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Iridium(III) Derivatives of Dithiophosphoric and Dithiophosphinic Acids

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H_2IrL_2(chel) compounds ($L = PPh_3$, $AsPh_3$; chel = O,O'*-disubstituted dithiophosphate, or* P,P*-disubstituted dithiophosphinates) were prepared. Structure proposals are made on the basis of i.r. and n.m.r. spectral evidence.*

Introduction

The preparation and properties of the coordinatively unsaturated iridium(III) hydrides $IrH_3(PPh_3)_2$, *I*, and $IrH_3(AsPh_3)_2$, *II*, have been reported.[1] The reaction of *I* and *II* with chelating mononegative ligands has been studied,[2] in the case of pentan-2-4-dionate of other β-diketonates, of N,N-dialkyl-dithiocarbamate, and of N,N-diethyldiselenocarbamate. Here preparation and properties of $H_2Ir^{III}L_2$(chel) ($L = PPh_3$, $AsPh_3$) are reported, where chel is the chelating anion, a *O,O'*-disubstituted dithiophosphate, $(RO)_2PS_2^-$, or a *P,P*-disubstituted dithiophosphinate, $R_2PS_2^-$, ligands known[3,4,5,6] to yield stable derivative of metallic and organometallic cations, suitable for spectroscopic studies.

Measuraments

Analytical and other data relating to the compounds prepared are given in Table I. ^1H n.m.r. data are given in Table II. The decomposition points were determined in the air and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 621, n.m.r. spectra by Dr. G. Bonora on a Perkin-Elmer R-10 instrument, operating at 33°C and 60.0 Mc, using tetramethylsilane as internal standard. Conductivity measurements were carried out for some compounds and their non-ionic nature was confirmed.

Discussion

The preparation of the compounds was generally carried out by reaction of the hydride *I* or *II* with the appropriate ligand, in form either of the acids or of the alkali salts in methanol-benzene suspension. The compounds (Table I) are crystalline, stable and white solids, with the exception of $Ir[S_2P(OEt)_2]_3$, VII, which is orange, like the analogous rhodium complex.[7] Elemental analyses, infrared and n.m.r. spectra established $H_2Ir(EPh_3)$(dithioligand) (E = P, As) as the correct formula.

The molecular weight determinations (Table I), in benzene or chloroform solution, allowed us to rule out associated structures, such as those suggested[4,5,8] for some dithiophosphate or dithiophosphinate in solution and such as those established[9] by X-rays in

Table I. Analytical, Molecular weight, and I.R. Data

Compound [a]	dec. point °C	Calculated C	H	M	Found C	H	M	ν(Ir—H) [e]
III	195	52.11	4.34	875	51.88	4.19	940	2210, 2143
IV	188	53.15	4.65	903	53.13	4.45	898	2190, 2127
V	199	54.03	3.75	1066	54.50	3.91	1145	2185, 2136
VI	181	48.33	4.23	993	48.63	4.23	1050	2115, 2085
VII [a]	125 [b]	19.24	4.04	747	19.97	4.19	735	— —
VIII	185	55.23	4.60	871	55.43	4.72	838	2242, 2140
IX	183	59.56	4.34	967	60.07	4.62	992 [d]	2160, 2131
X	176	49.94	4.37	961	49.53	4.47	940 [d]	2200, 2120

[a] All the compounds are white, except VII, which is orange; [b] Melting point; [c] by osmometry in 1% benzene solution at 37°C, unless stated otherwise; [d] by osmometry in 1% chloroform solution at 37°C; [e] nujol mull.

