

## DNMR SPECTROSCOPIC EVIDENCE FOR PHENYL GROUP EXCHANGE BETWEEN $C_6H_5Hg^+$ AND $Hg^{2+}$

PAUL PERINGER\* and PETER-PAUL WINKLER

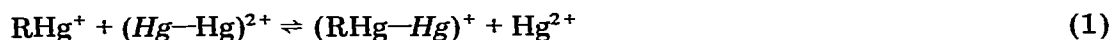
*Institut für Anorg. u. Analyt. Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck (Austria)*

(Received March 20th, 1980)

### Summary

The phenyl group transfer between  $[Hg(DMSO)_6](O_3SCF_3)_2$  and  $[C_6H_5Hg(DMSO)_2](O_3SCF_3)$  has been investigated by means of  $^1H$ ,  $^{13}C$  and  $^{199}Hg$  NMR spectroscopy. The bimolecular reaction is faster in methanol ( $k_2 = 1.3 \times 10^4$  l/mol s) than in DMSO.

In view of recent reports [1] concerning solid stable organomercury(I) compounds, this study was initially directed towards the question whether or not soluble organomercury(I) compounds are formed as short-lived intermediates during reaction 1.



This would involve a net transfer of a mercury atom, as has been observed [2] for the exchange between valency states I and II of mercury (eq. 2):



Phenylmercurytrifluoromethanesulfonate and mercury(I)trifluoromethanesulfonate in the form of its DMSO solvates were used in this experiment on the basis of solubility and stability considerations [3].

The addition of  $Hg_2^{2+}$  to a solution of  $C_6H_5Hg^+$  caused noticeable broadening of the  $C_6H_5Hg^+$   $^{199}Hg$  NMR signal. The  $Hg_2^{2+}$  signal on the other hand exhibited the same linewidth as observed in the absence of  $C_6H_5Hg^+$ . Although there was thus no  $^{199}Hg$  NMR evidence for reaction 1, the result suggested the occurrence of a reaction between  $C_6H_5Hg^+$  and  $Hg_2^{2+}$  species present in  $Hg_2^{2+}$  solutions as a result of the disproportionation 3.



Indeed, no  $^{199}Hg$  NMR resonance could be detected in equimolar solutions of

$C_6H_5Hg^+$  and  $Hg^{2+}$ . Reversibility was confirmed by the appearance of the signals of  $C_6H_5Hg^+$  and  $Hg_2^{2+}$  after addition of liquid mercury,  $Hg^{2+}$  having been reduced to  $Hg_2^{2+}$  according to eq. 3. A transfer of the phenyl group between  $C_6H_5Hg^+$  and  $Hg^{2+}$  thus seems to be indicated, eq. 4.



This is corroborated by the disappearance of  $^1H-^{199}Hg$  and  $^{13}C-^{199}Hg$  coupling patterns of  $C_6H_5Hg^+$  upon addition of  $Hg^{2+}$ , and by its reappearance at low temperatures. A concomitant broadening of the  $^{13}C(1)$  resonance of  $C_6H_5Hg^+$  was noted.

The dependence of the linewidth of the  $Hg^{2+}$  ( $C_6H_5Hg^+$ )  $^{199}Hg$  NMR signal on the concentration of  $C_6H_5Hg^+$  ( $Hg^{2+}$ ) as shown in Fig. 1 or Fig. 2 is consistent with second order kinetics, yielding bimolecular rate constants  $k_2 = 1.3 \times 10^4$  and  $k_2 = 2.4 \times 10^3$  l/mol s respectively. The different rate constants may be explained by assuming as the first step of reaction 4 a dissociation of the stable [4] hexakis-DMSO-mercury(II) complex. The coordination of DMSO in the solvate  $[C_6H_5Hg(DMSO)_2]O_3SCF_3$  is weaker than in  $[Hg(DMSO)_6](O_3SCF_3)_2$  as a consequence of the *trans* influence of the  $C_6H_5$  group, as can be seen from mercury-oxygen stretching vibrations in these compounds [3]. Thus, when an excess of  $C_6H_5Hg^+$  (Fig. 2) is used, the DMSO present from dissociation of the weakly coordinated  $[C_6H_5Hg(DMSO)_2]^+$  diminishes the dissociation of  $[Hg(DMSO)_6]^{2+}$ . This is supported by the observation of smaller  $k_2$  ( $3.1 \times 10^2$  l/mol s) when DMSO as solvent in place of methanol.

No reactions of type 4 comparable in rate have been found for  $C_6H_5HgCl/HgCl_2$  or  $C_6H_5HgOAc/Hg(OAc)_2$ .

