted in a regioisomeric mixture of monoadducts *rac*-**21** and *rac*-**22** in 58% and 12% yield, respectively, along with 16% of divinyl adduct *rac*-**23**. Extending the reaction time to 6 h caused diadduct *rac*-**23** to become the main reaction product (34%). The formation of the lactam addition product *rac*-**22** and diadduct *rac*-**23** is remarkable, because nucleophilic addition at C-3 has to be considered much more likely as this is a keto group in conjugation to the electron withdrawing coordinated arene. Presumably the formation of *rac*-**22** and *rac*-**23** is the result of an activation of the lactam carbonyl function by the neighboring keto group and the presence of the electron withdrawing tricarbonylchromium group, which might attract the nitrogen lone electron pair to some extent. *rac*-**21**–*rac*-**23** were characterized on the basis of their spectroscopic data. In particular, a comparison of the carbonyl absorptions of the complexes clearly reveals the identity of *rac*-**22** by the diagnostic benzylic ketone absorption at 1697 cm^{-1} (Table 1). The assignment as *exo* adducts was made in analogy with related tricarbonyl(1,2-indandione)chromium(0) adducts [27].



3. Conclusion

In conclusion, we reported a route to the tricarbonylchromium complex of *N*-methylisatin and some related ligands. Nucleophilic addition occurs preferentially at the keto carbonyl group, although addition at the lactam carbonyl group is observed as a minor reaction path as well. Under the reaction conditions applied an unusual transformation of a *N*-MEM to a *N*-MOM substituent was observed, which was highly accelerated by microwave irradiation.

4. Experimental

4.1. General

See Ref. [26]; melting points were determined with a Büchi apparatus according to Dr. Tottoli without any correction. *tert*-Butylmethyl ether (TBME), cyclohexane, petroleum ether (PE), and tetrahydrofuran (THF) were distilled from sodium–potassium alloy/benzophenone. Dichloromethane was dried over P_4O_{10} and distilled under argon. Ethyl acetate (EA) was dried over $CaCl_2$ and distilled under argon. Reagents were purchased and used without further purification or prepared according to the literature procedures. In the ^{13}C NMR spectra, according to APT and DEPT measurements, + indicates methylene or quarternary carbon atoms, whereas − indicates methyl or methyne carbon atoms. Unless otherwise indicated, new compounds were obtained with >95% purity (^1H NMR). Microwave irradiation was performed with an instrument CEM Discover.

4.2. (3,3-Dimethoxy-N-methyl)indolin-2-one (**9**)

0.1 g of *para*-toluenesulfonic acid was added to 10.000 g (62.1 mmol) of *N*-methylisatin (**8**) in 100 mL of methanol and 40 mL of 2,2-dimethoxypropane. The mixture was heated at reflux for 20 h, after which the solvent was removed at reduced pressure. The remaining crude product was purified by column chromatography at silica gel (300 × 30 mm, PE/TBME 4:1) affording 9.384 g (45.3 mmol, 73%) of **9** as a colorless solid (m.p. 82 °C).

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3028 (w), 2940 (w), 2831 (w, –OCH_3), 1726 (s, C═O), 1612 (m, O═C–NR_2), 1494 (m), 1473 (m), 1047 (s, C–O), 745 (m). ^1H NMR (400.1 MHz, TMS, $CDCl_3$): $\delta = 3.16$ (s, 3H, *N*-CH_3), 3.57 (s, 6H, OCH_3), 6.83 (m, $^3J_{7,6} = 7.8$ Hz, 1H, arom. H), 7.09 (m, $^3J_{5,4} = 7.4$ Hz, 1H, arom. H), 7.36 (m, $^3J_{6,7} = 7.8$ Hz, $^4J_{6,4} = 1.3$ Hz, 1H, arom. H), 7.41 (m, $^3J_{4,5} = 7.4$ Hz, $^4J_{4,6} = 1.3$ Hz, 1H, arom. H). ^{13}C NMR (100.6 MHz, TMS, $CDCl_3$, APT): $\delta = 25.8$ (−, *N*-CH_3), 50.8 (−, OCH_3), 97.0 [+, $C(OCH_3)_2$], 108.8 (−, arom. CH), 122.7 (−, arom. CH), 124.7 (−, arom. CH), 124.9 (+, arom. C_q), 130.7 (−, arom. CH), 143.4 (+, arom. C_q), 170.7 (+, C═O). MS *m*/*z* (%) = 207 (96) [M^+], 192 (16) [M^+-CH_3], 176 (100) [M^+-OCH_3], 164(80) [M^+-CH_3-CO], 146 (76), 134 (84), 118 (52), 105 (92) [$M^+-C_4H_6O_3$], 91 (35) [$M^+-C_5H_3O_3$], 77 (68) [$M^+-C_5H_9NO_3$], 63 (28). Anal. Calc. for $C_{11}H_{13}NO_3$ (207.13): C, 63.76; H, 6.32; N, 6.76. Found: C, 64.18; H, 6.23; N, 6.65%.

4.3. rac-Tricarbonyl[(3,3-dimethoxy-N-methyl)indolin-2-one] chromium(0) (rac-**10**)

(a) 2.0 g (9.7 mmol) of **9** and 3.30 g (15.0 mmol) of hexacarbonylchromium in 100 mL of dibutyl ether and 10 mL of THF was heated at reflux for 20 h. After cooling to 25 °C the mixture was filtered through a frit, and the solvent I removed at reduced pressure. The remaining crude product was purified by column chromatography at silica gel (200 × 30 mm, PE/TBME 2:1, then TBME). 599 mg (1.75 mmol, 18%) of *rac*-**10** as a bright yellow solid (m.p. 157 °C, dec.).

