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Polydentate ligands containing phosphorus
XV*. The synthesis and structure of η^4-1,5-cyclooctadiene-η^2-tris(diphenylthiophosphinoyl)methanidoiridium(I), (COD)Ir(TrisS$_3$)

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Abstract

η^4-1,5-Cyclooctadiene-η^2-tris(diphenylthiophosphinoyl)methanidoiridium(I), (COD)Ir(TrisS$_3$), was synthesized by the reaction of [(COD)IrCl]$_2$ with lithium tris(diphenylthiophosphinoyl)methanide, Li{[Ph$_2$P(S)]$_3$C}, in methylene chloride. A crystallographic structural determination was carried out on a yellow crystal in the monoclinic system of space group $P2_1/n$. The unit cell dimensions are $a = 10.826(3)$, $b = 21.659(6)$, $c = 17.487(5)$ Å, $\beta = 100.23(2)°$ and $Z = 4$. The coordination about iridium is square planar with the TrisS$_3^-$ ligand showing bidentate behavior with one of the P(S) groups being non-coordinated. The variable temperature ^{31}P{^{1}H} NMR spectra indicate fluxional behavior of the TrisS$_3^-$ ligand at room temperature and non-fluxional behavior at −80 °C.

Introduction

The recently discovered series of ligands of the type [Ph$_2$P(X)][Ph$_2$P(Y)][Ph$_2$P(Z)]CH, HTrisXYZ, where X, Y and Z are various combinations of lone pairs of electrons and the chalcogens O, S and Se [1, 2], their anionic derivatives TrisXYZ$^-$ [3] and their methyl analogues, e.g. (Me$_2$P)$_3$CH [4], {(Me$_2$P)$_3$C}$^-$ [5], [Me$_2$P(S)]$_3$CH [6] and {[Me$_2$P(S)]$_2$-[Ph$_2$P(S)]C}$^-$ [7] have shown very interesting chemistry and ligand behavior [8–12]. The most investigated of the anionic ligands, TrisS$_3^-$, can bond as a tridentate tripodal ligand [13] or as a bidentate ligand [14]. We report here the synthesis, structure and variable temperature ^{31}P{^{1}H} NMR of another complex of TrisS$_3^-$ in which the ligand is bidentate, viz. (COD)IrTrisS$_3$.

Experimental

Spectroscopy

NMR spectra (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) were obtained on an IBM WP200 spectrometer. Positive ^{31}P chemical shifts are reported to the high frequency ('downfield') side of 85% H$_3$PO$_4$. Carbon and proton chemical shifts are referenced to tetramethylsilane. Fast atom bombardment (FAB) mass spectra were obtained with a VG Analytical VG3070E instrument with *m*-nitrobenzyl alcohol as the supporting matrix.

Synthesis of (COD)Ir(TrisS$_3$)

The starting materials [(COD)IrCl]$_2$ [15] and LiTrisS$_3$ [3d] were prepared as previously described. A solution of 0.67 g (1.0 mmol) of LiTrisS$_3$ dissolved in 20 ml of CH$_2$Cl$_2$ was added dropwise with stirring to a solution of 0.336 g (0.50 mmol) of [COD)IrCl]$_2$ in 20 ml of CH$_2$Cl$_2$ under an inert atmosphere of Ar. The mixture was stirred for 12 h then filtered via cannula through Celite. The Celite was washed with two 5 ml portions of CH$_2$Cl$_2$, which were added to the filtrate. The solvent was removed under reduced pressure to yield a yellow–brown residue. The residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O at 0 °C to yield 0.71 g (74%) of (COD)IrTrisS$_3$, m.p. 162 °C (dec.). MW (calc.): 964.1. Found: FAB-MS: 965 (M+1, 100% rel. int.), 857 (M−COD+1, 46.3%), 856 (M−COD, 40.0%). FAB-MS: isotope abundance mass calculation for M+1(C$_{45}$H$_{43}$IrP$_3$S$_3$): 963 (51.1% of M+1 peak), 964 (27.5%), 965 (100%), 966 (51.0%), 967 (25.0%). Found: 963 (47.1%), 964 (50.9%), 965

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*For Part XIV see ref. 12.

