Half-Sandwich Pentamethylcyclopentadienyl Iridium Complexes Containing Sulfido and Selenido Ligands
X-Ray Crystal Structures of $Cp^*Ir(PMe_3)(S_6)$ and $Cp^*Ir(PMe_3)(Se_4)$

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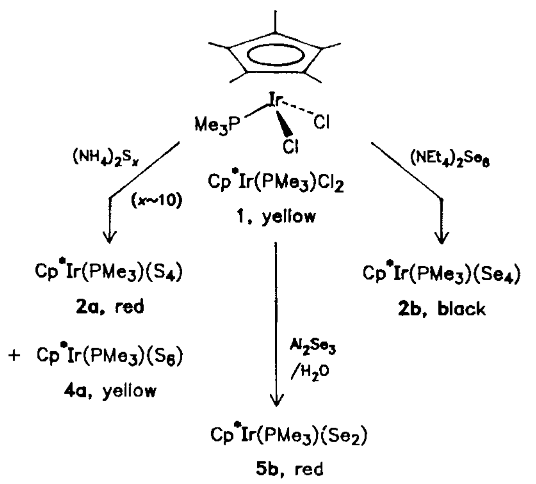
$Cp^*Ir(PMe_3)Cl_2$ (**1**) reacts with chalcogenide ligand sources such as $(NH_4)_2S_x$ ($x \approx 10$), $(NEt_4)_2Se_6$, and H_2Se to yield the half-sandwich complexes $Cp^*Ir(PMe_3)(S_n)$ [n = 4 (**2a**), 6 (**4a**)] and $Cp^*Ir(PMe_3)(Se_n)$ [n = 2 (**5b**), 4 (**2b**)]. Desulfurization of **4a** by PPh_3 leads to $Cp^*Ir(PMe_3)(S_5)$ (**3a**), while both **4a** and **3a** react with excess $P(nBu)_3$ to give **2a**. The geometries of the *cyclo*-oligochalcogenide ligands in **4a** and **2b** have been determined by X-ray crystallography.

Among the numerous transition metal cyclopentadienyl complexes with (unsubstituted) sulfur[1-4] and selenium[5] ligands, iridium compounds are missing so far. We therefore report on some mononuclear Cp*Ir complexes which we have obtained starting from $Cp^*Ir(PMe_3)Cl_2$ (**1**) (abbreviations: Cp = η^5-cyclopentadienyl, η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; Cp* = η^5-C_5Me_5).

Results and Discussion

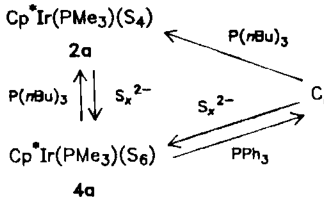
Bergman and co-workers[6] have found that the two halide ligands of **1** can be replaced by mercapto and alkylthio nucleophiles to give complexes of the type $Cp^*Ir(PMe_3)(SR)_2$ (R = H, Me, *t*Bu). We have similary observed that **1** reacts with ammonium polysulfide, $(NH_4)_2S_x$ ($x \approx 10$), in chloroform solution to produce a mixture of two *cyclo*-oligosulfido complexes $Cp^*Ir(PMe_3)(S_4)$ (**2a**) and $Cp^*Ir(PMe_3)(S_6)$ (**4a**) in almost quantitative yield. The products **2a** and **4a** can be separated by chromatography on silica gel, both are air-stable under ambient conditions. The corresponding *cyclo*-pentasulfido compound, **3a**, is not obtained in this reaction. This is surprising in view of the fact that sulfurization of $CpRh(PPh_3)_2$ with excess sulfur gives the *cyclo*-pentasulfido complex, $CpRh(PPh_3)(S_5)$, preferentially; the byproducts $CpRh(PPh_3)(S_4)$ and $CpRh(PPh_3)(S_6)$ convert spontaneously and quantitatively into $CpRh(PPh_3)(S_5)$ in solution[4].



The *cyclo*-pentasulfido complex **3a** is accessible by desulfurization of **4a** by using triphenylphosphane.

$$\underset{\textbf{4a}}{Cp^*Ir(PMe_3)(S_6)} + PPh_3 \xrightarrow[(CH_2Cl_2)]{40^\circ C} \underset{\textbf{3a}}{Cp^*Ir(PMe_3)(S_5)} + Ph_3PS$$

If excess tri-*n*-butylphosphane is used, both **4a** and **3a** are desulfurized to give **2a** in high yield (80–90%). The formation of dinuclear complexes is not observed, although compounds such as $Cp'_2Ti(\mu\text{-}S_2)_2TiCp'_2$[7] and $Cp^*(NO)M(\mu\text{-}S_2)_2M(NO)Cp^*$ (M = Cr, Mo, W)[8] are easily obtained from the corresponding mononuclear *cyclo*-pentasulfido half-sandwich complexes in the presence of tertiary phosphanes.



