

# Pentacarbonyl(2,6-diaminopyridine)chromium(0): synthesis and molecular structure

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## Abstract

Photolysis of hexacarbonylchromium(0) in the presence of 2,6-diaminopyridine in toluene solution at 10 °C yields pentacarbonyl(2,6-diaminopyridine)chromium(0), which could be isolated from solution as plate-like crystals and fully characterized by using the single crystal X-ray diffractometry and MS, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The complex was found to have the 2,6-diaminopyridine ligand bonded to the chromium atom through one of the NH<sub>2</sub> groups. A single crystal X-ray structure of the complex reveals that the coordination sphere around the chromium atom is a slightly distorted octahedron, involving five carbonyls and one 2,6-diaminopyridine ligand. Because of the steric requirement of 2,6-diaminopyridine the four equatorial carbonyl groups are bended away from the N-donor ligand. The pyridine plane makes an angle of 112.9(3)° with the OC–Cr–N bond axis. The Cr–C distances have values between 1.833(7) and 1.935(7) Å. The Cr–N distance is 2.236(5) Å.

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## 1. Introduction

Pentacarbonylpyridinemetall(0) complexes of the Group 6 elements have been known for a long time [1]. Since pyridine (py) acts as mainly  $\sigma$ -donor ligand with little  $\pi$ -accepting ability [2], the M–N bond in these low valent metal complexes is not very strong. Consequently, M(CO)<sub>5</sub>(py) complexes are quite labile toward ligand substitution reactions [3]. Group 6 metal carbonyl complexes of substituted pyridines are also known [4]. M(CO)<sub>5</sub>(L) complexes with L = 4-methylpyridine or 4-phenylpyridine have already been reported to be isolable [5–7]. 2-Substituted pyridine derivatives such as 2-cyanopyridine and 2-phenylpyridine form also

complexes of the M(CO)<sub>5</sub>L type [5,8], indicating that a non-bulky substituent in position 2 does not hinder the coordination of pyridine to a transition metal. Therefore, pyridine derivatives having ligating atoms in 2- or 6-position are expected to show more than one binding mode. For example, 2,6-diaminopyridine (dap) can bind the transition metal through a sp<sup>3</sup>-hybridized nitrogen of the amino groups and/or through the sp<sup>2</sup>-hybridized nitrogen of the aromatic ring. The former is a stronger  $\sigma$ -donor but much weaker  $\pi$ -acceptor than the latter. Here, we report the binding mode of 2,6-diaminopyridine (dap) in the Cr(CO)<sub>5</sub>(dap) complex, which was synthesized for the first time from the photolysis of Cr(CO)<sub>6</sub> in the presence of dap. In this new complex, the 2,6-diaminopyridine is bonded to the chromium through one of the amine groups as monodentate ligand, as determined by single crystal X-ray structural analysis as well as by NMR spectroscopy. Numerous complexes of the type Cr(CO)<sub>5</sub>(amine) have been known and used for the preparation of related compounds [3,9–11].

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## 2. Experimental

### 2.1. General remarks

All reactions and manipulations were carried out either in vacuum or under a dry and oxygen free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used.

Analytical grade and deuterated solvents, hexacarbonylchromium(0), 2,6-diaminopyridine were purchased from Merck GmbH, Darmstadt, Germany, and used as received. The photochemical reactions and other treatments of organometallic compounds such as purification and crystallization were followed by taking IR spectra from solutions on a Perkin–Elmer 16 PC FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX 400 (400.1 MHz for  $^1\text{H}$ ; and 100.6 MHz for  $^{13}\text{C}$  spectrometer). TMS was used as internal reference for  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts. Mass spectra were taken on a Finnigan MAT 8400 instrument.

Photochemical reactions were carried out in an immersion-well apparatus [12] (solidex glass,  $\lambda > 280$  nm) by using a Hanau TQ 150 high pressure mercury lamp (Quarzlampen GmbH, Hereaus, Germany) which was cooled by circulating water.

