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Preliminary communication

DITHIOFORMATO COMPLEXES OF THE PLATINUM METALS; SYNTHESIS AND PROTON NMR SPECTRA

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Summary

Proton NMR spectra of the dithioformate ligands in an extensive range of new platinum metal dithioformato complexes permit unambiguous assignment of stereochemistry.

The stereochemistry, structure and even the stoichiometry of products obtained on treatment of carbon disulphide with transition metal complexes are frequently subjects of doubt and speculation [1]. We now find that the dithioformate anion, one of the ligands commonly found in these systems [1-3], can be reliably detected and characterised by its IR and proton NMR spectra. Furthermore the NMR couplings of the dithioformate proton (HCS_2) to the hydride [^4J(HH)] and/or phosphorus donor ligands [^4J(PH)] are valuable sources of stereochemical information. To confirm these observations we have synthesised and characterised the most extensive series of dithioformate complexes reported to date.

The hydrides [$MHX(CO)(PPh_3)_3$] (M = Ru, Os; X = Cl, Br) [$MH(OCOCF_3)(CO)(PPh_3)_2$], [$RuH_2(PPh_3)_4$], [$OsH_4(PPh_3)_3$], [$IrHCl_2(PPh_3)_3$] (*trans* chlorides) and *mer*-[$IrH_3(PPh_3)_3$] react with carbon disulphide in boiling benzene to yield dithioformato derivatives [$M(S_2CH)X(CO)(PPh_3)_2$] (two isomeric forms), [$M(S_2CH)(OCOCF_3)(CO)(PPh_3)_2$], [$Ru(S_2CH)_2(PPh_3)_2$], [$Os(S_2CH)_2(PPh_3)_2$], [$Ir(S_2CH)Cl_2(PPh_3)_2$] and [$Ir(S_2CH)H_2(PPh_3)_2$], respectively. Each of these products shows IR [$\nu(HCS_2)$ ca. 1215-1235 w and 900-930 s cm^{-1}] and proton NMR spectra [HCS_2 multiplet τ ca. 0 to -5] characteristic of chelate dithioformate ligands (see Table 1). In contrast the complexes [$RuH_2(CO)(PPh_3)_3$], [$RuHCl(PPh_3)_3$] and [$RhH_2Cl(PPh_3)_3$] react to afford sulphur-containing products, currently under investigation, which do not display the spectral characteristics of dithioformate ligands but show instead very broad, strong IR bands at ca. 1280-1320 and/or 1000 cm^{-1}. Finally, under the conditions

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TABLE 1

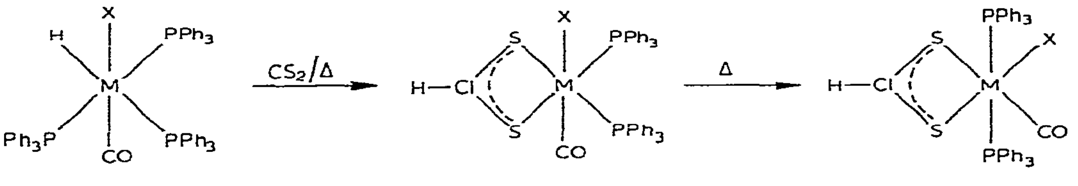
INFRARED AND NMR DATA FOR DITHIOFORMATO COMPLEXES

Complex	$\nu(S_2CH)$ (cm^{-1})		$\tau(S_2CH)$ (ppm)	$^4J(PH)_{trans}$ (Hz)	$^4J(PH)_{cis}$ (Hz)
$Ru(S_2CH)Cl(CO)(PPh_3)_2$ (Ia)	1230,	925, 920	−1.87	8.0	—
$Ru(S_2CH)Cl(CO)(PPh_3)_2$ (Ib)	1225, 1220,	930 (935)	−0.25	—	3.0
$Ru(S_2CH)Br(CO)(PPh_3)_2$ (Ia)	1235	925	−1.70	8.0	—
$Ru(S_2CH)Br(CO)(PPh_3)_2$ (Ib)	1225	925	−0 15	—	3.0
$Os(S_2CH)Cl(CO)(PPh_3)_2$ (Ia)	1235	920	−3.65	8.0	—
$Os(S_2CH)Cl(CO)(PPh_3)_2$ (Ib)	1235	920	−1.85	—	3.0
$Os(S_2CH)Br(CO)(PPh_3)_2$ (Ia)	1230	920	−3.45	8.5	—
$Os(S_2CH)Br(CO)(PPh_3)_2$ (Ib)	1222	920	−1.90	—	3 0
$Ru(S_2CH)(OCOCF_3)(CO)(PPh_3)_2$ (Ib)	1228	930	+0.05	—	2.75
$Os(S_2CH)(OCOCF_3)(CO)(PPh_3)_2$ (Ia)	1230	925	−3.58	8 25	—
$Ru(S_2CH)_2(PPh_3)_2$ (II) [a]	1220	920, 915, 908	−1.5	1.5	$\simeq 0$
$Os(S_2CH)_2(PPh_3)_2$ (II) [a]	1220, 1215	910, 902	−3.24	5.5	$\simeq 0$
$Ir(S_2CH)Cl_2(PPh_3)_2$ (III)	1230	915	−3.20	10.0	—
$Ir(S_2CH)H_2(PPh_3)_2$ (IV) [b]	1235	930	−3.37	—	ca. 3

[a] These spectra show additional IR bands at ca. 775 cm^{-1}. [b] IrH, τ 29.93 ppm; $^2J(PH)_{cis}$ 17 0 Hz; $^4J(HH)_{trans}$ 1.5Hz.