Reaction 4 shows that the *trans* effect order does not parallel the *trans* influence order: The value of  $J(^{13}C(1)-^{199}Hg)$  in (see Experimental section), affected primarily by  $\sigma$  bonds, is the largest for all the  $C_6H_5HgX$  compounds examined so far [5]. The position of  $X = CF_3SO_3$  in the *trans* effect order may be seen as a consequence of steric effects (the  $CF_3SO_3$  anion is believed to be

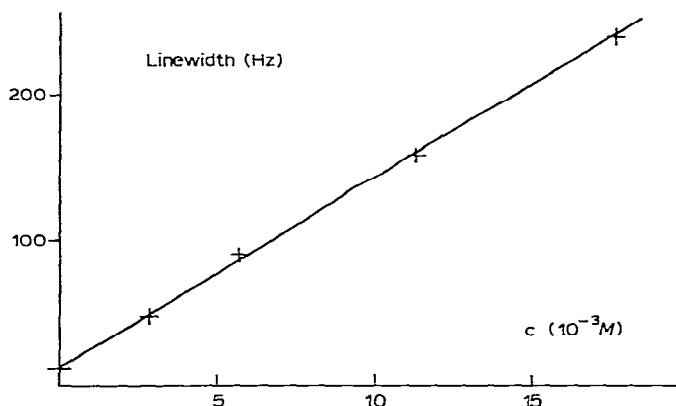


Fig. 1. Plot of the linewidth of 0.5 M  $Hg(DMSO)_6(O_3SCF_3)_2$  versus  $[C_6H_5Hg(DMSO)_2]O_3SCF_3$  in methanol.

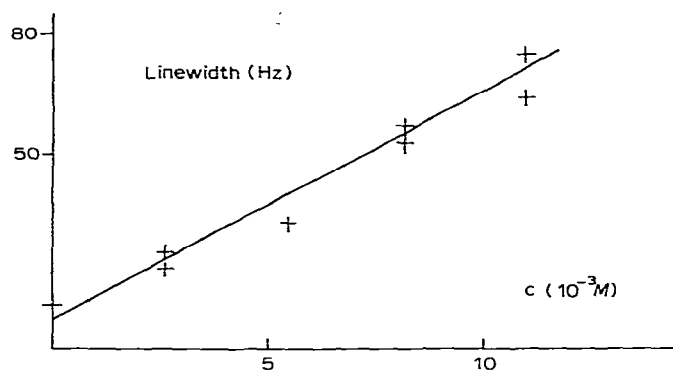


Fig. 2. Plot of the linewidth of 0.5 M  $C_6H_5Hg(DMSO)_2O_3SCF_3$  versus  $[Hg(DMSO)_6(O_3SCF_3)_2]$  in methanol.

essentially noncoordinating in solution) or of electronic features of the transition state.

Reaction 4 would be the first example of kinetic lability on the NMR time scale of a Hg—C bond of aryl—mercury compounds. The existence of the same type (eq. 5) of redistribution reaction for allylmercury compounds can be concluded from the change of the  $\sigma$  allyl type PMR spectrum of  $CH_2 = CH-CH_2HgX$  into a  $AX_4$  pattern upon addition of catalytic amounts of  $HgX_2$  [6].



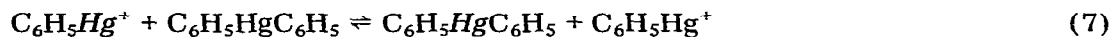
Reactions involving a corresponding “one alkyl exchange” (eq. 5, R = Me, Bu) were investigated [7] by isotope labelling techniques. The increase in rate found when X was changed paralleled the increasing ionicity of  $HgX_2$ . An estimation of  $k_2$  at 300 K for X =  $NO_3$  and R = Me from data measured at 273 K [7], assuming similar temperature dependence of the rate as for X = Br [7], yields  $k_2 = 7 \times 10^3$  l/mol s. A bimolecular electrophilic substitution at carbon with front side attack ( $S_E2$ ) was proposed for X with low affinity for Hg [7].

Complete self-symmetrization (eq. 6) has been reported for 2,3,5,6-tetrafluoro-4-methoxyphenylmercurytrifluoromethanesulfonate in acetone within

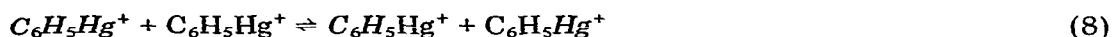


ten minutes [8]. No NMR signals of symmetrization products could be detected for phenylmercurytrifluoromethanesulfonate in acetone, although the absence of  $^{13}C-^{199}Hg$  coupling indicates the presence of small amounts of  $Hg^{2+}$  according to reaction 4.

