Synthesis and Reactivity of some Group VB Chalcogenide Cyclo-octa-1,5-diene Rhodium(I) and Iridium(I) Complexes

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Complexes of the type [(cod)MClL] (cod = cyclo-octa-1,5-diene; M = Rh or Ir, L = Me_3PS or Me_2PhPS; M = Rh, L = Me_2PhPSe or Me_3AsS; M = Ir, L = $MePh_2PS$), and related cations $[(cod)ML_2]^+$ [M = Rh, L = Me_3PS or Me_2PhPS; M = Rh or Ir, L_2 = $Ph_2P(S)CH_2P(S)Ph_2$] have been synthesised. The complexes [(cod)-IrClL] (L = Me_3PS or Me_2PhPS) undergo oxidative-addition reactions with anhydrous HCl to give [(cod)Ir(H)-Cl_2L]. For L = Me_2PhPS a second product can be isolated, *viz.* $[(cod)Ir(H)Cl_2]_2,C_6H_6$. This is the only product for the reaction where L = $MePh_2PS$. The hydrido-complexes [(cod)Ir(H)Cl_2L] immediately eliminate HCl in water and ethanol. Reaction of iodine with the complexes [(cod)IrClL] (L = Me_3PS or $MePh_2PS$) affords [(cod)IrCl(L)I_2]. The complexes have been characterised by i.r. and n.m.r. spectroscopy.

OVER the last decade considerable interest has been centred on oxidative-addition reactions of low-valent d^8 transition-metal complexes.[1] The tendency for these complexes to undergo such reactions depends markedly on the nature of the co-ordinated ligands. To date, most studies have involved the use of typical π-acceptors, for instance carbonyls,[1] phosphines,[1] and, more recently, isocyanides.[2] In contrast, single-crystal *X*-ray studies on the complexes $[(Me_3PS)Cr(CO)_5]$,[3] $[Cu(Me_3PS)_3]^+$,[4] and $[Co(Me_3AsS)_4]^{2+}$ [5] indicate that tertiary phosphine and arsine sulphides are moderate σ-donors with minimal π-acceptor properties. It was therefore of interest to examine the reactivity of complexes containing these ligands.

In this paper we report the preparation and characterisation of a series of rhodium(I) and iridium(I) complexes [(cod)MClL] (cod = cyclo-octa-1,5-diene, M = Rh or Ir, L = tertiary phosphine or arsine chalcogenide). Related cationic complexes are also described. Such complexes, in which an olefin and a chalcogen donor ligand are simultaneously co-ordinated to a transition metal, are not common. However recent studies have shown that complexes containing sulphide ligands are effective homogeneous catalysts for olefin hydrogenation.[6] During the course of this work oxidative-addition reactions of the analogous iridium phosphine complexes [(cod)IrClL] (L = $MePh_2P$ or Ph_3P) were reported.[7] Since both the phosphine and phosphine sulphide complexes have the same co-ordination number and ancillary ligands, an evaluation of the influence of the sulphur donor ligand on the oxidation-addition reactions is possible.

RESULTS AND DISCUSSION

Preparation of the Complexes.—The rhodium(I) complexes [(cod)RhClL] (L = Me_3PS, Me_2PhPS, Me_3AsS, or Me_2PhPSe) were synthesised *via* bridge-cleavage reactions on $[(cod)RhCl]_2$ with the appropriate chalcogenide in benzene solution at room temperatures. The corresponding iridium(I) complexes [(cod)IrClL] (L = Me_3PS, Me_2PhPS, or $MePh_2PS$) were isolated from an iridium(III) precursor $[(cod)IrHCl_2]_2$, in refluxing benzene, even in the presence of an excess of ligand. In contrast, excesses of phosphine and phosphite ligands react with the expulsion of cod to produce $[RhCl(PR_3)_3]$, $[Rh(PR_3)_4]^+$, or $[Rh(PR_3)_5]^+$,[8] and $Ir(H)Cl_2(PR_3)_3]$ [9] or $[Ir(PR_3)_5]^+$ [10] from the respective rhodium and iridium precursors. The ability of the phosphine sulphides to undergo bridge-splitting reactions is in accord with the expected decrease in basicity along the series $Me_3PS > Me_2PhPS > MePh_2PS > Ph_3PS$.[11] The Me_3PS complexes were obtained in good yield (80—90%), whereas we were unable to isolate Ph_3PS complexes and, for L = $MePh_2PS$, only the iridium complex could be obtained in reasonable yield (*ca.* 55%).

