Synthesis of η^6-(4a-Methyl-1,2,3,4-tetrahydro-4a*H*-carbazole)-tricarbonylchromium Complex and Stereoelectronic Behaviour with Organolithium Reagents: an Apparent Frontal Attack to the $(CO)_3Cr$ Group

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The synthesis of η^6-(4a-methyl-1,2,3,4-tetrahydro-4a*H*-carbazole)tricarbonylchromium (**3**) is described, and its reactivity with organolithium reagents have been analysed. The addition of RLi (R= H, Me, *n*-Bu, *tert*-Bu) to **3** affords the corresponding *endo/exo* tricarbonylchromium complexes of *cis*-4a-methyl-9a-substituted-1,2,3,4-tetrahydro-4a*H*-carbazole, which permit the consideration of the stereoelectronic behaviour of the tricarbonylchromium group on 4a-methyl and the 9a substituent or on the methylenes of the cyclohexene moiety in the complexes.

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Alkaloids containing the *cis*-fused tetrahydrocarbazole system exhibit a considerable diversity of structure and a wide variety of biological activities [1]. Thus, 9-(dimethylaminopropyl) derivatives of 4a-methyl-9a-substituted-1,2,3,4,4a,9a-hexahydrocarbazoles show a significant dopaminergic and serotoninergic activity [2a]. However, the *trans*-1,2,3,4,4a,9a-tetrahydrocarbazol-4-one was obtained by photochemistry cyclization [2b].

We reported a novel synthesis of 2'-substituted spiro[cycloalkane-1,3'-indolines] by reaction of the C=N bond in a spiro[cycloalkane-1,3'-3*H*-indole] with an organomagnesium reagent in the presence of copper(I) chloride, to give the 2'-R substituted (R= Me, Ph) derivatives, in nearly quantitative yield [3]. However, the same reaction in 2'-methylspiro[cyclohexan-1,3'-3*H*-indole] with methylmagnesium iodide gives the methyl insertion products on the 2'-methyl substituent in good yield, while the C=N addition product was not detected [4]. Reaction of 4a-methyl-1,2,3,4,-tetrahydro-1*H*-carbazole (**1**) with organomagnesium halides in the presence of cuprous chloride gives only the *cis*-4a,9a-dialkylhexahydrocarbazole derivatives through a radicalic mechanism [5].

The preparation of conjugated (η^6-Arene)tricarbonylchromium complexes enhances the nucleophilic addition to the conjugated positions. Thus, the molecular structure of 2'-methylspiro[cyclohexan-1,3'-3*H*-indole]tricarbonylchromium complex and the nucleophilic addition to the C=N double bond have been reported [6].

The complexes show characteristic properties due to the strong electron-withdrawing ability and steric bulkiness of tricarbonylchromium fragment, and significant applications in organic synthesis have been reported [7a-e]. The tricarbonyl group is well-known to stabilize both the benzylic carbanion and carbocation and apparently benzylic radical intermediates [7,8a-b]. Thus, the η^6-styrene-$Cr(CO)_3$ complex undergoes nucleophilic addition, facilitated by stabilisation of the benzylic carbanion by the tricarbonylchromium moiety [9].

The synthesis of compound **1** and their **3** complex was outlined to examine the nucleophilic addition on the conjugated C=N double bond and the *cis*-*trans* stereochemistry of the reaction employing organolithium reagents.

Results and Discussion.

Compound **1** was conveniently synthesized either by treatment of 1,2,3,4-tetrahydrocarbazolyl magnesium iodide with methyl iodide in dry tetrahydrofuran or by Fischer reaction of the phenylhydrazone of 2-methylcyclohexanone [10].

The reaction of compound **1** with methyllithium, in dry toluene as solvent and controlled temperature, permits the preparation of 4a,9a-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole in excellent yield, Table 1. The same method was applied to obtain the 9a-alkyl derivatives, by reaction of **1** and the appropriate organolithium reagent, generally in excellent yield. The reaction is particularly useful for the preparation of the hindered 9a derivatives such as, *n*-butyl or *tert*-butyl, Table 1.

