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Pentacarbonylchromium complexes containing the fluorinated isocyanide ligands H_2FCNC and HF_2CNC

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Abstract

Pentacarbonyl(fluoromethyl isocyanide)chromium and pentacarbonyl(difluoromethyl isocyanide)chromium have been prepared. The vibrational spectroscopic data for the compounds indicate that these isocyanide ligands have a lower π-acceptor/σ-donor ratio than trifluoromethyl isocyanide.

Introduction

Methyl isocyanide was the first to be prepared, and was made more than 100 years ago by Gautier [1]. Its perfluorinated derivative was first reported in 1967, by Makorov *et al.* [2]. The chemistry of trifluoromethyl isocynanide, however, remained unexplored until an efficient synthesis became available [3]. Our recent studies have shown that the introduction of fluorine into isocyanides has strong effects on their reactivity [4] and ligand behaviour [5]. Thus, trifluoromethyl isocyanide proved to be a strong π acceptor ligand, even stronger than the carbonyl and thiocarbonyl ligands [5]. As a consequence the CF_3NC ligand can take the bridging position in di- and tri-nuclear complexes at the expense of a carbonyl ligand [6].

Results and discussion

In studying the effect of fluorine substitution we become interested in the partially-fluorinated methyl isocyanides $CNCH_2F$ and $CNCHF_2$. As there was no obvious fluoroorganic starting material available we decided to form these species as ligands in transition metal complexes.

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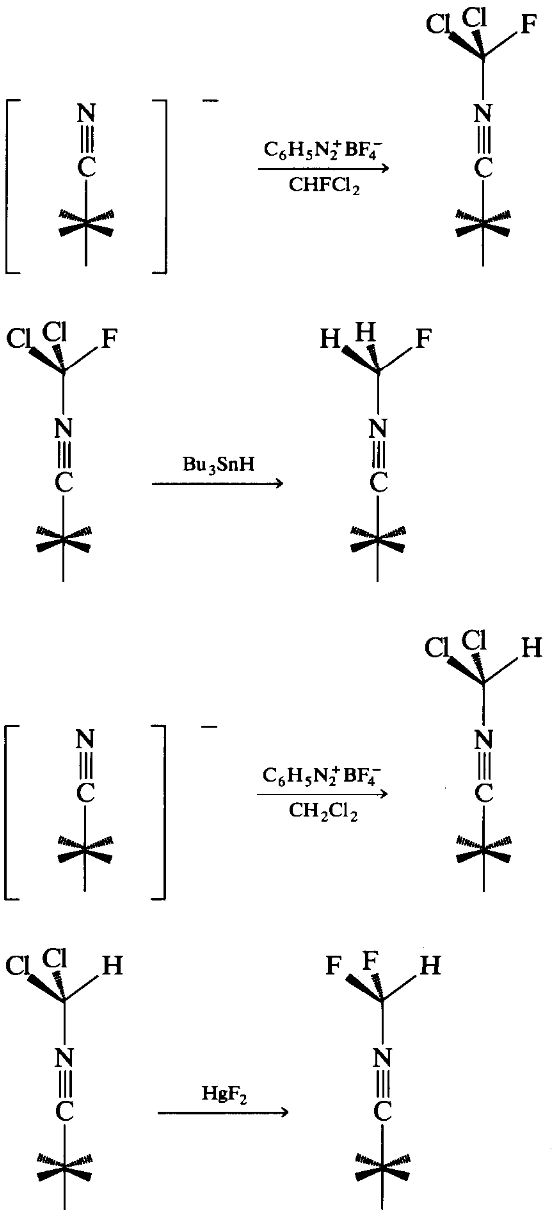

Scheme 1.

As shown by Fehlhammer *et al.* [7] pentacarbonyl(cyano)chromate undergoes radical alkylation (Scheme 1). If dichloromethane and dichlorofluoromethane are used as solvents the desired starting materials $(CO)_5Cr(CNCHCl_2)$ and $(CO)_5Cr(CNCCl_2F)$ can be prepared by known methods [7].

Pentacarbonyl(dichlorofluoromethyl isocyanide)chromium can be converted into pentacarbonyl(fluoromethyl isocyanide)chromium by use of tributyltin hydride as reducing agent. Reduction by zinc in diethyl ether in the presence of acetic acid results in accompanying attack on the C–F bond to give a mixture of the fluoromethyl isocyanide and the methyl isocyanide complex, as shown by ^1H NMR spectroscopy. These two compounds show very similar physical properties, *e.g.* solubility, volatility, and R_F values on thin layer chromatography plates, so that separation is very difficult.

Pentacarbonyl(difluoromethyl isocyanide)chromium was obtained by a halogen-exchange reaction with mercury fluoride as fluorinating agent. This seems to be better in this case than the Schwartz reagent SbF_3/SbF_5, that was used by Fehlhammer *et al.* to convert $(CO)_5Cr(CNCCl_3)$ into $(CO)_5Cr(CNCF_3)$ in trace amounts [8], because it is not oxidizing.

