ELSEVIER

Journal of Organometallic Chemistry 559 (1998) 131–140

Journal of Organometallic Chemistry

# Reduction of tricarbonyl($\eta^6$-Indole)chromium(0) complexes

F. Christopher Pigge *, Shiyue Fang, Nigam P. Rath

*Department of Chemistry, University of Missouri- St. Louis, St. Louis, MO 63121-4499, USA*

Received 7 November 1997

**Abstract**

Tricarbonyl($\eta^6$-indole)chromium(0) complexes substituted at the C2 and/or C3 positions have been reduced to the corresponding indoline complexes by the action of a hydride donor in trifluoroacetic acid. $NaBH_3CN$ and $NaBH_4$ were found to be superior to $Et_3SiH$ as hydride sources. In general, reductions involving the use of $NaBH_3CN$ were found to occur with greater stereoselectivity as compared to reductions using $NaBH_4$. With certain (indole)chromium complexes, this stereoselectivity was a result of preferential hydride addition from the *endo* face, as revealed by single crystal X-ray analysis. 

*Keywords:* (arene)chromium; Reduction; Indole; Indoline; Sodium cyanoborohydride

## 1. Introduction

The chemistry of tricarbonyl($\eta^6$-arene)chromium(0) complexes continues to attract a great deal of attention and these materials have emerged as versatile intermediates in organic synthesis [1]. Coordination of an arene moiety to the $Cr(CO)_3$ fragment renders the ring susceptible to lithiation as well as substitution by nucleophilic addition with high levels of regioselectivity [2]. In addition, the steric bulk of the metal fragment coupled to an ability to stabilize both positive and negative charge at benzylic positions facilitates stereocontrolled manipulation of functionality at sites adjacent to the arene ring [3]. Furthermore, the accessibility of enantiomerically pure planar-chiral arenechromium complexes has resulted in the development of new methodologies for asymmetric synthesis [1–3].

In connection with a program involving manipulation of ($\eta^6$-indoline)metal complexes, we required access to a variety of substituted ($\eta^6$-indoline)$Cr(CO)_3$ derivatives. Rather than preparing the indoline ligands in anticipation of subsequent complexation with a $Cr(CO)_3$ fragment, we instead envisioned an approach which involved the reduction of the corresponding (indole)$Cr(CO)_3$ complexes, in turn obtained from readily available indole precursors. (Indole)$Cr(CO)_3$ complexes are well-characterized organometallic species and have proven to be particularly useful intermediates in the synthesis of C4 and C7 substituted indole derivatives [4]. Significantly, however, the manipulation of (indole)$Cr(CO)_3$ complexes at positions adjacent to the aromatic ring (i.e. C2 and C3) has been scarcely explored [4]c. Reactions at these positions which deliver a saturated 5-membered ring would be expected to proceed with high levels of stereoselection given the presence of the metal center [1,3]; thus, a general means for contolling the relative (and potentially absolute) stereochemistry of the indoline ring system in these complexes might be realized. As an initial test of the efficacy of this approach, we have examined the reduction of several (indole)$Cr(CO)_3$ derivatives.

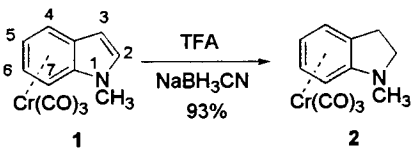
* Corresponding author. Tel.: +1 314 5165340; fax: +1 314 5165342.

0022-328X/98/$19.00 
*PII* S0022-328X(98)00403-3

## 2. Results and discussion

Indoles are typically reduced to indolines by treatment with a hydride reagent under acidic conditions [5]. Deuterium labeling studies indicate the reaction proceeds via initial protonation at C3 to generate an indolenium ion which is subsequently reduced by the hydride donor [6]. Accepting this mechanistic rationale, there were two principle concerns regarding the viability of this protocol for the reduction of (indole)chromium complexes. Firstly, there was no certainty that the metal complexes would be stable to the necessary acidic reaction conditions. Secondly, the $Cr(CO)_3$ fragment acts as a powerful electron withdrawing group and may reduce the nucleophilicity of the C2–C3 $\pi$ bond to such an extent that protonation at C3 is precluded [1–3]. Consequently, initial studies were performed on readily available (*N*-methylindole)$Cr(CO)_3$ **1** [7].

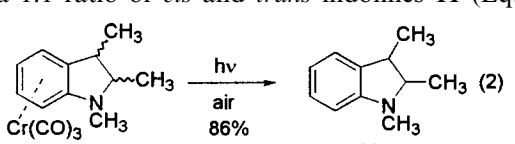
Addition of $NaBH_4$ to a degassed solution of **1** in acetic acid according to the procedure of Gribble [6] resulted only in recovery of unreacted starting material, even after prolonged reaction times and heating of the reaction mixture. Thus, while **1** remained intact under these conditions, it appeared that C3 protonation was indeed problematic. Application of a procedure reported by Ketcha for the reduction of electron deficient indoles was next examined [8]. Gratifyingly, addition of **1** to a degassed solution of trifluoroacetic acid (TFA) at 0°C resulted in immediate formation of a wine-red solution, presumably indicative of the intermediate indolenium ion. Careful addition of an excess (~5 equivalents) of $NaBH_3CN$ led to the rapid discharge of the red color concomitant with formation of the indoline complex **2** [9], isolated in 93% yield after aqueous work-up (Eq. (1)).




(1)

With an efficient procedure in hand, the reduction of (indole)$Cr(CO)_3$ complexes bearing substituents at the C2 and/or C3 positions was examined and the results of these efforts are summarized in Table 1. All of the chromium complexes used as starting materials were easily prepared from the corresponding indole and $Cr(CO)_6$ using standard procedures [4]c. At the outset, it was anticipated that these reductions would proceed with high levels of stereoselectivity in line with the well-known ability of the $Cr(CO)_3$ fragment to serve as a stereodirecting group [1,3]. Reduction of the 3-methylindole complex **3**, however, afforded only a 1.7:1 mixture of indoline complexes **4** and **5**, albeit in quite acceptable (75%) isolated yield. Stereochemical assignment of the products was made based upon comparison of the $^1$H-NMR chemical shift of the 3-methyl substituent. *Endo* oriented groups are observed to resonate at lower field than their analogous *exo* isomers due to the deshielding effect of the $Cr(CO)_3$ moiety [10]. While the major isomer **4** was formed through the expected reaction manifold involving C3 protonation from the sterically less hindered *exo* face (i.e. the face opposite the metal) the overall stereoselectivity was low, perhaps due to equilibration of the initially formed indolenium ion [6]. Reduction of the 2-methylindole isomer was found to proceed with much greater selectivity (entry 2), yielding a 4.5:1 mixture of isomers (as determined by $^1$H-NMR). Surprisingly however, the major product was found to be the *exo* isomer **7**, resulting from hydride addition to the putative indolenium ion from the sterically more hindered *endo* face. This stereochemical assignment was subsequently confirmed by X-ray crystal structure analysis of **7** after chromatographic separation of the products (Fig. 1). The crystal data for **7** are shown in Table 2. The origin of this unusual stereochemical outcome is neither readily apparent nor easily rationalized [11]. Nucleophilic additions (including hydride additions) to functional groups at benzylic or homobenzylic positions of (arene)$Cr(CO)_3$ complexes are well-known to proceed predominantly or exclusively via attack from the *exo* face [1,3]; including additions to structurally related spiroindolenine- and phenyl(imine)$Cr(CO)_3$ derivatives [12,13]. Hydride addition to a CO ligand to form a metal formyl species capable of acting as a hydride delivery agent is unprecedented in reactions involving (arene)$Cr(CO)_3$ complexes and is therefore highly unlikely. Chromium-hydride (Cr–H) complexes have been prepared from (arene)$Cr(CO)_3$ derivatives and organosilanes under photochemical reaction conditions [14], but it seems improbable that such complexes would be formed under the reaction conditions used in this study. Instead, it appears the nature of the reducing agent plays a critical role in determining product stereochemistry (vide infra).

