Synthesis, Characterization, and Some Reactions of the Tricarbonylchromium Complexes of 1,3-Indandione and Ninhydrin

Dirk Leinweber,[a] Rudolf Wartchow,[b] and Holger Butenschön*[a]

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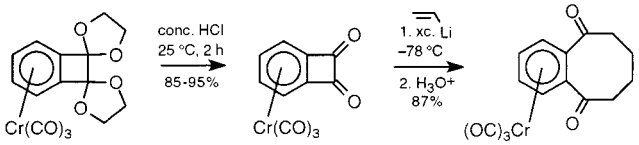
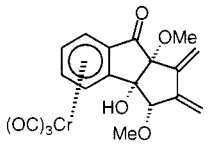
The syntheses and characterization of the tricarbonylchromium complexes of 1,3-indandione and ninhydrin are described. As the direct complexation proved unsuccessful, the acetal route was tried. Although some complexes were obtained, complex deacetalization did not work in the case of ninhydrin. Finally, the oxidation of tricarbonyl(η^6-1,3-indandione)chromium(0) with dimethyldioxirane gave the ninhydrin complex in 75% yield in equilibrium with the indantrione complex. The latter reacts in hetero Diels-Alder reactions with dienes with diastereoselective formation of spiro anellated pyran derivatives.

(η^6-Arene)tricarbonylchromium complexes with functionalized anellated rings deserve interest under a variety of aspects. Often their chemistry considerably differs from that of the uncoordinated arene for at least two reasons. First, the electron withdrawal of the tricarbonylchromium groups renders the anellated ring electron poor. This is especially the case when sp^2 hybridization of the benzylic carbon atoms facilitates the transfer of the tricarbonylchromium electron withdrawal to the anellated ring via resonance interactions. Second, the facial discrimination caused by complexation at only one side of the aromatic system decreases symmetry and as a consequence can induce changes to the stereoselectivity of chemical reactions at the anellated ring. Usually one observes attack of reagents from the face opposite to the tricarbonylchromium group. This point is of special importance when more than one reaction of this kind takes place at the anellated ring. As a consequence, the stereodirecting effect of tricarbonylchromium should be more clearly visible in the reactions of multifunctional anellated rings.

In our work this type of diastereoselectivity became obvious when (η^6-benzocyclobutenedione)tricarbonylchromium (**2**) was treated with nucleophiles: In contrast to the reactions of the uncoordinated ligand, only *cis* diaddition was observed with a number of nucleophiles. **2** can be obtained by hydrolysis of the diacetal **1** in high yield, which is now available by an improved synthesis.[1] The most striking observation in this context was the dianionic oxy-Cope rearrangement upon diaddition of vinyllithium to **2**, which resulted in the formation of benzocyclooctenedione complex **3** in high yield under mild reaction conditions.[2−4] This reaction involves both functionalities and is possible only because the diaddition to the keto functionalities takes place from the face opposite to the $Cr(CO)_3$ group in both cases. Dianionic oxy-Cope rearrangements starting from **2** are possible with a number of alkenylmetal reagents. In many cases a subsequent intramolecular aldol addition results in the formation of a highly functionalized benz-anellated diquinane, e.g. **4** from **2** and 1-lithio-1-methoxyallene.[3−5]



1 **2** **3**



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As **2** proved to be a starting material for diastereoselective reactions leading to highly functionalized anellated ring systems, we became interested in the next higher analogues, which are the tricarbonylchromium complexes **5** and **7** or **8** of 1,2-indandione and indantrione or ninhydrin, respectively. If similar chemistry were possible with these complexes, this would pave a way to benz-anellated cyclononanedione and hydrindane systems. The keto functionalities in complexes **5**−**8** should be rather electrophilic, because, as in **2**, the sp^2 hybridization of the benzylic carbon atoms should facilitate the electron withdrawal to the $Cr(CO)_3$ fragment. In **7** the central keto group at C-2 should be more electrophilic than the other two. A consequence is that the first nucleophilic addition will usually take place at C-2, which means that next in any case a neighbouring keto group is attacked, which is a precondition of oxy-Cope chemistry to happen. Here, we report on the synthesis of the tricarbonylchromium complexes **7** and **8**. On the way to these complexes it became clear that tricarbonyl(η^6-1,3-

[a] Institut für Organische Chemie, Universität Hannover, Schneiderberg 1B, D-30167 Hannover, Germany
Fax: (internat.) +49(0)511/762-4616
E-mail: holger.butenschoen@mbox.oci.uni-hannover.de
[b] Institut für Anorganische Chemie, Universität Hannover, Callinstraße 9, D-30167 Hannover, Germany

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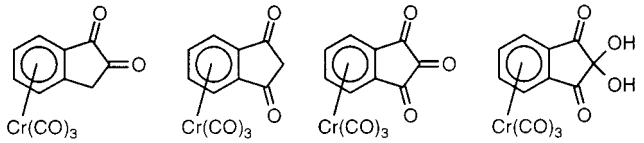
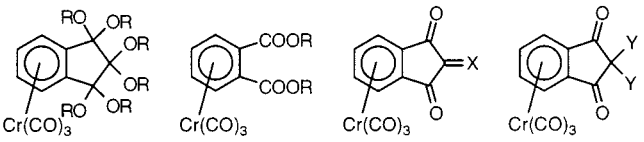
indandione)chromium(0) (**6**) plays a key role in the finally successful synthesis. The synthesis of **5** will be reported elsewhere.



5 **6** **7** **8**

As with benzocyclobutenedione, all attempts to directly coordinate the ligands by treatment of indantrione (**19**) or ninhydrin (**17**) with hexacarbonylchromium or triamminetricarbonylchromium were not successful and resulted in decomposed material only. A retrosynthetic analysis of the problem led to five different possible ways to **7** or **8** starting from **9**−**12** and **6**.

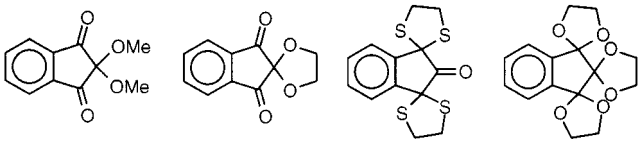


9 **10** **11** **12**

9 might be a precursor of **7** and **8** in an acetalization−complexation−deacetalization sequence, which had proven successful in the case of **2**. Similar to an earlier synthesis of ninhydrin (**17**) from diethyl phthalate,[6] **10** could undergo a Pummerer rearrangement upon treatment with dimethyl sulfoxide/sodium methanolate. **11** could be obtained from **6** and already contains all three sp^2 hybridized carbon atoms in the anellated ring. A change of the functional group X (diazo, oxime, enamine) by hydrolysis or oxidation to O would give **7** or **8**. Alternatively, **12** (Y = halogen) could be formed from **6** by halogenation, hydrolysis should give **7** or **8**. Finally, a direct oxidation of **6** to **7** or **8** must be considered. However, one would have to use an oxidation method which must not cause an oxidative decomplexation of the low valent chromium atom.

The Acetal Route

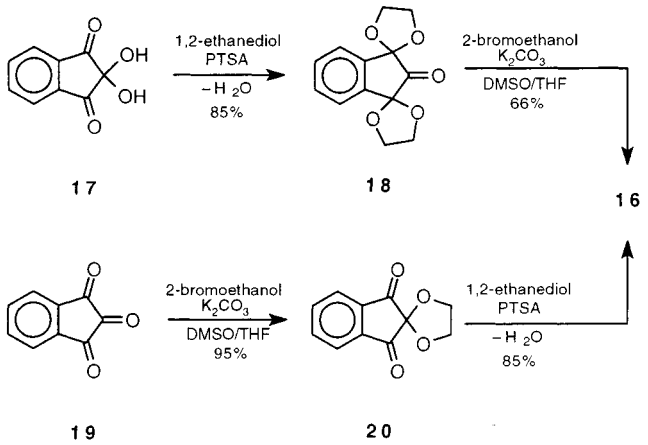
Indantrione (**19**) was obtained by treatment of commercially available ninhydrin (**17**) with boiling thionyl chloride in almost quantitative yield.[7] Because known acetals **13**−**15**[8−10] did not give satisfactory complexation results, new, thermally more stable indantrione acetals were envisaged as ligands for chromium complexes. The most promising acetal in this context is, of course, tris(ethylenedioxy)indane (**16**).



13 **14** **15** **16**

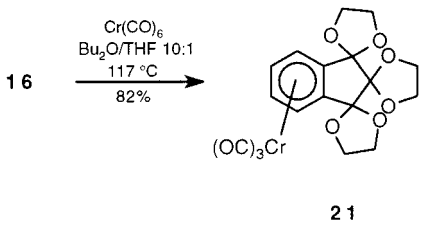
In a first attempt to prepare **16**, indantrione (**19**) or ninhydrin (**17**) were subjected to standard acetalization conditions [1,2-ethanediol, cat. *p*-toluenesulfonic acid (PTSA), aceotropic water removal with benzene]. Unexpected and in contrast to Schönberg's work,[10] bisacetal **18** was obtained in 85% yield. Although complexation of **18** was unsuccessful, the compound came out to be a valuable starting material for a new synthesis of benzocyclobutenedione by photodecarbonylation and subsequent deacetalization.[1]

While the acetalization under standard conditions took place only at the keto groups adjacent to the aromatic ring, selective acetalization was possible at C-2 using 2-bromoethanol/potassium carbonate.[9] Starting from ninhydrin (**17**) or indantrione (**19**) the sequence of acetalization reactions is interchangeable, so that either **18** or **20** are intermediates leading to **16**, the route via **20** giving higher yield.



17 **18** **19** **20**

Next, complexation of **16** was achieved by treatment with hexacarbonylchromium in dibutyl ether/THF (10:1) at 117°C in 82% yield. **21**, which is the first chromium complex of an indantrione acetal, was obtained as a yellow powder which was crystallized from diethyl ether/petroleum ether. In contrast to many similar compounds the crystalline material is air sensitive and decomposes within 24 h in the air. From ethyl acetate/petroleum ether (1:1) crystals of **21** suitable for an X-ray crystal structure analysis were grown at −30°C (Figure 1).



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The structure shows that the central ethylenedioxy group is bent towards the tricarbonylchromium group whereas the ethylenedioxy groups at C-1 und C-3 are bent away from the tricarbonylchromium group. This conformation minimizes steric interactions between the adjacent ethylenedioxy groups as well as the steric interaction between ethylenedioxy groups and the tricarbonylchromium fragment.

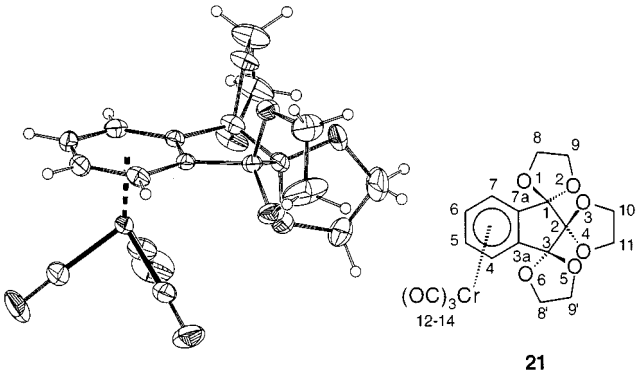
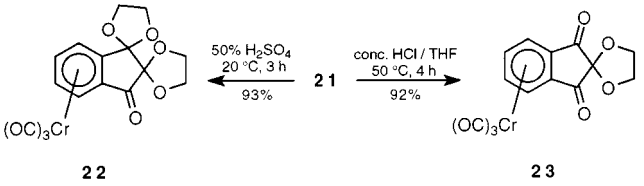


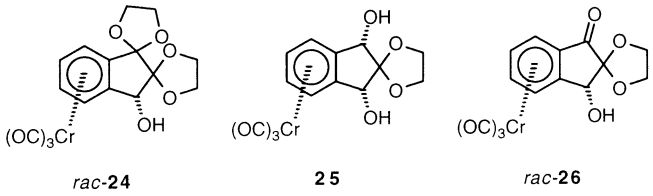
Figure 1. Structure in the crystal and numbering scheme of **21**.[11] Selected bond lengths [A]: C1−C2 1.557(3), C2−C3 1.565(4), C3−C3a 1.506(3), C3a−C4 1.408(3), C4−C5 1.395(4), C5−C6 1.400(4), C6−C7 1.392(4), C7−C7a 1.412(3), C7a−C3a 1.387(3), C7a−C1 1.502(3), C1−O1 1.403(3), C1−O2 1.423(3), C2−O3 1.408(3), C2−O4 1.400(3), Cr−C_{Arene} 2.209(2) − 2.218(2).

After the successful complexation of ligand **16** deprotection of the keto groups was attempted similar to the deprotection of **1**. Treatment of **21** with conc. hydrochloric acid at 20°C for 2 h resulted in the hydrolysis of only one ethylenedioxy group. Racemic **22** was isolated in 85% yield. However, the reaction had to be traced by TLC in order to avoid further hydrolysis. Pure **22** was obtained in 93% yield upon treatment of **21** with 50% sulfuric acid for 3 h at 20°C. Stronger reaction conditions (conc. HCl, 50°C, 4 h) provided 1,3-indandione complex **23** in 92% yield.

