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Phthalimide Tricarbonylchromium Complexes: Synthesis, Characterization, Nucleophilic Addition, and Unanticipated *syn* Adduct Formation upon Addition of Propynyllithium

Osama Mahmoud Ali Habib,[a,b] Zhirong Zhao-Karger,[a] Ismail Abdelshafy Abdelhamid,[a,c] Rudolf Wartchow,[d] and Holger Butenschön*[a]

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The complexation of phthalimide derivatives with hexacarbonylchromium in dibutyl ether/THF (10:1) afforded the corresponding tricarbonylchromium complexes, which were characterized spectroscopically. Subsequent nucleophilic addition with Grignard or organolithium reagents as well as with sodium tetrahydridoborate gave high yields of the corresponding *anti* adducts. However, in certain cases, addition of 1-lithio-1-methoxyallene, 1-propynyllithium, or ethenylmagnesium bromide, the unanticipated formation of the corresponding *syn* adducts was observed with the relative configuration of the propynyllithium adduct *rac*-**20** confirmed by a crystal structure analysis. The unusual stereochemistry is explained by the intermediacy of a highly resonance-stabilized acyliminium ion formed from the original *exo* adduct. Finally, dehydration of the methyl adduct made available the *exo*-methylene derivative *rac*-**37**, bearing another fully sp^2-hybridized ligand system. This compound was also characterized by a crystal structure analysis.

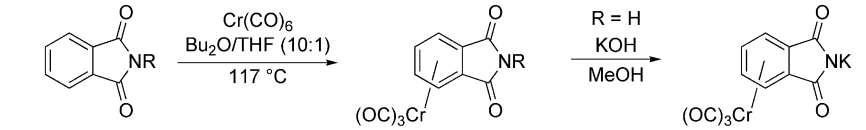
Introduction

One of the significant features of (arene)tricarbonylchomium complexes is the facial discrimination of the arene ligand.[1–7] This reduction in symmetry has been exploited in many stereoselective syntheses[1,6,8–12] as well as in asymmetric catalysis.[13–15] In particular, substituted (arene)tricarbonylchromium complexes with an annulated carbocycle, which allow for reaction at the annulated ring with high diastereoselectivity, have been widely investigated.[16,17] Planar chiral representatives often facilitate a transfer of their planar chirality into central chirality by the diastereoselective formation of an asymmetric carbon atom.[18,19] In comparison with complexes with annulated carbocycles, those with annulated heterocycles have been investigated to a much lesser extent although the incorporation of heteroatoms allows for a much larger diversity of compounds and chemical reactivity not given in the corresponding annulated carbocycles. In the context of our interest in the chemistry of (arene)tricarbonylchromium complexes with annulated heterocycles,[20] we report herein on the investigations of such complexes with phthalimide-derived ligands. The phthalimide ligand is attractive because it contains two carbonyl functions as well as an imide functionality. It is also related to the isoindolin-1-one system, which is a substructure of biologically active compounds.[21–25]

Results and Discussion

Phthalimide tricarbonylchromium complexes can be obtained by the direct complexation of the ligands with hexacarbonylchromium in boiling dibutyl ether/THF (10:1). In addition to the unsubstituted phthalimide complex **2**, we also prepared *N*-substituted derivatives **5**, **7**, **9**, and **11**. Yields were in the range of 20–71% and could not be improved upon by using (naphthalene)tricarbonylchromium as the complexation reagent.[26] The parent compound **2**, which to our surprise was unknown, was obtained in 71% yield as a red solid and characterized by spectroscopic methods. Complex **2** was easily deprotonated with potassium hydroxide in methanol to afford potassium phthalimide complex **3** in 93% yield. The *N*-methylphthalimide complex **5** was obtained from ligand **4** in 61% yield and the ethyl analogue **6** afforded complex **7** in 57% yield. In the context of our interest in oxyanion-accelerated reactions, particularly Cope rearrangements,[16,17,27–34] we focused on the *N*-vinyl-substituted derivative. Unfortunately, attempts to couple complex **2** with vinyl bromide in the presence of copper iodide failed.[35] However, the direct complexation of commercially available *N*-vinylphthalimide (**8**) gave the desired complex **9** in varying yields of 20–48% with *N*-vinylphthalimide recovery of around 40%. The moderate

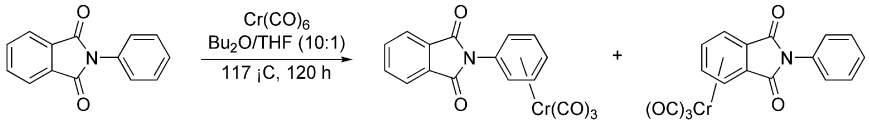
[a] Leibniz Universität Hannover, Institut für Organische Chemie, Schneiderberg 1B, 30167 Hannover, Germany
E-mail: holger.butenschoen@mbox.oci.uni-hannover.de
[b] Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, A. R. Egypt
[c] Department of Chemistry, Faculty of Science, Cairo University, 12613 Giza, A. R. Egypt
[d] Leibniz Universität Hannover, Institut für Anorganische Chemie, Callinstraße 9, 30167 Hannover, Germany



1: R = H
4: R = Me
6: R = Et
8: R = CH=CH_2
10: R = CH_2CH_2Br

2: R = H (71 %)
5: R = Me (61%)
7: R = Et (57 %)
9: R = CH=CH_2 (20-48 %)
11: R = CH_2CH_2Br (42 %)

3 (93 %)



12

13 (31 %)

14 (11 %)

yield is presumably due to the partial decomposition of **9** during the extended period of heating. Use of (naphthalene)tricarbonylchromium(0)[26,36] instead of hexacarbonylchromium(0), however, did not significantly improve the yield. 2-Bromoethyl derivative **11** was obtained in 42% yield from **11** in an attempt to improve the access to **9**.

When *N*-phenylphthalimide (**12**) was treated with $Cr(CO)_6$ under the usual reaction conditions moderate regioselectivity was observed reflecting the relative electron densities of the two arene rings in the ligand; as a result, complex **13** was obtained in 31% yield whereas coordination at the less electron-rich arene ring afforded complex **14** in only 11% yield. Complexes **13** and **14** were separated by column chromatography and were characterized separately. No bis(tricarbonylchromium) complex was obtained. All new complexes were characterized spectroscopically.

The phthalimide complexes prepared were subjected to nucleophilic addition reactions at one of the carbonyl functions. According to our experience with isatin complexes[20] and other complexes with annulated cycloalkenones,[27–29,37–39] nucleophilic attack from the face opposite the tricarbonylchromium moiety had to be expected for obvious steric reasons.[40–42] The results of the addition reactions of various nucleophiles at one of the carbonyl functions are summarized in Table 1.

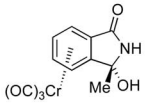
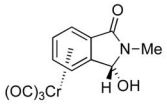
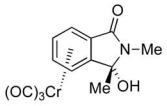
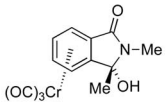
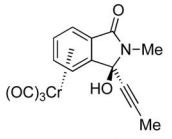
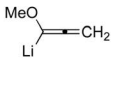
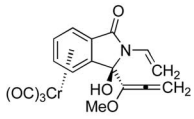
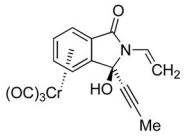
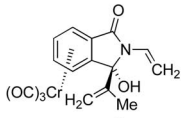
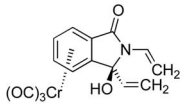
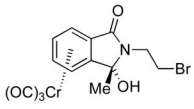
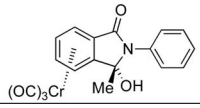
In all cases good-to-high yields of adducts were obtained, all of which contain a hemi-aminal substructure. However, presumably due to the stability of the amide bond, no ring-opening to the corresponding carbonyl compound was observed in the presence of acid. In most cases the reactions show the expected stereochemistry with nucleophilic attack from the face opposite the tricarbonylchromium group resulting in an *endo*-hydroxy substituent. However, entries 5–7 and 9 show the formation of the products *rac*-**18**, *rac*-**19**, *rac*-**20**, and *rac*-**22**, which were obtained in high yields with an unanticipated *exo*-hydroxy configuration. The products were characterized spectroscopically; the stereochemical assignments made are based on the crystal structure analyses of adducts *rac*-**17** and *rac*-**20** as well as on a careful analysis of the ^1H NMR spectra of the products.

The reduction of **5** with $NaBH_4$ gave alcohol *rac*-**16** in 65% yield. Enantioselective reduction was tried using Corey's oxazaborolidine method.[43] Although the chemical yield was 67%, the enantiomeric excess was only 31% according to Mosher's ester analysis. This may be due to the fact that reduction of **5** does not require the differentiation of two enantiotopic faces of one carbonyl function but the differentiation of two enantiotopic carbonyl groups in an asymmetric desymmetrization. Treatment of *N*-methylphthalimide complex **5** with methyllithium or methylmagnesium chloride resulted in the formation of the *exo*-methyl-*endo*-hydroxy complex *rac*-**17** in 81 or 93% yield, respectively. The relative configuration at the asymmetric carbon atom was established as *endo*-hydroxy-*exo*-methyl by X-ray crystal structure analysis (Figure 1). The structure shows the expected planar environment of the amide nitrogen atom. The tricarbonylchromium moiety adopts a conformation with one of the carbonyl ligands in an *anti* orientation with respect to the asymmetric carbon atom C2, presumably for steric reasons. Remarkably, the Cr1–C6 distance is significantly shorter than other distances between the chromium atom and the coordinated carbon atoms.

Upon the addition of propynyllithium[45,46] to one of the carbonyl functions in **5** as well as in **9**, the monoadducts *rac*-**18** and *rac*-**20** were formed in 90 and 89% yields, respectively, and characterized by their IR, NMR, and MS data. Contrary to expectation, the crystal structure analysis of *rac*-**20** (Figure 2) indicated that the isolated compound was not the anticipated *exo*-propynyl *endo*-hydroxy derivative but had the opposite relative configuration.

The analysis clearly indicates the *endo* position of the 1-propynyl group and the *exo* position of the hydroxy substituent. In addition, the *N*-vinyl group adopts a conformation coplanar to that of the phthalimide moiety with an s-*trans* conformation of the *N*-vinyl bond with respect to the remaining phthalimide carbonyl function. As in *rac*-**17**, the nitrogen atom has a planar environment. None of the car-

Table 1. Nucleophilic addition to phthalimide tricarbonylchromium complexes.