Both **2a** and **3a** take up sulfur from excess ammonium polysulfide, $(NH_4)_2S_x$, and **4a** is regenerated in moderate yields.

Only the *cyclo*-tetraselenido complex $Cp^*Ir(PMe_3)(Se_4)$ (**2b**) has been isolated from the reaction of **1** with the hexa-

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selenide salt $(NEt_4)_2Se_6$ at room temperature. If the selenium source is H_2Se (generated by hydrolysis of Al_2Se_3 in the reaction mixture), a diselenido complex **5b** is formed; the stable final product appears to be the phosphane-free tetramer, $Cp^*_4Ir_4(\mu\text{-}Se)_4$.

The Ph_3P analogs of **2a**, **4a**, and **2b** are readily prepared by starting from $Cp^*Ir(PPh_3)Cl_2$. The di- and oligonuclear chalcogenide derivatives of $Cp^*Ir(L)Cl_2$ [L = PMe_3 (**1**), PPh_3] will be described separately.

The composition of the new complexes **2a**–**4a**, **2b** and **5b** is unequivocally established by elemental analyses and the EI mass spectra which contain the molecular ion in all cases. The fragment of highest intensity is always $Cp^*Ir(E_2)^+$ [*m/z* = 392 (E = S) and 486 (E = Se)]. The ^1H-, ^{13}C-, and ^{31}P-NMR data are summarized in Table 1. X-ray crystallographic structure determinations were carried out for $Cp^*Ir(PMe_3)(S_6)$ (**4a**) and $Cp^*Ir(PMe_3)(S_4)$ (**2b**) in order to define the geometry of the *cyclo*-chalcogenide ligand within the sterically crowded coordination sphere of iridium (Figures 1 and 2).

Table 1. NMR spectroscopic characterization (all measurements in $CDCl_3$ at 0°C)

Compound	**1**	**2a**	**2b**	**3a**	**4a**	**5b**
^1H NMR						
$C_5(CH_3)_5$	1.68 s	1.81 d	1.84 d	1.72 d	1.72 d	1.85 d
$[^4J(P,H)]$	–	[2.7]	(1.8]	[2.3]	[2.7]	[1.8]
$P(CH_3)_3$	1.61 d	1.52 d	1.62	1.54 d	1.54 d	1.63 d
$[^2J(P,H)]$	[8.8]	[10.8]	[10.8]	[10.8]	[10.8]	[9.9]
^{13}C NMR						
$C_5(\mathit{C}H_3)_5$	8.9 s	9.3 s	9.7 s	8.7 s	8.8 s	9.6 s
$\mathit{C}_5(CH_3)_5$	91.0 d	96.7 s	96.3 d	97.0 d	97.2 s	96.2 d
$[^2J(P,C)]$	[3.4]		[2.3]			[2.3]
$P(CH_3)_3$	13.7	15.6 d	17.5 d	14.5 d	14.4 d	17.4
$[^1J(P,C)]$	[39.4]	[42.8]	[42.8]	[42.8]	[40.5]	[42.8]
^{31}P NMR	−27.0	−33.3	−37.5	−35.6	−36.1	−40.0