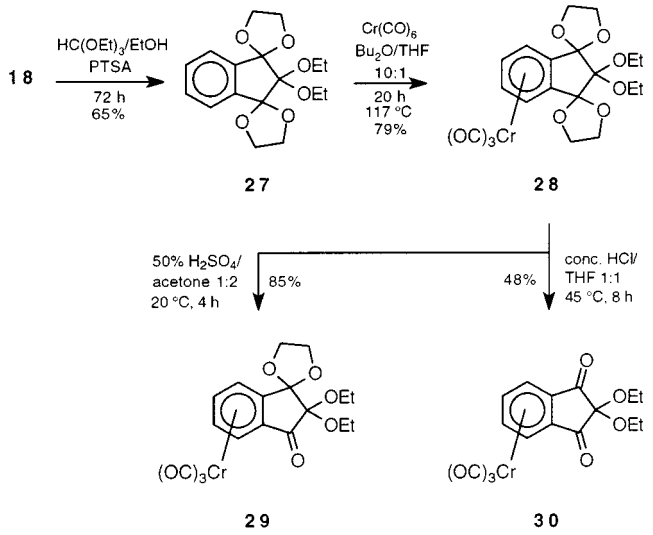


22 and **23** were characterized spectroscopically. The electron withdrawing effect of the benzylic keto group can nicely be observed by comparison of the carbonyl ligand absorptions in the IR spectra: Whereas these bands are observed at 1972 and at 1903 cm^{-1} for trisacetal **21**, the keto group in **22** reduces the carbonyl ligand backbonding as indicated by values of 1988 and 1922 cm^{-1} for this compound. This effect is even stronger for diketone **23**, the absorption bands appear at 1996 and 1925 cm^{-1}. A similar trend is seen for the ^{13}C NMR chemical shifts of the carbonyl ligand carbon atoms (**21**: δ = 231.1, **22**: δ = 228.9, **23**: δ = 226.7). In the mass spectra, all three compounds show a significant peak at *m/z* = 128, which has to be attributed to the η^6 coordinated benzynechromium cation.[12]

In order to deprotect all three keto functionalities a variety of reaction conditions for acetal hydrolysis were tried. Unfortunately all attempts failed: either the acetal group at C-2 could not be hydrolyzed or oxidative decomplexation and decomposition occurred. We concluded that the unprotected keto groups in **22** and **23** were incompatible with the desired hydrolysis. Therefore, **22** and **23** were reduced with sodium borohydride to give *rac*-**24** and **25** with complete diastereoselectivity in 96% and 89% yield, respectively. Hydrolysis of *rac*-**24** was only partly successful and gave complex *rac*-**26** in 76% yield upon treatment with 50% sulfuric acid in acetone, whereas attempts to hydrolyze **25** resulted in decomposed material only.



As the ethylenedioxy group at C-2 proved to be unexpectedly stable, we envisaged using an open-chain acetal instead. In this case, hydrolysis should be favored for entropic reasons. 2,2-Diethoxy derivative **27** was obtained from **18** by treatment with triethyl orthoformiate in the presence of PTSA in 65% yield and coordinated to tricarbonylchromium in 79% yield under standard conditions (dibutyl ether/THF, 10:1, 117°C, 20 h) to give complex **28**. Single deprotection of **28** to monoacetal **29** was achieved in 85%, whereas stronger reaction conditions resulted in deprotection at C-1 and C-3 only in moderate yield (48%) of **30**, which was characterized by ^1H-NMR and IR spectroscopy only.



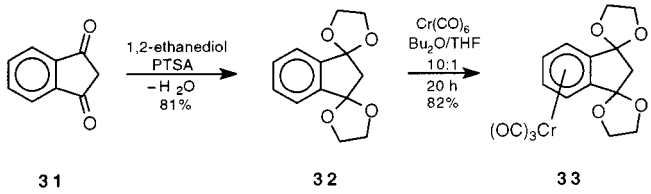
Although the acetal route so far resulted in the synthesis of a number of interesting, highly functionalized indanone and indandione complexes, it did so far not pave a way to the desired complexes **7** and **8**. Experiments directed to Pummerer rearrangements starting from phthalate complex **10** also gave only unsatisfactory results, usually only hydrolysis to the diacid complex is observed.[13] Therefore routes via 1,3-indandione complex **6** were tried next.

The 1,3-Indandione Route

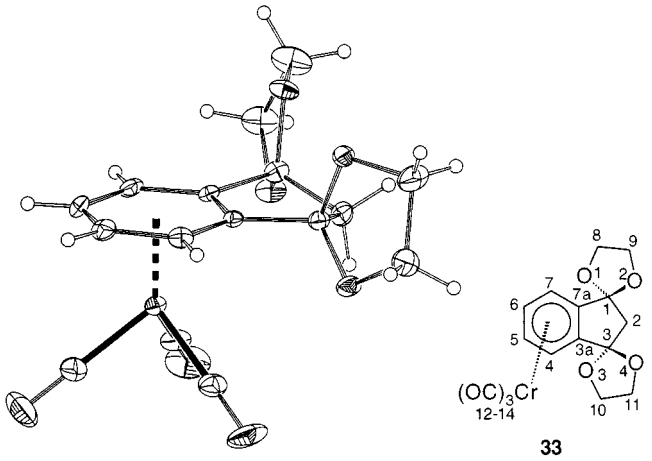
The synthesis of 1,3-indandione complex **6** deserves some interest because a number of syntheses of ninhydrin start from 1,3-indandione (**31**).[14] Usually the activated methylene group is functionalized and transformed into a (hy-

drated) keto group by hydrolytic or oxidative processes. We felt that such reaction sequences might eventually lead to **7** and **8**.

As the direct complexation of 1,3-indandione using hexacarbonylchromium failed, we resorted to the acetal route to prepare the complex. **31** was transformed to the new diacetal **32** under standard reaction conditions in 81% yield. It should be mentioned that benzene apparently is neccessary for aceotropic water removal; use of toluene instead resulted in a reduced yield of only 38% of **32**. The long reaction time is neccessary because shorter ones lead to significant amounts of monoacetal. Diacetal **32** can be coordinated to chromium by treatment with hexacarbonylchromium under standard reaction conditions to give **33** in 82% yield as an air sensitive yellow solid. Crystals of **33** suitable for an X-ray crystal structure analysis (Figure 2) were grown from ethyl acetate/petroleum ether (1:1).



31 32 33

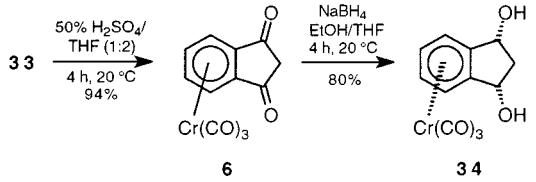


33

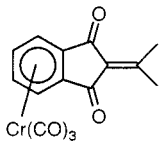
Figure 2. Structure in the crystal and numbering scheme of **33**.[11] Selected bond lengths [Å]: C1−C2 1.538(4), C2−C3 1.531(4), C3−C3a 1.514(4), C3a−C4 1.415(4), C4−C5 1.401(4), C5−C6 1.417(4), C6−C7 1.395(4), C7−C7a 1.413(4), C7a−C1 1.512(4), C3a−C7a 1.400(4), C1−O1 1.404(4), C1−O2 1.433(3), C3−O3 1.417(3), C3−O4 1.423(4), Cr−C_{Arene} 2.204(3) − 2.218(3).

The crystal structure shows that C-2 is slightly bent towards the tricarbonylchromium group, presumably as a result of the steric bulk of the adjacent ethylenedioxy substituents. However, this effect is much smaller than in **21**. Due to the smaller steric loading the bond lengths C1−C2 and C2−C3 in **33** [1.538(4), 1.531(4) Å] are significantly shorter than the corresponding bond lengths in **21** [1.557(3), 1.565(4) Å]. As in **21**, no CO ligand is located below the anellated ring.

Hydrolysis of the acetal functionalities in **33** was easily achieved by treatment with 50% sulfuric acid/THF (1:2) and gave tricarbonyl(η^6-1,3-indandione)chromium(0) (**6**) in 94% yield. Reduction of **6** with sodium borohydride gave a *cis* diol as a diastereomerically pure product; according to the usual attack of the nucleophile from the face opposite to the tricarbonylchromium group we assign formula **34** to this product.[2,4,15−18] Knoevenagel condensation product **35** was obtained as a side product of the acetal hydrolysis in 5% yield beside 90% of **6**, when the reaction was carried out in a 1:1 mixture of 50% sulfuric acid/acetone. **35** is the first complex in this series with three sp^2 hybridized carbon atoms in the anellated ring.



6 34



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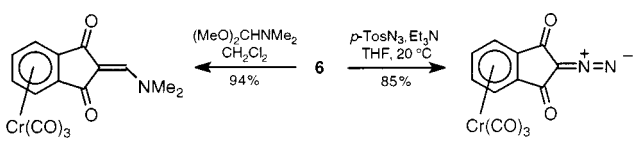
Functionalization of 6 at C-2

As there are some published syntheses of ninhydrin starting from 1,3-indandione (**29**) via functionalization at C-2 some experiments along these line were undertaken. First, introduction of an oxime function at C-2 was attempted by treatment of **6** with sodium nitrite in diluted sulfuric acid. Treatment of the desired oxime with formalin solution and sulfuric acid should lead to **8**.[19] However, in contrast to the uncoordinated 1,3-indandione (**31**), no reaction occurred with chromium complex **6**.

Next, **6** was treated with dimethylformamide dimethylacetal [dimethoxy(dimethylamino)methane] resulting in the formation of enamine **36** in 94% yield. It is known that hydrated 1,2,3-tricarbonyl compounds can be obtained from such enamines by oxidation with singulett oxygen or ozone.[20] Most recently a synthesis of thianinhydrin has been published in which the oxidation was performed with dimethyldioxirane (DDO),[21] which is an oxidant far more compatible with a low valent tricarbonylchromium complex than singulett oxygen or ozone.[22−26]



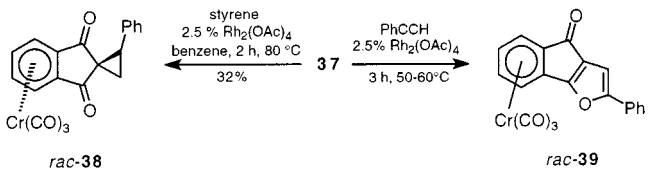
36 37

Another 1,3-indandione derivative which was transformed into ninhydrin by oxidation with DDO in high yield, is 2-diazo-1,3-indandione.[27] To test in how far similar chemistry would be possible with the corresponding chromium complex, **6** was treated with tosyl azide at 20°C

under basic reaction conditions to give 2-diazo-1,3-indandione complex **37** in 85% yield as an air stable solid. **36** and **37** were fully characterized by their spectroscopic data. The IR absorptions of the carbonyl ligands (**36**: $\tilde{\nu}$ = 1916, 1964 cm^{-1}, **37**: $\tilde{\nu}$ = 1944, 1996 cm^{-1}) as well as the chemical shifts of the ^{13}C-NMR signals of their carbon atoms (**36**: δ = 232.0, **37**: δ = 229.4) and their different colours (**36**: orange, **37**: brown) indicate that the ligands in **36** and **35** are much different from one another, the enamine substituted ligand of **36** being more electron rich than the diazo substituted ligand of **37**. The formation and stability of compounds **35**, **36**, and **37** show that 1,3-indandione complexes with an sp^2 hybridization at C-2 can exist, and we felt that the synthesis of the indantrione complex should also be possible despite its special electronic properties.

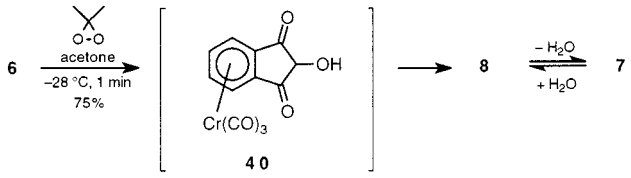
Next, oxidation of **36** and **37** with DDO was tried. The reagent was prepared according to the procedure by Adam et al.[28] **36** and **37** were carefully treated with DDO at −78, −28, and at 20°C. Use of up to 3 equiv. of DDO caused no reaction. Use of more than 3 equiv. of DDO caused a slow oxidative decomplexation of **36** at −78 and at −28°C, as well as at 20°C the decomplexation occurred immediately. With **37** slow oxidative decomplexation was observed at all three temperatures, when 5 equiv. of DDO were used. Longer reaction times did not change these results. Therefore, in contrast to their uncoordinated ligands, **36** and **37** prove to be unsuitable as precursors for **7** or **8**.

Two other experiments were carried out with diazo compound **37**. First, **37** was treated with styrene in the presence of rhodium(II) acetate. This salt causes loss of nitrogen with formation of a carbene. We were interested in the diastereoselectivity of the cycloaddition of the derived carbene with styrene and observed the formation of a diastereomerically pure spirocyclopropane derivative in 32% yield. Although we did not obtain crystals suitable for an X-ray crystal structure analysis, we regard the obtained complex as the *anti* diastereoisomer **38** for steric reasons. Next, **37** was treated with phenylethyne in the presence of rhodium(II) acetate. As result of a 1,3-dipolar cycloaddition, the anellated furan **39** was formed in 70% yield. The formation of **39** corresponds to the reaction of the uncoordinated ligand,[29] apparently the electron withdrawal of the tricarbonylchromium fragment does not influence the regioselectivity of the cycloaddition.