Entry	Phthalimide complex	Reagent	Product		Yield (%)
1	**2**	MeLi[a]		*rac*-**15**	84
2	**5**	$NaBH_4$		*rac*-**16**	65
3	**5**	MeLi		*rac*-**17**	81
4	**5**	MeMgCl[b]		*rac*-**17**	93
5	**5**			*rac*-**18**	90
6	**9**			*rac*-**19**	92
7	**9**			*rac*-**20**	89
8	**9**			*rac*-**21**	40[c]
9	**9**			*rac*-**22**	70
10	**11**	MeMgCl		*rac*-**23**	74
11	**12**	MeMgCl		*rac*-**24**	78

[a] 3.5 equiv. [b] 2 equiv. [c] In addition to *rac*-**20** (48%).

bonyl ligands is located below the annulated ring. In contrast to *rac*-**17**, the tricarbonylchromium group in *rac*-**20** adopts a conformation with one of the carbonyl ligands being in rather close proximity to the alkynyl substituent, both moieties adopting an almost parallel conformation. The distance between them (C10–C13 331.5, C11–O3 327.4 pm) is slightly less than the sum of the van der Waals radii of the respective atoms. The distance between the CO and the alkynyl triple bond is close to that between the cyclopentadienyl ligands in ferrocene (332 pm[47]). In this context it appears noteworthy that we, as well as others, showed

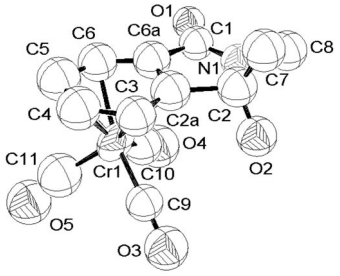


Figure 1. Crystal structure of *rac*-**17**.[44] Selected bond lengths [pm] and angles [°]: Cr1–C2a 2.18(2), Cr–C3 2.24(2), Cr1–C4 2.19(2), Cr1–C5 2.24(2), Cr1–C6 2.08(2), Cr1–C6a 2.27(2), C1–N1 1.31(3), C1–C6a 1.54(2), C2–N1 1.42(2), C2–C2a 1.63(3), C2–C7 1.52(3), C2–O2 1.31(2), N1–C8 1.47(2); N1–C2–C2a 99(1), O2–C2–C7 116(2), O2–C2–C2a 109(2), C2a–C2–C7 110(1), N1–C2–C7 112(2).

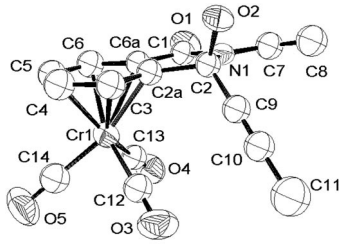


Figure 2. Crystal structure of *rac*-**20**.[44] Selected bond lengths [pm], bond angles [°], and torsional angles: Cr1–C2a 2.197(5), Cr1–C3 2.221(7), Cr1–C4 2.196(8), Cr1–C5 2.181(7), Cr1–C6 2.206(6), Cr1–C6a 2.170(4), Cr1–C12 1.813(6), Cr1–C13 1.840(8), Cr1–C14 1.837(6), C2a–C3 1.385(8), C2a–C6a 1.375(8), C3–C4 1.396(9), C4–C5 1.383(9), C5–C6 1.388(9), C6–C6a 1.408(9), C1–C6a 1.492(8), C1–O1 1.221(7), C1–N1 1.374(8), C2–C2a 1.534(8), C2–O2 1.434(7), C2–N1 1.482(7), C2–C9 1.448(8), C9–C10 1–143(8), C10–C11 1.50(1), N1–C7 1.410(8), C7–C8 1.317(9); N1–C1–O1 124.8(5), N1–C1–C6a 106.5(5), O1–C1–C6a 128.8(6), C1–N1–C7 122.3(5), C1–N1–C2 113.1(4), C2–N1–C7 124.6(4), N1–C7–C8 126.6(5), N1–C2–O2 110.5(4), N1–C2–C2a 101.5(4), N1–C2–C9 112.9(5), O2–C2–C2a 108.9(4), O2–C2–C9 108.2(5), C2a–C2–C9 114.8(5); C2–N1–C1–C6a –0.9(6), C2–N1–C7–C8 –6.5(9).

that intramolecular reactions are well possible between the alkynyl substituents of 1,1′-dialkynylferrocenes.[48–50] The practically parallel orientation of the two moieties is counterintuitive for steric reasons and suggests some attractive interaction between the carbonyl and the alkynyl π system in *rac*-**20**. The elemental cell has a center of symmetry and hence contains four molecules of opposite absolute configuration as two pairs, respectively. These molecules interact through hydrogen bridges between the hydroxy hydrogen atoms and the carbonyl oxygen atom of the other molecule (Figure 3). There are no clear steric reasons to explain the intramolecular parallel arrangement of one of the carbonyl ligands and the triple bond and thus we favor an electronic interaction between them as the reason for the unexpected conformation.

A careful comparison of the NMR spectroscopic data of *rac*-**17** and *rac*-**20** shows a significant difference in the chemical shifts of their hydroxy protons: Whereas the chemical shift of the hydroxy proton in *rac*-**17** is δ = 5.50 ppm, the corresponding absorption for *rac*-**20** appears at δ = 6.60 ppm. Presumably, this difference is due to the magnetic

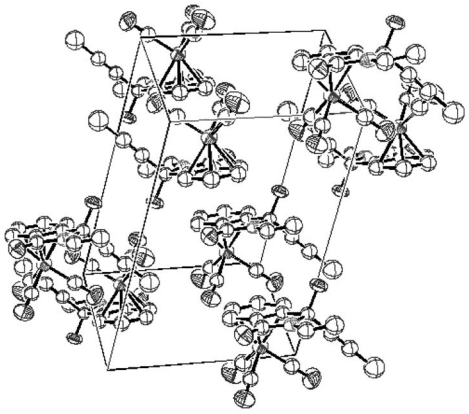


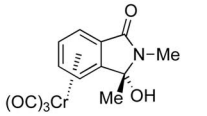
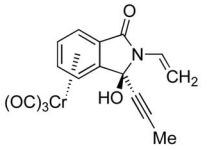
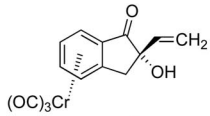
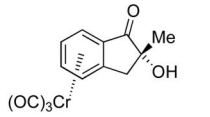
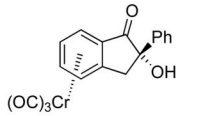
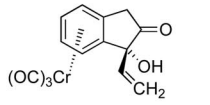
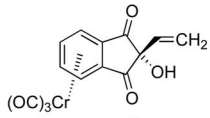
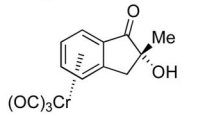
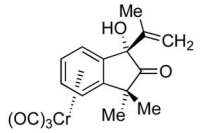
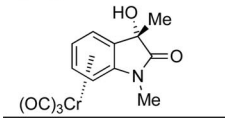
Figure 3. Elemental cell of *rac*-**20** in the crystal.[44]

anisotropy of the tricarbonylchromium group in *rac*-**17**, which is not manifest in *rac*-**20**. In this context a comparison with other related compounds is instructive. A selection of related compounds together with the chemical shifts of the corresponding hydroxy protons are reported in Table 2. According to these data the chemical shifts of *endo*-hydroxy protons are in the range of δ = 4.85–5.68 ppm, whereas the chemical shift of the *exo*-hydroxy proton in *rac*-**20** (δ = 6.60 ppm) significantly deviates from this range.

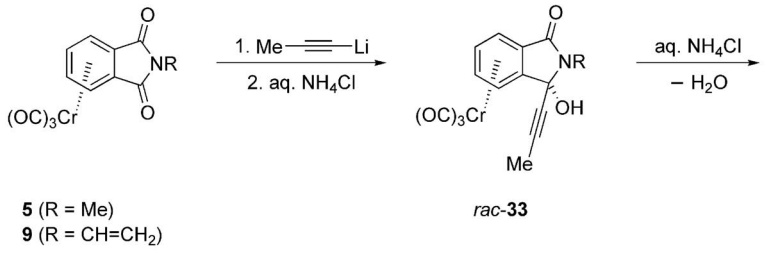
Based on the data in Table 2 the relative configurations of the products in Table 1, which were not characterized crystallographically, were assigned. In this context the addition of 2-propenyllithium gives an unexpected result: 2-Bromopropene was treated with lithium for 2 h in diethyl ether at reflux to generate 2-propenyllithium.[52] A solution of **9** was added dropwise at –78 °C and after stirring at this temperature for 2 h and the usual hydrolytic work-up two products were isolated. The major product, which was obtained in 48% yield, was *rac*-**20**, whereas the expected adduct *rac*-**21** was obtained in only 40% yield. Adduct *rac*-**21** was characterized spectroscopically; the chemical shift of the hydroxy proton is δ = 5.16 ppm, which is in accord with the *endo*-hydroxy configuration. Possibly, the methyl group attached to the vinyl moiety prevents the formation of the opposite diastereomer for steric reasons. However, the formation of a significant amount of *rac*-**20** is unusual and indicates the formation of a considerable amount of 1-propynyllithium prior to nucleophilic addition. Treatment of 2-bromo-3,3,3-trifluoropropene with 2 equiv. of lithium diisopropylamide has been reported to result in the formation of (3,3,3-trifluoropropynyl)lithium.[53] To explain our observation one has therefore to consider an HBr elimination caused by the basic 2-propenyllithium formed. Alternatively, one might consider a lithium hydride elimination from 2-propenyllithium followed by deprotonation of propyne.

Next, **9** was treated with vinylmagnesium bromide to introduce a second vinyl group. The reaction proceeded smoothly and gave adduct *rac*-**22** in 70% yield after work-up. The assigned configuration is based on the observation of the ^{1}H NMR signal of the hydroxy group, which appears

Table 2. Chemical shifts of the hydroxy protons in some tricarbonylchromium complexes. Relative configurations of *rac*-**17**, *rac*-**20**, *rac*-**25**, and *rac*-**26** have been confirmed crystallographically.

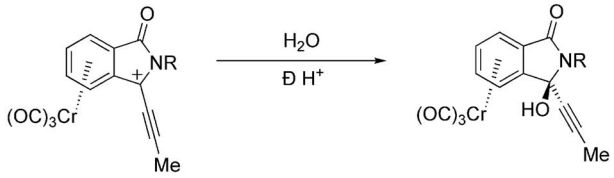
Compound		δ_{OH} [ppm]	Solvent	Reference
	*rac*-**17**	5.50	$CDCl_3$	this work
	*rac*-**20**	6.60	[D$_6$]acetone	this work
	*rac*-**25**	5.18	[D$_6$]acetone	[39]
	*rac*-**26**	4.85	[D$_6$]acetone	[39]
	*rac*-**27**	5.68	[D$_6$]acetone	[39]
	*rac*-**28**	5.45	[D$_6$]acetone	[39]
	*rac*-**29**	5.46	[D$_6$]acetone	[39]
	*rac*-**30**	5.14	[D$_6$]acetone	[51]
	*rac*-**31**	4.88	[D$_6$]acetone	[51]
	*rac*-**32**	5.22	[D$_6$]acetone	[20]

at δ = 6.31 ppm ($CDCl_3$), and the data given in Table 2. Whereas the configuration of *rac*-**22** is assigned only on the basis of the hydroxy ^{1}H NMR signal, the assignment of the configurations in *rac*-**17** and *rac*-**20** is beyond any doubt based on X-ray structure analyses. In contrast to *rac*-**17**, adducts *rac*-**19**, *rac*-**20**, and *rac*-**21** contain unsaturated substituents, which most likely is the reason for their unexpected configuration. The explanation that we propose involves a normal addition from the face opposite the tricarbonylchromium group in the first step. In the case of the addition of 1-propynyllithium to **9**, this results in *rac*-**33** after hydrolytic work-up with NH_4Cl. Subsequent protonation of the hydroxy group and dissociation of H_2O presumably results



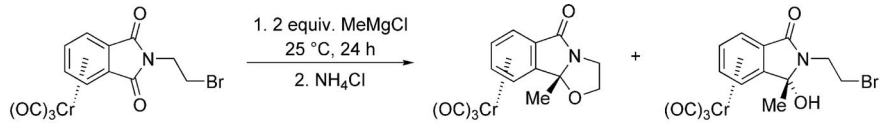
5 (R = Me)
9 (R = $CH=CH_2$)

rac-**33**



rac-**34**

rac-**18** (R = Me)
rac-**20** (R = $CH=CH_2$)



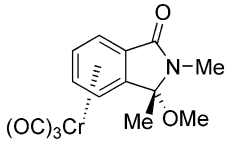
11

rac-**35** (46 %) + *rac*-**23** (13 %)

in the highly conjugated resonance-stabilized acyliminium cation *rac*-**34**. Nucleophilic attack of water from the face opposite $Cr(CO)_3$ then gives rise to the formation of the observed product *rac*-**20**. We think that addition of the nucleophile at the *exo* face followed by isomerization via a highly delocalized acyliminium ion intermediate explains all the cases in which the *exo*-hydroxy adducts were formed.