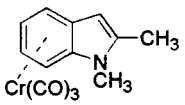
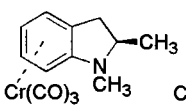
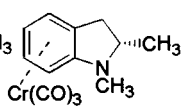
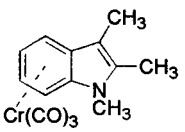
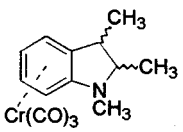
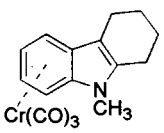
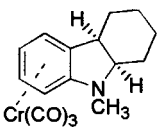
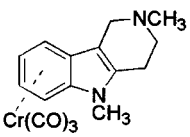
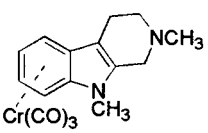
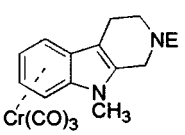
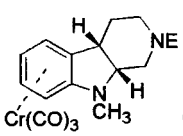
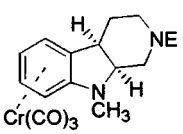
The 2,3-dimethylindole complex **9** was found to undergo reduction with no stereoselectivity as TLC and $^1$H-NMR revealed a complex mixture of what appeared to be all four possible stereoisomers (**10**) with none predominating. This lack of stereoselectivity was confirmed by oxidative removal of the metal center [3]c to give a 1:1 ratio of *cis* and *trans* indolines **11** (Eq. (2)).




(2)

In contrast, exposure of tetrahydrocarbazole complex **12** to these reaction conditions resulted in formation of

Table 1
Reduction of ($\eta^6$-indole)$Cr(CO)_3$ complexes with $NaBH_3CN$ in TFA

| Entry | Starting complex | Product(s) | Yield(%) |
|---|---|---|---|
| 1 |  **3** |  **4** (1.7)  **5** (1.0) | 75 |
| 2 |  **6** |  **7** (4.5)  **8** (1.0) | 87 |
| 3 |  **9** |  **10** | 85 |
| 4 |  **12** |  **13** | 84 |
| 5 |  **14** | N.R. | – |
| 6 |  **15** | N.R. | – |
| 7 |  **16** (E = $CO_2Me$) |  **17** (5.4)  **18** (1.0) | 83 |

a single *cis*-fused stereoisomer **13**. As the reduction of this ring system in the absence of metal complexation also generates a *cis* ring fusion [5], this stereochemistry was not unexpected. The interesting and unusual feature of this reaction was that the reduction had occurred exclusively from the *endo* face (as confirmed by X-ray cystallography [15]). A possible explanation for this outcome involves initial equilibration of indolenium ion intermediates such that the smallest C3 substituent (i.e. H) occupies the *endo* position. Hydride addition from the *endo* face then ensues to provide the preferred *cis* ring fusion.

As a final test of the scope of this reduction procedure, chromium complexes of the carboline ring system also were examined. As shown in entries 5 and 6, $\gamma$ and $\beta$ *N*-methylcarboline complexes **14** and **15** failed to react. However, the less basic carbamate substituted complex **16** underwent smooth reduction to afford a chromatograhphically separable 5.4:1 mixture of *cis*-fused isomers. The stereochemistry of the minor isomer (**18**) was established by X-ray crystallography and the molecular structure is shown in Fig. 2. The crystal data for **18** also are provided in Table 2. That the major product **17** was the isomeric *cis*-fused complex was

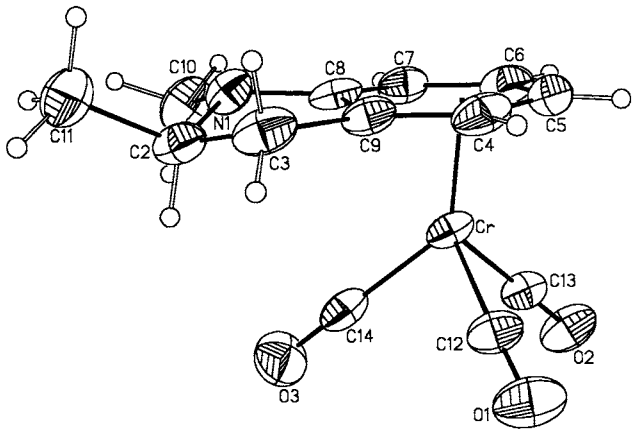



Fig. 1. Molecular structure of **7** (50% thermal ellipsoids). Selected bond distances (Å): Cr–C4 2.217; Cr–C5 2.223; Cr–C6 2.204; Cr–C7 2.268; Cr–C8 2.333; Cr–C9 2.258; Cr–C12 1.819; Cr–C13 1.840; Cr–C14 1.848.

established by comparison of the metal-free arenes obtained from both **17** and **18**, which were identical by $^{1}$H- and $^{13}$C-NMR (Eq. (3)).

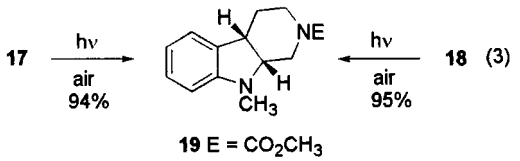



Table 2
Crystal data for complexes **7** and **18**

| | **7** | **18** |
|---|---|---|
| Molecular formula | $C_{13}H_{13}CrNO_3$ | $C_{17}H_{18}CrN_2O_5$ |
| Formula weight | 283.24 | 382.33 |
| $T$ (K) | 223(2) | 223(2) |
| Crystal dimensions (mm) | $0.30\times0.08\times0.02$ | $0.20\times0.15\times0.10$ |
| Space group | $P2_1/c$ | $P2_1/c$ |
| Crystal system | Monoclinic | Monoclinic |
| $a$ (Å) | 13.1585(2) | 11.3506(2) |
| $b$ (Å) | 7.39720(10) | 13.8699(2) |
| $c$ (Å) | 12.75950(10) | 10.9771(1) |
| $\beta$ (°) | 98.7760(10) | 105.435(1) |
| Vol (Å$^3$) | 1227.42(3) | 1665.81(4) |
| $Z$ | 4 | 4 |
| Density calcd (Mg m$^{-3}$) | 1.533 | 1.524 |
| Radiation ($\lambda$, Å) | Mo-K$_\alpha$ (0.71073) | Mo-K$_\alpha$ (0.71073) |
| $\mu$ (Mo-K$_\alpha$, cm$^{-1}$) | 9.30 | 7.18 |
| $F$ (000) | 584 | 792 |
| Scan type | $\omega$ | $\omega$ |
| $2\theta$ limit (°) | 50 | 52 |
| Tot. no. of refl. | 22 315 | 29 918 |
| Independent reflections | 2163 | 3256 |
| $R_1$ ($F$) | 7.6% | 4.6% |
| $wR_2$ ($F^2$) | 18.9% | 10.8% |
| GOF on $F^2$ | 1.067 | 1.076 |
| No. of parameters | 215 | 226 |
| Largest diff. peak (eÅ$^{-3}$) | 1.430 | 0.314 |