(b) 2.0 g (9.7 mmol) of **9** and 2.64 g (10.0 mmol) of Tricarbonyl(naphthalene)chromium(0) in 50 mL THF was heated at reflux for 15 h. The remaining crude product was purified by column chromatography at silica gel (200 × 30 mm, PE/TBME 2:1, then TBME). 1.76 g (5.1 mmol, 53%) of *rac*-**10.**

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3094 (w), 2922 (w), 2841 (w), 1952 (s, CrCO), 1887 (s, CrCO), 1838 (s, CrCO), 1737 (s, C═O), 1549 (s), 1463 (m), 1431 (m), 1354 (m), 1321 (s), 1267 (m), 1224 (m), 1108 (m, C–O), 1057 (s, C–O), 1075 (m), 1056 (s), 1041 (s), 1017 (s), 999 (s), 964 (m), 939 (m), 821 (s), 743 (m), 660 (s), 631 (s), 617 (s). ^1H NMR (200 MHz, acetone-d_6): $\delta = 3.08$ (s, 3H, *N*-CH_3), 3.50 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 5.20 (m, $J = 6.3$ Hz, $J = 6.4$ Hz, $J = 0.8$ Hz, 1H, arom. H), 5.59 (m, $J = 6.5$ Hz, $J = 0.8$ Hz, $J = 0.4$ Hz, 1H, arom. H), 5.94 (m, $J = 6.4$ Hz, $J = 6.5$ Hz, $J = 1.0$ Hz, 1H, arom. H), 6.35 (m, $J = 6.3$ Hz, $J = 1.0$ Hz, $J = 0.4$ Hz, 1H, arom. H). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.04$ (s, 3H, *N*-CH_3), 3.54 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 4.90 (m, 1H, arom. H), 5.01 (m, 1H, arom. H), 5.54 (m, 1H, arom. H), 5.91 (m, 1H, arom. H). ^{13}C NMR (100.6 MHz, $CDCl_3$ APT): $\delta = 26.0$ (−, *N*-CH_3), 50.6 (−, OCH_3), 51.3 (−, OCH_3), 71.1 (−, arom. CH), 83.4 (−, arom. CH), 92.2 (−, arom. CH), 92.6 (−, arom. CH), 93.9 (+, arom. C_q), 96.5 (+, arom. C_q), 124.5 [−, $C(OCH_3)_2$], 168.9 (+, C═O), 231.7 (+, CrCO). MS (70 eV, 70 °C): *m*/*z* (%) = 345 (2) [M^++2], 344 (6) [M^++1], 343 (17) [M^+], 312 (4) [M^+-OCH_3], 287 (7) [M^+-2CO], 259 (22) [M^+-3CO], 244 (56), 214 (24), 207 (20) [$M^+-Cr(CO)_3$], 176 (19), 147 (100) [Isatin], 132 (24), 118 (90), 91 (31), 77 (24), 64 (7), 52 (16) [^{52}Cr]. Anal. Calc. for $C_{14}H_{13}CrNO_6$ (343.16): C, 48.99; H, 3.82; N, 4.08. Found: C, 48.61; H, 4.15; N, 3.84%.

4.4. Tricarbonyl(N-methylisatin)chromium(0) (rac-**6**)

100 mg (0.3 mmol) of *rac*-**10** in 5 mL of formic acid was stirred at 25 °C for 1 h. After addition of 50 mL of water the mixture was extracted three times with 20 mL of dichloromethane each. After drying over magnesium sulfate,

filtration through a frit and solvent removal at reduced pressure the remaining crude product was purified by column chromatography (150 × 15 mm, PE/TBME 1:1, then EA) to give 70 mg (0.2 mmol, 81%) of *rac*-**6** as a purple solid (m.p. 185 °C).

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3092 (w), 2932 (w), 1963 (s, CrCO), 1893 (s, CrCO), 1868 (s, CrCO), 1737 (s, C═O, lactam), 1706 (m, C═O, ketone), 1611 (m), 1540 (s), 1454 (s), 1432 (s), 1341 (s), 1305 (s), 1243 (m), 1105 (m, C–O), 1071 (m, C–O), 1056 (s), 1027 (m), 860 (m), 834 (m), 798 (m), 755 (m), 649 (s), 617 (s), 593 (s). ^{1}H NMR (200 MHz, acetone-d_6): $\delta = 3.19$ (s, 3H, *N*-CH_3), 5.53 (m,$J = 6.4$ Hz, $J = 6.5$ Hz, 1H, arom. H), 5.83 (m, $J = 6.7$ Hz, 1H, arom. H), 6.49 (m, $J = 6.5$ Hz, $J = 6.7$ Hz, $J = 0.8$ Hz, 1H, arom. H), 6.62 (m,$J = 6.4$ Hz, $J = 0.8$ Hz, 1H, arom. H). ^{13}C NMR (100.6 MHz, acetone-d_6, APT): $\delta = 25.6$ (−, CH_3), 75.1 (−, arom. CH), 77.7 (+, arom. C_q), 85.7 (−, arom. CH), 91.3 (−, arom. CH), 96.1 (−, arom. CH), 129.2 (+, arom. C_q), 157.8 (+, NC═O), 179.1 (+, NC*C*═O), 231.1 (+, CrCO). MS (70 eV, 80°C): *m*/*z* (%) = 299 (5) [M^++2], 298 (11) [M^++1], 297 (40) [M^+], 241 (10) [M^+−2CO], 213 (100) [M^+−3CO], 191 (3), 176 (13), 161 (21) [M^+−$Cr(CO)_3$], 133 (8), 105 (14), 104 (14), 78 (9), 77 (8), 65 (4), 52 (70) [$^{52}Cr^+$]. HRMS ($C_{12}H_7CrNO_5$): Calcd.: 296.9730; found: 296.9729.

