Synthesis reactivity and molecular structure of 2'-methylspiro[cyclohexane-1,3'-3H-indole] chromium tricarbonyl complex

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Abstract

Synthesis of 2'-methylspiro[cyclohexane-1,3'-3H-indole] chromium tricarbonyl and structural analysis by spectroscopy and single-crystal X-ray techniques have been carried out. The reactivity of the C=N bond of indolenine with organometallic reagents has also been analysed. The reduction of 2'-methylspiro[cyclohexane-1,3'-3H-indole] chromium tricarbonyl with AlLiH$_4$ gave endo- and exo-complexes, which have been isolated and analysed by spectroscopic methods.

Keywords: Chromium; X-ray structure; Carbonyl; Synthesis; Reactivity; Spiroindolenine

1. Introduction

We have recently studied the reactivity of the C=N bond in spiroindolenine derivatives. Grignard reagents (R = Me; Ph) in the presence of cuprous chloride transform the spiro[cyclohexane-1,3'-3H-indole] into 2'-R spiro[1,3'-3H-cyclohexaneindoline] (R = Me; Ph) derivatives in quantitative yields [1]. Grignard (in the absence of cuprous chloride) or organolithium reagents gave 2'-substituted derivatives in very low yields (< 10%) [2].

Afterwards, 2'-methylspiro[cyclohexane-1,3'-3H-indole] 1 reacts with the methylmagnesium iodide in THF to give a methyl insertion on the 2'-methyl substitution in good yields [3], but the C=N addition product was not detected. The same Grignard reagent in the presence of cuprous chloride was inactive for both addition and insertion reactions.

Our objective was analysis of the reaction of the modified C=N bond and 2'-methyl substituent with Grignard or organolithium reagents in the 2'-methyl-spiro[cyclohexane-1,3'-3H-indole] chromium tricarbonyl complex 1-Cr(CO)$_3$.

2. Discussion

Formation of η^6-Cr(CO)$_3$ complexes enhances the reactivity and selectivity of the conjugated positions. The η^6-styrene-Cr(CO)$_3$ complex suffers double bond nucleophilic addition, which does not occur in the free styrene. The reaction is justified in terms of the carbanion stabilization on the benzylic position by the complex [4].

The synthesis of 1-Cr(CO)$_3$ was carried out by treatment of 1 with chromium hexacarbonyl in THF/dioxane (1:5), under rigorous dryness, argon atmosphere and sunlight coverture, in a Strohmeier type system [5], in good yield. Solvent mixture was very important for the complex formation, and when di-n-butyl ether/THF (9:1) was used, a brown oil was obtained which contained the free 2'-methylspiro derivative 1 and the C=N

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Table 1
Coordinates and thermal parameters of 1–Cr(CO)₃

Atom	x	y	z	U_{eq}
CR	0.2549(1)	0.1450(1)	0.3141(1)	342(1)
C15	0.1913(2)	0.3040(3)	0.3370(2)	455(9)
O15	0.1522(2)	0.4032(2)	0.3518(2)	690(9)
C16	0.1549(2)	0.1164(3)	0.1935(2)	443(9)
O16	0.0919(2)	0.0978(2)	0.1187(2)	707(9)
C17	0.1652(2)	0.0660(3)	0.4026(2)	485(10)
O17	0.1081(2)	0.0161(3)	0.4571(2)	807(10)
C1	0.3591(2)	−0.1090(2)	0.1705(2)	345(7)
C2	0.4617(2)	−0.1928(3)	0.1760(3)	469(10)
C3	0.4702(3)	−0.2917(3)	0.2714(3)	538(11)
C4	0.3740(3)	−0.3797(3)	0.2643(3)	601(12)
C5	0.2738(3)	−0.2982(3)	0.2657(3)	528(11)
C6	0.2622(2)	−0.1997(3)	0.1700(3)	429(9)
C7	0.3711(2)	−0.0023(2)	0.2587(2)	330(7)
C8	0.3779(2)	−0.0018(3)	0.3759(2)	394(8)
C9	0.3974(2)	0.1183(3)	0.4344(3)	481(10)
C10	0.4076(2)	0.2349(3)	0.3763(3)	525(11)
C11	0.3995(2)	0.2370(3)	0.2579(3)	468(10)
C12	0.3812(2)	0.1183(2)	0.2009(2)	376(8)
N1	0.3683(2)	0.1011(2)	0.083(2)	452(8)
C13	0.3547(2)	−0.0228(3)	0.0657(2)	414(9)
C14	0.3386(4)	−0.0779(4)	−0.0498(3)	653(14)