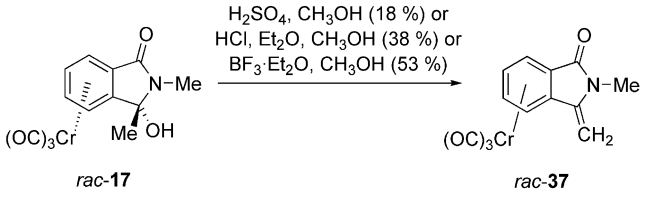
When *N*-(2-bromoethyl)phthalimide complex **11** was treated with methylmagnesium chloride at 25 °C instead of –78 °C, in addition to adduct *rac*-**23** (13%), the tricyclic oxazolidine *rac*-**35** was obtained in 46% yield as a result of a subsequent intramolecular Williamson ether synthesis.

In a similar, but intermolecular fashion, methyl ether *rac*-**36** was obtained in 73% yield from *rac*-**17** by treatment with sodium hydride followed by iodomethane.



rac-**36** (73 %)

In an attempt to invert the configuration[54] at C2, *rac*-**17** was treated with H_2SO_4/CH_3OH, $HCl/Et_2O/CH_3OH$, and $BF_3{\cdot}Et_2OH/\ CH_3OH$. In all three attempts, instead of the desired inversion, elimination with the formation of the new *exo*-methylene complex *rac*-**37** was observed in 18, 38, and 53% yields, respectively . Clearly, deprotonation of the intermediate acyliminium ion is highly favored over the nucleophilic attack of methanol.



rac-**17** *rac*-**37**

Complex *rac*-**37** is an unusual compound because it is a styrene complex with a fixed conformation. In contrast to other styrene tricarbonylchromium derivatives it is also an enamide. As in phthalimide complexes, the ligand atoms forming the bicyclic structure are sp^2-hybridized rendering

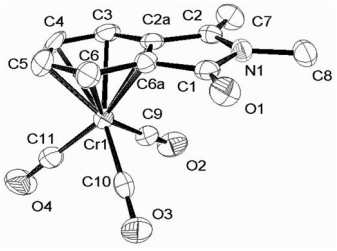
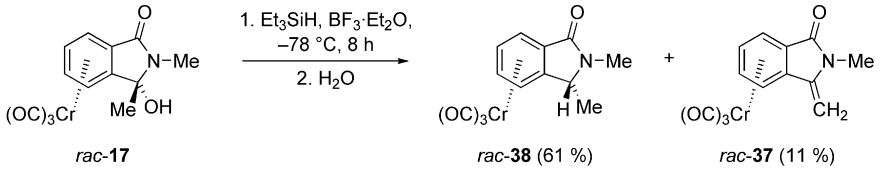


Figure 4. Crystal structure of *rac*-**37**.[44] Selected bond lengths [pm] and angles [°]: Cr1–C2a 220.1(5), Cr1–C3 223.4(5), Cr1–C4 221.1(5), Cr1–C5 220.9(5), Cr1–C6 219.9(6), Cr1–C6a 219.5(5), C1–N1 137.9(7), C1–O1 122.0(6), C1–C6a 147.8(7), N1–C2 139.1(7), N1–C8 145.5(6), C2–C2a 148.4(6), C2–C7 133.1(7), C2a–C6a 141.0(7), C2a–C3 139.2(7), C3–C4 141.4(7), C4–C5 139.0(8), C5–C6 139.9(8), C6–C6a 142.0(6); N1–C1–O1 126.6(5), O1–C1–C6a 128.1(5), N1–C1–C6a 105.2(4), C1–N1–C2 113.1(4), N1–C2–C2a 106.2(4), C6a–C2a–C2 106.4(4), C2a–C6a–C1 109.0(4).



the ligand planar. Complex *rac*-**37** was crystallized from CH_2Cl_2/hexane to give crystals suitable for X-ray crystal structure analysis (Figure 4).

Complex *rac*-**37** has a fully sp^2-hybridized ligand that is completely planar. This feature differs from certain benzocyclobutenedione complexes.[27] The tricarbonylchromium group shows a staggered conformation relative to the benzene ring with no CO ligand below the annulated ring. The measured bond lengths of the benzene ring vary slightly with C6–C6a being the longest. However, the effect is close to the standard deviations and must not be overinterpreted. Overall, the structure shows a quasi-plane of symmetry distorted only by the carbonyl versus the methylene moiety with the intracyclic angles at the annulated ring being 105° at C1 as well as at C2.

When *rac*-**17** was treated with triethylsilane in the presence of $BF_3{\cdot}Et_2O$ at –78 °C over 8 h, after aqueous workup a mixture was obtained consisting of *rac*-**37** (11%) as the side-product and *rac*-**38** (61%) as the main product, which was characterized spectroscopically. Although crystalline needles were obtained, it was not possible to generate crystals suitable for X-ray structure analysis. The relative configuration assigned is based on the assumed formation of the corresponding acyliminium cation from *rac*-**17** with subsequent hydride transfer from the hydrosilane from the face opposite the tricarbonylchromium group.

Conclusion

The investigation of phthalimide tricarbonylchromium complexes has shown that in certain cases nucleophilic addition leads to *syn* instead of the expected *anti* adducts. In addition to the crystal structure analysis of the propynyllithium adduct *rac*-**20**, the assignments of the relative configurations are based on a detailed comparison of the ^1H NMR chemical shifts of the hydroxy groups of several related tricarbonylchromium complexes, which show a systematic correlation with the corresponding configuration. Finally, dehydration of *rac*-**17** afforded the *exo*-methylene complex *rac*-**37**, which has a fully sp^2-hybridized ligand system with configurationally rigid, highly conjugated lactam and styrene substructures. Further investigations will be directed towards the synthesis of this compound in an enantiomerically pure form and a study of its reactivity.

Experimental Section

General: All operations were performed under argon using Schlenk technique. Reaction vessels were heated under reduced pressure with a heat gun and flushed with argon or nitrogen. This procedure was repeated three times. Solvents were dried and distilled before use. Diethyl ether and THF were distilled from sodium wire/benzophenone under nitrogen; petroleum ether (PE), *tert*-butyl methyl ether (TBME), and ethyl acetate were dried with calcium chloride. Hexane, dibutyl ether, dichloromethane, and acetonitrile were dried with calcium hydride. Column chromatography was carried out using flash chromatography.[55] Silica gel (J. T. Baker, ∅ = 40 μm) was degassed three times by heating under reduced pressure and then flushed with argon. IR: Perkin–Elmer FT 1710, Golden Gate ATR instruments; s = strong, m = middle, w = weak, br. = broad. MS: Finnegan AM 400 spectrometer (ionization potential 70 eV). FAB-MS: VG-Autospec spectrometer. LC–MS (ESI): Micromass LCT spectrometer with lock-spray unit (ESI), loop mode, HPLC Alliance 2695 column (Waters). HRMS: VG-Autospec or Micromass LCT spectrometer with lock-spray unit (ESI). ^1H NMR: Bruker WP 200 (200.1 MHz) and AVS 400 (400.1 MHz) spectrometers. ^{13}C NMR: Bruker AVS 200 (50.3 MHz) and AVS 400 (100.6 MHz) spectrometers. Chemical shifts δ refer to δ_{TMS} = 0.00 ppm or to solvent signals. The multiplicities of the signals were determined by ATP or DEPT measurements. Signals with negative phase for CH or CH_3 are labeled as "–", those with positive phase for C or CH_2 are labeled as "+".Melting points were measured with a Büchi apparatus. Elemental analyses (CHN) were carried out with an element Vario EL instrument with acetanilide as the standard.

General Procedure for the Synthesis of Tricarbonyl(phthalimide)-chromium(0) Complexes (GP1): The phthalimide and hexacarbonylchromium (1.1 equiv.) in dibutyl ether and THF (10:1) were heated at reflux for 17–48 h. After cooling to 25 °C, the reaction mixture was carefully filtered through a P4 frit covered with a 2 cm thick layer of silica gel. The solvents were removed under reduced pressure and the crude product was purified by flash chromatography at SiO_2 eluting with TBME/PE. The tricarbonyl(phthalimide)chromium(0) complexes were obtained as red, moderately air-stable solids.

Tricarbonyl(phthalimide)chromium(0) (2): Prepared by GP1. Phthalimide (**1**; 1.00 g, 6.8 mmol) and hexacarbonylchromium (1.65 g, 7.5 mmol) in dibutyl ether (80 mL) and THF (8 mL) were heated at reflux for 48 h. Flash chromatography (200 × 20 mm, TBME/PE, 3:1, then TBME) gave **2** (1.35 g, 4.8 mmol, 71%) as a red solid, m.p. 205 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3199 (m, NH), 1979 (s, CO), 1928 (s, CrCO), 1904 (m, CrCO), 1716 (m, NCO), 1605 (m), 1307 (s), 1052 (s) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 5.97 (s, 2 H, CHC*H*C*H*CH), 6.30 (s, 2 H, C*H*CHCHC*H*), 10.30 (s, 1 H, N-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 90.0 (–, *C*HCHCH*C*H), 94.6 (+, CHC_qC_qCH), 94.8 (–, CH*C*H*C*HCH), 168.8 (+, O*C*NH*C*O), 231.7 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 283 (17) $[M]^+$, 227 (7) $[M – 2\ CO]^+$, 199 (97) $[M – 3\ CO]^+$, 147 (97) $[M – Cr(CO)_3]^+$, 104 (82), 77 (12), 76 (98), 52 (100) $[Cr]^+$. HRMS: calcd. for $C_{11}H_5CrNO_5 – H$ 281.9495; found 281.94989. $C_{11}H_5CrNO_5$ (283.16): calcd. C 46.66, H 1.78, N 4.95; found C 46.91, H 1.82, N 4.99.