The monomeric complexes are moderately air-stable crystalline solids. I.r. spectra (Table 1) show the P=S and P=Se stretching frequencies to have decreased in the usual manner on co-ordination.[12] Although metal–sulphur and –chlorine modes may occur at similar frequencies,[13] a single strong band in the 270—290 cm^{-1} region is assignable to ν(M–Cl). N.m.r. data are given in Table 1. For the iridium complexes two separate bands are observed for the olefinic protons of the co-ordinated cod ligand, demonstrating the lack of a plane of symmetry perpendicular to the co-ordination plane. The rhodium complexes show only a broad singlet which suggests a rapid exchange process, as found in other similar systems.[14,15]

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Cationic complexes $[(cod)M\{Ph_2P(X)CH_2P(X)Ph_2\}]ClO_4$ (M = Rh or Ir, X = S; M = Rh, X = Se) have been isolated. Treatment of a suspension of the complex $[(cod)MCl]_2$ in methanol with $AgClO_4$, filtration of the resulting AgCl from the yellow solution, and addition of an equimolar proportion of the appropriate chelating chalcogenide ligand in dichloromethane, yields the products as air-stable crystalline solids. The iridium complex can also be prepared with greater difficulty from the iridium(III) complex $[(cod)Ir(H)Cl_2]_2$. Conductivity and molecular-weight measurements indicate the complexes are essentially 1 : 1 electrolytes. Treatment of the complexes with either an excess of the chelating phosphine sulphide or carbon monoxide does not readily displace the co-ordinated cyclo-octa-1,5-diene. With the monodentate phosphine sulphides cationic complexes $[(cod)RhL_2]Ph_4B$ (L = Me_3PS or Me_2PhPS) have been obtained, with difficulty and in low yield, by halide-ion displacement in methanol from either [(cod)RhClL] or $[(cod)RhCl]_2$ followed by precipitation as the tetraphenylborate salt. Support for the formulation comes from i.r. spectra which confirm the presence of tetraphenylborate anions,[16] but the insolubility of the complexes prevents conductivity or n.m.r. studies.

TABLE 1

Spectral data for the complexes

Compound	^{1}H N.m.r. [a]/τ		I.r. [b]/cm^{-1}	
	=CH–	Me–P(J_{P-H})	ν(P=S)	ν(M–Cl)
Me_3PS		8·21 (13·2)	565	
$[(cod)RhCl(Me_3PS)]$	5·82	8·05 (13·2)	542	273
$[(cod)IrCl(Me_3PS)]$	5·99, 6·46	7·99 (13·2)	538	286
Me_2PhPS		8·03 (13·2)	585	
$[(cod)RhCl(Me_2PhPS)]$	5·73	7·80 (13·8)	559	270
$[(cod)IrCl(Me_2PhPS)$	5·92, 6·39	7·65 (13·8)	553	284
$MePh_2PS$		7·82 (12·0)	619, 608	
$[(cod)IrCl(MePh_2PS)]$	6·06, 6·42	7·45 (13·8)	574	292
Me_3AsS		8·17	473 [c]	
$[(cod)RhCl(Me_3AsS)]$	5·81	7·97	452 [c]	271
Me_2PhPSe		7·82 (13·2)	495 [d]	
$[(cod)RhCl(Me_2PhPSe)]$	5·88	7·69 (13·8)	484 [d]	275
$Ph_2P(S)CH_2(S)PPh_2$		6·02 (13·4) [e]	628, 616, 596	
$[(cod)Rh(bdtm)]ClO_4$	5·67	5·37 (12·6) [e]	590, 583	
$[(cod)Ir(bdtm)]ClO_4$	5·87 6·62 [f,g]		584, 569	
$Ph_2P(Se)CH_2(Se)PPh_2$		5·17 (13·4) [e,i]	531	
$[(cod)Rh(bdsm)]ClO_4$	5·60	5·55 (10·8) [e]	530, 509	
$[(cod)Rh(Me_3PS)_2]Ph_4B$	[j]		536	
$[(cod)Rh(Me_2PhPS)_2]Ph_4B$	[j]		550	
$[(cod)Ir(H)Cl_2(Me_3PS)]$	5·52, 5·85 [h]	8·16 (12·6) [k]	537	290, 236 [l]
$[(cod)Ir(H)Cl_2(Me_2PhPS)]$	[j]		553	285, 242 [l]
$[(cod)Ir(H)Cl_2)]_2$ [m]	5·85 [i]			306, 274, 257 [n]
$[(cod)Ir(H)Cl_2]_2C_6H_6$	6·05 [i]			306, 281, 258 [o]
$[(cod)IrClI_2(Me_3PS)]$	4·35, 4·70	7·86 (13·8)	531	302, 161 [p]
$[(cod)IrClI_2(Me_3PS,I_2)]$	[j]		527	297, 165 [p]
$[(cod)IrClI_2(MePh_2PS)]$	4·50	7·74 (12·6)	562	[q]

