Journal of Organometallic Chemistry, 94 (1975) C3—C4

Preliminary communication

SYNTHESIS OF *trans*-AZOALKANE LIGANDS R—N=N—R BY DEHALOGENATION OF *N,N*-DIHALOALKYLAMINES, $RNCl_2$

GOTTFRIED HUTTNER*, H.-G. SCHMID, H. WILLENBERG and TH. STARK
Anorganisch Chemisches Institut der Technischen Universität, 8 München 2, Arcisstr. 21 (B.R.D.)

(Received May 15th, 1975)

Summary

N,N-Dihaloalkylamines, $RNCl_2$, are dehalogenated by organometallic sodium or lithium salts to give *trans*-azoalkanes, R—N=N—R, and their corresponding metal complexes.

Dehalogenation of *N,N*-dihaloalkylamines, $RNCl_2$, to give azoalkane compounds, R—N=N—R, has not previously been observed. We now report that azocyclohexane and its complexes may be prepared in substantial yields from *N,N*-dichlorocyclohexylamine, $C_6H_{11}NCl_2$, by using sodium or lithium salts of organometallic complexes as dehalogenating agents.

When a THF solution of $Na_2[Cr_2(CO)_{10}]$ is allowed to react with $C_6H_{11}NCl_2$ at −40 °C the azocyclohexane complex $(C_6H_{11}N{=}NC_6H_{11})Cr(CO)_5$ (I) may be isolated in yields of 68%. I is also obtained from the reaction of $C_6H_{11}NCl_2$ with THF solutions of $(CO)_5Cr[C(OLi)(n\text{-}C_4H_9)]$ in yields up to 52%, whereas with the corresponding acylate complexes of Mo and W, $(CO)_5M[C(OLi)(n\text{-}C_4H_9)]$ (M = Mo,W), only poor yields of the azocyclohexane complexes $(C_6H_{11}N{=}NC_6H_{11})M(CO)_5$ are obtained. Analogous syntheses of other azoalkane complexes starting from $i\text{-}C_3H_7NCl_2$ or $n\text{-}C_4H_9NCl_2$ have not yet been successful.

The yellow air-stable compound I melts at 96 °C with decomposition. In THF solution it dissociates completely to give $C_6H_{11}N{=}NC_6H_{11}$ and $THFCr(CO)_5$. This reaction is completely reversible and upon removal of THF I is recovered in quantitative yield. Similar but irreversible ligand exchange reactions occur with amines and phosphanes in benzene solutions at 20 °C to give the corresponding amine or phosphane adducts of $Cr(CO)_5$ in high yield.

The *trans* configuration of the azo ligand in I is proved by an independent synthesis of I from *trans*-$C_6H_{11}N{=}NC_6H_{11}$ and $THFCr(CO)_5$ **. The *trans* structure

---

*Correspondence should be addressed to this author.

**This method was introduced by Dr. M. Herberhold for the synthesis of complexes of various *cis*-azo ligands [1].

of the ligand in I has also been demonstrated by X-ray analysis.

The steric strain caused by the *trans* configuration of the bulky azo ligand may explain the reactivity of I, which makes it a useful reagent for the preparation of $LCr(CO)_5$ complexes.

Acknowledgements

We are indebted to Prof. Dr. Dr. h.c. E.O. Fischer for his continuous interest in this work. Financial support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. The Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften made available its computing facilities for the structural work.

Reference

1 M. Herberhold and W. Golla, Chem. Ber., 107 (1974) 3199.