4.5. 2,3-Dimethoxy-N-(para-nitrobenzyl)indolin-2-one (*11*)

(a) A suspension of 0.4984 g (1.8 mmol) of *N*-(*p*-nitrobenzyl)isatin (**10**) [33], 0.5 mL (4.6 mmol) of trimethylorthoformiate, and 0.734 g (0.1 mmol) of PTSA in 4 mL of methanol was heated at reflux till complete dissolution of all components. The mixture was stirred at 27 °C for 72 h, followed by addition of 5 mL of saturated aqueous $NaHCO_3$ and extraction with 3 × 2 mL of EA. The collected organic layers were washed twice with 5 mL of water and dried over K_2CO_3. After solvent removal at reduced pressure a yellow solid was obtained, which was purified by column chromatography at silica gel (80 × 25 mm, PE, PE/TBME 3:1, then TBME). 0.485 g (1.5 mmol, 84%) of **11** as a bright yellow solid (m.p. 120 °C).

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3084 (w), 2950 (w), 2833 (w, OCH_3), 1717 (s, C═O lactam), 1607 (m, C═O ketone), 1516 (m), 1488 (m), 1469 (m, NO_2), 1344 (m, NO_2), 1082 (s, C–O), 748 (m). ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 3.46$ (s, 6H, OCH_3), 5.04 (s, 2H, NCH_2), 7.01 (d, $J = 7.9$ Hz, 1H, arom. H), 7.11 (dt, $J = 7.6$ Hz, 0.6 Hz, 1H, arom. H), 7.36 (dt, $J = 7.8$ Hz, 1.2 Hz, 1H, arom. H), 7.49 (dd, $J = 7.4$ Hz, 0.7 Hz, 1H, arom. H), 7.55 + 8.23 (AA′BB′ line system, *p*-nitrophenyl H). ^{13}C NMR (100.6 MHz, BB, DMSO-d_6): $\delta = 41.9$ (NCH_2), 50.3 (OCH_3), 96.5 [$C(OCH_3)_2$], 109.8 (arom. CH), 122.8 (arom. CH), 123.9 (H*C*CNO_2), 124.3 (arom. C_q), 125.0 (arom. CH), 128.2 (H*C*CHCNO_2), 130.8 (arom. CH), 141.6 (arom. C_q), 143.7 (CNO_2), 147.0 (NCH_2C), 170.2 (C═O). MS (70 eV, 140 °C): *m*/*z* (%) = 328 (62) [M^+], 297 (72) [M^+−2CH_3−1], 253 (64) [M^+−2CH_3−NO_2], 223 (20), 192 (62) [M^+−$C_7H_6NO_2$], 164 (62), 132 (100) [M^+−2OCH_3−*p*-nitrobenzyl+2H]. HRMS $C_{17}H_{16}N_2O_5$: Calcd.: 328.1059; found: 328.1062.

4.6. N-(Methoxyethoxymethyl)isatin (*12*)

13 mL (114.8 mmol) of 1-(chloromethoxy)-2-methoxyethane was added dropwise at 0 °C to a solution of 8.000 g (54.4 mmol) of isatin in 50 mL of dichloromethane and 38 mL of ethyldiisopropylamine. After 15 min the solution was allowed to warm to 25 °C and was stirred for 24 h at this temperature. 50 mL of methanol was added to the red solution, which was stirred for another 10 min. After solvent removal at reduced pressure the obtained oil was dissolved in 25 mL of dichloromethane and washed twice with 10 mL of saturated aqueous NaCl. After drying of the collected organic layers and solvent removal at reduced pressure a red solid was obtained, which was purified by column chromatography at silica gel (200 × 40 mm, cyclohexane, cyclohexane/TBME 5:1, then TBME). 10.606 g (45.1 mmol, 83%) *N*-(2-methoxyethoxymethyl)isatin (**12**), bright orange solid (m.p. 66 °C).

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3061 (w), 2992 (w), 2882 (w, OCH_3), 1747 (s, C═O), 1635 (m), 1611 (s, O═C–NR_2), 1506 (m), 1473 (s), 1449 (m), 1065 (s, C–O–C), 752 (m). ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 3.21$ (s, 3H, CH_3), 3.46 + 3.68 [AA′BB′ line system, 2 × 2H, OCH_2CH_2O], 5.23 [s, 2H, NCH_2], 7.22 [dt, $J = 7.5$, 0.7 Hz, 1H, arom. H], 7.26 [d, $J = 8.0$ Hz, 1H, arom. H], 7.60 [d, $J = 7.5$ Hz, 1H, arom. H], 7.71 [dt, $J = 7.8$ Hz, 1.5 Hz, 1H, arom. H]. ^{13}C NMR (100.6 MHz, APT, acetone-d_6): $\delta = 77.9$ (CH_3), 88.3 (CH_2OCH_3), 90.3 (NCH_2), 91.5 ($CH_2CH_2OCH_3$), 131.7 (arom. CH), 137.8 (arom. C_q), 143.8 (arom. CH), 144.4 (arom. CH), 158.2 (arom. CH), 170.7 (arom. C_q), 178.3 (C═O), 203.1 (C-3). MS (70 eV, 80 °C): *m*/*z* (%) = 235 (56) [M^+], 146 (100) [M^+−$C_4H_9O_2$], 132 (53), 89 (97) [$CH_2OC_2H_4OCH_3$]. HRMS $C_{12}H_{13}NO_4$: Calcd.: 235.0845; found: 235.0847. MS (ESI) $C_{12}H_{13}NO_4$ [Na+ C_2H_3N]$^+$: Calcd.: 299.1008; found: 299.0997.

