Pentacarbonyl(4-phenylpyridine)-tungsten(0) and pentacarbonyl-(2-phenylpyridine)chromium(0)

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In pentacarbonyl(4-phenylpyridine)tungsten(0), [W(C$_{11}$H$_9$N)(CO)$_5$], the molecules have mm site symmetry and the pyridine ligand, with m symmetry, is completely planar. In pentacarbonyl(2-phenylpyridine)chromium(0), [Cr(C$_{11}$H$_9$N)(CO)$_5$], the molecules are in general positions and the phenyl and pyridine rings of the ligand are twisted by 67.7 (3)° with respect to one another by rotation about the C—C bond joining them. In both compounds, the axial M—C$_{carbonyl}$ bond $trans$ to the M—N$_{ligand}$ bond is significantly shorter than the equatorial M—C$_{carbonyl}$ bonds.

Comment

The molecular structures of pentacarbonyl(4-phenylpyridine)tungsten(0), (I) (Fig. 1), and pentacarbonyl(2-phenylpyridine)chromium(0), (II) (Fig. 2), along with that previously reported by Creaven et al. (2000) for pentacarbonyl(di-2-pyridylamine)tungsten(0), (III), are formally all very similar. Thus, in all three cases, the metal atom M (M is W or Cr) is six-coordinate in a distorted octahedral environment comprising five carbonyl ligands and the monodentate N-donor ligand. In every case, the M—C$_{carbonyl}$ bond axial and $trans$ to the M—N$_{ligand}$ bond is significantly shorter than the equatorial M—C bonds [see Tables 1 and 2 for (I) and (II), respectively; in (III), the axial bond is 1.967 (7) Å $versus$ 2.020 (7)–2.063 (8) Å for the equatorial bonds]. In addition, in all three cases, because the C$_{ax}$—M—C$_{eq}$ angles are all less than 90° [Tables 1 and 2 for (I) and (II), respectively; 84.9 (3)–89.2 (3)° for (III)], the M—C bonds are distributed in an umbrella-like manner, with M—C$_{ax}$ as the handle and M—C$_{eq}$ as the spokes.

The variously substituted N-donor pyridine ligands are, of course, totally different throughout the series. In (I), the

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N-donor ligand has m symmetry and is therefore completely planar. Due to the mm site symmetry of the molecule as a whole, the N-donor ligand plane bisects the angles of one pair of opposite C$_{eq}$—W—C$_{eq}$ angles. Table 1 shows that the endocyclic angles at N, C5, C6 and C9 are all less than the ideal value of 120°, which is consistent with elongation of the ligand in the direction from N to C9, although the discrepancy decreases from atom to atom in the series, in the order given above. Similar discrepancies, but fewer in number and with no real regularity, are found in the pyridine ligands of (II) (at N and C7; Table 2) and (III) [116.6 (6) and 115.9 (7)° at the donor and free pyridine N, respectively].
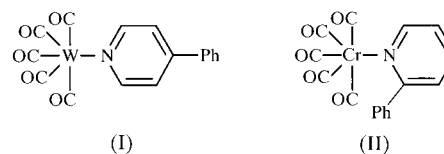
In (I), the pyridine ligand is attached to the M(CO)$_5$ fragment in an end-on manner. In (II) and (III), the mode of attachment is sideways on, brought about by the presence in each case of a substituent species in the 2-position. Despite this, the pyridine ligand in (III), although not constrained by symmetry, is still essentially planar and is oriented with respect to the equatorial carbonyl groups in much the same way as the corresponding ligand in (I).

The situation is very different in the case of (II). Here, in the absence of the bridging amine link present in (III), the phenyl and pyridine rings are twisted through 67.7 (3)° [estimated from the dihedral angles in Table 2; this angle is calculated as 67.44 (15)° by $MPLA$ in $SHELXL$97 (Sheldrick, 1997)] in order to avoid impossibly short non-bonding intramolecular contacts.