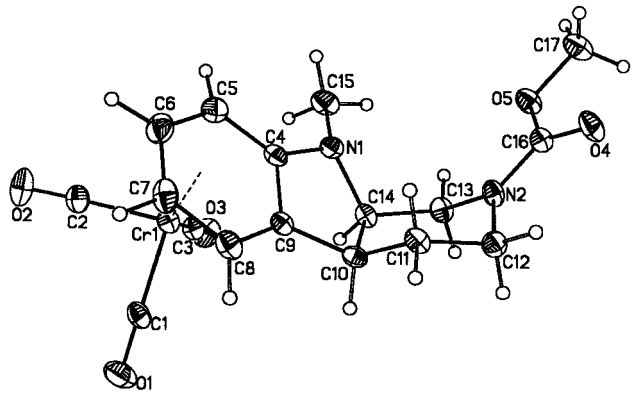
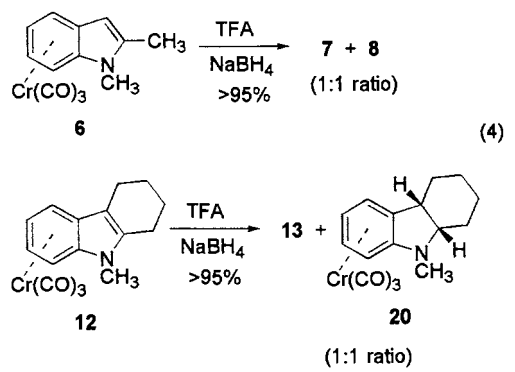


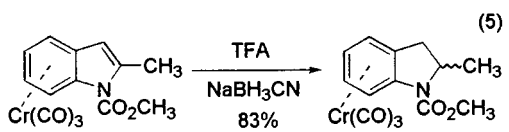

Fig. 2. Molecular structure of **18** (50% thermal ellipsoids). Selected bond distances (Å): Cr–4 2.332; Cr–C5 2.266; Cr–C6 2.193; Cr–C7 2.209; Cr–C8 2.228; Cr–C9 2.266; Cr–C1 1.835; Cr–C2 1.828; Cr–C3 1.836.

In this instance the predominant reaction pathway involves reduction of the carboline from the *exo* face. Evidently, the presence of the carboline N atom influences the course of the reaction (as compared to the carbazole reduction shown in entry 4), perhaps by inhibiting C3 equilibration.

The choice of $NaBH_3CN$ as the hydride source in these reactions was predicated upon the reported stability of this reagent to the acidic reaction conditions [8]. However, the rapidity with which these (indole)$Cr(CO)_3$ reductions occur suggested that less toxic and less expensive $NaBH_4$ may serve as a viable alternative reducing agent. Thus, complexes **6** and **12** were subjected to the standard reduction conditions (TFA, 0°C) with $NaBH_4$ substituted for $NaBH_3CN$ (Eq. (4)). Surprisingly, while the reaction proceeded to produce the corresponding indoline complexes in virtually quantitative yield, no stereoselectivity was observed for either substrate. Complex **6** yielded a ~1:1 mixture of C2 epimers **7** and **8** (as determined by $^{1}$H-NMR spectroscopy) compared to a 4.5:1 ratio when using $NaBH_3CN$. Complex **12**, which was found to undergo $NaBH_3CN$-mediated reduction with complete stereoselectivity, afforded a 1:1 mixture of **13** and **20**. The stereochemistry in **20** was established by X-ray crystallography [15].

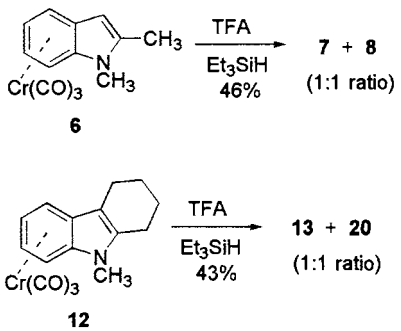


The absence of any stereoselectivity in the reductions involving $NaBH_4$, while unexpected, does seem to provide some insight into the factors responsible for the selectivity observed in the $NaBH_3CN$-mediated reductions. Addition of $NaBH_4$ to a solution of acetic acid (and presumably trifluoroacetic acid as well) is known to result in rapid evolution of 3 equivalents of $H_2$ with concomitant formation of triacetoxyborohydride [16]. It seems reasonable to expect that some sort of acetoxyborohydride is also being generated from $NaBH_3CN$; however, this species must be sufficiently different (perhaps due to the presence of a CN ligand) as to result in a more selective (perhaps less reactive) reducing agent relative to $NaBH_4$. The reasons for the *endo* selectivity exhibited by the $NaBH_3CN$/TFA reagent combination, especially with regard to the reduction of a conformationally unbiased indole complex such as **6**, remain obscure. Perhaps solvation of the intermediate indolenium ion and/or boron-nitrogen pairing result in increased steric bulk at the *exo* face, thereby causing the reduction to occur predominantly from the *endo* face. The steric environment and/or basicity of the indole nitrogen atom must also play a role as reduction of the carbamate derivative **21** with $NaBH_3CN$ was found to yield a 1:1 mixture of indoline complexes **22** and **23** (Eq. (5)). It also should be pointed out that the different selectivities observed when using $NaBH_4$ and $NaBH_3CN$ would seem to rule out the possibility that these reductions are proceeding through initial protonation at C2 followed by hydride addition to C3 [17].




**21** **22** (*exo* $CH_3$) **23** (*endo* $CH_3$) **22:23** = 1:1 (5)

Finally, in an effort to determine if some sort of 'Cr–H' species may be playing a role in these reductions, the use of $Et_3SiH$ as a hydride source was examined [18]. As mentioned previously, chromium hydrides have been obtained from organosilanes and (arene)$Cr(CO)_3$ complexes [14]. Additionally, $Et_3SiH$ has been used for the reduction of benzylic cations generated from arene–chromium complexes [3]b. Once again, **6** and **12** were used as substrates in order to compare any stereoselectivity pattern. In both instances, a ~1:1 mixture of the corresponding indolines was produced (Eq. (6)). Furthermore, this reagent combination resulted in greatly diminished yields and required prolonged reaction times. Given the lack of any stereoselectivity in these organosilane reductions, the intervention of metal-hydride intermediates seems unlikely.