Direct Oxidation of 6: Formation of the Ninhydrin Complex

The direct oxidation of 1,3-indandione to ninhydrin was performed by Teeters and Shriner as early as 1933 with selenium dioxide.[30] The oxidation of 1,3-diphenyl-1,3-propanedione to 1,3-diphenyl-1,2,3-propanetrione with Dess-Martin periodane has been reported by Golec et al. more recently.[31] However, both reagents led to oxidative decomplexation or decomposition when applied to **6**. The oxidation of 1,3-diphenyl-1,3-propanedione to 1,3-diphenyl-1,2,3-propanetrione and its hydrate has also been performed by Adam et al. with 4 equiv. of dimethyldioxirane (DDO) in 98% yield.[32] When 1,3-indandione complex **6** was treated with 3 equiv. of DDO in acetone at −28°C, a fast reaction occurred. An intermediate, presumably **40**, was observed by TLC, and after hydrolysis and purification by column chromatography, tricarbonyl(η^6-ninhydrin)chromium(0) (**8**) was isolated in 75% yield as a red-brown, moderately air sensitive solid. The reaction could be stopped at the intermediate step, when only 1 equiv. of DDO was used. Unfortunately, attempts to isolate and characterize the intermediate so far failed, because the compound rapidly decomposed during the column chromatography. The MS and IR spectra obtained are in accord with **40**. To our knowledge this is the first example of oxidation at a carbon atom with DDO in a tricarbonylchromium complex. Although DDO has been used as an oxidative decomplexation reagent,[33] we do not observe any decomposition in the reaction reported here.



As the final reaction product only **8** was detected by TLC. However, in addition to the complete set of signals of ninhydrin complex **8** the complete set of signals of indantrione complex **7** was observed in the ^{13}C-NMR spectrum, indicating an equilibrium between **8** and **7**.[34] **8** and **7** were characterized spectroscopically by ^{1}H- and ^{13}C-NMR as well as by their IR and mass spectra. In addition, there is an X-ray structure analysis of **8**, which confirms its constitution. However, the crystal quality was only poor so that structural data cannot be discussed here. The chemical shift of the carbon atoms of the carbonyl ligands in **7** is δ = 227.4 (in [D_6]acetone). This documents that **7** is more electron poor than its lower homologue **2** whose carbonyl ligand ^{13}C-chemical shift is δ = 228.3 (in [D_8]THF).[35] Unfortunately, the IR absorptions of **7** could not yet be determined, because the complex exists only in equilibrium with **8**, but according to the known correlation between ^{13}C-NMR shift of carbonyl ligands and the IR absorptions of these ligands the smaller ^{13}C-NMR chemical shift can be taken as evidence for a reduced back bonding of the carbonyl ligands in **7** as compared to those in **2**.[35,36] The mass spectrum of ninhydrin complex **8** does not show a molecular ion peak at *m/z* = 314. The highest signal is observed at *m/z* = 296 corresponding to the dehydrated indantrione complex **7**. The base peak is observed at *m/z* = 128 corre-

sponding to the η^6 benzyne-Cr^+ ion which was observed and characterized in the mass spectrum of **2** already.[12]

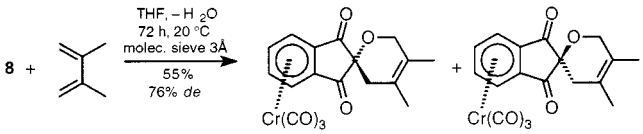
One important problem, which we could not solve so far, is the dehydration of ninhydrin complex **8** with formation of pure indantrione complex **7**. This might be possible either by physical or by chemical methods. Attempts to dehydrate **8** by drying at 20°C or at 50°C at 10^{-3} bar failed. At higher temperatures thermal decomposition was observed. This is in accord with the behaviour of uncomplexed ninhydrin (**17**), which affords heating up to 190°C to loose part of its hydrate water.[7] Attempts to remove the hydrate water azeotropically (benzene, 80°C, cat. PTSA) gave only a black suspension of decomposed material. As uncomplexed ninhydrin (**17**) can be dehydrated to indantrione (**19**) by treatment with molecular sieves (3Å),[37] **8** was treated for some time in that way. Although a darkening of the colour of the solution from orange-red to dark red was observed, no enrichment of the dehydrated complexes was detected. More experiments along this line are under way in our laboratory.

Chemical methods to dehydrate **8** cause problems: Usually, ninhydrin (**17**) is dehydrated by boiling it in thionyl chloride,[7] a prohibitive procedure for low valent metal complexes. The presumably increased reactivity of **7** as compared to **8** does not render a reaction with reagents like trimethyl orthoformiate or 2,2-dimethoxypropane promising, because an immediate addition of the side product methanol to **7** has to be expected. Similar reactions were observed upon treatment of ninhydrin (**17**) with acetanhydride or acetyl chloride.[38] One promising way, which is being tested in our group is the reaction of ninhydrin (**17**) with trimethylsilyl chloride under basic reaction conditions followed by elimination of hexamethyldisiloxane.[39]

Reactions of Ninhydrin Complex 8

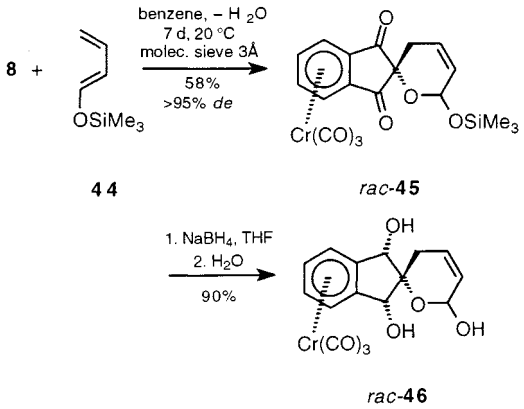
Hetero-Diels–Alder reactions are an important tool in the synthesis of heterocycles.[40] Aldehydes and electron deficient ketones can serve as heterodienophiles in such reations leading to 5,6-dihydro-2*H*-pyrans, which are valuable intermediates in natural product syntheses, especially in carbohydrate chemistry.[41] Indantrione (**19**) is one of the few ketones reported to undergo this reaction with the central keto group.[37] The regioselectivity of this reaction is a result of the electron distribution in indantrione (**19**) with the central keto group being the most electron deficient one. With respect to complexes **7** and **8** we were interested to know in how far the equilibrium mixture of the ninhydrin and the indantrione complexes would react in a hetero-Diels–Alder fashion. Due to the electron withdrawal of the tricarbonylchromium group the regioselectivity of the reaction did not neccessarily have to be the same as in the reaction of uncomplexed indantrione (**19**): The benzylic keto groups are more electrophilic than in the ligand, and the difference in electrophilicity between them and C-2 decreases. Finally, we wanted to verify the suggestion that the diene would diastereoselectively attack the heterodienophile from the face opposite to the tricarbonylchromium group to some extent.

In a first experiment ninhydrin complex **8** was treated wih 2,3-dimethyl-1,3-butadiene (**41**) in THF for 72 h at 20°C in the presence of some molecular sieves (3 Å). Cycloadducts **42** and **43** were obtained in 55% yield as a mixture of diastereomers (*de* = 76%, ^{13}C NMR, ^{1}H NMR) in addition to 13% of unreacted **8**, which was recovered. **42** and **43** were identified spectroscopically, including comparison of the data with those of the known ligand.[37] So far we did not succeed in a separation of the diastereomers and were thus unable to confirm their relative configurations beyond any doubt. However, for steric reasons we assume an attack of the diene at the face opposite to the tricarbonylchromium group to be preferred, and in accord with results of similar reactions reported here we suggest **42** to be the major diastereomer.



41 **42** **43**

Next, 1-trimethylsilyl-1,3-butadiene (**44**) was tested. The reaction resulted in the formation of cycloadduct *rac*-**45** in 58% yield as a single diastereomer (*de* > 95%, ^{1}H NMR,^{13}C NMR). In this case, 20% of unreacted starting material **8** were recovered. To determine the relative configuration of the cycloadduct at C-2, *rac*-**45** was reduced with sodium borohydride to give *rac*-**46** in 90% yield. Such a reduction is known to give the *endo* alcohol as a result of hydride attack from the face opposite to the tricarbonylchromium group.[42,43] NOE experiments confirmed the assigned relative configuration: Irradiation at the resonance frequency of the benzylic protons gave an NOE at the methylene protons and vice versa. In conclusion, **8** had diastereoselectively been attacked by the diene from the face opposite to the tricarbonylchromium group.[44]



44 *rac*-**45**

rac-**46**

A similar result was obtained upon treatment of ninhydrin complex **8** with 1-methoxy-3-trimethylsiloxy-1,3-butadiene (**47**, Danishefsky diene[45]). Complex *rac*-**48** was obtained as an orange-red solid in 78% yield (*de* > 95%, ^{1}H NMR, ^{13}C NMR) as a result of a hetero-Diels–Alder

cycloaddition followed by hydrolysis of the intermediate silyl enol ether. In addition, 23% unreacted starting material **8** were recovered. To our surprise we found that *rac*-**48** does not easily undergo a methanol elimination to **49**. Fortunately, crystals suitable for an X-ray crystal structure analysis (Figure 3) were obtained from dichloromethane/petroleum ether.

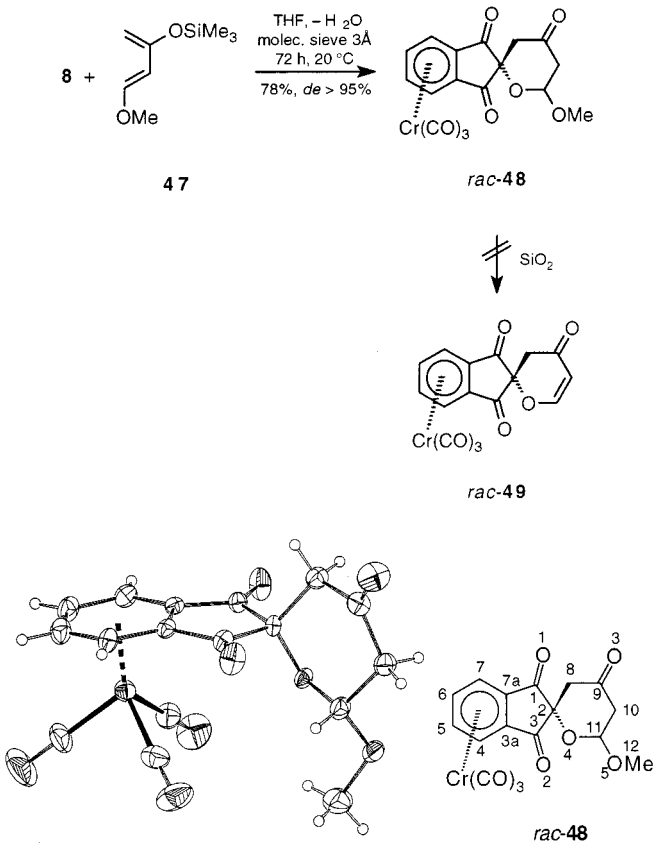


Figure 3. Structure in the crystal and numbering scheme of **48**.[11] Selected bond lengths [A]: C1−C2 1.546(5), C2−C3 1.544(5), C3−C3a 1.462(5), C4−C5 1.400(5), C5−C6 1.403(5), C6−C7 1.369(5), C7−C7a 1.411(5), C7a−C1 1.450(5), Cr−C_{Arene} 2.170(4)−2.213(3).

The structure confirms the NOE results and is the proof that the diene in these reactions attacks from the face of the ligand opposite to the tricarbonylchromium group. The spiro-anellated heterocycle shows a chair conformation, and presumably due to the steric demand of the spiro-anellated ring no carbonyl ligand is located below the five-membered ring.

The successful hetero-Diels−Alder reactions starting from ninhydrin complex **8** show that this compound may be used as a substitute of the dehydrated indantrione complex **7**. We currently investigate reactions of **8** and related complexes in more depth with some emphasis on addition reactions of organometallic substrates to the keto groups in the anellated ring.

Experimental Section

General: All operations were performed in flame-dried reaction vessels in an argon atmosphere using the Schlenk technique. Diethyl ether, dibutyl ether, dioxane, THF, petroleum ether (40−70°C), pentane, hexane, heptane, and benzene were distilled from sodium-potassium alloy/benzophenone. Dichloromethane was distilled from calcium chloride. − ^{1}H NMR: Bruker WP 80 (80 MHz), WP 200 SY (200.1 MHz), AM 400 (400.1 MHz). − ^{13}C NMR: Bruker WP 200 SY (50.3 MHz), AM 400 (100.1 MHz). Signal multiplicities were determined with APT and DEPT techniques. Chemical shifts refer to $\delta_{TMS} = 0$ or to residual solvent signals.[46,47] Air sensitive samples were prepared and sealed in an argon atmosphere. − IR: Perkin-Elmer FT-IR 580 and 1710. − MS: Finnigan MAT 112, 312 at 70 eV. − HRMS: Finnigan MAT 312, VG Autospec, peak matching with PFK. − Combustion analyses: Heraeus CHN Rapid. − Melting points (uncorr.) were determined in sealed glass tubes with an apparatus according to Dr. Tottoli. − Column chromatography: Silica gel (J. T. Baker, 40 μm) was degassed by heating it with a heat gun at reduced pressure followed by setting it under normal pressure with argon. This sequence was repeated five times. Separations were performed using flash chromatography.[48] Unless otherwise indicated, chiral compounds were obtained as racemates.