$U_{eq} = 1/3\Sigma[U_{ij}a_i^* a_j^* a_i a_j \cos(a_i, a_j)]\times10^4.$

reduction product 2′-methylspiro[cyclohexane-1,3′-(2′,3′)-dihydroindole], while complex 1-Cr(CO)₃ was not detected.

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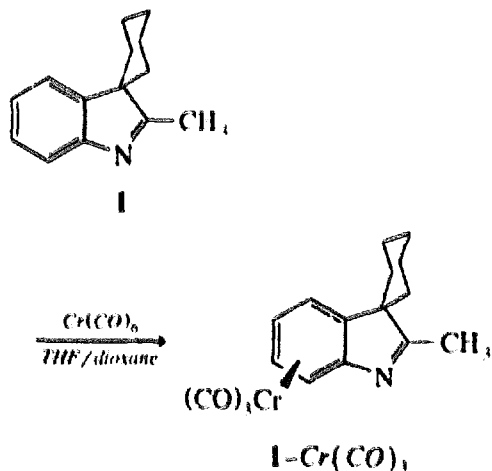
1-Cr(CO)₃

2.1. Molecular structure of η⁶-2′-methylspiro[cyclohexane-1,3′-3H-indole] chromium tricarbonyl, 1-Cr(CO)₃

Table 1 shows the atomic coordinates and Table 2 shows the bond distances and angles for the chromium tricarbonyl complex.

The molecule consists of an apparent conjugate indolenine with a methyl substituent in 2′, a spiro cyclohexane-1,3′ bonded and a chromium tricarbonyl moiety π-associate to the benzene ring.

The molecular structure is illustrated in Fig. 1 [6]. Bond distances and angles in chromium tricarbonyl

Table 2
Bond distances (Å) and angles (°) for 1–Cr(CO)₃

Cr–C15	1.845(3)	C1–C7	1.513(3)
Cr–C16	1.837(3)	C1–C13	1.528(4)
Cr–C17	1.831(3)	C2–C3	1.518(5)
Cr–C7	2.259(2)	C3–C4	1.513(5)
Cr–C8	2.231(3)	C4–C5	1.525(5)
Cr–C9	2.203(3)	C5–C6	1.519(4)
Cr–C10	2.202(3)	C7–C8	1.397(4)
Cr–C11	2.237(3)	C7–C12	1.423(4)
Cr–C12	2.235(3)	C8–C9	1.418(4)
Cr–CO	1.728(1)	C9–C10	1.390(4)
C15–O15	1.149(4)	C10–C11	1.410(5)
C16–O16	1.150(3)	C11–C12	1.396(4)
C17–O17	1.149(4)	C12–N1	1.414(4)
C1–C2	1.556(4)	N1–C13	1.288(4)
C1–C6	1.541(4)	C13–C14	1.487(4)
C15–Cr–C16	88.8(1)	C1–C6–C5	112.6(2)
C15–Cr–C17	89.3(1)	C1–C7–C12	106.7(2)
C16–Cr–C17	88.0(1)	C1–C7–C8	134.0(2)
Cr–C15–O15	179.6(3)	C8–C7–C12	119.2(2)
Cr–C16–O16	179.3(3)	C7–C8–C9	119.2(2)
Cr–C17–O17	179.2(3)	C8–C9–C10	120.7(3)
C7–C1–C13	98.8(2)	C9–C10–C11	121.1(3)
C6–C1–C13	112.7(2)	C10–C11–C12	117.9(3)
C6–C1–C7	116.8(2)	C7–C12–C11	121.9(2)
C2–C1–C13	107.6(2)	C11–C12–N1	126.2(3)
C2–C1–C7	110.3(2)	C7–C12–N1	111.9(2)
C2–C1–C6	109.9(2)	C12–N1–C13	106.3(2)
C1–C2–C3	112.6(2)	C1–C13–N1	116.1(2)
C2–C3–C4	111.2(3)	N1–C13–C14	121.5(3)
C3–C4–C5	110.5(3)	C1–C13–C14	122.4(2)
C4–C5–C6	111.2(3)		