## 3. Conclusions

The reagent combination of $NaBH_3CN$ in TFA efficiently reduces (indole)$Cr(CO)_3$ derivatives to the corresponding indoline complexes. With certain substrates this reduction proceeds with good to excellent levels of stereoselectivity through a reaction manifold apparently involving preferential addition of hydride to the nominally sterically more hindered *endo* face. It is noteworthy, however, that, in general, well defined and predictable stereoselectivities are absent. These results are somewhat unexpected given the high degree of stereocontrol exerted by the $Cr(CO)_3$ moiety in numerous other closely related processes. Nonetheless, this study does demonstrate the ability to manipulate the pyrrole ring of chromium-complexed indoles in a synthetically useful manner. Studies examining alternative means of functionalizing the indole nucleus expected to exhibit higher stereoselectivities are currently underway.

## 4. Experimental

### 4.1. General

All reactions were performed under a blanket of dry dinitrogen. Reagents and solvents available from commercial sources were used as received unless otherwise noted. Tetrahydrofuran was distilled from a Na/benzophenone ketyl. $CDCl_3$ was purified by passage through a short column of basic alumina. Thin layer chromatography (TLC) was performed using Whatman precoated TLC plates, silica gel 60F-254, 0.25 μm thickness. Flash column chromatography was performed using Selecto Scientific silica gel 60 (230–400 mesh). $^1H$- and $^{13}C$-NMR spectra were obtained using a Varian XL-300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts ($\delta$) are reported relative to residual $CHCl_3$ ($\delta = 7.26$ ppm for $^1H$ and 77.0 ppm for $^{13}C$). Infrared spectra were recorded on a Perkin–Elmer Model 1600 FTIR spectrophotometer. Melting points were determined using a Thomas-Hoover melting point apparatus and are uncorrected. Combustion analyses were obtained from Atlantic Microlabs, Norcross, GA.

### 4.2. General procedure for the synthesis of ($\eta^6$-indole)$Cr(CO)_3$ complexes

All new chromium-indole complexes (except **15**) were prepared from $Cr(CO)_6$ in $n$-$Bu_2O$/THF according to the general procedure described by Widdowson [4]c. The complexes were isolated as yellow to orange solids by a single recrystallization of the crude reaction mixture. All yields are unoptimized.

#### 4.2.1. Tricarbonyl($\eta^6$-1,3-dimethylindole)chromium(0) (3)

Application of the standard procedure to 1.50 g (10.33 mmol) 1,3-dimethylindole afforded 1.16 g (40%) of **3**, m.p. 116–119°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 2.23 (s, 3H), 3.63 (s, 3H), 5.10 (t, 1H, $J = 6.1$ Hz), 5.41 (t, 1H, $J = 6.0$ Hz), 5.99 (d, 1H, $J = 6.6$ Hz), 6.27 (d, 1H, $J = 6.6$ Hz), 6.81 (s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$ 9.41, 32.85, 77.18, 86.80, 88.27, 90.79, 100.81, 104.35, 117.51, 131.84, 234.59. IR (thin film) $\nu$ ($cm^{-1}$) 1962, 1840. Anal. Calcd. for $C_{13}H_{11}CrNO_3$: C 55.52; H 3.94; N 4.98. Found: C 55.45; H 3.91; N 4.91.

#### 4.2.2. Tricarbonyl($\eta^6$-1,2-dimethylindole)chromium(0) (6)

1.50 g (10.33 mmol) 1,2-dimethylindole afforded **6** (1.27 g, 44%), m.p. 115–117°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 2.32 (s, 3H), 3.56 (s, 3H), 5.09 (t, 1H, $J = 5.9$ Hz), 5.34 (t, 1H, $J = 6.1$ Hz), 5.97 (d, 1H, $J = 6.9$ Hz), 6.06 (s, 1H), 6.28 (d, 1H, $J = 7.1$ Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 13.18, 29.78, 77.29, 87.54, 89.10, 89.98, 100.97, 101.80, 117.26, 143.70, 235.07. IR (thin film) $\nu$ ($cm^{-1}$) 1928, 1825. Anal. Calcd. for $C_{13}H_{11}CrNO_3$: C 55.52; H 3.94; N 4.98. Found: C 55.43; H 4.04; N 4.90.

#### 4.2.3. Tricarbonyl($\eta^6$-1,2,3-trimethylindole)chromium(0) (9)

The general procedure as applied to 1.50 g (9.42 mmol) 1,2,3-trimethylindole yielded 1.76 g (63%) **9**, m.p. 118–122°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 2.15 (s, 3H), 2.24 (s, 3H), 3.54 (s, 3H), 5.08 (t, 1H, $J = 6.0$ Hz), 5.35 (t, 1H, $J = 6.4$ Hz), 5.96 (d, 1H, $J = 6.3$ Hz), 6.22 (d, 1H, $J = 7.0$ Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 8.71, 10.66, 29.92, 77.28, 86.99, 87.86, 90.17, 101.54, 108.43, 117.01, 138.84, 235.23. IR (thin film) $\nu$ ($cm^{-1}$) 1924, 1825. Anal. Calcd. for $C_{14}H_{13}CrNO_3$: C 56.95; H 4.44; N 4.74. Found: C 56.77; H 4.46; N 4.69.

#### 4.2.4. Tricarbonyl($\eta^6$-N-methyl-1,2,3,4-tetrahydrocarbazole)chromium(0) (12)

From 2.00 g (10.80 mmol) $N$-methyltetrahydrocarbazole was obtained 2.65 g (76%) **12**, m.p. 120–123°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 1.70–2.00 (br. m, 4H), 2.40–2.70 (br. m, 4H), 3.50 (s, 3H), 5.09 (br. s, 1H), 5.32 (br. s, 1H), 6.00 (br. s, 1H), 6.17 (br. s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$ 15.40, 20.54, 22.18, 22.48, 29.35, 77.77, 87.35, 87.46, 89.72, 100.83, 111.18, 116.90, 142.15, 235.38. IR (thin film) $\nu$ ($cm^{-1}$) 1932, 1840. Anal. Calcd. for $C_{16}H_{15}CrNO_3$: C 59.81; H 4.71; N 4.36. Found: C 59.95; H 4.72; N 4.33.

#### 4.2.5. Tricarbonyl($\eta^6$-2,5-dimethyl-1,2,3,4-tetrahydro-$\gamma$-carboline)chromium(0) (14)

Subjection of 1.14 g (5.69 mmol) 2,5-dimethyltetrahydro-$\gamma$-carboline [19] to the standard complexation procedure afforded 0.69 g (36%) **14**, m.p. 145–148°C. $^1$H-NMR ($CDCl_3$) $\delta$ 2.53 (s, 3H), 2.69–2.74 (m, 3H), 2.82–2.87 (m, 1H), 3.46–3.62 (m, 2H), 3.51 (s, 3H), 5.08 (t, 1H, $J = 5.7$ Hz), 5.33 (t, 1H, $J = 5.5$ Hz), 5.99 (d, 1H, $J = 6.6$ Hz), 6.11 (d, 1H, $J = 6.0$ Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 22.93, 29.51, 45.42, 50.70, 51.62, 77.57, 87.05, 87.23, 89.87, 98.80, 109.60, 117.00, 140.04, 235.00. IR (thin film) $\nu$ ($cm^{-1}$) 1940, 1842. Anal. Calcd. for $C_{16}H_{16}CrN_2O_3$: C 57.14; H 4.80; N 8.33. Found: C 56.92; H 4.84; N 8.22.

