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Complex Iridium(III) Hydrides with Dithiocarbamate and Xantate Groups

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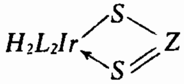
After the synthesis of the iridium(III) hydrides $IrH_3[P(C_6H_5)_3]_2$[1] *and* $IrH_3[As(C_6H_5)_3]_2$,[2] *the reactions of these co-ordinatively unsaturated intermediates have been studied with chelating mononegative ligands having oxygen (β-diketonates)*[3] *or sulphur [0,0′-dialkyldithiophosphates (A), 0,P-dialkyldithiophosphinates (B)]*[4] *as donor atoms. In this note the derivatives with chel = N,N′-diethyldithiocarbamate (C) and 0-ethylxanthate (D) are reported. They are the first examples of iridium(III) derivatives of dithiocarbamate and xanthate and also the first examples of hydrido complexes with these ligands. They were prepared so that the study of ligands with two sulphur atoms could be completed and were chosen in order to study the effect of varying the Z group in the chelating moiety of the compounds of the type*  $H_2L_2Ir\langle S_2 \rangle Z$ *[A), Z = P(OR)₂; B), Z = PR₂; C), Z = CNR₂; D), Z = COR].*

Experimental Section

Some properties of the new compounds are reported in Table I. Molecular weight determinations (±5%) were carried out in benzene solution (ca. 1%) on a Mechrolab Osmometer 301-A. Melting points were determined in the air on a Leitz apparatus. Infrared spectra were recorded on Perkin Elmer 237 or 621 spectrometer. ^1H n.m.r. spectra (Table II) were recorded on a P.E. R-10 instrument operating at 60 Mc./sec. and 33°C, using tetramethylsilane as internal standard and $CDCl_3$ as solvent.

The new compounds are indefinitely stable to air, soluble in chloroform, benzene, methylene chloride and insoluble in alcohols and in acetone. All of them are diamagnetic as shown by their n.m.r. spectra.

Starting Material. $IrH_3[P(C_6H_5)_3]_2$[1] and $IrH_3[As(C_6H_5)_3]_2$ were prepared according to the procedure previously described.[5,2]

Dihydridodiethyldithiocarbamatobis(triphenylphosphine)iridium(III), $IrH_2[S_2CN(C_2H_5)_2]\ [P(C_6H_5)_3]_2$, I.

A solution of sodium diethyldithiocarbamate (0.2 g, 1.2 mmoles) in acetone (10 ml) was added, drop by drop, to a suspension of $IrH_3(PPh_3)_2$ (0.72 g, 1 mmol) in benzene (100 ml), under reflux and with stirring until a yellow colour appeared (ca. 20 mins). After filtering to remove a small amount of unreacted $IrH_3(PPh_3)_2$ and concentrating under reduced pressure to 50 ml, ethanol was added (2:1) and a pale yellow product (0.4 g) was obtained, which was filtered off and reprecipitated from benzene solution by the addition of ethanol.

Anal. Calcd for $C_{41}H_{42}IrNP_2S_2$: C, 56.79; H, 4.89; N, 1.61; S, 7.39%. Found: C, 56.35; H, 5.02; N, 1.33; S, 7.71.

Infrared spectrum (Nujol and C_4Cl_6 mulls, cm^{-1}): 2125s, 2085s, 2070sh, 1480s, 1425s, 1360w, 1340w, 1295m, 1260s, 1210s, 1180w, 1140s, 1090s, 1065m, 1025w, 1005w, 1000w, 915w, 850w, 830w, 780w, 740s, 700, 617w, 594w, 575w, 545s, 517s, 508s, 500s, 454w 447w, 437m, 427w, 421m, 402w, 359w, 324w, 320w, 298w, 262w, 251w.

Dihydridodiethyldithiocarbamatobis(triphenylarsine)iridium(III), $IrH_2[S_2CN(C_2H_5)_2]\ [As(C_6H_5)_3]_2$, II.

This compound was prepared analogously to compound I, from $IrH_3(AsPh_3)_2$ (0.8 g, 1 mmol) and sodium diethyldithiocarbamate (0.2 g, 1.2 mmoles).

