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Reactions of Diphenyldithiophosphoric and Diphenyldithiophosphinic Acids with Nucleophilic Ruthenium(0), Rhodium(I), Iridium(I) and Platinum(0) Complexes

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The reaction of $Ru(CO)_3(PPh_3)_2$ with diphenyldithiophosphoric, $(PhO)_2PSSH$, and diphenyldithiophosphinic (Ph_2PSSH) acids yields new monomeric complexes of the type $Ru(CO)_2(PPh_3)_2(SSPR_2)_2$ (R = Ph, OPh); no evidence has been found for the formation of hydrido derivatives. The same reactions with trans-$Ir(CO)(PPh_3)_2Cl$ and $Pt(PPh_3)_4$ lead to the hydrido derivatives $Ir(CO)H(PPh_3)_2(SSPR_2)Cl$ and $PtH(PPh_3)_2(SSPR_2)$ in which the dithio ligand acts as monodentate. MeI and EtI react at sulphur of coordinated dithio ligand of the hydrido complexes giving, as final products, the ester R_2PSSR' (R' = Me, Et) and $Ir(CO)H(PPh_3)_2ClI$ or $Pt(PPh_3)_2I_2$. The possible *mechanism of these reactions is discussed.*

The structure of the new complexes is established on the basis of the i.r. spectroscopic data.

Introduction

The oxidative addition reaction of protonic acids to low oxidation state complexes of transition metals has been the subject of recent work and an extensive range of hydrido complexes have been prepared by this procedure[1–4]. It appears that the acidity cannot be the sole factor responsible for the propensity of acids to add to low oxidation state transition metal complexes, evidence being presented that both the acidity of the protonic acid and the nephelauxetic effect of the conjugate base are responsible for the formation of stable hydrides[5,6].

We have recently described the syntheses and some reactions of diphenyldithiophosphato and dicyclohexyldithiophosphinato complexes of rhodium(I) and iridium(I)[7]. This paper deals with the reactions of diphenyldithiophosphoric and diphenyldithiophosphinic acids with low oxidation state complexes of ruthenium(O), rhodium(I), iridium(I) and platinum(O). Before this work, the $IrH_2L_2(S–S)$ (L = PPh_3, $AsPh_3$; S–S = O,O′-disubstituted dithiophosphate or P,P′-disubstituted dithiophosphinate) complexes are the only hydridodithiophosphato and hydridodithiophosphinato compounds which have been reported[8].

Experimental

The starting materials $Ru(CO)_3(PPh_3)_2$[9], $Rh(CO)(PPh_3)_2Cl$[10], $Ir(CO)(PPh_3)_2Cl$[11], $Ir(CO)H(PPh_3)_3$[12], $Pt(PPh_3)_4$[13], Ph_2PSSH[14] and $(PhO)_2PSSH$[15] were prepared following methods reported in the literature. Other chemicals were reagent grade and were used without purification. I.r. spectra were recorded with a Perkin–Elmer 457 spectrophotometer. Molecular weights were determined with a Knauer vapour-pressure osmometer. Elemental analyses were by Bernhardt, Mülheim, Germany. All reactions were carried out under an atmosphere of oxygen-free nitrogen.

Dicarbonylbis(diphenyldithiophosphato)bis(triphenylphosphine)ruthenium(II), $Ru(CO)_2(PPh_3)_2[SSP(OPh)_2]_2$

A dichloromethane solution of $(PhO)_2PSSH$ was added dropwise to $Ru(CO)_3(PPh_3)_2$ (0.250 g, 0.35 mmol) dissolved in the same solvent. The progress of the reaction was followed by i.r. spectroscopy. The mixture was stirred for about 10 min and then partial evaporation of the solvent *in vacuo,* followed by addition of hexane, afforded a yellow solid. The pure product was obtained after recrystallization from dichloromethane–hexane. The complex *dicarbonylbis(diphenyldithiophosphinato) bis (triphenylphosphine)ruthenium(II)* was prepared similarly from $Ru(CO)_3(PPh_3)_2$ and the appropriate acid.

Carbonylchloro(diphenyldithiophosphato)hydridobis(triphenylphosphine)iridium(III), $Ir(CO)ClH(PPh_3)_2[SSP(OPh)_2]$

To a solution of *trans*-$Ir(CO)(PPh_3)_2Cl$ (0.400 g, 0.51 mmol) in degased benzene (50 ml) was added a solution of $(PhO)_2PSSH$ in the same solvent dropwise until the yellow colour of the solution just disappeared (about 3 min). Evaporation under reduced pressure gave an oil which was crystallised from ether and successively from dichloromethane–pentane as white crystals. Similarly prepared, as white crystals, using diphenyldithiophosphoric acid, was *carbonylchloro(diphenyldithiophosphinato) hydridobis (triphenylphosphine)iridium(III).*