The planarity of the pyridine ligands in (I) and (III) is reflected in the manner in which the molecules are packed in the unit cells. In (I), the molecules are first of all arranged linearly, head to tail, in the b direction. These rows, with the orientation of the molecules alternating from row to row, form layers parallel to [100], with the pyridine ligands face to face and completely superimposed, and c/2 [3.933 (2) Å] apart. In (III), the pyridine ligands are again face to face but in columns, with coordinates of the form $(0, y, 0)$ and $(\frac{1}{2}, y, \frac{1}{2})$, related pair-
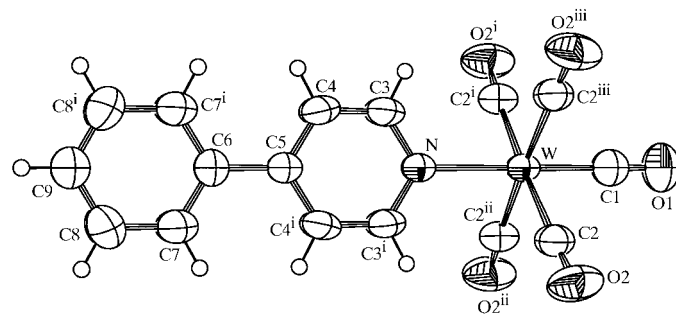

Figure 1
The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $x, y, \frac{1}{2} - z$; (iii) $1 - x, y, z$].

wise by crystallographic centres of symmetry and therefore strictly parallel to one another, and $b/2$ [3.592 (3) Å] apart. No such interactions are found in (II).
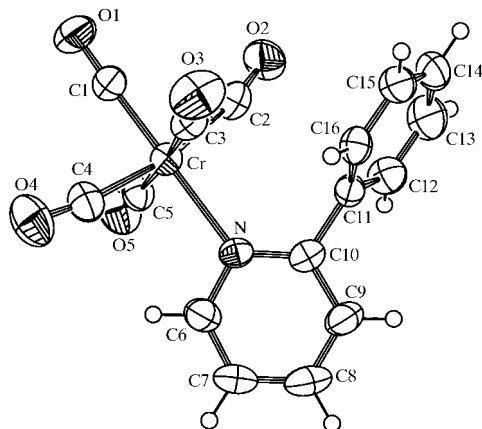

Figure 2
The molecular structure of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

For (I), and for (III) reported previously by Creaven *et al.* (2000), the complex W(CO)₅·THF (THF is tetrahydrofuran) was prepared by photolyis of W(CO)₆ in argon-purged THF. Addition of a solution of the appropriate pyridine ligand, also in THF, to the filtered solution of the solvate complex, and removal of the solvent under reduced pressure, yielded the crude product. The same procedure was used for the preparation of (II), except that diethyl ether was used as the solvent in place of THF. For all three compounds, recrystallization from de-aerated toluene provided crystals suitable for analysis.

Compound (I)

Crystal data

[W(C₁₁H₉N)(CO)₅]	Mo $K\alpha$ radiation
$M_r = 479.09$	Cell parameters from 14
Orthorhombic, $Cmcm$	reflections
$a = 12.538\ (4)$ Å	$\theta = 12.5–14.0°$
$b = 16.239\ (6)$ Å	$\mu = 7.236\ \mathrm{mm}^{-1}$
$c = 7.866\ (5)$ Å	$T = 298\ (2)$ K
$V = 1601.6\ (13)$ Å³	Plate, yellow
$Z = 4$	$0.56 \times 0.24 \times 0.10$ mm
$D_x = 1.987\ \mathrm{Mg\ m}^{-3}$	

Data collection

Nicolet $P3$ diffractometer	$\theta_{max} = 30.07°$
$\theta/2\theta$ scans	$h = 0 \to 17$
Absorption correction: ψ scan	$k = 0 \to 22$
(North *et al.*, 1968)	$l = 0 \to 11$
$T_{min} = 0.188$, $T_{max} = 0.485$	2 standard reflections
1251 measured reflections	every 50 reflections
1251 independent reflections	intensity decay: none
1136 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 0.5806P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.083$	$(\Delta/\sigma)_{max} < 0.001$
1251 reflections	$\Delta\rho_{max} = 0.96$ e Å⁻³
71 parameters	$\Delta\rho_{min} = -1.35$ e Å⁻³
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °) for (I).

