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Note

Synthesis and X-ray structure of [acenaphthene–chromium(0)-dicarbonyl-tri(2,3,5-trimethylphenyl)phosphite]

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Abstract

The compound [acenaphthene–$Cr(CO)_2$-tri(2,3,5-trimethylphenyl)phosphite] has been obtained by reacting $[C_{12}H_{10}Cr(CO)_3]$ with the phosphite in UV light. The complex has been characterized by elemental analysis, ^1H NMR and ^{13}C NMR spectra, and X-ray analysis. Crystals are orthorhombic, space group *Pbca*, $Z=8$, with the cell dimensions $a=22.067(1)$, $b=17.563(1)$, $c=18.784(1)$ Å. Owing to the steric requirements the phosphite is located opposite to the non-bonded rings of the acenaphthene and the Cr–P–O angles from the three 2,3,5-trimethylphenyl groups differ from each other distinctly (115.2, 120.9 and 121.8°).

Key words: Crystal structures; Chromium complexes; Acenaphthene complexes; Carbonyl complexes; Phosphite complexes

Introduction

Complexes of unsymmetrically substituted naphthalenes have been used to study the influence of different substitution patterns on their reactivity upon complexation. This has been realized by the replacement of one Cp ligand from ferrocene by methyl- and dimethylnaphthalenes [1] and by tetra- to octamethylnaphthalenes [2].

The complexation of substituted naphthalenes to chromiumtricarbonyl has been studied with a few examples which were used for the separation of isomers by gas chromatography [3] or by column liquid chromatography [4]. The complex $2,3\text{-}(Me_3SiO)_2C_{10}H_6Cr(CO)_3$ has been used for its conversion to the 1,2-dihydroxy derivative [5] and a substituted naphthalene–$Cr(CO)_3$ was studied with its inter-ring rearrangement of the $Cr(CO)_3$ group [6].

With the substitution of one carbonyl yielding [arene $Cr(CO)_2L$], the influence of voluminous P ligands on the bonding of the naphthalene and the conformation of its substituents can be studied and varied conveniently. As one interesting example the structure of [octamethylnaphthalene–$Cr(CO)_3$] and [OMN–$Cr(CO)_2P\phi_3$] have been compared [7]. Other structural and spectroscopic studies of similar arene–chromium complexes are mainly restricted to hexaethylbenzene and its complexes $[(\eta^6\text{-}Et_6C_6)Cr(CO)_2L]$ [8, 9].

We have started a project using acenaphthene as the arene in complexes [acenaphthene–$Cr(CO)_2L$] with L = triarylphosphites, expecting additional structural and spectroscopic information by use of the ethylene bridge of the acenaphthene.

Experimental

Preparation and spectroscopic characterization of the complex

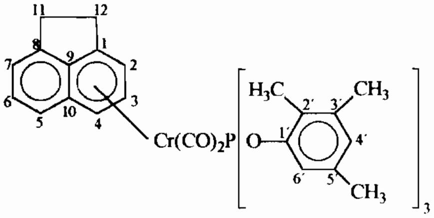
Tri(2,3,5-trimethylphenyl)phosphite was prepared according to a literature procedure [10]. $Cr(CO)_6$ was reacted to give $(NH_3)_3Cr(CO)_3$ [11], which was used for the preparation of [acenaphthene–$Cr(CO)_3$] [12] according to a literature method [6]. The ligand substitution in [acenaphthene–$Cr(CO)_3$] with the phosphite using UV light and the purification of the complex by chromatography are standard procedures [9].

[Acenaphthene–$Cr(CO)_2$-$P(OC_6H_2(CH_3)_3)_3$]: red crystals (10% based on $Cr(CO)_6$, m.p. 143 °C. *Anal.* Calc. for $C_{41}H_{43}O_5PCr$: C, 70.5; H, 6.2. Found: C, 70.3; H, 5.9%.

Molecular mass 698.8 g/mol; MS: $[M^+]$ peak 698.19 (relative intensity 5.7%), $[M^+-2CO]$ 641.93 (6.07%), $[M^+-2CO$ and ACN] 488.48 (100%).

^{31}P NMR (90 MHz, $CDCl_3$, 80% D_3PO_4 as external standard) 132 ppm; the uncomplexed phosphite at 202 ppm.

^1H NMR (400 MHz, $CDCl_3$, resonances in ppm, reference TMS, numbering from Scheme 1): H(5): 7.06 (d, 7.1 Hz, 1H); H(7): 6.93 (d, 5.4 Hz, 1H); H(6): 7.13



Scheme 1.