cod = Cyclo-octa-1,5-diene; bdtm = bis(diphenylphosphinothioyl)methane; and bdsm = bis(diphenylphosphinoselenoyl)methane

[a] In $CDCl_3$, except where indicated. Diene CH_2 resonances obscured by Me–P. [b] As Nujol mulls. [c] ν(As=S). [d] ν(P=Se). [e] P–CH_2–P. [f] $(CD_3)_2CO$ solution. [g] Includes P–CH_2–P. [h] Benzene solution. [i] $(CD_3)_2SO$ solution. [j] Insufficient solubility for n.m.r. [k] τ(Ir–H) 22·06. [l] ν(Ir–H) 2 210 cm^{-1}. [m] From ref. 7. [n] ν(Ir–H) 2 260 cm^{-1}. [o] ν(Ir–H) 2 259 cm^{-1}. [p] ν(M–I). [q] Poorly resolved spectra, not readily assigned.

Reaction of the Complexes [(cod)IrClL] (L = *Tertiary Phosphine Sulphide*) *with* HCl.—Only the iridium(I) complexes are oxidised by hydrogen chloride. The isolated products (see accompanying Scheme) depend both on the nature of the phosphine sulphide ligand L and the solvent employed. Thus, under anhydrous conditions, suspensions of the complexes [(cod)IrClL] (L = Me_3PS or Me_2PhPS) in ether, reacted with an excess of HCl to give the hydrido-complexes $[(cod)Ir(H)Cl_2L]$, as moderately air-stable cream solids. I.r. spectra (Table 1) indicate that, as for the analogous phosphine complexes, the hydride ligand is *trans* to a chloride.[7] The ν(Ir–H) mode was observed as a single band at *ca.* 2 210 cm^{-1} within the region expected for a hydride ligand *trans* to a halide, and the two Ir–Cl modes at *ca.* 290 and 240 cm^{-1} are respectively consistent with chloride *trans* to a co-ordinated double bond and chloride *trans* to a hydride ligand.[7] Immediate elimination of HCl occurs when the hydrido-complexes are treated with water or ethanol yielding the original irridium(I) complexes. This behaviour is in contrast to that observed for the phosphine analogues $[(cod)Ir(H)Cl_2(PR_3)]$, which can be isolated from methanol solution, but is reminiscent of the behaviour of those complexes containing sterically bulky ligands, *e.g.* $[Ir(H)Cl_2(CO)(PBu^t{}_2Et)_2]$.[17] Isolatable complexes, containing a hydride ligand co-ordinated in the presence