#### 4.2.6. Tricarbonyl($\eta^6$-2-carbomethoxy-9-methyl-1,2,3,4-tetrahydro-$\beta$-carboline)chromium(0) (16)

**16** (0.93 g, 52%) was obtained from 1.13 g (4.63 mmol) of the corresponding $\beta$-carboline derivative [20], m.p. 167–168°C (dec). $^1$H-NMR ($CDCl_3$, mixture of rotamers) $\delta$ 2.71 (br. m, 2H), 3.54 (s, 3H), 3.79 (s, 3H), 3.85–3.91 (m, 2H), 4.43 (m, 1H), 4.71 (m, 1H), 5.12 (t, 1H, $J = 6.4$ Hz), 5.36 (t, 1H, $J = 6.1$ Hz), 6.02 (d, 1H, $J = 6.4$ Hz), 6.19 (d, 1H, $J = 6.3$ Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 21.26, 30.07, 41.54, 41.78, 53.31, 83.17, 87.30, 87.68, 90.28, 99.65, 110.18, 117.24, 137.58, 155.73, 234.91. IR (thin film) $\nu$ ($cm^{-1}$) 1942, 1844, 1684. Anal. Calcd. for $C_{17}H_{16}CrN_2O_5$: C 53.68; H 4.24; N 7.37. Found: C 53.61; H 4.25; N 7.25.

#### 4.2.7. Tricarbonyl($\eta^6$-N-carbomethoxy-2-methylindole)chromium(0) (21)

Complex **21** (1.40 g, 82%) was obtained from 1.00 g (5.28 mmol) $N$-carbomethoxy-2-methylindole, m.p. 149–150°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 2.53 (s, 3H), 4.10 (s, 3H), 5.17 (t, 1H, $J = 6.3$ Hz), 5.29 (t, 1H, $J = 6.6$ Hz), 6.02 (d, 1H, $J = 6.6$ Hz), 6.15 (s, 1H), 6.79 (d, 1H, $J = 7.2$ Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 17.11, 54.47, 83.05, 87.03, 89.39, 90.32, 102.03, 107.83, 114.69, 143.39, 151.66, 234.12. IR (thin film) $\nu$ ($cm^{-1}$) 1948, 1872, 1846, 1740. Anal. Calcd. for $C_{14}H_{11}CrNO_5$: C 51.70; H 3.41; N 4.31. Found: C 51.64; H 3.43; N 4.20.

#### 4.2.8. Tricarbonyl($\eta^6$-2,9-dimethyl-1,2,3,4-tetrahydro-$\beta$-carboline)chromium(0) (15)

The preparation of **15** using the general procedure described above was unsuccessful. Thus, the following procedure was employed: $Cr(CO)_6$ (1.26 g, 6.27 mmol) and 40 ml $CH_3CN$ were combined in a 250 ml round bottom flask and vigorously refluxed for 18 h. The $CH_3CN$ was then removed in vacuo to afford

$(CH_3CN)_3Cr(CO)_3$ as a yellow solid [21]. The $\beta$-carboline derivative [20] in 40 ml of THF was then added directly to the flask and the resulting mixture was warmed in a 40°C water bath for 48 h. The THF was evaporated under reduced pressure and the residue was mixed with ether and filtered through a pad of Celite®. The filtrate was concentrated and the residue purified by flash column chromatography using EtOAc:$Et_2O$:MeOH (7:2:1) as the eluent. Fractions containing the desired complex were combined and concentrated to afford a yellow solid which was further purified by recrystallization from $CH_2Cl_2$/hexanes. **15** (0.75 g, 53%) was obtained as yellow needles, m.p. 160–161°C. $R_f$ (7:2:1 EtOAc:$Et_2O$:MeOH) = 0.20. $^1$H-NMR ($CDCl_3$) $\delta$ 2.55 (s, 3H), 2.67–2.83 (m, 4H), 3.38–3.61 (m, 2H), 3.49 (s, 3H), 5.10 (t, 1H, $J$ = 6.3 Hz), 5.34 (t, 1H, $J$ = 6.5 Hz), 6.00 (d, 1H, $J$ = 6.8 Hz), 6.20 (d, 1H, $J$ = 6.4 Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 21.33, 29.77, 45.84, 51.36, 52.24, 77.78, 87.53, 87.67, 90.18, 100.12, 109.35, 117.37, 139.92, 235.24. IR (thin film) $\nu$ ($cm^{-1}$) 1938, 1846. Anal. Calcd. for $C_{16}H_{16}CrN_2O_3$: C 57.14; H 4.80; N 8.33. Found: C 57.05; H 4.90; N 8.31.

### 4.3. General procedure for reduction of (indole)chromium complexes using $NaBH_3CN$

The procedure used for the reduction of unsubstituted indole complex **1** [7] is representative. Approximately 10 ml of trifluoroacetic acid (TFA) was cooled to 0°C in an ice bath and deoxygenated by bubbling $N_2$ through the solution for 10 min. Complex **1** (250 mg, 0.94 mmol) was added to the TFA in one portion, resulting in formation of a deep burgundy solution. An excess of solid $NaBH_3CN$ was then carefully added in small portions over 15 min until the red color had been completely discharged (~5 equivalents were necessary). At this time, TLC indicated complete consumption of **1**. The reaction was then quenched by the dropwise addition of water (25 ml) over 45 min. Ether was then added and the layers were separated. The yellow organic solution was washed sequentially with several portions of $H_2O$, 5% aqueous NaOH solution, $H_2O$, and brine. The organic phase was then dried over anhydrous $MgSO_4$, filtered through a pad of basic alumina, and concentrated under reduced pressure to afford **2** (235 mg, 93%) as a bright yellow solid. No further purification was necessary as this material was homogeneous by $^1$H-NMR and TLC. The spectral properties of **2** were identical to those reported in the literature [9].