### 2.2. $\text{Cr}(\text{CO})_5(2,6\text{-diaminopyridine})$

A solution of 0.50 g (2.3 mmol)  $\text{Cr}(\text{CO})_6$  and 0.50 g (4.6 mmol) 2,6-diaminopyridine in toluene (150 ml) was irradiated for 150 min at 10 °C. The solution was filtered and the volatiles were removed by evaporation in vacuum. The brown residue was dissolved in 2 ml dichloromethane and transferred on to a silica gel column of 15 cm length and 2 cm diameter, packed with hexane. An orange fraction containing the complex  $\text{Cr}(\text{CO})_5(2,6\text{-diaminopyridine})$  was eluted with a 1:5 mixture of dichloromethane and *n*-hexane. Recrystallization from toluene gave plate-like orange crystals of  $\text{Cr}(\text{CO})_5(\text{C}_5\text{H}_7\text{N}_3)$ : 0.26 g, 38% yield; m.p. 82 °C (dec); MS:  $m/z$  301 ( $\text{M}^+$ ); IR (*n*-hexane)  $\nu(\text{CO}) = 2068.7$  (w), 1934.5 (vs), 1890.0 (s)  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR ( $d_2$ -dichloromethane)  $\delta = 221.42$  ( $\text{CO}_{\text{trans}}$ ), 214.38 ( $\text{CO}_{\text{cis}}$ ), 165.40 (C2), 159.38 (C6), 140.71 (C4), 104.61 (C3), 100.89 (C5) ppm;  $^1\text{H}$  NMR ( $d_2$ -dichloromethane)  $\delta = 9.64$  (d, H3), 9.00 (dd, H4), 8.64 (d, H5), 3.60 (s,  $\text{NH}_2$ ), 2.10 (s,  $\text{NH}_2$ ) ppm;  $J(\text{H}3\text{--H}4) = 2.8$ ,  $J(\text{H}4\text{--H}5) = 8.2$  Hz.

### 2.3. X-ray diffraction structure analysis

An orange thin plate single crystal was glued to a thin glass fiber and inserted in a glass capillary tube, which was then mounted on a RIGAKU-AFC7S diffracto-

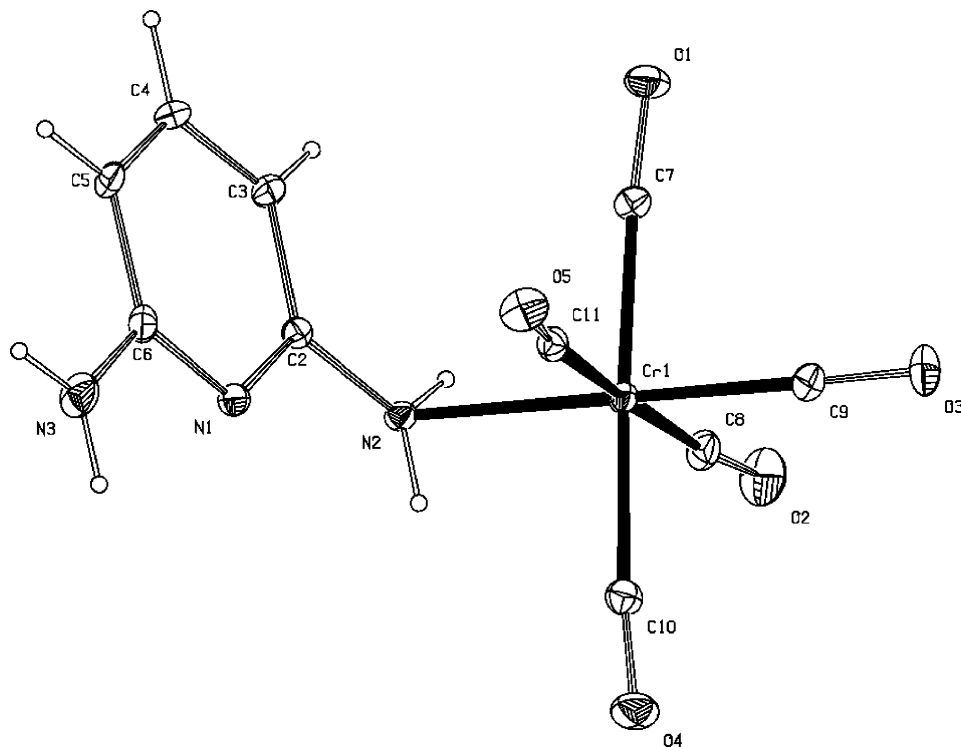


Fig. 1. ORTEP drawing of the  $\text{Cr}(\text{CO})_5(2,6\text{-diaminopyridine})$  molecule with the atom numbering scheme. Each atom is represented by ellipsoids of thermal vibration, scaled to enclose 30% of electron density and H atoms are shown as small circles with arbitrary radii.