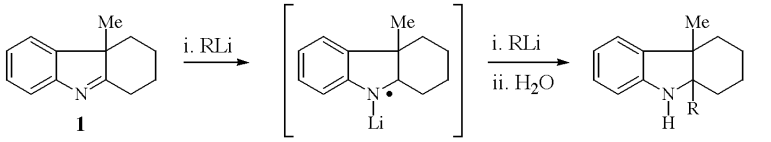
Table 1

Preparation of the 9a-Substituted derivatives **2b-d**

RLi	Equiv.	T (°)	t (h)	9a-R(%)
Methyl	2	-10	3	87
n-Butyl	1.25	0	3	97
tert-Butyl	3	-10	5	45

Experimental evidence for the 9a radical-anion intermediate was found by epr for the reaction of 4a-methylcarbazolenine **1** and methyllithium in toluene at room temperature [11]. Hence, the reaction proceeds through a single electron transfer mechanism from the RLi reagent giving the 9a radical intermediate that couples with the radical R of the organolithium reagent [12], Scheme 1.

Scheme 1



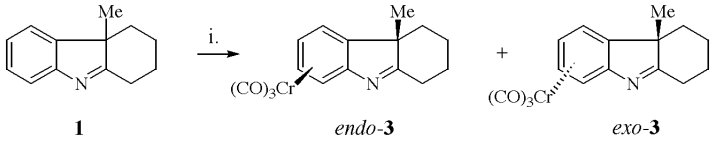
R = H, **2a**: Me, **2b**; *n*-Bu, **2c**; *tert*-Bu, **2d**.

Reaction mechanism of **1** with organolithium reagents.

The synthesis of **3**, tricarbonylchromium complex of **1**, was undertaken to enhance the polarisation of the conjugate C=N double bond by the electron-withdrawing effect of the tricarbonylchromium group. The complex **3** was obtained by transmetallation of **1** with hexacarbonylchromium in 1,4-dioxane/THF (3:1) at 150°, under argon atmosphere and rigorous dry and darkness conditions, in good yield (75%), as a mixture of isomers, using a Strohmeier apparatus [13] to avoid the sublimation and the hazard of inhalation of the reagent, Scheme 2.

While the *exo* **3** isomer, with 4a-methyl and tricarbonylchromium groups on opposite sides of the mean molecular plane, was isolated as orange crystals, the *endo*-isomer was isolated as an unstable yellow crystalline solid that partially decomposes during the chromatographic separation, Scheme 2.

Scheme 2



1 *endo*-**3** *exo*-**3**

i. $Cr(CO)_6$, Dioxane/THF (3:1), 150°. **3**, 75%, *endo/exo*, 1:2.

Preparation of tricarbonylchromium complex, **3**.

The ^1H NMR spectrum shows two signals for the methyl group which were assigned to the *endo* and *exo* isomers of **3**, on the basis of the recognised deshielding effect produced by the tricarbonylchromium group on the 4a-methyl substituent [9]. Thus, the methyl group appears at 1.51 and 1.42 ppm in the *endo* and *exo* isomers respectively in a 1:2 ratio.

The major *exo* isomer in the mixture, evidence that the tricarbonylchromium group and the methylene groups (at position 1 and 3 or 2 and 4 in a half-chair of the cyclohexene conformation), show a tolerable steric bulkiness effect and is the more stable (crystallographic molecular model) [14]. In contrast, the *endo* isomer with the tricarbonylchromium group and 4a-methyl substituent on the same face show an important steric bulkiness effect and hence, the *endo* isomer is unstable.

The reaction of lithium aluminium hydride with **3** (*endo/exo*, 1:2) in THF, gives the two isomers, *exo*-**4a** (42%) and *endo*-**4a** (40%) [15] in practically 1:1 ratio (by ^1H NMR); the methyl group appears at 1.22 and 1.31 ppm for the *exo* and *endo* isomers respectively.

Moreover, both *exo* and *endo* isomers, by oxidative demetallation with iodine yield only *cis*-4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole; the hydrochloride derivative shows identical spectral and melting point data with that of a sample obtained by direct reaction of the uncomplexed **1** with lithium aluminium hydride.