#### 4.3.1. Endo- and exo-tricarbonyl($\eta^6$-1,3-dimethylindoline)chromium(0) (**4** and **5**)

Using the procedure described above, **3** (300 mg, 1.07 mmol) yielded a 1.7:1.0 mixture of indoline isomers **4** and **5**, respectively (226 mg, 75%) which were not separated. The ratio of **4**:**5** was determined by comparison of the $^1$H-NMR integrations corresponding to the 3-methyl signal. For the *endo* 3-methyl isomer **4**: $^1$H-NMR ($CDCl_3$) $\delta$ 1.32 (d, 3H, $J$ = 6.5 Hz), 2.66 (s, 3H), 2.79 (m, 1H), 3.06 (m, 1H), 3.50 (t, 1H, $J$ = 8.8 Hz), 4.63 (d, 1H, $J$ = 6.2 Hz), 4.74 (m, 1H), 5.48 (m, 2H). $^{13}$C-NMR ($CDCl_3$) $\delta$ 17.61, 33.65, 34.41, 61.41, 69.95, 81.71, 92.23, 95.45, 105.51, 137.12, 234.46. *exo* 3-methyl isomer **5**: $^1$H-NMR ($CDCl_3$) $\delta$ 1.22 (d, 3H, $J$ = 6.9 Hz), 2.66 (s, 3H), 3.02 (m, 1H), 3.16 (m, 1H), 3.40 (t, 1H, $J$ = 8.8 Hz), 4.74 (m, 1H), 4.86 (t, 1H, $J$ = 6.1 Hz), 5.34 (t, 1H, $J$ = 6.3 Hz), 5.53 (m, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$ 21.59, 33.65, 34.36, 61.09, 71.58, 83.73, 92.23, 94.36, 104.37, 135.14, 234.34. An analytical sample of the mixture was obtained by recrystallization from $CH_2Cl_2$/hexanes: IR (thin film) $\nu$ ($cm^{-1}$) 1935, 1840. Anal. Calcd. for $C_{13}H_{13}CrNO_3$: C 55.12; H 4.63; N 4.95. Found: C 55.21; H 4.57; N 4.89.

#### 4.3.2. Exo- and endo-tricarbonyl($\eta^6$-1,2-dimethylindoline)chromium(0) (**7** and **8**)

Treatment of **6** (300 mg, 1.07 mmol) as described above afforded a 4.5:1.0 mixture of **7** and **8**, respectively (264 mg, 87%). The ratio of products was determined by comparison of the $^1$H-NMR integrations corresponding to the 2-methyl signal. *exo* isomer **7**: $^1$H-NMR ($CDCl_3$) $\delta$ 1.30 (d, 3H, $J$ = 6.2 Hz), 2.51 (m, 1H), 2.62 (s, 3H), 2.90 (dd, 1H, $J$ = 7.5, 15.0 Hz), 3.51 (m, 1H), 4.71 (d, 1H, $J$ = 6.6 Hz), 4.87 (t, 1H, $J$ = 6.3 Hz), 5.34 (t, 1H, $J$ = 6.4 Hz), 5.52 (d, 1H, $J$ = 6.2 Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 18.26, 32.63, 36.04, 61.21, 72.00, 84.13, 92.26, 94.17, 98.60, 136.17, 234.52. *endo* isomer **8**: $^1$H-NMR ($CDCl_3$) $\delta$ 1.39 (d, 3H, $J$ = 6.8 Hz), 2.51 (m, 1H), 2.73 (s, 3H), 3.17 (m, 1H), 3.87 (m, 1H), 4.75 (m, 2H), 5.40 (m, 1H), 5.59 (d, 1H, $J$ = 6.0 Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 17.06, 29.95, 35.10, 58.83, 70.17, 82.43, 93.70, 94.79, 96.08, 135.91, 235.18. An analytical sample of **7** was obtained by flash column chromatography (3:1 hexanes:ether, $R_f$ = 0.43) followed by recrystallization from ether/hexanes. M.p. 103–105°C (dec). IR (thin film) $\nu$ ($cm^{-1}$) 1931, 1833. Anal. Calcd. for $C_{13}H_{13}CrNO_3$: C 55.12; H 4.63; N 4.95. Found: C 54.96; H 4.60; N 4.91.

#### 4.3.3. Tricarbonyl($\eta^6$-1,2,3-trimethylindoline)chromium(0) (**10**)

Complex **9** (500 mg, 1.69 mmol) was treated as described above to yield **10** (425 mg, 85%) as a complex mixture of stereoisomers. Without further characterization, **10** was dissolved in ether and irradiated with a 125 W tungsten lamp at rt in the presence of air for 48 h. The oxidized chromium salts were filtered off through a pad of Celite® and the filtrate was concentrated under reduced pressure to afford 198 mg (86%) of a 1:1 mixture of *cis* and *trans* 1,2,3-trimethylindoline (**11**), identical by $^1$H-NMR to an authentic mixture [22].

#### 4.3.4. Exo-tricarbonyl($\eta^6$-N-methylhexahydrocarbazole)chromium(0) (**13**)

Reduction of **12** (300 mg, 0.93 mmol) according to the procedure described above gave **13** (254 mg, 84%). An analytical sample was obtained by recrystallization from $CH_2Cl_2$/hexanes. M.p. 102–104°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 1.13–1.27 (m, 3H), 1.52–1.68 (m, 3H), 1.81 (m, 1H), 2.05 (m, 1H), 2.58 (s, 3H), 2.66 (m, 1H), 3.29 (m, 1H), 4.80 (d, 1H, $J = 6.8$ Hz), 4.90 (t, 1H, $J = 6.2$ Hz), 5.37 (t, 1H, $J = 6.3$ Hz), 5.45 (d, 1H, $J = 6.2$ Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$ 20.43, 23.59, 24.32, 30.88, 32.06, 38.82, 64.09, 73.71, 84.85, 91.34, 93.87, 105.11, 134.97, 234.69. IR (thin film) $\nu$ ($cm^{-1}$) 1947, 1848. Anal. Calcd. for $C_{16}H_{17}CrNO_3$: C 59.44; H 5.30; N 4.33. Found: C 59.41; H 5.34; N 4.26.

#### 4.3.5. Endo- and exo-tricarbonyl($\eta^6$-2-carbomethoxy-9-methylhexahydro-$\beta$-carboline)chromium(0) (**17** and **18**)

Reduction of **16** (394 mg, 1.04 mmol) produced a separable 5.4:1.0 mixture of **17** and **18**, respectively. The products were isolated by flash column chromatography (1:1 hexanes:$Et_2O$). Major *endo* isomer **17**: 277 mg, 70%. $R_f$ (1:1 hexanes:$Et_2O$) = 0.10. M.p. 142–143°C (dec). $^1$H-NMR ($CDCl_3$, mixture of rotamers) $\delta$ 2.08 (m, 1H), 2.24 (m, 1H), 2.77 (s, 3H), 3.34 (m, 2H), 3.48 (m, 1H), 3.65 (m, 1H), 3.73 (s, 3H), 3.87 (m, 1H), 4.01 (m, 0.5H), 4.15 (m, 0.5H), 4.63 (m, 2H), 5.60 (m, 2H). $^{13}$C-NMR ($CDCl_3$, mixture of rotamers) $\delta$ 28.62, 29.05, 30.44, 36.61, 38.28, 41.78, 52.92, 62.00, 67.77, 79.99, 80.13, 82.90, 94.54, 96.73, 101.03, 156.18, 156.74, 234.72. IR (thin film) $\nu$ ($cm^{-1}$) 1940, 1866, 1842, 1698. Anal. Calcd. for $C_{17}H_{18}CrN_2O_5$: C 53.40; H 4.75; N 7.33. Found: C 53.16; H 4.69; N 7.27. Minor *exo* isomer **18**: 51 mg, 13%. $R_f$ (1:1 hexanes:$Et_2O$) = 0.30. M.p. 158–159°C (dec). $^1$H-NMR ($CDCl_3$, mixture of rotamers) $\delta$ 1.54 (m, 1H), 1.92 (m, 1H), 2.67 (s, 3H), 3.02 (m, 2H), 3.19 (m, 1H), 3.41 (m, 1H), 3.70 (s, 3H), 3.86 (m, 1H), 4.32 (m, 1H), 4.79 (d, 1H, $J = 6.6$ Hz), 4.90 (t, 1H, $J = 6.1$ Hz), 5.39 (t, 1H, $J = 6.2$ Hz), 5.51 (d, 1H, $J = 5.8$ Hz). $^{13}$C-NMR ($CDCl_3$, mixture of rotamers) $\delta$ 29.35, 32.39, 37.53, 41.02, 41.79, 52.95, 63.60, 73.14, 84.86, 91.60, 94.31, 102.11, 107.98, 135.13, 156.29, 234.37. IR (thin film) $\nu$ ($cm^{-1}$) 1948, 1842, 1694. Anal. Calcd. for $C_{17}H_{18}CrN_2O_5$: C 53.40; H 4.75; N 7.33. Found: C 53.48; H 4.83; N 7.33. Oxidative removal of the chromium (as described for **10**) from separate solutions of **17** and **18** afforded the same carboline derivative (**19**) in $>90\%$ yield. $^1$H-NMR ($CDCl_3$) $\delta$ 1.60–1.72 (m, 1H), 1.88–1.98 (m, 1H), 2.77 (s, 3H), 3.17–3.41 (m, 4H), 3.59 (m, 1H), 3.70 (s, 3H), 4.08 (m, 1H), 6.51 (d, 1H, $J = 7.8$ Hz), 6.71 (t, 1H, $J = 7.4$ Hz), 7.06 (d, 1H, $J = 7.1$ Hz), 7.12 (t, 1H, $J = 7.7$ Hz).

