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Exo- and Endo-Tricarbonyl\((4b,5,6,7,8,8a\text{-}\eta)-\text{Cis-N-}
Methyl-2,3,4,4a,9,9a-Hexahydro-1H- Carbazole\]Chromium(0)

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References


exo- and endo-Tricarbonyl[(4b,5,6,7,8,8a-\(\eta^6\)-N-methyl-2,3,4,4a,9,9a-hexahydro-1H-carbazole)chromium(0)]

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Abstract

Acid-mediated hydride reduction of tricarbonyl(\(\eta^6\)-N-methyl-1,2,3,4-tetrahydrocarbazole)chromium(0) affords either the cis-fused exo-hexahydrocarbazole-chromium(0) complex \(\{[\text{Cr} (\text{C}_2\text{H}_7\text{N})(\text{CO})_3]\}, \) (I) exclusively, or a separable mixture of (I) and the endo-isomer \(\{[\text{Cr} (\text{C}_2\text{H}_7\text{N})(\text{CO})_3]\}, \) (II), depending upon the choice of hydride donor. The conformations of the hexahydrocarbazole systems differ in the orientation of the indoline moiety with respect to the saturated hexahydrocarbazole rings. The isolation of the exo-isomer is unusual, as this complex arises via reaction at the sterically more hindered endo face of the coordinated ligand.

Comment

The chemistry of (\(\eta^6\)-arene)tricarbonylchromium complexes continues to attract much attention, owing to the multitude of reactions in which the bound arene can participate (Semmelhack, 1995). Moreover, most transformations of chromium-complexed arenes proceed with excellent levels of stereoselectivity, as a consequence of the stereodirecting effect of the Cr(CO)₃ fragment (Davies & McCarthy, 1995). In a study aimed at extending this useful reactivity profile to include stereo-controlled manipulations of \(\eta^6\)-coordinated indoles, the acid-mediated hydride reduction of (indole)Cr(CO)₃ complexes has been explored (Pigge et al., 1998). It is in connection with this project that the title complexes, (I) and (II), were prepared and structurally characterized.

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. The exclusive production of the exo-isomer, (I), under the initial set of reaction conditions is significant, as this complex results from reaction at the nominally sterically more hindered endo face of the coordinated indole ligand. Such endo-selective reactions of (arene)chromium complexes have rarely been observed (Sur et al., 1996). It is also noteworthy that (I) and (II) represent two of only a few structurally characterized (\(\eta^6\)-indoline)—transition metal complexes (Chen et al., 1997; Heaton et al., 1993; Dickens et al., 1989).

Bond distances and angles for the two complexes are quite similar, with the major structural difference being the stereochemistry of the carbazole ring fusion relative to the Cr(CO)₃ group. The average Cr—CO distances are 1.834 (2) and 1.832 (4) Å, and the average OC—Cr—CO angles are 88.16 (9) and 88.04 (8)°, for compounds (I) and (II), respectively. The Cr(CO)₃ fragment adopts a partially eclipsed conformation with the coordinated arene, and the three CO ligands are aligned over C5, C7, and C8a. Such a conformation is typical in Cr(CO)₃ complexes of arenes bearing an electron-releasing substituent (Solladie-Cavallo, 1985). The Cr—C arene distances vary in the ranges 2.202 (2)—2.346 (2) Å and 2.200 (2)—2.390 (2) Å in (I) and (II), respectively. The distance from the Cr atom to the centroid of the aromatic ring is 1.757 in (I) and 1.773 Å in (II). The bond distances and angles within the aromatic ring itself are quite similar, with the major structural difference being the stereochemistry of the carbazole ring fusion relative to the Cr(CO)₃ group.
and 1.410 (3) Å, and 119.9 (4) and 119.9 (4)°, for (I) and (II), respectively]. The indoline ring in both complexes (mean plane calculations include atoms C4a, C4b, C5–C8, C8a, C9a and N9) adopts an envelope conformation in which all the atoms are approximately coplanar except C9a, which constitutes the 'flap' of the envelope and which deviates from the indoline mean plane by 0.237(1) in (I) and 0.118(1) Å in (II), toward the face of the arene occupied by the Cr(CO)3 fragment. The saturated six-membered carbocyclic ring (C1–C4, C4a, C9a) exists in a chair conformation in both complexes. The attached N atom occupies an axial position in (I) and an equatorial position in (II). The conformational preferences observed in (I) and (II) presumably reflect a minimization of interactions between the bound ligand and the Cr(CO)3 fragment, although examination of molecular models did not reveal any significant steric constraints present in either complex, regardless of the conformation adopted by the cyclohexane ring. The C–C distances and angles in the saturated carbocyclic rings are in the ranges 1.515 (3)–1.556 (2) Å and 109.3 (2)–116.29 (14)°, respectively. These values are similar to the distances and angles found in a structurally characterized metal-free cis-hexahydrocarbazole derivative (McLean et al., 1970). The crystal packing of the molecules indicates a weak interaction of one of the carbonyl O atoms (O3) with an aromatic H atom [O3–H5(1 + x, y, z) = 2.55 Å and O3–H6A(–x + 1/2, y– 1/2, –z + 1/2) = 2.54 Å for (I) and (II), respectively].