Hence, during the reaction time, the *endo*-**3** complex was completely consumed to give the main *endo-cis*-**4a** complex while the more stable *exo*-**3** complex was partially consumed to give *exo-cis*-**4a** and some amount of the *exo*-**3** complex was recovered.

The tricarbonylchromium group in the *exo*-**3** blocks the opposite arene face to the 4a methyl group, and the nucleophilic attack to the C=N bond, must take place in *anti* (*dorsal* attack) to this π-bonded group, giving the *exo-cis*-4a-methyl-9a-(substituted)tricarbonylchromium isomer. However, the tricarbonylchromium group in the *endo*-**3** blocks the same arene face to the 4a methyl group, and the

nucleophilic attack to the C=N bond, must take place in *syn* (frontal attack) to this π-bonded group, giving the main *endo-cis*-4a-methyl-9a-(substituted) tricarbonylchromium isomer. The *trans* isomer was not detected.

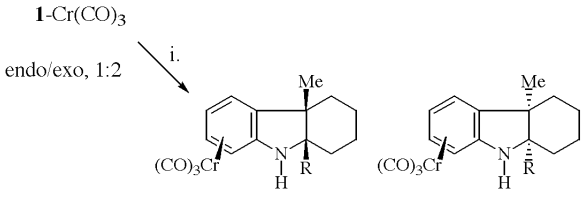
The above results agree well with the experimental data obtained previously by Oishi [15] for the preparation of **4a** complex (R=H), by transmetallation of **2a** with $Cr(CO)_6$ giving the *endo*-**4a** complex as the main isomer (by ^{1}H NMR, *endo/exo*, 10:1). This fact seems consistent with the strongest steric bulkiness interaction between the tricarbonylchromium and the methylene groups of the twisted cyclohexane ring in the *exo-cis*-**4a** complex, being the *endo-cis*-**4a** isomer the more stable one.

On the other hand, the reaction of the **3** complex (*endo*/*exo*, 1:2) with methyllithium in dry toluene at room temperature affords both isomers, *exo*-**4b** and *endo*-**4b**, (*endo/exo*, 3:2 ratio); by ^{1}H NMR, the 4a and 9a methyl signals appear at 1.34 and 1.39 for the *endo-cis*-**4b** and 1.08 and 1.19 ppm for the *exo-cis*-**4b** complexes respectively. Moreover, the uncomplexed *cis*-**2b** product was isolated in 9% yield by partial decomposition of **4b** complexes.

The major *endo-cis*-**4b** isomer arises of a frontal attack of the nucleophile to the C=N bond by the same face as the tricarbonylchromium group in the *endo*-**4b**, while the minor *exo-cis*-**4b** isomer arises of a dorsal attack.

However, by oxidative demetallation with iodine in THF, was only obtained *cis*-4a,9a-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole; the hydrochloride derivative shows identical spectral and melting point data with that of a sample obtained by direct reaction of **1** with methyllithium in dry toluene. The *trans* isomer was not detected, Scheme 3.

Scheme 3



i. RLi/toluene, r.t.

R = H, *endo*-**4a**/*exo*-**4a**	50:50
R = Me, *endo*-**4b**/*exo*-**4b**	60:40
R = *n*-Bu, *endo*-**4c**/*exo*-**4c**	68:32

The reaction of **3** (*endo*/*exo*, 1:2) with *n*-butyllithium in dry toluene gives *endo-cis*-**4c** and *exo-cis*-**4c** (*endo/exo*, 68:32) by ^{1}H NMR; the 4a-methyl group appears at 1.36 and 1.10 ppm for the *endo* and the *exo* isomer respectively. Moreover, the uncomplexed *cis*-**2c** product was isolated in 13% yield by partial decomposition of the **4c** complexes.

However, by oxidative demetallation of the complex with iodine in THF, was only obtained *cis*-4a-methyl-9a-(*n*-butyl)-1,2,3,4,4a,9a-hexahydrocarbazole as an oil in quantitative yield; the hydrochloride derivative shows identical spectral and melting point data with that of a sample obtained by reaction of **1** with *n*-butyllithium in dry toluene. The *trans* isomer was not detected, Scheme 3.

