Bis(diethyl sulfide)bis(2,4,6-trimethylphenyl)iridium(II) and Related Compounds†

Andreas A. Danopoulos,[a] **Geoffrey Wilkinson,***[,a] **Bilquis Hussain-Bates**[b] **and Michael B. Hursthouse***[,b]

[a] *Johnson Matthey Laboratory, Chemistry Department, Imperial College, London SW7 2AY, UK*

[b] *Department of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB, UK*

The interaction of *mer*-$IrCl_3(SEt_2)_3$ with $Mg(mes)_2(thf)_2$ [mes = mesityl (2,4,6-trimethylphenyl), thf = tetrahydrofuran] in Et_2O-thf gives *trans*-$Ir(mes)_2(SEt_2)_2$ **1**. With PMe_3 **1** gives *trans*-$Ir(mes)_2(PMe_3)_2$ **2**; both compounds are paramagnetic. With NO, **2** reacts to form the formally iridium(III) complex $Ir(mes)_2(NO)(PMe_3)_2$ **4** that has a bent IrNO group, while H_2 gives the known hydride $IrH_5(PMe_3)_2$. With CO **1** forms the square iridium(I) complex $Ir(mes)(CO)_2(SEt_2)$ **3**. The *trans*-square planar molecules of compound **1** lie on centres of symmetry; Ir–S and Ir–C 2.298(4) and 2.09(1) Å, respectively, with a unique S–Ir–C angle of 88.2(3)°. Molecules of **2** are also *trans* square planar, but lie in general positions; Ir–P 2.302(4), 2.305(4) Å, Ir–C 2.097(9), 2.112(9) Å and P–Ir–C 89.6(3)–90.5(3)°. The crystal structure of **4** contains two crystallographically independent molecules, both of which lie on two-fold axes, coincident with the Ir–N bond. The geometry is slightly distorted square pyramidal; N–Ir–P and N–Ir–C 91.7(2) (× 2) and 99.1(3), 99.3(3)°, respectively. The Ir–N, Ir–P and Ir–C bond lengths are 1.90(1), 1.91(1); 2.324(5), 2.328(4); and 2.186(9), 2.182(12) Å, respectively. The bent Ir–N–O system [133.7(10) and 133.4(8)°] is disordered over two sites related by the two-fold axes, but in a single molecule is fixed in one position and believed to associate, *via* O ··· P interaction, with the phosphorus atom of one phosphine.

Interaction of $Li(C_6H_2Pr^i_3\text{-}2,4,6)$ (LiR) and $RhCl_3(tht)_3$ (tht = tetrahydrothiophene) forms the square rhodium(II) compounds, *trans*-$RhR_2(tht)_2$, whose X-ray crystal structure was determined; by contrast the use of lithium mesityl ($C_6H_2Me_3$-2,4,6) gave $Rh(mes)_3$.[1] While the interaction of $IrCl_3(tht)_3$ with Mg(mes)Br gives $Ir(mes)_3$ [2a] and anhydrous $IrCl_3$ with Li(mes) gives $Ir(mes)_4$,[2b] the interaction of either LiR or Mg(mes)Br with the halides gave non-crystallisable intractable oils. However, by use of the diethyl sulfide complex *mer*-$IrCl_3(SEt_2)_3$ and $Mg(mes)_2(thf)_2$ (thf = tetrahydrofuran) we have obtained *trans*-$Ir(mes)_2(SEt_2)_2$.

Mononuclear iridium(II) species are rare[3] and there has been no recent work. The best characterised compounds are those of Shaw and co-workers[4a] that have chelate (O,P) ligands as in $Ir[P(Bu^t)_2C_6H_4O]_2$; two such compounds were characterised by X-ray diffraction.[4b] The species $[IrR'(CO)(PPh_3)_3]^+$, R′ = Me, Ph or CH_2CN, were generated in solution electrochemically and characterised only by IR and EPR spectroscopy.[5]

Analytical and physical data for new compounds are given in Table 1

Table 1 Analytical and physical data for iridium compounds*

Compound	Colour	M.p./°C	Analysis (%) C	H	N
1 $Ir(mes)_2(SEt_2)_2$	Green	135–136	50.2 (51.1)	6.7 (6.9)	
2 $Ir(mes)_2(PMe_3)_2$	Purple	*ca.* 234 (decomp.)	50.4 (50.4)	7.1 (6.9)	
3 $Ir(mes)(CO)_2(SEt_2)$	Yellow	*ca.* 180 (decomp.)	38.2 (38.3)	4.9 (4.7)	
4 $Ir(mes)_2(NO)(PMe_3)_2$	Yellow	*ca.* 100 (decomp.)	46.5 (47.0)	6.3 (6.5)	2.2 (2.3)
5 $Ir(mes)_2(py)_2$	Yellow-green	*ca.* 140 (decomp.)	55.8 (56.1)	6.9 (7.0)	4.4 (4.7)

* For mass spectra see Experimental section.

Results and Discussion

The interaction of *mer*-$IrCl_3(SEt_2)_3$ with excess of $Mg(mes)_2(thf)_2$ leads to *trans*-$Ir(mes)_2(SEt_2)_2$ **1** as green, air-sensitive crystals. Although *fac*-$IrCl_3(SEt_2)_3$ does react it gives only an oily intractable mixture; use of mesityllithium gives only $Ir(mes)_3$. Although **1** can be obtained using Et_2O alone as solvent, the yields are increased to *ca.* 27% when tetrahydrofuran is introduced as described in the Experimental section. The reaction is clearly a complicated one and other unidentified products are also formed.

