Neutron Diffraction Study of *fac*-$[IrH_3(PPh_2Me)_3]\cdot MeOH$ †

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The structure of the methanol solvate of the facial isomer of $[IrH_3(PPh_2Me)_3]$ has been analysed by neutron diffraction. Data were obtained at 55 ± 0.1 K using a single crystal of volume 17.6 mm^3 and the structure refined to final agreement factors of $R(F^2) = 0.053$ and $R'(F^2) = 0.064$ for 1615 reflections. The Ir atom is situated on a three-fold rotation axis. Distances and angles correspond well to those expected for a complex with normal terminal H atoms: Ir–H 1.627(4), Ir–P 2.314(2) Å; H–Ir–H 83.4(2), P–Ir–P 98.6(1), and H–Ir–P 88.5(2), 169.1(2)°. As expected, the overall geometry of the complex is distorted octahedral, with the hydrogen ligands compressed together by the steric bulk of the phosphines, as evidenced by the H–Ir–H ($< 90°$) and P–Ir–P ($> 90°$) angles. The compound crystallizes in the rhombohedral space group $R3$, with $a = 10.367(1)$ Å and $\alpha = 108.19(6)°$ at $T = 55 \pm 0.1$ K.

As part of our continuing studies of polyhydride/phosphine metal complexes of the type MH_xL_y (L is a tertiary phosphine)[1–5] we report here a single-crystal neutron diffraction study of *fac*-$[IrH_3(PPh_2Me)_3]$. Molecules of the type MH_xL_y have been the subject of renewed interest, stimulated by the discovery of the existence of the 'non-classical' $M(\eta^2\text{-}H_2)$ dihydrogen ligand[6,7] and its complete structural characterization *via* X-ray and neutron diffraction studies on $[Fe(\eta^2\text{-}H_2)H(Ph_2PCH_2CH_2PPh_2)]^+$ [8] and $[Fe(\eta^2\text{-}H_2)H_2(PEtPh_2)_3]$.[9] Polyhydride/phosphine complexes have also featured prominently in the controversy surrounding the T_1 criterion for identifying non-classical dihydride complexes.[10–12] Recent neutron diffraction work by various groups[13–17] has shown that, for the most part, these polyhydride–phosphine complexes have 'classical' structures. One compound of this class, $[ReH_7\{P(C_6H_4Me\text{-}p)_3\}_2]$,[17] has an especially intriguing 'intermediate' structure in which the H $\cdots$ H distance has a value (1.36 Å) midway between that of classical (≈ 1.9 Å)[3–5,13–16] and non-classical (≈ 0.9 Å)[6–9] structures.

For the iridium polyhydride family, neutral complexes tend to have classical structures[5,18–20] while cationic complexes are believed to be non-classical, at least in solution.[21] A notable exception is the neutral non-classical tetrahydride complex $[Ir(H_2)H_2Cl(PR_3)_2]$ (R = Pr^i, C_6H_4 or Bu^t).[22] The cationic species $[IrH_3(C_5H_5)(PMe_3)]^+$, originally believed to be non-classical based on NMR measurements,[23] subsequently was shown by neutron diffraction to be classical, with the extremely large observed proton–proton coupling constants being due to quantum-mechanical exchange coupling.[18] In the present study, we extend our earlier work[5] on $[IrH_5(PPr^i_3)_2]$ to the trihydride species *fac*-$[IrH_3(PPh_2Me)_3]$. Like most other members of the neutral iridium polyhydride family, this compound has a classical structure.

Experimental

Synthesis.—The compound *fac*-$[IrH_3(PPh_2Me)_3]$ was synthesised in a manner similar to that described by Chatt *et al.*[24] The compound $IrCl_3\cdot 3H_2O$ (1.82 g, 5.16 mmol) was mixed with concentrated HCl (1 cm^3) in ethanol (10 cm^3). The mixture was heated for 45 min at 78 °C, upon which the colour changed from brown to green. This solution was cooled to room temperature, liquid PPh_2Me (4.34 cm^3, 23.2 mmol) was added by syringe, and the solution was heated at 80 °C for 6 h. After cooling, the solution was filtered, the filtrate evaporated to dryness, and the residue extracted with toluene (5 × 20 cm^3). After concentration to about 15 cm^3, the solution was cooled to −15 °C to give pale yellow crystals of $[IrCl_3(PPh_2Me)_3]$ (*ca.* 70% yield) (Found: C, 51.85; H, 4.20). Calc. for $C_{39}H_{39}Cl_3IrP_3$: C, 52.10; H, 4.35%).