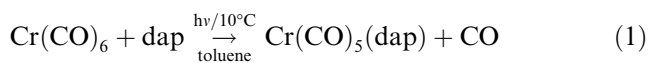
meter operating in  $\omega/2\theta$  scan mode [13]. The cell parameters were determined from a least-squares refinement of 25 centered reflections in the range of  $10.01 \leq \theta \leq 13.92^\circ$ . During data collection, three standard reflections were periodically measured every 150 reflection and showed no significant intensity variation. X-ray diffraction data were collected at  $T = 293 \pm 2$  K with graphite-monochromated Mo  $K\alpha$  radiation in the range of  $2.30\text{--}32.51^\circ$ . Absorption correction (PSI  $\Psi$ -Correction) was applied (with *trans.* factors: 0.8485–0.9985). The structure was solved by direct methods using the program SHELXS97 [14] and refined by a full-matrix least-squares procedure on  $F^2$  using the SHELXL97 [15]. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms were placed geometrically in calculated positions, 0.93 Å for the phenyl group and 0.96 Å for the methyl group from their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . After final refinement, it was obtained that the highest peak with the residual electron density of 0.78 and distance 0.92 Å from Cr1 and also the deepest hole with the residual electron density of  $-0.51$  and distance of 0.94 Å from Cr1.

An ORTEP drawing [16] of the  $\text{Cr}(\text{CO})_5(\text{dap})$  molecule, was prepared by using PLATON [17], is given in Fig. 1. The packing diagram of  $\text{Cr}(\text{CO})_5(\text{dap})$  in unit cell is given in Fig. 2. Crystal and experimental data are

given in Table 1, selected bond lengths and angles are given in Table 2.

### 3. Results and discussion

UV irradiation of  $\text{Cr}(\text{CO})_6$  in the presence of excess 2,6-diaminopyridine (dap) at  $10^\circ\text{C}$  in toluene solution leads to the formation of pentacarbonyl(2,6-diaminopyridine)chromium(0) complex according to Eq. (1).



The photolytic conversion of  $\text{Cr}(\text{CO})_6$  to  $\text{Cr}(\text{CO})_5(\text{dap})$  was followed by IR spectroscopy. The absorption band at  $1983.2\text{ cm}^{-1}$  due to CO stretching of the parent carbonyl complex decreases while three new features of the product grow in concomitantly as the reaction proceeds. The absorption band of  $\text{Cr}(\text{CO})_6$  disappeared almost completely after 150 min of irradiation, leaving mainly three new bands of the product  $\text{Cr}(\text{CO})_5(\text{dap})$  in the CO stretching region. The  $\text{Cr}(\text{CO})_5(\text{dap})$  complex could be isolated from the solution by column chromatography on silica gel and recrystallization from toluene as plate-like orange crystals. This new complex was fully characterized by single crystal X-ray diffraction, MS, IR, and NMR spectroscopy.