The compound is paramagnetic and the X-band EPR spectrum at 77 K (Fig. 1) is similar to that for the monomeric $RhR_2(thf)_2$.[1] The crystal structure of **1** has been determined by X-ray diffraction. A diagram of the molecule is shown in Fig. 2; bond lengths and angles are given in Table 2. Not unexpectedly, the structure and geometry parameters are similar to those of the rhodium(II) tetrahydrothiophene complex. The metal atom lies on a centre of symmetry, giving an accurately planar IrC_2S_2 unit. The unique C–Ir–S angle is 88.2(3)°. The angle between the plane of the aryl ring and the co-ordination plane is 77.8°. The Ir–C and Ir–S distances and the near-tetrahedral angles at sulfur suggest that the ligand–metal bonding is pure σ in character. For comparison, the M–C and M–S distances in the rhodium(II) complex[1] are 2.109(10) and 2.291(5) Å, respectively.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI units employed: atm = 101 325 Pa, cal = 4.184 J.

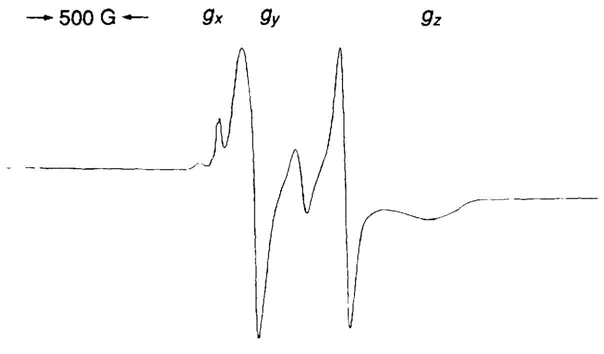

Fig. 1 The X-band EPR spectrum of *trans*-Ir(mes)$_2$(SEt$_2$)$_2$ in toluene at 77 K; g_x = 2.29, g_y = 2.14, g_z = 1.90 (G = 10^{-4} T)

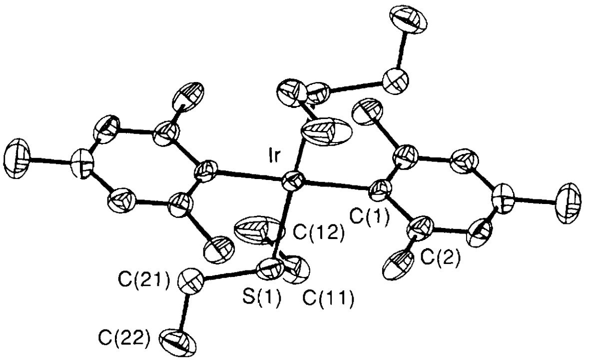

Fig. 2 The structure of *trans*-Ir(mes)$_2$(SEt$_2$)$_2$

Table 2 Bond lengths (Å) and angles (°) for Ir(mes)$_2$(SEt$_2$)$_2$

S(1)–Ir	2.298(4)	C(1)–Ir	2.092(11)
C(11)–S(1)	1.809(11)	C(21)–S(1)	1.822(13)
C(2)–C(1)	1.410(13)	C(6)–C(1)	1.433(13)
C(3)–C(2)	1.387(15)	C(161)–C(2)	1.571(15)
C(4)–C(3)	1.399(16)	C(5)–C(4)	1.388(15)
C(141)–C(4)	1.519(17)	C(6)–C(5)	1.372(14)
C(121)–C(6)	1.529(15)	C(12)–C(11)	1.479(18)
C(22)–C(21)	1.525(16)		
C(1)–Ir–S(1)	88.2(3)	S(1)–Ir–S(1B)	180.0(1)
C(1)–Ir–C(1B)	180.2(2)	S(1)–Ir–C(1B)	91.8(3)
C(11)–S(1)–Ir	112.0(5)	C(21)–S(1)–Ir	113.4(4)
C(21)–S(1)–C(11)	100.7(6)	C(2)–C(1)–Ir	121.0(7)
C(6)–C(1)–Ir	125.5(8)	C(6)–C(1)–C(2)	113.2(9)
C(3)–C(2)–C(1)	123.5(9)	C(161)–C(2)–C(1)	118.7(9)
C(161)–C(2)–C(3)	117.7(10)	C(4)–C(3)–C(2)	121.4(11)
C(5)–C(4)–C(3)	116.4(10)	C(141)–C(4)–C(3)	121.2(12)
C(141)–C(4)–C(5)	122.4(11)	C(6)–C(5)–C(4)	122.4(10)
C(5)–C(6)–C(1)	123.0(10)	C(121)–C(6)–C(1)	118.6(9)
C(121)–C(6)–C(5)	118.3(9)	C(12)–C(11)–S(1)	117.1(9)
C(22)–C(21)–S(1)	112.2(9)		

