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Preliminary Communication

BIS-ARYL CHROMIUM COMPLEXES CONTAINING THE DIMETHYLDITHIOCARBAMATE ANION AND OTHER CHELATE LIGANDS

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Summary

The complex $CrCl_2(Me_2dtc)bipy$ reacts with aryl Grignard reagents to yield $R_2Cr(Me_2dtc)bipy$ ($R = C_6H_5, CH_3C_6H_4$) as orange, air and moisture stable compounds. Other complexes $CrCl_2(L)py_2$, $L = Me_2dtc^-, sal^-, acac^-$ react with aryl Grignards to give related organo derivatives which are air and moisture sensitive.

Organometallic compounds of Cr(III) containing chelating acid-base ligands have not been studied as extensively as the analogous Co(III) derivatives [1]. Perfluoroalkyl derivatives containing quadridentate and bidentate salicylaldimines [2], salicylaldehyde, acetylacetone [2] and dithiocarbamates [3] have been reported but as yet neither aryl nor alkyl derivatives have been obtained. The complex $CH_3Cr(salen)H_2O$ reported by Dey and De [4] has not been isolated [5] when attempting to follow the sparse experimental details originally given.

Bis-aryl chromium derivatives have now been isolated containing chelating dimethyldithiocarbamate groups (Me_2dtc^-) by reaction of phenyl or p-tolyl magnesium bromide on the complex $CrCl_2(Me_2dtc)bipy$ in tetrahydrofuran solution. The orange complexes are prepared in high yield and are obtained from solution as monohydrates. The lattice water was not readily detected from the infra-red spectra of the compounds but could be demonstrated by n.m.r. examination of solutions in $CDCl_3$.

The magnetic moment of $(C_6H_5)_2Cr(Me_2dtc)bipy$ at 293°K is 3.85 B.M., slightly higher than the spin only value as has been observed for other chromium organo derivatives [2, 3].

The compounds are stable to both air and water and this property appears related to the presence of the two chelate groups. The reaction of $CrCl_2(Me_2dtc)py_2$ with the p-tolyl Grignard reagent gave a deep red crystalline product presumably $(p\text{-}CH_3C_6H_4)_2Cr(Me_2dtc)py_2$ which decomposed rapidly in the presence of traces of air and moisture.

The compound $CrCl_2(Me_2dtc)bipy$ is readily prepared by the reaction of $CrCl_2(CH_3CN)_2$ with tetramethyl-thiuramdisulphide in the presence of bipyridyl but other examples of the type $CrCl_2LB$ have been prepared where L = the anions of salicylaldehyde or acetylacetone and B = bipy or two moles of pyridine, by reaction of the free ligand on $CrCl_3(THF)_3$ in an appropriate refluxing solvent such as benzene or pyridine followed by addition of the B ligand bipyridyl or pyridine.

The complexes with pyridine coordinated to Cr all readily react with aryl Grignard reagents to give organometallic compounds but the compounds are very sensitive to air and moisture and have not yet been fully characterised.

A comparison of the greater reactivity with water of $Cr(C_6H_5)_3(THF)_3$ [6] and p-$CH_3C_6H_4CrCl_2(THF)_3$ [7] compared to $[R_2Cr(bipy)_2]^+$, R = C_6H_5 [8], 2-$CH_3OC_6H_4$ [9] seems to indicate the importance of chelate groups in suppressing reaction with water, for aryl chromium derivatives.

The series of bis-chelate - bis-organo Cr compounds $[R_2Cr(bipy)_2]^+$ where R = C_6H_5 [8], 2-$CH_3OC_6H_4$ [9], $(CH_3)_3SiCH_2$ [10], have been shown to have the organo groups in a cis-arrangement, the possible alternative trans complex being destabilized by steric hindrance between the hydrogens of two bipyridyl groups arranged in a plane [11]. There should be little or no direct interaction between bipyridyl and a dithiocarbamate ring and the present compounds ought therefore to be free to adopt either a cis or trans arrangement of organo groups.

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