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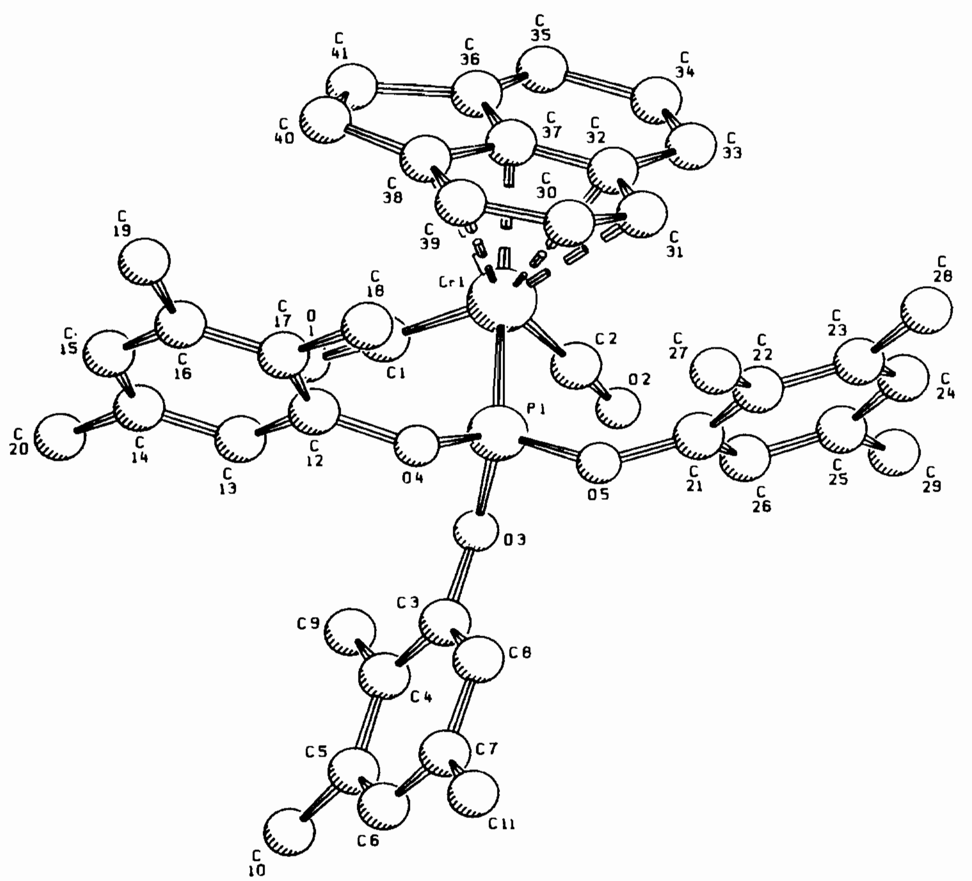

Fig. 1. Representation of the complex [acenaphthene–$Cr(CO)_2$-tri(2,3,5-trimethylphenyl)phosphite] with the numbering of the atoms.

('t', 1H); H(6′) and H(4′): 7.11 (s, 1H) and 6.71 (s, 1H); H(4): 4.91 (d, 6.4 Hz, 1H); H(3): 4.84 (m, 1H); H(2): 4.45 (m, 1H); CH_2(11) and CH_2(12): 3.38 (m, 1H), 3.22 (m, 1H), 3.04 (m, 1H), 2.96 (m, 1H); CH_3 (3′) and CH_3(5′): 2.25 (s, 6H); CH_3(2′): 2.19 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$, resonances in ppm, numbering as in Scheme 1; p, s, t, q = primary, secondary, tertiary and quartary carbon from a spin echo experiment): C(2′) 151.0 (q); C(8) 148.0 (q); C(3′) and C(5′) 137.7 and 135.1 (q); C(5), C(6) and C(7) 130.5, 126.9 and 125.7 (t); C(1′) 124.8 (q); C(4′) and C(6′) 122.5 and 119.4 (t); C(1), C(9) and C(10) 112.6, 105.9 and 104.2 (q); C(2), C(3) and C(4) 92.2, 85.2 and 83.6 (t); C(11) and C(12) 29.75 and 29.35 (s); C(methyl 3′) and C(methyl 5′) 21.5 and 21.0 (p); C(methyl 2′) 20.5 (p).

X-ray structure of [acenaphthene–$Cr(CO)_2$-$P(2,3,5\text{-}Me_3C_6H_2O)_3$]

Single crystals were obtained by slow crystallization from a heptane/CH_2Cl_2 mixture. A red crystal having approximate dimensions 0.55×0.025×0.05 mm was mounted on an Enraf-Nonius Turbo-CAD4 diffractometer. The unit cell was determined and refined from 54 selected reflexions with $55 \leq 2\theta \leq 70°$.