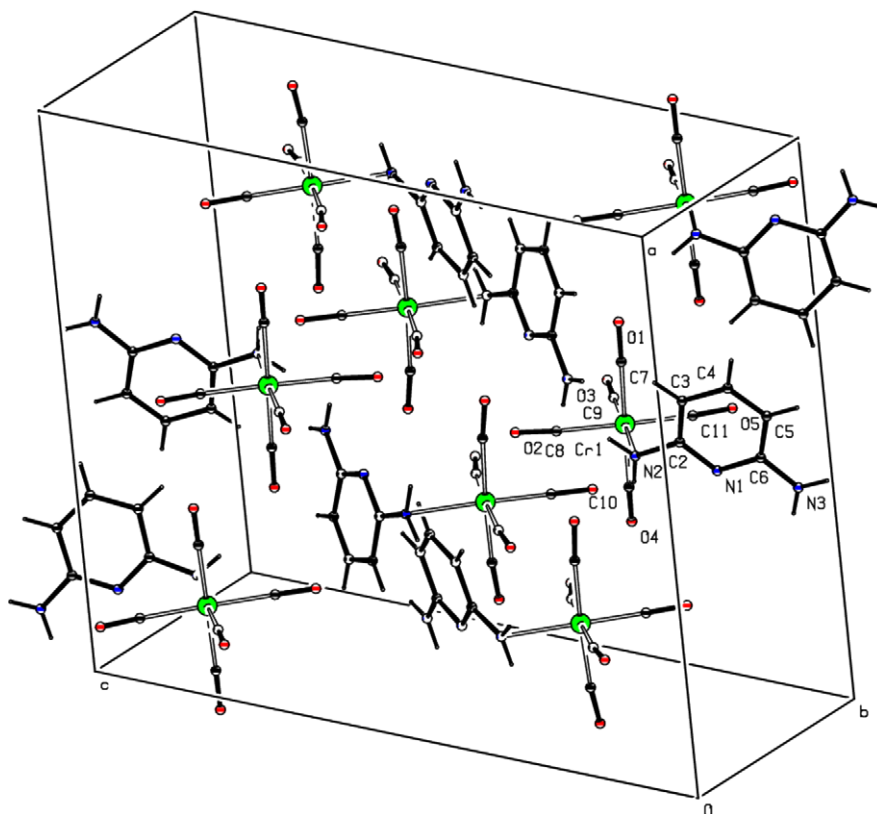


Fig. 2. The unit cell and the molecular packing of  $\text{Cr}(\text{CO})_5(2,6\text{-diaminopyridine})$ .

Table 1

Crystal and experimental X-ray data for Cr(CO)<sub>5</sub>(2,6-diaminopyridine)

Empirical formula	C <sub>10</sub> H <sub>7</sub> N <sub>3</sub> O <sub>5</sub> Cr
Formula weight (g/mol)	301.18
Crystal color/habit	Orange/thin plate
Crystal size (mm)	0.25 × 0.05 × 0.30
Temperature (K)	293 (2)
Wavelength (Å)	0.71069
Crystal system	Orthorhombic
Lattice type	Primitive
Space group [No.]	<i>Pbc</i> [#60]
<i>a</i> (Å)	16.997 (6)
<i>b</i> (Å)	7.338 (5)
<i>c</i> (Å)	20.687 (6)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	2580 (2)
<i>Z</i>	8
Density (calc) (Mg/m <sup>3</sup> )	1.551
$\mu$ (cm <sup>-1</sup> )	0.906
$\theta$ Range (°)	2.30–32.51
Index ranges	0 ≤ <i>h</i> ≤ 25, 0 ≤ <i>k</i> ≤ 11, −31 ≤ <i>l</i> ≤ 0
Reflections collected/unique	4669/4144
Absorption correction	$\Psi$ -correction
Refinement method	Full-matrix least-squares refinement on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4669/0/173
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.915
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0613, <i>wR</i> <sub>2</sub> = 0.1521
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.2917, <i>wR</i> <sub>2</sub> = 0.2501
Largest differential peak, hole (e Å <sup>-3</sup> )	0.780 and −0.510

Crystallographic data (excluding structure factors) for structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition No. CCDC 231116. Copies of the data can be obtained, free of charge, on applicant to the Cambridge Crystallographic Data Centre (CCDC) 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