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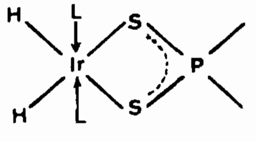
Table II. ^1H n.m.r. data [a]

Compound and	Solvent	Hydride			Other Ligands Methyl		Methylene		Aromatic
III,	C_6D_6	29.8 dT	6	18	7.15 D	19	—	—	1.85-2.25; 2.60-3.1
III,	$CDCl_3$	30.0 dT	6	18	7.15 D	14	—	—	2.1-2.8
IV,	C_6D_6	29.8 dT	5	18	9.19 T	7	6.68 dQ	10	1.8-2.25; 2.7-3.1
IV,	$CDCl_3$	30.4 dT	5	19	9.15 T	7	6.85 dQ	. . .	2.17-2.85
V,	$CDCl_3$	30.8 dT	6	19	—	—	—	—	2.3-3.4
VI,	$CDCl_3$	24.4 S	—	—	broad multiplet,		8-10		2.5-3.2
VI,	C_6D_6	23.5 S	—	—	broad multiplet,		8.5-9.5		2.4-3.2
VII,	$CDCl_3$	—	—	—	8.62 T	7	5.70 dQ	3,7	—
VIII,	$CDCl_3$	31.7 dT	5	19	complex multiplet, 8.5-10				2.1-3.2
IX,	$CDCl_3$	32.2 dT	4	18	—	—	—	—	2.2-3.1
X,	$CDCl_3$	24.5 S	—	—	broad absorption, 8.5-10				2.91 S

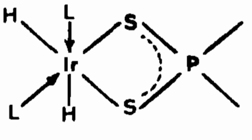
[a] Spectra recorded at 60 Mc in saturated solution at 33°C; [b] S, Singulet; D, Doublet; T, Triplet; Q, Quartet; M, Multiplet; d, double.

the case of $Co(S_2PEt_2)_2$ or $Ni(S_2PEt_2)_2$. These last results and the structure determination carried out for $V[S_2P(OEt)_2]_3$,[10] $Ni(S_2PPh_2)_2$,[11] and $Ni[S_2P(OMe)_2]_2$,[12] suggest that the dithioligand employed behave generally as chelate anion, although 2,9-dimethyl-1,10-phenanthrolinebis(*O,O'*-dimethyldithiophosphate)nickel(II) has been quite recently shown[13] to contain a non chelating dithiophosphate group.

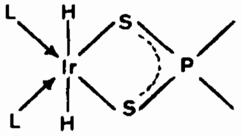
The related iridium(III) complexes $H_2Ir(PPh_3)_2$(β-diketonato), and $H_2Ir(AsPh_3)_2$(β-diketonato) have been shown[1c,2] to contain a six-coordinate iridium(III) atom. On this ground, and on the evidence given by the X-ray structure of the related dithiophosphates and dithiophosphinates,[9,10,11,12] the compounds here reported are likely to have a octahedral arrangement of ligands, that is, either A, or B, or C



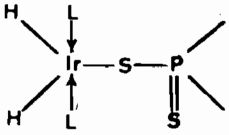
A



B



C



D

The presence of two infrared iridium-hydrogen stretching bands, in all the hydride complexes reported rules out structure C, which requires only one infrared active Ir–H vibration. Structure B requires the presence of two non-equivalent L ligands, while the ^1H n.m.r. spectrum indicated that the L ligands are equivalent . The observed position and number of the ν(Ir–H) is in agreement with structure A, which requires a n.m.r. spectrum where the hydride signal is split into a triplet with the observed magnitude of J(H–Ir–P).[14]

The presence of a double triplet (J≅4-6 cps) in the hydride part of the n.m.r. spectra of compounds III, IV, V, VIII and IX can be explained assuming either a geminal H–H coupling, or an equilibrium in the solution between structure A and structure D, or a coupling with the phosphorous nucleus of the dithiophosphate or dithiophosphinate ligand. Geminal H–H coupling in hydride complexes has been reported but it requires magnetical non-equivalence of the hydrido groups; a similar case was observed[2] for $H_2Ir(PPh_3)_2$(1,1',1"-trifluoropentan-2,4-dionate). Because no similar asymmetry is present here, geminal H–H coupling is not considered to be a valid explanation. An equilibrium between structure A and D cannot be accepted to explain the hydride double triplet; doubling of the P– or O– alkyl signals would also be required, and to explain our spectra the equilibrium composition should, surprisingly, be 50-50% for all compounds III, IV, V, VIII and IX. A coupling between the phosphorous nucleus of the dithioligand and the hydride-coupled phosphorus nuclei of the PPh_3 groups can be accepted.