4.7. 3,3-Dimethoxy-N-(methoxyethoxymethyl)indolin-2-one (*13*) and 3,3-dimethoxy-N-(methoxymethyl)indolin-2-one (*14*)

A solution of 10.606 g (45.1 mmol) of **12** and 0.641 g (3.4 mmol) of *para*-toluenesulfonic acid in 75 mL of methanol and 15 mL (137.0 mmol) of trimethylorthoformiate was stirred for 48 h at 20 °C. After addition of 100 mL of saturated aqueous $NaHCO_3$ the mixture was extracted three times with 15 mL of EA each. The collected organic layers were washed twice with 550 mL of water each and dreid over K_2CO_3. After solvent removal at reduced pressure a brown solid was obtained, which was subjected to column chromatography (150 × 40 mm, cyclohexane/TBME 10:1, cyclohexane/TBME 3:1, then TBME/ethyl acetate 2:1). I: 5.075 g (21.4 mmol, 40%) of **14**, bright yellow solid (m.p. 53 °C). II: 4.738 g (16.9 mmol, 37%) of **13**, viscous red-brown oil.

Compound **13**: IR (ATR): $\tilde{\nu}/cm^{-1}$ 3058 (w), 2943 (w), 2834 (w, –OCH_3), 1734 (s, C=O), 1614 (m, O=C–NR_2), 1487 (m), 1468 (m), 1061 (s, C–O), 753 (m). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.33$ (s, 3H, CH_2OCH_3), 3.51 (m, $J = 4.6$ Hz, 2H, $CH_2CH_2OCH_3$), 3.55 [s, 6H, $C(OCH_3)_2$], 3.66 [m, $J = 4.6$ Hz, 2H, CH_2OCH_3], 5.18 [s, 2H, NCH_2], 7.08 (d, $J = 7.8$ Hz, 1H, arom. H), 7.14 (dt, $J = 7.6$ Hz, 0.8 Hz, 1H, arom. H), 7.26 (dt, $J = 7.8$ Hz, 1.3 Hz, 1H, arom. H), 7.41 (d, $J = 7.4$ Hz, 1H, arom. H). ^{13}C NMR (100.6 MHz, APT, $CDCl_3$): $\delta = 50.9$ [$C(OCH_3)$], 59.0 (CH_2OCH_3), 68.0 (CH_2OCH_3), 70.2 (NCH_2), 71.5 ($CH_2CH_2OCH_3$), 97.3 [$C(OCH_3)_2$], 110.5 (arom. CH), 123.3 (arom. CH), 124.6 (arom. C_q), 124.9 (arom. CH), 130.9 (arom. CH), 141.7 (arom. C_q), 171.3 (C=O). MS (70 eV, 25 °C): m/z (%) = 281 (69) [M^+], 250 (41) [M^+-CH_3O], 222 (19) [$M^+-C_3H_7O$], 206 (19) [$M^+-C_3H_7O_2$], 192 (100) [$M^+-C_4H_9O_2$], 179 (21) [$M^+-C_4H_9NO_2$], 146 (60) [$C_4H_9O_2-CH_3O-CH_3$], 132 (70). HRMS $C_{14}H_{19}NO_5$: Calcd.: 281.1262; found: 281.1263.

Compound **14**: IR (ATR): $\tilde{\nu}/cm^{-1}$ 3057 (w), 2942 (w), 2832 (w, –OCH_3), 1734 (s, C=O), 1613 (m, O=C–NR_2), 1487 (m), 1468 (m), 1060 (s, C–O), 752 (m). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.32$ (s, 3H, CH_2OCH_3), 3.56 [s, 6H, $C(OCH_3)_2$], 5.09 (s, 2H, NCH_2), 7.04 (d, $J = 7.8$ Hz, 1H, arom. H), 7.12 (dt, $J = 7.6$ Hz, 0.9 Hz, 1H, arom. H), 7.36 (dt, $J = 7.8$ Hz, 1.2 Hz, 1H, arom. H), 7.42 (d, $J = 7.3$ Hz, 1H, arom. H). ^{13}C NMR (100.6 MHz, APT, $CDCl_3$): $\delta = 51.0$ [$C(OCH_3)_2$], 56.4 (CH_2OCH_3), 71.2 (NCH_2), 97.4 [$C(OCH_3)_2$], 102.0 (arom. CH), 123.3 (arom. CH), 124.6 (arom. C_q), 125.0 (arom. CH), 130.9 (arom. CH), 141.7 (arom. C_q), 171.4 (C=O). MS (70 eV, 25 °C): m/z (%) = 237 (69) [M^+], 206 (57) [M^+-CH_3O], 192 (78) [$M^+-C_2H_5O$], 178 (91) [$M^+-C_2H_5NO$], 162 (79) [$M^+-C_2H_5NO_2$], 146 (73) [$M^+-C_2H_5O-CH_3O-CH_3$], 132 (100). MS (ESI) $C_{12}H_{15}NO_4$ [Na+H_3CCN]: Calcd.: 301.1164; found: 301.1170.

4.8. *rac*-Tricarbonyl[3,3-dimethoxy-N-(methoxyethoxymethyl)indolin-2-one]chromium(0) (*rac*-**15**)

1.000 g (3.6 mmol) of **13** and 0.932 g (4.4 mmol) of tricarbonyl(naphthalene)chromium(0) in 50 mL of THF was heated at reflux for 39 h. After cooling to 25 °C and filtration the solvent was removed at reduced pressure. The remaining material was purified by column chromatography (60 × 20 mm, PE, PE/TBME 4:1, then EA) giving 0.207 g (0.5 mmol, 15%) of *rac*-**15** as a dark orange, viscous oil.