No DNMR spectroscopic evidence could be found for the occurrence of reaction 7.



Reaction 8 seems unlikely in acetone because  $^{13}C-^{199}Hg$  spin—spin coupling has been observed in other solvents (see Experimental part).



## Experimental

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{199}\text{Hg}$  NMR spectra were recorded on a Bruker WP-80 multinuclear spectrometer.  $[\text{C}_6\text{H}_5\text{Hg}(\text{DMSO})_2]\text{O}_3\text{SCF}_3$  and  $[\text{Hg}(\text{DMSO})_6](\text{O}_3\text{SCF}_3)_2$  were prepared as described elsewhere [3]. A solution of  $\text{Hg}_2^{2+}$  was obtained by treating  $[\text{Hg}(\text{DMSO})_6](\text{O}_3\text{SCF}_3)_2$  in methanol with elementary mercury [3]. Unless otherwise stated, the measurements were carried out in methanolic solution at 300 K. Only freshly prepared solutions of  $\text{C}_6\text{H}_5\text{Hg}^+$  and  $\text{Hg}_2^{2+}$  were used because slow oligomercuration is observed, especially at elevated temperatures.

### $^{13}\text{C}$ and $^1\text{H}$ NMR spectroscopic data for $\text{C}_6\text{H}_5\text{HgO}_3\text{SCF}_3$

1 M in DMSO:  $\delta^{13}\text{C}(1)$  143.6,  $\delta^{13}\text{C}(2)$  137.1,  $\delta^{13}\text{C}(3) = \delta^{13}\text{C}(4)$  128.8 ppm  
 $^1J(^{13}\text{C}-^{199}\text{Hg})$  3110,  $^2J(^{13}\text{C}-^{199}\text{Hg})$  128,  $^3J(^{13}\text{C}-^{199}\text{Hg})$  248,  $^3J(^1\text{H}-^{199}\text{Hg})$  242,  
 $^4J(^1\text{H}-^{199}\text{Hg})$  69 Hz. 4 M in dioxane:  $\delta^{13}\text{C}(1)$  139.9,  $\delta^{13}\text{C}(2)$  137.0,  $\delta^{13}\text{C}(3) =$   
 $\delta^{13}\text{C}(4)$  127.7 ppm  $^1J(^{13}\text{C}-^{199}\text{Hg})$  2918,  $^2J(^{13}\text{C}-^{199}\text{Hg})$  134,  $^3J(^{13}\text{C}-^{199}\text{Hg})$   
 247 Hz.

## Acknowledgements

We thank Professors A. Engelbrecht and K.E. Schwarzhan for making this work possible and the Fonds zur Förderung der Wissenschaft, Wien for allowing access to the NMR spectrometer.

## References

- 1 E.T. Blues, D. Bryce-Smith and H. Karimpour, *J. Chem. Soc. Chem. Commun.*, (1979) 1043.
- 2 P. Peringer, *J. Chem. Research*, in the press.
- 3 P. Peringer, *J. Inorg. Nucl. Chem.*, in the press.
- 4 M. Sandström, I. Persson and S. Ahrland, *Acta Chem. Scand. A*, 32 (1978) 607.
- 5 P.L. Goggin, R.J. Goodfellow, D.M. McEwan, A.J. Griffiths and K. Kessler, *J. Chem. Research (M)*, (1979) 2315; A.P. Tupiauskas, N.M. Sergeev, Y.A. Ustynyuk and A.N. Kashin, *J. Magn. Reson.*, 7 (1972) 124; N.K. Wilson, R.D. Sehr and P.D. Ellis, *J. Magn. Reson.*, 21 (1976) 437; A.J. Brown, O.N. Howarth and P. Moore, *J. Chem. Soc. Dalton Trans.*, (1976) 1584; J. Browning, P.L. Goggin, R.J. Goodfellow, N.W. Hurst, L.G. Mallinson and M. Murray, *J. Chem. Soc. Dalton Trans.*, (1978) 872.
- 6 reviewed in V.S. Petrosyan and O.A. Reutov, *J. Organometal. Chem.*, 76 (1974) 123.
- 7 E.D. Hughes, C.K. Ingold, F.G. Thorpe and H.C. Volger, *J. Chem. Soc.*, (1961) 1133.
- 8 G.B. Deacon and D. Tunaley, *J. Organometal. Chem.*, 156 (1978) 403.