The molecular structure of the complex elucidated by X-ray diffractometry is shown in Fig. 1, and the X-ray structural data are given in Table 2. In essence, the metal atom has a pseudo-octahedral arrangement of six ligands, one dap and five carbonyls. The dap ligand is bonded to the chromium through one of the amine nitrogen atoms (Fig. 1). The metal–carbon bond distance for CO in *trans*-position to the dap ligand [Cr–C9 = 1.833(7) Å] is slightly shorter than those for the four equatorial CO ligands [Cr–C7 = 1.873(6), Cr–C8 = 1.904(7), Cr–C10 = 1.935(7), and Cr–C11 = 1.896(6) Å], as observed in the analogous Cr(CO)<sub>5</sub>(piperidine) complex [18]. The differences observed in the Cr–CO bond distances for the carbonyl groups cis to the dap ligand seemingly originate from the orientation of the pyridine moiety and from crystal packing effects [19]. The difference in Cr–CO bond distances between *cis*- and *trans*-carbonyls in Cr(CO)<sub>5</sub>(dap)

Table 2

Selected bond lengths (Å) and angles (°) of the Cr(CO)<sub>5</sub>(dap) molecule

Bond lengths (Å)		Bond angles (°)	
Cr1–C7	1.873(6)	C9–Cr1–C7	88.1(3)
Cr1–C11	1.896(6)	C9–Cr1–C11	89.7(3)
Cr1–C8	1.904(7)	C7–Cr1–C11	89.5(3)
Cr1–C10	1.935(7)	C9–Cr1–C8	87.4(3)
Cr1–N2	2.236(5)	C7–Cr1–C8	90.2(3)
O1–C7	1.157(6)	C11–Cr1–C8	177.0(3)
O3–C9	1.161(8)	C9–Cr1–C10	88.6(3)
O5–C11	1.143(7)	C7–Cr1–C10	176.6(3)
O4–C10	1.129(7)	C11–Cr1–C10	89.6(3)
O2–C8	1.139(8)	C8–Cr1–C10	90.4(3)
N2–C2	1.431(7)	C9–Cr1–N2	177.4(2)
C6–N1	1.342(7)	C7–Cr1–N2	91.2(2)
C6–N3	1.354(8)	C11–Cr1–N2	92.8(2)
C6–C5	1.396(9)	C8–Cr1–N2	90.1(2)
C2–N1	1.325(7)	C10–Cr1–N2	92.2(2)
C2–C3	1.390(8)	O3–C9–Cr1	178.6(6)
C4–C5	1.355(9)	O1–C7–Cr1	175.4(6)
C4–C3	1.396(9)	O2–C8–Cr1	173.9(7)
		O5–C11–Cr1	173.1(5)
		C2–N2–Cr1	112.9(3)
		N1–C6–N3	116.5(6)
		N1–C6–C5	121.7(6)
		N3–C6–C5	121.8(6)
		O4–C10–Cr1	174.0(6)
		N1–C2–C3	124.9(5)
		N1–C2–N2	114.9(5)
		C3–C2–N2	120.2(5)
		C2–N1–C6	117.5(5)
		C5–C4–C3	119.9(6)
		C4–C5–C6	119.7(6)
		C4–C3–C2	116.2(6)

Esd's are given parentheses.

is in accord with the notion of an enhanced chromium (d<sub>π</sub>) → carbonyl (π\*) back-donation arising from the fact that the π-accepting ability of amine is much less than that of carbon monoxide.

The metal–nitrogen bond distance [Cr–N2 = 2.236(5) Å] is slightly longer than that in the analogous Cr(CO)<sub>5</sub>(pyridine) complex [18] [Cr–N = 2.194(4) Å], because the dap ligand is bonded to the metal through the amine nitrogen atom, having much less π-accepting ability than the pyridine sp<sup>2</sup>-nitrogen atom. The pyridine plane makes an angle of 112.9(3)° with the C9–Cr–N2 bond axis. One also observes a noticeable difference in nitrogen–carbon bond distances in the coordinated dap ligand. The nitrogen–carbon bond distance of the coordinated amine group [C2–N2 = 1.431(7) Å] is longer than that of the non-coordinating amine group [C6–N3 = 1.354(8) Å]. This confirms the coordination of the dap ligand through one NH<sub>2</sub> group acting as strong σ-donor.

Because of the presence of the bulky 2,6-diaminopyridine ligand, the four equatorial carbonyls are bent away as seen from the C9–Cr–C bond angles being smaller than 90° [C9–Cr–C7 = 88.1(3), C9–Cr–C8 = 87.4(3), C9–Cr–C10 = 88.6(3), C9–Cr–C11 = 89.7(3)°].

