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O,O'-Dithiophosphato and P,P-Dithiophosphinato Complexes of Iridium(I)

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The complexes $Ir(CO)_2(S–S)$ (I; $S–S^- = (C_6H_{11})_2PSS^-$ or $(PhO)_2PSS^-$) and $Ir(chel)(S–S)$ (II; chel = 1,5-cyclooctadiene) have been synthesised by the reactions of $[\{Ir(CO)_3Cl\}_n]$ and $[Ir(chel)Cl]_2$ with $(C_6H_{11})_2PSSNH_4$ and $(PhO)_2PSSNH_4$. Complexes II react with CO and triphenylphosphine giving $Ir(CO)_2(S–S)$ and $Ir(PPh_3)_2(S–S)$ respectively. Triphenylphosphine and triethylphosphine, L, react differently with $Ir(CO)_2[SSP(C_6H_{11})_2]$ and $Ir(CO)_2[SSP(OPh)_2]$, the products of the reactions being $Ir(CO)L[SSP(C_6H_{11})_2]$ and $Ir(CO)_2L_2[SSP(OPh)_2]$. In the latter compounds the $SSP(OPh)_2$ group behaves as unidentate ligand. 1,2-Bis(diphenylphosphino)ethane,L–L, reacts with complexes I cleaving the metal–sulphur bonds and giving $[Ir(CO)(L–L)_2](S–S)$ in which the $S–S^-$ is a counterion.

Some oxidative addition reactions on compounds I are also reported and the results compared with those obtained for analogous rhodium(I) substrates.

Introduction

Transition metal complexes having co-ordinated as bidentate ligand O,O'-dithiophosphate, $(RO)_2PSS^-$, or P,P'-dithiophosphinate, R_2PSS^-, show an interesting reactivity; they, in fact, can react with neutral ligands by stepwise cleavage of metal–sulphur bonds to give products with unidentate co-ordinated or ionic dithioligand and this type of reaction is influenced by the nature of the neutral reactant[1–9].

Recently it has been observed that dithio-complexes can react with neutral ligands giving compounds in which the central metal shows a different formal oxidation state[10].

Furthermore several intra and intermolecular rearrangements in complexes containing co-ordinated dithiophosphate or dithiophosphinate groups have been observed, depending on the experimental conditions[11].

The reactivity of dithiophosphato and dithiophosphinato complexes is, consequently, particular and different from that shown by other compounds containing dithio-ligands such as dialkyl- and diaryldithiocarbamate[12].

Recently we studied the preparation and the reactivity, including some oxidative addition reactions, of $RhL_2(S–S)$ and $Rh(chel)(S–S)$ complexes (L = CO, PPh_3; chel = cycloocta-1,5-diene; $S–S^- = (PhO)_2PSS^-$ and $(C_6H_{11})_2PSS^-$) and the results indicated that the presence of weak Rh–CO and Rh–chel bonds determined by the co-ordinated dithio-ligands is a very important factor governing the type of reaction products[13]. This paper reports on the preparation and the reactivity of analogous iridium(I) complexes $Ir(CO)_2(S–S)$ (*I*) and Ir(chel)(S–S) (*II*) with the aim of studying the effect of the central metal on the reactivity of the substrates.

Results and Discussion

The poly(tricarbonylchloroiridium), $[\{Ir(CO)_3Cl\}_n]$, reacts in methanol or benzene under reflux with the ammonium salt of dicyclohexyldithiophosphinate, $(C_6H_{11})_2PSSNH_4$, giving with high yield $Ir(CO)_2[SSP(C_6H_{11})_2]$; a similar reaction occurs using the ammonium salt of O,O'-dithiophosphate, $(PhO)_2PSSNH_4$, but in this case the compound $Ir(CO)_2[SSP(OPh)_2]$ was formed in poor yield. The complexes Ir(chel)(S–S) (chel = 1,5-cyclooctadiene) were similarly obtained by reacting $[Ir(chel)Cl]_2$ with $(C_6H_{11})_2SSPNH_4$ or $(PhO)_2PSSNH_4$ in benzene solution, as described in the experimental section.

All the compounds are yellow or orange–yellow crystalline solids, nonconducting in dichloromethane solution, soluble in common organic solvents including saturated hydrocarbons. The bidentate behaviour of the dithio-ligands used to prepare these iridium(I) complexes is indicated both by conductivity and molecular weight measurements, these latter showing that all the compounds are monomers, thus excluding any associated structure in solution.