This view can explain the double triplet observed in the n.m.r. spectra of compounds III, IV, V, VIII, and IX, and the absence of splitting in compound VI and X, where L = $AsPh_3$. The amount of coupling is rather small, 4-6 cps, and, consequently, this type of coupling could not be observed[3] on more distant protons, such as those of the methyl groups in $Me_2TlS_2P(OR')_2$.[3] The coupling must take place not mainly by the way of the sulphur and iridium atoms, but also by some other mechanism. Otherwise, being the phosphorus nucleus of PPh_3 and of the hydride nuclei separated by the same number of bonds from the phosphorus nucleus of the dithioligand, the coupling should be possible even in the case of the arsine derivatives VI and IX.

The additional way by which coupling might be transmitted is the interaction of the ring current of an aryl ring of the phosphines with the electronic density localized on the chelated moiety. This interaction is possible with phosphines where the radius

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of the tricovalent phosphorus (1.10 A) is smaller than the radius of the tricovalent arsenic (1.21 A); further, ^{75}As has spin 3/2 and a finite electric quadrupole moment, so that every coupling by this way cannot be operative on a ^{75}As nucleus.

Additional support can be found for this way of explaining a long-range effect. The following table gives the τ values for the O-alkyl groups of different dithiophosphates ($CDCl_3$ solution):

	τCH_3	τCH_2
$(CH_3O)_2PS_2Tl$	6.33	—
$[(CH_3O)_2PS_2]_2Zn$	6.19	—
$H_2Ir(PPh_3)_2[S_2P(OCH_3)_2]$	7.20	—
$Me_2TlS_2P(OEt)_2$	8.65	5.88
$Et_2TlS_2P(OEt)_2$	8.66	5.90
$TlS_2P(OEt)_2$	8.70	5.90
$Ir[S_2P(OEt)_2]_3$	8.58	5.64
$H_2Ir(PPh_3)_2[S_2P(OEt)_2]$	9.19*	6.68*
	9.15	6.85

* Benzene solution.

It is evident that the τ values of the dihydrido-iridium(III) compounds are exceptional and that solvent effect is small even on going from benzene to chloroform. For example, metal and organometal dithiocarbamate (*e.g.*, $Zn(S_2CNEt_2)_2$, $R_3Sn(S_2CNEt_2)$, $R_2Sn(S_2CNEt_2)_2$) as well as alkyl dithiocarbamate (*e.g.* EtS–C(S)–NEt_2) have all quite similar τ values (8.70±0.04 τ for CH_3 and 6.17+0.05 τ for CH_2).[15]

The abnormally high values (Δτ up to 1τ) observed for iridium hydride dithiophosphates compared to other dithiophosphates, could be due either to hydride *trans*-effect, or to long range shielding from aryl groups of PPh_3 ligands. The first explanation is not to be preferred; a stronger perturbation than the introduction of two H^- such as a difference of two in the formal oxidation state (from Tl^I to Tl^{III}) produces nearly no change on τ value. Similarly, on related chelated complexes:[16] in $(CO)_2$Rhacac the effect of changing carbonyls with other ligands on the shifts of the methyl groups bonded to the acetylacetonato ring is not so big: *e.g.* 7.89τ in $(CO)_2$Rhacac and 8.16 in (norbornadiene)Rhacac, both in CCl_4.

Therefore the abnormally high values recorded for the dihydridoiridium(III) complexes might be rather due to long range shielding on the O-bonded alkyl groups by phenyl group of the phosphine ligand.

This shielding explains also the lack of the generally remarkable low field shifting on going from aromatic to $CDCl_3$ solvent. The order of magnitude of such a shielding from an aromatic molecule in chelated molecules can be judged by a solvent effect[17] on $(CO)_2$Iracac: τ(CH_3) was found to be 8.42 and 7.90, and τ(CH) was found to be 4.85 and 4.26 in C_6H_6 and CS_2 solution respectively.