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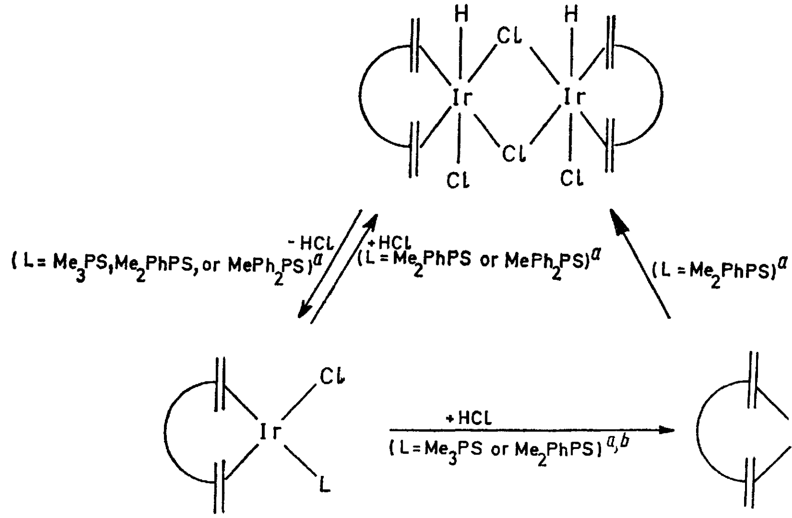
of a sulphide ligand, appear to be somewhat limited[18] although they have been postulated as intermediates, *e.g.*[19] in the oxidation of the complex [(CO)RhCl(Et_2S)$_2$] to [(CO)RhCl_3(Et_2S)$_2$] by HCl. Similarly it has been suggested[6] that a rhodium(III) hydrido-species [L_3RhH_2-(olefin)] (L = Cl, Et_2S, or solvent molecule) is important in the catalytic hydrogenation of olefins using the complex [RhCl_3(Et_2S)$_3$].



SCHEME Solvents: ^{a} benzene, ^{b} ether

The influence of the tertiary phosphine sulphide, L, on the stability of the iridium(III) complexes [(cod)Ir(H)Cl_2L] is more clearly demonstrated by the protonation reactions in benzene. Treatment of a benzene solution of the complex [(cod)IrClL] (L = Me_3PS) with anhydrous HCl yielded the same product as isolated from the ether reaction, *i.e.* [(cod)Ir(H)Cl_2(Me_3PS)]. However when L = Me_2PhPS, two hydridic species were isolated, *viz.* the expected hydrido-complex [(cod)Ir(H)Cl_2(Me_2PhPS)] and an insoluble product, identified as [(cod)Ir(H)Cl_2]$_2$,C_6H_6. The presence of a molecule of benzene of solvation is confirmed by the characteristic resonance of appropriate intensity at τ 2·62 in the n.m.r. and a band at 702 cm^{-1} in the i.r. spectrum.[9] The action of HCl on the complex [(cod)-IrCl($MePh_2PS$)] yielded [(cod)Ir(H)Cl_2]$_2$,C_6H_6 as the only detectable hydrido-complex, as well as the free chalcogenide ligand. This complex can also be obtained by shaking [(cod)Ir(H)Cl_2(Me_2PhPS)] in benzene, indicating that it occurs from a dimerisation and concurrent chalcogenide expulsion [equation (1)]. The tendency for this reaction to occur follows the order of

$$2[(cod)Ir(H)Cl_2L] \xrightarrow{C_6H_6} [(cod)Ir(H)Cl_2]_2,C_6H_6 + 2L \quad (1)$$
$$(L = Me_2PhPS \text{ or } MePh_2PS)$$

decreasing basicities of the tertiary phosphine sulphides.

