Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Novel heterogeneous binuclear dithiocarbamate complexes

W.K. GLASS and T. SHIELS
Chemistry Department, University College, Belfield, Dublin (Ireland)

(Received December 17th, 1971)

An unsuccessful attempt has previously been made to incorporate dithiocarbamates in heteronuclear metal complexes[1]. We prepared π-$C_5H_5(CO)_3MoSnCl_3$ and π-$C_5H_5(CO)_3WSnCl_3$ by standard methods[2] and reacted these in turn with $NaS_2CN(CH_3)_2$ and $NaS_2CN(C_2H_5)_2$ to give complexes of the general formula π-$C_5H_5(CO)_3M$–$SnCl_2R$, where M = Mo,W and R = $S_2CN(CH_3)_2$, $S_2CN(C_2H_5)_2$. The reactions were carried out in acetone, under a nitrogen atmosphere in the dark, using 1/1 molar ratios of reactants. After 1 hour, the acetone was removed under reduced pressure and the resulting solid extracted with hot benzene, treated with decolourizing charcoal and recrystallized from a methylene chloride–heptane mixture. Excellent analytical figures corresponding to the general formula π-$C_5H_5(CO)_3M$–$SnCl_2R$ were obtained for these products.

The structure of these complexes is presumably analogous to π-$C_5H_5(CO)_3MoSnCl[\pi$-$C_5H_5Fe(CO)_2]_2$[3]. The cyclopentadienyl group occupies three of the coordination positions around the molybdenum or tungsten, the structure thus being essentially a trigonal-capped metal atom (M) at the apex of a square pyramid. The tin atom is centred in a distorted tetrahedral grouping.

In the infrared, five bands (instead of the three expected) are exhibited in the carbonyl stretching region between 2035 and 1935 cm^{-1} for each compound. A typical spectrum is shown in Fig. 1. Jetz and Graham reported extra carbonyl bands for the complex π-$C_5H_5(CO)_2FeSi(Cl)_2CH_3$[4] and explained these in terms of different rotamers caused by restricted rotation about the Fe–Si bond.

Although infrared absorption bands due to the π-C_5H_5 group occur in the spectra of these complexes in the 1000 ± 70 cm^{-1} region (suggested by Bradley and Gitlitz[5] as a criterion for distinguishing unidentate and bidentate dithiocarbamates) our spectra suggest unidentate coordination. Again the partial double bond character of the C–N bond is evident from its stretching vibration which occurs at ca. 1525 cm^{-1} in these complexes.

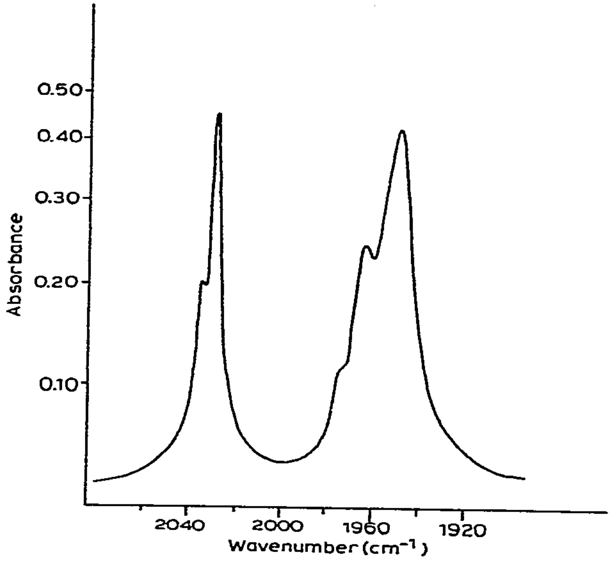

Fig. 1. The carbonyl stretching frequencies for the complex π-$C_5H_5(CO)_3Mo-SnCl_2S_2CNMe_2$, obtained in CS_2 solution.

