

Preliminary communication

N-ALKYL- AND N-ARYL-THIOFORMAMIDO COMPLEXES OF THE PLATINUM GROUP METALS

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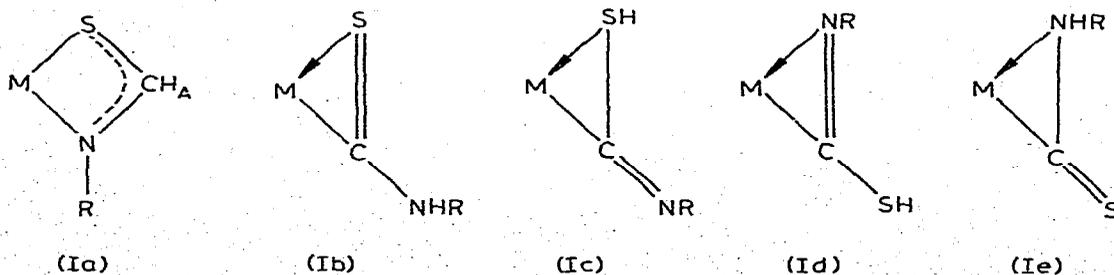
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Summary

Alkyl- and aryl-isothiocyanates undergo insertion reactions with platinum metal hydrides to yield the corresponding *N*-alkyl- and *N*-aryl-thioformamido ($S\cdots CH\cdots NR$) derivatives, the structure and stereochemistry of which have been deduced using 1H NMR data.

As part of a study of small ring chelates we have recently reported the formation of new dithioformato complexes by insertion of carbon disulphide into platinum metal hydride bonds [1]. We now find that alkyl- and aryl-isothiocyanates $RNCS$ ($R = Me$ or Ph) undergo analogous reactions to yield products containing the novel *N*-alkyl- and *N*-aryl-thioformamido ligands ($S\cdots CH\cdots NR$). Thus the hydrides $[MHX(CO)(PPh_3)_3]$ ($M = Ru$ or Os ; $X = Cl$ or Br) $[RuH_2(PPh_3)_4]$ and $[IrHCl_2(PPh_3)_3]$ (*trans*-chlorides) react with isothiocyanates $RNCS$ in boiling benzene or toluene to yield new complexes $[MX(S\cdots CH\cdots NR)(CO)(PPh_3)_2]$ (two isomers), $[Ru(S\cdots CH\cdots NR)_2(PPh_3)_2]$ and $[Ir(S\cdots CH\cdots NR)Cl_2(PPh_3)_2]$ (two isomers), respectively. On the basis of infrared spectra which show weak bands at ca. 1290–1200 and ca. 930–890 cm^{-1} , similar to those observed for the corresponding dithioformato derivatives, but no evidence of $\nu(NH)$ or $\nu(SH)$ vibrations the thioformamido ligands are assigned structure Ia in preference to the feasible



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alternatives Ib–Ie. The infrared spectra also show a very strong band at ca. 1500 (R = Ph) or 1570 cm^{-1} (R = Me) tentatively attributed to $\nu(\text{C}\cdots\text{NR})$. The structural assignment is supported by the ^1H NMR spectra each of which displays a sharp multiplet, relative intensity one, [proton H_A in Ia] at ca. -0.5 to 2.0 ppm on the τ scale, similar to those found for the corresponding dithioformates. The fine structure of these multiplets reflects the symmetry properties of the complexes and the asymmetric nature of the thioformamido ligands. Thus the products $[\text{M}(\text{S}\cdots\text{CH}\cdots\text{NR})\text{X}(\text{CO})(\text{PPh}_3)_2]$ formed under mild conditions show low-field doublet of doublet patterns [$^4J(\text{PH})_{\text{trans}}$ ca. 8–9 and ca. 2–3 Hz]