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(100%), 966 (69.8%), 967 (16.1%). $^{31}P\{^1H\}$ NMR (23 °C, $CDCl_3$, 80.90 MHz): 38.1 (s). $^{31}P\{^1H\}$ NMR (−80 °C, CH_2Cl_2 with a concentric capillary of d_6-acetone to provide lock, 80.90 MHz): 40.0 (t, $^2J[P(S)_{coord}–P(S)_{free}] = 14.6$, 1P, $P(S)_{free}$), 31.4 (d, $J = 14.6$, 2P, $P(S)_{coord}$). $^{13}C\{^1H\}$ NMR (23 °C, $CDCl_3$, 50.29 MHz): 135.0 (d, $^1J(^{31}P–^{13}C) = 92.1$, Ph–C(1)), 133.4 (d, $^2J(P–C) = 9.4$, Ph–C(2,6)), 130.1 (s, Ph–C(4)), 127.2 (d, $^3J(P–C) = 13.2$, Ph–C(3, 5)), 66.7 (s, COD–CH), 31.7 (s, COD–CH_2). ^1H NMR (23 °C, $CDCl_3$, 200 MHz): 7.94–7.84 (m, *ortho*-Ph), 7.27–7.07 (m, *meta-*, *para*-Ph), 3.75 (br s, COD–CH), 2.18–2.15 (br m, COD–CH_2, 4H), 1.67–1.59 (m, COD–CH_2, 4H).

Crystallographic structural determination of (COD)IrTrisS$_3$

A yellow single crystal of (COD)IrTrisS$_3$, grown from CH_2Cl_2/EtOH, was used in the crystallographic structural determination. Details concerning the crystal data collection and data refinement are given in Table 1.

Results and discussion

The reaction of $[(COD)IrCl]_2$ and LiTrisS$_3$ (1:2 molar ratio) in methylene chloride yields (COD)IrTrisS$_3$ in good yield. The ^{31}P NMR spectrum at room temperature is a singlet, which indicates that all three P(S) groups are equivalent, either stereochemically in a static structure, or more likely, due to averaging in a fluxional/exchange kinetic process. At −80 °C the ^{31}P spectrum is of an AX_2-type with a doublet at 31.4 ppm and a triplet at 40.0 ppm with a $^2J(P–P)$ of 14.6 Hz. This is consistent with a square planar coordination geometry about iridium with two P(S) groups coordinated (31.4 ppm) and one P(S) group non-coordinated (40.0 ppm). This coordination geometry has also been observed in similar $TrisO_nS_{3-n}^-$ complexes (where $n = 0$, 2 and 3) of rhodium(I), iridium(I) and platinum(II), in particular: (COD)Ir(TrisO$_3$) [16], (COD)Rh(TrisS$_3$) [14b], (CO)$_2$IrTrisS$_3$ [14b], (Et$_3$P)PtCl(TrisS$_3$) [14a] and (COD)Rh(TrisO$_2$S) [12].

The molecular structural determination of (COD)Ir(TrisS$_3$) has confirmed the bidentate nature of TrisS$_3$. Figure 1 gives the ORTEP view of the molecule with only the *ipso* carbons of the phenyl groups displayed for purposes of clarity. Figure 2 gives a better perspective of the iridium coordination and of the folding of the six-membered chelate ring. Selected bond lengths and angles are given in Tables 2 and 3, respectively. Table 4 gives the atomic coordinates.

TABLE 1. Crystal and refinement data

Compound	(COD)Ir(TrisS$_3$)
Formula	$C_{45}H_{42}IrP_3S_3$
Formula weight	964.1
Crystal color, habit	yellow rectangular prism
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.826(3)
b (Å)	21.659(6)
c (Å)	17.487(5)
β (°)	100.23(2)
V (Å^3)	4035(2)
Z	4
D_{calc} (g/cm^3)	1.587
Crystal size (mm)	0.2×0.2×0.4
μ(Mo Kα) (mm^{-1})	3.593
Diffractometer	Siemens R3m/V
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	298
2θ Range (°)	3.5–50.0
Scan type	Wyckoff
Monochromator	highly oriented graphite crystal
Index ranges	$0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 25$ $-20 \leqslant l \leqslant 20$
No. reflections measured	7741
No. independent reflections ($R_{int} = 5.85\%$)	7116
Observed reflections ($F > 3.0\sigma(F)$)	4886
Absorption correction	semi-empirical
Transmission factors; max, min.	0.9598, 0.5981
Refinement system	Siemens SHELXTL PLUS (VMS)
Solution	direct methods
No. parameters refined	470
R^a (%)	5.33
$R_w{}^b$ (%)	4.48
Goodness-of-fit^c	1.18

$^a R = \Sigma|F_o - F_c|/\Sigma F_o$. $^b R_w = \Sigma|(F_o - F_c)(w)^{1/2}|/\Sigma F_o(w)^{1/2}$. $^c GOF = [\Sigma\{(w)(F_o - F_c)^2\}/M - N]^{1/2}$, where M = no. of observed reflections and N = no. of parameters refined.