Reaction of the Complexes [(cod)IrClL] *with Iodine.*—The iridium(I) complexes undergo oxidative-addition reactions with iodine, although the isolation of solid products with consistent analyses is difficult. Thus the complex [(cod)IrCl(Me_3PS)] when treated with the stoicheiometric amount of iodine yielded [(cod)IrClI_2-(Me_3PS)]. I.r. spectral data (Table 1) are consistent with *trans*-addition of the halogen;[7] bands at *ca.* 300 and *ca.* 160 cm^{-1} were assignable to the Ir–Cl and Ir–I stretching modes respectively. When an excess of iodine was used in the reaction, the isolated product analysed as [(cod)IrClI_2(Me_3PS,I_2)]. This complex is a non-electrolyte and has an i.r. spectrum (Table 1) almost identical to that observed for [(cod)IrClI_2-(Me_3PS)]. The free tertiary phosphine sulphides themselves readily form adducts,[20] R_3PS,I_2 in which the iodine is bonded to the sulphur atom. The reaction of iodine with the analogous rhodium complexes yielded insoluble products which could not be completely characterised. Further oxidative-addition reactions on these complexes (with Cl_2 and MeI for example) were complicated by attack occurring at the co-ordinated phosphine sulphide ligand, so far precluding the isolation of any pure products.

EXPERIMENTAL

I.r. spectra (4 000—250 cm^{-1}) were recorded using a Beckmann IR20 spectrophotometer and a R.I.I.C. FS-720 interferometer (400—40 cm^{-1}). N.m.r. spectra were measured using a JEOL JNM-C-60 HL spectrometer. Molecular-weight data were recorded on a Hitachi–Perkin-Elmer vapour-pressure osmometer. Microanalyses were carried out by Dr. Campbell, Otago. Analytical data are summarised in Table 2.

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[19] F. Faraone, R. Pietropaolo, and S. Sergi, *J. Organometallic Chem.*, 1970, **24**, 797.

[20] R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, 1962, **1**, 771; W. Tefteller and R. A. Zingaro, *ibid.*, 1966, **5**, 2151.

All reactions were performed under an atmosphere of oxygen-free nitrogen; all complexes isolated were washed with n-pentane, unless otherwise stated, and dried *in vacuo* at 25 °C. Benzene and ether were sodium dried; other laboratory grade solvents were used as purchased. Trimethylphosphine sulphide (Maybridge Chemical Co.) was used as obtained, while dimethylphenylphosphine sulphide [11] and selenide,[21] methyldiphenylphosphine sulphide,[11] and trimethylarsine sulphide [22] were prepared from literature methods.

Preparation of the Complexes.—[(cod)IrClL] (L = Me_3PS, Me_2PhPS, or $MePh_2PS$). These were obtained by similar methods of which the following is typical. To a suspension of the finely ground complex [(cod)Ir(H)Cl_2] (0·25 g, 0·34 mmol) in benzene (10 cm^3) was added Me_3PS (0·084 g, 0·78 mmol) in benzene (5 cm^3) and the mixture was heated under reflux (20 min) on a water-bath, HCl being liberated. The solution was filtered and the solvent was reduced to below half its original volume, whereupon a first crop of yellow crystals was collected. A second crop was isolated upon addition of n-pentane or n-hexane to the mother liquor. The *crystals* were washed with ether, then n-pentane; yield 80% (0·25 g). Pure chalcogenide complexes could not be isolated where L = Ph_3PS or Me_3AsS. I.r. measurements on the latter product showed no band in the 400—500 cm^{-1} range for ν(As=S). The complexes were non-electrolytes in nitrobenzene and a molecular-weight determination for [(cod)IrCl(Me_3PS)] in chloroform gave 407 (calc. 444).