TABLE 1

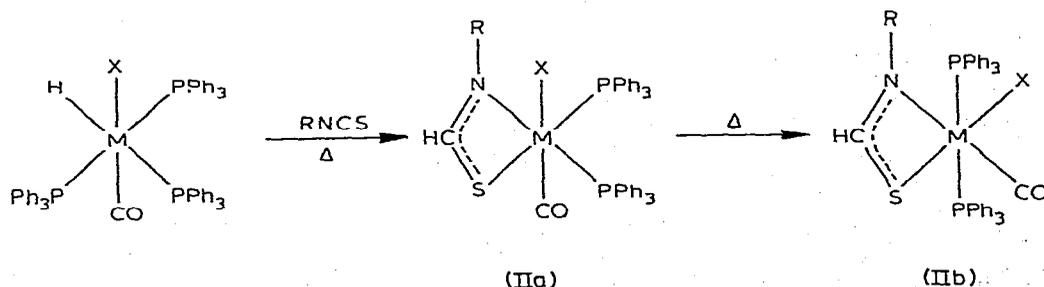
NMR DATA^{a,b} FOR *N*-ALKYL- AND *N*-ARYL-THIOFORMAMIDO COMPLEXES

Complex	Number	$\tau(\text{CH}_A)$	$^4J(\text{PH}_A)_{\text{trans}}$	$^4J(\text{PH}_A)_{\text{cis}}$
$\text{Ru}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	IIb	1.82(t)		2.5
$\text{Ru}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Br}(\text{CO})(\text{PPh}_3)_2$	IIb	1.83(t)		2.5
$\text{Os}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	IIa	0.15(d of d)	8.0/2.0	
$\text{Os}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	IIb	0.65(t)		2.5
$\text{Os}(\text{S}\cdots\text{CH}\cdots\text{NMe})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	IIa	$-0.42(\text{d of d})$	8.5/3.5	
$\text{Os}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Br}(\text{CO})(\text{PPh}_3)_2$	IIa	0.26(d of d)	9.0/3.0	
$\text{Os}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Br}(\text{CO})(\text{PPh}_3)_2$	IIb	0.62(t)		2.5
$\text{Ir}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Cl}_2(\text{PPh}_3)_2$	IIIb	$-0.26(\text{t})$		2.5
$\text{Ir}(\text{S}\cdots\text{CH}\cdots\text{NMe})\text{Cl}_2(\text{PPh}_3)_2$	IIIa	$-0.26(\text{d of d})$	10.0/4.0	
$\text{Ir}(\text{S}\cdots\text{CH}\cdots\text{NPh})\text{Br}_2(\text{PPh}_3)_2$	IIIb	$-0.29(\text{t})$		2.5
$\text{Ru}(\text{S}\cdots\text{CH}\cdots\text{NPh})_2(\text{PPh}_3)_2$	IV	1.14(d)	2.5	
$\text{Ru}(\text{S}\cdots\text{CH}\cdots\text{NMe})_2(\text{PPh}_3)_2$	IV	1.30(d)	3.0	

^aNMR spectra taken in CDCl_3 (R = Ph) or CD_2Cl_2 (R = Me); d = doublet, t = triplet, couplings ± 0.3 Hz.

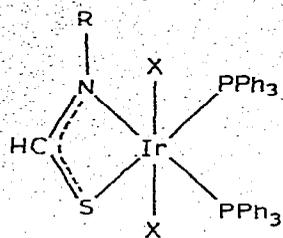
^bMeNCS derivatives show additional couplings [$^4J(\text{HH}_A) \leq 1$ Hz] between methyl protons and H_A .

indicative of stereochemistry (IIa). The isomeric species $[\text{M}(\text{S}\cdots\text{CH}\cdots\text{NR})\text{X}(\text{CO})(\text{PPh}_3)_2]$ obtained using more vigorous conditions and/or longer reaction times display low-field triplets [$^4J(\text{PH})_{\text{cis}}$ ca. 2.5 Hz] consistent with stereochemistry IIb*. These assignments parallel those made for the corresponding dithioformates and are in accord with the expected reaction sequence :

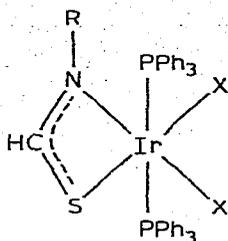


Similarly, using the NMR data given in Table 1, the products obtained on treating $[\text{IrHCl}_2(\text{PPh}_3)_3]$ with MeNCS and PhNCS are assigned structures IIIa (R = Me, X = Cl) and IIIb (R = Ph, X = Cl), respectively. Finally, the complexes

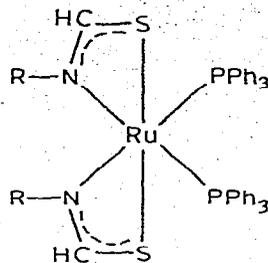
*Infrared data ($\nu(\text{CO})$ ca. 1900–1930 cm^{-1}) are consistent with CO *trans* to nitrogen rather than sulphur [1, 2].



(IIIa)



(III b)



(IV)

$[\text{Ru}(\text{S}\cdots\text{CH}\cdots\text{NR})_2(\text{PPh}_3)_2]$ are tentatively assigned stereochemistry IV analogous to that established [3] for the pyridine-2-thiolato complex $[\text{Ru}(\text{SC}_5\text{H}_4\text{N})_2(\text{PPh}_3)_2]$ [4].

References

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