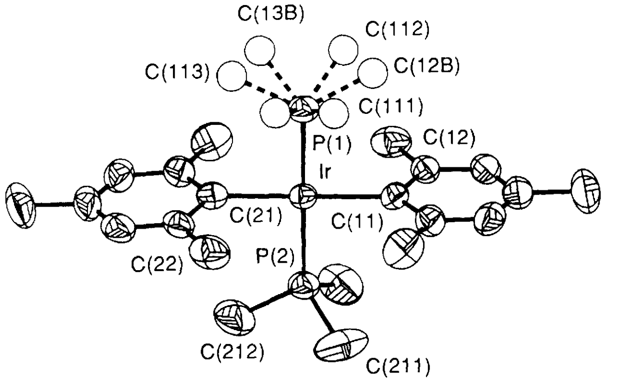

Fig. 3 The structure of *trans*-Ir(mes)$_2$(PMe$_3$)$_2$

Table 3 Bond lengths (Å) and angles (°) for Ir(mes)$_2$(PMe$_3$)$_2$

P(1)–Ir	2.302(4)	P(2)–Ir	2.305(4)
C(11)–Ir	2.112(9)	C(21)–Ir	2.097(9)
C(111)–P(1)	1.838(19)	C(112)–P(1)	1.795(19)
C(113)–P(1)	1.845(19)	C(11B)–P(1)	1.811(26)
C(12B)–P(1)	1.829(31)	C(13B)–P(1)	1.825(28)
C(211)–P(2)	1.832(12)	C(212)–P(2)	1.790(11)
C(213)–P(2)	1.832(10)	C(12)–C(11)	1.422(9)
C(16)–C(11)	1.426(11)	C(13)–C(12)	1.399(11)
C(121)–C(12)	1.529(12)	C(14)–C(13)	1.365(13)
C(15)–C(14)	1.381(12)	C(141)–C(14)	1.552(13)
C(16)–C(15)	1.385(11)	C(161)–C(16)	1.500(13)
C(22)–C(21)	1.431(10)	C(26)–C(21)	1.413(11)
C(23)–C(22)	1.395(12)	C(221)–C(22)	1.519(13)
C(24)–C(23)	1.374(13)	C(25)–C(24)	1.378(13)
C(241)–C(24)	1.523(13)	C(26)–C(25)	1.385(11)
C(261)–C(26)	1.523(12)		
P(2)–Ir–P(1)	178.9(1)	C(11)–Ir–P(1)	90.5(3)
C(11)–Ir–P(2)	89.6(3)	C(21)–Ir–P(1)	90.3(3)
C(21)–Ir–P(2)	89.7(3)	C(21)–Ir–C(11)	177.3(2)
C(111)–P(1)–Ir	114.6(6)	C(112)–P(1)–Ir	116.3(6)
C(113)–P(1)–Ir	117.9(7)	C(211)–P(2)–Ir	114.4(5)
C(212)–P(2)–Ir	118.1(4)	C(213)–P(2)–Ir	114.2(4)
C(12)–C(11)–Ir	121.5(6)	C(16)–C(11)–Ir	123.9(6)
C(22)–C(21)–Ir	121.4(6)	C(26)–C(21)–Ir	123.0(6)
C(112)–P(1)–C(111)	101.8(9)	C(113)–P(1)–C(111)	98.4(8)
C(113)–P(1)–C(112)	105.1(9)	C(212)–P(2)–C(211)	102.7(7)
C(213)–P(2)–C(211)	103.8(6)	C(213)–P(2)–C(212)	101.7(6)
C(16)–C(11)–C(12)	114.6(7)	C(13)–C(12)–C(11)	122.1(8)
C(121)–C(12)–C(11)	119.0(7)	C(121)–C(12)–C(13)	118.9(7)
C(14)–C(13)–C(12)	120.9(8)	C(15)–C(14)–C(13)	119.1(9)
C(141)–C(14)–C(13)	120.3(10)	C(141)–C(14)–C(15)	120.6(10)
C(16)–C(15)–C(14)	121.1(9)	C(15)–C(16)–C(11)	122.1(8)
C(161)–C(16)–C(11)	119.6(8)	C(161)–C(16)–C(15)	118.2(8)
C(26)–C(21)–C(22)	115.4(8)	C(23)–C(22)–C(21)	120.7(9)
C(221)–C(22)–C(21)	119.5(8)	C(221)–C(22)–C(23)	119.9(8)
C(24)–C(23)–C(22)	122.8(9)	C(25)–C(24)–C(23)	116.9(9)
C(241)–C(24)–C(23)	120.4(10)	C(241)–C(24)–C(25)	122.6(11)
C(26)–C(25)–C(24)	122.9(9)	C(25)–C(26)–C(21)	121.4(8)
C(261)–C(26)–C(21)	119.2(8)	C(261)–C(26)–C(25)	119.4(9)

Reactions.—The diethyl sulfide ligands in compound **1** are labile and readily substituted by PMe$_3$, PMe$_2$Ph or PEt$_2$Ph; the yields of the phosphine complexes are essentially quantitative. The purple crystalline solids are moderately air sensitive and the solutions are paramagnetic (Evans' NMR method) but EPR silent. The structure of the PMe$_3$ derivative Ir(mes)$_2$(PMe$_3$)$_2$ **2** has been determined, Fig. 3 and Table 3. The molecule lies in a general position in the unit cell but has an approximate centrosymmetric structure except for a two-fold disorder of one of the two PMe$_3$ groups. The maximum deviation for atoms defining the co-ordination plane is 0.04 Å for C(21). The two aryl groups make dihedral angles of 89.8 and 88.1° with this plane. There is no significant difference between the Ir–C distances in this complex and the thioether adduct **1**, but the equivalence of the Ir–S distance in **1** and the Ir–P distance in **2** suggests some small enhancement of the Ir–P interaction through π bonding.