**Experimental**

Treatment of (η⁶-N-methyl-1,2,3,4-tetrahydrocarbazole)Cr(CO)3 with NaBH3CN in trifluoroacetic acid afforded the exo-hexahydrocarbazole complex, (I), as the sole product in 84% isolated yield. Substitution of NaBH4 for NaBH3CN in the reaction produced a separable 1:1 mixture of (I) and the endo-isomer, (II), in 95% yield. Full experimental details, including spectroscopic data, for the synthesis of (I) and (II) have been published elsewhere (Pigge et al., 1998). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexanes into a methylene chloride solution of (I) and a diethyl ether solution of (II).

**Compound (I)**

**Crystal data**

\[
\text{[Cr(C_{13}H_{17}N)(CO)_{3}]} \\
M_r = 323.31 \\
\text{Monoclinic} \\
P2_1/c \\
a = 7.3756 (1) \text{ Å} \\
b = 21.9934 (2) \text{ Å} \\
c = 9.6991 (1) \text{ Å} \\
\beta = 108.843 (1)^\circ \\
V = 1489.02 (3) \text{ Å}^3 \\
Z = 4 \\
D_\text{r} = 1.442 \text{ Mg m}^{-3} \\
D_\text{m} \text{ not measured}
\]

**Data collection**

Siemens CCD diffractometer

\[
\text{3102 reflections with } l > 2\sigma(l)
\]

Absorption correction: empirical (Blessing, 1995)

\[
R_{\text{int}} = 0.029 \\
\theta_{\text{max}} = 28^\circ \\
T_{\text{min}} = 0.78, T_{\text{max}} = 0.98 \\
25368 \text{ measured reflections} \\
3596 \text{ independent reflections}
\]

**Refinement**

Refinement on \(F^2\)

\[
R(F^2 > 2\sigma(F^2)) = 0.032 \\
\omega R(F^2) = 0.082 \\
S = 1.081 \\
3596 \text{ reflections} \\
190 \text{ parameters} \\
H \text{ atoms not refined}
\]

\[
w = 1/\sigma^2(F^2) + (0.0352P)^2 + 0.6246P \\
\text{where } P = (F^2 + 2F^2)^{1/2}
\]

**Compound (II)**

**Crystal data**

\[
\text{[Cr(C_{13}H_{17}N)(CO)_{3}]} \\
M_r = 323.31 \\
\text{Mo Kα radiation} \\
\lambda = 0.71073 \text{ Å}
\]
A New Ni(dmit)$_2$ Salt with a Paramagnetic Cation: [Cu(bpy)$_3$][Ni(C$_3$S$_5$)$_2$]

**Abstract**

The cation of the title compound, tris(2,2'-bipyridyl)-copper(II) bis[bis(2-thioxo-1,3-dithiole-4,5-dithiolato-$S^4$,S$_5$)nickelate(III)], [Cu(C$_{10}$H$_8$N$_2$)$_3$][Ni(C$_3$S$_5$)$_2$], has crystallographic twofold rotation symmetry with all Cu—N distances almost equivalent in an octahedral environment. The NiS$_4$ coordination of the anion is significantly distorted from a square-planar geometry.

**Comment**

The synthesis of molecular conductors containing localized magnetic moments is a new challenge in the

**References**


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