TABLE 2

Colours, melting points, and analytical data (%) for the complexes

Compound	Colour [a]	M.p. (t°/C)	Found (calc.)		
			C	H	Cl
[(cod)RhCl(Me_3PS)]	y	140 [b]	37·6 (37·2)	5·9 (6·0)	10·0 (10·0)
[(cod)IrCl(Me_3PS)]	y	190 [b]	30·0 (29·8)	4·7 (4·8)	8·2 (8·0)
[(cod)RhCl(Me_2PhPS)]	y	137—139	46·4 (46·1)	5·6 (5·6)	8.8 (8·5)
[(cod)IrCl(Me_2PhPS)]	y	163—165	38·3 (38·0)	4·7 (4·6)	8·0 (7·0)
[(cod)IrCl($MePh_2PS$)]	y	95—100 [b]	43·6 (44·4)	4·3 (4·4)	7·4 (6·2)
[(cod)RhCl(Me_3AsS)]	y	168—170	33·2 (33·2)	5·5 (5·3)	8·7 (8·9)
[(cod)RhCl(Me_2PhPSe)]	y	128—130	41·7 (41·5)	5·2 (5·0)	7·6 (7·6)
[(cod)Rh(bdtm)]ClO_4	y	*c*	52·0 (52·2)	4·6 (4·5)	8·2 (8·4) [d]
[(cod)Ir(bdtm))]ClO_4	y	*c*	47·4 (46·7)	4·2 (4·0)	7·4 (7·6) [d]
[(cod)Rh(Me_3PS)$_2$]Ph_4B	ob	*c*	60·0 (61·1)	6·1 (6·7)	
[(cod)Rh(Me_2PhPS)$_2$]Ph_4B	ob	*c*	66·3 (66·2)	5·7 (6·2)	
[(cod)Ir(H)Cl_2(Me_3PS)]	*c*	155—160	27·1 (27·5)	4·4 (4·6)	14·4 (14·8)
[(cod)Ir(H)Cl_2(Me_2PhPS)]	*c*	*c*	34·6 (35·4)	4·4 (4·5)	13·9 (13·1)
[(cod)Ir(H)Cl_2]$_2$,C_6H_6	c	>200	32·7 (32·1)	4·0 (3·9)	
[(cod)IrClI_2(Me_3PS)]	db	124—127	19·3 (18·9)	3·1 (3·0)	37·0 (36·4) [e]
[(cod)IrClI_2(Me_3PS,I_2)]	db	105—108	13·9 (13·9)	2·1 (2·2)	52·5 (53·3) [e]
[(cod)IrClI_2($MePh_2PS$)]	db	85—90 [b]	28·9 (30·65)	3·0 (3·0)	30·4 (30·9) [e]

cod = Cyclo-octa-1,5-diene and bdtm = bis(diphenylphosphinothioyl)methane.

[a] y = Yellow, c = cream, ob = orange-brown, db = dark brown. [b] Decomposition point. [c] Not recorded. [d] S. [e] I.

[(cod)RhClL] (L = Me_3PS, Me_2PhPS, Me_3AsS, or Me_2PhPSe). These were obtained by similar methods of which the following is typical. To a solution of the complex [(cod)RhCl]$_2$ (0·32 g, 0·65 mmol) in benzene (10 cm^3) was added Me_3PS (0·145 g, 1·34 mmol) dissolved in benzene (5 cm^3). The mixture was shaken (5 min) at room temperature, filtered, and reduced to half its original volume on a rotatory evaporator, whereupon a first crop of yellow crystals was obtained. A second crop was isolated upon reduction of volume of the mother liquor and the addition of n-pentane. The *crystals* were washed with ether and n-pentane; yield 90% (0·42 g). For L = $MePh_2PS$, no reaction occurred at room temperature, but on heating under reflux (2 h) an oil was isolated which did show a band at 582 cm^{-1} in the i.r. spectrum, indicative of the presence of co-ordinated P=S. The complexes were non-electrolytes in nitrobenzene, and a molecular-weight determination for [(cod)RhCl(Me_3AsS)] in chloroform gave 385 (calc. 398).

Cyclo-octa-1,5-*dienebis*(*trimethylphosphine sulphide*)*rhodium*(I) *tetraphenylborate*. To a suspension of the complex [(cod)RhCl]$_2$ (0·15 g, 0·3 mmol) in methanol (10 cm^3) was added Me_3PS (0·144 g, 1·33 mmol) dissolved in methanol (5 cm^3) and the mixture was shaken for 15 min. Sodium tetraphenylborate (0·20 g, 0·6 mmol) in methanol (4 cm^3) was added to the filtered solution to effect precipitation of the brown *product* in 22% yield (0·066 g). An alternative synthesis was effected by the reaction of the complex [(cod)RhCl(Me_3PS)] with Me_3PS in benzene followed by precipitation of the product with sodium tetraphenylborate.