The reaction of **3** (*endo*/*exo*, 1:2) with *tert*-butyllithium in toluene affords an unstable oil complex (**4d**) which decomposes in silica gel column chromatography to the *cis*-4a-methyl-9a-*tert*-butyl derivative (**2d**). Treatment of **4d** complex with iodine in THF gives only compound *cis*-**2d** as an oil; hydrochloride 187-190°.

On the basis of the above experiments, it can be concluded that organolithium reagents react more rapidly with *endo* **3** than with the *exo* isomer, which can be justified by the greater stability of the transition state formed by the nucleophile with the *endo-cis*-$Cr(CO)_3$ than with the *exo-cis*-$Cr(CO)_3$ isomer.

To probe this supposition, the **4b** complex was prepared by transmetallation of the hexahydrocarbazole *cis*-**2b** with hexacarbonylchromium in 1,4-dioxane/THF (3:1) under rigorous dry and darkness conditions and argon atmosphere. The product was obtained in good yield (63%), as a mixture of *endo*-**4b** and *exo*-**4b** isomers in 12:1 ratio.

The structural interpretation about the more stable *endo-cis*-**4**(**a-c**) isomer is related to the saturated cyclohexane ring. The presence of the *cis*-9a substituent (hydrogen, methyl, *n*-butyl) in the corresponding complexes, produces a twisted cyclohexane chair conformation necessary to avoid the contacts with the 4a-methyl substituent and with the tricarbonylchromium group. However, in the *exo-cis* isomer (**4a-c**), the methylene at 1 and 3 positions (or 2 and 4) in a chair conformation are also close to the tricarbonylchromium group. This approach seems to be the most important bulkiness contact and hence, the resulting complex is less stable than their *endo-cis* isomers. This interpretation accords well with the low transformation of the *exo*-**3** to the *exo-cis*-**4**(**a-c**) isomer with the organolithium reagent (*exo*-**3**: MeLi, 20%; *n*-Bu-Li, 15%). Moreover, the same steric effect can be related with the presence in the reaction of the decomposition product *cis*-4a-methyl-9a-substituted-1,2,3,4a,9a-hexahydrocarbazole, which increases with the volume of the 9a-substituent.

Although, in general the reaction of **3** with the organolithium reagents proceeds well in toluene while it does not take place in ethereal solvents (THF or diethyl ether). This fact could permit an interpretation of the reaction of the *endo*-**3** isomer and the organolithium reagent through an electron transfer mechanism affording a more stable *endo-cis* complex, by analogy with the reaction of **1** with the organolithium reagent in toluene [11]. However, the steric bulkiness considerations through a radical mechanism of the organolithium and the C=N bond to give the main *endo* isomer could give a similar outcome as that of the ionic one.

A characteristic feature of the (η^6-arene)-$Cr(CO)_3$ complexes, useful for rapid identification is the presence of two intense carbonyl stretching bands in the IR spectrum. Complex **3** (KBr) shows these bands at 1940 and 1850 cm^{-1}. On the basis of local C3v symmetry for the tricarbonylchromium group, these bands have been assigned to a non-degenerate symmetric vibration (A1) and a doubly-degenerate asymmetric vibration (E) [16].

EXPERIMENTAL

Melting points were determined in open capillary tubes or in a Reichert hot stage microscope and are uncorrected. Infrared spectra were recorded using a Perkin Elmer 681 spectrophotometer. ^1H NMR spectra were recorded at 200 MHz using a Bruker WM-200-SY spectrometer; ^{13}C NMR spectra were recorded at 50 MHz, in $CDCl_3$. Chemical shifts are given in ppm, using TMS as internal reference. Mass spectra were recorded using electronic impact technique at 70 eV, using a Hewlett-Packard SP85 spectrometer. Elemental analyses were performed with a LECO CHN-600. All solvents and chemicals were reagent grade.

Synthesis of 4a-Methyl,9a-substituted-1,2,3,4,4a,9a-hexahydrocarbazoles, **2b-d**, General Procedure.