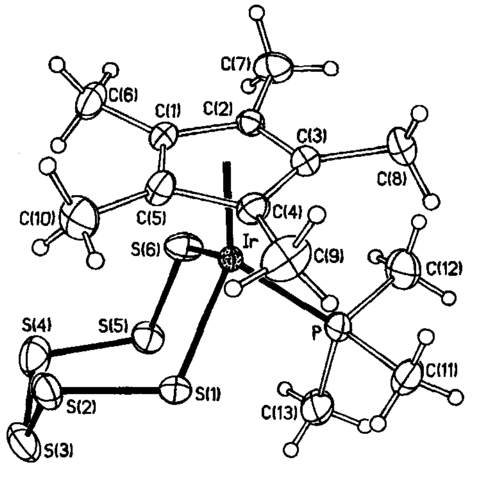


Figure 1. Molecular structure of $Cp^*Ir(PMe_3)(S_6)$ (**4a**) in the crystal. Selected bond distances [Å] and angles [°]: Ir–Cp* (ring center) 1.889(2), Ir–P 2.266(2), Ir–S(1) 2.358(2), Ir–S(6) 2.345(3), S(1)–S(2) 2.036(3), S(2)–S(3) 2.060(4), S(3)–S(4) 2.037(5), S(4)–S(5) 2.056(3), S(5)–S(6) 2.036(3); Cp*–Ir–P 130.1(2), Cp*–Ir–S(1) 122.1(2), Cp*–Ir–S(6) 119.5(2), P–Ir–S(1) 86.1(1), P–Ir–S(6) 89.1(1), S(1)–Ir–S(6) 101.1(1), Ir–S(1)–S(2) 111.6(1), S(1)–S(2)–S(3) 108.6(2), S(2)–S(3)–S(4) 107.5(2), S(3)–S(4)–S(5) 105.9(2), S(4)–S(5)–S(6) 109.5(2), Ir–S(6)–S(5) 120.3(1)

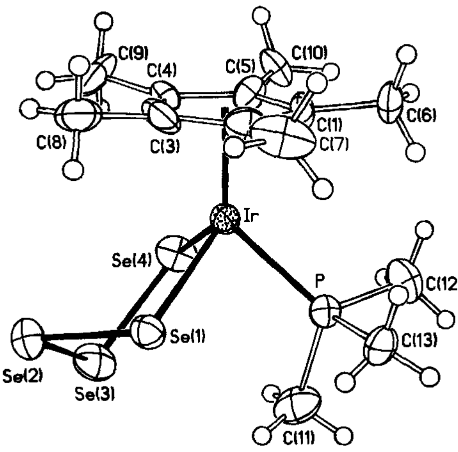
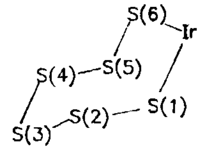
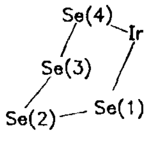


Figure 2. Molecular structure of $Cp^*Ir(PMe_3)(S_4)$ (**2b**) in the crystal. Selected bond distances [Å] and angles [°]: Ir–Cp* (ring center) 1.862(2), Ir–P 2.260(5), Ir–Se(1) 2.468(2), Ir–Se(4) 2.472(2), Se(1)–Se(2) 2.336(3), Sc(2)–Se(3) 2.313(3), Se(3)–Se(4) 2.361(3); Cp*–Ir–P 132.1(1), Cp*–Ir–Se(1) 122.4(1), Cp*–Ir–Se(4) 119.8(1), P–Ir–Se(1) 86.4(1), P–Ir–Se(4) 89.4(2), Se(1)–Ir–Se(4) 96.8(1) Ir–Se(1)–Se(2) 102.3(1), Se(1)–Se(2)–Se(3) 97.8(1), Se(2)–Se(3)–Se(4) 98.4(1), Ir–Se(4)–Se(3) 108.1(1)

Compounds **4a** and **2b** both crystallize as discrete molecules without significant intermolecular contacts. The structures are very similar and are based on a three-legged piano-stool geometry. Of primary interest is the conformation of the cycloalkane-analogous iridium-chalcogen ring systems; in both cases these conformations are similar to the parent cycloalkanes. In both cases the Ir atom, instead of occupying the uniquely puckered site in these odd-membered rings, occupies the site most remote from the unique site.



Iridium–sulfur ring system in **4a**



Iridium–selenium ring system in **2b**

The cyclopentane-analogous ring in **2b** is puckered at Se(2); the remaining four atoms form an almost perfect plane (the maximum deviation is less than 0.01 Å). The cycloheptane-analogous ring in **4a** has the chair conformation, the unique site being S(3). The deviations from planarity for the two four-membered planes [Ir, S(1), S(5), S(6)] and [S(1), S(2), S(4), S(5)] are greater than in **2b**, especially for the metal-containing plane in which S(6) is elevated by 0.14 Å. As a result of the placement of the metal atom in the ring system, these complexes are chiral. By chance, in both cases crystal growth has provided a spontaneous enantiomeric resolution.

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Experimental

IR: Perkin-Elmer 983G. – ^{1}H, ^{13}C, ^{31}P NMR: Jeol FX 90Q, $CDCl_3$ solutions, 0°C. – EI-MS: Varian MAT 8500 (70 eV); the most intense peak of the isotope pattern is listed. – The starting compounds $[Cp^*IrCl_2]_2$[9], $Cp^*Ir(PMe_3)Cl_2$[10], and $(NEt_4)_2Se_6$[11] were prepared according to the literature. All reactions and manipulations were routinely carried out under purified argon. Silica gel (Merck Kieselgel 60) for column chromatography (CC) was activated at 600°C overnight and stored under argon.