Tricarbonyl(potassium phthalimide)chromium(0) (3): Potassium hydroxide (0.10 g, 1.8 mmol) in ethanol (5.6 mL) was added dropwise

to tricarbonyl(phthalimide)chromium (**2**; 0.51 g, 1.8 mmol) in ethanol (5.2 mL) and the mixture was stirred for 2 h at 50 °C, the color of the solution changing from red to orange. The mixture was cooled to 25 °C and **3** precipitated as an orange solid. After filtration, **3** (0.54 g, 1.7 mmol, 93%) was obtained as an orange, air-stable solid, m.p. > 300 °C. IR (ATR): $\tilde{\nu}$ = 3080 (w), 1963 (s, CrCO), 1894 (s, CrCO), 1768 (m, NCO), 1693 (s, NCO), 1580 (s), 1379 (m), 1298 (w), 1125 (w), 1088 (w), 1051 (w), 793 (w), 711 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 5.69 (m, 2 H, CHC*H*C*H*CH), 6.00 (m, 2 H, C*H*CHCHC*H*) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 87.9 (–, *C*HCHCH*C*H), 92.9 (–, CH*C*H*C*HCH), 94.0 (+, CHC_qC_qCH), 168.9 (+, O*C*NH*C*O), 232.6 (+, CrCO) ppm. LC–MS (ESI): calcd. for $C_{11}H_4CrKNO_5$ [+H] 321.9130; found 321.9133.

Tricarbonyl(*N*-methylphthalimide)chromium(0) (5): Prepared by GP1. *N*-Methylphthalimide[56] (**4**; 1.00 g, 6.2 mmol) and hexacarbonylchromium (1.50 g, 6.8 mmol) in Bu$_2$O (70 mL) and THF (7 mL) were heated at reflux for 35 h. Column chromatography (200 × 20 mm, PE/TBME, 1:3) gave **5** (1.13 g, 3.80 mmol, 61%) as a deep-red solid, m.p. 196 °C. IR (ATR): $\tilde{\nu}$ = 3082 (w), 2961 (w), 1974 (s, CO), 1894 (s, CO), 1761 (m), 1698 (s), 1432 (m), 1371 (m), 1249 (w), 1203 (w), 1141 (w), 1080 (w), 1005 (m), 954 (w), 846 (w), 799 (w), 751 (w), 703 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 3.13 (s, 3 H, CH$_3$), 5.52 (s, 2 H, CHC*H*C*H*CH), 6.05 (s, 2 H, C*H*CHCHC*H*) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT): δ = 24.5 (–, C-8), 87.3 (–, *C*HCHCH*C*H), 90.6 (–, CH*C*H*C*HCH), 90.8 (+, CHC_qC_qCH), 167.2 (+, O*C*NH*C*O], 228.9 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 297 (53) [M]$^+$, 241 (20) [M – 2 CO]$^+$, 213 (97) [M – 3 CO]$^+$, 161 (25) [M – Cr(CO)$_3$]$^+$, 117 (10), 104 (12), 76 (19), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{12}H_7CrNO_5$ 296.9729; found 296.9727. $C_{12}H_7CrNO_5$ (297.19): calcd. C 48.50, H 2.37, N 4.71; found C 48.94, H 2.50, N 4.78.

Tricarbonyl(*N*-ethylphthalimide)chromium(0) (7): Prepared by GP1. *N*-Ethylphthalimide[57] (**6**; 1.10 g. 6.2 mmol) and hexacarbonylchromium (1.50 g, 6.8 mmol) in dibutyl ether (70 mL) and THF (7 mL) were heated at reflux for 30 h. Flash chromatography (200 × 20 mm, TBME/PE, 3:1) gave **7** (1.134 g, 3.8 mmol, 57%) as a deep-red solid, m.p. 111 °C. IR (ATR): $\tilde{\nu}$ = 3080 (w), 2960 (w), 1971 (s, CrCO), 1893 (s, CrCO), 1765 (m, NCO), 1704 (s, NCO), 1439 (m), 1374 (m), 1265 (w), 1189 (w), 1155 (w), 1033 (w), 893 (w), 872 (w), 842 (w), 755 (w), 703 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 1.26 (t, ^3J = 6.3 Hz, 3 H, CH$_3$), 3.70 (q, ^3J = 6.5 Hz, 2 H, CH$_2$), 5.52 (s, 2 H, CHC*H*C*H*CH), 6.06 (s, 2 H, C*H*CHCHC*H*) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT): δ = 13.6 (–, C-9), 33.8 (+, C-8), 87.5 (–, C- *C*HCHCH*C*H), 90.7 (–, CH*C*H*C*HCH), 91.0 (+, CHC_qC_qCH), 167.2 (+, O*C*NH*C*O), 229.0 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 311 (25) [M]$^+$, 255 (9) [M – 2 CO]$^+$, 227 (99) [M – 3 CO]$^+$, 175 (15) [M – Cr(CO)$_3$]$^+$, 133 (11), 77 (11), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{13}H_9CrNO_5$ 310.9886; found 310.9888. $C_{13}H_9CrNO_5$ (311.21): calcd. C 50.50, H 2.28, N 4.53; found C 50.23, H 2.74, N 4.61.

Tricarbonyl(*N*-vinylphthalimide)chromium(0) (9): a) Prepared by GP1. *N*-Vinylphthalimide (**8**; 320 mg, 1.9 mmol) and hexacarbonylchromium (450 mg, 2.0 mmol) in Bu$_2$O (40 mL) and THF (4 mL) were heated for 24 h at reflux. Flash chromatography (200 × 20 mm, TBME/PE, 2:1) afforded **9** (278 mg, 0.9 mmol, 45%) as a deep-red solid, m.p. 204 °C (dec.). b) *N*-Vinylphthalimide (**8**; 0.5 g, 2.8 mmol) and tricarbonyl(naphthalene)chromium(0) (0.8 g, 3.1 mmol) in THF (50 mL) were heated at reflux for 15 h and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (200 × 20 mm, PE/TBME, 1:1, then 1:2) to afford **9** (0.35 g, 1.1 mmol, 40%). IR (ATR): $\tilde{\nu}$ = 3088 (w, =CH), 1980 (s, CrCO), 1894 (s, CrCO), 1771 (m, NCO), 1711 (s, NCO), 1635 (w), 1526 (w), 1425 (w), 1401 (w), 1367 (s), 1306 (m), 1225 (m), 1167 (m), 1139 (m), 1079 (w), 1016 (m), 984 (w), 899 (w), 873 (m), 831 (m), 757 (w), 718 (m), 698 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 5.07 (d, $^3J_{cis}$ = 9.8 Hz, 1 H, =CH*H*), 5.46 (dd, *J* = 2.5, 4.3 Hz, 2 H, CHC*H*C*H*CH), 6.03 (m, 3 H, C*H*CHCHC*H*, =C*H*H), 6.75 (m, 1 H, NC*H*=CH$_2$) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT): δ = 87.2 (–, *C*HCHCH*C*H), 89.6 (+, CHC_qC_qCH), 90.8 (–, CH*C*H*C*HCH), 105.9 (+, =CH$_2$), 123.3 (–, *C*H=CH$_2$), 165.6 (+, O*C*NC*O*), 228.5 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 309 (45) [M]$^+$, 253 (32) [M – 2 CO]$^+$, 225 (83) [M – 3 CO]$^+$, 209 (46), 173 (33) [M – Cr(CO)$_3$]$^+$, 154 (13), 129 (8), 108 (10), 97 (35), 80 (28), 69 (63), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{13}H_7CrNO_5$ 308.9729; found 308.9729. $C_{13}H_9CrNO_5$ (311.21): calcd. C 50.17, H 2.91, N 4.50; found C 50.18, H 2.75, N 4.58.

Tricarbonyl[*N*-(2-bromoethyl)phthalimide]chromium(0) (11): Prepared by GP1. *N*-(2-Bromoethyl)phthalimide (**10**; 1.00 g, 3.9 mmol, **10**) and hexacarbonylchromium (0.95 g, 4.3 mmol) in Bu$_2$O (60 mL) and THF (6 mL) were heated at reflux for 17 h. Flash chromatography (200 × 20 mm, PE/TBME, 1:3) gave **11** (0.64 g, 1.6 mmol, 42%) as a red solid, m.p. 127 °C. IR (ATR): $\tilde{\nu}$ = 3032 (w), 2961 (w), 1974 (s, CrCO), 1894 (s, CrCO), 1761 (m, NCO), 1698 (s, NCO), 1432 (m), 1371 (m), 1249 (w), 1203 (w), 1141 (w), 1080 (w), 1005 (m), 954 (w), 846 (w), 799 (w), 751 (w), 703 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 3.5 (t, ^3J = 6.8 Hz, 2 H, CH$_2$Br), 4.0 (t, ^3J = 6.9 Hz, 2 H, NCH$_2$), 5.53 (m, 2 H, CHC*H*C*H*CH), 6.05 (m, 2 H, C*H*CHCHC*H*) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT, HMQC): δ = 28.7 (+, CH$_2$Br), 42.3 (+, NCH$_2$), 86.2 (–, *C*HCHCH*C*H), 91.1 (–, CH*C*H*C*HCH), 92.5 (+, CHC_qC_qCH), 166.3 (+, O*C*NC*O*], 232.9 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 391 (11) + 389 (11) [M]$^+$, 335 (4) + 333 (4) [M – 2 CO]$^+$, 311 [M – Br]$^+$, 305 (11), 307 (10) [M – 3 CO]$^+$, 277 (70), 279 (67) [M – (CO)$_4$]$^+$, 253 (3), 255 (4) [M – Cr(CO)$_3$]$^+$, 227 [M – Br – 3(CO)]$^+$, 174 [M – Br – Cr(CO)$_3$]$^+$, 160 (39), 130 (67), 102 (13), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{13}H_8BrCrNO_5$ 388.8991; found 388.8991. $C_{13}H_8BrCrNO_5$ (390.11): calcd. C 40.02, H 2.07, N 3.59; found C 40.43, H 2.14, N 3.61.

Tricarbonyl[(η^6-*N*-phenyl)phthalimide]chromium(0) (13) and Tricarbonyl[*N*-phenyl(η^6-phthalimide)]chromium(0) (14): Prepared by GP1. *N*-Phenylphthalimide (**10**; 1.5 g, 6.7 mmol) and hexacarbonylchromium (1.63 g, 7.4 mmol) in Bu$_2$O (100 mL) and THF (10 mL) were heated at reflux for 48 h. Flash chromatography (200 × 20 mm, PE/TBME, 1:3, then TBME) gave **13** (0.75 g, 2.0 mmol, 31%) as a yellow solid (m.p. 162 °C) and **14** (0.26 g, 0.7 mmol, 11%) as a red solid (m.p. 157 °C). **13**: IR (ATR): $\tilde{\nu}$ = 3103 (w), 1958 (s, CrCO), 1863 (s, CrCO), 1778 (m, NCO), 1711 (s, NCO), 1526 (m), 1460 (m), 1355 (m), 1223 (w), 1078 (w), 1046 (w), 878 (w), 812 (w), 794 (w), 713 (w), 670 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 5.3 (t, *J* = 5.6 Hz, 1 H, *p*-H), 5.4 (t, *J* = 5.9 Hz, 2 H, *m*-H), 5.9 (d, *J* = 6.3 Hz, 2 H, *o*-H), 7.8 (s, 2 H, CHC*H*C*H*CH), 7.9 (s, 2 H, C*H*CHCHC*H*) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT, HMQC): δ = 89.4 (–, *o*-CH), 90.7 (–, *m*-CH), 90.8 (–, *p*-CH), 106.3 (+, N*C*CH), 124.0 (–, *C*HCHCH*C*H), 130.9 (+, CHC_qC_qCH), 135.0 (–, CH*C*H*C*HCH), 166.1 (+, O*C*NC*O*), 231.9 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 359 (5) [M]$^+$, 303 (9) [M – 2 CO]$^+$, 275 (100) [M – 3 CO]$^+$, 223 (10) [M – Cr(CO)$_3$]$^+$, 153 (11), 77 (16), 52 (79) [Cr]$^+$. HRMS: calcd. for $C_{17}H_9NO_5Cr$ 358.9886; found 358.9888. $C_{17}H_9CrNO_5$ (359.26): calcd. C 56.84, H 2.53, N 3.90; found C 57.13, H 2.27, N 4.11. **14**: IR (ATR): $\tilde{\nu}$ = 3088 (w), 1980 (s, CrCO), 1934 (s, CrCO), 1895 (s, CrCO), 1711 (s, NCO), 1499 (m), 1406 (w), 1373 (s), 1224 (w), 1116 (w), 1063 (w), 879 (w), 848 (w), 760 (w), 705 (w), 689 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 5.5 (s, 2 H, CHC*H*C*H*CH), 6.1 (s,