The compound $LiAlH_4$ (0.5 g) was added in small portions to a solution of $[IrCl_3(PPh_2Me)_3]$ (0.785 g, 0.887 mmol) in tetrahydrofuran (thf) (50 cm^3). The colour changed immediately from pale yellow to colourless, and this suspension was stirred at 40 °C for about 1 h. After cooling, the excess of $LiAlH_4$ was destroyed by adding Pr^iOH in thf. The suspension was pumped to dryness and the residue extracted with MeOH (5 × 10 cm^3); the extract was concentrated to one-third of the initial volume and pentane (50 cm^3) added to give $[IrH_5(PPh_2Me)_2]$ (0.28 g, 0.47 mmol). After filtering off the solid $[IrH_5(PPh_2Me)_2]$, the mother-liquor was concentrated *in vacuo* to dryness, leaving a semi-solid material. This was extracted with toluene (5 × 5 cm^3) and treated with MeOH (10 cm^3). The solution was then maintained at −15 °C, to yield a single large crystal of $[IrH_3(PPh_2Me)_3]\cdot MeOH$ and several smaller ones, over a period of about 2 weeks. Measurement of the crystal density was not attempted in view of the sensitivity of the compound to air and moisture (Found: C, 58.05; H, 5.55. Calc. for $C_{40}H_{46}IrOP_3$: C, 58.00; H, 5.60%).

Neutron Diffraction.—The large, prismatic, lemon-yellow single crystal of the compound was used for the neutron diffraction experiment. It was mounted on an aluminium pin under a nitrogen atmosphere in a glove-box. A quartz cap was applied to prevent decomposition while indexing the faces of the crystal outside the glove-box. The capped sample was then sealed inside an aluminium can, placed inside a closed-cycle helium refrigerator and then mounted on a four-circle diffractometer at the Brookhaven High Flux Beam Reactor. A germanium (220) monochromator was employed to obtain a neutron beam of wavelength 1.1595(1) Å (calibrated with KBr, $a_0 = 6.6000$ Å at 295 K). Diffraction data were collected[25] in the rhombohedral setting of space group $R3$ at 55 ± 0.1 K.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

The temperature of 55 K was chosen for data collection in order to be well above a reversible phase transition observed to occur at 36 K. Upon initial cooling of the crystal to 20 K a sharp reduction in peak intensity was observed for the (5,5,5) reflection (rhombohedral setting) on the three-fold axis, accompanied by a splitting of the peak into three components. This splitting disappeared when the crystal was reheated through the transition. The sample temperature was monitored by a platinum resistor which was calibrated against the magnetic phase transition of an FeF_2 crystal at 78.38(1) K.[26] The unit-cell parameters at 55 ± 0.1 K were determined by a least-squares procedure based on the $\sin^2\theta$ values of 32 reflections ($46 < 2\theta < 53°$), and are listed in Table 1.

Intensity measurements were carried out by the θ–2θ step-scan technique. The scan width for low-angle data ($5 < 2\theta < 60°$) was 3.2° with 80 steps per scan. The scan width for high-angle data ($60 \leqslant 2\theta < 110°$) was determined by the formula $\Delta(2\theta) = [0.42(1 + 11.5 \tan\theta)]$ and the step adjusted to give 60–90 steps per scan. Counts were accumulated at each step for approximately 1.6 s, the exact time being determined by monitoring the incident beam intensity. The intensities of two check reflections were monitored at 100-reflection intervals: $(-1,3,-5)$, $(-1,6,1)$ for the low-angle data and (1,1,8), (3,12,4) for the high-angle data. No significant variation in the intensity of these reflections was observed during the course of data collection.

Integrated intensities were calculated estimating the background from the first and last tenth of each scan. Lorentz and absorption corrections were applied, the latter by means of numerical integration over a Gaussian grid of 8 × 8 × 6 points along a^*, b^* and c^*, respectively,[27] to yield 3298 F_o^2 values. The maximum and minimum calculated transmission coefficients were 0.666 and 0.529, respectively. The 3298 values of F_o^2 were averaged over the $\bar{3}$ Laue symmetry to give 1615 independent values for subsequent structure refinement. The agreement factor for averaging was $R_{\text{int}} = \Sigma_{hkl}\Sigma_i^{n_i}|F_{oi}^2 - F_o^2|/\Sigma_{hkl}\, n_iF_o^2 = 0.036$.