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Carbonyldihydridotris(triphenylphosphine)iridium(III) Diphenyldithiophosphinate Salt, $[Ir(CO)H_2(PPh_3)_3]SSPPh_2$

A solution of diphenyldithiophosphinic acid in benzene was added dropwise to a solution of $Ir(CO)H(PPh_3)_3$ (0.300 g, 0.29 mmol) in the same solvent, until the yellow colour was just discharged (2 min). The mixture was stirred for 5 min, then the solvent was removed under reduced pressure and the residual oil was treated with ether and successively crystallised from dichloromethane–hexane as white crystals. The tetraphenylborate salt was obtained by adding $NaBPh_4$ dissolved in methanol to a solution of $[Ir(CO)H_2(PPh_3)_3]SSPPh_2$ in the same solvent. The complex *carbonyldihydridotris (triphenylphosphine) iridium (III) diphenyldithiophosphate* was prepared similarly from $Ir(CO)H(PPh_3)_3$ and the appropriate acid.

Cis-bis(triphenylphosphine)diphenyldithiophosphatohydridoplatinum(II), cis-$PtH(PPh_3)_2[SSP(OPh)_2]$

To a filtered solution of $Pt(PPh_3)_4$ (0.40 g, 0,32 mmol) in benzene (40 ml), $(PhO)_2PSSH$ in the same solvent was added dropwise until the yellow colour of the solution just disappeared (3 min). The solvent was evaporated off and the crude product crystallised several times form dichloromethane–ether. Cis-*bis(triphenylphosphine) diphenyldithiophosphinatohydridoplatinum(II)* was prepared similarly.

Reactions of $Ir(CO)H(PPh_3)_2(SSPR_2)Cl$ with MeI or EtI

No reaction was observed when $Ir(CO)H(PPh_3)_2(SSPR_2)Cl$ and MeI or EtI were left to react at room temperature. A suspension of $Ir(CO)H(PPh_3)_2(SSPR_2)Cl$ in MeI or EtI (4 ml) was heated under reflux with stirring for *ca.* 3 h. The solvent was evaporated off and the crude product washed with ether and crystallised from dichloromethane–hexane gave always $Ir(CO)H(PPh_3)_2ClI$. By evaporation of the ether solution a white solid was obtained; the elemental analyses of these products are consistent with the esters R_2PSSR' (R' = Me, Et) (Found C, 60.52; H, 5.02; S, 25.3%; $C_{13}H_{13}PS_2$ requires C, 59.07; H, 4.95; S, 24.25%. Found C, 53.4; H, 4.73; S, 22.3%; $C_{13}H_{13}O_2PS_2$ requires C, 52.69; H, 4.42; S, 21.63%).

Reactions of $PtH(PPh_3)_2(SSPR_2)$ with MeI or EtI

$PtH(PPh_3)_2(SSPR_2)$ does not react at room temperature with MeI or EtI while when the suspension was heated to reflux for *ca.* 4 h a reaction occurs. The solvent was evaporated off and the crude product washed with ether and crystallised from dichloromethane–hexane gave a yellow solid characterised as $Pt(PPh_3)_2I_2$. By evaporation of the ether solution a white solid was obtained; analytical data of the products obtained are sonsistent with those of the esters R_2PSSR' (R' = Me, Et).

Results and Discussion

The new complexes described are air-stable crystalline solids, monomeric in benzene solution, soluble in benzene, acetone and dichloromethane but not sufficiently to obtain satisfactory ^1H n.m.r. spectra in the hydride region. Howing to this reason, stereochemical assignments for the new complexes have been made using i.r. data and, where necessary, chemical evidence. Analytical results and pertinent i.r. spectral data for all compounds prepared are given in Table I.

Ruthenium Complexes

Tricarbonylbis(triphenylphosphine)ruthenium(0) reacts with diphenyldithiophosphoric and diphenyldithiophosphinic acids in benzene solution to give the yellow crystalline products $Ru(CO)_2(PPh_3)_2(SSPR_2)_2$ (R = Ph, OPh). No evidence was obtained for the formation of hydrido complexes in these reactions. The products are similar to those observed in the reaction of $Ru(CO)_3(PPh_3)_2$ with trifluoroacetic[16] or carboxylic[17] acids. No hydrido complex was obtained in the reaction of $Ru_3(CO)_{12}$ with Ph_2PSSH and the only product was the dicarbonyl complex $Ru(CO)_2(SSPPh_2)_2$ in which the dithio ligands are chelating agents[18]; in contrast, the same reaction with carboxylic acids gives hydrido complexes.