To a solution of 4a-methyl-1,2,3,4-tetrahydro-4a*H*-carbazole (**1**) (1.5 g, 8.1 mmol) in dry toluene (19 ml), at -10°, under an argon atmosphere, was added a solution of the organolithium reagent (12.5 mmol) in hexane or THF. The solution was stirred at -10° for 3 hours and hydrolysed with toluene:water 1:1 (25 ml). The organic layer was separated and the solvent removed at reduced pressure yielding a residual brown oil that was extracted with dichloromethane, dried on Na_2SO_4 and filtered. The solvent was removed at reduced pressure and the residual orange oil purified by column chromatography using hexane:ethyl acetate (4:1) as the eluent. The 4a-methyl-9a-substituted-1,2,3,4,4a,9a-hexahydrocarbazole (**2b-d**) were obtained as yellow oils, which were crystallized as the hydrochloride derivative as white solids.

cis-4a,9a-Dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole (**2b**).

Compound **2b** was obtained as a light yellow oil, hydrochloride m.p. 222-224°, 1.41 g, 87% yield. IR (Film): 3340, 740 cm^{-1}. ^1H NMR ($CDCl_3$): 1.10 (s, 3H), 1.18 (s, 3H), 1.3-1.7 (m, 7H, $(CH_2)_3$, H-1), 1.85 (m, 1H), 3.33 (s, 1H), 6.62 (d, 1H, J = 7.3 Hz), 6.76 (t, 1H, J= 6.8 Hz); 6.98 (m, 2H). ^{13}C NMR ($CDCl_3$): 22.0, 22.3, 22.4, 34.6, 36.3, 45.8, 65.7, 110.1, 118.4, 121.5, 126.6, 138.1, 148.4. MS (70 eV): m/z 201 (M^+, 30), 186 (100), 158 (19), 146 (49), 144 (73).

Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.41; H, 9.34; N, 7.15.

cis-4a-Methyl-9a-*n*-butyl-1,2,3,4,4a,9a-hexahydrocarbazole (**2c**).

Compound **2c** was obtained as a light yellow oil, hydrochloride mp 221-223°, 1.9 g, 97% yield. IR (Film): 3350, 730 cm^{-1}. ^1H NMR ($CDCl_3$): 0.86 (t, 3H, J = 5,0 Hz), 1.05 (s, 3H), 1.2-1.7 (m, 13H), 1.85 (m, 1H), 3,31 (s, 1H), 6.52 (d, 1H, J = 7.8 Hz), 6.66 (t, 1H, J = 7.2 Hz), 6.95 (m, 2H). ^{13}C-NMR ($CDCl_3$): 14.1, 22.2, 22.5, 23.5, 26.4, 31.5, 32.5, 34.8, 46.8, 67.7, 110.5, 118.5, 121.4, 126.7, 138.5, 148.5. MS (70 eV): m/z 243 (M^+, 10), 186 (100), 144 (28), 143 (10), 130 (6).

Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.6; H, 10.45; N, 5.8.

cis-9a-*tert*-Butyl-4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (**2d**).

Compound **2d** was obtained as a light yellow oil (hydrochloride mp 187-190°), 0.9 g, 45% yield. IR (Film): 3400, 735 cm^{-1}. ^1H NMR ($CDCl_3$): 1.00 (s, 9H), 1.45 (s, 3H), 1.3-1.9 (m, 8H), 3.80 (s, 1H), 6.52 (d, ^1H, J = 7.2 Hz), 6.65 (t, 1H, J = 6.5 Hz), 6.85 (d, 1H, J = 6.5 Hz), 6.98 (t, 1H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$): 21.4, 22.4, 23.3, 28.4, 29.0, 39.8, 41.1, 48.3, 72.7, 107.5, 117.3, 119.8, 126.6, 140.0, 149.3. MS (70 eV): m/z 243 (M^+, 1), 186 (100), 144 (40), 130 (11), 93 (19).

Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.54; H, 10.20; N, 5.45.

η^6-(4a-Methyl-1,2,3,4-tetrahydro-4a*H*-carbazole) tricarbonylchromium (**3**), General Procedure.