Cyclo-octa-1,5-*dienebis*(*dimethylphenylphosphine sulphide*)-*rhodium*(I) *tetraphenylborate*. In a similar manner to that described in the preceding preparation, Me_2PhPS (0·19 g, 1·12 mmol) dissolved in methanol (5 cm^3) was added to a suspension of the complex [(cod)RhCl]$_2$ (0·12 g, 0·25 mmol) in methanol (10 cm^3) and the mixture was shaken (15 min), filtered, and sodium tetraphenylborate (0·086 g, 0·25 mmol) in methanol (4 cm^3) added. The brown *product* was obtained in 20% yield (0·084 g).

[*Bis*(*diphenylphosphinothioyl*)*methane*](*cyclo-octa*-1,5-*diene*)*rhodium*(I) *perchlorate*. Silver(I) perchlorate (0·085 g, 0·4 mmol) in methanol (6 cm^3) was added to the finely ground complex [(cod)RhCl]$_2$ (0·097 g, 0·1 mmol) suspended in methanol (2 cm^3). The mixture was shaken (20 min) and then filtered to remove AgCl. Bis(diphenylphosphinothioyl)methane (0·18 g, 0·4 mmol) in dichloromethane (15 cm^3) and methanol (5 cm^3) was added to the filtrate and

[21] P. Nicpon and D. W. Meek, *Inorg. Chem.*, 1966, **5**, 1297.

[22] R. A. Zingaro, R. E. McGlothin, and R. M. Hedges, *Trans. Faraday Soc.*, 1963, **59**, 798.

the mixture shaken (30 min). The total volume of the solution was reduced to less than half under vacuum and a crop of yellow *crystals* were obtained, in 55% yield (0·17 g). The complex was recrystallised from methanol. This complex was a uni-univalent electrolyte in nitromethane; its conductivity was 81 Ω^{-1} cm^2 at 20 °C, which was in the range expected (70—90 Ω^{-1} cm^2). In acetone, a determination of the molecular weight resulted in a value of 429, which is significantly higher than half of the calculated molecular weight (365) suggesting incomplete dissociation of the perchlorate ion; in fact in chloroform a value of 687 was observed, suggesting little ionisation of the perchlorate ion. The corresponding diselenide complex was prepared in a similar manner but the C and H figures were consistently high (Found: C, 50·0; H, 4·8. Calc. for $C_{33}H_{34}ClIrO_4P_2Se_2$: C, 46·5; H, 4·0%).

[*Bis*(*diphenylphosphinothioyl*)*methane*](*cyclo-octa*-1,5-*diene*)*iridium*(I) *perchlorate, method* A. A slight excess of the finely ground complex $[(cod)Ir(H)Cl_2]_2$ (0·125 g, 0·17 mmol) was added to silver(I) perchlorate (0·13 g, 0·63 mmol) in methanol (5 cm^3). After shaking (20 min), the solution was filtered to remove AgCl and bis(diphenylphosphinothioyl)methane (0·14 g, 0·31 mmol) dissolved in acetone (10 cm^3) was added to the filtrate with shaking (5 min). The volume of the resulting solution was reduced to less than half under reduced pressure and a difficult precipitation of the yellow-brown *solid* was effected after the addition of n-hexane to the cooled solution; yield 50% (0·14 g). The complex was recrystallised from methanol. This complex was a uni-univalent electrolyte in nitromethane, its conductivity being 80 Ω^{-1} cm^2 at 20 °C. A molecular-weight determination in acetone gave a value of 587 (calc. for a 1 : 1 electrolyte, 423), suggesting incomplete dissociation.

Method B. This method was similar to that of the rhodium analogue above. The complex $[(cod)IrCl]_2$ (0·103 g, 0·15 mmol) was added to silver(I) perchlorate (0·063 g, 0·3 mmol) in methanol (5 cm^3). After filtering the solution, bis(diphenylphosphinothioyl)methane (0·137 g, 0·3 mmol) in acetone (10 cm^3) was added and, on reduction of volume, the *product* was obtained in 55% yield.