Amines such as pyridine and 4-*tert*-butylpyridine (L) react with compound **1** to give green-yellow, paramagnetic powders analysing for Ir(mes)$_2$L$_2$ but crystals suitable for X-ray study were not obtained.

The interaction of compound **1** with CO at ambient temperature and pressure produces Ir(mes)(CO)$_2$(SEt$_2$) **3**, characterised analytically and spectroscopically; the only related sulfide is the halide-bridged polymer[6] [*cis*-IrCl(CO)$_2$-(SEt$_2$)]$_n$. The reaction of **1** with CO is quite different from the reaction[1] of RhR$_2$(tht)$_2$ with CO which involves reversible addition. The iridium complex gives products other than **3**

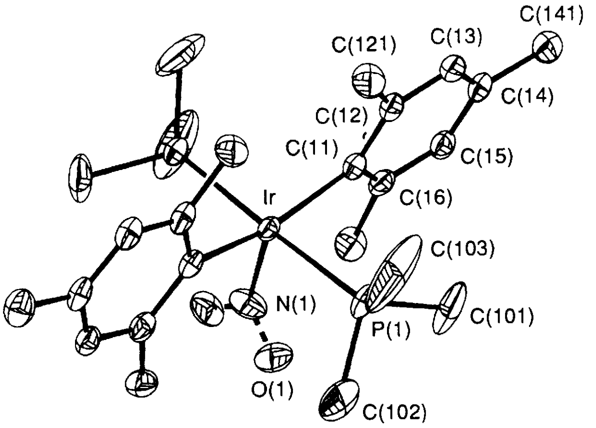

Fig. 4 The structure of molecule 1 of $Ir(mes)_2(NO)(PMe_3)_2$

Table 4 Selected bond lengths (Å) and angles (°) for $Ir(mes)_2(NO)(PMe_3)_2\cdot 0.5Et_2O$

N(1)–Ir(1)	1.903(14)	N(2)–Ir(2)	1.909(13)
P(1)–Ir(1)	2.324(5)	P(2)–Ir(2)	2.328(4)
C(11)–Ir(1)	2.186(9)	C(21)–Ir(2)	2.182(12)
N(1)–O(1)	1.067(19)	N(2)–O(2)	1.057(16)
P(1)–Ir(1)–P(1B)	176.6(1)	P(2)–Ir(2)–P(2B)	176.6(1)
C(11)–Ir(1)–C(11B)	161.8(2)	C(21)–Ir(2)–C(21B)	161.4(2)
P(1)–Ir(1)–N(1)	91.7(2)	P(2)–Ir(2)–N(2)	91.7(2)
C(11)–Ir(1)–N(1)	99.1(3)	C(21)–Ir(2)–N(2)	99.3(3)
C(11)–Ir(1)–P(1)	88.4(4)	C(21)–Ir(2)–P(2)	88.4(3)
O(1)–N(1)–Ir(1)	133.7(10)	O(2)–N(2)–Ir(2)	133.4(8)
C(101)–P(1)–Ir(1)	116.2(6)	C(201)–P(2)–Ir(2)	116.2(4)
C(102)–P(1)–Ir(1)	115.2(7)	C(202)–P(2)–Ir(2)	115.3(5)
C(102)–P(1)–C(101)	103.6(8)	C(203)–P(2)–Ir(2)	113.9(5)
C(12)–C(11)–Ir(1)	118.3(7)	C(22)–C(21)–Ir(2)	118.4(8)
C(16)–C(11)–Ir(1)	126.0(7)	C(26)–C(21)–Ir(2)	125.3(7)

according to NMR spectra of the initial solutions but these have not been identified.

The interaction of compound **2** with H_2 (1 atm for 1 h or 4 atm for 15 min) gives essentially quantitative yields of the known,[7] air-sensitive, classical iridium(v) hydride $IrH_5(PMe_3)_2$ identified by ^1H and ^{31}P NMR spectra (see Experimental section). The previous synthesis involved initial interaction of $IrCl_3(PMe_3)_3$ with $LiAlH_4$ followed by hydrolysis. The present reaction presumably involves oxidative addition of hydrogen and hydrogenolysis of the Ir–C bond to give mesitylene, which was detected by ^1H NMR spectroscopy.

Interaction of compound **1** with nitric oxide at low temperatures in toluene gives $Ir(mes)_2(NO)(PMe_3)_2$ **4** where the iridium is in oxidation state III as the IrNO bond is bent (see crystal structure below); **4** has a characteristic[8] band for bent M–NO at 1519 cm^{-1} in the IR spectrum.