Anal. Calcd for $C_{41}H_{42}As_2IrNS_2$: C, 51.47; H, 4.44; N, 1.46; S, 6.72%. Found: C, 51.1; H, 4.30; N. 1.52; S, 6.2%.

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Table I. Iridium(III) hydrides dithiocomplexes and some their properties.

Compound		Colour	m.p. °C [a]	M.W. calcd.	M.W. found	ν(Ir-H) (cm^{-1}) [b]
I	$IrH_2[P(C_6H_5)_3]_2[S_2CN(C_2H_5)_2]$	pale yellow	193	867	868	2125-2085
II	$IrH_2[As(C_6H_5)_3]_2[S_2CN(C_2H_5)_2]$	yellow	198	955	978	2085-2040
III	$IrH_2[P(C_6H_5)_3]_2(S_2COC_2H_5)$	pale yellow	190	840	880	2150-2100
IV	$IrH_2[As(C_6H_5)_3]_2(S_2COC_2H_5)$	pale yellow	199	928	960	2095-2065

[a] Uncorrected (± 2°C). [b] Nujol mull.

Table II. ^1H Nuclear Magnetic Resonance Data. *J*-Values in c./sec. Aromatic bands omitted. $CDCl_3$ solvent.

	H^-						
Compound	τ	Moltiplicity and [relative area]	Coupling constant	τ	CH_3 multiplicity	τ	CH_2 multiplicity
I	29,5	triplet [2]	16.1	9.2	triplet [6]	7	quadruplet [4]
II	31	singlet [2]	—	9.20	triplet [6]	6.85	quadruplet [4]
III	29.2	triplet [2]	15.6	8.95	triplet [3]	6.22	quadruplet [2]
IV	30.4	singlet [2]	—	8.95	triplet [3]	6.25	quadruplet [2]

Infrared spectrum (Nujol and C_4Cl_6 mulls, cm^{-1}): 2085s, 2040s, 1560m, 1495sh, 1490s, 1480s, 1430, 1370s, 1350m, 1295m, 1265m, 1210s 1180w, 1140s, 1095w, 1075s, 1000m, 910w, 850w, 815w, 770w, 735sh, 700s, 693s, 688s, 670w, 611w, 578w, 566w, 480m, 473m, 465s, 453w, 395w, 356w, 344sh, 327s, 319sh, 312sh, 271w, 261w.

Dihydrido-0-ethylxanthatobis(triphenylphosphine)iridium(III), $IrH_2(S_2COC_2H_5)[P(C_6H_5)_3]_2$, III.

By a procedure similar to that described above for the compound I, 0.3 g of the compound III were obtained by reacting $IrH_3(PPh_3)_2$ (0.72 g, 1 mmol) and sodium xanthate (0.17 g, 1.2 mmoles).

Anal. Calcd for $C_{39}H_{37}IrOS_2$: C, 55.75; H, 4.44; S, 7.63%. Found: C, 56.2; H, 4.4; S, 7.01%.

Infrared spectrum (Nujol and C_4Cl_6 mulls, cm^{-1}): 2150m, 2100m, 1560w, 1480s, 1450s, 1440sh, 1430s, 1375sh, 1355s, 1320w, 1300sh, 1290m, 1230sh, 1210s, 1175m, 1160m, 1135sh, 1120w, 1080s, 1075sh, 1060w, 1050s, 1025w, 1005m, 1000sh, 880w, 860w, 840w, 820m, 810w, 765w, 730s, 700s, 690s, 615w, 601w, 545m, 517s, 503s, 456w, 440w, 438sh, 430w, 419w, 358w, 340w, 274w, 250w.

Dihydrido-0-ethylxanthatobis(triphenylarsine)iridium(III),
$Irh_2(S_2COC_2H_5[As(C_6H_5)_3]_2$, IV.

The preparation of this compound was carried out in a similar way to that of compound I. By reacting for *ca* 2 hrs $IrH_3(AsPh_3)_2$ (0.8 g, 1mmol) in acetone (100 ml) and sodium 0-ethylxanthate (0.17 g, 1.2 mmoles) in acetone (20 ml), a pale-yellow precipitate (0.4 g) was deposited, which was separated by filtration, reprecipitated from benzene solution by the addition of ethanol, to eliminate the solvate acetone showed by means IR and ^1H n.m.r. spectra.