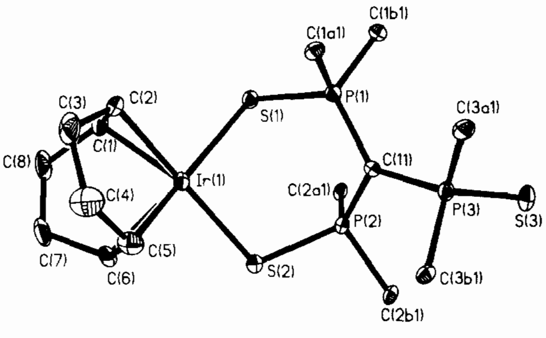

Fig. 1. ORTEP diagram of $(C_8H_{12})Ir\{[SP(C_6H_5)_2]_3C\}$ with H atoms omitted and showing only the *ipso* carbons of the phenyl groups.

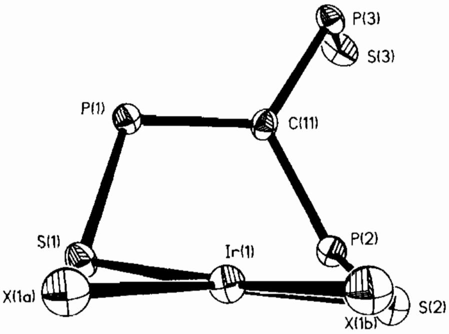

Fig. 2. ORTEP diagram of $C_8H_{12}Ir\{[SP(C_6H_5)_2]_3C\}$ showing the chelate ring and coordination geometry about iridium. X(1a) and X(1b) are the centroids of the C(1)–C(2) and C(5)–C(6) double bonds, respectively.

TABLE 2. Selected bond lengths (Å) in $C_8H_{12}Ir\{[SP(C_6H_5)_2]_3C\}$

Ir(1)–S(1)	2.382(2)	Ir(1)–S(2)	2.326(3)
Ir(1)–C(1)	2.142(10)	Ir(1)–C(2)	2.152(10)
Ir(1)–C(5)	2.108(9)	Ir(1)–C(6)	2.141(8)
S(1)–P(1)	2.031(3)	S(2)–P(2)	2.039(3)
S(3)–P(3)	1.972(4)	P(1)–C(1A1)	1.832(9)
P(1)–C(1B1)	1.825(8)	P(1)–C(11)	1.742(8)
P(2)–C(2A1)	1.828(8)	P(2)–C(2B1)	1.825(9)
P(2)–C(11)	1.758(9)	P(3)–C(3A1)	1.831(10)
P(3)–C(3B1)	1.829(8)	P(3)–C(11)	1.789(9)
C(1)–C(2)	1.429(16)	C(1)–C(8)	1.504(14)
C(2)–C(3)	1.511(14)	C(3)–C(4)	1.485(16)
C(4)–C(5)	1.507(16)	C(5)–C(6)	1.379(14)
C(6)–C(7)	1.544(15)	C(7)–C(8)	1.477(15)
Ir(1)–X(1a)[a]	2.025	Ir(1)–X(1b)[a]	2.010

[a] X(1a) and X(1b) are the centroids of the C(1)–C(2) and C(5)–C(6) double bonds, respectively.