W—C1	1.955 (10)	W—N	2.273 (8)
W—C2	2.037 (5)		
C1—W—C2	88.44 (12)	C7ⁱ—C6—C7	116.7 (9)
C3—N—C3ⁱ	114.0 (9)	C8ⁱ—C9—C8	119.1 (12)
C4ⁱ—C5—C4	114.8 (8)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Compound (II)

Crystal data

[Cr(C₁₁H₉N)(CO)₅]	$D_x = 1.498\ \mathrm{Mg\ m}^{-3}$
$M_r = 347.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 14
$a = 6.223\ (4)$ Å	reflections
$b = 13.635\ (12)$ Å	$\theta = 7.5–10.0°$
$c = 18.170\ (9)$ Å	$\mu = 0.767\ \mathrm{mm}^{-1}$
$\beta = 92.60\ (5)°$	$T = 298\ (2)$ K
$V = 1540.1\ (18)$ Å³	Block, yellow green
$Z = 4$	$0.56 \times 0.50 \times 0.20$ mm

Data collection

Nicolet $P3$ diffractometer	$\theta_{max} = 30.06°$
$\theta/2\theta$ scans	$h = 0 \to 8$
Absorption correction: refined from	$k = 0 \to 19$
ΔF (*XABS*2.0; Parkin *et al.*, 1995)	$l = -25 \to 25$
$T_{min} = 0.691$, $T_{max} = 0.858$	2 standard reflections
4494 measured reflections	every 50 reflections
4494 independent reflections	intensity decay: none
1781 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0310P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.087$	$+ 1.0286P]$
$wR(F^2) = 0.157$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.026$	$(\Delta/\sigma)_{max} < 0.001$
4494 reflections	$\Delta\rho_{max} = 0.35$ e Å⁻³
208 parameters	$\Delta\rho_{min} = -0.42$ e Å⁻³
H-atom parameters constrained	

Table 2
Selected geometric parameters (Å, °) for (II).

Cr—C1	1.821 (5)	Cr—C5	1.910 (6)
Cr—C4	1.892 (6)	Cr—C2	1.926 (6)
Cr—C3	1.897 (6)	Cr—N	2.216 (4)
C1—Cr—C4	85.4 (2)	C1—Cr—C2	83.0 (2)
C1—Cr—C3	88.7 (2)	C10—N—C6	115.8 (4)
C1—Cr—C5	88.9 (2)	C6—C7—C8	118.0 (5)
N—C10—C11—C12	−114.7 (5)	N—C10—C11—C16	69.1 (6)
C9—C10—C11—C12	66.2 (6)	C9—C10—C11—C16	−109.9 (5)

As a result of the *mm* molecular symmetry of (I), the asymmetric unit consists of less than half the molecule. Thus, the 4c (*mm*) sites contain, in addition to W, C1 and O1 of the axial carbonyl ligand and N, C5, C6 and C9 of the 2-phenylpyridine ligand. Atoms C3, C4, C7 and C8 are in the 8g (*m*) sites. In forming the complete molecule, these last (C3, C4, C7 and C8) are replicated with the symmetry operation $(1 - x, y, \frac{1}{2} - z)$. Atoms C2 and O2 in the 16h general positions are the sole representatives of the set of four equatorial carbonyl ligands. The remaining members of the set are generated by

the above symmetry operation together with $(x, y, \frac{1}{2} - z)$ and $(1 - x, y, z)$. The comparatively high R value achieved for the structure of (II) is a source of some concern. This may be due in part to a comparatively poor quality and weakly diffracting sample crystal. However, it was noted that the original yellow–green crystal became opaque and colourless in the course of data collection. It is thus possible that partial decomposition of the sample crystal has had a deleterious effect upon the intensity data, although the intensity standard reflection measurements suggested that this was not the case. In both refinements reported here, H atoms were placed in calculated positions (C—H = 0.93 Å) and refined using a riding model, with $U_{iso} = 1.2U_{eq}$ of the C atom to which they were attached.

For both compounds, data collection: $P3$ software (Nicolet, 1980); cell refinement: $P3$ software; data reduction: $RDNIC$ (Howie, 1980); program(s) used to solve structure: $MULTAN$87 (Debaerdemaeker *et al.*, 1987); program(s) used to refine structure: $SHELXL$97

(Sheldrick, 1997); molecular graphics: $ORTEP$-3 (Farrugia, 1997); software used to prepare material for publication: $SHELXL$97.

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