1,3-Bis(ethylenedioxy)-2-indanone (18): A solution of 5.00 g (28.1 mmol) of ninhydrin (**17**), 4.00 g (3.6 mL, 64.5 mmol) of 1,2-ethanediol, and 150 mg (1.0 mmol) of *para*-toluenesulfonic acid (PTSA) in 100 mL of benzene is heated at reflux for 20 h. The solution changes its colour from yellow to colourless. After solvent removal at reduced pressure a colourless solid is obtained, which is dissolved in 50 mL of ethyl acetate. The solution is washed three times each with 10 mL of a saturated aqueous solution of sodium bicarbonate and water. After filtration of the crude product through a short silica gel column with diethyl ether as the eluent 5.90 g (23.9 mmol, 85%) of **18** is obtained as a colourless powder (m. p. 105°C, DSC), which becomes yellow in the light. − IR (KBr): $\tilde{\nu}$ = 2973 (w) cm^{-1}, 2905 (w), 1777 (m, CO), 1471 (w), 1330 (m), 1310 (m), 1229 (w), 1029 (s, acetal-C−O), 945 (m), 864 (w), 765 (m), 740 (w). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.28 + 4.39 [2m, 4 H + 4 H, 8(8′)-H, 9(9′)-H], 7.57 (s, 4 H, arom. H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 66.5 [+, C-8(8′) or C-9(9′)], 66.6 [+, C-8(8′) or C-9(9′)], 101.4 [+, C-1(3)], 124.8 [−, C-4(7)], 132.0 [−, C-5(6)], 138.5 [+, C-3a(7a)], 209.4 (+, C-2). − MS (70 eV, 20°C): *m/z* (%) = 248 (2) [M^+], 220 (34) [M^+ − CO], 188 (7), 176 (10), 162 (7), 148 (100) [$C_9H_8O_2^+$], 133 (18), 104 (51), 88 (23), 77 (31). − $C_{13}H_{12}O_5$ (248.23): calcd. C 62.90, H 4.87; found C 62.52, H 4.88.

2-Ethylenedioxy-1,3-indandione (20):[9] A suspension of 1.00 g (6.2 mmol) of indantrione (**19**), 0.51 mL (7.2 mmol) of 2-bromoethanol and 3 mL of THF is mixed with 1.00 g (7.2 mmol) of potassium carbonate and 3 mL of DMSO. After 24 h at 40°C the yellow-brown suspension is added to 20 mL of water, causing formation of a yellow precipitate. This is filtered off, washed with water until no more potassium carbonate can be detected (pH). After drying at 0.001 mbar 1.21 g (5.9 mmol, 95%) of **20** is obtained as a bright yellow powder (m. p. 138°C), which was identified spectroscopically.[9,10]

1,2,3-Tris(ethylenedioxy)indane (16): a) 4.00 g (19.6 mmol) of **20**, 6.90 g (6.2 mL, 111.1 mmol) of 1,2-ethanediol, and 15 mg (0.1 mmol) of PTSA in 100 mL of benzene is heated at reflux with azeotropic water removal. The yellow colour of the solution fades out during this time. After solvent removal a colourless solid remains, which is recrystallized from ethyl acetate. 4.60 g (15.8 mmol, 81%) of **16** is obtained as colourless, long needles (m. p. 180°C).

b) A suspension of 4.00 g (16.1 mmol) of **18**, 1.36 mL (19.2 mmol) of 2-bromoethanol, and 8 mL of THF is mixed with 2.60 g (19.2 mmol) of potassium carbonate and 8 mL of DMSO. The yellow mixture is stirred for 24 h at 50°C and becomes white. THF is

removed at reduced pressure, and DMSO is removed by filtration. The white residue is washed with water until a pH indicator does no more show basic reaction. After recrystallization from ethyl acetate 3.10 g (10.6 mmol, 66%) of **16** is isolated as colourless, long needles.

16: IR (KBr): $\tilde{\nu}$ = 2991 (w) cm^{-1}, 2955 (w), 2884 (m), 1472 (w), 1321 (w), 1294 (w), 1270 (m), 1206 (w), 1157 (w), 1078 (m), 1042 (s, acetal-C−O), 1008 (m), 980 (m), 956 (m), 868 (w), 785 (m), 655 (w). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.15 [s, 4 H, 9(9′)-H], 4.23 [s, 8 H, 8(8′)-H, 10(10′)-H], 7.42 (s, 4 H, arom. H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 66.4 [+, C-8(8′), C-(10,10′)], 66.8 [+, C-9(9′)], 109.1 [+, C-1(3)], 112.2 (+, C-2), 123.1 [−, C-4(7)], 130.3 [−, C-5(6)], 139.9 [+, C-3a(7a)]. − MS (70 eV, 70°C): *m/z* (%) = 294 (4) [M^+ + 2], 293 (12) [M^+ + 1], 292 (70) [M^+], 220 (89), 176 (13), 148 (100) [$C_9H_8O_2^+$], 133 (26), 104 (39), 88 (11), 76 (20). − HRMS, $C_{15}H_{16}O_6$: calcd. 292.09668, found 292.09494. − $C_{15}H_{16}O_6$ (292.09): calcd. C 61.64, H 5.52; found C 61.58, H 5.45.

Tricarbonyl[η^6-1,2,3-tris(ethylenedioxy)indane]chromium(0) (21): A mixture of 2.00 g (6.8 mmol) of **16** and 1.65 g (7.5 mmol) of hexacarbonylchromium(0) in 100 mL of dibutyl ether and 10 mL of THF is heated at reflux for 20 h, the colour changing to dark yellow. The solvent is condensed at reduced pressure at 50°C into a cold trap, and the remaining solid is recrystallized from diethyl ether/petroleum ether. 2.40 g (5.6 mmol, 82%) of **21**, yellow, long needles (m. p. 210°C). − IR (KBr): $\tilde{\nu}$ = 2965 (w) cm^{-1}, 2896 (w), 1972 (s, CO), 1903 (s, CO), 1474 (w), 1275 (m), 1227 (w), 1128 (w), 1069 (m), 1039 (s, acetal-C−O), 1011 (w), 980 (w), 955 (w), 916 (w), 819 (w), 665 (m), 626 (m). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.98−4.35 [m, 12 H, 8(8′)-H, 9(9′)-H, 10-H, 11-H], 5.23 + 5.37 (AA′BB′ line system, 2 × 2 H, arom. H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 66.5 (+, C-10 or C-11), 66.6 [+, C-8(8′) or C-9(9′)], 66.8 (+, C-10 or C-11), 67.4 [+, C-8(8′) or C-9(9′)], 84.4 [−, C-4(7)], 90.9 [−, C-5(6)], 107.7 [+, C-1(3) or C-3a(7a)], 108.5 [+, C-1(3) or C-3a(7a)], 109.7 (+, C-2), 231.1 (+, CO). − MS (70 eV, 100°C): *m/z* (%) = 430 (3) [M^+ + 2], 429 (4) [M^+ + 1], 428 (13) [M^+], 372 (23) [M^+ − 2 CO], 344 (33) [M^+ − 3 CO], 292 (16), 256 (39), 228 (11), 212 (100) [$(C_9H_4O_3)Cr^+$], 148 (21), 128 (27), 104 (14). − HRMS, $C_{18}H_{16}CrO_9$: calcd. 428.01994, found 428.02011. − $C_{18}H_{16}CrO_9$ (428.32): calcd. C 50.48, H 3.77; found C 50.45, H 3.77.

Crystal Structure Analysis of 21:[11] $C_{18}H_{16}CrO_9$, yellow, crystal size 0.40 × 0.40 × 0.25 mm, *a* = 8.506(2), *b* = 17.211(3), *c* = 12.532(2) Å, α = 90, β = 94.13(2), γ = 90°, *V* = 1829.9(6) Å^3, $d_{calcd.}$ = 1.555 gcm^{-1}, μ = 6.80 cm^{-1}, *Z* = 4, crystal system monoclinic, space group $P2_1/a$ (Nr. 14), Stoe IPDS diffractometer, λ = 0.71073 Å, 125 exposures, $2\Theta_{max}$ 56.2°, 16285 measured reflections (±*h*, ±*k*, ±*l*), 4292 independent (R_{int} = 0.03) and 2876 observed reflections [$I > 2\sigma(I)$], 255 refined parameters, H atoms included into the refinement using the riding model, R_1 = 0.0392, wR_2 = 0.1141 based on F^2, min., max. residual electron density −0.30, 0.36 eÅ^{-3}; programs used: SHELXS-86, SHELXL-93. CCDC = 101981.

Tricarbonyl[η^6-2,3-bis(ethylenedioxy)-1-indanone]chromium(0) (22): 200 mg (0.5 mmol) of **21** is treated with 10 mL of conc. hydrochloric acid. The green-yellow mixture is stirred at 25°C for 2 h, the colour changes to orange-yellow. The reaction is traced by TLC [ethyl actate, R_f(**21**) = 0.24, R_f(**22**) = 0.59, R_f(**23**) = 0.69]. When no more **21** and only a minimum amount of **23** is detected, 80 mL of water is added, and the mixture is extracted three times each with 40 mL of diethyl ether. The collected organic layers are washed three times each with 20 mL of water, dried with $MgSO_4$, and filtered. The solvent is removed at reduced pressure, and the orange solid obtained is recrystallized from diethyl ether/petroleum ether. 153 mg (0.4 mmol, 85%) of **22**, orange crystals (m. p. 175°C, dec.). − IR (KBr): $\tilde{\nu}$ = 3079 (w) cm^{-1}, 2963 (w), 2905 (w), 1986 (s, CO), 1929 (s, CO), 1727 (s, CO), 1520 (w), 1471 (w), 1431 (w), 1276 (w), 1186 (m), 1076 (w), 1033 (s, acetal-C−O), 951 (w), 898 (w), 804 (w), 720 (w), 649 (m), 615 (m). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.02−4.53 (m, 8 H, CH_2), 5.23−5.92 (ABCD line system, 4 H, arom. H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 66.7 (+, CH_2), 66.8 (+, CH_2), 67.1 (+, CH_2), 67.9 (+, CH_2), 84.2 (−, C-5 or C-6), 84.8 (−, C-5 or C-6), 90.4 (−, C-3a), 92.1 (+, C-2), 93.1 (−, C-7), 103.7 (+, C-3 or C-7a), 105.6 (+, C-3 or C-7a), 113.8 (+, C-3a), 196.2 (+, C-1), 228.9 (+, CO). − MS (70 eV, 100°C): *m/z* (%) = 386 (2) [M^+ + 2], 385 (4) [M^+ + 1], 384 (8) [M^+], 340 (24), 300 (14) [M^+ − 3 CO], 284 (10), 256 (28), 228 (8), 212 (100) [$(C_9H_4O_3)Cr^+$] , 184 (8), 148 (8), 128 (43) [$(C_6H_4)Cr^+$], 104 (10), 91 (16), 80 (24). − HRMS, $C_{16}H_{12}CrO_8$: calcd. 383.99372, found 383.99432. − $C_{16}H_{12}CrO_8$ (383.99): calcd. C 50.01, H 3.15; found C 48.46, H 3.21.

Tricarbonyl(η^6-2-ethylenedioxy-1,3-indandione)chromium(0) (23): A solution of 1.00 g (2.3 mmol) of **21** in 20 mL of THF is treated with 50 mL of conc. hydrochloric acid. The initially yellow solution is stirred at 50°C until no more **22** is detected by TLC (ca. 4 h, vide supra). 100 mL of water is added to the dark red solution, which then is extracted five times with 40 mL of diethyl ether each. The collected organic layers are washed three times each with 40 mL of water, dried with $MgSO_4$, and filtered. The solvent is removed at reduced pressure, and the red solid obtained is recrystallized from diethyl ether/petroleum ether. 0.73 g (2.1 mmol, 92%) of **23**, red crystals (m. p. 170°C, dec.). − IR (KBr): $\tilde{\nu}$ = 3101 (w) cm^{-1}, 2904 (w), 1996 (s, CO), 1925 (s, CO), 1746 (s, CO), 1723 (s, CO), 1514 (w), 1472 (w), 1192 (s, acetal-C−O), 1146 (m), 1020 (s), 951 (m), 905 (w), 838 (w), 739 (w), 666 (w), 647 (s), 607 (s), 516 (w). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.41 (AA′BB′ line system, 4 H, CH_2), 5.69 + 5.88 (AA′BB′ line system, 2× 2 H, arom. H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 67.9 (+, CH_2), 68.1 (+, CH_2), 85.8 [−, C-5(6)], 92.8 [−, C-4(7)], 95.4 (+, C-2), 96.1 [+, C-3a(7a)], 193.2 [+, C-1(3)], 226.7 (+, CO). − MS (70 eV, 100°C): *m/z* (%) = 340 (28) [M^+], 284 (13) [M^+ − 2 CO], 256 (27) [M^+ − 3 CO], 212 (100) [$(C_9H_4O_3)Cr^+$], 184 (8), 128 (39) [$(C_6H_4)Cr^+$], 104 (8), 91 (5), 80 (6), 76 (7). − HRMS, $C_{14}H_8CrO_7$: calcd. 339.96751, found 339.96847. − $C_{14}H_8CrO_7$ (339.97): calcd. C 49.43, H 2.37; found C 49.44, H 2.66.