Dichloro(*cyclo-octa*-1,5-*diene*)*hydrido*(*trimethylphosphine sulphide*)*iridium*(III). The finely ground complex $[(cod)IrCl(Me_3PS)]$ (0·05 g) was placed in dry ether (15 cm^3) in which about half of the complex dissolved. Into this suspension, dry HCl gas was bubbled (5 min) and the mixture shaken for a further 5 min. A cream *precipitate* appeared and the mixture was taken to dryness under vacuum; yield 70% (0·4 g). It immediately lost HCl in the presence of water or ethanol. The same product could be isolated from benzene solution.

Dichloro(*cyclo-octa*-1,5-*diene*)(*dimethylphenylphosphine sulphide*)*hydridoiridium*(III). Dry HCl gas was bubbled into a suspension of the complex $[(cod)IrCl(Me_2PhPS)]$ (0·05 g) in dry ether (12 cm^3) for 5 min, followed by shaking (10 min). The solvent was removed under vacuum to yield the cream *complex* in 60% yield (0·32 g). The complex was dehydrohalogenated in chloroform, alcohol, and water.

Di-μ-*chloro-bis*[*chloro*(*cyclo-octa*-1,5-*diene*)*hydridoiridium*-(III)]–*benzene, method* A. When dry HCl gas was bubbled into a solution of the complex $[(cod)IrCl(Me_2PhS)]$ (0·1 g) in benzene (10 cm^3) an insoluble cream *complex* precipitated in 60% yield (0·07 g). The presence of a benzene molecule of solvation was shown by n.m.r. and i.r. studies (band at 702 cm^{-1}). The filtrate contained the hydrido-complex described above, *i.e.* $[(cod)Ir(H)Cl_2(Me_2PhPS)]$.

Method B. When the complex $[(cod)Ir(H)Cl_2(Me_2PhPS)]$ was shaken in benzene for 10 min the *product* was obtained in 80% yield.

Method C. When dry HCl gas was bubbled into a solution of the complex $[(cod)IrCl(MePh_2PS)]$ (0·1 g) in benzene (8 cm^3) the *product* precipitated in 80% yield.

Chloro(*cyclo-octa*-1,5-*diene*)*di-iodo*(*trimethylphosphine sulphide*)*iridium*(III). Iodine (0·06 g, 0·24 mmol) in benzene (5 cm^3) was added slowly to the complex $[(cod)IrCl(Me_3PS)]$ (0·09 g, 0·24 mmol) in benzene (8 cm^3). On removal of half the solvent under vacuum, a brown *precipitate* appeared upon slow addition of n-hexane to the solution cooled in an ice-bath. It was washed with ether followed by n-hexane; yield 60% (0·083 g).

Chloro(*cyclo-octa*-1,5-*diene*)*di-iodo*(*trimethylphosphine sulphide*)*iridium*(III)–*iodine*. The complex $[(cod)IrCl(Me_3PS)]$ (0·09 g, 0·25 mmol) in benzene (8 cm^3) was added to iodine (0·12 g, 0·48 mmol) in benzene (5 cm^3). On removal of most of the solvent under reduced pressure and on the slow addition of n-hexane to the cooled solution, a dark brown *precipitate* in 30% yield (0·057 g) was obtained. It was washed with ether followed by n-hexane.

Chloro(*cyclo-octa*-1,5-*diene*)(*diphenylmethylphosphine sulphide*)*di-iodoiridium*(III). Iodine (0·06 g, 0·24 mmol) in benzene (5 cm^3) was added slowly to the complex $[(cod)IrCl(MePh_2PS)]$ (0·14 g, 0·24 mmol) in benzene (8 cm^3). A small amount of a brown precipitate appeared which was filtered off. The filtrate was taken to below half volume under vacuum, and n-hexane slowly added to the solution which was cooled in an ice-bath. A brown precipitate was obtained after some difficulty. It was washed with ether followed by n-hexane; yield 0·09 g, 45%. The initial brown precipitate in this reaction, though obtained in low yields, was consistent with a complex containing a higher iodine content but it could not be completely characterised.

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