In a Strohmeier type system [14], under darkness and argon atmosphere, was placed 4a-methyl-1,2,3,4-tetrahydro-4a*H*-carbazole (3 g, 0.016 mol) in dry THF (50 ml), and hexacarbonylchromium (3.45 g, 0.016 mol) in dry 1,4-dioxane (150 ml). The mixture was warmed at 150° for 4 days and after solvent evaporation at reduced pressure, a yellow oil was obtained (3.89 g, 75%), as a mixture of isomers *endo*:*exo* (by ^1H NMR, 1:2), that was purified by silica gel column chromatography using ethyl acetate:hexane (1:1) as eluent. The *exo*-**3** was obtained as an orange oil, which was precipitated in hexane as an orange solid, mp 118-120°, 2.59 g (67%); the *endo*-**3**, yellow solid, mp 105-109°, 0.15 g (decomposes during the silica gel column purification).

exo-**3**.

This compound has IR (KBr): 1940, 1850, 1590, 665, 625 cm^{-1}. ^1H NMR ($CDCl_3$): 1.37 (s, 3H), 1.2-1.9 (m, 4H), 2.31 (m, 2H), 2.57 (m, 1H), 2.72 (m, 1H), 4.89 (m, 1H), 5.52 (m, 1H), 5.71 (m, 1H), 5.88 (m, 1H). MS (70 eV): m/z 321 (M^+, 8), 265 (1), 237 (100), 220 (8), 195 (11), 184 (5), 80 (14), 52 (94).

Anal. Calcd. for $C_{16}H_{15}NO_3Cr$: C, 59.82; H, 4.71; N, 4.36. Found: C, 60.14; H, 4.41; N, 4.78.

endo-**3**.

This compound has IR (KBr): 1935, 1850, 1590, 670, 625 cm^{-1}. ^1H NMR ($CDCl_3$): 1.52 (s, 3H), 1.2-1.9 (m, 4H), 2.31 (m, 2H), 2.57 (m, 1H), 2.72 (m, 1H), 4.89 (m, 1H), 5.52 (m, 1H), 5.71 (m, 1H), 5.88 (m, 1H). MS (70 eV): m/z 321 (M^+, 12), 265 (5), 237 (100), 220 (11), 195 (10), 184 (7), 80 (15), 52 (90).

Anal. Calcd. for $C_{16}H_{15}NO_3Cr$: C, 59.82; H, 4.71; N, 4.36. Found: C, 59.64; H, 4.25; N, 4.28.

Reaction of **3** with $LiAlH_4$, *endo*- and *exo*-**4a**.

To a solution of $LiAlH_4$ (0.302 g, 7.96 mmol) in dry THF (3 ml) was added a solution of **3** (*endo*:*exo*, 1:2) (0.639 g, 1.99 mmol) in dry THF (8 ml), under darkness and argon atmosphere. The mixture was stirred at room temperature for 2 hours and hydrolysed with THF:H_2O 1:1 (20 ml), extracted with diethyl ether (20 ml) and dried on $MgSO_4$. After, the mixture was filtered and the solvent removed under reduced pressure, giving a

yellow oil as an *endo:exo* (1:1) mixture, which was purified by silica gel column chromatography using hexane:ethyl acetate 5:1 as the eluent. Three compounds were isolated: the *endo-cis*-**4a** isomer, as a yellow crystalline solid, mp 146-148° [15], 256 mg, 40**%** yield; the *exo-cis*-**4a** isomer, as a yellow solid, mp 155-157°, 268 mg, 42**%** yield; the uncomplexed compound **2a**, 55 mg, 7% yield, as a light yellow oil, hydrochloride mp 222-224°.

endo-cis-**4a**.