Tricarbonyl[η^6-2,3-bis(ethylenedioxy)-*endo*-1-indanol]chromium(0) (24): 0.20 g (5.7 mmol) of sodium borohydride is added to a solution of 1.75 g (4.6 mmol) of **22** in 60 mL of THF/ethanol (1:1). Within 1 min the colour changes from red to yellow. The mixture is stirred for 2 h at 25°C, then 100 mL of water is added. The mixture is extracted three times with 50 mL of diethyl ether each. The collected organic layers are washed three times each with 30 mL of water, dried with $MgSO_4$, and filtered. After solvent removal at reduced pressure a yellow solid is obtained which is purified by column chromatography at silica gel (diethyl ether/petroleum ether, 1:1, length 20 cm, ∅ 3 cm). 1.70 g (4.4 mmol, 96%) of **24** (*de* > 95%, NMR), bright yellow solid (m. p. 160°C, dec.). − IR (KBr): $\tilde{\nu}$ = 3626 (w, OH) cm^{-1}, 3100 (w), 2962 (w), 2899 (w), 1976 (s, CO), 1898 (s, CO), 1434 (w), 1262 (m), 1203 (w), 1035 (m), 949 (w), 663 (w), 629 (m). − ^{1}H NMR (200.1 MHz, [D$_6$]acetone): δ = 3.50 (d, 1 H, $^3J_{1,OH}$ = 10.0 Hz, OH), 3.93−4.37 (m, 8 H, acetal-H), 4.88 (d, 1 H, $^3J_{1,OH}$ = 10.0 Hz, 1-H), 5.44−5.70 (m, 4 H, arom. H). − ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 65.4 (+, CH_2), 65.5 (+, CH_2), 66.2 (+, CH_2), 66.8 (+, CH_2), 70.6 (−, C-1), 86.4 (−, C-4 or C-7), 86.9 (−, C-4 or C-7), 92.6 (−, C-5 or C-6), 93.1 (−, C-5 or C-6), 108.3 (+, C-2 or C-3), 108.5 (+, C-2 or C-3), 112.1

(+, C-3a or C-7a), 114.6 (+, C-3a or C-7a), 232.9 (+, CO). − MS (70 eV, 140°C): *m/z* (%) = 387 (3) [M^+ + 1], 386 (9) [M^+], 330 (36) [M^+ − 2 CO], 302 (54) [M^+ − 3 CO], 256 (9), 242 (42), 214 (98) [$(C_9H_6O_3)Cr^+$], 198 (8), 186 (55), 173 (100), 158 (13), 133 (11), 105 (15), 89 (18), 52 (75). − HRMS, $C_{16}H_{14}CrO_8$: calcd. 386.00938, found 386.00955. − $C_{16}H_{14}CrO_8$ (386.01): calcd. C 49.75, H 3.65; found C 49.86, H 3.70.

Tricarbonyl(η⁶-2-ethylenedioxy-*endo*-1,*endo*-3-indandiol)-chromium(0) (25): 67 mg (1.8 mmol) of sodium borohydride is added to an orange solution of 250 mg (0.7 mmol) of **23** in THF/ethanol (1:1). The mixture is stirred for 2 h at 2°C, and the colour changes to yellow. 50 mL of water is added, and the mixture is extracted three times with 20 mL of diethyl ether each. The collected organic layers are washed three times each with 30 mL of water, dried with $MgSO_4$, and filtered. After solvent removal at reduced pressure a bright yellow solid is obtained, which is recrystallized from diethyl ether/petroleum ether. 214 mg (0.6 mmol, 89%) of **25** (*de* > 95%, NMR), bright yellow solid (m. p. 175°C, dec.). − IR (KBr): $\tilde{\nu}$ = 3551 (m, OH) cm^{-1}, 3110 (w), 2900 (w), 1963 (s, CO), 1865 (s, CO), 1475 (w), 1435 (w), 1396 (m), 1263 (w), 1278 (m), 1196 (m), 1181 (m), 1123 (w), 1095 (w), 1047 (m), 1015 (m), 955 (w), 672 (m), 634 (m). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.63 (d, 2 H, $^3J_{1(3),OH}$ = 12.0 Hz, OH), 4.11−4.31 (m, 4 H, CH_2), 4.84 [d, 2 H, $^3J_{1(3),OH}$ = 12.0 Hz, 1(3)-H], 5.33 + 5.49 (AA′BB′ line system, 4 H, arom. H). − ^{13}C NMR (100.6 MHz, [D_6]DMSO): δ = 65.0 (+, CH_2), 66.7 (+, CH_2), 72.1 [−, C-1(3)], 87.4 [−, C-4(7)], 92.8 [−, C-5(6)], 114.1 [+, C-3a(7a)], 115.4 (+, C-2), 233.9 (+, CO). − MS (70 eV, 100°C): *m/z* (%) = 345 (3) [M^+ + 1], 344 (10) [M^+], 288 (41) [M^+ − 2 CO], 260 (100) [M^+ − 3 CO], 242 (10), 212 (8), 214 (8), 199 (30), 182 (34), 170 (90), 131 (42), 118 (55), 102 (41), 91 (44), 76 (36). − HRMS, $C_{14}H_{12}CrO_7$: calcd. 343.99881, found 343.99894. − $C_{14}H_{12}CrO_7$ (344.00): calcd. C 48.85, H 3.51; found C 49.78, H 3.91.

Tricarbonyl(η⁶-2-ethylenedioxy-*endo*-3-hydroxy-1-indanone)-chromium(0) (26): At 0°C 30 mL of 50% sulfuric acid is added slowly to a solution of 1.24 g (3.2 mmol) of **24** in 60 mL of acetone. Within 4 h the colour changes from yellow to deep red. 150 mL of ice water is added, and the mixture is extracted three times with 40 mL of diethyl ether each. The collected organic layers are washed three times with 30 mL of water each, dried with $MgSO_4$, and filtered. After solvent removal at reduced pressure an orange solid is obtained which is purified by column chromatography at silica gel (diethyl ether/petroleum ether, 1:1, length 50 cm, ∅ 3 cm). 0.83 g (2.4 mmol, 76%) of **26**, orange solid (m. p. 160°C). − IR (KBr): $\tilde{\nu}$ = 3532 (m, OH) cm^{-1}, 3412 (br), 3096 (w), 2960 (w), 2904 (w), 1972 (s, CO), 1892 (s, CO), 1728 (s, CO), 1524 (m), 1432 (w), 1388 (w), 1264 (w), 1200 (m), 1168 (m), 1116 (m), 1036 (m), 1020 (m), 952 (m), 904 (w), 652 (m), 612 (m). − ^{1}H NMR (400.1 MHz, [D_6]-acetone): δ = 4.13−4.36 (m, 4 H, CH_2), 4.48 (br, 1 H, OH), 5.20 (d, 1 H, $^3J_{3,OH}$ = 6.8 Hz, 3-H), 5.67 (t, 1 H, $^3J_{5,6}$ = $^3J_{6,7}$ = 6.3 Hz or $^3J_{4,5}$ = $^3J_{5,6}$ = 6.3 Hz, 5-H or 6-H), 5.79 (d, 1 H, $^3J_{6,7}$ = $^3J_{4,5}$ = 6.3 Hz, 4-H or 7-H), 5.89 (d, 1 H, $^3J_{6,7}$ = $^3J_{4,5}$ = 6.3 Hz, 4-H or 7-H), 6.04 (t, 1 H, $^3J_{5,6}$ = $^3J_{6,7}$ = 6.3 Hz or $^3J_{4,5}$ = $^3J_{5,6}$ = 6.3 Hz, 5-H or 6-H). − ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 66.2 (+, CH_2), 66.3 (+, CH_2), 69.4 (−, C-3), 86.0 (−, C-4 or C-7), 86.2 (−, C-4 or C-7), 91.5 (−, C-6), 92.7 (+, C-2), 95.3 (−, C-5), 104.6 (+, C-3a), 122.6 (+, C-7a), 197.1 (+, C-1), 230.3 (+, CO). − MS (70 eV, 130°C): *m/z* (%) = 344 (3) [M^+ + 2], 343 (5) [M^+ + 1], 342 (15) [M^+], 286 (36) [M^+ − 2 CO], 258 (35) [M^+ − 3 CO], 214 (93) [$(C_9H_6O_3)Cr^+$], 186 (75), 183 (63), 174 (19), 158 (18), 151 (10), 133 (8), 123 (12), 115 (7), 109 (38), 105 (25), 95 (15), 89 (23), 77 (18), 52 (100) [^{52}Cr]. − HRMS, $C_{14}H_6CrO_7$: calcd. 341.98316, found 341.98465. − $C_{14}H_6CrO_7$ (341.98): calcd. C 49.14, H 2.95; found C 48.97, H 2.99.

2,2-Diethoxy-1,3-bis(ethylenedioxy)indane (27): A mixture of 1.00 g (4.00 mmol) of **18**, 0.48 mL (8.00 mmol) of anhydrous ethanol, 1.18 mL (8.00 mmol) of triethyl orthoformiate, and 50 mg (0.30 mmol) of PTSA is stirred for 72 h at 25°C. Then 10 mL of a saturated aqueous solution of sodium carbonate is added, and the mixture is extracted three times with 5 mL of ethyl acetate each. The collected organic layers are washed three times wih 2 mL of water each and are then dried with potassium carbonate. After solvent removal at reduced pressure a colourless solid is obtained which is recrystallized from diethyl ether/petroleum ether, (2:1). 0.84 g (2.6 mmol, 65%) of **27**, colourless solid (m. p. 109°C). − IR (KBr): $\tilde{\nu}$ = 2974 (m) cm^{-1}, 2929 (w), 2899 (m), 1479 (w), 1390 (w), 1320 (w), 1267 (m), 1229 (m), 1117 (m), 1083 (s), 1050 (s, acetal-C−O), 1005 (m), 964 (m), 776 (m), 645 (w). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.21 (t, 6 H, ^3J = 7.0 Hz, CH_3), 3.86 (q, 4 H, ^3J = 7.0 Hz, CH_2CH$_3$), 4.18−4.30 (m, 8 H, CH_2CHH_2), 7.38 (s, 4 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.6 (−, CH_3), 58.3 (+, CH_2CH_3), 65.2 (+,CH_2CH_2), 105.4 (+, C-2), 111.1 [+, C-1(3)], 122.8 [−, C-4(7)], 129.6 [−, C-5(6)], 140.3 [+, C-3a(7a)]. − MS (70 eV, 70°C): *m/z* (%) = 323 (2) [M^+ + 1], 322 (5) [M^+], 292 [21], 265 (5), 249 (9), 221 (20), 193 (24), 177 (13), 162 (8), 149 (100) [$C_9H_9O_2^+$], 133 (16), 121 (10), 104 (54), 76 (28). − HRMS, $C_{17}H_{22}O_6$: calcd. 322.14164, found 322.14163. − $C_{17}H_{22}O_6$ (322.14): calcd. C 63.34, H 6.88; found C 63.09, H 6.63.

Tricarbonyl[η⁶-2,2-diethoxy-1,3-bis(ethylenedioxy)indane]-chromium(0) (28): A mixture of 460 mg (1.4 mmol) of **27** and 471 mg (2.1 mmol) of hexacarbonylchromium(0) in 50 mL of dibutyl ether and 5 mL of THF is heated at reflux for 20 h. The solution changes its colour from colourless to yellow. Upon cooling to room temperature a yellow solid precipitates. After addition of 20 mL of petroleum ether the crystallization is completed at −30°C for 16 h. After decanting the solvent mixture and drying at 0.001 mbar 504 mg (1.1 mmol, 79%) of **28** is obtained as a yellow solid (m. p. 215°C, dec.). − IR (KBr): $\tilde{\nu}$ = 2976 (w) cm^{-1}, 2904 (w), 1976 (s, CO), 1912 (s, CO), 1864 (s, CO), 1480 (w), 1440 (w), 1284 (w), 1256 (m), 1232 (m), 1116 (w), 1096 (w), 1048 (m), 1000 (w), 660 (m), 624 (m). − ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 1.18 (t, 3 H, ^3J = 7.2 Hz, CH_3), 1.21 (t, 3 H, ^3J = 7.2 Hz, CH_3), 3.67 (q, 2 H, ^3J = 7.2, CH_2CH$_3$), 3.94 (q, 2 H, ^3J = 7.2, CH_2CH$_3$), 4.08−4.31 (m, 8 H, CH_2CH_2), 5.46 + 5.62 (AA′BB′ line system, 4 H, arom. H). − ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 14.8 (−, CH_3), 14.8 (−, CH_3), 57.6 (+, CH_2CH_3), 57.9 (+, CH_2CH_3), 65.3 (+, CH_2CH_2), 65.8 (+,CH_2CH_2), 85.4 [−, C-4(7)], 92.2 [−, C-5(6)], 104.5 (+, C-2), 110.35 [+, C-3a(7a) or C-1(3)], 110.41 [+, C-3a(7a) or C-1(3)], 232.1 (+, CO). − MS (70 eV, 140°C): *m/z* (%) = 458 (4) [M^+], 402 (66) [M^+ − 2 CO], 374 (51) [M^+ − 3 CO], 330 (29), 286 (26), 258 (79), 242 (61), 226 (34), 212 (94) [$(C_9H_4O_3)Cr^+$], 198 (85), 173 (28), 157 (88), 148 (51), 128 (33), 104 (37), 52 (100) [^{52}Cr]. − HRMS, $C_{20}H_{22}CrO_9$: calcd. 458.06689, found 458.06690. − $C_{20}H_{22}CrO_9$ (458.07): calcd. C 52.41, H 4.83; found C 52.53, H 4.86.