2 H, C*H*CHCHC*H*), 7.28 (m, 2 H, *m*-H), 7.39 (m, 1 H, *p*-H), 7.51 (m, 2 H, *o*-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT, HMQC): δ = 87.5 (–, CH*C*H*C*HCH), 90.1 (+, CHC_qC_qCH), 90.8 (–, CH*C*H*C*HCH), 126.7 (–, *m*-C), 128.7 (–, *p*-C), 129.2 (–, *o*-C), 130.9 (+, N*C*CH), 166.3 (+, O*C*N*C*O), 228.7 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 359 (12) $[M]^+$, 303 (6) [M – 2 CO]$^+$, 275 (100) [M – 3 CO]$^+$, 223 (64) [M – Cr(CO)$_3$]$^+$, 179 (46), 105 (12), 77 (18), 52 (67) $[Cr]^+$. HRMS: calcd. $C_{17}H_9CrNO_5$ 358.9886; found 358.9888. $C_{17}H_9CrNO_5$ (359.26): calcd. C 56.84, H 2.53, N 3.90; found C 57.09, H 2.69, N 4.09.

General Procedure for Nucleophilic Addition to *N*-Substituted Tricarbonyl(phthalimide)chromium Complexes (GP2): The complex in THF or diethyl ether was added dropwise at –78 °C to a cooled solution (–78 °C) of the nucleophile in THF or Et_2O. After stirring the mixture for 2–16 h at –78 °C under TLC control, it was hydrolyzed by addition of satd. aq. NH_4Cl or 1 M HCl at –78 °C. After warming to 25 °C the mixture was extracted with portions of ethyl acetate (15 mL) until the aqueous layer remained colorless. The collected organic layers were washed with water and dried with $MgSO_4$, filtered through a P4 frit covered with a layer of silica gel (2 cm). After the removal of solvent under reduced pressure the crude product was purified by flash chromatography (SiO_2, 200 × 20 mm).

***rac*-Tricarbonyl(*endo*-3-hydroxy-*exo*-3-methylisoindolin-1-one)-chromium(0) (*rac*-15):** Prepared by GP2. Complex **2** (0.30 g, 1.0 mmol) in THF (30 mL) and methyllithium (2.2 mL, 1.6 M in diethyl ether, 3.5 mmol) were stirred for 3 h at –78 °C and column chromatography (TBME) gave *rac*-**15** (0.27 g, 0.9 mmol, 84%) as a yellow solid, m.p. 178 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3390–3308 (w, br., OH, NH), 2982 (w), 1976 (s, CrCO), 1885 (s, CrCO), 1719 (m, NC=O), 1681 (m, NC=O), 1431 (w), 1400 (m), 1156 (m), 1090 (m), 1074 (w), 1057 (w), 1027 (m), 949 (m), 877 (w), 840 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.86 (s, 3 H, CH_3), 5.54 (s, 1 H, OH), 5.63 (m, 1 H, HOCCC*H*), 5.86 (m, 2 H, HOCCCHC*H*C*H*), 6.27 (d, *J* = 6.4 Hz, 1 H, HOCCCHCHCHC*H*), 8.17 (s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 27.3 (–, CH_3), 86.0 (–, COH), 87.1 (–, HOCCCHCHCH*C*H), 91.5 (–, HOCC*C*H), 93.0 (–, HOCCCH*C*H), 96.1 (–, HOCCCHCH*C*H), 99.0 (+, HOCC*C*CO), 119.9 (+, CHOC*C*), 167.5 (+, HOCC*C*O), 233.6 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 299 (3) $[M]^+$, 282 (5) [M – OH]$^+$, 281 (24) [M – H_2O]$^+$, 243 (2) [M – 2 CO]$^+$, 225 (12) [M – H_2O – 2 CO]$^+$, 215 (5) [M – 3 CO]$^+$, 198 (23) [M – OH – 3 CO]$^+$, 197 (94) [M – H_2O – 3 CO]$^+$, 163 (1) [M – $CrCO_3$]$^+$, 145 (36) [M – H_2O – $CrCO_3$]$^+$, 132 (7), 117 (6), 103 (10), 90 (11), 76 (12), 52 (100) $[Cr]^+$. HRMS: calcd. for $C_{12}H_9CrNO_5$ 298.9886; found 298.9886. $C_{12}H_9CrNO_5$ (299.20): calcd. C 48.17, H 3.03, N 4.68; found C 48.51, H 3.19, N 4.88.

***rac*-Tricarbonyl(*N*-methyl-*endo*-3-hydroxyisoindolin-1-one)chromium(0) (*rac*-16):** Complex **5** (0.20 g, 0.7 mmol) in THF/H_2O (1:1, 30 mL) and $NaBH_4$ (0.04 g, 1.0 mmol) in THF (1 mL) were mixed at –78 °C and then stirred for 0.5 h at 0 °C. After addition of hydrochloric acid (1 M, 5 mL) and extraction with ethyl acetate (3 × 15 mL) the product was isolated by column chromatography (SiO_2, 200 × 20 mm, ethyl acetate) to give *rac*-**16** (0.13 g, 0.4 mmol, 65%) as a yellow solid, m.p. 139 °C. IR (ATR): $\tilde{\nu}$ = 3150 (w, OH), 3087 (w), 1961 (s, CrCO), 1917 (s, CrCO), 1879 (s, CrCO), 1675 (s, NCO), 1541 (w), 1421 (m), 1395 (m), 1247 (w), 1094 (m), 1036 (m), 938 (w), 827 (w), 792 (m), 759 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, [D$_6$]acetone, HMQC): δ = 2.94 (s, 3 H, CH_3), 5.63–5.70 (m, 2 H, HOCCCHC*H*C*H*), 5.96 (m, 2 H, HOC*H*CCHCHCHC*H*), 6.06 (m, 2 H, HOCHCC*H*, OH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 26.1 (–, CH_3), 81.1 (–, HO*C*), 86.9 (–, HOCCCHCHCH*C*H), 89.9 (–, HOCC*C*H), 92.4 (–, HOCCCH*C*H), 93.8 (–, HOCCCHCH*C*H), 98.9 (+, HOCC*C*CO), 115.5 (+, HOC*C*), 165.8 (+, HOCN*C*), 232.7 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 299 (31) $[M]^+$, 243 (10) [M – 2 CO]$^+$, 215 (66) [M – 3 CO]$^+$, 213 (11) [M – 3 CO – 2H]$^+$, 198 (10) [M – 3 CO – OH]$^+$, 197 (11) [M – 3 CO – H_2O]$^+$, 187 (66) [M – 4 CO]$^+$, 163 (15) [M – Cr(CO)$_3$]$^+$, 162 (15) [M – Cr(CO)$_3$ – H]$^+$, 164 (100) [M – Cr(CO)$_3$ – OH]$^+$, 118 (28), 91 (37), 77 (26), 52 (74) $[Cr]^+$. HRMS: calcd. for $C_{12}H_9CrNO_5$ 298.9886; found 298.9889. $C_{12}H_9CrNO_5$ (299.21): calcd. C 48.17, H 3.03, N 4.68; found C 48.57, H 3.14, N 4.76.

***rac*-Tricarbonyl(*N*-methyl-*endo*-3-hydroxy-*exo*-3-methylisoindolin-1-one)chromium(0) (*rac*-17):** a) Prepared by GP2. Complex **5** (0.436 g, 1.5 mmol) in THF (15 mL) and methyllithium (3.8 mL, 1.6 M in diethyl ether, 6.0 mmol) were stirred for 3 h at –78 °C and column chromatography (TBME) gave *rac*-**17** (0.373 g, 1.2 mmol, 81%) as yellow crystals from CH_2Cl_2/hexanxe (1:3), m.p. 158 °C (dec.). b) Prepared by GP2. Complex **5** (0.50 g, 1.7 mmol) in THF (30 mL) and methylmagnesium chloride (1.4 mL, 3 M in THF, 4.2 mmol) were stirred for 2 h and column chromatography with ethyl acetate as eluent gave *rac*-**17** (0.49 g, 1.6 mmol, 93%). IR (ATR): $\tilde{\nu}$ = 3172 (w, OH), 2982 (w), 1952 (s, CrCO), 1869 (s, CrCO), 1669 (s, NCO), 1542 (w), 1482 (w), 1420 (m), 1373 (m), 1261 (w), 1225 (m), 1187 (w), 1151 (m), 1090 (m), 1074 (w), 1057 (w), 1027 (m), 949 (m), 806 (w), 774 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, CCH_3), 2.91 (s, 3 H, NCH_3), 5.50 (s, 1 H, OH), 5.65–5.71 (m, 2 H, HOCCCHC*H*C*H*), 5.90 (d, *J* = 6.2 Hz, 1 H, HOCCCHCHCH*C*H), 6.16 (d, *J* = 6.2 Hz, 1 H, HOCCC*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 24.7 (–, NCH_3), 26.7 (–, C*C*H$_3$), 87.7 (–, HOCCCHCHCH*C*H), 88.4 (+, HOC), 90.2 (–, HOCCCHCH*C*H), 93.5 (–, HOCC*C*H), 95.4 (–, HOCCCH*C*H), 99.5 (+, HOC*C*), 121.7 (+, HOCC*C*CH), 166.2 (+, HOCCC*C*O), 234.0 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 313 (56) $[M]^+$, 295 (10), 257 (23) [M – 2 CO]$^+$, 230 (43) [M – 3 CO]$^+$, 211 (82), 201 (67), 213 (85), 201 (16), 171 (11), 160 (100) [M – Cr(CO)$_3$ – OH]$^+$, 146 (43), 130 (31), 117 (15), 103 (40), 91 (47), 77 (43), 52 (74) $[Cr]^+$. HRMS: calcd. for $C_{13}H_{11}CrNO_5$ 313.0042; found 313.0042.