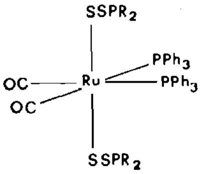
The monomeric formulation of compounds $Ru(CO)_2(PPh_3)_2(SSPR_2)_2$ has been established from molecular weight determination in benzene solution. The i.r. spectra of the complexes exhibit bands in the region associated with co-ordinated terminal carbonyl, triphenylphosphine ligand and dithiophosphato- or dithiophosphinato group. Recently, characteristic bands of the co-ordination mode of the dithio ligand in the ν(P–S) stretching region have been assigned[18–20] The i.r. spectra of $Ru(CO)_2(PPh_3)_2(SSPR_2)_2$ compounds in the ν(P–S) stretching region are rather complicated, showing absorptions due to the tertiary phosphine as well as the dithiophosphato- or dithiophosphinato groups; the presence of the carbonyl bending vibration in this region is a complicating factor. Thus, the presence of the bands at 642 and 540 cm^{-1} in the $Ru(CO)_2(PPh_3)_2(SSPPh_2)_2$ complex must be considered with caution as diagnostic of unidentate co-ordination of the dithio ligand. In the $Ru(CO)_2(PPh_3)_2[SSP(OPh)_2]$ complex, only an i.r. absorption at 535 cm^{-1} can be considered characteristic of monodentate $-SSP(OPh)_2$ co-ordination. Two strong bands appearing at about 2050 and 2000 cm^{-1} are assigned to the terminal carbonyl stretching vibrations and indicate that the two carbonyl groups, in the $Ru(CO)_2(PPh_3)_2(SSPR_2)_2$ complexes, are in *cis* arrangement. Significantly, the ν(CO) stretching frequencies for $Ru(CO)_2(PPh_3)_2(SSPR_2)_2$ complexes are similar to those observed for analogous trifluoroacetato[16] and acetato[17] compounds, and on the basis of the arguments

TABLE I. Analytical Data (%)[a] and Characteristic I.r. Spectral Data (cm^{-1}).

Complex	Colour	C	H	S	Cl	ν(CO)[b]	ν(M–H)[b]
$Ru(CO)_2(PPh_3)_2(SSPPh_2)_2$	Yellow	62.99 (63.09)	4.27 (4.27)	10.81 (10.86)		2050vs 1998vs	
$Ru(CO)_2(PPh_3)_2[SSP(OPh)_2]_2$	Yellow	59.81 (59.84)	4.11 (4.05)	10.41 (10.30)		2055vs 1995vs	
$Ir(CO)H(PPh_3)_2(SSPPh_2)Cl$	White	57.12 (57.10)	4.08 (4.01)	6.20 (6.22)	3.52 (3.44)	2035vs	2185m
$Ir(CO)H(PPh_3)_2[SSP(OPh)_2]Cl$	White	55.24 (55.39)	3.77 (3.89)	5.89 (6.03)	3.18 (3.33)	2040vs	2205m
$[Ir(CO)H_2(PPh_3)_3]SSPPh_2$	White	63.81 (63.94)	4.42 (4.56)	6.03 (5.09)		2010s	2110s 2155sh
$[Ir(CO)H_2(PPh_3)_3]SSP(OPh)_2$	White	62.28 (62.36)	4.55 (4.45)	5.01 (4.96)		2010s	2110s 2155sh
$Ir(CO)H(PPh_3)_2ClI$	Pale yellow	48.76 (48.93)	3.51 (3.44)		3.96[c] (3.90)	2025vs	2195s[d]
$PtH(PPh_3)_2(SSPPh_2)$	White	59.67 (59.43)	4.38 (4.25)	6.72 (6.61)			2148m
$PtH(PPh_3)_2[SSP(OPh)_2]$	White	57.61 (57.53)	4.15 (4.12)	6.32 (6.40)			2165m–s
$Pt(PPh_3)_2I_2$	Yellow	44.52 (44.41)	3.14[e] (3.10)				

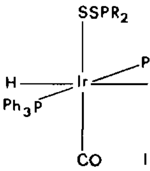
[a] Calculated values in parentheses. [b] Nujol mulls. [c] I, 13.85(13.97). [d] ν(Ir–Cl) 312 cm^{-1}. [e] I, 26.11(26.07).

reported in reference 17 for the acetato compounds, we consider that the complexes $Ru(CO)_2(PPh_3)_2(SSPR_2)_2$ have probably the following structure: ·



Rhodium and Iridium Complexes

Diphenyldithiophosphoric or diphenyldithiophosphinic acids react with *trans*-$Ir(CO)(PPh_3)_2Cl$ giving $Ir(CO)H(PPh_3)_2(SSPR_2)Cl$ compounds. They are white, air-stable crystalline solids, monomeric and non-conducting in benzene solution. If octahedral six-co-ordination is assumed for the iridium(III) ion, then the dithio ligand acts as monodentate ligand. The phosphine ligands are almost always *trans* to each other in related complexes[2,21–24]; then three isomers (Figure 2) are possible for the Hydrido complexes prepared:



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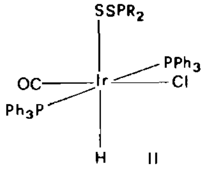
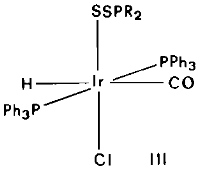


II



III

A single absorption band at 275 cm^{-1} in the Ir–Cl stretching region and the ν(Ir–H) at about 2200 cm^{-1} indicate that Cl is *trans* to a hydrido ligand (structure I) and allow to rule out the structure II wherein the CO is *trans* to Cl (in this case the ν(Ir–Cl) stretching frequency should have appeared at 300–315 cm^{-1} [25]). A ν(Ir–H) value at lower wavenumbers than that observed should be expected for the structure III where a *trans* H–Ir–CO geometry is present.

The complex *trans*-$Rh(CO)(PPh_3)_2Cl$ does not react at room temperature with R_2PSSH acids, confirming that rhodium(I) complexes are less effective in the oxidative additions and in the stabilisation of hydrido species than the analogous iridium(I) compounds. The reaction of diphenyldithiophosphinic acid with $Rh(PPh_3)_3Cl$ has been previously[26] reported and gives the $[Rh(PPh_3)(SSPPh_2)]_2$ complex by a mechanism probably involving addition of Ph_2PSSH to the rhodium(I) complex followed by *cis*-elimination of HCl.

$Ir(CO)H(PPh_3)_2(SSPR_2)Cl$ complexes react with R'I (R' = Me, Et) to give $Ir(CO)H(PPh_3)_2ClI$[27] and the ester R_2PSSR' which has not been fully characterised (see Experimental). Sulphur atoms in the prepared hydridodithiophosphato- and hydridodithiophosphinato iridium(III) complexes are nucleophilic centers and can undergo electrophilic attack in the reactions with alkyl iodides. A mechanism involving an electrophilic attack of the alkyl group at sulphur with formation of a labile cationic complex which in turn undergoes a fast rearrangement involving the coordination of the halogen to the metal seems then reasonable for the described reactions. We are unable to establish the structure of the cationic intermediate because it is not possible to indicate which sulphur atom undergoes the electrophilic attack. The proposed mechanism can be related to the known alkylation reaction of sulphur in metal complexes[28–30].

The carbonyl hydride $Ir(CO)H(PPh_3)_3$ reacts immediately in benzene solution with diphenyldithiophosphoric or diphenyldithiophosphinic acids to give $[Ir(CO)H_2(PPh_3)_3]SSPR_2$; on adding $NaBPh_4$ in methanol to a solution containing the cationic complex in the same solvent, the salt $[Ir(CO)H_2(PPh_3)_3]BPh_4$ was obtained, confirming that the dithio ligand is not a co-ordinated ion. The hydrido cation $[Ir(CO)H_2(PPh_3)_3]^+$ has been previously described[26] and our spectroscopic data are in agreement with them.

Platinum Complexes

Tetrakis(triphenylphosphine)platinum(0) also undergoes oxidative addition reaction with diphenyldithiophosphoric or diphenyldithiophosphinic acids, giving the hydrido complexes $PtH(PPh_3)_2(SSPR_2)$. The i.r. spectra of these compounds show the ν(Pt–H) at about 2150 cm^{-1}; in the far-infrared spectrum of $PtH(PPh_3)_2(SSPPh_2)$, besides absorptions due to the tertiary phosphine as well as the dithio ligand, there appear bands at 545 and 655 cm^{-1} which are very close to those reported[20] as characteristic of monodentate $-SSPPh_2$ co-ordination in platinum(II) complexes. This is consistent with a square-planar structure and allows us to establish that the prepared complexes are not five-co-ordinate hydrido species of platinum(II).

$PtH(PPh_3)_2(SSPR_2)$ compounds react with MeI or EtI giving *trans*-$Pt(PPh_3)_2I_2$ as final product. The formation of the di-iodide complex indicates that the reaction takes place by two steps: (i) electrophilic attack of the alkyl group at the sulphur atom of co-ordinated dithio ligand with formation of a cationic labile intermediate which in turn yields the free ester R_2PSSR' ($R' = Me, Et$) (see Experimental) by co-ordination of iodide to metal, as observed in the analogous reaction of $Ir(CO)H(PPh_3)_2(SSPR_2)Cl$; (ii) reductive elimination of methane or ethane from a transient intermediate platinum(IV) complex formed by oxidative addition of MeI or EtI to a platinum(II) hydrido complex[31]. Owing to the lack of kinetic data, we cannot establish which step is the first among the two.

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