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3088 (w), 2945 (w), 2836 (w, –OCH_3), 1963 (s, CrCO), 1877 (s, CrCO), 1744 (s, C=O), 1615 (s), 1551 (m), 1461 (m), 1348 (m), 1067 (s, C–O–C), 760 (m). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.37$ (s, 3H, CH_2OCH_3), 3.56 (s, 3H, C_qOCH_3), 3.65 (s, 3H, C_qOCH_3), 4.91 (t, $J = 6.0$ Hz, 1H, arom. H), 4.97 (d, $^2J = -11.7$ Hz, 1H, NCH_2), 5.08 (d, $^2J = -11.4$ Hz, 1H, NCH_2), 5.32 (d, $J = 6.0$ Hz, 1H, arom. H), 5.53 (t, $J = 6.0$ Hz, 1H, arom. H), 5.87 (d, $J = 5.8$ Hz, 1H, arom. H); signals for the CH_2CH_2 protons (3.5–3.8) could not be assigned because of signal overlap. –^{13}C NMR (100.6 MHz, APT, $CDCl_3$): $\delta = 50.5$ (C_qOCH_3), 51.3 (C_qOCH_3), 59.2 (CH_2OCH_3), 68.9 (CH_2OCH_3), 70.7 (NCH_2), 73.2 (C-7), 84.1 (C-6), 91.5 (C-5), 92.4 (C-4), 93.7 ($CH_2CH_2OCH_3$), 96.7 (C-3) 102.3 (C-3a), 122.4 (C-7a) 168.9 (C-2), 231.6 (CO). MS (70 eV, 140°C): m/z (%) = 416 (10), [M^+-1], 386 (8) [M^+-OCH_3-1], 253 (64), 317 (100), [$M^+-CH_3-(CO)_3-1$], 178 (31) [$M^+-C_4H_9NO_2-Cr(CO)_3-1$]. HRMS $C_{17}H_{19}CrNO_8$: Calcd.: 417.0515; found: 417.0516.

4.9. *rac*-Tricarbonyl[3,3-dimethoxy-N-(methoxymethyl)-indolin-2-one]chromium(0) (*rac*-**16**)

0.550 g (2.3 mmol) of **14** and 0.522 g (2.4 mmol) of tricarbonyl(naphthalene)chromium(0) in 20 mL of THF was heated at reflux for 40 h. After cooling to 25 °C and filtration the solvent was removed at reduced pressure. The remaining material was purified by column chromatography (50 × 20 mm, PE, PE/TBME 3:1, then EA) giving 0.164 g (0.4 mmol, 19%) of *rac*-**16** as an orange, viscous oil.

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3100 (w), 2945 (w), 2797 (w, –OCH_3), 1960 (s, CrCO), 1867 (s, CrCO), 1739 (s, C=O), 1614 (s), 1548 (m), 1458 (m, Aryl-C=C), 1347 (m), 1063 (s, C–O–C), 749 (m). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.36$ (s, 3H, CH_2OCH_3), 3.56 (s, 3H, C_qOCH_3), 3.66 (s, 3H, C_qOCH_3), 4.84 (d, $^2J = -11.2$ Hz, 1H, NCH_2), 4.90 (t, $J = 6.1$ Hz, 1H, 7-H), 5.02 (d, $^2J = -11.2$ Hz, 1H, NCH_2), 5.25 (d, $J = 6.3$ Hz, 1H, 4-H), 5.53 (t, $J = 6.1$ Hz, 1H, 6-H), 5.89 (d, $J_{H,H} = 6.1$ Hz, 1H, 5-H). ^{13}C NMR (100.6 MHz, APT, $CDCl_3$): $\delta = 50.6$ ($C_q\ _CH_3$), 51.3 ($C_q\ _CH_3$), 57.2 (CH_2OCH_3), 71.9 (NCH_2), 73.0 (C-4), 83.9 (C-7), 91.6 (C-5), 92.5 (C-6), 93.6 (C-3a), 96.7 (C-7a), 122.4 (C-3), 169.0 (C-2), 231.6 (CO). MS (70 eV, 90°C): m/z (%) = 373 (17) [M^+], 317 (13) [M^+-2CO], 289 (20) [M^+-3CO], 237 (44) [$M^+-Cr(CO)_3$], 206 (29) [$M^+-Cr(CO)_3-CH_3O$], 178 (100) [$M^+-Cr(CO)_3-C_2H_2NO$], 175 (19) [$M^+-Cr(CO)_3-2\times CH_3O$], 146 (58) [$M^+-Cr(CO)_3-CH_3O-CH_3-C_2H_2O$]. HRMS $C_{15}H_{15}CrNO_7$: Calcd.: 373.0255; found: 373.0254.

4.10. 3,3-Diethoxy-N-(ethoxymethyl)indolin-2-one (**18**) and 3,3-diethoxy-N-(methoxyethoxymethyl)indolin-2-one (**19**)

A solution of 2.026 g (8.6 mmol) of **12** and 0.139 g (0.7 mmol) of *para*-toluenesulfonic acid in 20 mL of ethanol and 3 mL (18.2 mmol) of trimethylorthoformiate was stirred for 48 h at 22 °C. After addition of 30 mL of saturated aqueous $NaHCO_3$ the mixture was extracted three times with 15 mL of ethyl acetate each. The collected organic layers were washed twice with 50 mL of water each and dried over K_2CO_3. After solvent removal at reduced pressure a brown solid was obtained, which was subjected to column chromatography (150 × 40 mm, cyclohexane/EE

100:1, cyclohexane/EE 50:1, then TBME). I: 0.675 g (2.4 mmol, 28%) of **18**, yellow oil. II: 1.153 g (3.7 mmol, 43%) of **19**, viscous orange oil.