Tricarbonyl(η⁶-2,2-diethoxy-3-ethylenedioxy-1-indanone)-chromium(0) (29): 30 mL of 50% sulfuric acid is carefully added at 0°C to a solution of 400 mg (0.87 mmol) of **28** in 70 mL of acetone. The yellow solution is stirred for 4 h at 20°C, the colour changing to dark red. After addition of 100 mL of ice water the mixture is extracted three times with 30 mL of *tert*-butylmethyl ether (TBME) each. The collected organic layers are washed three times each with 20 mL of a saturated aqueous solution of sodium carbonate and another three times each with 20 ml of water. After drying with

potassium carbonate, filtration, and solvent removal at reduced pressure a red solid is obtained which is purified by column chromatography at silica gel (TBME/petroleum ether, 2:1, length 25 cm, ∅ 3 cm). 306 mg (0.74 mmol, 85%) of **29**, orange solid (m. p. 175°C, dec.). − IR ($CHCl_3$): $\tilde{\nu}$ = 3047 (w) cm^{-1}, 2980 (w), 2900 (w), 1992 (s, CO), 1936 (s, CO), 1728 (m, ketone), 1516 (w), 1424 (w), 1392 (w), 1260 (w), 1228 (w), 1176 (m), 1072 (m), 1048 (m), 1008 (w), 956 (w), 820 (w), 648 (w), 608 (w). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.10−1.40 (m, 6 H, CH_3), 3.60−3.94 (m, 4 H, CH_2CH_3), 4.35−4.50 (m, 4 H, CH_2CH_2), 5.23 (t, 1 H, ^3J = 6.0, Hz, 5-H or 6-H), 5.41 (d, 1 H, ^3J = 6.0 Hz, 4-H or 7-H), 5.65 (t, 1 H, ^3J = 6.0, Hz, 5-H or 6-H), 5.79 (d, 1 H, ^3J = 6.0 Hz, 4-H or 7-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.5 (CH_3), 16.2 (CH_3), 60.2 (CH_2CH_3), 60.7 (CH_2CH_3), 66.4 (CH_2CH_2), 67.6 (CH_2CH_2), 83.5 (CH, C-4 or C-5 or C-6 or C-7), 86.3 (CH, C-4 or C-5 or C-6 or C-7), 90.2 (CH, C-4 or C-5 or C-6 or C-7), 91.6 (C_q, C-2), 94.8 (CH, C-4 or C-5 or C-6 or C-7), 98.8 (C_q, C-3), 109.1 (C_q, C-3a), 118.1 (C_q, C-7a), 194.4 (C_q, C-1), 229.8 (C_q, CO). − MS (70 eV, 25°C): *m/z* (%) = 416 (2) [M^+ + 2], 415 (6) [M^+ + 1], 414 (14) [M^+], 358 (72), [M^+ − 2 CO], 330 (69) [M^+ − 3 CO], 301 (18), 186 (57), 272 (26), 258 (74), 212 (100) [(indantrione)Cr^+], 185 (54), 173 (55), 157 (90), 148 (40), 128 (65), 104 (56), 96 (59).

(η^6-2,2-Diethoxy-1,3-indandione)chromium(0) (30): 30 mL of conc. hydrochloric acid is added at 20°C to a solution of 150 mg (0.33 mmol) of **28** in 30 mL of THF. The solution is stirred for 8 h at 45°C, changing its colour from yellow to dark red. After addition of 100 mL of ice water the mixture is extracted three times each with 30 mL of TBME. The collected organic layers are washed three times each with 20 mL of a saturated aqueous solution of sodium carbonate and another three times each with 20 mL of water. After drying with potassium carbonate, filtration, and solvent removal at reduced pressure a brown oil is obtained which is purified by column chromatography at silica gel (TBME/petroleum ether, 1:1, length 20 cm, ∅ 3 cm). Fraction I: 59 mg (0.16 mmol, 48%) of **30**, red solid (m. p. 165°C, dec.). II: 25 mg (0.06 mmol, 18%) of **29**.

30: IR ($CHCl_3$): $\tilde{\nu}$ = 3045 (w) cm^{-1}, 2980 (w), 2960 (w), 2008 (s, CO), 1944 (s, CO), 1744 (m. ketone-CO), 1720 (m, ketone-CO), 1600 (w), 1260 (w), 1176 (w), 1140 (w), 1100 (w), 1056 (w), 956 (w), 636 (w), 600 (w). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.23 (m, 6 H, CH_2CH_3), 3.90−4.10 (m, 4 H, OCH_2CH_3), 5.65 + 5.88 (AA′BB′ line system, 4 H, arom. H).

1,3-Bis(ethylenedioxy)indane (32): A solution of 2.00 g (13.7 mmol) of 1,3-indandione (**31**)[49], 1.83 mL (32.9 mol) of 1,2-ethanediol, and 0.02 g (0.1 mmol) of PTSA is heated at reflux with azeotropic water removal for 48 h, the solution becoming deep red. After solvent removal at reduced pressure a red, greasy solid is obtained, which is crystallized from ethyl acetate/petroleum ether (1:1). 2.60 g (11.1 mmol, 81%) of **32** as a colourless solid (m. p. 144°C). − IR (KBr): $\tilde{\nu}$ = 3052 (w) cm^{-1}, 2976 (w), 2896 (m), 1460 (w), 1320 (m), 1268 (m), 1128 (m), 1064 (m), 1036 (s, acetal-C-O), 940 (m), 804 (m), 772 (m). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.58 (s, 2 H, 2-H), 4.10 + 4.21 [AA′BB′, 2× 2 H, 8(8′)-H, 9(9′)-H], 7.37−7.49 (m, 4 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 50.0 (+, C-2), 66.2 [+, C-8(8′), C-(9,9′)], 113.4 [+, C-1(3)], 123.6 [−, C-4(7)], 130.9 [−, C-5(6)], 143.1 [+, C-3a(7a)]. − MS (70 eV, 25°C): *m/z* (%) = 235 (2) [M^+ + 1], 234 (7) [M^+], 190 (14), 174 (14), 162 (93), 146 (22), 135 (19), 118 (13), 105 (100) [$C_7H_5O^+$], 76 (30). − HRMS, $C_{13}H_{14}O_4$: calcd. 234.08920, found 234.08902. − $C_{13}H_{14}O_4$ (234.09): calcd. C 66.66, H 6.02; found C 66.61, H 5.89.

Tricarbonyl[η^6-1,3-bis(ethylenedioxy)indane]chromium(0) (33): A mixture of 1.30 g (5.6 mmol) of **32** and 2.00 g (9.1 mmol) of hexacarbonylchromium(0) in 120 mL of dibutyl ether and 12 mL of THF is heated at reflux for 20 h. The initially colourless solution becomes dark yellow. The reaction mixture is filtered through silica gel (length 10 cm, ∅ 3 cm). Unreacted starting material is eluted with diethyl ether/petroleum ether (1:1), then the product is eluted with ethyl acetate. The solvent is removed at reduced pressure, and 1.70 g (4.6 mmol, 82%) of **33** is obtained as a yellow powder (m. p. 245°C, dec.). − IR (KBr): $\tilde{\nu}$ = 3084 (w) cm^{-1}, 2984 (w), 2956 (w), 2880 (w), 1956 (s, CO), 1896 (s, CO), 1316 (m), 1280 (m), 1116 (m), 1072 (s, acetal-C−O), 1036 (m), 948 (m), 820 (m), 656 (s), 632 (m). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.33 (d, 1 H, $^2J_{anti\text{-}2,syn\text{-}2}$ = −14.0 Hz, *syn*-2-H or *anti*-2-H), 2.63 (d, 1 H, $^2J_{anti\text{-}2,syn\text{-}2}$ = −14.0 Hz , *syn*-2-H or *anti*-2-H), 4.00−4.35 (m, 8 H, OCH_2CH_2O), 5.28 + 5.42 (AA′BB′ line system, 2× 2 H, arom. H). − ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 42.2 (+, C-2), 65.0 (+, OCH_2), 66.0 (+, OCH_2), 88.0 [−, C-4(7)], 94.1 [−, C-5(6)], 110.8 [+, C-1(3)], 113.5 [+, C-3a(7a)], 232.5 (+, CO). − MS (70 eV, 90°C): *m/z* (%) = 371 (1) [M^+ + 1], 370 (2) [M^+], 286 (11) [M^+ − 3 CO], 234 (8), 214 (16), 190 (15), 174 (24), 162 (96), 146 (52), 135 (40), 119 (35), 105 (100) [$C_7H_5O^+$], 90 (39), 76 (84), 52 (44). − HRMS, $C_{16}H_{14}CrO_7$: calcd. 370.01446, found 370.01437. − $C_{16}H_{14}CrO_7$ (370.01) : calcd. C 51.90, H 3.81; found C 51.91, H 3.82.

Crystal Structure Analysis of 33:[11] $C_{16}H_{14}CrO_7$, yellow, *a* = 8.335(1), *b* = 10.064(1), *c* = 18.695(2) Å, α = 90, β = 100.84(1), γ = 90°, *V* = 1540.2 Å^3, $d_{calcd.}$ = 1.597 gcm^{-1}, μ = 7.80 cm^{-1}, *T* = 200 K, *Z* = 4, monoclinic, space group $P2_1/c$ (Nr. 14), Stoe IPDS diffractometer, λ = 0.71073 Å, 133 exposures, $2\Theta_{max}$ 56°, 15000 measured reflections (±*h*, ±*k*, ±*l*), 3516 independent and 1799 observed reflections [$I > 2\sigma(I)$], 218 refined parameters, H atom positions found and included using the riding model, R_1 = 0.0443, wR_2 = 0.0673, min., max. residual electron density −0.54, 0.38 e$\mathring{A}^{-3}$; programs used: SHELXS-86, SHELXL-93. CCDC 102125.

Tricarbonyl(η^6-1,3-indandione)chromium(0) (6) and Tricarbonyl[η^6-2-(2-methylethylene)-1,3-indandione]chromium(0) (35): a) A solution of 3.00 g (8.2 mmol) of **33** in 100 mL of THF is mixed with 50 mL of 50% sulfuric acid. A red solution is formed, whose colour continuously deepens. After 4−5 h no more **33** is detected by TLC, and 100 mL of water is added. The mixture is extracted three times with 50 mL each of diethyl ether, and the collected organic layers are washed three times with 20 mL each of a saturated aqueous solution of sodium bicarbonate. After drying with $MgSO_4$, filtration, and solvent removal at reduced pressure 2.17 g (7.7 mmol, 94%) of **6** is obtained as a red-brown solid (m. p. 125°C).

b) 50 mL of 50% sulfuric acid is slowly added to a solution of 4.40 g (11.9 mmol) of **33** in 50 mL of acetone. Immediately a deep red solution is formed, which is stirred for 4 h at 25°C. 100 mL of ice water is added, and the mixture is extracted three times each with 30 mL of diethyl ether. The collected organic layers are washed three times each with 50 mL of water, dried with $MgSO_4$, filtered, and the solvent is removed at reduced pressure. A brown solid is obtained which is purified by column chromatography at silica gel (diethyl ether/petroleum ether, 1:1, then diethyl ether, length 30 cm, ∅ 5 cm). Fraction I: 190 mg (0.6 mmol, 5%) of **35**, orange-brown solid (m. p. 151°C). II: 3.00 g (10.7 mmol, 90%) of **6**.

6: IR (KBr): $\tilde{\nu}$ = 3100 (w) cm^{-1}, 2960 (w), 2920 (w), 1995 (s, CO), 1942 (s, CO), 1907 (s, CO), 1740 (m, CO), 1709 (s), 1364 (w), 1252 (m), 650 (m), 604 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.29 (d, 1 H, $^2J_{anti\text{-}2,syn\text{-}2}$ = −21.9 Hz, *syn*-2-H or *anti*-2-H), 3.36 (d, 1 H, $^2J_{anti\text{-}2,syn\text{-}2}$ = −21.9 Hz , *anti*-2-H or *syn*-2-H), 6.07 + 6.18 (AA′BB′ line system, 2× 2 H, arom. H). − ^{13}C NMR (100.6

MHz, [D$_6$]acetone): δ = 43.7 (+, C-2), 88.3 [−, C-4(7)], 95.9 [−, C-5(6)], 102.8 [+, C-3a(7a)], 195.9 [+, C-1(3)], 230.2 (+, CO). − MS (70 eV, 80°C): *m/z* (%) = 284 (5) [M$^+$ + 2], 283 (16) [M$^+$ + 1], 282 (44) [M$^+$], 254 (2) [M$^+$ − CO], 226 (44) [M$^+$ − 2 CO], 198 (52) [M$^+$ − 3 CO], 146 (44), 119 (13), 104 (43), 90 (27), 76 (48), 52 (100) [^{52}Cr]. − HRMS, $C_{12}H_6CrO_5$: calcd. 281.96203, found 281.96196. − $C_{12}H_6CrO_5$ (281.96): calcd. C 51.08, H 2.14; found C 51.17, H 2.38.