TABLE 3. Selected bond angles (°) in $C_8H_{12}Ir\{[SP(C_6H_5)_2]_3C\}$

S(1)–Ir(1)–S(2)	95.3(1)	S(1)–Ir(1)–C(1)	90.0(2)
S(2)–Ir(1)–C(1)	152.7(3)	S(1)–Ir(1)–C(2)	89.1(2)
S(2)–Ir(1)–C(2)	167.2(3)	C(1)–Ir(1)–C(2)	38.9(4)
S(1)–Ir(1)–C(5)	155.8(3)	S(2)–Ir(1)–C(5)	89.8(3)
C(1)–Ir(1)–C(5)	96.3(4)	C(2)–Ir(1)–C(5)	81.5(4)
S(1)–Ir(1)–C(6)	165.7(3)	S(2)–Ir(1)–C(6)	87.0(3)
C(1)–Ir(1)–C(6)	81.8(4)	C(2)–Ir(1)–C(6)	91.7(4)
C(5)–Ir(1)–C(6)	37.9(4)	Ir(1)–S(1)–P(1)	108.3(1)
Ir(1)–S(2)–P(2)	109.3(1)	S(1)–P(1)–C(1A1)	107.9(3)
S(1)–P(1)–C(1B1)	103.9(3)	C(1A1)–P(1)–C(1B1)	103.6(4)
S(1)–P(1)–C(11)	112.0(3)	C(1A1)–P(1)–C(11)	114.3(4)
C(1B1)–P(1)–C(11)	114.2(4)	S(2)–P(2)–C(2A1)	110.4(3)
S(2)–P(2)–C(2B1)	102.4(3)	C(2A1)–P(2)–C(2B1)	103.3(4)
S(2)–P(2)–C(11)	114.8(3)	C(2A1)–P(2)–C(11)	110.8(4)
C(2B1)–P(2)–C(11)	114.3(4)	S(3)–P(3)–C(3A1)	109.9(3)
S(3)–P(3)–C(3B1)	112.7(3)	C(3A1)–P(3)–C(3B1)	100.7(4)
S(3)–P(3)–C(11)	114.5(3)	C(3A1)–P(3)–C(11)	111.9(4)
C(3B1)–P(3)–C(11)	106.3(4)	Ir(1)–C(1)–C(2)	70.9(6)
Ir(1)–C(1)–C(8)	111.8(7)	C(2)–C(1)–C(8)	123.6(9)
Ir(1)–C(2)–C(1)	70.2(6)	Ir(1)–C(2)–C(3)	112.8(6)
C(1)–C(2)–C(3)	121.7(8)	C(2)–C(3)–C(4)	114.1(10)
C(3)–C(4)–C(5)	115.3(9)	Ir(1)–C(5)–C(4)	112.4(7)
Ir(1)–C(5)–C(6)	72.4(5)	C(4)–C(5)–C(6)	123.0(10)
Ir(1)–C(6)–C(5)	69.8(5)	Ir(1)–C(6)–C(7)	112.0(6)
C(5)–C(6)–C(7)	125.7(10)	C(6)–C(7)–C(8)	114.9(8)
C(1)–C(8)–C(7)	116.0(10)	P(1)–C(1A1)–C(1A2)	121.1(7)
P(1)–C(11)–P(3)	125.7(5)	P(2)–C(11)–P(3)	118.7(4)
S(1)–Ir(1)–X(1a)[a]	89.5	P(1)–C(11)–P(2)	115.4(5)
X(1a)–Ir(1)–X(1b)[a]	87.5	S(2)–Ir(1)–X(1b)[a]	88.3

[a] X(1a) and X(1b) are the centroids of the C(1)–C(2) and C(5)–C(6) double bonds, respectively.

The coordination about iridium (S1, S2, X1a and X1b, where X1a and X1b are the centroids of the C1–C2 and C5–C6 double bonds, respectively) is a slightly distorted square plane with a twist of 9° between the dihedral planes S1–Ir–S2 and X1a–Ir–X1b. The iridium bond distances to the centroids of the double bonds are 2.025 and 2.010 Å, which are slightly shorter than the average of 2.098 Å for the four double bonds in the five coordinate iridium complex $(COD)_2IrSnCl_3$ [17]. The structure of the coordinated COD ligand is otherwise normal [12, 14b, 17, 18].

The $TrisS_3^-$ is bound to Ir via two sulfur atoms with an average bond length of 2.354 Å, essentially the same as the 2.359 Å observed in $(CO)_2Ir(TrisS_3)$ [14b]. The third P(S) group is not coordinated and is in fact pointed away from iridium. The coordinated P(S) groups have P–S bond lengths of 2.031(3) and 2.039(3) Å compared to the shorter non-coordinated P–S bond length of 1.972(4) Å. It is generally true that phosphine chalcogenide bonds lengthen upon coordination as is observed here. The P–C bonds within the chelate ring, 1.742(8) and 1.758(9) Å, are slightly shorter than the P–C distance (1.789 Å) of the non-coordinated P(S) group. The $TrisS_3^-$ ligand remains planar at the central carbon, which lies only 0.028 Å out of the plane of the three phosphorus atoms. The bond length and bond angle data suggest that considerable delocalization remains within the ligand when complexed as a bidentate ligand, which has been noted previously for $TrisS_3^-$ [14b], $TrisO_3^-$ [19] and $TrisO_2S^-$ [12]. Figure 2 shows that P2 lies very close (0.419 Å) to the best plane of S1, S2, X1a and X1b, so that four members of the chelate ring Ir, S1, S2 and P2 are nearly planar with P1 and C11 forming a two-atom 'flap' of a folded envelope, similar to the familiar folded envelope (with a one-atom flap) of five-membered rings. The structure of the $TriS_3^-$ ligand in $(COD)IrTrisS_3$ is essentially the same in all respects as was observed for $(CO)_2IrTrisS_3$ [14b].