Crystal Structure Analysis of *rac*-17:[44] $C_{13}H_{11}CrNO_5$, molecular weight 313.25, crystal system monoclinic, space group *P*21/*c*, *a* = 13.448(6), *b* = 6.432(2), *c* = 15.779(8) Å, *α* = 90, *β* = 105.29(6), *γ* = 90°, *V* = 1316.5(10) Å^3, *Z* = 4, $d_{calcd.}$ = 1.580 g/cm^3, *F*(000) = 640*e*, *μ* = 0.887 mm^{-1}, crystal color red, crystal size 0.11 × 0.04 × 0.02 mm, Stoe IPDS (Area Detector) diffractometer, *T* = 300(2) K, *λ*(Mo-$K_α$) = 0.71073 Å, θ_{min} = 2.68°, θ_{max} = 24.53°, –15 ≤ *h* ≤ 14, –7 ≤ *k* ≤ 7, –17 ≤ *l* ≤ 18, no absorption correction, no extinction correction, 6010 collected, 2117 unique reflections [*R*(int) = 0.2967], refinement program: SHELXL-93, refinement by full-matrix least-squares method (F^2), *S* = 0.839, *R* indices [$I > 2\sigma(I)$]: R_1 = 0.1055, wR_2 = 0.1488, *R* indices (all data): R_1 = 0.3936, wR_2 = 0.2076, min./max. residual electron density: –0.331/0.476 Å^{-3}, completeness of data 99.3%.

***rac*-Tricarbonyl[*exo*-3-hydroxy-*endo*-3-(1-propynyl)-*N*-methylisoindolin-1-one]chromium(0) (*rac*-18):** Prepared by GP 2. At –78 °C, butyllithium (2.9 mL, 4.6 mmol, 1.6 M in hexane) was added to 1-bromo-1-propene (505 mg, 4.2 mmol) in THF (10 mL) and the mixture was stirred for 2 h.[45] Complex **5** (305 mg, 1.0 mmol) in THF (15 mL) was added and the mixture stirred at –78 °C for 2 h followed by the addition of methanol (20 mL) and column chromatography (petroleum ether/TBME, 1:4, then ethyl acetate) gave *rac*-**18** (0.9 mmol, 90%) as a red-orange solid, m.p. 133 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3435 (w, OH), 2253 (w, C≡C), 2120 (w),

1969 (s, CrCO), 1881 (s, CrCO), 1674 (m, NCO), 1544 (w), 1477 (w), 1415 (w), 1366 (w), 1259 (m), 1206 (s), 1165 (w), 1091 (m), 1015 (s), 796 (s), 652 (m), 619 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.88 (s, 3 H, CCH_3), 2.95 (s, 3 H, NCH_3), 5.69–5.76 (m, 2 H, HOCCCHC*H*C*H*CH), 5.95 (m, 1 H, HOCCC*H*CHCHCH or HOCCCHCHCHC*H*), 6.15 (m, 1 H, HOCCC*H*CHCHCH or HOCCCHCHCHC*H*), 6.82 (s, 1 H, OH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 3.82 (–, C*C*H$_3$), 25.0 (–, NCH_3), 76.8 (+, HOC), 82.5 (+, H_3CC*C*), 84.6 (+, H_3C*C*), 87.4 (–, HOCCCHCHCH*C*H), 89.8 (–, HOCC*C*HCHCHCH), 93.3 (–, HOCCCH*C*HCHCH or HOCCCHCH*C*HCH), 94.4 (–, HOCCCH*C*HCHCH or HOCCCHCH*C*HCH), 97.3 (+, HOCC*C*CO), 119.1 (+, HOC*C*CCO), 165.7 (+, NCO), 233.2 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 337 (45) [M]$^+$, 297 (58), 281 (23) [M – 2 CO]$^+$, 253 (63) [M – 3 CO]$^+$, 235 (59), 225 (33), 213 (85), 201 (16) [M – Cr(CO)$_3$]$^+$, 184 (70), 161 (52), 128 (28), 117 (26), 104 (32), 91 (17), 77 (48), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{15}H_{11}CrNO_5$ 337.0042; found 337.0042.

***rac*-Tricarbonyl[*exo*-3-hydroxy-*endo*-3-(1-methoxypropa-1,2-dienyl)-2-methylisoindolin-1-one]chromium(0) (*rac*-19):** Prepared by GP2. Complex **5** (0.265 g, 0.9 mmol) in THF (10 mL) and 1-lithio-1-methoxyallene [prepared by dropwise addition of butyllithium (13 mL, 1.6 M in hexane, 1.8 mmol) to methoxyallene (0.127 g, 1.8 mL) in diethyl ether (5 mL) followed by stirring for 2 h at –78 °C] were stirred for 2 h at –78 °C and hydrolyzed with satd. aq. NH_4Cl (10 mL). Purification by column chromatography (petroleum ether/TBME, 1:2, then ethyl acetate) gave *rac*-**19** (0.301 g, 0.8 mmol, 92%) as an orange solid, m.p. 109 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3421 (w, OH), 2961 (w), 1974 (s, CrCO), 1881 (s, CrCO), 1678 (m, CO), 1535 (w), 1392 (w), 1260 (w), 1096 (m), 1010 (m), 799 (m), 651 (m), 621 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.84 (s, 3 H, NMe), 3.38 (s, 3 H, OMe), 5.62–5.70 (m, 2 H, HOCCCHC*H*C*H*CH), 5.76 (d, ^2J = 8.9 Hz, 1 H, CH_2), 5.84 (d, ^2J = 8.9 Hz, 1 H, CH_2), 5.95 (d, J = 6.1 Hz, 1 H, HOCCCHCHCHC*H*), 6.06 (d, J = 6.2 Hz, 1 H, HPCCC*H*CHCHCH), 6.09 (s, 1 H, OH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 25.2 (–, NCH_3), 57.9 (–, OCH_3), 87.6 (–, HOCC*C*H), 88.6 (+, COH), 89.8 (–, HOCCHCHCH*C*H), 93.2 (–, HOCCCH*C*HCHCH or HOCCCHCH*C*HCH), 94.5 (–, HOCCCH*C*HCHCH or HOCCCHCH*C*HCH), 96.6 (+, CH_2), 98.7 (+, HOCC*C*CO), 118.9 (+, HOC*C*CCO), 134.4 (+, *C*OCH_3), 166.8 (+, NCO), 198.2 (+, *C*CH_2), 233.5 (+, CrCO) ppm. MS (70 eV, 130 °C): *m*/*z* (%) = 367 (24) [M]$^+$, 311 (28) [M – 2 CO]$^+$, 283 (94) [M – 3 CO]$^+$, 265 (29), 251 (64), 235 (59), 214 (61), 199 (12), 182 (89), 162 (22), 143 (12), 127 (17), 115 (12), 77 (19), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{13}H_{13}CrNO_3$ 283.0300; found 283.0301.

***rac*-Tricarbonyl[*exo*-3-hydroxy-*endo*-3-(1-propynyl)-2-vinylisoindolin-1-one]chromium(0) (*rac*-20):** Prepared by GP2. At –78 °C butyllithium (1 mL, 0.6 mmol, 1.6 M in hexane) was added to 1-bromo-1-propene (130 mg, 1.1 mmol) in THF (8 mL) and the mixture was stirred at –78 °C for 2 h.[45] Complex **9** (83 mg, 0.3 mmol) in THF (10 mL) was added at –78 °C and the mixture was stirred for 18 h at –78 °C followed by hydrolysis with 1 M hydrochloric acid (5 mL) and column chromatography (PE/TBME, 1:3, then ethyl acetate). Complex *rac*-**20** (84 mg, 0.2 mmol, 89%) was formed as a red-orange solid. Single crystals suitable for X-ray analysis were obtained by recrystallization in CH_2Cl_2/hexane (5:1), m.p. 182 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3320 (w, OH), 1975 (s, CrCO), 1907 (s, CrCO), 1702 (s), 1260 (m), 1096 (m), 1017 (m), 798 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.94 (s, 3 H, CH_3), 4.76 (d, $^3J_{cis}$ = 9.8 Hz, 1 H, *E*-CH_2), 5.49 (d, $^3J_{trans}$ = 16.4 Hz, 1 H, *Z*-CH_2), 5.78 (m, 2 H, HOCCCHC*H*C*H*CH), 5.97 (m, 1 H, HOCCC*H*CHCHCH or HOCCCHCHCHC*H*), 6.28 (m, 1 H, HOCCC*H*CHCHCH or HOCCCHCHCHC*H*), 6.60 (s, 1 H, OH), 6.70 (dd, $^3J_{cis}$ = 9.8, $^3J_{trans}$ = 16.9 Hz, 1 H, C*H*CH_2) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 4.02 (–, CH_3), 76.5 (+, COH), 83.7 (+, HOC*C*CCH_3), 86.4 (+, HOCC*C*CH_3), 87.1 (–, HOCCCHCHCH*C*H), 90.5 (–, HOCCC*H*CHCHCH), 93.8 (–, HOCCCHCH*C*HCH), 95.2 (–, HOCCCH*C*HCHCH), 95.5 (+, HOC*C*CO), 100.6 (+, CH_2), 117.7 (+, HOC*C*CCO), 126.9 (–, *C*HCH_2), 164.8 (+, HOCC*C*O), 232.8 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 349 (28) [M]$^+$, 309 (38), 293 (24) [M – 2 CO]$^+$, 265 (54) [M – 3 CO]$^+$, 247 (55), 237 (35), 225 (62), 213 (19) [M – Cr(CO)$_3$]$^+$, 196 (61), 167 (77), 149 (58), 130 (25), 115 (59), 104 (50), 89 (24), 76 (55), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{16}H_{11}NO_5Cr$ 349.0042; found 349.0042.

Crystal Structure Analysis of *rac*-20:[44] $C_{16}H_{11}CrNO_5$, molecular weight 349.26, crystal system triclinic, space group $P\bar{1}$, a = 6.970(1), b = 9.211(3), c = 12.608(3) Å, α = 103.15(2), β = 105.27(2), γ = 91.74(2)°, V = 756.9(3) Å^3, Z = 2, $d_{calcd.}$ = 1.533 g/cm^3, $F(000)$ = 356*e*, μ = 0.780 mm^{-1}, crystal color red, Stoe IPDS (area detector) diffractometer, T = 300(2) K, λ(Mo-K_α) = 0.71073 Å, θ_{min} = 2.28°, θ_{max} = 26.25°, $-8 \le h \le 8$, $-11 \le k \le 11$, $-15 \le l \le 15$, no absorption correction, no extinction correction, 10788 collected, 2787 unique reflections [R(int) = 0.1234], refinement program: SHELXL-93, refinement by full-matrix least-squares method (F^2), S = 0.846, R indices [I>2σ(I)]: R_1 = 0.0527, wR_2 = 0.0707, R indices (all data): R_1 = 0.1736, wR_2 = 0.0870, min./max. residual electron density: –0.523/0.365 Å^{-3}, completeness of data 93%.