Generally, when steric effects from crystal packing or crowding of bulky ligands around the central metal do not occur, complexes containing dithiophosphate or dithiophosphinate co-ordinated groups are found to have a planar arrangement for the MSSP grouping[14]. Accordingly, the iridium(I) compounds here reported are likely to have a square-planar structure. As expected, i.r. spectra in the CO stretching region of *I* complexes show two very strong bands at about 2000 and 2060 cm^{-1}.

When carbon monoxide was bubbled through a dichloromethane solution containing *II*, the complexes *I* were obtained and no formation of five-co-ordinate compounds was observed.

Similarly, triphenylphosphine reacts with *II* giving substitution products of 1,5-cyclooctadiene, $Ir(PPh_3)_2(S–S)$. In no case was cleavage of iridium–sulphur

TABLE. Analytical Data and CO Stretching Frequencies (cm^{-1}).

Compound	Colour	Molecular Weight[a, b]	Analyses, %[a]				ν(CO) (nujol mulls)
			C	H	S	Halogen	
$Ir(CO)_2[SSP(C_6H_{11})_2]$	Orange	488 (509)	33.07 (32.99)	4.39 (4.35)	12.46 (12.58)		2043 vs, 1985 vs
$Ir(CO)_2[SSP(OPh)_2]$	Orange	518 (529)	31.82 (31.75)	1.96 (1.90)	12.13 (12.11)		2048 vs, 1997 vs
$Ir(1,5\text{-}C_8H_{12})[SSP(C_6H_{11})_2]$	Yellow	546 (562)	42.84 (42.76)	6.21 (6.10)	11.57 (11.41)		
$Ir(1,5\text{-}C_8H_{12})[SSP(OPh)_2]$	Yellow	574 (582)	41.52 (41.29)	3.96 (3.81)	11.32 (11.02)		
$Ir(PPh_3)_2[SSP(C_6H_{11})_2]$	Red-brown	965 (978)	58.88 (58.94)	5.41 (5.35)	6.51 (6.55)		
$Ir(PPh_3)_2[SSP(OPh)_2]$	Red-brown	974 (998)	57.84 (57.76)	4.16 (4.04)	6.37 (6.42)		
$Ir(CO)(PPh_3)[SSP(C_6H_{11})_2]$	Yellow	756 (744)	50.11 (50.05)	5.08 (5.01)	8.48 (8.61)		1955 vs
$Ir(CO)_2(PPh_3)_2[SSP(OPh)_2]$	Yellow		57.08 (56.97)	3.96 (3.92)	6.15 (6.08)		2002 vs, 1945 vs
$[Ir(CO)(Ph_2PC_2H_4PPh_2)_2]SSP(C_6H_{11})_2$	Pale-yellow		61.12 (61.06)	5.47 (5.52)	5.08 (5.01)		1938 vs
$[Ir(CO)(Ph_2PC_2H_4PPh_2)_2]SSP(OPh)_2$	Pale-yellow		60.18 (60.13)	4.45 (4.50)	4.58 (4.94)		1935 vs
$Ir(CO)_2[SSP(C_6H_{11})_2]Cl_2$	Yellow	565 (580)	28.72 (28.96)	3.87 (3.82)	10.96 (11.04)	12.08 (12.21)	2130 vs, 2085 vs
$Ir(CO)_2[SSP(C_6H_{11})_2]Br_2$	Yellow	638 (669)	25.37 (25.11)	3.42 (3.31)	9.72 (9.57)	23.65 (23.87)	2132 vs, 2082 vs
$Ir(CO)_2[SSP(C_6H_{11})_2]I_2$	Red-brown	734 (763)	22.08 (22.02)	2.97 (2.90)	8.52 (8.40)	33.16 (33.24)	2122 vs, 2080 vs
$Ir(CO)_2(CH_3)[SSP(C_6H_{11})_2]I$	Yellow	632 (651)	27.53 (27.65)	3.81 (3.86)	9.78 (9.84)	19.35 (19.47)	2100 vs, 2038 vs

[a] Calculated values in parentheses. [b] In benzene solution.

bond observed, as confirmed by conductivity measurements and elemental analysis data.