CO = centroid of benzene ring.

complex are given in Table 2. The Cr atom deviates slightly above the centre of the benzene ring. The distances of the chromium to benzene ring range from 2.202(3) up to 2.259(2) Å; the distance of the chromium to the centroid of the benzene ring being 1.728(1) Å.
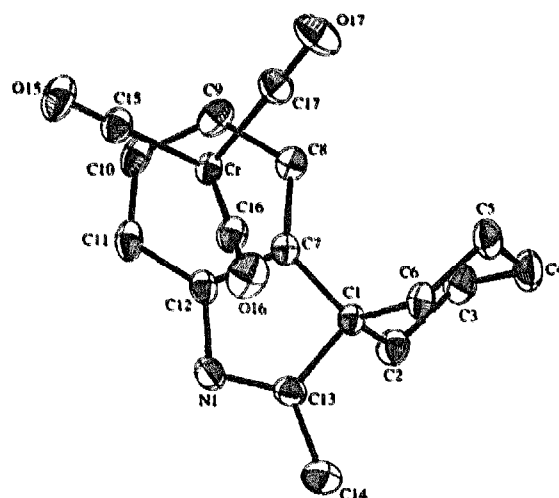

Fig. 1. ORTEP [6] view of the molecule. Thermal ellipsoids are shown at the 30% probability level.

2.2. Cr(CO)₃ moiety

The configuration of the tricarbonyl group with respect to the benzene ring was found to be between staggered and eclipsed with the carbonyl groups being located near C8, C10, and C12, Fig. 2. The σ-bond distances Cr–CO are 1.831(3), 1.837(3), and 1.845(3) Å for C17, C16 and C15 respectively, while the C–O bonds are 1.15 Å. The bond angles C–Cr–C for the Cr(CO)₃ group range from 88.0(1) to 89.3(1)°. The Cr–arene bond distances are of three types: Cr–C9 and Cr–C10 2.20 Å, Cr–C8, Cr–C11 and Cr–C12 2.23–2.24 Å, while the enlargement Cr–C7 2.26 Å is probably due to the sterical hindrance of the spiranic substituent. In the solid state mono- and disubstituted benzene–Cr(CO)₃ complexes have a tendency to adopt the eclipsed conformation, unless strong steric effects are involved [7].

2.3. Indolenine ring
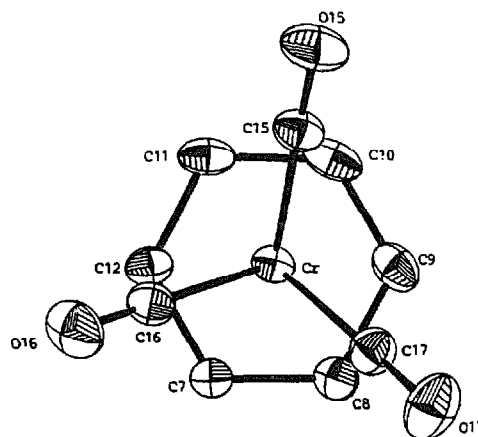
The bond distances in the benzene ring show normal values (ranging from 1.396(4) to 1.423(4) Å). Remarkable in the pyrroline ring are the N1 bond distances C12–N1 1.414(4) and N1=C3 1.288(4) Å, the latter is larger than the normal values (similar C=N bonds range from 1.26–1.27 Å [8]), due to the withdrawing electronic effect of the Cr(CO)₃ group in the complex. Bond angles in the pentagonal ring are: in N1, C12–N1–C13 106.3(2)°, and in C13, N1–C13–C1 116.1(2)°, N1–C13=C14 121.5(3)°. Carbon atoms in the benzene ring are coplanar with C8 at 0.08(3) Å in the maximum deviation towards the Cr, while N1 and C1 deviate 0.038(2) Å towards and −0.094(2) Å away from the Cr atom respectively.

