

Preliminary communication

THE REACTIONS OF $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{L})]$ ($\text{L} = \text{R}_3\text{P}$ OR RNC) WITH CARBON DISULPHIDE AND ORGANOISOTHIOCYANATES

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Summary

The reactions of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PR}_3)]$ or $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]/\text{R}_3\text{P}$ mixtures ($\text{R} = \text{alkyl or aryl}$) with CS_2 in refluxing CS_2 or $\text{CS}_2/\text{toluene}$ gives rise to $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{CS})]$, $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{CS}_2)]$, $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{CS}_3)]$, and $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\text{CS})(\text{S})]$ in reasonable yields. The corresponding reactions using PhNCS give $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{PhNCS})]$ and a polymeric species which appears to be $[\text{Co}_4(\eta\text{-C}_5\text{H}_5)_4(\text{PhNCS})]$. Similar products are obtained with $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNR})]$ or $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]/\text{RNC}$ mixtures.

Recently, Werner and his coworkers have reported the preparations of $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\text{CS})(\text{S})]$ [1] and $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{CS})]$ [2] by involved routes, whilst $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CS}_2)]$ has also been obtained using a multi-step process [3]. This has prompted us to publish a preliminary account of our studies of the chemistry of $[\text{Co}(\eta\text{-C}_5\text{H}_5)]/\text{CS}_2$ systems which show that there are simple and direct routes to a wide variety of compounds related to those mentioned above.

When solutions of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PR}_3)]$ or of equimolar amounts of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ and PR_3 ($\text{R} = \text{alkyl or aryl}$) in carbon disulphide are heated under reflux for 1–3 days, many products are formed. So far we have been able to separate only three by column chromatography and isolate them in reasonable yields ($> 1\%$); they are orange $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{CS})]$, deep red $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)(\eta^2\text{-CS}_2)]$ and red $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{CS}_3)]$. Yields vary with the phosphine but typical values when $\text{PR}_3 = \text{PPh}_3$ are 10, 25, and 17% respectively. If toluene is added to the reaction mixture to raise the reaction temperature, a fourth major product is formed, Werner's trinuclear complex $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\text{CS})(\text{S})]$ [1]. It increases in importance with increasing temperature and longer reaction times. The source of Werner's complex appears to be $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{CS}_2)]$ which, when $\text{PR}_3 = \text{PPh}_3$, decomposes to it in ca. 35% yield after 4 h in refluxing toluene or four days at 25°C under the influ-

ence of UV radiation. The sulphur atoms in all four types of complexes exhibit their expected basic properties and form adducts with alkyl halides or Lewis acids, e.g. $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CS})\cdot\text{HgCl}_2]$, $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CS}_2)\cdot 2\text{SnCl}_2]$, $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{P}^i\text{Bu}_3)(\text{CS}_3\text{Me})]\text{I}$, and $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\text{CS})(\text{S})\cdot\text{AgBF}_4]$.

A similar series of reactions and products are obtained when the phosphines are replaced by organoisocyanides.

In parallel with our studies involving carbon disulphide we have also pursued the chemistry of related molecules such as organoisoithiocyanates. $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{PhNCS})]$ may be obtained in good yield by the UV irradiation of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CS}_2)]$ and PhNCS, and is also a product of the reaction of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CO})]$ with PhNCS in refluxing benzene. A polymeric species is also formed in this reaction which may be an analogue of Werner's complex, but both analytical and ^1H NMR data are consistent with a $[\text{Co}_4(\eta\text{-C}_5\text{H}_5)_4(\text{PhNCS})]$ formulation. Its structure is currently being determined [4]. $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{PhNCS})]$ appears to be the first stable organoisoithiocyanate complex of a first row transition metal to have been reported. The more normal reaction involves ligand fragmentation.

References

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