Experimental Section

Bis(*triphenylphosphine*)(O,O′-*dimethyldithiophosphato*)*dihydridoiridium*(*III*). III. To a methanol solution (50 ml) of potassium *O*,*O*′-dimethyldithiophosphate (0.2 g, 1 mM) a suspension of tris(triphenylphosphine)trihydridoiridium(III), *I*, (0.718 g, 1 m*M*) in benzene (100 ml) was added. After 48 hrs the solution was evaporated to dryness, the residue was extracted with benzene (20 ml) and the crude product was precipitated by adding methanol. The analytical sample (0.4 g) was obtained after two additional crystallizations from benzene/methanol, in form of white small crystals.

Bis(*triphenylphosphine*)(O,O′-*diethyldithiophosphato*) *dihydridoiridium*(*III*). *IV*. At 50-60°C, tris(triphenylphosphine)trihydridoiridium(III), *I*, (0.719 g) was added to a benzene solution (100 ml) of *O*,*O*′-diethyldithiophosphoric acid (0.186 g). When gas evolution stopped (*ca.* 1 hr), the filtered solution was concentrated to *ca.* 20 ml and the crude product was precipitated by addition of methanol. After two additional crystallizations from benzene/methanol, white, thin needles of the product IV were obtained.

Bis(*triphenylphosphine*)(O,O′-*di*(p-*chloro*)*phenyldithiophosphato*)*dihydridoiridium*(*III*). V. It was prepared similarly to *III*, but at 64° for 24 hrs and under stirring; yield 0,7 g.

Bis(*triphenylarsine*)(O,O′-*diethyldithiophosphato*)-*dihydridoiridium*(*III*). VI. Bis(triphenylarsine)trihydridoiridium(III) *II* (0.808 g, 1 m*M*) in benzene (100 ml) was treated with a methanol solution (150 ml) of potassium *O*,*O*′-diethyldithiophosphate (0.225 g) for 12 hrs under stirring. The solution was then concentrated to small volume and a large excess of methanol was added, to yield a greenish solid. Chromatography on alumina (grade II) of the benzene solution of the greenish solid, yielded the product VI, isolated by adding methanol to the residue from the first benzene eluates.

Tris(O,O′-*diethyldithiophosphato*)*iridium*(*III*). VII. An aqueous solution (50 ml) of sodium hexachloroiridate(III) (0.948 g) was treated with an aqueous solution (50 ml) of sodium *O*,*O*′-diethyldithiophosphate (1.176 g) and the resulting green solution was treated under reflux 5-6 hrs. A brown precipitate formed, and was filtered (0.6 g). As it is very soluble in all the organic solvents tried, it was purified by chromatography on alumina (grade II) of a benzene solution. An orange band developped, which was isolated and yielded the product VII, (0.5 g) on evaporation.

Bis(*triphenylphosphine*)(P,P-*diethyldithiophosphinato*)*dihydridoiridium*(*III*). VIII. A benzene suspension (120 ml) of bis(triphenylphosphine)trihydridoiridium(III) *I* (0.719 g, 1 m*M*) was added to a methanol solution (80 ml) of sodium *P*,*P*-diethyldithiophosphinate (0,176 g). After 24 hrs at 64° under stirring, the filtered solution was evaporated to a small volume; on addition of metha-

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nol a crude product precipitated, which was purified on alumina (grade II) using a benzene solution: product VIII (0.2 g) was obtained on evaporation.

Bis(triphenylphosphine)(P,P-*diphenyldithiophosphinato)dihydridoiridium(III)*. IX. The compound (0.7 g) was obtained as above (compound VIII) reaction time being 48 hrs at room temperature.

Bis(triphenylarsine)(P,P-*diethyldithiophosphinato)dihydridoiridium(III)*. X. The compound (0.4 g) was obtained as compound IX.

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