The structure analysis was carried out in the hexagonal setting[†] of space group $R3$ (no. 146), initially with data having $F_o^2 > 3\sigma(F_o^2)$ (1341 reflections). This initial refinement employed differential Fourier synthesis[28] with the starting model defined by non-hydrogen atom positions taken from a preliminary X-ray analysis.[‡,29] All H atoms belonging to the iridium complex were located in difference scattering-density maps and positional parameters were refined to convergence.

Subsequent full-matrix least-squares refinement using all data with the program UPALS[30] converged at $R(F^2) = 0.115$, a rather high value. Fourier difference maps at this stage revealed the presence of a methanol solvate molecule, as confirmed by elemental analysis (see above). The disordered methanol solvate was refined isotropically and all other atoms anisotropically to give at convergence a final $R(F^2) = 0.053$, $R'(F^2) = 0.064$, $S = 1.81$ for 277 parameters. Refinement was on F_o^2 with weights $w = [\sigma^2_{\text{count}}(F_o^2) + (0.02F_o^2)^2]^{-1}$. The neutron scattering lengths ($b \times 10^{-14}$ m) used were 1.06, 0.6648, −0.3741, 0.513 and 0.5803 for the Ir, C, H, P and O atoms, respectively.[31]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Views of the molecular core, the entire molecule of $[IrH_3(PPh_2Me)_3]$, and the methanol solvate are given in Figs. 1, 2 and 3 respectively. Table 1 gives a summary of the crystal

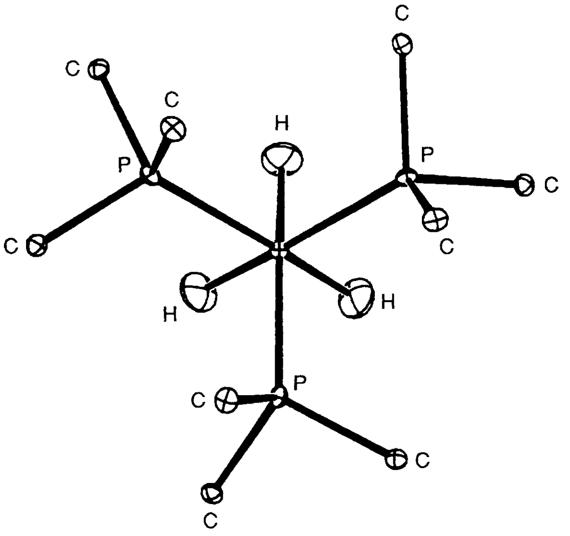

Fig. 1 An ORTEP plot[32] of the core of *fac*-$[IrH_3(PPh_2Me)_3]$. A crystallographic three-fold rotational axis passes through the molecule