This compound has IR (KBr): 3380, 1940, 1850, 1550, 680, 630 cm^{-1}. ^1H NMR (acetone-d_6): 1.31 (s, 3H), 1.3-1.7 (m, 7H), 1.90 (m, 1H, H-1), 3.44 (m, 1H, H-9a), 4.89 (t, 1H, J= 6.2 Hz, H-6), 5.06 (d, 1H, J= 6.6 Hz, H-8), 5,34 (s br, 1H, NH), 5.64 (t, 1H, J= 6.5 Hz, H-7), 5.71 (d, 1H, J= 6.2 Hz, H-5). MS (70 eV): m/z 323 (M^+, 11), 267 (9), 240 (20), 239 (77), 237 (36), 186 (23), 144 (27), 130 (24), 80 (18), 52 (100).

Anal. Calcd. for $C_{16}H_{17}NO_3Cr$: C, 59.45; H, 5.29; N, 4.33. Found: C, 59.75; H, 5.45; N, 4.52.

exo-cis-**4a**.

This compound has IR (KBr): 3405, 1940, 1850, 1550, 680, 630 cm^{-1}. ^1H NMR ($CDCl_3$): 1.22 (s, 3H), 1.5-1.9 (m, 6H), 2.10 (m, 2H), 3.36 (dd, 1H, J= 10.0 and 5.5 Hz, H-9a), 4.83 (t, 1H, J= 6.3 Hz, H-6), 5.03 (d, 1H, J= 6.7 Hz, H-8), 5,58 (s br, 1H, NH), 5.69 (t, 1H, J= 6.3 Hz, H-7), 5.83 (d, 1H, J= 6.4 Hz, H-5). MS (70 eV): m/z 323 (M^+, 19), 267 (13), 240 (25), 239 (100), 186 (25), 144 (26), 130 (26), 80 (13), 52 (52).

Anal. Calcd. for $C_{16}H_{17}NO_3Cr$: C, 59.45; H, 5.29; N, 4.33. Found: C, 59.37; H, 5.72; N, 4.45.

Reaction of **3** with Organolithium Reagents, General Procedure.

To a solution of **3** (*endo/exo*, 1:2) (0.4 g, 1.25 mmol) in dry toluene (12 ml), under darkness and argon atmosphere, was added the corresponding organolithium reagent (2,4 mmol). After 5 hours, the mixture was hydrolysed with THF:H_2O 1:1 (10 ml), extracted with diethyl ether (20 ml) and dried on $MgSO_4$. After filtration the solvent was removed at reduced pressure to give a residual brown oil as a mixture of the *endo* and *exo* isomers, that was purified on a silica gel column chromatography using hexane:ethyl acetate (4:1) as the eluent.

exo-cis-**4b**, *endo*-**4b**.

Following the general procedure, **3** (*endo/exo*, 1:2) and MeLi (1,6 *M* in hexane; 1.5 ml, 2.4 mmol) give: a) *endo-cis*-**4b**, as a yellow solid (164 mg, 39%), mp 130-132°; b) *exo-cis*-**4b**, as a yellow solid (109 mg, 26%), mp 138-140°; c) the uncomplexed compound **2b**, light yellow oil (13 mg, 9%), hydrochloride m.p. 222-224°.

endo-cis-**4b**.

This compound has IR (KBr): 3360, 1930, 1840, 1540, 670, 620 cm^{-1}. ^1H NMR (MeOD): 1.34 (s, 3H), 1.39 (s, 3H), 1.3-1.7 (m, 8H), 4.90 (m, 1H), 5.01 (d, 1H, J= 6.8 Hz), 5,53 (m, 2H). MS (70 eV): m/z 337 (M^+, 24), 281 (16), 253 (100), 201 (18), 186 (59), 158 (14), 144 (47), 130 (14), 52 (50).

Anal. Calcd. for $C_{17}H_{19}NO_3Cr$: C, 60.53; H, 5.68; N, 4.15. Found: C, 60.74; H, 5.35; N, 4.18.

exo-cis-**4b**.

This compound has IR (Film): 3355, 1940, 1845, 1540, 670, 630 cm^{-1}. ^1H NMR (MeOD): 1.08 (s, 3H), 1.19 (s, 3H), 1.3-1.8 (m, 5H), 2.00 (m, 2H), 2.50 (m, 1H), 3.80 (br s, 1H), 4.77 (t, 1H, J = 6.2 Hz), 4.95 (m, 1H), 5.61 (t, 1H, J = 6.4 Hz), 5.68 (d, 1H, J = 6.4 Hz). MS (70 eV): m/z 337 (M^+, 20), 281 (14), 253 (100), 201 (17), 186 (60), 158 (13), 144 (50), 130 (14), 52 (51).