Compound **18**: IR (ATR): $\tilde{\nu}/cm^{-1}$ 3057 (w), 2980 (w), 2836 (w, –OCH_3), 1736 (s, C=O), 1615 (m, O=C–NR_2), 1488 (m), 1469 (m), 1044 (s, C–O), 756 (m). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.16$ [t, $J = 7.0$ Hz, 3H, $CH_2OCH_2CH_3$], 1.23 [t, $J = 7.0$ Hz, 6H, $C(OCH_2CH_3)_2$], 3.53 [q, 2H, $J = 6.9$ Hz $CH_2OCH_2CH_3$], 3.68–3.84 [m, 2H, $C(OCH_2CH_3)_2$], 3.90–3.98 [m, 2H, $C(OCH_2CH_3)_2$], 5.13 [s, 2H, NCH_2] 7.06 [dd, $J = 7.8$ Hz, 3.4 Hz, 1H, arom. H], 7.11 [dt, $J = 7.5$ Hz, 2.2 Hz, 1H, arom. H] 7.34 (dt, $J = 7.8$ Hz, 0.8 Hz, 1H, arom. H), 7.42 (d, $J = 7.2$ Hz, 1H, arom. H). ^{13}C NMR (100.6 MHz, APT, $CDCl_3$): $\delta = 15.0$ ($CH_2OCH_2CH_3$), 15.4 [$C(OCH_2CH_3)_2$], 59.0 [$C(OCH_2CH_3)_2$], 64.4 ($CH_2OCH_2CH_3$), 69.8 (NCH_2), 97.3 [$C(OCH_2CH_3)_2$], 110.4 (arom. CH), 123.2 (arom. CH), 124.9 (arom. CH), 125.4 (arom C_q), 130.7 (arom. CH), 141.8 (arom C_q), 171.7 (C=O). MS (70 eV): m/z (%) = 279 (24) [M^+], 265 (24), 251 (14), 234 (23), 220 (31), 206 (48), 192 (52), 175 (26), 160 (25), 148 (48), 146 (100) [$M^+-2C_2H_5O-C_2H_5$] 132 (63), 104 (13), 90 (41). LC–MS (ESI+) $C_{12}H_{15}NO_4$ [Na+C_2H_3N]: Calcd.: 343.1636; found: 343.1634. HRMS $C_{15}H_{21}NO_4$: Calcd.: 279.1471; found: 279.1471.

Compound **19**: IR (ATR): $\tilde{\nu}/cm^{-1}$ 3058 (w), 2930 (w), 2832 (w, –OCH_3), 1736 (s, C=O), 1614 (m, O=C–NR_2), 1488 (m), 1468 (m), 1062 (s, C–O), 757 (m). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.23$ [t, $J = 7.0$ Hz, 6H, $C(OCH_2CH_3)_2$]3.34 (s, 3H, CH_2OCH_3), 3.46 (m, $J = 4.6$ Hz, 2H, NCH_2OCH_2), 3.64 (m, $J = 4.6$ Hz, 2H, CH_2OCH_3), 3.76–3.83 (m, 2H, OCH_2CH_3), 3.90–3.98 (m, 2H, OCH_2CH_3), 5.19 (s, 2H, NCH_2), 7.35 (dt, $J = 7.8$ Hz, 4.6 Hz, 1H, arom. H), 7.42 (d, $J = 7.5$ Hz, 1H, arom. H); two signals for arom. h between 7.06 and 7.13 cannot be assigned due to signal overlap. ^{13}C NMR (100.6 MHz, APT, $CDCl_3$): $\delta = 15.4$ (OCH_2CH_3), 59.0 (OCH_3), 59.1 (OCH_2CH_3), 68.0 (NCH_2OCH_2), 70.3 (NCH_2), 71.5 (CH_2OCH_3), 97.3 [$C(OCH_2CH_3)_2$], 110.5 (arom. CH), 123.3 (arom. CH), 124.9 (arom. CH), 125.4 (arom. C_q), 130.7 (arom. CH), 141.6 (arom. C_q), 171.8 (C=O). MS (70 eV): m/z (%) = 309 (14) [M^+], 295 (17), 281 (13), 264 (17), 220 (23), 192 (75), 162 (18), 148 (48), 132 (70), 119 (30) [$M^+-C(C_2H_5O)_2-C_4H_9O_2+1$], 104 (13), 90 (30). LC–MS (ESI+) $C_{16}H_{23}NO_5$ [Na]: Calcd.: 332.1479; found: 332.1474. HRMS $C_{16}H_{23}NO_5$: Calcd.: 309.1573; found: 309.1576.

*4.11. rac-Tricarbonyl[endo-3-hydroxy-exo-3-methyl-N-methylindolin-2-one]chromium(0) (rac-**20**)*

At −78 °C, 1 mL (1.6 mmol) of 1.6 M methyllithium in diethyl ether was added to 150 mg (0.51 mmol) of *rac*-**6**. After stirring for 20 min at −78 °C, 10 mL of saturated aqueous NH_4Cl was added, and the mixture was allowed to warm to 25 °C. The layers were separated, and the aqueous layer was extracted three times with 30 mL of TBME each. After drying over $MgSO_4$ and solvent removal at reduced pressure the remaining material was purified by column chromatography at alumina (150 × 15 mm, TBME, then methanol) affording 105 mg (0.3 mmol, 65%) of *rac*-**20** as a yellow solid [m.p. 117 °C, *de* > 95% (NMR)].