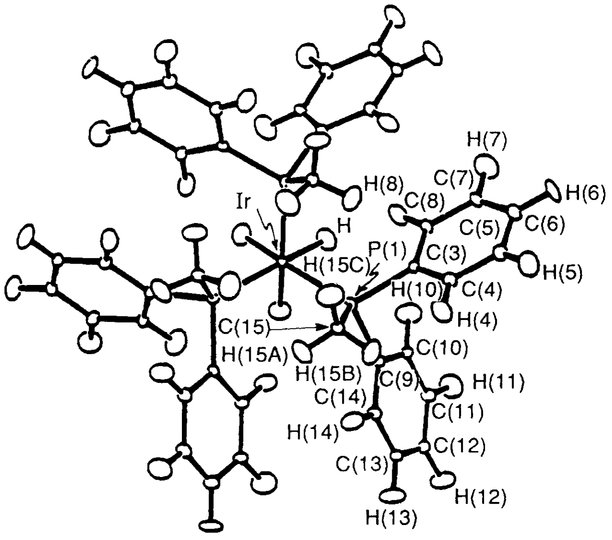

Fig. 2 Complete molecular plot of *fac*-$[IrH_3(PPh_2Me)_3]$

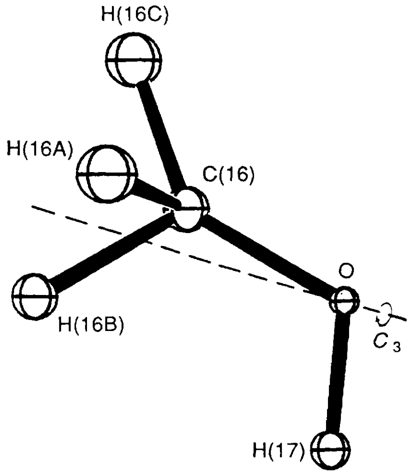

Fig. 3 An ORTEP plot[32] of the methanol molecule of solvation in *fac*-$[IrH_3(PPh_2Me)_3]$. Only one of the three disordered orientations is shown

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[†] Miller indices were transformed from the rhombohedral (r) to the hexagonal (h) setting using the following transformation: $h^h = h^r - k^r$, $k^h = k^r - l^r$ and $l^h = h^r + k^r + l^r$.

[‡] Carried out at ambient temperature on a small chip cut off from the large crystal. Hexagonal unit-cell constants: $a = 16.860(12)$, $c = 11.150(9)$ Å. A model consisting of the non-hydrogen atom skeleton of the molecule was refined to yield agreement factors of $R = 0.044$ and $R' = 0.058$. No attempt was made to determine the absolute configuration.

Table 1 Summary of crystal data and experimental parameters* for *fac*-$[IrH_3(PPh_2Me)_3]\cdot MeOH$

a/Å	16.794(3)
c/Å	11.006(3)
Z	3
U/Å^3	2689(1)
M	828.0 (includes MeOH)
D_c/kg m^{-3}	1.52 × 10^{-3}
μ/m^{-1}	238
Crystal faces	[{100} {110} {1$\bar{1}$0}]
U/m^3	17.6 × 10^{-8}
Data limits/°	$5 < 2\theta < 110$
Hemisphere sampled	[$\pm h$, $+k$, $\pm l$]

* Values for a rhombohedral setting: $a = 10.367(1)$ Å, $\alpha = 108.19(6)°$, $Z = 1$ and $U = 896.3(3)$ Å^3.

Table 2 Positional parameters[a] for *fac*-$[IrH_3(PPh_2Me)_3]\cdot MeOH$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
H	0.0740(3)	−0.0008(1)	−0.0947(3)
Ir	0.0000(0)	0.0000(0)	0.0000(0)
P(1)	−0.1204(2)	−0.0004(2)	0.1017(2)
C(3)	−0.2268(1)	−0.1117(1)	0.1219(2)
C(4)	−0.2479(1)	−0.1835(1)	0.0406(2)
C(5)	−0.3307(1)	−0.2664(1)	0.0498(2)
C(6)	−0.3934(1)	−0.2789(1)	0.1412(2)
C(7)	−0.3727(1)	−0.2082(1)	0.2240(2)
C(8)	−0.2903(1)	−0.1248(1)	0.2135(2)
C(9)	−0.1698(1)	+0.0622(1)	0.0248(2)
C(10)	−0.2164(1)	+0.0250(1)	−0.0851(2)
C(11)	−0.2585(1)	0.0662(1)	−0.1477(2)
C(12)	−0.2528(1)	0.1469(1)	−0.1026(2)
C(13)	−0.2045(1)	0.1856(1)	0.0044(2)
C(14)	−0.1641(1)	0.1430(1)	0.0688(2)
C(15)	−0.0994(1)	0.0488(1)	0.2551(2)
H(4)	−0.1982(3)	−0.1739(3)	−0.0299(4)
H(5)	−0.3458(3)	−0.3218(3)	−0.0133(4)
H(6)	−0.4573(3)	−0.3438(3)	0.1491(4)
H(7)	−0.4207(3)	−0.2166(3)	0.2954(4)
H(8)	−0.2769(3)	−0.0701(3)	0.2771(4)
H(10)	−0.2203(3)	−0.0368(3)	−0.1211(4)
H(11)	−0.2964(3)	0.0345(3)	−0.2300(4)
H(12)	−0.2865(3)	0.1787(3)	−0.1501(4)
H(13)	−0.2000(4)	0.2483(3)	0.0397(4)
H(14)	−0.1275(3)	0.1741(3)	0.1533(4)
H(15A)	−0.0054(3)	−0.0918(3)	0.3152(4)
H(15B)	−0.0382(3)	0.1172(3)	0.2528(4)
H(15C)	−0.1563(3)	0.0554(3)	0.2915(4)
O[b]	0.0000(0)	0.0000(0)	0.6138(6)
C(16)[b]	−0.0361(8)	0.0328(8)	0.6687(9)
H(17)[b]	−0.0288(11)	0.0322(11)	0.7543(12)
H(16A)[b]	−0.0569(20)	−0.0767(20)	0.5946(27)
H(16B)[b]	0.0267(17)	0.0011(27)	0.5263(17)
H(16C)[b]	−0.0215(20)	−0.0772(19)	0.6652(25)

