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Key indicators

Single-crystal X-ray study  
 T = 100 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
 R factor = 0.041  
 wR factor = 0.120  
 Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

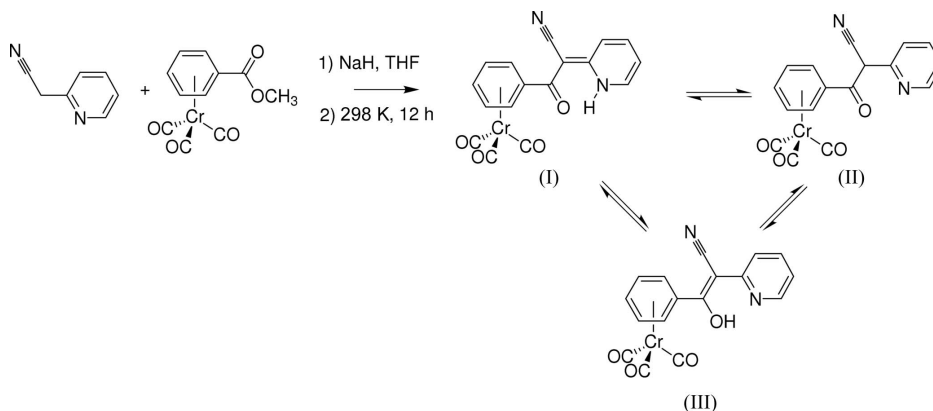
$[\eta^6\text{-2-Benzoyl-2-(1,2-dihydropyridin-2-ylidene)acetonitrile}] \text{tricarboxylchromium(0)}$

The structure of the title compound,  $[\text{Cr}(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O})(\text{CO})_3]$ , at 173 K has molecules arranged in a herring-bone pattern. The side chain of the arenechromium unit is planar and tilted by approximately  $24^\circ$  to the benzene ring.

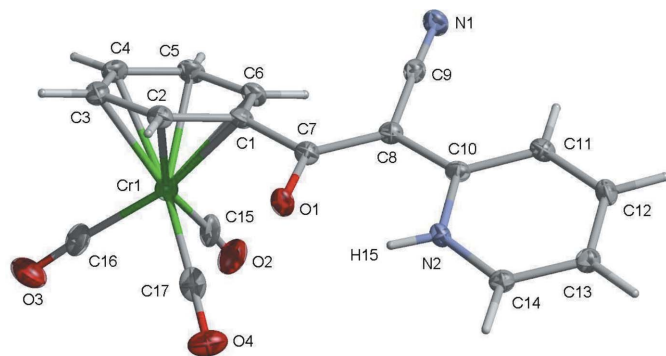
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Comment

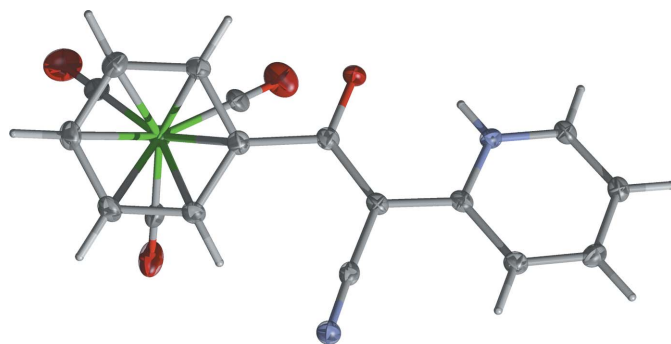
The structure of the title compound, (I) (Fig. 1), reveals a Cr-arene centroid distance of 1.724 Å and all Cr-C(arene) distances are approximately equal (Table 1). The three carbonyl groups are equidistant from Cr. Displacement parameters of carbonyl atoms O3 and O4 suggest rotation around the metal, while O2 appears to swing beneath it, affecting the Cr-CO vibrational modes. The three metal carbonyls adopt a staggered conformation with respect to the benzene ring C atoms (Fig. 2), and one of them is directly eclipsed with the side-chain carbonyl group. However, for monosubstituted arenetricarbonylchromium complexes (Morris, 1995), an eclipsed conformation is usually favored.



