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Preliminary communication

THE SYNTHESIS AND FLUXIONAL BEHAVIOUR OF THE COMPLEXES $Cp_2Ru_2(CO)_3(CNR)$

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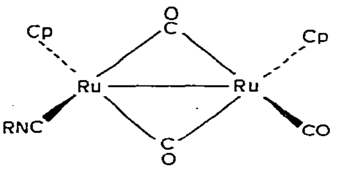
Summary

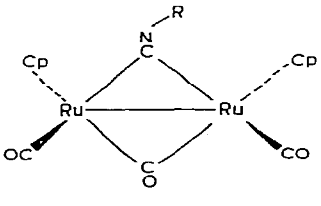
The isonitrile complexes $Cp_2Ru_2(CO)_3(CNR)$ ($Cp = \eta^5\text{-}C_5H_5$; R = Me, Et, i-Pr, t-Bu) exist as *cis/trans* mixtures of bridged and terminal isonitrile isomers. NMR studies show that they are fluxional, and obey the Adams—Cotton mechanism.

Of the mechanisms postulated for the bridge-terminal exchange observed in fluxional polynuclear transition metal carbonyls, perhaps that for which the greatest experimental support is available, at least for dimeric species, is the Adams—Cotton mechanism. For example, ^{13}C and ^{1}H NMR studies not only on the dimer $Cp_2Fe_2(CO)_4$ [1], but also on several of its isonitrile substitution products [2,3] are in agreement with the mechanistic predictions. NMR studies of the analogous $Cp_2Ru_2(CO)_4$ (I) yield little information, as down to −80°C, only one CO resonance is observed. We wish to report the synthesis and variable temperature ^{13}C NMR spectra of the isonitrile substitution products $Cp_2Ru_2(CO)_3(RNC)$ (R = Me, Et, i-Pr and t-Bu).

These complexes may be synthesized by reaction of a small excess of the isonitrile with I in refluxing xylene, followed by chromatography on alumina. Infrared spectra show the presence of *cis* and *trans* forms of both the terminal (II) and bridged (III) isonitrile isomers. We assign the nine bands observed in the spectrum (hexane) of the ethyl isonitrile derivative as follows (relative intensities in parentheses): (a) 2124 cm^{-1} (3), terminal CN vibration of *cis*-II



(II) cis



(III) cis

and *trans*-II; the low intensity and broadness may mask the presence of the two bands which are observed in the analogous iron complex; (b) 2004(75) and 1975 cm^{-1} (10), symmetric terminal CO vibration of *cis*-III and *trans*-III, respectively. The latter is symmetry forbidden for *trans*-I, but allowed, although perhaps weakly, for *trans*-III due to the non-linear nature of the CNR ligand in a bridging position [4]; (c) 1963(sh) and 1958 cm^{-1}(100), overlapping asymmetric terminal CO vibration of *cis*-III and *trans*-III and terminal CO vibration of *cis*-II and *trans*-II; (d) 1809 cm^{-1} (55), coincident bridging CO vibration of *cis*-III and *trans*-III; (e) 1774 cm^{-1} (15), coincident bridging CO vibration of *cis*-II and *trans*-II; (f) 1735(25) and 1706 cm^{-1} (15), bridging CN vibration of *trans*-III and *cis*-III.

Frequency values for the iron complex are very similar, but relative intensities show a much greater propensity in the ruthenium complexes towards occupation of the bridging position by the isonitrile; the proportion of the bridging isomer increases in the same order t-Bu < i-Pr < Et < Me. Furthermore, infrared studies of I show clearly the presence of a nonbridged isomer [5]; spectra of the isonitrile derivatives show no evidence for detectable concentrations of a non-bridged species.

Variable temperature ^{13}C NMR spectra of the ethyl isonitrile derivative [CH_2Cl_2/CD_2Cl_2; Cr(acac)$_3$] in the region 80—260 ppm (Fig. 1) show a low temperature limiting spectrum obtained at −70°C; the assignments follow from

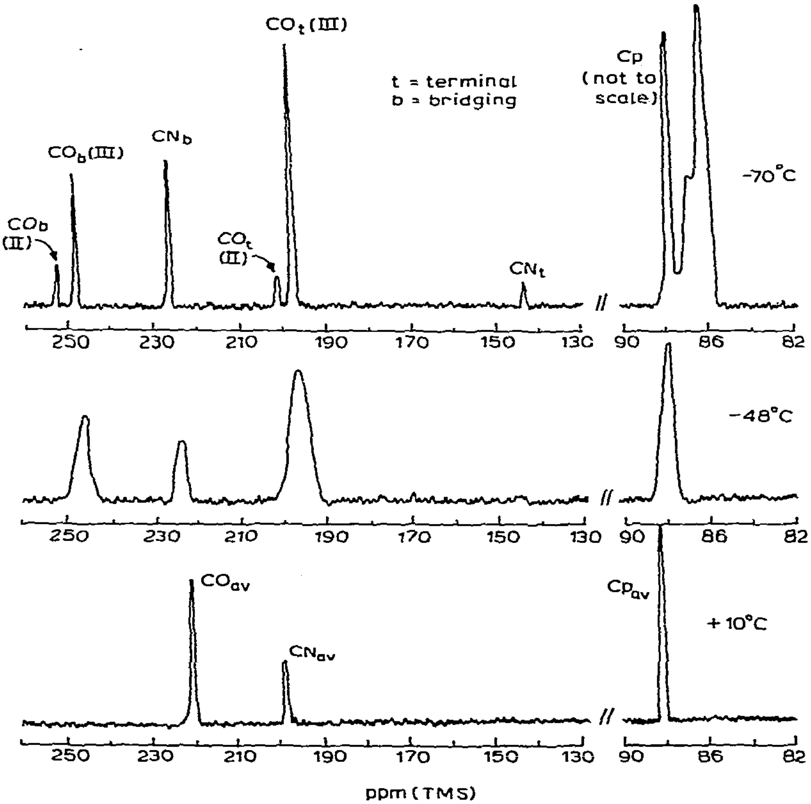


Fig. 1. ^{13}C NMR spectra of $Cp_2Ru_2(CO)_3(EtNC)$.

intensities and previous work on related iron complexes [3]. Although infrared spectra indicate *cis* and *trans* forms of both II and III, only two isomers are apparent from the ^{13}C NMR spectra. Results from ^{1}H NMR spectra indicate that this is due to coincidence of *cis* and *trans* signals, rather than rapid *cis—trans* interconversion. Raising of the temperature results in collapse of both CO and CNR resonances to yield finally the high temperature limiting spectrum at +10°C. The other complexes behave similarly, and the results are in agreement with the Adams—Cotton mechanism. A comparison with the analogous iron complexes reveals (a) a significantly lower barrier to exchange for ruthenium; with similar chemical shift differences, low temperature limiting spectra may be obtained for iron at −20 to −30°C.

(b) For the ruthenium complexes, the averaged CO and CN resonances are not in the position calculated from chemical shift differences and relative isomer populations at −70°C. The results indicate an increase in the population of the terminal isonitrile isomer with increasing temperature; this is in contrast to the iron complexes, where variable temperature infrared studies show that the terminal isonitrile isomer concentration is inversely proportional to temperature, and (c) two Cp resonances are observed for the bridging ruthenium isonitrile isomer, indicating that at −70°C, nitrogen inversion is also slow on the NMR time scale [6]. Down to −110°C, only one resonance is observed for the iron complex.

A full report on the isonitrile derivatives of the series $Cp_2M_2(CO)_4$ (M = Fe, Ru, Os) will be published on completion of work on the osmium complexes.

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