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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1217). Services for accessing these data are described at the back of the journal.

References

Bresciani-Pahor, N., Forcolin, M., Marzilli, L. G., Randaccio, L., Summers, M. F. & Toscano, P. J. (1985). *Coord. Chem. Rev.* **63**, 1–125.

Bresciani-Pahor, N., Randaccio, L., Toscano, P. J. & Marzilli, L. G. (1982). *J. Chem. Soc. Dalton Trans.* pp. 567–572.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Randaccio, L., Bresciani-Pahor, N., Zangrando, E. & Marzilli, L. G. (1989). *Chem. Soc. Rev.* **18**, 225–250.

Savage, H. F. J., Lindley, P. F., Finney, J. L. & Timmins, P. A. (1987). *Acta Cryst.* B**43**, 280–295.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SHELXTL Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Toscano, P. J., Swider, T. F., Marzilli, L. G., Bresciani-Pahor, N. & Randaccio, L. (1983). *Inorg. Chem.* pp. 3416–3421.

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

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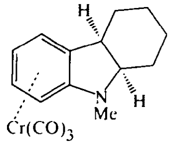
Abstract

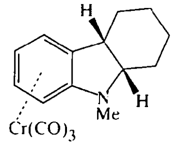
Acid-mediated hydride reduction of tricarbonyl(η^6-*N*-methyl-1,2,3,4-tetrahydrocarbazole)chromium(0) affords either the *cis*-fused *exo*-hexahydrocarbazole–chromium(0) complex {[$Cr(C_{13}H_{17}N)(CO)_3$], (I)} exclusively, or a separable mixture of (I) and the *endo*-isomer {[$Cr(C_{13}H_{17}N)(CO)_3$], (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 (η^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 stereocontrolled manipulations of η^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.



(I)



(II)

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 (η^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) 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 typical for both complexes [mean values are 1.410 (3)

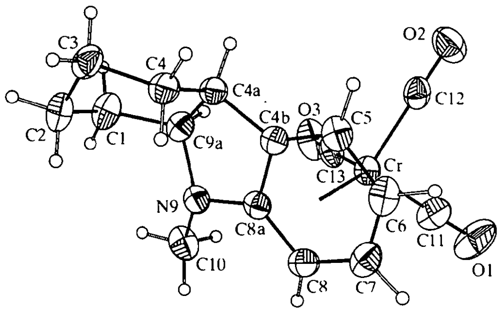


Fig. 1. View of (I) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

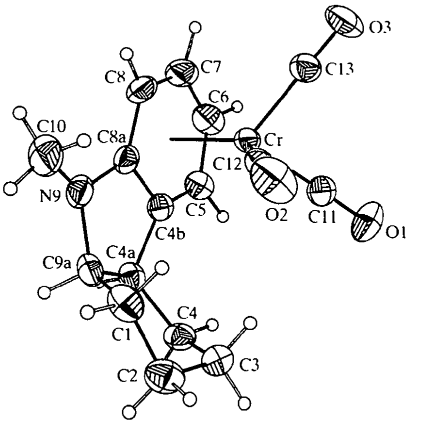


Fig. 2. View of (II) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

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—H6*A*($-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$) = 2.54 Å for (I) and (II), respectively].

Experimental

Treatment of (η^6-*N*-methyl-1,2,3,4-tetrahydrocarbazole)Cr(CO)$_3$ with NaBH$_3$CN in trifluoroacetic acid afforded the *exo*-hexahydrocarbazole complex, (I), as the sole product in 84% isolated yield. Substitution of NaBH$_4$ for NaBH$_3$CN 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

[Cr($C_{13}H_{17}N$)(CO)$_3$]
M_r = 323.31
Monoclinic
$P2_1/c$
a = 7.3756 (1) Å
b = 21.9934 (2) Å
c = 9.6991 (1) Å
β = 108.843 (1)°
V = 1489.02 (3) Å^3
Z = 4
D_x = 1.442 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 2–28°
μ = 0.777 mm^{-1}
T = 218 (2) K
Hexagonal plate
0.33 × 0.30 × 0.10 mm
Light yellow