#### 4.3.6. Exo- and endo-tricarbonyl($\eta^6$-1-carbomethoxy-2-methylindoline)chromium(0) (**22** and **23**)

Reduction of **21** (300 mg, 0.92 mmol) afforded a separable, ~1:1 mixture of **22** and **23** in 83% overall yield. The products were separated by flash column chromatography (4:1 hexanes:$Et_2O$). The structures were assigned on the basis of the $^1$H-NMR chemical shifts of the 2-methyl substituents (vide supra). *exo*-methyl isomer **22**: 109 mg, 36%. $R_f$ (1:1 hexanes:$Et_2O$) = 0.42. M.p. 89–90°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 1.40 (d, 3H, $J = 6.4$ Hz), 2.65 (dd, 1H, $J = 5.9$, 16.0 Hz), 3.36 (dd, 1H, $J = 9.5$, 16.0 Hz), 3.86 (s, 3H), 4.50 (m, 1H), 4.99 (t, 1H, $J = 6.3$ Hz), 5.36 (t, 1H, $J = 6.6$ Hz), 5.63 (d, 1H, $J = 6.1$ Hz), 6.21 (br. s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$ 22.20, 35.87, 53.45, 56.29, 80.46, 87.17, 91.75, 92.93, 99.91, 142.78, 153.61, 233.35. IR (thin film) $\nu$ ($cm^{-1}$) 1955, 1864, 1716. Anal. Calcd. for $C_{14}H_{13}CrNO_5$: C 51.38; H 4.00; N 4.28. Found: C 51.46; H 4.07; N 4.17. *endo*-methyl isomer **23**: 141 mg, 47%. $R_f$ (1:1 hexanes:$Et_2O$) = 0.26. M.p. 138–140°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 1.52 (d, 3H, $J = 6.5$ Hz), 2.60 (dd, 1H, $J = 2.8$, 16.0 Hz), 3.33 (dd, 1H, $J = 10.4$, 16.0 Hz), 3.84 (s, 3H), 4.43 (br. m, 1H), 5.03 (t, 1H, $J = 6.3$ Hz), 5.38 (t, 1H, $J = 6.6$ Hz), 5.50 (d, 1H, $J = 6.4$ Hz), 6.46 (br. s, 1H). $^{13}$C-NMR ($CDCl_3$) $\delta$ 20.28, 34.91, 53.34, 55.26, 81.87, 88.27, 90.69, 92.44, 98.11, 135.90, 153.00, 233.53. IR (thin film) $\nu$ ($cm^{-1}$) 1966, 1864, 1716. Anal. Calcd. for $C_{14}H_{13}CrNO_5$: C 51.38; H 4.00; N 4.28. Found: C 51.35; H 3.99; N 4.22.

### 4.4. General procedure for reduction of (indole)chromium complexes using $NaBH_4$

A procedure identical to the one described above was used except that $NaBH_4$ was substituted for $NaBH_3CN$. Reduction of complex **6** afforded a mixture of **7** and **8** ($>95\%$ yield) in a ratio of 1:1 as determined by $^1$H-NMR. Reduction of **12** produced a separable 1:1 mixture of **13** and isomeric indoline **20** as determined by $^1$H-NMR and X-ray analysis [15]. Spectral and analytical data for **20** are given below.

### 4.5. General procedure for reduction of (indole)chromium complexes using $Et_3SiH$

The procedure used for the reduction of **12** is representative. Triethylsilane (2.20 ml, 13.60 mmol) was added to ~15 ml deoxygenated TFA. Complex **12** (0.55 g, 1.70 mmol) was added in one portion and the resulting wine-red solution was warmed in a 50–55°C oil bath. The reaction was monitored by TLC. After 72 h, no starting material remained and the reaction was allowed to cool to rt. The solution was carefully poured into ~50 ml of 15% aq. NaOH solution and extracted

with ether ($2 \times 50$ ml). The combined ether extracts were washed with brine and dried over anhydrous $MgSO_4$. Filtration through a pad of basic alumina and evaporation of the solvent gave an oily yellow solid which was subjected to flash column chromatography (3:1 hexanes:$CH_2Cl_2$). Two yellow bands were eluted. The first ($R_f = 0.31$ (3:1 hexanes:$Et_2O$)) was found to contain indoline complex **13** (115 mg, 21%). The second fraction ($R_f = 0.21$ (3:1 hexanes:$Et_2O$)) consisted of isomeric indoline complex **20** (123 mg, 22%). An analytical sample of **20** was obtained by recrystallization from ether/hexanes. M.p. 135–138°C (dec). $^1$H-NMR ($CDCl_3$) $\delta$ 1.44–2.18 (m, 8H), 2.73 (s, 3H), 3.22 (m, 1H), 3.64 (m, 1H), 4.62 (d, 1H, $J = 7.0$ Hz), 4.67 (t, 1H, $J = 6.0$ Hz), 5.54 (m, 2H). $^{13}$C-NMR ($CDCl_3$) $\delta$ 19.97, 20.28, 20.85, 26.14, 30.06, 37.55, 63.26, 68.70, 80.26, 93.55, 96.21, 101.39, 136.60, 235.10. IR (thin film) $\nu$ ($cm^{-1}$) 1940, 1840. Anal. Calcd. for $C_{16}H_{17}CrNO_3$: C 59.44; H 5.30; N 4.33. Found: C 59.48; H 5.37; N 4.40.

The same procedure applied to complex **6** afforded a 1:1 mixture ($^1$H-NMR) of **7** and **8** in 46% overall yield.

