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Linkage Isomers of the Cyanate Group: *O*-Cyanato- and *N*-Cyanato-tris(triphenylphosphine)rhodium(I)

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Summary The first example of solid linkage isomers containing *N*- and *O*-bonded cyanate groups is reported with the compounds $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$; the i.r. spectra of the isomers are discussed, and the solvent-dependence of the mode of co-ordination is noted.

O-Bonded cyanates in inorganic systems are rare and are characterised only with difficulty. The hexa-*O*-cyanates of Mo^{III}, Re^{IV}, and Re^{V} were assigned on the basis of their lowered (relative to the free ion) CO stretching frequencies,[1] and the same arguments (together with some mass spectral data) were used for $(cp)_2M(OCN)_2$ (M = Zr, Hf) cp = cyclopentadienyl).[2] Although the peak in question was not identified in $(cp)_2Ti(OCN)_2$ other spectral measurements indicated its similarity to the corresponding zircocene and hafnocene compounds and it was assigned a similar structure. Recently, however, Burmeister *et al.*[3] have re-examined the above metallocenes and concluded from dipole-moment measurements that they should be formulated $(cp)_2Ti(NCO)_2$ and $(cp)_2Zr(OCN)_2$. This conflicts with ^{14}N n.m.r. measurements on the former which show a downfield shift relative to the free cyanate ion;[4] such a shift has been taken as being indicative of *O*-bonding.[5] We now report the preparation and properties of the first solid linkage isomers to be isolated which involve the cyanate group, the compounds $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$.

Treatment of $Rh(PPh_3)_3Cl$ with Ph_4As in MeCN yields a yellow solid, whereas the addition of EtOH to the reaction mixture results in an orange solid. The two compounds both give identical *X*-ray fluorimetric analyses[6] for $Rh(PPh_3)_3$'CNO'.† The i.r. spectrum of the orange product (KBr disc) shows a sharp peak at 2215 cm^{-1} ($A = 9\cdot0 \times 10^{4}$ $\mathrm{M}^{-1}\,cm^{-2}$), whereas the yellow product has a broader CN stretching frequency at 2230 cm^{-1} ($A = 12\cdot7 \times 10^{4}$ $\mathrm{M}^{-1}\,cm^{-2}$). The yellow product is insoluble in MeCN, but the orange product dissolves to give a non-conducting solution which has a spectrum with a peak at 2220 cm^{-1} (A $8\cdot1 \times 10^{4}$ $\mathrm{M}^{-1}\,cm^{-2}$). (^{14}N N.m.r. results show that EtOCN is stable in MeCN but isomerises in EtOH: the integrated intensities for EtOCN in these two solvents are $8\cdot0$ and $17\cdot0 \times 10^{4}$ $\mathrm{M}^{-1}\,cm^{-2}$ respectively.[7])

The above results show that the orange product may be formulated as $Rh(PPh_3)_3OCN$ since the integrated intensity of the CN stretching frequency is reduced below that of the free ion, whereas the yellow isomer has an integrated intensity greater than that of the free ion, typical of an *N*-cyanato-compound.[8] Further support for these formulations comes from the NCO deformation modes which occur at 592 cm^{-1} for the yellow isomer, but at 607 and 590 cm^{-1} for the orange. The removal of the degeneracy of the corresponding NCS mode due to the lower symmetry of the non-linear M–SCN group has been used as a criterion for *S*-bonding in thiocyanate co-ordination.[9] The Rh–OCN unit might also be expected to be non-linear, in which case

† We use the notation 'CNO' to indicate that the mode of co-ordination of the cyanate group is unspecified.

if the degeneracy of the deformation mode is removed then two bands would be predicted for the orange $Rh(PPh_3)_3OCN$, and only one for the yellow $Rh(PPh_3)_3NCO$, as is indeed observed.

The region in which the CO stretching frequency occurs is obscured by Ph_3P vibrations. The compounds also form adducts with dioxygen, and hence also with Ph_3PO which also vibrates in this region, very readily, so that considerable precautions have to be taken to prevent contact with oxygen. The only band which could possibly be due to the CO stretching frequency is that at 1318 cm^{-1} in $Rh(PPh_3)_3$-OCN; no counterpart is seen for the isomer. This frequency is towards the lower end of the range observed for *N*-cyanato-compounds, and above the free ion value and the values assigned previously for *O*-cyanates.[9] However, the low intensity of the CO stretching frequency in general, the complications arising from Fermi resonance with the overtone of the deformation mode to which have been attributed the decrease in this frequency, and the recent conclusions regarding the uncertainty of the mode of co-ordination in $(cp)_2M(CNO)_2$† compounds, which provide 50% of the data justifying the use of this frequency, mean that it is a criterion of uncertain reliability. The difficulties of identifying the fundamental band in question and making a definite assignment in this region of the spectrum preclude any firm conclusions on this point, although an increase in ν_{CO} on co-ordination through oxygen was predicted theoretically for the cyanate group.[10] A band is observed at 332 cm^{-1} in $Rh(PPh_3)_3OCN$ which is assigned to the Rh–OCN stretching frequency. No similar band has been observed above 250 cm^{-1} in $Rh(PPh_3)_3NCO$, nor in $Rh(PPh_3)_3NCS$.[7]

The mode of co-ordination of the cyanate group, like that of the thiocyanate group,[11] depends on the nature of the solvent. This is indicated by the different methods of preparation of these isomers, and by the fact that both compounds dissolved in $CHCl_3$ give identical solutions with ν_{CN} at 2235 cm^{-1} ($A = 17 \times 10^4$ M^{-1} cm^{-2}); similarly in benzene ν_{CN} occurs at 2227 cm^{-1} ($A = 19 \times 10^4$ M^{-1} cm^{-2}) for each isomer.

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