An X-ray crystal structure determination of compound **4** shows the crystal to contain two symmetry-independent molecules, each of which, however, lies on a two-fold axis of symmetry. The Ir–N–O system is bent and the oxygens are disordered over two symmetry-related positions in each molecule. A diagram of molecule 1 is shown in Fig. 4 whilst geometry parameters for both are given in Table 4. Perusal of this Table shows the close similarity between the two molecules. In view of the P–Ir–P and C–Ir–C angles, the common geometry is best described as square pyramidal, with the nitrosyl in the axial site. This gives a close analogy with the related complex $Ir(NO)Cl_2(PPh_3)_2$[9] where the P–Ir–P angle is 170.2(1)° and the Cl–Ir–Cl angle 157.4(1)°. The analogy extends to the relative orientation of the nitrosyl group which in **4**, as in the dichloride, lies very close to the N–Ir–P plane; the dihedral angle between the planes ONIr and NIrP is *ca.* 3° in both molecules.

Mingos and Ibers[9] suggested that such an orientation may well be indicative of some form of NO phosphine interaction, and Robinson and co-workers[10] showed that a 'bisecting', 45° orientation, found in a (nitrosyl)bis(phosphine)bis(trifluoroacetyl)rhodium complex, was probably a result of steric interactions. In order to explore the factors which may contribute to support of the structure found for compound **4**, we have made an analysis of the steric interactions and possible molecular dynamics using van der Waals potentials calculations.

Using the CHEMX modelling package and incorporating only van der Waals interactions, the bent NO group was systematically rotated about the Ir–N bond and the remaining ligands allowed to move, *via* metal–ligand bond rotations, to minimise the total steric energy. The experimentally determined NO orientation seems to be in a shallow and broad well, greater than 90° wide; the total steric energy increases only by *ca.* 2 kcal mol^{-1} for a twist of 45°. There is a barrier, some 10 kcal high, at about 90° rotation. This result suggests that the orientation found for the NO group is not sterically controlled, and is a result of some form of nitrosyl–phosphine interaction, presumably $O \cdots P$. This would explain the NMR results discussed below which show non-equivalence of the PMe_3 groups.

The ^{31}P NMR spectrum of compound **4** at 25 °C consists of an AB quartet [centred at δ −30, ^2J(P–P) = 397 Hz], indicative of two magnetically inequivalent P nuclei, which does not change from −80 to +80 °C. This precludes *trans* or *cis* square-pyramidal C_{2v} geometries for the five-co-ordinate species where the PMe_3 groups would have been equivalent. A trigonal-bipyramidal geometry with phosphines occupying axial and equatorial positions and equatorial mesityl groups would have been a possibility were it not for the magnitude of ^2J(P–P) which indicates that the phosphine groups remain *trans* in solution.[11] The ^1H NMR spectrum does, however, show a reversible temperature dependence for the CH_3 groups of PMe_3. At −80 °C there is a deceptively simple, non-binomial triplet which at −50 °C becomes a doublet, at −40 °C a doublet of doublets, at −30 °C an apparent doublet of triplets, at −20 °C a doublet of quartets, and at 0 °C a doublet of triplets. The whole CH_3 region collapses at +10 °C to a broad line which finally splits to give the spectrum observed at 25 °C which persists from +20 °C to +60 °C. The system can be described as $A_9XX'A_9'$ and a general analysis has been given.[12] The ^1H NMR bands of the mesityl groups are temperature independent.

The above results suggest that the solid-state structure is retained in solution over the temperature range studied. The phosphorus atoms, although equivalent by symmetry (not taking the rigidity of the Ir–NO function into account) become magnetically inequivalent due to the interaction of one of these groups with the nitrosyl oxygen atom. This interaction is evidently strong enough to persist up to +80 °C when decomposition becomes evident, probably *via* O transfer to P since Me_3PO can initially be detected in the ^1H NMR spectra. The final product is a green solution having a broad isotropic EPR spectrum, but no metal complex could be isolated.

The temperature dependence of the ^1H NMR spectrum can, on the other hand, be explained by the rotations in the trimethylphosphine ligand that is *not* interacting with IrNO about the P–C and P–Ir bonds with concomitant variations of ^2J(P–H) and ^4J(P–H) and subsequent change in line shape in the methyl region as expected.[12]

Finally, whilst O_2, halogens, N_2O, CS_2 and alkyl hydroperoxides all react with compound **2** at 25 °C, no crystalline products could be obtained. There is no reaction with acetic acid, alcohols, dialkyl peroxides or catechol at temperatures up to *ca.* 100 °C.

Table 5 Crystal data and details of refinement

Compound	**1**	**2**	**4**
Formula	$C_{26}H_{42}IrS_2$	$C_{24}H_{40}IrP_2$	$C_{24}H_{40}IrNOP_2\cdot0.5C_4H_{10}O$
M	610.97	582.75	649.82
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$
a/Å	8.307(2)	9.622(3)	13.070(3)
b/Å	8.387(4)	14.034(2)	28.358(5)
c/Å	10.537(1)	19.255(1)	16.364(4)
α/°	86.39(2)	90	90
β/°	78.56(2)	98.09(2)	113.38(4)
γ/°	66.66(2)	90	90
U/Å^3	660.56	2574.21	5567.15
Z	1	4	8
D_c/g cm^{-3}	1.54	1.50	1.55
F(000)	307	1164	2616
μ/cm^{-1}	51.9	52.9	47.9
Total data measured	4807	7841	9452
No. of unique reflections	3132	4013	4773
No. of observed reflections $[F_o > 3\sigma(F_o)]$	2950	3586	4575
No. of parameters	158	283	336
Weighting scheme parameter *g* in $w = 1/[\sigma^2(F) + gF^2]$	0	0	0
Final *R*	0.0593	0.0378	0.0381
Final *R*′	0.0604	0.0385	0.0410