Accordingly, all the N2–Cr–C bond angles to the equatorial carbonyls are greater than 90° [N2–Cr–C7 = 91.2(2), N2–Cr–C8 = 90.1(2), N2–Cr–C10 = 92.2(2), N2–Cr–C11 = 92.8(2)°].

The IR spectrum of Cr(CO)<sub>5</sub>(dap) in solution exhibits three prominent absorption bands at 2068.7, 1934.5, and 1890.0 cm<sup>-1</sup> in the CO stretching vibrational region. The three-band ν(CO) pattern indicates that the C<sub>4v</sub> symmetry of M(CO)<sub>5</sub> skeleton, commonly observed for M(CO)<sub>5</sub>L complexes [20], can also be adopted for Cr(CO)<sub>5</sub>(dap); ν(CO) modes: 2 A<sub>1</sub> (IR active), E (IR active), and B<sub>1</sub> (IR inactive).

The <sup>13</sup>C NMR spectrum of Cr(CO)<sub>5</sub>(dap) shows two signals for the carbonyl groups at 221.42 and 214.38 ppm in ≈1:4 intensity ratio [21]. The appearance of only one signal for the four equatorial CO groups indicates that the molecule is fluxional with respect to rotation about the metal–nitrogen bond axis in solution. In the <sup>13</sup>C–{<sup>1</sup>H} NMR spectrum, the complex Cr(CO)<sub>5</sub>(dap) shows five signals for the carbons of dap at 165.40 (C2), 159.38 (C6), 140.71 (C4), 104.61 (C3), and 100.89 (C5) ppm, in accord with the unsymmetric coordination of dap through one NH<sub>2</sub> group to the metal atom. All the carbon signals of the dap ligand exhibit a coordination shift to the lower magnetic field depending upon the closeness of the carbon atom to the coordination site. The <sup>13</sup>C NMR chemical shifts of the free 2,6-diaminopyridine (dap) molecule in dichloromethane are 158.32 (C2, C6), 139.36 (C4), and 97.20 (C3, C5) ppm.

The <sup>1</sup>H NMR spectrum of the free 2,6-diaminopyridine (dap) in dichloromethane gives a singlet at 4.56 (NH<sub>2</sub>), a doublet at 5.74 (H3, H5), and a triplet 7.07 (H4) ppm with a coupling constant of 7.8 Hz. The Cr(CO)<sub>5</sub>(dap) complex shows two signals at 2.10 and 3.60 ppm for the NH<sub>2</sub> groups, a doublet at 9.64 (H3), a doublet of doublet at 9.00 (H4), and a doublet at 8.64 (H5) ppm; with the coupling constants of *J*(H3–H4) = 2.8, *J*(H4–H5) = 8.2 Hz. The <sup>1</sup>H NMR signals of aromatic protons of 2,6-diaminopyridine show remarkable shifts to the lower magnetic field upon coordination. This indicates that 2,6-diaminopyridine acts as a strong electron donor in coordinating to the chromium atom.

2,6-Diaminopyridine has three nitrogen atoms each with a lone pair. All of three can potentially coordinate to a transition metal atom, separately or simultaneously, acting as mono- or multi-dentate ligand, respectively. The amine nitrogen atoms are almost purely σ-donor, and stronger donor than the sp<sup>2</sup> hybridized nitrogen of the ring. The latter nitrogen atom has also some π-accepting ability, albeit very weak. In the Cr(CO)<sub>5</sub>(dap) complex, the σ electron donation from dap to the metal

enhances the metal → carbonyl back bonding and, thus, strengthens the Cr–CO bonds. As a consequence of this Cr–CO bond strengthening, the Cr(CO)<sub>5</sub>(dap) complex is inert toward further CO substitution. The prolonged irradiation of Cr(CO)<sub>5</sub>(dap) in solution does not give any further CO substitution, which would lead to the formation of Cr(CO)<sub>4</sub>(dap) having the 2,4-diaminopyridine as bidentate ligand.

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