Proton ^1H NMR spectra show no evidence for isomerism. This could be due to the relatively slow time scale of this physical method. A singlet attributed to the π-C_5H_5 group occurs at τ4.23 for each of the molybdenum complexes and at τ4.11 and 4.13 for the methyl- and ethyl-tungsten compounds respectively. The deshielding effect with increased size of the metal atom could be due to greater back-donation into the π-cyclopentadienyl ring.

In the new complexes reported here two possible explanations could be advanced for the spectrum in the carbonyl stretching region, namely isomers due to hindered rotation within the $Sn(Cl)_2R$ group ($R = S_2CN(CH_3)_2, S_2CN(C_2H_5)_2$) or to hindered rotation about the metal—tin bond. We prefer the latter and suggest as possible rotamers those given in Fig. 2.

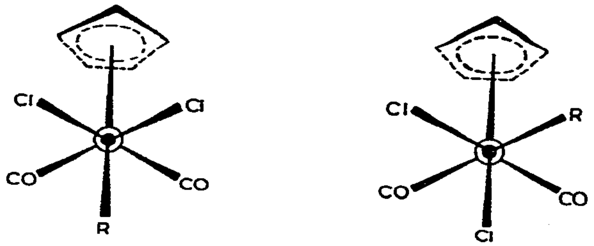

Fig. 2. Possible rotamers for the complexes π-$C_5H_5(CO)_3M-Cl_2R$, the third carbonyl group on the metal atom M being staggered.

REFERENCES

1 F. Bonati and G. Mingetti, *J. Organometal. Chem.*, 16 (1969) 332.
2 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 179; F. Bonati, S. Cenini and R. Ugo, *J. Chem. Soc. (A)*, (1967) 932.
3 J.E. O'Connor and E.R. Corey, *J. Amer. Chem. Soc.*, 89 (1967) 3930.
4 W. Jetz and W.A.G. Graham, *J. Amer. Chem. Soc.*, 89 (1967) 2773.
5 D.C. Bradley and M.H. Gitlitz, *J. Chem. Soc. (A)*, (1969) 1152.

BOOK REVIEW

Annual Reports in Organic Synthesis–1970; ed. by J. McMurry and R. B. Miller, Academic Press, New York, 1971, xvi+399 pages (paperback), $7.50.

Organometallic chemistry has come to play an important role in organic synthesis; organometallic compounds are finding valuable application both as stoichiometric and catalytic reagents. The book under discussion is the first volume of an intended annual series whose purpose is to survey current developments in organic synthesis. The authors' approach is similar to that of "*Reactionae Organicae*" published in "*Synthesis*", only even more streamlined: the information is conveyed almost solely by means of chemical equations. The obvious advantage of this method of presentation is that it allows rapid skimming of the material presented since an equation can convey much information and requires only little reading time. However, a brief, informative title and a few lines of text for each reference thus "abstracted" (as in "*Reactionae Organicae*") would be helpful; the first to state the nature of the conversion involved, the second to provide a minimum of information concerning scope and mechanism and any unusual reaction conditions. But, as the authors point out, it is the principal purpose of this series merely to alert the interested chemist to new chemistry; for details, the reader is urged to consult the original literature.

As an organometallic chemist active at the periphery of synthetic organic chemistry, your reviewer has found this an interesting and useful book. Many examples of the application of organometallics in organic synthesis escape us because they are hidden away in long organic papers that the organometallic chemist rarely reads in detail. This volume makes it possible and easy to become aware of many of these new applications. In this book one finds examples of the use in synthesis of many organometallic reagents and intermediates, such as organolithium and organomagnesium reagents, organoboranes and organoalanes, organometallic and metal hydrides, metal carbonyls, halomethylmercury and -zinc compounds, inorganic complexes such as $(Ph_3P)_3RhCl$, to mention just a few. Many of the reactions cited indeed are useful or potentially useful in synthesis, but some are not, despite the authors' claim to include only "reactions and methods which are new, synthetically useful and reasonably general." For instance, the reduction of carboxylic acids and ketones with $(\pi\text{-}C_5H_5)_2ZrH_2$ is an interesting, but hardly a useful reaction.