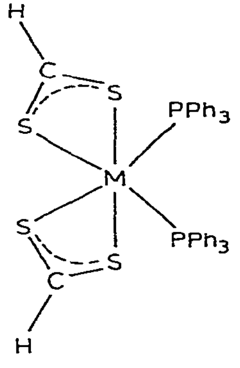
employed in these reactions, the complexes $[OsH_2(CO)(PPh_3)_3]$ and *fac*-$[IrH_3(EPh_3)_3]$ (E = As, P) appear inert to carbon disulphide.

The stereochemistry of the new dithioformato complexes can be unambiguously established by their proton NMR spectra. Thus the products $[M(S_2CH)X(CO)(PPh_3)_2]$, formed under mild conditions, show low-field proton NMR triplets $[^4J(PH)_{trans}$ ca. 8 Hz] indicative of stereochemistry type Ia. The isomeric species $[M(S_2CH)X(CO)(PPh_3)_2]$, obtained using more vigorous conditions and/or longer reaction times, display low-field triplets $[^4J(PH)_{cis}$ ca. 3 Hz] consistent with stereochemistry Ib. These assignments are in accord with the expected reaction sequence:

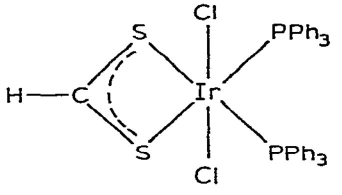


(Ia) (Ib)

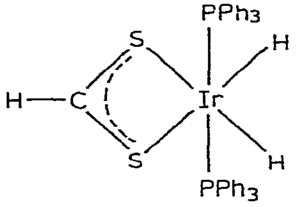
Likewise the osmium complex $[Os(S_2CH)(OCOCF_3)(CO)(PPh_3)_2]$ $[^4J(PH)_{trans}$ 8.25 Hz] has stereochemistry Ia ($X = OCOCF_3$) whereas the more labile ruthenium analogue $[^4J(PH)_{cis}$ 2.75 Hz] possesses stereochemistry Ib ($X = OCOCF_3$). The bis(dithioformato) complexes $[M(S_2CH)_2(PPh_3)_2]$ have relatively small P—H couplings $[^4J(PH)_{trans}$ ca. 1.5-5.5, $^4J(PH)_{cis} \approx 0$ Hz] and each therefore displays only a narrow doublet at low field. However, this is sufficient to confirm the *cis* stereochemistry II previously established for the ruthenium derivative by X-ray diffraction methods [4]. Finally, the low-field triplet $[^4J(PH)_{trans}$ 10.0 Hz] is indicative of stereochemistry III for $[Ir(S_2CH)Cl_2(PPh_3)_2]$ whereas the triplet of triplets pattern [τ −3.37, $^4J(PH)_{cis}$ ca. 3, $^4J(HH)_{trans}$ 1.5 Hz] observed for the dihydrido complex $[Ir(S_2CH)H_2(PPh_3)_2]$ establishes stereochemistry IV and is fully consistent with the high-field proton pattern [τ 29.93 triplet of doublets, $^{2}J(\mathrm{PH})_{cis}$ 17.0, $^{4}J(\mathrm{HH})_{trans}$ 1.5 Hz].



(II)

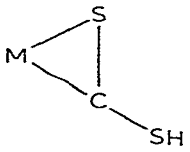


(III)

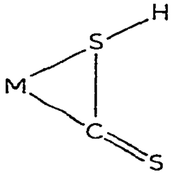


(IV)

These data amply demonstrate that NMR couplings of the dithioformate proton are a valuable source of stereochemical information. Furthermore, equivalent coupling of the dithioformate proton to two ^{31}P nuclei (Ia and Ib) or two ^{1}H nuclei (IV) clearly favours the symmetrical structure shown for the dithioformate ligands in I-IV and virtually eliminates the asymmetric alternatives:



and



References

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2 R.O. Harris, N.K. Hota, L. Sadavoy and J.M.C. Yuen, J. Organometal. Chem , 54 (1973) 259.
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Erratum

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page C14, line 11 should read:

atom. Thus the line width at half height for the C_α signal of $[(OC)_9Co_3CCHC_9H_{19}]^+$