IR (ATR): $\tilde{\nu}/cm^{-1}$ 3342 (m, OH), 3102 (w), 2965 (w), 2923 (w), 2871 (w), 1954 (s, CrCO), 1867 (s, CrCO), 1712 (s, C=O), 1613 (m), 1556 (m), 1460 (m), 1423 (m), 1355 (s), 1312 (m), 1215 (s), 1149 (S, C–O), 1096 (s, C–O), 1074 (m), 1024 (m), 825 (m), 750 (m). ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 1.61$ (s, 3H, C_qCH_3), 3.08 (s, 3H, NCH_3), 5.14 (m, $^3J_{5,4} = 6.3$ Hz, 1H, 5-H), 5.22 (s, 1H, OH), 5.56 (m, $^3J_{7,6} = 6.4$ Hz, 1H, 7-H), 5.86 (m, $^3J_{6,7} = 6.4$ Hz, 1H, 6-H), 6.19 (m,$^3J_{4,5} = 6.3$ Hz, 1H, 4-H). ^{13}C NMR (100.6 MHz, acetone-d_6, APT/HMQC): $\delta = 25.9$ (−, C-9), 26.0 (−, C-8), 72.8 (+, C-3), 73.6 (−, C-7), 85.1 (−, C-5), 92.4 (−, C-4), 95.3 (−, C-6), 103.2 (+, C-3a), 127.1 (+, C-7a), 178.0 (+, C-2), 233.9 (+, CrCO). MS (70 eV): m/z (%) = 313 (58) [M^+], 257 (23) [M^+-2CO], 229 (71) [M^+-3CO], 211 (100) [$M^+--3CO-H_2O$], 177 (23) [$M^+-Cr(CO)_3$], 161 (72) [$M^+-Cr(CO)_3-OH$], 146 (50) [$M^+-Cr(CO)_3-H-2CH_3$], 130 (50) [$M^+-Cr(CO)_3-OH-2CH_3$], 118 (60) [$M^+-Cr(CO)_3-OH-CH_2-2CH_3$], 91 (32), 77(44). HRMS ($C_{13}H_{11}CrNO_5$): Calcd.: 313.0043; found: 313.0042.

*4.12. rac-Tricarbonyl[endo-3-hydroxy-N-methyl-exo-3-vinylindolin-2-one]chromium(0) (rac-**21**), rac-tricarbonyl-[endo-2-hydroxy-N-methyl-exo-2-vinylindolin-2-one]-chromium(0) (rac-**22**), and rac-tricarbonyl[endo-2-endo-3-dihydroxy-N-methyl-exo-2-exo-3-divinylindolin-2-one]-chromium(0) (rac-**23**)*

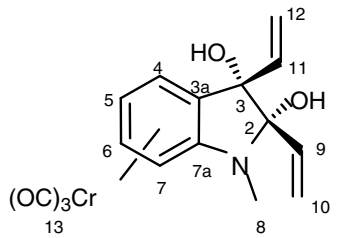
(a) 7 mL (7.0 mmol) of a 1 M solution of vinylmagnesium bromide in THF was added drowise at −78 °C to 502 mg (1.7 mmol) of *rac*-**6** in 40 mL of THF. After stirring at −78 °C for 2 h the mixture was warmed to 23 °C and stirred at this temperature for 40 min, 3 h, or 16 h. After cooling the mixture to −78 °C, 10 mL of water and 30 mL of saturated aqueous ammonium chloride was added. After warming to 23 °C the mixture was stirred for 15 min. The mixture was extracted 6 times with 15 mL of TBME each, and the collected organic layers were dried over $MgSO_4$, filtered. After solvent removal at pressure the mixture was separated by column chromatography (200 × 30 mm, PE/TBME 5:1, 3:1, 1:1, then TBME). I: 89 mg (0.3 mmol, 16%) [3 h: 131 mg, 0.4 mmol, 25%; 16 h: 113 mg, 0.3 mmol, 32%] of *rac*-**23** as an orange oil. II: 80 mg (0.3 mmol, 15%) [3 h: 63 mg, 0.2 mmol, 13%; 6 h: 29 mg, 0.1mmol, 9%] of *rac*-**22** as a red solid (m.p. 154.8 °C, dec.). III: 376 mg (1.2 mmol, 68%) [3 h: 215 mg, 0.7 mmol, 43%; 6 h: 103 mg, 0.3 mmol, 32%] of *rac*-**21** as a red solid (m.p. 132.4 °C, dec.).

(b) At −78 °C, 2.7 mL (2.7 mmol) of a 1 M solution of vinylmagnesium bromide in THF was added to 200 mg (0.7 mmol) of *rac*-**6** in 20 mL of THF. After stirring at −78 °C for 2 h, 5 mL of water and 15 mL of saturated

aqueous NH_4Cl was added at this temperature. The layers were separated, and the aqueous layer was extracted three times with 20 mL of TBME each. After drying of the collected organic layers over $MgSO_4$ and solvent removal at reduced pressure the remaining material was subjected to column chromatography at (SiO_2, 150×20 mm, PE/TBME, then TBME). I: 163 mg (0.4 mmol, 58%) of *rac*-**21**, red solid (m.p. 132.4 °C, dec.). II: 35 mg (0.1 mmol, 15%) of *rac*-**22**, red solid (m.p. 154.8 °C, dec.).

rac-**21:** IR (ATR): $\tilde{\nu}/cm^{-1}$ 3370 (m, OH), 3112 (w), 2971 (w), 1946 (s, CrCO), 1870 (s, CrCO), 1724 (s, C=O), 1613 (m), 1548 (m), 1358 (m), 1261 (m), 1210 (m), 1114 (s, C–O), 1071 (m, C–O), 982 (m), 936 (s), 815 (m), 796 (m), 664 (s), 624 (s). ^{1}H NMR (400.1 MHz, acetone-d_6): $\delta = 3.09$ (s, 3H, NCH_3), 5.15 (m, 1H, 5-H), 5.28–5.42 (m, 2H, $=CH_2$), 5.59 (m, 1H, 7-H), 5.61 (s, 1H, OH), 5.89 (m, 1H, 6-H), 6.0–6.10 (m, 2H, 4-H, =CH). ^{13}C NMR (100.6 MHz, acetone-d_6, APT + HMQC): $\delta = 25.4$ (−, NCH_3), 72.8 (−, C-7), 75.7 (+, C-3a), 84.3 (−, C-5), 92.3 (−, C-4), 94.6 (−, C-6), 100.4 (+, C-3), 115.9 (+, $=CH_2$), 126.5 (+, C-7a), 136.9 (–H) 175.3 (+, C-2), 233.0 (+, CrCO). MS (70 eV, 120°C): *m/z* (%) = 327 (9) [M^++2], 326 (15) [M^++1], 325 (50) [M^+], 269 (11) [M^+−2CO], 241 (41) [M^+−3CO], 223 (100) [M^+−−3CO−H_2O], 197 (24), 189 (29) [M^+−$Cr(CO)_3$], 173 (30), 144 (20), 115 (10), 91 (8) [$PhCH_2^+$], 73 (38), 52 (18) [^{52}Cr]. HRMS ($C_{14}H_{11}CrNO_5$): Calcd.: 325.0042; found: 325.0042.