The pyrroline ring is virtually planar with C1 in the maximum deviation, −0.029(2) Å, away from the Cr atom. The dihedral angle between the two benzene and pyrroline rings is 2.4(1)°.

The spirocyclohexane ring is in a chair conformation, and is nearly perpendicular to the indoline plane (96.5(1)°), with interesting structural facts around C1:(a) bond distances C1–C2 and C1–C6 1.556(4) and 1.541(4) Å respectively, which are larger than the nor-

mal values in contrast with the remaining bond distances in the cyclohexane ring; (b) the bond angle C7–C1–C13 98.8(2)° is the shortest in the pyrroline ring.

The contacts between molecules are of the order of van der Waals radii.

2.4. Reactivity of 2'-methylspiro[cyclohexane-1,3'-3H-indole] chromium tricarbonyl 1

The reactivity of 2'-methylspiro derivative complex 1–Cr(CO)₃ has been analysed with Grignard reagents in the presence of cuprous chloride, but unfortunately under these conditions the complex was destroyed. In the absence of cuprous chloride but with excess methylmagnesium iodide in diethyl ether (or THF) the complex was partially destroyed, but in the reaction mixture NMR detected two singlets at 1.20 and 1.25 ppm assigned to the addition product in very low yield (10% by NMR), which could not be isolated purely. Moreover, the 2'-ethyl derivative product, which is obtained from methyl insertion on the 2'-position (in the same reaction from free 2'-methyl derivative 1) was not detected in the reaction mixture.

However, the reaction of the 1–Cr(CO)₃ complex with aluminum lithium hydride in THF gave the reduction products in high yield (90%). Two stable isomers

Fig. 2. Projection of Cr(CO)₃ on the benzene ring plane.
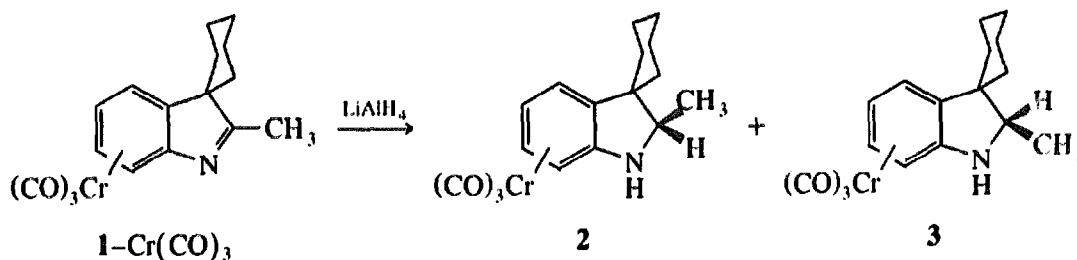
Scheme 1.

were isolated by silica gel column chromatography, in the relation 62:38, corresponding to attack of the hydride by the opposite face to the chromium carbonyl ligand 3 (endo) or by the same one 2 (exo) respectively (Scheme 1).

The main endo-isomer shows the methyl and chromium tricarbonyl groups at the same face, and this relative position of the groups is observed in the NMR as a deshielding of the methyl in 2'-position (at 1.37 ppm), while the minor isomer (endo) shows the methyl and chromium tricarbonyl in the opposite face, with NMR giving the methyl group at 1.22 ppm (since protons located in the same plane with the $Cr(CO)_3$ moiety are known to shift to lower field [9]).

A characteristic feature of $Cr(CO)_3(\eta^6\text{-indoline})$ complexes, useful for rapid identification, is the presence in solution of two CO intense IR bands. In complexes 2 and 3 the CO band appears at 1935 and 1930 cm^{-1} and at 1830 and 1845 cm^{-1} respectively for endo 3 and exo 2 isomers.