***rac*-Tricarbonyl[*endo*-3-hydroxy-*exo*-3-(1-methylethenyl)-*N*-vinylisoindolin-1-one]chromium(0) (*rac*-21):** Prepared by GP2. 2-Bromopropene (279 mg, 2.31 mmol) was added dropwise to lithium sand (25 mg, 3.6 mmol) in diethyl ether (10 mL) and heated at reflux for 2 h. The resulting solution of 2-lithiopropene was cooled to –78 °C and **9** (143 mg, 0.5 mmol) in THF (10 mL) was added dropwise. The mixture was stirred for 2 h at –78 °C, hydrolyzed with 1 M hydrochloric acid (10 mL), and purified by column chromatography (PE/TBME, 1:1 to 1:2) to give *rac*-**21** (65 mg, 0.2 mmol, 40%) as a yellow solid, m.p. 113 °C (dec.). Elution with ethyl acetate gave *rac*-**20** (79 mg, 0.2 mmol, 48%). ***rac*-21:** IR (ATR): $\tilde{\nu}$ = 3368 (w, OH), 1960 (s, CrCO), 1884 (s, CrCO), 1721 (w), 1675 (m, CO), 1638 (m), 1317 (m), 1175 (m), 1117 (m), 1022 (m), 996 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.47 (s, 3 H, CH_3), 4.58 (d, $^3J_{cis}$ = 9.8 Hz, 1 H, *E*-CHCH_2), 5.20 (d, $^3J_{trans}$ = 16.4 Hz, 1 H, *Z*-CHCH_2), 5.33 (m, 1 H, H_3CCC*H*$_2$), 5.16 (s, 1 H, OH), 5.79–5.82 (m, 3 H, HOCCCHC*H*C*H*CH, H_3CCC*H*$_2$), 5.97–6.01 (m, 2 H, HOCCC*H*CHCHC*H*), 6.70 (m, 1 H, C*H*CH_2) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, HMQC): δ = 18.6 (–, CH_3), 86.7 (–, HOCC*C*HCHCH*C*H or HOCCCHCHCH*C*H), 89.5 (–, HOCC*C*HCHCH*C*H or HOCCCHCHCH*C*H), 91.6 (+, HOC), 93.3 (–, HOCCCH*C*HCHCH or HOCCCHCH*C*HCH), 95.2 (–, HOCCCH*C*HCHCH or HOCCCHCH*C*HCH), 97.0 (+, HOC*C*CO), 99.3 (+, CH*C*H$_2$), 117.1 (+, H_3CC*C*H$_2$), 119.4 (+, HOCCCCO), 127.2 (–, *C*HCH_2), 144.3 (+, H_3C*C*), 165.7 (+, HOCCCC*C*O), 233.1 (+, CrCO) ppm. MS (70 eV, 115 °C): *m*/*z* (%) = 351 (34) [M]$^+$, 295 (43) [M – 2 CO]$^+$, 267 (87) [M – 3 CO]$^+$, 249 (71), 239 (20), 221 (43), 208 (11), 198 (91), 182 (30), 173 (14), 154 (18), 128 (18), 115 (22), 91 (13), 77 (22), 69 (29), 52 (100) [Cr]$^+$. HRMS: calcd. for $C_{16}H_{13}NO_5Cr$ 351.0199; found 351.0199.

***rac*-Tricarbonyl(*exo*-3-hydroxy-*endo*-3,*N*-divinylisoindolin-1-one)chromium(0) (*rac*-22):** Prepared by GP 2. Complex **9** (210 mg, 0.7 mmol) in THF (15 mL) and vinylmagnesium bromide (1.4 mL,

1.4 mmol, 1 M in THF) were stirred for 2 h at –78 °C and purification by column chromatography (TBME) gave *rac*-**22** (161 mg, 0.5 mmol, 70%) as an orange-yellow solid, m.p. 151 °C. IR (ATR): $\tilde{\nu}$ = 3285 (w, OH), 1972 (s, CrCO), 1884 (s, CrCO), 1673 (m, CO), 650 (s) cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 4.65 (d, $^3J_{cis}$ = 9.9 Hz, 1 H, *E*-CHCH_2), 5.27 (d, $^3J_{trans}$ = 16.4 Hz, 1 H, *Z*-CHCH_2), 5.59 (m, 1 H, CCHCH_2), 5.69 (m, 1 H, CCHCH_2), 5.87–5.94 (m, 4 H, HOCC*H*C*H*C*H*C*H*), 6.08 (m, 1 H, C*C*HCH$_2$), 6.31 (s, 1 H, OH), 6.71 (dd, $^3J_{trans}$ = 17.0, $^3J_{cis}$ = 9.8 Hz, 1 H, NCH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, HMQC): δ = 86.5 (–, arom. CH), 91.6 (–, HOCCCHCHCH*C*H), 93.4 (–, arom. CH), 93.5 (+, HOC), 96.7 (–, arom. CH), 97.1 (+, HOCC*C*CO), 100.6 (+, NCH*C*H$_2$), 115.5 (+, HOC*C*CCO), 119.7 (+, HOCCH*C*H$_2$), 127.2 (–, NCH), 138.6 (–, HOCCH), 165.5 (+, HOCCCC*C*O), 233.2 (+, CrCO) ppm. MS (70 eV, 110 °C): *m*/*z* (%) = 337 (46) $[M]^+$, 281 (41) $[M – 2\ CO]^+$, 253 (82) $[M – 3\ CO]^+$, 235 (67), 225 (42), 207 (54), 207 (20) $[M – Cr(CO)_3]^+$, 184 (87), 159 (80), 130 (57), 115 (33), 103 (57), 91 (11), 77 (75), 52 (100) $[Cr]^+$. HRMS: calcd. for $C_{15}H_{11}NO_5Cr$ 337.0042; found 337.0043.

***rac*-Tricarbonyl[*N*-(2-bromoethyl)-*endo*-3-hydroxy-*exo*-3-methylisoindolin-1-one]chromium(0) (*rac*-23):** Prepared by GP2. Complex **11** (0.30 g, 0.8 mmol) in THF (30 mL) and methylmagnesium chloride (0.5 mL, 1.5 mmol, 3 M in THF) were stirred at –78 °C for 10 h and purification by column chromatography (ethyl acetate) gave *rac*-**23** (0.23 g, 0.65 mmol, 74%) as a yellow solid, m.p. 128 °C. IR (ATR): $\tilde{\nu}$ = 3370 (br., OH), 1977 (s, CrCO), 1900 (s, CrCO), 1878 (s, CrCO), 1739 (s, NCO), 1376 (s), 1226 (m), 1109 (m), 1090 (m), 949 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.94 (s, 3 H, CH_3), 3.64 (t, ^3J = 7.9 Hz, 2 H, CH_2Br), 3.83 (t, ^3J = 8.0 Hz, 2 H, NCH_2), 5.73 (m, 2 H, HOCCCHC*H*C*H*CH), 5.93 (m, 2 H, *H*OCCC*H*), 6.39 (d, J = 6.1 Hz, 1 H, HOCCCHCHCHC*H*) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 25.5 (–, CH_3), 29.1 (+, CH_2Br), 41.4 (+, NCH_2), 86.2 (–, HOCCCHCHCH*C*H), 88.4 (+, HOCC*C*CO), 91.2 + 92.3 (–, HOCCCH*C*H*C*HCH), 95.9 (–, HOCC*C*HCHCHCH), 97.5 (+, HOC), 117.4 (+, HOC*C*CCO), 166.4 (+, NCO), 232.9 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 407 + 405 (2, 2) $[M]^+$, 390 + 388 (19, 20) $[M – OH]^+$, 389 + 387 (48, 48) $[M – H_2O]^+$, 351 + 349 (3, 3) $[M – 2\ CO]^+$, 333 + 331 (15, 15) $[M – 2\ CO – H_2O]^+$, 323 + 321 (1, 1) $[M – 3\ CO]^+$, 305 + 303 (11, 11) $[M – 3\ CO – H_2O]^+$, 295 + 293 (4, 4) $[M – 4\ CO]^+$, 277 + 275 (99, 100) $[M – 4\ CO]^+$, 253 + 251 (10, 9) $[M – Cr(CO)_3 – H_2O]^+$, 196 (65), 172 (41), 158 (22), 77 (12), 52 (60) $[Cr]^+$. HRMS: calcd. for $C_{14}H_{12}BrCrNO_5$ 404.9304; found 404.9307.

***rac*-Tricarbonyl(*endo*-3-hydroxy-*exo*-3-methyl-*N*-phenylisoindolin-1-one)chromium(0) (*rac*-24):** Prepared by GP2. Complex **12** (0.30 g, 0.8 mmol) in THF (30 mL) and methylmagnesium chloride (0.6 mL, 1.6 mmol, 3 M in THF) were stirred at –78 °C for 10 h and purification by column chromatography (ethyl acetate) gave *rac*-**24** (0.24 g, 0.6 mmol, 78%) as a yellow solid, m.p. 148 °C. IR (ATR): $\tilde{\nu}$ = 3400 (w, OH), 3070 (w), 1963 (s, CrCO), 1958 (s, CrCO), 1889 (s, CrCO), 1700 (s, NCO), 1499 (m), 1383 (m), 1217 (w) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone, HMQC): δ = 1.73 (s, 3 H, CH_3), 5.72 (s, 1 H, HOCCCHCHC*H*CH), 5.94 (s, 1 H, HOCCCHC*H*CHCH), 6.00 (m, 1 H, HOCCC*H*CHCHCH), 6.11 (s, 1 H, OH), 6.45 (s, 1 H, HOCCCHCHCHC*H*), 7.4 (m, 5 H, Ph-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 24.7 (–, CH_3), 85.5 (–, HOCCCHCHCH*C*H), 89.1 (+, HOC), 90.5 (–, HOCC*C*HCHCHCH), 91.4 (–, HOCCCH*C*HCHCH), 95.3 (–, HOCCCHCH*C*HCH), 97.1 (+, CHOCC*C*CO), 116.5 (+, HOC*C*CCO), 123.3 (–, *p*-CH), 127.5 (–, *m*-CH), 128.8 (–, *o*-CH), 132.1 (+, *ipso*-C), 164.8 (+, NCO), 232.2 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 274 (4) $[M – 3\ CO – OH]^+$, 273 (3) $[M – 3\ CO – H_2O]^+$, 239 (2) $[M – Cr(CO)_3]^+$, 223 (100) $[M – Cr(CO)_3 – O]^+$, 222 (7) $[M – Cr(CO)_3 – OH]^+$, 179, 147, 104, 76, 52 $[Cr]^+$. $C_{18}H_{13}CrNO_5$ (375.30): calcd. C 57.61, H 3.49, N 3.73; found C 57.85, H 3.34, N 3.86.

***rac*-Tricarbonyl[9b-*exo*-methyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one]chromium(0) (*rac*-35):** Prepared by GP 2. Complex **11** (0.30 mg, 0.8 mmol) in THF (30 mL) and methylmagnesium chloride (0.5 mL, 1.5 mmol, 3 M in THF) were stirred at 25 °C for 24 h and column chromatography (TBME/petroleum ether, 1:1, then ethyl acetate) gave *rac*-**35** (0.12 g, 0.4 mmol, 46%) as a yellow solid (m.p. 107 °C) and *rac*-**23** (0.04 g, 0.01 mmol, 13%). ***rac*-35:** IR (ATR): $\tilde{\nu}$ = 1950 (s, CrCO), 1889 (s, CrCO), 1865 (s, CrCO), 1709 (s, NCO), 1413 (m), 1375 (s), 1258 (m), 1142 (m), 1075 (m), 1045 (m), 1019 (m), 798 (m) 695 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]-acetone): δ = 1.82 (s, 3 H, CH_3), 3.51 (m, 1 H, NCH_2), 4.08 (m, 2 H, OCH_2), 4.26 (m, 1 H, NCH_2), 5.77 (m, 1 H, H$_3$CCCCHCHCHC*H*), 5.93 (t, J = 6.1 Hz, 1 H, H$_3$CCCCHC*H*CHCH), 5.95 (d, J = 6.2 Hz, 1 H, H$_3$CCCC*H*CHCHCH), 6.44 (d, J = 6.1 Hz, 1 H, H$_3$CCCCHCHC*H*CH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 20.9 (–, CH_3), 42.1 (+, NCH_2), 68.6 (+, OCH_2), 86.0 (–, CH), 90.5 (–, CH), 91.9 (–, CH), 95.2 (–, CH), 95.1 (+, H$_3$C*C*), 97.0 (+, H$_3$CCC*C*CO), 113.1 (+, H$_3$CC*C*CCO), 165.9 (+, NCO), 231.7 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 325 (42) $[M]^+$, 269 (13) $[M – 2\ CO]^+$, 241 (66) $[M – 3\ CO]^+$, 213 (44) $[M – 4\ CO]^+$, 189 (2) $[M – Cr(CO)_3]^+$, 174 (49) $[M – Cr(CO)_3 – CH_3]^+$, 147 (27), 130 (36), 102 (11), 77 (21), 52 (100) $[Cr]^+$. HRMS: calcd. for $C_{14}H_{11}CrNO_5$ 325.0042; found 325.0039. $C_{14}H_{11}CrNO_5$ (325.24): calcd. C 51.70, H 3.41, N 4.31; found C 51.85, H 3.24, N 4.26.