Sulfurization of $Cp^*Ir(PMe_3)Cl_2$ (**1**): A solution of excess ammonium polysulfide[12], $(NH_4)_2S_x$ ($x \approx 10$), in 2.5 ml of methanol was added dropwise to the yellow solution of 0.22 g (0.46 mmol) of **1** in 80 ml of $CHCl_3$. The color turned red immediately. The solution was stirred at room temp. for 3 h, then brought to dryness and the residue separated by CC on silica gel. Three zones were eluted successively which contained S_6 (pentane/CH_2Cl_2 2:1), $Cp^*Ir(PMe_3)(S_6)$ (**4a**, yellow, pentane/CH_2Cl_2 1:2), and $Cp^*Ir(PMe_3)(S_4)$ (**2a**, red, CH_2Cl_2). The *cyclo*-sulfido complexes **2a** and **4a** were recrystallized from $CHCl_3$/pentane at −25°C to give 0.15 g (61%) of red prisms of **2a** and 0.10 g (38%) of yellow-orange plates of **4a**.

(Pentamethylcyclopentadienyl)(cyclo-tetrasulfido)(trimethylphosphane)iridium (**2a**): M.p. 206°C. – MS: *m/z* (%) = 532 (20) $[M^+]$, 468 (20) $[M^+ - 2S]$, 436 (4) $[M^+ - 3S]$, 421 (6) $[M^+ - 3S - CH_3]$, 392 (100) $[M^+ - 2S - PMe_3]$.

$C_{13}H_{24}IrPS_4$ (531.8) Calcd. C 29.36 H 4.55 S 24.10
Found C 29.32 H 4.56 S 23.90

(Pentamethylcyclopentadienyl)(cyclo-hexasulfido)(trimethylphosphane)iridium (**4a**): M.p. 190°C. – MS: *m/z* (%) = 596 (0.3) $[M^+]$, 564 (2) $[M^+ - S]$, 532 (22) $[M^+ - 2S]$, 468 (25) $[M^+ - 4S]$, 436 (7) $[M^+ - 5S]$, 421 (8) $[M^+ - 5S - CH_3]$, 392 (100) $[M^+ - 4S - PMe_3]$.

$C_{13}H_{24}IrPS_6$ (595.9) Calcd. C 26.20 H 4.05 S 32.28
Found C 26.22 H 4.03 S 32.00

Desulfurization of $Cp^*Ir(PMe_3)(S_6)$ (**4a**)

a) *With Triphenylphosphane:* A yellow solution containing 0.12 g (0.21 mmol) of **4a** and 0.08 g (0.30 mmol) of triphenylphosphane in 80 ml of CH_2Cl_2 was kept under reflux for 40 min. Workup by CC on silica gel gave Ph_3PS (colorless, eluted with pentane/CH_2Cl_2 2:1, $Cp^*Ir(PMe_3)(S_5)$ (**3a**) (yellow-orange, eluted with pentane/CH_2Cl_2 1:2, and small amounts of $Cp^*Ir(PMe_3)(S_4)$ (**2a**) (red, eluted with neat CH_2Cl_2). Recrystallization from $CHCl_3$/pentane at −25°C left 0.10 g (88.5%) of yellow-orange needles of **3a** and ca. 0.01 g (9.4%) of red prisms of **2a**.

(Pentamethylcyclopentadienyl)(cyclo-pentasulfido)(trimethylphosphane)iridium (**3a**): M.p. 196°C. – MS: *m/z* (%) = 564 (2) $[M^+]$, 532 (24) $[M^+ - S]$, 500 (1) $[M^+ - 2S]$, 468 (26) $[M^+ - 4S]$, 436 (6) $[M^+ - 4S]$, 421 (8) $[M^+ - 4S - CH_3]$, 392 (100) $[M - 2S - PMe_3]$.

b) *With Tri-n-butylphosphane:* A threefold excess of tri-n-butylphosphane (0.23 g, 1.14 mmol) was used to abstract sulfur from **4a** (0.20 g, 0.38 mmol) in CH_2Cl_2 solution (80 ml). The color changed from yellow to red. The product **2a** (0.15 g, 84%) was isolated by CC on silica gel. The analogous desulfurization of $Cp^*Ir(PMe_3)(S_5)$ (**3a**) gave **2a** in 87% yield.