### 4.6. X-ray diffraction data collection for complexes 7 and 18

Crystals of appropriate dimensions were mounted on glass fibers in random orientation. Preliminary examination and data collection were performed using a Siemens SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer using graphite monochromated Mo-$K_\alpha$ radiation equipped with a sealed tube X-ray source (40 kV $\times$ 50 mA) at $-50$°C. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in $\omega$) scans. A total of 5554 frames of intensity data were collected with a frame width of 0.3° in $\omega$ and counting time of 10 s frame$^{-1}$ at a crystal to detector distance of 4.930 cm. The double pass method of scanning was used to exclude any noise. Data were collected for a total time of 26.2 h. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART software package was used for data collection as well as frame integration [23]. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of $xyz$ centroids of 8192 reflections ($\theta < 25.0$°). Empirical absorption correction was applied to the data using SADABS based upon the Laue symmetry equivalent reflections [24]. The integration process yielded 22315 and 29918 reflections of which 2163 ($2\theta < 50$°) and 3256 ($2\theta < 52$°) were independent reflections for **7** and **18**, respectively.

Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package [25]. The structures were solved by Patterson Methods and refined successfully in the space group $P2_1/c$. Full-matrix least squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were refined isotropically for **7** and were treated using appropriate riding model (AFIX m$^3$) for **18**. The final residual values for **7** and **18** were $R(F) = 7.6$ and 4.6% for 1550 and 2386 observed reflections [$I > 2\sigma(I)$]; $wR(F^2) = 18.9$ and 10.8% for all data, respectively. Crystal data and structure refinement parameters are listed in Table 2. A projection view of the molecules with non-hydrogen atoms represented by 50% thermal ellipsoids and showing the atom labeling is shown in Figs. 1 and 2.

## 5. Supplementary Material

A complete listing of all cystallographic data, including tables of bond distances and angles, atomic coordinates, geometrical parameters, positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for non-hydrogen atoms, and calculated and observed structure factors, is available from the authors upon request. This information will be deposited with the Cambridge Crystallographic Database.

## Acknowledgements

The authors wish to thank the University of Missouri Research Board and the Department of Chemistry, University of Missouri-St. Louis for generous financial support.

## References

[1] M. Uemura, in: L.S. Liebeskind (Ed.), Advances in Metal-Organic Chemistry, vol. 2, JAI Press, Greenwich, CT, 1991, p. 195.
[2] (a) M.F. Semmelhack, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, pp. 979–1038. (b) M.J. Siwek, J.R. Green, Chem. Commun. (1996) 2359. (c) R.A. Ewin, A.M. MacLeod, D.A. Price, N.S. Simpkins, A.P. Watt, J. Chem. Soc. Perkin Trans. 1 (1997) 401.
[3] (a) S.G. Davies, T.D. McCarthy, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 1039. (b) S.G. Davies, T.J. Donohoe, Synlett (1993) 323. (c) S.G. Davies, S.J. Coote, C.L. Goodfellow, in: L.S. Liebeskind (Ed.), Advances in Metal-Organic Chemistry, vol. 2, JAI Press, Greenwich, CT, 1991, p. 1.
[4] (a) M.F. Semmelhack, P. Knochel, T. Singleton, Tetrahedron Lett. 34 (1993) 5051. (b) M.F. Semmelhack, H. Rhee, Tetrahedron Lett. 34 (1993) 1399. (c) N.F. Masters, N. Mathews, G. Nechvatal, D.A. Widdowson, Tetrahedron 45 (1989) 5955. (d) P.J. Beswick, C.S. Greenwood, T.J. Mowlem, G. Nechvatal, D.A. Widdowson, Tetrahedron 44 (1988) 7325.

[5] (a) G.W. Gribble, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 8, Pergamon, Oxford, 1991, p. 603. (b) T.J. Donohoe, R. Garg, C.A. Stevenson, Tetrahedron Asymmetry 7 (1996) 317.
[6] G.W. Gribble, P.D. Lord, J. Skotnicki, S.E. Dietz, J.T. Eaton, J.L. Johnson, J. Am. Chem. Soc. 96 (1974) 7812.
[7] M.F. Semmelhack, W. Wulff, J.L. Garcia, J. Organomet. Chem. 240 (1982) C5.
[8] D.M. Ketcha, B.A. Lieurance, Tetrahedron Lett. 30 (1989) 6833.
[9] B. Ohlsson, C. Ullenius, J. Organomet. Chem. 350 (1988) 35.
[10] A. Meyer, O. Hofer, J. Am. Chem. Soc. 102 (1980) 4410.
[11] For other examples of apparently *endo* selective reactions involving (arene)chromium complexes, see: (a) S. Sur, S. Ganesh, D. Pal, V.G. Puranik, P. Chakrabarti, A. Sarkar, J. Org. Chem. 61 (1996) 8362. (b) S. Ganesh, K.M. Sathe, M. Nandi, P. Chakrabarti, A. Sarkar, J. Chem. Soc. Chem. Commun. (1993) 224.
[12] J.G. Rodríguez, A. Urrutia, I. Fonseca, J. Sanz, J. Organomet. Chem. 522 (1996) 231.
[13] (a) D.M. David, L.A.P. Kane-Maguire, S.G. Pyne, J. Chem. Soc. Dalton Trans. (1994) 289. (b) N. Taniguchi, M. Uemura, Synlett (1997) 51.
[14] For examples, see: (a) B.R. Jagirdar, R. Palmer, K.J. Klabunde, L.J. Radonovich, Inorg. Chem. 34 (1995) 278. (b) G.N. Glavee, B.R. Jagirdar, J.J. Schneider, K.J. Klabunde, L.J. Radonovich, K. Dodd, Organometallics 11 (1992) 1043. (c) E. Matarasso-Tchiroukhine, G. Jaouen, Can. J. Chem. 66 (1988) 2157. (d) U. Schubert, J. Müller, H.G. Alt, Organometallics 6 (1987) 469.
[15] Details of this crystal structure will be published elsewhere.
[16] D.A. Evans, K.T. Chapman, E.M. Carreira, J. Am. Chem. Soc. 110 (1988) 3560.
[17] Such a reaction pathway has been observed with certain indoles: R.J. Sundberg, The Chemistry of Indoles, Academic Press, New York, 1970.
[18] $Et_3SiH$ has been used in the reduction of metal-free indoles: A.E. Lanzilotti, R. Littell, W.J. Fanshawe, T.C. McKenzie, F.M. Lovell, J. Org. Chem. 44 (1979) 4809.
[19] R.G.W. Spickett, J. Med. Chem. 9 (1966) 436.
[20] B.E. Ho, K.E. Walker, Org. Synth. 51 (1971) 136.
[21] D.P. Tate, W.R. Knipple, J.M. Augl, Inorg. Chem. 1 (1962) 433.
[22] Available from Aldrich Chemical Co., Milwaukee, WI.
[23] Siemens Analytical X-ray, Madison, WI, 1995.
[24] R.H. Blessing, Acta Crystallogr. A51 (1995) 33.
[25] G.M. Sheldrick, Siemens Analytical X-ray Division, Madison, WI, 1995.