Both isocyanide complexes are crystalline air-stable compounds with low melting points and high volatility. They have been fully characterized spectroscopically. The complex $(CO)_5Cr(CNCH_2F)$ exhibits the expected doublet in the ^1H spectrum and triplet in the ^{19}F NMR spectrum. A triplet and a doublet, respectively, are observed in the ^1H and ^{19}F NMR spectra of $(CO)_5Cr(CNCHF_2)$. The ^{13}C NMR spectra exhibit signals at 79.6 (CH_2F, $^1J(CF) = 205$ Hz), 176.8 (CN), 214.5 (CO, *cis*) 216.0 (CO, *trans*) and 101.7 (CHF_2, $^1J(CF) = 256.4$ Hz, $^1J(CH) = 219.7$ Hz), 192.5 (CN), 213.1 (CO, *cis*) 213.7 (CO, *trans*) for $(CO)_5Cr(CNCH_2F)$ and $(CO)_5Cr(CNCHF_2)$, respectively. As for most $(CO)_5CrL$ complexes, the resonances of the CO ligand *trans* to the ligand appear at lower field than those of the CO ligands in the *cis* position. However, this chemical shift difference is rather small for the difluoromethyl isocyanide ligand. For the trifluoromethyl isocyanide ligand even the resonance of the *trans*-CO ligand is at higher field than that of the *cis*-CO ligands. This reflects the fall in the π-acceptor/σ-donor ratio on going from trifluoromethyl isocyanide to methyl isocyanide.

A related effect can be observed in the IR spectra of these compounds. Although a complete assignment of the CO and CN vibration modes is hindered by the strong coupling of the CO stretching mode with the CN stretching, the E mode can be easily assigned as it is the strongest absorption in the IR spectrum. Furthermore, this E(CO) mode should show only a weak coupling to the A_1(CN) mode. Nevertheless the energy of this absorption depends on the relative π-acceptor/σ-donor ratio of the ligand L. A plot of the wavenumbers for this E mode against the degree of fluorination is the increase to be linear. Thus, the π-acceptor/σ-donor ratio of isocyanides increases steadily with the number of fluorine atoms on the methyl group.

Attempts to isolate the free isocyanides from these complexes are under study.

Experimental

Pentacarbonyl(dichlorofluoromethyl isocyanide)chromium [7], pentacarbonyl(dichloromethyl isocyanide)chromium [7] and mercury fluoride [9] were prepared by published procedures. Tributyltin hydride (Aldrich) was used as received. All reactions were carried out in dry solvents under argon by standard Schlenck and vacuum-line techniques.

Pentacarbonyl(fluoromethyl iscyanide)chromium $(CO)_5Cr(CNCH_2F)$. A sample of $(CO)_5Cr(CNCCl_2F)$ (2.2 g, 6.9 mmol) was dissolved in 40 ml of n-hexane. Bu_3SnH (6 ml) was added at ambient temperature from a syringe. The mixture was heated under reflux for 1 h, then allowed to cool to room temperature and filtered through silica ($l = 8$ cm). The organo-tin compounds were eluted with *ca.* 100 ml of pentane and the product was then eluted with 300 mL of dichloromethane. The solvent was removed under vacuum and the residue sublimed at 30°C/10^{-2} mbar on to a receiver cooled to -20°C to give 1.39 g (82%) of colourless needles, m.p. 46°C. MS (80 eV): $m/e = 251$ (M^+), 139 ($M^+ - 4CO$), 111 ($M^+ + 5CO$), 41 (CrF^+), 52 (Cr^+). IR (n-pentane) $\nu = 2136$(w), 2054(w), 1969(vs), 1937(w) cm^{-1}. IR (gaseous): $\nu = 2140$(w), 2057(w), 1981(s), 1950(w), 734(m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.95 ($^2J(HF) = 48.1$ Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$ ref.): δ -176.2 ppm. ^{13}C NMR ($CDCl_3$): δ 79.6 (CH_2F) $^1J(CF) = 205$ Hz), 176.8 (CN), 214.5 (CO, *cis*), 216.0 (CO, *trans*) ppm.

Pentacarbonyl(difluoromethyl isocyanide)chromium *$(CO)_5Cr(CNCHF_2)$.* To a suspension of H_gF_2 (15 g, 62.9 mmol) in 250 mL of 1,1,2-trichloro-1,2,2-trifluoroethane were added $(CO)_5Cr(CNCCl_2H)$ (6.4 g, 19.9 mmol). The mixture was stirred for 16 h at ambient temperature and the mercury compounds were then removed by centrifugation. Solvent was then removed under vacuum and the residue sublimed at 30°C/10^{-2} mbar on to a receiver cooled to -20°C to give 4.5 g (84%) of pale yellow crystals, m.p. 27°C. MS (80 eV) m/e 269 (M^+), 157 ($M^+ - 4CO$), 129 ($M^+ - 5CO$), 78 ($CrCN^+$), 52 (Cr^+). IR (n-pentane): $\nu = 2135$(w), 2016(w), 1979(vs), 1946(m) cm^{-1}. IR (gaseous): $\nu = 1992$, 1363, 1116, 681, 660 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.49 ppm ($^2J(HF) = 63.5$ Hz). ^{19}F NMR ($CDCl_3$, $CFCl_3$, ref.): δ -86.4 ppm. ^{13}C NMR ($CDCl_3$): δ 101.4 (CHF_2) $^1J(CH) = 219.7$ Hz, $^1J(CF) = 256.4$ Hz), 192.5 (CN), 213.1 (CO, *cis*), 213.7 (CO, *trans*) ppm.

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