Selenization of $Cp^*Ir(PMe_3)Cl_2$ (**1**)

a) *With $(NEt_4)_2Se_6$:* A stirred solution of **1** (0.25 g, 0.53 mmol) in 60 ml of DMF was treated dropwise with a solution of 0.59 g (0.80 mmol) of $(NEt_4)_2Se_6$[11] in DMF (20 ml). The color of the solution changed gradually from dark green to brown and to dark red, and a brown precipitate of selenium was formed. The reaction mixture was stirred for 16 h, and the filtered solution was concentrated to a volumne of 5 ml. Upon CC on silica gel, a dark red band containing **2b** was collected by using pentane/CH_2Cl_2 (1:2). Recrystallization from hexane/chloroform at −25°C gave 0.35 g (92%) of dark red prisms of **2b**.

(Pentamethylcyclopentadienyl)(cyclo-tetraselenido)(trimethylphosphane)iridium (**2b**): M.p. 229°C. – MS: *m/z* (%) = 720 (30) $[M^+]$, 562 (46) $[M^+ - 2Se]$, 486 (100) $[M^+ - 2Se - PMe_3]$, 405 (16) $[M^+ - 3Se - PMe_3]$.

$C_{13}H_{24}IrPSe_4$ (719.4) Calcd. C 21.70 H 3.36 Se 43.90
Found C 21.85 H 3.36 Se 43.60

b) *With H_2Se:* Water (0.04 g, 2.2 mmol) was slowly added to a suspension of Al_2Se_3 (0.19 g, 0.63 mmol) in a $CHCl_3$/THF (1:1) solution (100 ml) of $Cp^*Ir(PMe_3)Cl_2$ (**1**) (0.30 g, 0.63 mmol) at ambient temperature. In the course of 2 d, the color changed from yellow-orange to dark red. The reaction mixture was filtered, the filtrate brought to dryness, and the residue purified both by CC on silica gel (pentane/CH_2Cl_2 1:2 as eluant) and recrystallization from hexane/chloroform mixtures at −25°C to give 0.05 g (14%) of dark red crystals of **5b**.

Table 2. Crystallographic data for $Cp^*Ir(PMe_3)(S_6)$ (**4a**) and $Cp^*Ir(PMe_3)(Se_4)$ (**2b**)

	4a	**2b**
	(a) Crystal Parameters	
Formula	$C_{13}H_{24}IrPS_6$	$C_{13}H_{24}IrPSe_4$
Formula weight	595.87	719.35
Crystal system	monoclinic	orthorhombic
Space group	$P2_2$	$P2_12_12_1$
a, Å	8.847(1)	8.803(3)
b, Å	13.654(2)	13.857(5)
c, Å	8.885(2)	15.588(4)
β, deg.	108.97(1)	
V, Å^3	1015.0(3)	1961.9(11)
Z	2	4
Cryst. dimens., mm	0.22 × 0.30 × 0.32	0.36 × 0.36 × 0.38
Cryst. color	orange	dark red
D(calc.), g · cm^3	1.950	2.435
μ(Mo-K_α), cm^{-1}	76.3	157.4
Temp., K	297	297
Transm., T(max)/T(min)	0.105/0.072	0.009/0.003
	(b) Data Collection	
Diffractometer	Nicolet R3m	
Monochromator	graphite	
Radiation	Mo-K_α (λ = 0.71073 Å)	
2Θ scan range, deg	4–60	4–55
Data collected	$\pm h, \pm k, +l$	$+h, +k, +l$
Rflns. collected	5866 (two forms)	2521
Indpt. rflns.	5848	2498
Indpt. obsvd. rflns. $F_0 \geq n\sigma(F_0)$	5266 (n = 4)	1957 (n = 3)
Std. rflns.	3 std/197 reflns	3 std/197 rflns
	(c) Refinement	
$R(F)$, %	3.37	4.43
$R(wF)$, %	4.42	4.72
Δ/σ(max)	0.05	0.03
$\Delta(\varrho)$, e Å^{-3}	2.47	1.18
N_0/N_v	27.3	11.2
GOOF	0.880	1.020