Data collection

Siemens CCD diffractometer
ω scans
Absorption correction: empirical (Blessing, 1995)
T_{min} = 0.78, T_{max} = 0.98
25 368 measured reflections
3598 independent reflections

3102 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 28°
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 30$
$l = 0 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.082
S = 1.081
3596 reflections
190 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.6246P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.291 e Å^{-3}
$\Delta\rho_{min}$ = −0.313 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

[Cr($C_{13}H_{17}N$)(CO)$_3$]
M_r = 323.31

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/n$
$a = 9.5188$ (1) Å
$b = 10.3406$ (1) Å
$c = 14.6223$ (2) Å
$\beta = 91.379$ (1)°
$V = 1438.86$ (3) Å^3
$Z = 4$
$D_x = 1.492$ Mg m^{-3}
D_m not measured

Cell parameters from 8192 reflections
$\theta = 2$–28°
$\mu = 0.804$ mm^{-1}
$T = 293$ (2) K
Rectangular
0.4 × 0.3 × 0.1 mm
Yellow

Data collection

Siemens CCD diffractometer
ω scans
Absorption correction: empirical (Blessing, 1995)
$T_{\min} = 0.77$, $T_{\max} = 0.91$
28 024 measured reflections
3476 independent reflections

3034 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 28°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.030$
3463 reflections
190 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.6378P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.299$ e Å^{-3}
$\Delta\rho_{\min} = -0.477$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection was carried out by a Siemens CCD X-ray diffractometer at 218 K. Data were collected by the double-pass method using the CCD area-detector system. The first 50 frames of data were recollected at the end of data collection to monitor crystal decay. H atoms were treated using appropriate riding models.

For both compounds, data collection: *SMART* (Siemens, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1997); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL-Plus*.

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References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Chen, S., Vasquez, L., Noll, B. C. & DuBois, M. R. (1997). *Organometallics*, **16**, 1757–1764.

Davies, S. G. & McCarthy, T. D. (1995). *Comprehensive Organometallic Chemistry* II, edited by E. W. Abel, F. G. A. Stone & G. Wilkinson, Vol. 12, pp. 1039–1070. Oxford: Elsevier Science Ltd.

Dickens, P. J., Slawin, A. M. Z., Widdowson, D. A. & Williams, D. J. (1989). *Tetrahedron Lett.* **29**, 103–106.

Heaton, S. B., Jones, G. B. & Pennington, W. T. (1993). *Acta Cryst.* C**49**, 1749–1753.

McLean, S., Trotz, U. O., Dichman, K. S., Fawcett, J. K. & Nyburg, S. C. (1970). *Tetrahedron Lett.* pp. 4561–4564.

Pigge, F. C., Fang, S. & Rath, N. P. (1998). *J. Organomet. Chem.* **559**, 131–140.

Semmelhack, M. F. (1995). *Comprehensive Organometallic Chemistry* II, edited by E. W. Abel, F. G. A. Stone & G. Wilkinson, Vol. 12, pp. 979–1038. Oxford: Elsevier Science Ltd.

Sheldrick, G. M. (1997*a*). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXS97. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1998). *SHELXTL-Plus.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1997). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Solladie-Cavallo, A. (1985). *Polyhedron*, **4**, 901–927.

Sur, S., Ganesh, S., Pal, D., Puranik, V. G., Chakrabarti, P. & Sarkar, A. (1996). *J. Org. Chem.* **61**, 8362–8363.

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A New Ni(dmit)$_2$ Salt with a Paramagnetic Cation: [Cu(bpy)$_3$][Ni(C$_3$S$_5$)$_2$]$_2$

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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$_5$)$_2$]$_2$, 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

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