Anal. Calcd. for $C_{17}H_{19}NO_3Cr$: C, 60.53; H, 5.68; N, 4.15. Found: C, 60.16; H, 5.44; N, 4.62.

endo- and *exo*-**4c**.

Following the general procedure, **3** (*endo/exo*, 1:2) and *n*-BuLi (1,6 *M* in hexane; 1.5 ml, 2.4 mmol) give: a) *endo-cis*-**4c**, (166 mg, 41.5%), as a yellow-orange solid, mp 148-151°; b) *exo-cis*-**4c**, as an orange oil that precipitates in hexane to give an orange solid, mp 160-163° (78 mg, 19.5%); c) the uncomplexed compound **2c** (29 mg, 13%), as a light yellow oil, hydrochloride mp 221-223°.

endo-cis-**4c**.

This compound has IR (film): 3400, 3290, 1940, 1840, 670, 620 cm^{-1}. ^1H NMR ($CDCl_3$): 0.96 (m, 3H), 1.1-1.7 (m, 8H), 1.36 (s, 3H, *endo*), 1.88 (m, 1H), 2.45 (m, 1H), 2.70 (m, 1H), 4.8-5.1 (m, 2H), 5.5-5.7 (m, 2H). MS (70 eV): m/z 379 (M^+, 7), 323 (4), 296 (18), 295 (64), 293 (27), 237 (9), 186 (45), 157 (6), 144 (49), 80 (26), 52 (100).

Anal. Calcd. for $C_{20}H_{25}NO_3Cr$: C, 63.31; H, 6.64; N, 3.69. Found: C, 63.59; H, 6.92; N, 3.75.

exo-cis-**4c**.

This compound has IR (film): 3400, 3280, 1940, 1840, 665, 625 cm^{-1}. ^1H NMR ($CDCl_3$): 0.96 (m, 3H), 1,10 (s, 3H, exo), 1.1-1.7 (m, 8H), 2.45 (m, 1H), 4.8-5.1 (m, 2H), 5.5-5.7 (m, 2H). MS (70 eV): m/z 379 (M^+, 7), 323 (4), 296 (18), 295 (64), 293 (27), 237 (9), 186 (45), 157 (6), 144 (49), 80 (26), 52 (100).

Anal. Calcd. for $C_{20}H_{25}NO_3Cr$: C, 63.31; H, 6.64; N, 3.69. Found: C, 63.39; H, 6.42; N, 3.44.

η6-(4a,9a-Dimethyl-1,2,3,4-tetrahydro-4a*H*-carbazole) tricarbonylchromium (**4b**).

Following the above procedure to prepare the **3** complex, 4a,9a-dimethyl-1,2,3,4-tetrahydro-4a*H*-carbazole (**2b**) (0.503 g, 2.5 mmol) in dry THF (10 ml), and hexacarbonylchromium (0.447 g, 2.5 mmol) in dry 1,4-dioxane (30 ml) give a yellow-orange oil (0.532 g, 63%), as a mixture of isomers *endo:exo* (12:1). The *exo*-**4b** complex was obtained as an orange solid (0.041 g), mp 138-140°; the *endo*-**4b**, yellow solid, mp 130-132°, (0.492 g). The spectral and analytical data are described above.

Decomplexation of the $Cr(CO)_3$ Complexes.

To a solution of the $Cr(CO)_3$ complex (0.24 mmol) in THF (10 ml) was added iodine (80 mg, 0.31 mmol) in THF (5 ml). After 1 hour at room temperature, the residual iodine was eliminated with an aqueous solution of $Na_2S_2O_3$ (10 ml, 15%). The reaction mixture was extracted with diethyl ether (20 ml) and dried with Na_2SO_4. After solvent elimination, the free compounds (**2a-d)** were obtained in practically quantitative yield.

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