rac-**22:** IR (ATR): $\tilde{\nu}/cm^{-1}$ 3374 (m, OH), 3089 (w), 2963 (w), 2926 (w), 2852 (w), 1958 (s, CrCO), 1896 (s, CrCO), 1857 (s, CrCO), 1697 (s, C=O), 1641 (m), 1613 (m), 1552 (s), 1473 (m), 1417 (m), 1302 (m), 1259 (m), 1088 (m, C–O), 1063 (m, C–O), 996 (s, C–O), 945 (s), 892 (m), 795 (s), 655 (s), 629 (s), 604 (s). ^{1}H NMR (200.1 MHz, acetone-d_6): $\delta = 2.90$ (s, 3H, NCH_3), 5.22 (m, 1H, 5-H), 5.32–5.50 (m, 3H, 4-H, $=CH_2$), 5.70–5.83 (m, 1H, =CH), 6.19–6.24 (m, 2H, 7-H, 6-H), 6.29 (s, 1H, OH). ^{13}C NMR (100.6 MHz, BB, acetone-d_6): $\delta = 27.4$ (C-8), 70.6 (C-7), 79.7 (C-3a), 84.4 (C-5), 90.6 (C-2), 91.5 (C-4), 99.5 (C-6), 119.0 (C-10), 134.7 (C-9), 142.2 (C-7a), 198.5 (C-3), 233.2 (C-11). MS (70 eV, 130 °C): *m/z* (%) = 325 (45) [M^+], 241 (59) [M^+−3CO], 223 (100) [M^+−3CO−H_2O], 189 (56) [M^+−$Cr(CO)_3$], 174 (10) [M^+−$Cr(CO)_3$−CH_3], 173 (53) [M^+−$Cr(CO)_3$−O], 160 (57) [M^+−$Cr(CO)_3$−CO−1], 144 (51) [M^+−$Cr(CO)_3$−OH−C_2H_3−1], 134 (16), 117 (14), 105 (16), 91 (19), 77 (41), 69 (30), 52 (73) [$^{52}Cr^+$]. HRMS ($C_{14}H_{11}CrNO_5$): Calcd.: 325.0042; found: 325.0046.



rac-**23**: IR (ATR): $\tilde{\nu}/cm^{-1}$ 3364 (m, OH), 3081 (w), 2963 (m), 1951 (s, CrCO), 1859 (s, CrCO), 1704 (m), 1614 (m), 1547 (m), 1472 (m), 1261 (s), 1091 (s, C–O), 1019 (m, C–O), 936 (m), 799 (s), 669 (m), 630 (m). ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 2.71$ (s, 3H, 8-H), 4.76 (s, 1H, 2-COH), 5.03 (dt, $J_{H,H} = 6.2$ Hz, 0.7 Hz, 1H, 5-H), 5.15 (dd, $J_{H,H} = 10.7$ Hz, 1.4 Hz, 1H, 12-H), 5.16 (d, $J_{H,H} = 6.8$, 1H, 7-H), 5.21 (s, 1H, OH 3-COH), 5.24 (dd, $J_{H,H} = 17.2$ Hz, 1.4 Hz, 12-H), 5.39 (dd, $J_{H,H} = 10.5$ Hz, 1.8 Hz, 1H, 10-H), 5.54 (dd, $J_{H,H} = 17.2$ Hz, 1.8 Hz, 1H, 10-H), 5.72 (dd, $J_{H,H} = 6.3$ Hz, 1.1 Hz, 1H, 7-H), 5.73 (dd, $J_{H,H} = 17.2$, 10.7 Hz, 1H, 9-H), 5.79 (dt, $J_{H,H} = 6.5$ Hz, 1.0 Hz, 1H, 6-H), 5.88 (dd, $J_{H,H} = 17.2$, 10.7 Hz, 1H, 11-H). ^{13}C NMR (100.6 MHz, BB, acetone-d_6): $\delta = 28.6$ (C-8), 72.5 (C-7), 81.7 (C-3a), 84.2 (C-5), 93.7 (C-4), 97.1 (C-3), 97.3 (C-6), 101.6 (-C-2), 114.4 (C-12), 119.6 (C-10), 134.1 (C-7a), 137.2 (C-9), 139.5 (C-11), 235.4 (C13). *m/z* (%) = 353 (22) [M^+], 269 (8) [M^+−3CO], 251 (14) [M^+−3CO−H_2O], 235 (14) [M^+−3CO−2OH], 182 (100) [M^+−$Cr(CO)_3$−2OH−1], 172 (70) [M^+−$Cr(CO)_3$−OH−C_2H_3−1], 158 (56) [M^+−$Cr(CO)_3$−OH−C_2H_3], 146 (63) [M^+−$Cr(CO)_3$−OH−C_2H_3−CH_3], 115 (38) [M^+−$Cr(CO)_3$−2OH−$2C_2H_3$−CH_3], 105 (45), 91 (70), 81 (79), 67 (57), 52 (56) [$^{52}Cr^+$]. HRMS ($C_{14}H_{11}CrNO_5$): Calcd.: 353.03553; found: 353.03561.

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