***rac*-Tricarbonyl(*endo*-3-methoxy-*exo*-3,*N*-dimethylisoindolin-1-one)chromium(0) (*rac*-36):** At –78 °C NaH (0.03 g, 1.3 mmol) was added to *rac*-**17** (0.30 g, 1.0 mmol) in THF (40 mL). Then iodomethane (0.18 g, 1.3 mmol) was added at –78 °C and the mixture was stirred for 4 h. After solvent removal to around 5 mL under reduced pressure the residue was diluted with water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The crude product was purified by column chromatography (SiO_2, 200 × 20 mm, TBME) to give *rac*-**36** (0.23 g, 0.7 mmol, 73%) as a yellow solid, m.p. 114 °C. IR (ATR): $\tilde{\nu}$ = 1957 (s, CrCO), 1892 (s, CrCO), 1863 (s, CrCO), 1709 (s, NCO), 1416 (m), 1375 (s), 1257 (m), 1142 (m), 1075 (m), 1045 (m), 1019 (m), 798 (m), 694 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D$_6$]acetone, HMQC): δ = 1.80 (s, 3 H, CCH_3), 2.79 (s, 3 H, OCH_3), 2.86 (s, 3 H, NCH_3), 5.66 (t, J = 5.9 Hz, 1 H, H$_3$COCCCHCHC*H*CH), 5.93 (m, 2 H, H$_3$COCCCHC*H*C*H*CH), 6.33 (d, J = 6.3 Hz, 1 H, H$_3$COCCCHCHCHC*H*) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 23.8 (–, NCH_3), 24.9 (–, CCH_3), 49.8 (–, OCH_3), 85.8 (–, H$_3$COCC*C*HCHCHCH), 91.60 (–, H$_3$COCCCHCHCH*C*H), 91.75 (–, H$_3$COCCCH*C*HCHCH), 91.77 (+, H$_3$CO*C*), 96.2 (–, H$_3$COCCCHCH*C*HCH), 99.1 (+, H$_3$COCC*C*CO), 113.2 (+, H$_3$COC*C*CCO), 165.8 (+, NCO), 232.7 (+, CrC) ppm. MS (70 eV): *m*/*z* (%) = 327 (11) $[M]^+$, 296 (5) $[M – CH_3O]^+$, 295 (9) $[M – CH_3OH]^+$, 271 (4) $[M – 2\ CO]^+$, 243 (28) $[M – 3\ CO]^+$, 212 (19) $[M – 3\ CO – CH_3O]^+$, 211 (70) $[M – 3\ CO – CH_3OH]^+$, 160 (82) $[M – Cr(CO)_3 – CH_3O]^+$, 159 (23) $[M – Cr(CO)_3 – CH_3OH]^+$, 130 (27), 103 (15), 91 (13), 77 (22), 52 (100) $[Cr]^+$. HRMS: calcd. for $C_{14}H_{13}CrNO_5$ 327.0199; found 327.0202.

Tricarbonyl(*N*-methyl-3-methylene-2,3-dihydroisoindol-1-one)chromium(0) (*rac*-37): At –78 °C $BF_3{\cdot}Et_2O$ (2 mL, 48% BF_3) was added to *rac*-**17** (0.20 g, 0.7 mmol) in THF (30 mL). The mixture was stirred at –78 °C for 10 h. After solvent removal under reduced pressure the mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 20 mL). The crude product was purified by column chromatography (TBME/petroleum ether, 4:1) to give *rac*-

37 (0.10 g, 0.3 mol, 53%) as an orange solid, m.p. 85 °C. IR (ATR): $\tilde{\nu}$ = 3095 (w, $=CH_2$), 1965 (s, CrCO), 1889 (s, CrCO), 1703 (s, NCO), 1642 (s), 1532 (w), 1433 (m), 1381 (m), 1302 (w), 1080 (m), 1029 (m), 841 (w), 770 (w), 697 (m) cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$, HMQC): δ = 3.23 (s, 3 H, CH_3), 4.88 (d, ^2J = 2.5 Hz, 1 H, CH_2), 5.04 (d, ^2J = 2.6 Hz, 1 H, CH_2), 5.30 (t, J = 6.5 Hz, 1 H, $H_2CCCCHCHCHCH$), 5.60 (t, J = 6.5 Hz, 1 H, $H_2CCCHCHCHCH$), 5.81 (d, J = 6.3 Hz, 1 H, $H_2CCCCHCHCH$), 6.14 (d, J = 6.3 Hz, 1 H, $H_2CCCCHCHCHCH$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.3 (–, CH_3), 82.6 (–, $H_2CCCCHCHCHCH$), 88.4 (–, $H_2CCCCHCHCHCH$), 88.8 (–, $H_2CCCHCHCHCH$), 89.4 (+, CH_2), 90.5 (+, $H_2CCCCCO$), 93.2 (–, $H_2CCCCHCHCHCH$), 102.0 (+, $H_2CCCCCO$), 141.2 (+, H_2CC), 165.3 (+, NCO), 230.6 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 295 (18) $[M]^+$, 239 (11) $[M – 2\ CO]^+$, 211 (89) $[M – 3\ CO]^+$, 159 (100) $[M – Cr(CO)_3]^+$, 131 (15) $[M – 4\ CO]^+$, 130 (78) $[M – Cr(CO)_3 – H]^+$, 116 (11) $[M – Cr(CO)_3 – CH_3]^+$, 103 (17), 90 (17), 77 (19), 52 (90) $[Cr]^+$. HRMS: calcd. for $C_{13}H_9CrNO_4$ 294.9937; found 294.9935. $C_{13}H_9CrNO_4$ (295.21): calcd. C 52.89, H 3.07, N 4.74; found C 52.57, H 2.97, N 4.82.

Crystal Structure Analysis of *rac*-37:[44] $C_{13}H_9CrNO_4$, molecular weight 295.21, crystal system triclinic, space group $P\bar{1}$, a = 8.959(4), b = 10.384(4), c = 14.826(7) Å, α = 73.16(5), β = 84.76(5), γ = 67.22(5)°, V = 1216.8(9) $Å^3$, Z = 4, $d_{calcd.}$ = 1.611 g/cm^3, $F(000)$ = 600, μ = 0.95 mm^{-1}, crystal color orange, Stoe IPDS (area detector) diffractometer, T = 298(2) K, λ(Mo-K_α) = 0.71073 Å, θ_{min} = 2.2°, θ_{max} = 26.3°, $-11 \le h \le 11$, $-12 \le k \le 12$, $-18 \le l \le 18$, absorption correction method multi-scan, T_{min} = 0.789, T_{max} = 0.893, no extinction correction, 15364 collected, 4506 unique reflections [R(int) = 0.108], refinement program: SHELXL-97, refinement by full-matrix least-squares method (F^2), S = 1.05, R indices [$I>2\sigma(I)$]: R_1 = 0.0631, wR_2 = 0.1552, R indices (all data): R_1 = 0.0963, wR_2 = 0.1458, min./max. residual electron density: –0.481/0.89 $Å^{-3}$, completeness of data 92%.

Tricarbonyl(*endo*-3,*N*-dimethyl-2,3-dihydroisoindol-1-one)chromium(0) (*rac*-38): At –78 °C triethylsilane (1 mL, 0.728 g, 6.3 mmol) and $BF_3{\cdot}Et_2O$ (1 mL, 48% BF_3) were added to *rac*-**17** (0.40 g, 1.3 mmol) in THF (40 mL). After stirring for 8 h at –78 °C the solvent was removed under reduced pressure and water (30 mL) was added. The mixture was extracted with ethyl acetate (3 × 30 mL) and the crude product was purified by column chromatograph (200 × 20 m, TBME/petroleum ether, 2:1, then 4:1) to give *rac*-**38** (0.23 g, 0.8 mmol, 61%) as a yellow solid (m.p. 134 °C) and *rac*-**37** (0.04 g, 0.1 mmol, 11%). *rac*-**38**: IR (ATR): $\tilde{\nu}$ = 3058 (w, CH), 1964 (s, CrCO), 1871 (s, CrCO), 1688 (s, NCO), 1551 (w), 1424 (m), 1394 (s), 1261 (m), 1150 (m), 1066 (m), 771 (m) cm^{-1}. ^1H NMR (400.1 MHz, [D_6]acetone, HMQC, HMBC): δ = 1.60 (d, ^3J = 6.5 Hz, 3 H, CCH_3), 3.01 (s, 3 H, NCH_3), 4.64 (q, ^3J = 6.1 Hz, 1 H, H_3CCH), 5.62 (t, J = 6.1 Hz, 1 H, $H_3CCHCCHCHCHCH$), 5.84 (t, J = 6.0 Hz, 1 H, $H_3CCHCCHCHCHCH$), 5.90 (d, J = 5.9 Hz, 1 H, $H_3CCHCCHCHCH$), 6.29 (d, J = 6.1 Hz, 1 H, $H_3CCHCCHCHCHCH$) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone, HMBC): δ = 18.6 (–, CCH_3), 26.3 (–, NCH_3), 55.9 (–, H_3CCH), 85.4 (–, $H_3CCHCCHCHCHCH$), 90.6 (–, $H_3CCHCCHCHCHCH$), 91.1 (–, $H_3CCHCCHCHCHCH$), 95.0 (–, $H_3CCHCCHCHCHCH$), 100.0 (+, $H_3CCHCCCO$), 117.3 (+, $H_3CCHCCCO$), 165.8 (+, NCO), 233.0 (+, CrCO) ppm. MS (70 eV): *m*/*z* (%) = 297 (26) $[M]^+$, 241 (8) $[M – 2\ CO]^+$, 213 (96) $[M – 3\ CO]^+$, 161 (43) $[M – Cr(CO)_3]^+$, 146 (100) $[M – Cr(CO)_3 – CH_3]^+$, 130 (15), 103 (17), 91 (30), 77 (22), 76 (11), 52 (89) $[Cr]^+$. HRMS: calcd. for $C_{13}H_{11}CrNO_4$ 297.0093; found 297.0093.

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