On the basis of local C3v symmetry for the $Cr(CO)_3$ group, these bands have been assigned to a non-degenerate symmetric vibration (A1) and a doubly-degenerate asymmetric vibration (E) [10].

Finally, complexes 2 and 3 were destroyed with an iodine solution in tetrachloromethane to obtain the same free molecular compound in quantitative yields.

3. Experimental

Melting points were determined using a Reichert stage microscope and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 681 spectrophotometer. Nuclear magnetic resonance spectra were recorded at 200 MHz using a Bruker WM-200-SY spectrometer, chemical shifts are given in δ using TMS as internal reference. Chemical shifts are given relative to internal tetramethylsilane. Mass spectra were recorded using a Hewlett-Packard SP85 spectrometer. Elemental analyses were performed with a LECO CHN-600.

3.1. Synthesis of $\eta^6(2'\text{-methylspiro[cyclohexane-1,3'-3H-indole]}$ chromium tricarbonyl 1-Cr(CO)_3

In a Strohmeier type system [5], previously flamed and purged with argon and covered from sunlight, was placed 1.5 g of 2'-methylspiro[cyclohexane-1,3'-3H-indole] in 120 ml of dioxane/THF 5:1. To this mixture was added 2.07 g (9.4 mmol) of chromium hexacarbonyl, and then the mixture was warmed at intense reflux temperature (bath at 140°C) for four days. The mixture was cooled under argon atmosphere and filtered to eliminate the chromium salts. The solvent was then removed and the orange solid recrystallized from hex-

ane. The η^6-complex 1-Cr(CO)_3 was obtained as a stable orange solid, m.p. 124–125°C, 1.84 g, 73% yield.

IR (KBr): 1945, 1855 (C=O); 1590 (C=N); 1550 (Ar); 665 and 620 (ArH).

^{1}H-NMR ($CDCl_3$): 1.2–1.9 (m, 10H, $(CH_2)_5$); 2.30 (s, 3H, CH_3-2'); 4.87 (t, 1H, $J = 6.3$ Hz, H-5'); 5.56 (t, 1H, $J = 6.4$ Hz, H-6'); 5.68 (d, 1H, $J = 6.1$ Hz, H-7'); 6.23 (d, 1H, $J = 6.2$ Hz, H-4').

^{13}C-NMR ($CDCl_3$): 16.7 (CH_3-2'); 21.2 (C-3, C-5); 24.6 (C-4); 32.8 and 35.0 (C-6 and C-2); 58.8 (C-3'); 83.3 (C-7'); 84.7 (C-4'); 93.9 (C-6'); 94.9 (C-5'); 114.8 (C-4'a); 131.2 (C-7'a); 193.6 (C-2'); 217.1 (CO).

Anal. Found: C, 60.55; H, 5.47; N, 4.33. $C_{17}H_{17}NO_3Cr$ Calc.: C, 60.89; H, 5.11; N, 4.18%.

3.2. Reaction of 1-Cr(CO)_3 with H_4AlLi

In a round-bottomed flask, previously flamed and in argon atmosphere, was placed 137 mg (3.6 mmol) of H_4AlLi in 3 ml of dry THF. The bottom was covered from sunlight and a solution of 200 mg (0.6 mmol) of 1-Cr(CO)_3 in 6 ml of dry THF was added. After 2 h at room temperature, the mixture was hydrolysed with 10 ml of THF/H_2O 1:1, and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate. The desecant was then filtered and the solvent evaporated to give an orange oil, which was purified by silica gel column chromatography using hexane/THF 5:1. Two compounds were isolated and identified as the isomers endo-η^6-(2'-methylspiro[cyclohexane-1,3'-(2',3')-dihydroindole] chromium tricarbonyl (3, stable yellow solid, m.p. 149–151°C, 113 mg, 56% yield) and exo-η^6-(2'-methylspiro[cyclohexane-1,3'-(2',3')-dihydroindole] chromium tricarbonyl (2, yellow solid, m.p. 134–136°C, 69 mg, 34% yield).