Crystal data: space group *Pbca* (orthorhombic), $a = 22.0669(6)$, $b = 17.5633(8)$, $c = 18.7838(5)$ Å, $V = 7280.0(4)$ Å^3, $Z = 8$, $D = 1.276$ g cm^{-3}, $\mu = 3.37$ mm^{-1}. Intensities were measured with Cu Kα radiation $\lambda = 1.5418$ Å, ω–2θ scan, $2 \leq 2\theta \leq 70°$.

A total of 3442 reflections with $I > 2\sigma(I)$ was used in the structure determination and refinement (programme SHELX-76). The hydrogen atoms were placed in geometrical positions and refined ridden on the carbon atoms bearing them. See also 'Supplementary material'.

Discussion

With the exchange of one carbonyl ligand in [acenaphthene–$Cr(CO)_3$] by tri(2,3,5-trimethylphenyl)-phosphite the spectroscopic properties of the complex change distinctly. Due to the phosphite being a weaker π-acceptor the CO stretching vibrations shift from 1967.5, 1901.9 and 1892.3 cm^{-1} in [acenaphthene–$Cr(CO)_3$] to 1911.6 and 1863.3 cm^{-1} in [acenaphthene –$Cr(CO)_2$-$P(OAr)_3$]. In the ^1H NMR spectrum of [acenaphthene–$Cr(CO)_2$-$P(OAr)_3$] compared to that of [acenaphthene–$Cr(CO)_3$] the influence of the phosphite

TABLE 1. Selected interatomic distances (Å) and angles (°) of [acenaphthene–$Cr(CO)_2$-$P(OAr)_3$]; Ar = 2,3,5-trimethylphenyl

Cr–C1	1.79(1)	Cr–C30	2.18(1)	Cr–P1–O3	115.2(2)
Cr–C2	1.82(1)	Cr–C31	2.23(1)	Cr–P1–O4	121.8(2)
C2–O2	1.15(1)	Cr–C32	2.33(1)	Cr–P1–O5	120.9(2)
C1–O1	1.17(1)	Cr–C37	2.25(1)	Cr–C1–P	91.2(3)
Cr–P1	2.20(0)	Cr–C38	2.22(1)	Cr–C2–P	89.4(3)
		Cr–C39	2.21(1)	Cr–C1–C2	85.7(2)

is shown by higher complexation shifts of the arene protons' resonances, especially in the acenaphthene part, which is bonded to the chromium. In addition for the phosphite complex all four methylene protons of the acenaphthene gave separated multiplets, whereas in [acenaphthene–$Cr(CO)_3$] the four protons appear as a broad unresolved multiplet at 3.36–3.52 ppm. Equivalent to this result both carbon atoms of the methylene groups register separately in the ^{13}C NMR spectra for the phosphite complex but not for [acenaphthene–$Cr(CO)_3$].

The structure of [acenaphthene–$Cr(CO)_2$-$P(OAr)_3$] is represented in Fig. 1 and some selected interatomic bond distances and angles from the inner core of the complex are given in Table 1. In the complex the phosphite is located opposite to the non-bonded ring of the acenaphthene. (This is different to the complex [napththalene–$Cr(CO)_2$-$P(OC_6H_5)_3$] [13], where one of the CO ligands takes that position.) It is due to some steric interaction, as indicated by the angles of the three substituents at the phosphorus.

The angle Cr–P1–O3 is smaller than the other two (Table 1), which carry the 2,3,5-trimethylphenyl groups that are closer to the acenaphthene (Fig. 1).

The pronounced difference between the two angles C38–C37–C36 (110.8°) and C31–C32–C33 (126.0°) in the complexed acenaphthene is similar to that in the free acenaphthene (112.4° and 128.4° [14]). Compared to the free acenaphthene [14] the C–C bonds in the complex are not altered appreciably. A deviation from planarity is registered for the anellated 5-ring; C41 is bent versus the chromium by about 9° (it deviates 0.14 Å from a plane formed by the carbon atoms of the 5-ring). The deflection of C40 from planarity is very small. The slight asymmetry in the bonding of the chromium to the ring with the distances to the central carbon atoms slightly longer than to the other four carbon atoms corresponds with the data for other naphthalene–chromium complexes [7, 15].

Supplementary material

Tables of final atomic coordinates, anisotropic temperature factors, leasts squares planes, full interatomic distances and angles as well as a listing of observed and calculated structure factors may be obtained from author D.S.

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