Table 3. Atomic coordinates (× 10^4) and isotropic thermal parameters ($Å^2 \times 10^3$) for Cp*Ir(PMe_3)(S_6) (**4a**); * equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U*
Ir	410.3(2)	5000	3177.5(2)	26.6(1)
S(1)	-788(2)	4810(2)	405(2)	47(1)
S(2)	-3215(2)	4879(3)	-253(3)	58(1)
S(3)	-3943(3)	6240(2)	-1220(3)	70(1)
S(4)	-3839(3)	7166(2)	608(4)	71(1)
S(5)	-1457(3)	7473(2)	1691(3)	49(1)
S(6)	-537(3)	6552(2)	3568(3)	47(1)
P	2452(2)	5731(2)	2597(3)	39(1)
C(1)	-714(8)	4311(5)	4907(9)	34(2)
C(2)	947(8)	4571(5)	5696(8)	30(2)
C(3)	1899(8)	3959(5)	5031(8)	34(2)
C(4)	857(9)	3429(5)	3744(9)	36(2)
C(5)	-786(11)	3627(6)	3732(12)	37(3)
C(6)	-2099(10)	4690(6)	5333(12)	49(3)
C(7)	1498(11)	5202(5)	7142(9)	48(3)
C(8)	3671(9)	3844(7)	5720(11)	50(3)
C(9)	1341(12)	2658(6)	2810(12)	56(4)
C(10)	-2218(11)	3115(6)	2666(12)	55(3)
C(11)	3596(10)	4874(10)	1823(11)	56(3)
C(12)	3918(12)	6328(8)	4256(13)	68(4)
C(13)	1997(12)	6673(8)	1084(12)	65(4)

Table 4. Atomic coordinates (× 10^4) and isotropic thermal parameters ($Å^2 \times 10^3$) for Cp*Ir(PMe_3)(S_4) (**2b**); * equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U*
Ir	1105.0(7)	5612.8(5)	3376.4(4)	41.7(2)
Se(1)	1057(2)	5598(2)	4959(1)	53(1)
Se(2)	-1381(2)	5018(2)	5251(2)	71(1)
Se(3)	-1187(3)	3567(2)	4526(2)	79(1)
Se(4)	-518(3)	4177(2)	3163(1)	66(1)
P	3155(6)	4638(4)	3479(3)	61(2)
C(1)	1999(18)	6602(15)	2384(11)	49(6)
C(2)	1668(23)	7171(15)	3181(12)	59(6)
C(3)	99(28)	7087(15)	3339(12)	68(7)
C(4)	-598(21)	6558(15)	2710(12)	55(6)
C(5)	544(19)	6216(13)	2093(12)	49(5)
C(6)	3419(22)	6636(18)	1950(17)	82(9)
C(7)	2890(36)	7761(17)	3595(15)	94(11)
C(8)	-704(37)	7656(20)	4021(13)	105(12)
C(9)	-2289(22)	6378(18)	2580(19)	84(10)
C(10)	209(23)	5752(16)	1286(10)	62(7)
C(11)	2957(31)	3556(16)	4119(16)	86(10)
C(12)	3954(32)	4157(23)	2480(16)	103(12)
C(13)	4765(20)	5211(19)	3954(15)	83(9)

(Pentamethylcyclopentadienyl)diselenido(trimethylphosphane)iridium (**5b**): M.p. 220°C. – MS: m/z (%) = 562 (40) [M^+], 486 (100) [$M^+ - PMe_3$], 482 (42) [M^+ – Se], 406 (22) [M^+ – Se – PMe_3].

X-ray Structure Determinations for **4a** *and* **2b**: Crystal data are shown in Table 2. Specimens were mounted on glass fibers with epoxy cement. Photographic evidence and systematic absences for **2b** in the data uniquely determined the space group as orthohombic $P2_12_12_1$, whereas for **4a** the alternatives were $P2_1/m$ and $P2_1$. The latter non-centrosymmetric alternative was chosen based on the asymmetry of the IrS_6 ring and chemically reasonable results of refinement. Corrections for absorption were performed on isotropic models by a method which obtains an empirical absorption tensor from an expression relating F_o and F_c[13]. – The structures were solved by heavy-atom methods and completed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, and hydrogen atom positions were idealized. The correct enantiomorph was assigned by refining a multiplicative term (η) for $\Delta f''$: for **4a**, η = 1.00(2); for **2b**, η = 1.12(6). All computations used SHELXTL (5.1) (G. Sheldrick, Nicolet Corp., Madison, WI, USA). Atomic coordinates for **4a** and **2b** are given in Tables 3 and 4.

Further details of the crystallographic structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, F.R.G., on quoting the depository number CSD-55566, thc names of the autors, and the journal citation.

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