Triphenylphosphine reacts differently with $Ir(CO)_2[SSP(C_6H_{11})_2]$ and $Ir(CO)_2[SSP(OPh)_2]$, the product of the former reaction being $Ir(CO)(PPh_3)[SSP(C_6H_{11})_2]$ in which the metal remains four-co-ordinate and retains the bidentate dithio-ligand. A compound showing two very strong ν(CO) bands and nonconducting in CH_2Cl_2 was obtained from the same reaction of $Ir(CO)_2[SSP(OPh)_2]$ with PPh_3. On the basis of elemental and i.r. analysis we formulate it as $Ir(CO)_2(PPh_3)_2[SSP(OPh)_2]$ in which the $SSP(OPh)_2$ group behaves as unidentate ligand. Spectroscopic data, however, do not allow the assignement of any structure for this compound to be made.

Steric effects due to co-ordinated dithio-ligand are generally small and the different behaviour of $Ir(CO)_2[SSP(C_6H_{11})_2]$ and $Ir(CO)_2[SSP(OPh)_2]$ might be attributed to electronic effects. Since the $-SSP(OPh)_2$ group should be a stronger π-acceptor than $-SSP(C_6H_{11})_2$, the π-component of the iridium–sulphur bond must be more important in $Ir(CO)_2[SSP(OPh)_2]$ than in $Ir(CO)_2[SSP(C_6H_{11})_2]$ and, therefore, in the former complex a stronger metal–sulphur bond should be expected. Although i.r. evidence is not conclusive, this is indirectly supported by the fact that ν(CO) are lower in $Ir(CO)_2$(S–S) when S–S is $-SSP(C_6H_{11})_2$. We cannot explain, then, the reason of the cleavage of iridium–sulphur bond in the reaction of $Ir(CO)_2[SSP(OPh)_2]$ with PPh_3. PEt_3 reacts similarly; however, using this ligand we could not obtain pure products and our observations are based on i.r. data.

Pyridine, which is a stronger σ-donor and poorer π-acceptor than tertiary phosphines, does not react with complexes *I*; in other cases similar reactions were found to be influenced by the nature of the neutral reacting ligand[5].

By adding to a pentane solution of *I* an excess of 1,2-bis(diphenylphosphino)ethane, L–L, the complexes [Ir(CO)(L–L)$_2$](S–S) were obtained with high yield. We could confirm that S–S$^-$ is a counterion in these compounds because on adding $NaBPh_4$ dissolved in methanol to [Ir(CO)(L–L)$_2$](S–S) in the same solvent the compound [Ir(CO)(L–L)$_2$]BPh_4 was obtained. As expected, the i.r. spectra of [Ir(CO)(L–L)$_2$]

(S–S) show a strong ν(CO) band at about 1940 cm^{-1} which disappears on heating for a few minutes the compounds in toluene because formation of [Ir(L–L)$_2$] (S–S) does occur. A similar reaction was observed for [Ir(CO)(L–L)$_2$]Cl[15]. 2,2′-Bipyridyl and PhSC$_2$H$_4$SPh do not react with *I* even when refluxed in heptane.

In a previous paper[13] we reported on the reactions of Rh(CO)$_2$(S–S) and Rh(chel)(S–S) with covalent molecules such as Cl$_2$, Br$_2$, I$_2$,CH$_3$I,CH$_3$CH=CHCl,H$_2$ and we observed formation of binuclear oxidation products and, in the case of the reaction with CH$_3$I, five-co-ordinated rhodium(III) acetyl compounds. These results demonstrate that Rh(CO)$_2$(S–S) and Rh(chel) (S–S) are co-ordinatively unsaturated species and that the Rh–CO bond in six co-ordinate rhodium(III) complexes, firstly obtained by oxidative addition, is weak, thereby favouring molecular rearrangements. The Ir–CO bond in six-co-ordinate iridium(III) complexes should be stronger than in analogous rhodium(III) compounds owing to a greater occurrence of back donation from the metal atom to the antibonding CO orbitals and a different behaviour in oxidative addition reactions should be expected.

By adding dropwise a pentane solution of Cl$_2$, Br$_2$, I$_2$ to Ir(CO)$_2$[SSP(C$_6$H$_{11}$)$_2$] dissolved in the same solvent, solid products were obtained which show two strong bands in the CO stretching region at higher wavenumbers than in the starting material as expected for an halogen *trans*-addition. These compounds can be formulated as Ir(CO)$_2$(S–S)X$_2$ (X$_2$ = Cl$_2$,Br$_2$,I$_2$); the presence of two halogen atoms in *trans*-position is confirmed by the far i.r. spectrum of Ir(CO)$_2$(S–S) Cl$_2$ which shows only one band ν(Ir–Cl) at 322 cm^{-1}. Probably, a *trans*-addition occurs also in the reaction with CH$_3$I; the complex Ir(CO)$_2$[SSP(C$_6$H$_{11}$)$_2$] (CH$_3$)I shows in fact, two strong bands in the CO stretching region and no molecular rearrangement was observed on leaving the reaction mixture standing for a long time. We exclude also any possibility of attack on the sulphur atom because the ν(CO) values observed are high and characteristic of iridium(III) species.

