Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

An N-unprotected Fischer pyrrolidinylidene complex

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Received 27 January 2000
Accepted 15 March 2000

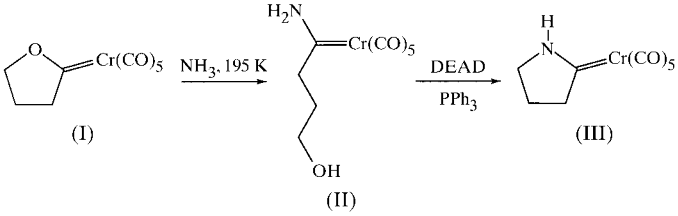
Data validation number: IUC0000082

The synthesis and crystal structure of pentacarbonyl(pyrrolidin-2-ylidene)chromium(0), $[Cr(C_4H_7N)(CO)_5]$, is reported. The compound shows strong interaction between the lone pair at nitrogen and the carbene C atom, and weak intermolecular hydrogen bonds.

Comment

Fischer aminocarbene complexes are versatile reagents for stereoselective organic synthesis (Dötz, 1984; Hegedus, 1995; Wulff, 1995; Barluenga, 1996). Cycloalkylidene complexes are potential precursors for spiro-cycloaddition and annelation reactions. Oxacyclopentylidene complexes are readily accessible by cyclization of alkynols at the metal template (Dötz *et al.*, 1987) and can be transformed into azacyclopentylidene (pyrrolidinylidene) complexes by an efficient one-pot procedure recently described by us (Haase & Dötz, 1999). The protocol is characterized by smooth conditions and provides the first generally applicable (Haase *et al.*, 1999; Dötz *et al.*, 1997) access to N-unprotected azacyclopentylidene complexes.

The structure of (III) was determined by X-ray crystallography to study the ring conformation and bond lengths in the absence of steric hindrance induced by substituents at the N atom. Complex (III) shows a ^3E conformation, with an angle of 11.3 (3)° between the C4/N1/C1/C2 and C4/C3/C2 planes, C3 lying 0.181 (4) Å above the C4/N1/C1/C2 plane. Characteristic details are the planarity at the N and the carbene C atom which indicates the strong π-interaction between these atoms, supported by the very short nitrogen–carbene bond of 1.296 (2) Å and the minor distortions from an exact trigonal environment of the Nsp^2 atom [C1—N1—H1 121.7 (14)°]. In contrast, known *N*-methyl-substituted azacyclopentylidene complexes show major steric interactions between the pentacarbonylchromium fragment and the *N*-methyl group resulting in C1—N1—NCH$_3$ angles of 125.8 (Dötz *et al.*, 1997) or 127.7° (Dötz *et al.*, 1999) and longer nitrogen–carbene bonds (1.313 and 1.3059 Å, respectively). Complex (III) shows almost ideal octahedral coordination around the Cr atom. The Cr—C distance of the *trans*-carbonyl group is between 0.014 and 0.035 Å shorter than to the *cis*-carbonyl ligands, as expected for Fischer carbene complexes (Fischer, 1974). The crystal structure is stabilized by weak intermolecular hydrogen bonds between the N1 H atom and the O1E^i atom of a carbonyl ligand [N1—H1 0.86, H1$\cdots$O1E^i 2.26 (2), N1$\cdots$O1E^i 3.069 (2) Å and N1—H1$\cdots$O1E^i 157°; symmetry code: (i) $x + 1, y, z$].



Experimental

Pentacarbonyl(oxacyclopentylidene)chromium(0), (I), was subjected to ammonolysis and the intermediate formed, *i.e.* acyclic aminocarbene complex (II), was recyclized under Mitsunobu conditions overnight. Recrystallization of the pure product from *n*-pentane/dichloromethane yielded complex (III) as yellow crystals in 65% overall yield.

Crystal data

$[Cr(C_4H_7N)(CO)_5]$
$M_r = 261.16$
Orthorhombic, $P2_12_12_1$
$a = 6.7152$ (3) Å
$b = 10.1507$ (5) Å
$c = 15.5447$ (9) Å
$V = 1059.59$ (9) Å^3
$Z = 4$
$D_x = 1.637$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 14785 reflections
$\theta = 3.3$–27.3°
$\mu = 1.083$ mm^{-1}
$T = 123$ (2) K
Plate, yellow
0.40 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Rotation in φ and ω, 2° scans
14 711 measured reflections
2630 independent reflections
2402 reflections with $I > 2\sigma(I)$

$R_{int} = 0.035$
$\theta_{max} = 28.28°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.057$
$S = 1.017$
2630 reflections
148 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983); 1097 Friedel pairs
Flack parameter = −0.015 (17)

All H atoms were located by a difference Fourier synthesis and refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}$(C or N)], using a riding model with C—H = 0.99 Å, while the coordinates of the H(N) atom were refined.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction:

DENZO–SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

We thank the Fonds der Chemischen Industrie and the Graduiertenkolleg 'Spektroskopie isolierter und kondensierter Moleküle' for financial support.

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Acta Cryst. (2000). C**56**, e174–e175 Martin Nieger *et al.* • $[Cr(C_4H_7N)(CO)_5]$ **e175**