Anal. Calcd for $C_{39}H_{37}As_2IrOS_2$: C, 50.47; H, 4.02; S, 6.91; 0, 1.72%. Found: C, 50.26; H 4.05; S, 6.83; 0, 2.08%.

Infrared spectrum (Nujol and C_4Cl_6 mulls, cm^{-1}): 2095m, 2065m, 1570w, 1480w, 1460w, 1430s, 1390w, 1370w, 1290w, 1220s, 1180sh, 1160m 1070w, 1050m, 1020w, 1000w, 800w, 780w, 740s, 730s, 690s, 670w, 490w, 480w, 470m, 460w, 330m, 320m.

From the mother liquor of the crude precipitate, a second crude products was obtained, which showed in the IR and ^1H n.m.r. spectra presence of a triarsine hydride compound which was not characterized.

Results and Discussion

The compounds obtained are reported with some of their properties in Table I. They were obtained by reaction of $IrH_3L_2[L = P(C_6H_5)_3; As(C_6H_5)_3]$ with the sodium salt of the appropriate ligand in a warm mixture of acetone/benzene. Elemental analyses, infrared and ^1H n.m.r. spectra established IrH_2L_2(dithioligand) as the correct formulae.

Molecular weight determination (Table I) ruled out any associated structure, such as these established for other derivatives of the dithioligands[6].

The related iridium(III) complexes, $IrH_2PPh_3)_2$(β-diketonate) and $IrH_2(AsPh_3)_2$(β-diketonate),[3] have been shown to contain a six-cordinate iridium(III) atom. On this basis and on evidence given by the X-ray structure of dithiocarbamates and xanthates of trivalent metals, the compounds reported here are likely to be hexaco-ordinate: a higher co-ordination number is exluded by the determination of the molecular weight, while a lower co-ordination number would require a monodentate dithioligand. A monodentate dithiocarbamate group can sometimes be found, when, otherwise, a seven-co-ordinate complex would result, as in $Ru(NO)(S_2CN(C_2H_5)_2)_3$,[7] in $Rh(PPh_3)(S_2CN(CH_3)_2)_3$[8], and according to the dipole moment, in $As^{III}(S_2CN(C_2H_5)_2)_3$[9].

The presence of two Ir-H stretching bands in the i.r. spectra of the isolated hydride complexes (Table I) ruled out a trans arrangement of the hydride li-

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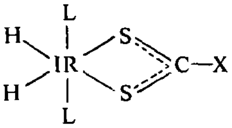
gands, which would require only one infrared active Ir-H vibration at lower frequency (*ca.* 1700 as against *ca.* 2000 cm^{-1})(10). On the other hand, a structure with a hydride ligand *trans* to a L group is ruled out by the fact that the ^{1}H n.m.r. spectra of the phosphine derivatives show only a triplet with a small *J*(H-Ir-P). These data and the observed stretching band ν(Ir-H) are in agreement with the structure:



(L = PPh_3, $AsPh_3$; X = $N(C_2H_5)_2$, OC_2H_5).

The i.r. spectrum below *ca.* 1660 cm^{-1} (Experimental Section) is rather complicated and therefore it is impossible to use the so called «infrared criterion»[11] to chek that the dithioligand is bidentate; however, there is evidence for the presence of the required ν (C=N) at *ca.* 1490 cm^{-1}, [12] of ν (C–S) at *ca.* 1050 cm^{-1}, [13] and of ν(Ir–S) at *ca.* 350 cm^{-1}, [14]. The values found for ν (C=$\overset{+}{N}$) are those required for both the ester and the metal salts of dithiocarbamic acid and suggest a substancial contribution of the form: $[\bar{S}_2C=\overset{+}{N}R_2]^-$.[12,15]

Altough a remarkable difference in the stability of dithiocarbamate and xanthate complexes has often been found,[9] no such difference is evident here, probably due to the presence of the triphenylphosphine groups.

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