H$_2$ and O$_2$ do not react at atmospheric pressure with Ir(CO)$_2$(S–S) compounds nor does an excess of CH$_3$COCl dissolved in pentane.

Ir(CO)$_2$[SSP(OPh)$_2$] reacts with Cl$_2$,Br$_2$,I$_2$,CH$_3$I giving more than one product. The i.r. spectrum of the obtained material in the CO stretching region shows, besides the two bands which are due to the neutral exa-co-ordinate iridium(III) compound, another band at about 2090 cm^{-1}. The intensity ratio of these bands does not change on refluxing the reaction mixture in CH$_2$Cl$_2$ for several hours and this allows us to exclude any rearrangement process occuring under equilibrium conditions. Attempts to separate the mixture components by chromatography on alumina did not give pure products.

Experimental

The poly(tricarbonylchloroiridium), [{Ir(CO)$_3$Cl}$_n$], was a commercial product; [(1,5–C$_8$H$_{12}$) IrCl]$_2$ was prepared from [(C$_8$H$_{14}$)$_2$IrCl]$_2$[16], following the method reported by Mestroni *et al.*[17] The salt (PhO)$_2$PSSNH$_4$ was prepared as described by Fletcher *et al.*[18] Other chemicals were reagent grade and were used without purification. I.r. spectra were recorded with a Perkin–Elmer 457 spectrometer; molecular weights were determined with a Knauer wapour pressure osmometer; a Conductivity Meter WTW LBR was used for conductivity measurements.

Elemental analyses were by Bernhardt, Mikroanalytisches Laboratorium, Mülheim, Germany.

All reactions were carried out under an atmosphere of oxygen-free nitrogen, although this precaution could probably be dispensed with in most cases.

Analytical data and ν(CO) stretching frequencies are reported in the table.

Dicarbonyl(P,P′-dicyclohexyldithiophosphinato) iridium(I), [Ir(CO)$_2$[SSP(C$_6$H$_{11}$)$_2$]

A suspension of poly(tricarbonylchloroiridium), [Ir(CO)$_3$Cl]$_n$ (0.400 g; 1.28 mmol) and (C$_6$H$_{11}$)$_2$PSSNH$_4$ (0.37 g; 1.30 mmol) in anhydrous benzene or methanol (150 ml) was refluxed for *ca.* 2.5 h. The yellow-orange solution was filtered and evaporated *in vacuo*; extraction with warm hexane gives, after partial evaporation of the solvent, the product as yellow–orange crystals (yield 82%). Dicarbonyl(O,O′-diphenyldithiophosphato)iridium(I),Ir(CO)$_2$[SSP(OPh)$_2$], was prepared in the same way from [{Ir(CO)$_3$Cl}$_n$] and (PhO)$_2$PSSNH$_4$ (molar ratio 1:1.2), and was isolated as yellow–orange crystals (yield 27%).

(Cycloocta-1,5-diene)(P,P′-dicyclohexyldithiophosphinato)iridium(I), Ir(1,5-C$_8$H$_{12}$)[SSP(C$_6$H$_{11}$)$_2$]

To a solution of [(1,5-C$_8$H$_{12}$)IrCl]$_2$ (0.592 g; 1.2 mmol) in benzene, (C$_6$H$_{11}$)$_2$PSSNH$_4$ (0.70 g; 2.5 mmol) was added and the mixture was refluxed for *ca.* 2 h. The solution was evaporated off; extraction with hexane gives, after evaporation of the solvent, the product as yellow crystals (yield 86%).

(Cycloocta-1,5-diene)(O,O′-diphenyldithiophosphato)iridium(I), Ir(1,5-C$_8$H$_{12}$)[SSP(OPh)$_2$], was similarly prepared from [(1,5-C$_8$H$_{12}$)IrCl]$_2$ (0.350 g; 0.71 mmol) and (PhO)$_2$PSSNH$_4$ (0.45 g; 1.5 mmol) and was obtained as yellow crystals (yield 81%).