Table 6 Fractional atomic coordinates (× 10^4) for $Ir(mes)_2(SEt_2)_2$

Atom	*x*	*y*	*z*
Ir	0	0	0
S(1)	1759(3)	−1298(3)	1505(2)
C(1)	2282(10)	−1024(10)	−1444(9)
C(2)	3520(12)	−229(11)	−1735(10)
C(3)	4977(12)	−766(13)	−2749(11)
C(4)	5312(13)	−2156(13)	−3569(11)
C(5)	4132(12)	−2982(12)	−3294(10)
C(6)	2688(12)	−2456(10)	−2294(9)
C(11)	3089(13)	−3576(12)	1134(11)
C(12)	2135(19)	−4760(14)	1311(15)
C(21)	485(12)	−1430(14)	3101(10)
C(22)	1676(17)	−2164(16)	4105(12)
C(121)	1408(14)	−3387(13)	−2122(11)
C(161)	3162(14)	1442(13)	−943(13)
C(141)	6891(16)	−2717(17)	−4690(14)

Table 7 Fractional atomic coordinates (× 10^4) for $Ir(mes)_2(PMe_3)_2$

Atom	*x*	*y*	*z*
Ir	4936.8(3)	92.7(2)	2405.3(2)
P(1)	6390(3)	−372(2)	1615(1)
P(2)	3458(3)	531(2)	3193(1)
C(11)	3631(8)	822(5)	1604(4)
C(12)	3874(9)	1792(5)	1444(5)
C(13)	3018(10)	2283(7)	914(5)
C(14)	1922(12)	1838(8)	515(6)
C(15)	1657(10)	892(8)	643(5)
C(16)	2476(10)	393(6)	1170(5)
C(21)	6268(9)	−568(6)	3220(5)
C(22)	6040(10)	−1530(6)	3424(5)
C(23)	6867(11)	−1934(7)	4003(6)
C(24)	7936(12)	−1447(8)	4400(5)
C(25)	8176(10)	−526(8)	4199(5)
C(26)	7377(10)	−86(6)	3635(5)
C(121)	5084(11)	2323(7)	1877(6)
C(141)	1000(14)	2388(10)	−80(7)
C(161)	2136(12)	−637(7)	1275(7)
C(221)	4865(11)	−2108(6)	3014(6)
C(241)	8851(15)	−1940(10)	5005(6)
C(261)	7678(12)	948(7)	3467(7)
C(211)	1659(13)	86(11)	2979(8)
C(212)	3915(15)	181(9)	4090(6)
C(213)	3239(15)	1821(7)	3276(7)
C(111)	5590(21)	−1206(13)	938(11)
C(112)	7008(23)	556(14)	1094(12)
C(113)	7965(22)	−1075(14)	1946(11)
C(11B)	6411(35)	−1644(21)	1460(18)
C(12B)	6010(39)	107(22)	725(19)
C(13B)	8249(33)	−99(19)	1857(17)

Group site occupancies for C(111), C(112), C(113) and C(11B), C(12B), C(13B) are 0.547 69 and 0.452 31 respectively.

Experimental

Microanalyses were by MEDAC Ltd, Brunel University and Imperial College Laboratories. General techniques have been described.[13] The NMR data were obtained on a JEOL EX-270 spectrometer at 270 (^{1}H) or 100 MHz (^{31}P) or a FX90Q (89.55, ^{1}H; 36.2 MHz, ^{31}P) referenced internally on residual H impurity in the solvent (δ 7.15, C_6D_6; 7.26, $CDCl_3$) and to external H_3PO_4. Mass spectra were by electron impact and the isotopic envelope was calculated for ^{191}Ir (37.3%), ^{193}Ir (62.7%).

Commercial chemicals were from Aldrich; $Mg(mes)_2(thf)_2$ was prepared as described.[14] Nitric oxide (British Oxygen Co.) was passed through a bed of NaOH pellets and a copper spiral cooled in solid CO_2.

The literature preparation of $IrCl_3(SEt_2)_3$[15] using $(NH_4)_2IrCl_6$ as source gives both *mer* and *fac* isomers. The following procedure gives good yields (85–90%) of essentially pure *mer* isomer according to NMR spectra. A mixture of Johnson Matthey $IrCl_3\cdot nH_2O$ (*ca.* 53% Ir; 3.0 g, 8.5 mmol) in 2-methoxyethanol (HPLC grade, 50 cm^3) and Et_2S (2.5 g, 27 mmol) was refluxed for 1 h in air. After cooling to 20 °C and filtering off any undissolved material, water was added to the filtrate until precipitation of yellow needles of the *mer* product was complete. The crystals were dried at 80 °C for 12 h under vacuum.

trans-*Bis(diethyl sulfide)bis(*2,4,6-*trimethylphenyl)iridium*(II) **1**.—To a stirred suspension of *mer*-$IrCl_3(SEt_2)_3$ (0.7 g, 1.23 mmol) in Et_2O (30 cm^3) at −78 °C was added, *via* a cannula, a suspension of $Mg(mes)_2(thf)_2$ (1.26 g, 3.1 mmol) in Et_2O (50 cm^3) and the mixture allowed to warm to room temperature when the colour changed from yellow to brown. After *ca.* 12 h of stirring, thf (30 cm^3) was added and the mixture refluxed (3 h) after which the volatiles were removed under vacuum. The brown residue was extracted with hexane (3 × 50 cm^3), the extracts combined, filtered and concentrated to *ca.* 10 cm^3 when green-brown crystals appeared. Cooling (−20 °C) for 12 h gave compound **1**. Yield: 0.2 g, 27% based on $IrCl_3(SEt_2)_3$.