35: IR (KBr): $\tilde{\nu}$ = 3075 (w) cm^{-1}, 3036 (w), 2906 (w), 1996 (s, CO), 1940 (s, CO), 1716 (m), 1676 (m), 1612 (m), 1420 (w), 1404 (w), 1372 (w), 1252 (w), 1132 (w). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.59 (s, 6 H, CH_3), 5.58 + 5.99 (AA′BB′ line system, 4 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.8 (−, CH_3), 87.7 [−, C-4(7)], 93.2 [−, C-5(6)], 99.9 [+, C-3a(7a)], 125.2 (+, = *C*(CH$_3$)$_2$), 172.5 (+, C-2), 189.5 [+, C-1(3)], 229.6 (+, CO). − MS (70 eV, 100°C): *m/z* (%) = 323 (1) [M$^+$ + 1], 322 (5) [M$^+$], 321 (16), 266 (17) [M$^+$ − 2 CO], 236 (100) [M$^+$ − 3 CO], 223 (9), 186 (4), 167 (4), 115 (6), 52 (82). − HRMS, $C_{15}H_{10}CrO_5$: calcd. 321.99333, found 321. 99332.

Tricarbonyl(η^6-*endo*-1,*endo*-3-indanediol)chromium(0) (34): In a 100 mL Schlenk flask a solution of 100 mg (0.35 mmol) of **6** in 20 mL of THF and 50 mL of ethanol and 50 mg (1.32 mmol) of sodium borohydride are mixed. Within 4 h at 25°C the colour of the mixture changes from red-brown to yellow-orange. 60 mL of water is added, and the mixture is extracted three times each with 15 mL of diethyl ether. The collected organic layers are washed three times each with 10 mL of water, dried with $MgSO_4$, and filtered. After solvent removal at reduced pressure 80 mg (0.28 mmol, 80%) of **34** (*de* > 95%, NMR) is obtained as a yellow powder, which is recrystallized from ethyl acetate (m. p. 205°C, dec.). − IR (KBr): $\tilde{\nu}$ = 3586 (w, OH) cm^{-1}, 3430 (w, OH), 3080 (w), 2960 (w), 1960 (s, CO), 1880 (s, CO), 1450 (w), 1100 (m), 1090 (w), 1040 (m), 802 (m), 668 (w), 640 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.80 (dq, 1 H, $^2J_{\text{syn-2,}anti\text{-2}}$ = −11.6 Hz, $^3J_{\text{syn-2,1(3)}}$ = 9.2 Hz or $^3J_{\text{anti-2,1(3)}}$ = 9.2 Hz, *syn*-2-H or *anti*-2-H), 2.66 (dq, 1 H, $^2J_{\text{syn-2,}anti\text{-2}}$ = −11.6 Hz, $^3J_{\text{syn-2,1(3)}}$ = 6.6 Hz or $^3J_{\text{anti-2,1(3)}}$ = 6.6 Hz, *syn*-2-H or *anti*-2-H), 4.75 [m, 2 H, 1(3)-H], 4.95 (m, 2 H, OH), 5.50 + 5.63 (AA′BB′ line system, 2× 2 H, arom. H). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 41.9 (+, C-2), 70.0 [+, C-1(3)], 89.2 [−, C-4(7)], 93.7 [−, C-5(6)], 120.9 [+, C-3a(7a)], 235.2 (+, CO). − MS (70 eV, 120°C): *m/z* (%) = 288 (2) [M$^+$ + 2], 287 (9) [M$^+$ + 1], 286 (32) [M$^+$], 230 (47) [M$^+$ − 2 CO], 202 (50) [M$^+$ − 3 CO], 184 (72), 166 (18), 132 (39), 116 (100) [$C_8H_4O_2^+$], 103 (42), 89 (47), 69 (49), 52 (60). − HRMS, $C_{12}H_{10}CrO_5$: calcd. 285.99333, found 285.99322. − $C_{12}H_{10}CrO_5$ (285.99): calcd. C 50.36, H 3.52; found C 50.43, H 3.60.

Tricarbonyl[η^6-2-(*N*,*N*-dimethylaminomethylene)-1,3-indandione]-chromium(0) (36): A solution of 300 mg (1.06 mmol) of **6** and 0.27 mL (2.12 mmol) of dimethylformamide dimethylacetal [dimethoxy-(dimethylamino)methane] in 1 mL of anhydrous dichloromethane is stirred for 16 h at 25°C with formation of an orange suspension. The solvent is removed at reduced pressure, and the orange-brown residue is purified by column chromatography at silica gel (ethyl acetate/diethyl ether, 1:1, length 15 cm, ∅ 3 cm). 337 mg (1.00 mmol, 94%) of **36** as an orange solid (m. p. 190°C, dec.). − IR (KBr): $\tilde{\nu}$ = 3444 (br) cm^{-1}, 2960 (w), 2936 (w), 1964 (s, CO), 1916 (s, CO), 1880 (s, CO), 1696 (m, CO), 1644 (s), 1612 (s), 1536 (w), 1484 (w), 1432 (m), 1380 (s), 1136 (w), 1004 (w), 660 (m), 624 (m). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.52 (s, 1 H, CH_3), 3.75 (s, 3 H, CH_3), 5.86 (s, 2 H, arom. H), 6.11 (s, 2 H, arom. H), 7.46 [s, 1 H, =C*H*-N(CH$_3$)$_2$]. − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 43.6 (−, CH_3), 47.8 (−, CH_3), 88.7 (−, C-4, C-7), 94.8 (−, C-5, C-6), 99.7 (+, C-2), 100.7 (+, C-3a, C-7a), 153.7 [+, = *C*H-N(CH$_3$)$_2$], 185.5 (+, C-1 or C-3), 188.5 (+, C-1 or C-3), 232.0 (+, CO). − MS (70 eV, 160°C): *m/z* (%) = 339 (1) [M$^+$ + 2], 338 (5) [M$^+$ + 1], 337 (20) [M$^+$], 281 (19) [M$^+$ − 2 CO], 253 (69) [M$^+$ − 3 CO], 238 (100) [(C$_{11}$H$_8$NO$_2$)Cr$^+$], 223 (6), 210 (13), 197 (10), 181 (7), 153 (8), 95 (18), 52 (53). − HRMS, $C_{15}H_{11}CrNO_5$: calcd. 337.00423, found 337.00293. − $C_{15}H_{11}CrNO_5$ (337.00): calcd. C 53.42, H 3.29, N 4.15; found C 52.70, H 3.35, N 3.97.

Tricarbonyl(η^6-2-diazo-1,3-indandione)chromium(0) (37): 0.16 mL (1.24 mmol) of triethylamine is added to a solution of 250 mg (0.89 mmol) of **6** in 5 mL of THF. 250 mg (1.27 mmol) of *para*-tosyl azide is added, and after 30 min no more **6** is detected by TLC. The solvent is removed at reduced pressure, and the dark brown, solid residue is purified by column chromtography (diethyl ether/petroleum ether, 1:2, then 1:1, length 20 cm, ∅ 3 cm). 233 mg (0.76 mmol, 85%) of **37** as a red-brown solid (m. p. 135°C). − IR ($CHCl_3$): $\tilde{\nu}$ = 3034 (w) cm^{-1}, 2360 (w), 2340 (w), 2124 (s, CN_2), 1996 (s, CO), 1944 (s, CO), 1716 (w, CO), 1688 (s, CO), 1600 (w), 1400 (w), 1344 (s), 1196 (w), 1140 (w), 640 (m), 604 (m). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 5.58 + 5.99 (AA′BB′ - System, 2× 2 H, arom. H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 70.4 (+, C-2), 87.7 [−, C-4(7)], 92.1 [−, C-5(6)], 97.8 [+, C-3a(7a)], 181.2 [+, C-1(3)], 229.4 (+, CO). − MS (70 eV, 110°C): *m/z* (%) = 310 (1) [M$^+$ + 2], 309 (3) [M$^+$ + 1], 308 (11) [M$^+$], 307 (43) [M$^+$ − 1], 252 (29) [M$^+$ − 2 CO], 224 (57) [M$^+$ − 3 CO], 196 (52), 168 (92), 140 (82), 114 (13), 90 (14), 80 (11), 52 (100) [^{52}Cr]. − HRMS, $C_{12}H_4CrN_2O_5$: calcd. 307.95253, found 307.95224. − $C_{12}H_4CrN_2O_5$ (308.16): calcd. C 46.77, H 1.31, N 9.09; found C 46.80, H 1.42, N 9.02.

Tricarbonyl{η^6-2-phenylspiro(cyclopropane-1,2′-[2*H*]inden)-1′,3′-dione}chromium(0) (38): A solution of 250 mg (0.82 mmol) of **37**, 0.94 mL (854 mg, 8.20 mmol) of phenylethene, and 10 mg (0.02 mmol) of rhodium(II) acetate in 30 mL of anhydrous benzene is heated at reflux for 2 h. The solvent is removed at reduced pressure, and the black residue is purified by column chromatography at silica gel (diethyl ether/petroleum ether, 1:1, length 20 cm, ∅ 3 cm). 100 mg (0.26 mmol, 32%) of **38** (*de* > 95%, NMR, presumably the *exo* diastereomer) as an orange-red solid (m. p. 152°C). − IR (KBr): $\tilde{\nu}$ = 3068 (w) cm^{-1}, 2960 (w), 1988 (s, CO), 1924 (s, CO), 1744 (w, ketone), 1700 (m, ketone), 1384 (w), 1308 (w), 1260 (w), 1220 (w), 1160 (w), 1096 (w), 1040 (w), 812 (w), 704 (w), 644 (w), 608 (w). − ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.23 (dd, 1 H, $^2J_{1,1}$ = − 4.4 Hz, $^3J_{1,2}$ = 9.0 Hz, 1-H), 2.49 (dd, 1 H, $^2J_{1,1}$ = − 4.4 Hz, $^3J_{1,2}$ = 9.0 Hz, 1-H), 3.43 (t, 1 H, $^3J_{1,2}$ = 9.0 Hz, 2-H), 6.00−6.30 (ABCD line system, 4 H, arom. H), 7.21−7.43 (m, 5 H, phenyl-H). − ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 22.2 (+, C-1), 41.0 (+, C-2′), 41.8 (−, C-2), 87.6 (−, C-5′ or C-6′), 87.7 (−, C-5′ or C-6′), 94.5 (−, C-4′ or C-7′), 94.6 (−, C-4′ or C-7′), 99.9 (+, C-3a′ or C-7a′), 101.1 (+, C-3a′ or C-7a′), 127.5 (−, C-6), 127.8 (−, C-5 or C-7), 129.4 (−, C-4 or C-8), 133.5 (+, C-3), 193.2 (+, C-1′ or C-3′), 195.2 (+, C-1′ or C-3′), 229.7 (+, CO). − MS (70 eV, 140°C): *m/z* (%) = 386 (3) [M$^+$ + 2], 385 (7) [M$^+$ + 1], 384 (14) [M$^+$], 328 (8) [M$^+$ − 2 CO], 300 (100) [M$^+$ − 3 CO], 248 (11), 171 (25), 155 (22), 140 (8), 107 (18), 91 (65), 52 (63). − HRMS, $C_{20}H_{12}CrO_5$: calcd. 384.00898, found 384.01050.

