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TRIFLUOROMETHYLISOCYANIDE, PREPARATION, REACTIVITY AND LIGAND BEHAVIOUR

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Trifluoromethylisocyanide, CF_3NC, can be prepared by elimination of halogene from $CF_3N{=}CX_2$ (X=Cl, Br) with magnesium in THF. Both conformers of $CF_3N{=}CHF$, $CF_3N{=}CHCl$ and $CF_3N{=}CHBr$ are formed when the hydrogen halides are reacted with isocyanide. The equilibrium of the Z and E conformer of these compounds has been studied by variable temperature nmr measurements. The N-trifluoromethylhalogenemethanimenes dimerize slowly forming the corresponding aminomethanimines $CF_3N{=}C(H)N(CF_3)(CX_2H)$. CF_3NC is a strong π-accepting ligand. This has been demonstrated by the synthesis of several transition metal complexes like $Ni(CNCF_3)_4$, $Ni_2Cp_2(CNCF_3)_2$, $\overset{*}{Cp}Co(CNCF_3)_2$ and $\overset{*}{Cp}CoI_2(CNCF_3)$. In competition with the carbonyl-ligand CF_3NC seems to prefer the bridging position. This is demonstrated in $Fe_3(\mu\text{-}CNCF_3)(CO)_{11}$, which contains a stable trifluoromethylisocyanide bridge, both in the solid state and in solution. Reaction of $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ with CF_3NC in the molar ratio 1:1 leads to formation of $Mo_2Cp_2(CO)_4(\eta^2\text{-}\mu\text{-}CNCF_3)$. According to the spectroscopic data the bridging CF_3NC ligand functions as a four electron donor. If an excess of CF_3NC is used $[MoCp(CO)_2(\mu\text{-}CNCF_3)]_2$ can be isolated as an unstable product. $[MoCp(CO)_2(\mu\text{-}CNCF_3)]_2$ undergoes cleavage of the metal-metal-bond and carbon-carbon-bond formation between the two coordinated isocyanide ligands. The new $F_3CN{=}C{=}C{=}NCF_3$ ligand bridges two $MoCp(CO)_2$ fragments.