[a] Based on hexagonal setting of space group *R*3. Parameters with zero estimated standard deviation (e.s.d.) were held fixed. [b] Of solvent molecule.

Table 3 Bond distances (Å) for *fac*-$[IrH_3(PPh_2Me)_3]\cdot MeOH$

H–Ir	1.627(4)	Phenyl carbon–hydrogen	
Ir–P(1)	2.314(2)	C(4)–H(4)	1.092(4)
P(1)–C(3)	1.850(3)	C(5)–H(5)	1.084(5)
P(1)–C(9)	1.829(3)	C(6)–H(6)	1.086(5)
P(1)–C(15)	1.831(3)	C(7)–H(7)	1.083(5)
		C(8)–H(8)	1.086(4)
Carbon–carbon bonds		C(10)–H(10)	1.082(5)
C(3)–C(4)	1.397(3)	C(11)–H(11)	1.082(4)
C(3)–C(8)	1.402(2)	C(12)–H(12)	1.087(4)
C(4)–C(5)	1.395(3)	C(13)–H(13)	1.089(5)
C(5)–C(6)	1.394(3)	C(14)–H(14)	1.093(4)
C(6)–C(7)	1.396(3)	average	1.086(4)
C(7)–C(8)	1.397(3)		
C(8)–C(3)	1.402(2)		
C(9)–C(10)	1.406(2)		
C(9)–C(14)	1.399(3)		
C(10)–C(11)	1.395(3)	Methyl carbon–hydrogen	
C(11)–C(12)	1.401(3)	C(15)–H(15A)	1.085(5)
C(12)–C(13)	1.393(3)	C(15)–H(15B)	1.094(5)
C(13)–C(14)	1.400(3)	C(15)–H(15C)	1.092(4)
average	1.398(3)	average	1.090(5)

Table 4 Bond angles (°) for *fac*-$[IrH_3(PPh_2Me)_3]\cdot MeOH$

H–Ir–H′	83.4(2)	H–C–C angles	
H–Ir–P(1)	169.1(2)	H(4)–C(4)–C(3)	118.9(3)
H–Ir–P(1′)	88.3(2)	H(4)–C(4)–C(5)	120.4(3)
H–Ir–P(1″)	88.7(2)	H(5)–C(5)–C(4)	120.0(3)
P(1)–Ir–P(1′)	98.6(1)	H(5)–C(5)–C(6)	119.8(3)
C(3)–P(1)–Ir	117.2(1)	H(6)–C(6)–C(5)	120.3(3)
C(9)–P(1)–C(15)	102.5(1)	H(6)–C(6)–C(7)	120.0(3)
C(9)–P(1)–C(3)	98.7(1)	H(7)–C(7)–C(6)	120.7(3)
C(9)–P(1)–Ir	115.0(1)	H(7)–C(7)–C(8)	119.4(3)
C(15)–P(1)–C(3)	102.4(1)	H(8)–C(8)–C(3)	120.7(3)
C(15)–P(1)–Ir	118.3(1)	H(8)–C(8)–C(7)	118.5(3)
C(4)–C(3)–P(1)	118.9(1)	H(10)–C(10)–C(9)	119.7(3)
C(8)–C(3)–P(1)	121.2(1)	H(10)–C(10)–C(11)	119.6(3)
C(10)–C(9)–P(1)	117.1(1)	H(11)–C(11)–C(10)	119.3(3)
C(14)–C(9)–P(1)	124.1(1)	H(11)–C(11)–C(12)	120.8(3)
		H(12)–C(12)–C(11)	120.3(3)
C–C–C angles		H(12)–C(12)–C(13)	120.1(3)
C(4)–C(3)–C(8)	118.7(2)	H(13)–C(13)–C(12)	119.7(3)
C(5)–C(4)–C(3)	120.8(2)	H(13)–C(13)–C(14)	119.8(3)
C(6)–C(5)–C(4)	120.2(2)	H(14)–C(14)–C(9)	120.5(3)
C(5)–C(6)–C(7)	119.7(2)	H(14)–C(14)–C(13)	119.2(3)
C(6)–C(7)–C(8)	119.9(2)	average	119.9(3)
C(3)–C(8)–C(7)	120.8(2)		
C(14)–C(9)–C(10)	118.8(2)	H(15A)–C(15)–P(1)	108.8(3)
C(9)–C(10)–C(11)	120.8(2)	H(15B)–C(15)–P(1)	108.5(3)
C(10)–C(11)–C(12)	120.0(2)	H(15C)–C(15)–P(1)	113.6(3)
C(11)–C(12)–C(13)	119.6(2)	H(15A)–C(15)–H(15B)	108.8(4)
C(12)–C(13)–C(14)	120.5(2)	H(15A)–C(15)–H(15C)	109.0(4)
C(9)–C(14)–C(13)	120.3(2)	H(15B)–C(15)–H(15C)	108.2(4)
average	120.0(2)		