Treatment of tricarbonyl( $\eta^6$ -methylbenzoate)chromium(0) with 2-cyanomethylpyridinyl sodium unexpectedly afforded (I) rather than tautomeric forms (II) or (III). Atom H15 was refined isotropically and unrestrained, and found to be bound to N2 at 0.79 (3) Å. It is involved in an intramolecular N2-H15...O1 hydrogen bond [ $\text{N}2 \cdots \text{O}1 = 2.579(3) \text{ \AA}$ ,  $\text{O}1 \cdots \text{H}15 = 1.92(3) \text{ \AA}$  and  $\text{N}2-\text{H}15 \cdots \text{O}1 = 140(3)^\circ$ ]. Further support for the assignment of tautomer (I) is lent by the extremely high chemical shift of 17.3 p.p.m. in  $\text{CDCl}_3$  recorded in the  $^1\text{H}$  NMR spectrum. This is much further downfield than standard shifts for hydroxy or methine protons as found in the other two tautomers. This tautomer form with an intramolecular N-H...O hydrogen bond is observed in the free arene, the 2-acylalkylated pyridine derivative (Abramovitch *et al.*, 1976).



**Figure 1**  
The molecular structure of (I) with 50% probability displacement ellipsoids, showing the out-of-plane positioned side chain relative to the benzenechromium unit.



**Figure 2**  
Top view of (I), showing the staggered conformation of the tricarbonylchromium fragment relative to the arene side chain.

## Experimental

Handling of arenechromium solutions was under an inert atmosphere using deoxygenated solvents. Synthesis of tricarbonyl( $\eta^6$ -methylbenzoate)chromium(0) has been described elsewhere (Mahaffey & Pauson, 1990). NaH (0.89 g, 2.5 mmol, 60% in mineral oil) in tetrahydrofuran (THF) (5 ml) was stirred at 263 K before adding 2-cyanomethylpyridine (0.225 ml, 2.0 mmol) by microsyringe. After 2 h at 263 K, tricarbonyl( $\eta^6$ -methylbenzoate)chromium(0) (0.54 g, 2.0 mmol) dissolved in THF (5 ml) was added by syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight. After concentration, the solids were dissolved in THF (5 ml) before H<sub>2</sub>O (15 ml) was added, and the mixture was extracted with 15 and then 40 ml portions of EtOAc. The combined organic extracts were dried *in vacuo*, yielding a red solid that was recrystallised from MeOH to give 50 mg (20%) of (I) in yellow flakes. Air-stable, diffraction-quality crystals were obtained by recrystallisation from a solvent mixture of approximately 1:2 Et<sub>2</sub>O/hexanes at 253 K.

### Crystal data

[Cr(C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O)(CO)<sub>3</sub>]  
*M<sub>r</sub>* = 358.27  
 Orthorhombic, *Pbca*  
*a* = 13.6266 (4) Å  
*b* = 10.3234 (3) Å  
*c* = 20.6939 (6) Å  
*V* = 2911.07 (15) Å<sup>3</sup>

*Z* = 8  
*D<sub>x</sub>* = 1.635 Mg m<sup>-3</sup>  
 Cu *K*α radiation  
 $\mu$  = 6.71 mm<sup>-1</sup>  
*T* = 100 K  
 Block, yellow  
 0.12 × 0.06 × 0.03 mm

### Data collection

Bruker Proteum diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2000)  
*T*<sub>min</sub> = 0.500, *T*<sub>max</sub> = 0.824

55017 measured reflections  
 2700 independent reflections  
 2456 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.057  
 $\theta$ <sub>max</sub> = 69.1°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR*(*F*<sup>2</sup>) = 0.120  
*S* = 1.09  
 2700 reflections  
 221 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 4.6385P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.83 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.78 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cr1—C15	1.854 (3)	Cr1—C4	2.227 (3)
Cr1—C16	1.859 (3)	Cr1—C1	2.228 (3)
Cr1—C17	1.876 (3)	Cr1—C2	2.238 (3)
Cr1—C6	2.210 (3)	Cr1—C3	2.240 (3)
Cr1—C5	2.212 (3)	O3—C16	1.112 (4)
C15—Cr1—C16	84.52 (12)	C16—Cr1—C17	86.18 (13)
C15—Cr1—C17	86.66 (12)		
C6—C1—C7—O1	-153.5 (3)	O1—C7—C8—C10	4.8 (4)
C2—C1—C7—O1	21.4 (3)	C1—C7—C8—C10	-175.9 (2)
C6—C1—C7—C8	27.2 (4)	N2—C10—C8—C7	4.4 (4)
C2—C1—C7—C8	-158.0 (2)	C11—C10—C8—C7	-176.3 (2)
O1—C7—C8—C9	-169.3 (2)	N2—C10—C8—C9	178.9 (2)
C1—C7—C8—C9	10.1 (4)	C11—C10—C8—C9	-1.9 (4)

Refinement of all H atoms was done using isotropic idealised riding models in all cases except for the nitrogen-bound H15, which was refined isotropically with free coordinates. Forcing the position of the N-bound hydrogen on to the oxygen produced higher *wR2*, *R1*, and goodness of fit values.

Data collection: *PROTEUM2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Raster3d* (Merritt & Bacon, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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