Table 8 Fractional atomic coordinates ($\times 10^4$) for Ir(mes)$_2$(NO)(PMe$_3$)$_2$·0.5Et$_2$O

Atom	*x*	*y*	*z*
Ir(1)	0	344.6(1)	2500
Ir(2)	0	2844.8(1)	7500
N(1)	0	1016(4)	2500
N(2)	0	3518(4)	7500
O(1)	424(12)	1276(5)	2280(10)
O(2)	640(11)	3774(4)	7717(9)
P(1)	1181(2)	320(1)	1750(2)
P(2)	1931(2)	2821(1)	8251(2)
C(11)	1452(7)	223(3)	3740(6)
C(12)	1827(7)	−248(3)	3966(7)
C(13)	2806(8)	−324(3)	4716(7)
C(14)	3492(7)	4(4)	5265(7)
C(15)	3115(7)	462(3)	5052(7)
C(16)	2131(7)	580(3)	4327(6)
C(21)	218(6)	2721(3)	6263(6)
C(22)	311(6)	3080(3)	5683(6)
C(23)	565(7)	2960(3)	4956(6)
C(24)	732(7)	2489(3)	4749(6)
C(25)	608(7)	2153(3)	5284(6)
C(26)	355(7)	2254(3)	6035(6)
C(101)	2621(9)	465(6)	2396(9)
C(102)	800(12)	704(7)	769(10)
C(103)	1280(16)	−237(6)	1268(15)
C(121)	1191(9)	−669(4)	3430(8)
C(141)	4586(8)	−111(4)	6046(7)
C(161)	1877(9)	1098(3)	4187(8)
C(201)	2727(9)	2969(6)	7609(7)
C(202)	2490(10)	2265(5)	8732(16)
C(203)	2480(10)	3233(7)	9189(9)
C(221)	188(8)	3601(3)	5819(7)
C(241)	1040(8)	2392(4)	3968(6)
C(261)	252(9)	1833(3)	6563(7)
O(20)	5000	1146(10)	7500
C(1)	4209(17)	1253(8)	7505(15)
C(2)	3541(36)	1138(14)	7947(30)
C(2B)	3105(34)	1290(14)	7051(28)

trans-*Bis*(2,4,6-*trimethylphenyl*)*bis*(*trimethylphosphine*)-*iridium*(II) **2**.—To compound **1** (0.2 g, 0.3 mmol) in Et$_2$O (20 cm^3) was added an excess of PMe$_3$ (0.2 cm^3) when the solution became purple. Removal of volatiles after 2 h and extraction of the residue with hot hexane (3 × 20 cm^3) followed by cooling (−20 °C, *ca.* 5 h) of the filtered solution gave an essentially quantitative yield of **2** as light purple hexagonal plates that can be handled in air for short periods.

The same procedure gave the PMe$_2$Ph (m.p. 205–207 °C) and PEtPh$_2$ complexes as purple prisms from Et$_2$O; they were characterised by analysis.

cis-*Dicarbonyl*(*diethyl sulfide*)(2,4,6-*trimethylphenyl*)-*iridium*(I) **3**.—To a solution of compound **1** (0.05 g, 0.08 mmol) in thf (10 cm^3) was introduced CO for 5 min when the colour changed from brown-green to yellow. Removal of volatiles, extraction of the residue with hexane (3 × 10 cm^3), filtration and concentration (*ca.* 2 cm^3) followed by cooling (−20 °C) produced yellow needles in essentially quantitative yields. Mass spectrum: m/z 448 $(M)^+$, 430 $(M - \mathrm{CO})^+$, 402 $(M - 2\mathrm{CO})^+$ and 338 $(M - \mathrm{mes})^+$. IR (hexane): 2043 and 1971 cm^{-1} (CO). ^{1}H NMR (C$_6$D$_6$): δ 0.6 (t, 6 H, *Me*CH$_2$S), 2.1 (q, 4 H, MeC*H*$_2$S), 2.2 (s, 3 H, *p*-Me), 2.65 (s, 6 H, *o*-Me) and 6.98 (s, 2 H, aromatic H).

trans-(*Nitrosyl*)*bis*(2,4,6-*trimethylphenyl*)*bis*(*trimethylphosphine*)*iridium*(III) **4**.—Through a solution of compound **2** (0.1 g, 0.17 mmol) in toluene (20 cm^3) at −78 °C was passed NO for 10 min when the purple solution became brown. Warming and work-up as above, extraction of the residue with hexane (3 × 20 cm^3), concentration (to 5 cm^3) and cooling (5 h, −20 °C) gave yellow needles in quantitative yield. X-Ray-quality crystals were best obtained from Et$_2$O. IR (Nujol): 1519 cm^{-1} (NO). NMR (C$_6$D$_6$, 25 °C): ^{1}H, δ 1.05 (t, 18 H, PMe$_3$), 1.87 (s, 6 H, *p*-Me), 2.15 (s, 6 H, *o*-Me), 2.25 (s, 6 H, *o*-Me) and 6.9 (s, 4 H, aromatic H); ^{31}P, δ −30 [AB quartet, ^2J(P–P) = 397 Hz]. For variable-temperature NMR spectra see text.