data and experimental parameters, Table 2 the final atomic positions, while Tables 3 and 4 give bond distances and angles respectively.

A closely related molecule, *fac*-$[IrH_3(PPhMe_2)_3]$, was analysed by us earlier with X-ray diffraction.[1] That study did not reveal the hydrogen-atom positions, but indicated a molecule with approximate C_{3v} symmetry with Ir–P distances of 2.296(3), 2.296(3) and 2.291(3) Å and P–Ir–P angles of 101.4(1), 102.1(1) and 99.5(1)°: in short, a distorted octahedron with three missing facial H atoms. Unlike the present compound, the Ir atom of the $PPhMe_2$ derivative is not situated on a crystallographic three-fold axis. An even earlier X-ray study of the meridional isomer of $[IrH_3(PPh_3)_3]$ did reveal the locations of the H atoms, but their positions were not refined.[35]

In the present study the iridium complex is distorted octahedral. The distances and angles in the metal hydride are normal, including Ir–H 1.627(4) Å. This value may be compared with terminal Ir–H distances from other neutron diffraction studies: 1.587(3) Å in $[IrH_3(C_5H_5)(PMe_3)]^+[BF_4]^-$,[18] 1.589(3) Å in $[(Et_3P)_2Pt(\mu\text{-}H)_2IrH_2(PEt_3)_2]^+[BPh_4]^-$,[34] 1.594(3) Å in $[IrH_2(C_5Me_5)(SiEt_3)_2]$,[35] 1.58(1) Å in $[IrH_2Cl(PMe_2Ph)_3]$,[19] 1.617(8) Å in $[IrHCl_2(PMe_2Ph)_3]$,[20] and 1.606(5) Å in $[IrH_5(PPr^i_3)_2]$.[5] The angles between the ligands in our complex deviate significantly from the ideal octahedral value of 90°. Thus, the P–Ir–P angle of 98.6(1)° is markedly larger than the H–Ir–H angle of 83.4(2)°. This difference is due to steric effects; the methyldiphenylphosphine ligands are much bulkier than the hydride ligands, causing compression of the H–Ir–H angle.

An analysis of the mean-square displacement (m.s.d.) parameters for the iridium complex revealed that the average difference in C and H m.s.d.s along the C–H bonds is 64(46) × 10^{-24} m^2, with the hydrogen atoms always moving more than the carbons. This average difference, which reflects mainly the zero-point motion, is very similar to that usually found for such bonds. The precision is rather low, due to the fact that the thermal parameters are rounded off and are only accurate to *ca.* 10% for the non-hydrogen atoms. In view of this limited precision we have not examined the details of the motion of the hydrogen atoms relative to the phenyl planes. For the Ir–H bond, the difference in m.s.d.s along the bond is 89 × 10^{-24} m^2, with the hydrogen atom moving more, as expected.

The methanol solvate has its carbon atom C(16) displaced from the three-fold rotation axis, resulting in a three-fold disorder of the molecule (Fig. 3). Deviations of the methanol bond distances and angles from commonly accepted values are likely to be a consequence of this disorder.

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