3.2.1. endo-Isomer

IR (KBr): 3380 (NH); 1935; 1855 and 1830 (C=O); 1545 (ArH); 670, 620 (ArH).

^{1}H-NMR (acetone-d_6): 1.37 (d, 3H, $J = 6.5$ Hz, CH_3-2'); 1.3–2.0 (m, 10H, $(CH_2)_5$); 3.81 (c, 1H, $J = 6.5$ Hz, H-2'); 4.91 (t, 1H, $J = 6.5$ Hz, H-5'); 5.06 (d, 1H, $J = 5.7$ Hz, H-7'); 5.38 (br s, 1H, NH); 5.62 (t, 1H, $J = 6.1$ Hz, H-6'); 5.77 (d, 1H, $J = 6.1$ Hz, H-4').

Anal. Found: C, 60.19; H, 6.02; N, 4.35. $C_{17}H_{19}NO_3Cr$ Calc.: C, 60.53; H, 5.68; N, 4.15%.

3.2.2. exo-Isomer

IR (film): 3380 (NH); 1930, 1880 and 1845 (C=O); 1550 (ArH); 670 and 620 (ArH).

^{1}H-NMR (acetone-d_6): 1.22 (d, 3H, $J = 6.5$ Hz, CH_3-2'); 1.3–2.1 (m, 10H, $(CH_2)_5$); 3.45 (c, 1H, $J = 6.5$ Hz, H-2'); 4.88 (t, 1H, $J = 6.5$ Hz, H-5'); 5.03 (d, 1H, $J = 5.7$ Hz, H-7'); 5.52 (br s, 1H, NH); 5.70 (t, 1H, $J = 6.1$ Hz, H-6'); 6.15 (d, 1H, $J = 6.1$ Hz, H-4').

Anal. Found: C, 60.37; H, 5.92; N, 4.29. $C_{17}H_{19}NO_3Cr$ Calc.: C, 60.53; H, 5.68; N, 4.15%.

3.3. X-ray analysis of the $1-Cr(CO)_3$ complex

Crystals of $1-Cr(CO)_3$ of composition $C_{17}H_{17}NO_3Cr$ were grown from an ethyl acetate solution.

A yellow crystal of $0.38 \times 0.32 \times 0.21$ mm^3 was used for X-ray structure determination. 96 reflections up to $2\theta = 61°$ were measured on a Philips PW 1100 diffractometer for the refinement of the lattice constants.

These crystals are monoclinic and belong to the space group $P2_1/a$. Accurate cell constants were $a = 12.736(1)$, $b = 10.188(1)$, $c = 11.984(1)$ Å, $\beta = 96.497(5)°$, $V = 1545.0(1)$ Å^3, $Z = 4$, $D_c = 1.442(3)$ g cm^{-3}, $M = 335.32$, $F(000) = 696$, $\mu = 7.516(4)$ cm^{-1}. Intensities were collected in $\omega-2\theta$ scan mode using Mo Kα ($\lambda = 0.7107$ Å) radiation with a graphite monochromator ($-16 < h < 16; 0 < k < 13; 0 < l < 15$) up to $\theta = 25°$. Two reference reflections after every 90 min showed negligible variation. From 2721 reflections measured, 2410 were considered observed with the $I > 3\sigma(I)$ criterion.

The structure was solved by direct methods (SIR92) [11] and difference Fourier techniques; no absorption correction was applied ($\mu = 7.516$ cm^{-1}). All calculations were carried out with the program XRAY80 [12] on a VAX 6410 computer. The structure was refined using full-matrix least-squares. All non-H atoms were refined with anisotropic thermal parameters. H-atoms were found in the difference Fourier map and refined isotropically. The refinement converged at $R = 0.033$. All the geometric calculations were performed with the program PARST [13]; scattering factors and anomalous dispersion were taken from the International Tables for X-ray Crystallography [14].

Acknowledgements

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