Reaction of Compound **2** *with Dihydrogen.*—A solution of compound **2** (0.1 g, 0.17 mmol) in thf (10 cm^3) in a Fisher–Porter bottle under N$_2$ was pressurised (80 psi, *ca.* 5.5 × 10^5 Pa) with H$_2$; the purple solution became yellow within 5 min. After pressure release and removal of volatiles the residue was crystallised as yellow needles from hexane after reduction in volume to *ca.* 2 cm^3 at −78 °C (2 h). The ^{1}H NMR spectrum identified IrH$_5$(PMe$_3$)$_2$.[7] NMR (C$_6$D$_6$): ^{1}H, δ −9.42 [t, 5 H, IrH$_5$, ^2J(P–H) = 11.7 Hz] and 1.6 (m, 18 H, PMe$_3$); ^{31}P-{^{1}H}, δ −53 (s) selectively decoupling CH$_3$; −53 [sext, ^2J(P–H) = 11.7 Hz].

trans-*Bis*(*pyridine*)*bis*(2,4,6-*trimethylphenyl*)*iridium*(II) **5**.—To compound **1** (0.05 g, 0.1 mmol) in Et$_2$O (20 cm^3) was added an excess of pyridine (0.2 cm^3) and the mixture stirred for 2 h. Removal of volatiles from the green-yellow solution and washing of the residue with hexane followed by dissolution in CH$_2$Cl$_2$ (10 cm^3) and addition of hexane gave a precipitate of **5**. The EPR spectrum is similar to that of **1**.

Crystallography.—Crystals used for the X-ray work were sealed in capillaries under argon. All crystallographic data were recorded using a Delft Instruments FAST TV Area detector diffractometer situated at the window of a rotating-anode generator equipped with a molybdenum anode and graphite monochromator, giving λ(Mo-Kα) = 0.710 69 Å. Slightly more than one hemisphere of data was recorded as previously outlined,[16] with a crystal-to-detector distance of 40 mm and a detector swing angle of 25°. The range of coverage of θ was thus −10 to >30° in the equatorial plane. The measurement of $\chi = 0$ 'main' regions and $\chi = 90°$ 'cusp' regions gave a minimum of 95% of all data accessible in the specified θ range, plus additional reflections outside the range in particular areas of reciprocal space. All reflections were included in the processing and merging, but only those with $F > 3\sigma(F)$ for the subsequent calculations. The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. Absorption corrections were applied using the DIFABS method.[17] Non-hydrogen atoms were refined anisotropically, except the disordered methyl carbons in compound **2**. All hydrogens were included in idealised positions with group U_{iso} values for **1** and **2**, except for those on the disordered methyl carbons in **2**, but only aryl hydrogens were included for **4**. Crystal data and experimental details are given in Table 5. Tables of fractional atomic coordinates are given in Tables 6–8. The CHEMX modelling package was from Chemical Design Ltd, Oxford, April 1991 release.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for provision of X-ray facilities (to M. B. H.) and Johnson Matthey plc for a loan of iridium.

References

1 R. S. Hay-Motherwell, S. U. Koschmieder, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 2821.
2 (*a*) R. S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, in the press; (*b*) *Polyhedron*, 1991, **10**, 1457.
3 N. Serpone and M. A. Jamieson, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, p. 1120.

4 (*a*) H. D. Empsall, P. N. Heys, W. S. McDonald, M. C. Norton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1978, 1119 and refs. therein; (*b*) R. Mason, K. M. Thomas, H. D. Empsall, S. R. Fletcher, P. N. Heys, E. M. Hyde, C. E. Jones and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1974, 612.

5 S. Zecchin, G. Zotti and G. Pilloni, *J. Organomet. Chem.*, 1985, **294**, 37.

6 P. Piraino, F. Faraone and R. Pietropaolo, *J. Chem. Soc., Dalton Trans.*, 1972, 2319.

7 E. K. Barefield, *Inorg. Synth.*, 1974, **15**, 34.

8 B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, 1966, **7**, 277.

9 D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

10 A. M. R. Galas, M. B. Hursthouse, D. S. Moore and S. D. Robinson, *Inorg. Chim. Acta*, 1983, **77**, L135.

11 P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, 1979.

12 R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.

13 A. A. Danopoulos, A. C. C. Wong, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 315.

14 W. Seidel and J. Bürger, *Z. Anorg. Allg. Chem.*, 1978, **447**, 195.

15 G. B. Kaufman, *Inorg. Synth.*, 1963, **7**, 224.

16 A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 1855.

17 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 1980.

Received 26*th June* 1992; *Paper* 2/03384D