Fast atom bombardment mass spectra of $(COD)IrTrisS_3$ gave strong peaks at $M+1$ and at $M-(COD)$ indicating the molecule is sufficiently stable to allow molecular weight determination via

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}[a]
Ir(1)	262(1)	1096(1)	8998(1)	32(1)
S(1)	−1055(2)	1005(1)	7758(1)	34(1)
S(2)	2054(2)	719(1)	8595(1)	37(1)
S(3)	2612(2)	1561(1)	5553(1)	47(1)
P(1)	−376(2)	1571(1)	7003(1)	30(1)
P(2)	1794(2)	730(1)	7412(1)	31(1)
P(3)	2207(2)	1904(1)	6524(1)	32(1)
C(1)	−1343(9)	998(6)	9549(6)	57(5)
C(2)	−1174(8)	1636(5)	9388(5)	45(4)
C(3)	−652(11)	2088(5)	10023(6)	70(5)
C(4)	740(11)	2108(6)	10204(8)	84(6)
C(5)	1397(9)	1560(5)	9925(6)	51(4)
C(6)	1230(9)	964(5)	10165(5)	48(4)
C(7)	334(10)	763(6)	10714(6)	70(5)
C(8)	−1001(11)	718(6)	10346(6)	73(5)
C(1A1)	−715(7)	2369(4)	7248(5)	33(3)
C(1A2)	−1383(8)	2762(4)	6697(6)	41(3)
C(1A3)	−1735(9)	3339(5)	6913(7)	57(4)
C(1A4)	−1439(10)	3516(5)	7681(8)	64(5)
C(1A5)	−768(10)	3134(5)	8235(6)	55(4)
C(1A6)	−375(8)	2567(5)	8014(6)	45(4)
C(1B1)	−1426(8)	1439(4)	6079(5)	33(3)
C(1B2)	−963(8)	1470(4)	5385(5)	40(3)
C(1B3)	−1780(9)	1372(5)	4685(5)	51(4)
C(1B4)	−3027(9)	1258(5)	4666(6)	57(4)
C(1B5)	−3491(9)	1246(5)	5355(6)	56(4)
C(1B6)	−2701(8)	1339(4)	6048(6)	41(3)
C(2A1)	818(7)	79(4)	7008(5)	31(3)
C(2A2)	185(9)	97(5)	6248(6)	47(4)
C(2A3)	−589(9)	−385(5)	5948(6)	57(4)
C(2A4)	−699(10)	−895(5)	6391(6)	61(5)
C(2A5)	−55(11)	−921(5)	7135(6)	67(5)
C(2A6)	702(9)	−440(5)	7451(5)	46(4)
C(2B1)	3347(8)	525(4)	7223(5)	34(3)
C(2B2)	3464(9)	232(5)	6514(5)	46(4)
C(2B3)	4650(11)	76(5)	6385(8)	67(5)
C(2B4)	5704(10)	200(5)	6925(9)	74(6)
C(2B5)	5575(9)	478(5)	7609(8)	63(5)
C(2B6)	4413(8)	641(4)	7747(6)	46(4)
C(3A1)	1587(8)	2688(4)	6353(6)	39(3)
C(3A2)	1055(9)	2864(5)	5603(6)	54(4)
C(3A3)	658(11)	3468(6)	5435(7)	77(6)
C(3A4)	795(11)	3896(6)	6012(8)	72(5)
C(3A5)	1285(10)	3727(5)	6756(7)	60(5)
C(3A6)	1682(8)	3132(5)	6933(6)	44(4)
C(3B1)	3604(7)	2051(4)	7257(5)	32(3)
C(3B2)	4774(8)	2118(4)	7054(6)	45(4)
C(3B3)	5794(8)	2269(5)	7613(7)	57(4)
C(3B4)	5659(9)	2364(5)	8366(6)	57(4)
C(3B5)	4502(9)	2304(5)	8575(6)	53(4)
C(3B6)	3469(9)	2141(4)	8028(5)	41(3)
C(11)	1200(7)	1428(4)	6981(5)	31(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

this method. The correlation coefficient for the observed versus calculated isotopic abundance mass distribution (see 'Experimental') is 0.89 and indicates that FAB-MS is a useful method for molecular weight determination of reasonably heavy molecules of this type.

Supplementary material

Tables of a complete listing of bond lengths, bond angles, anisotropic displacement coefficients, H atom coordinates and isotropic displacement coefficients (4 pages) and calculated and observed structure factors (26 pages) are available from the authors.

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