Tricarbonyl{η^6-3-oxa-2-phenylcyclopenta[*a*]inden-8(8a)-one}chromium(0) (39): A mixture of 230 mg (0.77 mmol) of **37** and 10 mg (0.02 mmol) of rhodium(II) acetate in 7.0 mL of phenylethyne is stirred for 3 h at 50−60°C. After removal of the phenylethyne at 0.001 mbar a dark brown solid is obtained, which is purified by column chromatography at silica gel (diethyl ether/petroleum ether, 1:1, length 20 cm, ∅ 3 cm). 207 mg (0.54 mmol, 70%) of **39** as a

dark brown solid (m. p. 162°C, dec.). – IR (KBr): $\tilde{\nu}$ = 3100 (w) cm^{-1}, 2960 (w), 2924 (w), 1996 (s, CO), 1976 (s, CO), 1892 (s, CO), 1700 (s, ketone), 1524 (w), 1476 (w), 1260 (m), 1164 (w), 1136 (w), 1096 (m), 1064 (m), 1020 (m), 872 (m), 800 (m), 764 (m), 652 (m), 600 (m). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.39–6.16 (ABCD line system, 4 H, arom. H), 6.76 (s, 1 H, 3-H), 7.33–7.70 (m, 5 H, phenyl-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 83.1 (CH, C-6′ or C-7′ or C-8′ or C-9′), 86.7 (CH, C-6′ or C-7′ or C-8′ or C-9′), 90.2 (CH, C-6′ or C-7′ or C-8′ or C-9′), 91.1 (CH, C-6′ or C-7′ or C-8′ or C-9′), 97.0 (C_q, C-5a′ or C-9a′), 98.1 (C_q, C-5a′ or C-9a′), 100.8 (CH, C-3), 124.3 [CH, C-12′(16′) or C-13′(15′)], 127.2 (C_q, C-4), 129.0 [CH, C-12′(16′) or C-13′(15′)], 129.1 (CH, C-14′), 129.2 (C_q, C-11′), 162.4 (C_q, C-2), 168.9 (C_q, C-5), 181.9 (C_q, C-10′), 230.5 (C_q, CO). – MS (70 eV, 140°C): *m/z* (%) = 384 (2) [M^+ + 2], 383 (5) [M^+ + 1], 382 (14) [M^+], 326 (13) [M^+ – 2 CO], 298 (100) [M^+ – 3 CO], 270 (8), 246 (14), 189 (20), 140 (4), 105 (5), 77 (6), 52 (66). – HRMS, $C_{20}H_{10}O_5Cr$: calcd. 381.99333, found 381.99063.

Tricarbonyl(η^6-indantrione)chromium(0) (7) and Tricarbonyl(η^6-ninhydrin)chromium(0) (8): 300 mg (1.06 mmol) of **6** is mixed with 32.0 mL (3.2 mmol) of a –28°C cold 0.1 M solution of dimethyldioxirane in acetone. **6** completely reacts within one minute. The obtained dark brown solution is stirred for 5 min at –28°C. Then 100 mL of water is added, and the mixture is extracted three times each with 30 mL of diethyl ether. After drying of the collected organic layers with $MgSO_4$ the solvent is removed at reduced pressure, and the black residue is purified by column chromatography at silica gel (diethyl ether/petroleum ether, 1:1, length 20 cm, ∅ 3 cm). 249 mg (0.79 mmol, 75%) of **8** as a brown solid (m. p. 105°C, dec.). The NMR spectra show the presence of some **7**.[50]

8: IR (KBr): $\tilde{\nu}$ = 3396 (w, OH) cm^{-1}, 3092 (w), 1996 (s, CO), 1936 (s, CO), 1744 (s, ketone), 1716 (s, ketone), 1260 (w), 1188 (w), 1092 (w), 1020 (w), 996 (w), 936 (w), 640 (m), 596 (m). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 6.15 (s, 4 H, arom. H), 6.70 (s, 1 H, *endo*-OH or *exo*-OH), 6.83 (s, 1 H, *endo*-OH or *exo*-OH). – ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 86.6 (+, C-2), 87.1 [–, C-4(7)], 95.1 [–, C-5(6)], 96.5 [+, C-3a(7a)], 193.7 [+, C-1(3)], 228.5 (+, CO). – MS (70 eV, 110°C): *m/z* (%) = 297 (5) [M^+ + 1 – H_2O], 296 (22) [M^+ – H_2O], 212 (54) [(indantrione)Cr^+], 184 (15), 128 (100) [(C_6H_4)Cr^+], 104 (12), 80 (14). – HRMS, $C_{12}H_6CrO_7$: calcd. 295.94130, found 295.94122.

7: ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 6.30 + 6.43 (AA′BB′ line system, 2 + 2 H, arom. H). – ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 88.1 [–, C-4(7)], 95.9 [–, C-5(6)], 100.1 [+, C-3a(7a)], 178.3 [+, C-1(3)], 187.1 (+, C-2), 227.4 (+, CO).

Tricarbonyl[η^6-(1,3-dioxoindane)-2-*spiro*-2′-(4′,5′-dimethyl-3′,6′-dihydro-2′*H*-pyrane)]chromium(0) (42/43): 157 mg (1.91 mmol) of 2,3-dimethyl-1,3-butadiene (**41**) is added to a solution of 150 mg (0.48 mmol) of **8** in 5 mL of THF. After addition of 200 mg of molecular sieves (3 Å) the mixture is allowed to stand for 72 h at 20°C. The red solution is then separated from the molecular sieves, and the solvent is removed at reduced pressure. The crude product is purified by column chromatography (TBME/petroleum ether, 1:4, length 30 cm, ∅ 3 cm). Fraction I: 100 mg (0.27 mmol, 55%) of **42**/**43** as an orange-red solid (mixture of diastereomers, *de* = 76%, NMR). II: 20 mg (0.06 mmol, 13%) of **8**.

42/**43**: IR (KBr): $\tilde{\nu}$ = 3084 (w) cm^{-1}, 2960 (w), 2920 (w), 2860 (w), 1992 (s, CO), 1932 (s, CO), 1736 (s, ketone), 1704 (s, ketone), 1636 (w), 1616 (w), 1448 (w), 1424 (w), 1284 (w), 1260 (w), 1144 (w), 1092 (m), 1028 (m), 800 (w), 640 (m), 604 (m). – **42**: ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 1.61 (s, 3 H, OCH_2CCH_3), 1.69 (s, 3 H, CCH_2CCH_3), 2.29 (s, 2 H, CCH_2), 4.26 (s, 2 H, OCH_2), 6.05–6.14 (m, 4 H, arom. H). – ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 12.9 (–, CCH_2CCH_3), 17.4 (–, OCH_2CCH_3), 31.1 (+, CCH_2), 67.2 (+, OCH_2), 73.5 (+, C-2), 86.9 [–, C-4(7)], 94.9 [–, C-5(6)], 97.6 [+, C-3a(7a)], 119.1 (+, CCH_2CCH_3), 123.9 (+, OCH_2CCH_3), 195.6 [+, C-1(3)], 228.6 (+, CO). – **42**/**43**: MS (70 eV, 140°C): *m/z* (%) = 378 (32) [M^+], 322 (27) [M^+ – 2 CO], 294 (59) [M^+ – 3 CO], 276 (25), 264 (36), 212 (94) [(indantrione)Cr^+], 155 (27), 128 (55, $C_6H_4Cr^+$), 112 (24), 99 (100), 76 (23), 52 (94) [^{52}Cr]. – HRMS, $C_{13}H_8O_5Cr$: calcd. 378.01955, found 378.01849.

Tricarbonyl[η^6-(1,3-dioxoindane)-2-*spiro*-2′-(3′-trimethylsiloxy-6′-dihydro-2′*H*-pyrane)]chromium(0) (45): 387 mL (2.39 mmol) of 1-(trimethylsiloxy)butadiene (**44**) is added to a solution of 150 mg (0.48 mmol) of **8** in anhydrous benzene. After addition of 200 mg of molecular sieves the mixture is allowed to stand for 7 d at 20°C. The red solution is separated from the molecular sieves, and the solvent is removed at reduced pressure. The crude product is purified by column chromatography (TBME/petroleum ether, 1:1, length 30 cm, ∅ 3 cm). Fraction I: 121 mg (0.28 mmol, 58%) of **45** as an orange-red solid (*de* > 95%, NMR; m. p. 202°C). II: 30 mg (0.09 mmol, 20%) of **8**.

45: IR (KBr): $\tilde{\nu}$ = 3084 (w) cm^{-1}, 2960 (w), 2924 (w), 2012 (s, CO), 1932 (s, CO), 1736 (s, ketone), 1704 (s, ketone), 1508 (w), 1420 (w), 1400 (w), 1280 (w), 1252 (w), 1228 (w), 1188 (w), 1168 (w),1084 (w), 1044 (m), 888 (w), 864 (w), 844 (m), 640 (w), 596 (m). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 0.15 (s, 9 H, $OSiMe_3$), 2.36 (m, 1 H, CH_2), 2.52 (m, 1 H, CH_2), 5.81 (m, 1 H, CH_2CH), 5.90–5.96 (m, 2 H, $OCHOSiMe_3$, CH_2CHCH), 6.10 + 6.15 (AA′BB′ line system, 2 + 2 H, arom. H). – ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = – 0.4 (–, $OSiMe_3$), 26.2 (+, CH_2), 75.3 (+, C-2), 86.9 (–, C-4 or C-7), 87.5 (–, C-4 or C-7), 91.0 (–, $OCHOSiMe_3$), 94.8 (–, C-5 or C-6), 95.3 (–, C-5 or C-6), 97.1 (+, C-3a or C-7a), 97.2 (+, C-3a or C-7a), 122.5 (–, CH_2CH), 129.3 (–, CH_2CHCH), 193.7 (+, C-1 or C-3), 196.2 (+, C-1 or C-3), 228.7 (+, CO). – MS (70 eV, 150°C): *m/z* (%) = 439 (4) [M^+ + 1], 438 (6) [M^+], 354 (20) [M^+ – 3 CO], 339 (100) [M^+ – 3 CO – CH_3], 321 (33), 296 (7), 268 (10), 247 (17), 212 (13), 197 (15), 139 (7), 126 (32), 99 (14), 73 (28), 52 (59). – HRMS, $C_{19}H_{18}CrO_7Si$: calcd. 438.02269, found 438.02249.

Tricarbonyl[η^6-(1,3-dioxoindane)-2-*spiro*-2′-(3′-methoxy-4′,4′,6′,6′-tetrahydro-2′*H*-pyran-5′-one)]chromium(0) (48): 583 mL (3.60 mmol) of 1-methoxy-3-trimethylsiloxy-1,3-butadiene (**47**) is added to a solution of 380 mg (1.20 mmol) of **8** in 10 mL of anhydrous THF. After addition of 200 mg of molecular sieves (3 Å) the mixture is allowed to stand for 72 h at 20°C. The red solution is separated from the molecular sieves, and the solvent is removed at reduced pressure. The crude product is purified by column chromatography (TBME/petroleum ether, 1:1, then TBME, length 30 cm, ∅ 3 cm). Fraction I: 87 mg (0.28 mmol, 23%) of **8**. II: 347 mg (0.88 mmol, 78%) of **48**, orange-red solid (*de* > 95%, NMR; m. p. 195°C).

IR (KBr): $\tilde{\nu}$ = 3084 (w) cm^{-1}, 2972 (w), 2920 (w), 2848 (w), 2000 (s, CO), 1940 (s, CO), 1740 (s, ketone), 1712 (s, ketone), 1512 (w), 1448 (w), 1396 (w), 1264 (w), 1204 (w), 1176 (w), 1040 (m), 980 (w), 924 (w), 640 (m), 604 (m). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 2.61 [dd, 1 H, ^2J = –17.1 Hz, ^3J = 3.6 Hz, OCH(OMe)CH_2], 2.67 [d, 1 H, ^2J = –16.5 Hz, CCH_2C(O)], 2.99 [d, 1 H, ^2J = –17.1 Hz, ^3J = 3.6 Hz, OCH(OMe)CH_2], 3.08 (d, 1 H, ^2J = –16.5 Hz, CCH_2C(O)], 3.55 (s, 3 H, OCH_3), 6.15 + 6.18 (AA′BB′, 4 H, arom. H). – ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 38.9 [CH_2, CH(OMe)CH_2], 45.3 [CH_2, CCH_2C(O)], 55.0 (CH_3, OCH_3), 75.3 (C_q, C-2), 87.1 (CH, C-4 or C-7), 87.4 (CH, C-4 or C-7), 94.9 (CH, C-5 or C-6), 95.3 (CH, C-5 or C-6), 96.5 (C_q, C-3a or C-7a),

97.5 (C_q, C-3a or C-7a), 100.1 [CH, OCH(OMe)], 193.5 (C_q, C-1 or C-3), 196.3 (C_q, C-1 or C-3), 200.5 [C_q, $CH_2C(O)$], 228.5 (C_q, CO). − MS (70 eV, 150°C): *m/z* (%) = 398 (32) [M^+ + 2], 397 (9) [M^+ + 1], 396 (22) [M^+], 365 (2), 312 (36) [M^+ − 3 CO], 280 (31) [M^+ − 3 CO − CH_3OH], 270 (25), 256 (61), 238 (11), 226 (13), 212 (41), 146 (6), 128 (19), 104 (16), 96 (13), 52 (100) [^{52}Cr].

Crystal Structure Analysis of *rac*-48:[11] $C_{17}H_{12}CrO_8$, red, crystal size 0.07 × 0.12 × 0.15 mm, a = 8.304(2), b = 21.332(3), c = 10.110(2) Å, α = 90, β = 110.38(2), γ = 90°, V = 1678.8(6) Å^3, $d_{calcd.}$ = 1.568 gcm^{-3}, μ = 7.3 cm^{-1}, Z = 4, crystal system monoclinic, space group $P2_1/a$ (Nr. 14), Stoe IPDS diffractometer, λ = 0.71073, 150 exposures $2\Theta_{max}$ 48°, 9612 measured reflections (±h, ±k, ±l), 2484 independent and 1085 observed reflections [$I > 2\sigma(I)$], 235 refined parameters, H atoms included using the riding model, $R_{1\,=\,0}$.0345, wR_2 = 0.0516 {$w = 1/[\sigma 2(F_0^2)]$}, min., max. residual electron density −0.23, 0.18 eÅ^{-3}; programs used: SHELXS-86, SHELXL-93. CCDC 102146.

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