Absorption of Carbon Monoxide by Ir(1,5-C$_8$H$_{12}$) (S–S) Complexes

When CO is bubbled through a CH$_2$Cl$_2$ solution containing Ir(1,5-C$_8$H$_{12}$)(S–S) for about 15 min the i.r. spectrum in the CO stretching region shows two bands which are close to those observed for Ir(CO)$_2$ (S–S) complexes. The solvent was evaporated off and the pure product Ir(CO)$_2$(S–S) was obtained by crystallization from pentane.

Reaction of Ir(1,5-C_8H_{12})(S–S) Complexes with PPh_3

To a benzene solution of Ir(1,5-C_8H_{12})(S–S), PPh_3 was added (molar ratio about 1:2.3) and the mixture was stirred for about 4 h. The solvent was evaporated and by crystallization from hexane the products Ir$(PPh_3)_2$(S–S) were obtained.

Carbonyltriphenylphosphine(P,P'-dicyclohexyldithiophosphinato)iridium(I), Ir(CO)(PPh_3)[SSP$(C_6H_{11})_2$]

An excess of triphenylphosphine was added to a solution of Ir$(CO)_2$[SSP$(C_6H_{11})_2$] in pentane and the mixture was stirred for about 30 min. A yellow solid was formed and this was filtered and washed several times with pentane.

Dicarbonylbis(triphenylphosphine)(O,O'-diphenyldithiophosphato)iridium(I), Ir$(CO)_2(PPh_3)_2$[SSP$(OPh)_2$]

A small excess of triphenylphosphine was added to a pentane solution of Ir$(CO)_2$[SSP$(OPh)_2$]. A yellow solid was formed immediately; after about 20 min this was filtered and washed several times with pentane.

Carbonylbis[1,2-bis(diphenylphosphino)ethane] iridium(I) P,P'-dicyclohexyldithiophosphinate Salt, [Ir(CO)$(Ph_2PC_2H_4PPh_2)_2$]SSP$(C_6H_{11})_2$

1,2-bis(diphenylphosphino)ethane in excess was added to a solution containing Ir$(CO)_2$[SSP$(C_6H_{11})_2$] dissolved in pentane and the mixture was left with vigorous stirring for about 20 min. A pale-yellow solid was obtained; this was separated by filtration and washed several times with pentane in order to remove the excess of the ligand.

Carbonylbis[1,2-bis(diphenylphosphino)ethane]iridium(I) O,O'-diphenyldithiophosphate salt, [Ir(CO)$(Ph_2PC_2H_4PPh_2)_2$]SSP$(OPh)_2$, was obtained similarly.

The complex [Ir(CO)$(Ph_2PC_2H_4PPh_2)_2$]BPh_4 was obtained by adding $NaBPh_4$ dissolved in methanol to a solution of [Ir(CO)$(Ph_2PC_2H_4PPh_2)_2$](S–S) in the same solvent.

Dichlorodicarbonyl(P,P'-dicyclohexyldithiophosphinato)iridium(III), Ir$(CO)_2$[SSP$(C_6H_{11})_2$]Cl_2

A pentane solution of Cl_2 was added dropwise to Ir$(CO)_2$[SSP$(C_6H_{11})_2$] dissolved in the same solvent. A yellow solid was formed. The progress of the reaction was followed by i.r. spectroscopy and the addition of Cl_2 was stopped when the i.r. spectrum showed disappearance of the ν(CO) of the starting substrate. The solid formed was separated by filtration, washed several times with pentane and dried.

Dibromodicarbonyl(P,P'-dicyclohexyldithiophosphinato)iridium(III), Ir$(CO)_2$[SSP$(C_6H_{11})_2$]Br_2 and diidodicarbonyl(P,P'-dicyclohexyldithiophosphinato)iridium (III), Ir$(CO)_2$[SSP$(C_6H_{11})_2$]I_2, were prepared and isolated similarly, respectively as yellow and red-brown solids.

Dicarbonyliodomethyl(P,P'-dicyclohexyldithiophosphinato)iridium(III), Ir$(CO)_2$[SSP$(C_6H_{11})_2$](CH_3)I

CH_3I (44 ml) and Ir$(CO)_2$[SSP$(C_6H_{11})_2$] (0.210 g) were left to react with stirring. After about 10 h, the i.r. spectrum of the mixture in CH_2Cl_2 indicated that the reaction was complete. The solvent was evaporated *in vacuo* and the crude product obtained was crystallized from CH_2Cl_2–pentane and then from benzene–methanol to give a yellow solid.

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