tion, both crystallized and uncrystallized samples of tetra-*p*-tolylsilane showed an unassigned singlet at 442 cps. (6% of total aromatic hydrogens).

This work was supported in part by the Office of Naval Research. We are indebted to Prof. H. GILMAN for a sample of tetra-*m*-tolylsilane and to the Dow Corning Corporation for a gift of dimethylchlorosilane.

Chemistry and Life Sciences Laboratory
Research Triangle Institute,
Durham, North Carolina (U.S.A.)

COLIN G. PITT
KENNETH R. SKILLERN

1 K. MOEDRITZER, *Organometal. Chem. Rev.*, 1 (1966) 179.
2 G. FRITZ, *Z. Anorg. Allgem. Chem.*, 273 (1953) 275.
3 H. GILMAN AND D. H. MILES, *J. Org. Chem.*, 23 (1958) 326.
4 H. GILMAN, R. A. TOMASI AND D. WITTENBERG, *J. Org. Chem.*, 24 (1959) 821.
5 L. E. NELSON, N. C. ANGELOTTI AND D. R. WEYENBERG, *J. Am. Chem. Soc.*, 85 (1963) 2662.
6 N. S. NAMETKIN, V. M. VDOVIN AND P. L. GRINDBERG, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1964) 1133; D. R. WEYENBERG AND L. E. NELSON, *J. Org. Chem.*, 30 (1965) 2618.
7 A. J. CHALK AND J. F. HARROD, *J. Am. Chem. Soc.*, 87 (1965) 16.
8 R. K. INGHAM AND H. GILMAN, in F. G. A. STONE AND W. A. G. GRAHAM, *Inorganic Polymers*, Academic Press, New York, 1962, pp. 335–337.
9 H. A. CLARK, A. F. GORDON, W. C. YOUNG AND M. J. HUNTER, *J. Am. Chem. Soc.*, 73 (1951) 3798; M. L. JOSIEN AND J. M. LEBAS, *Bull. Soc. Chim. France*, 23 (1956) 53.
10 C. EABORN, *Organosilicon Compounds*, Butterworth, London, 1960, pp. 51–55.
11 R. A. BENKESER AND F. J. RIEL, *J. Am. Chem. Soc.*, 73 (1951) 3472.
12 W. A. PICCOLI, G. G. HABERLAND AND R. L. MERKER, *J. Am. Chem. Soc.*, 82 (1960) 1883.
13 M. KANAZASHI, *Bull. Chem. Soc. Japan*, 26 (1953) 493.
14 A. V. TOPCHIEV, N. S. NAMETKIN AND A. A. SHCHERBAKOVA, *Dokl. Akad. Nauk. SSSR*, 86 (1952) 559.
15 H. GILMAN AND G. N. R. SMART, *J. Org. Chem.*, 15 (1950) 720.

Received June 30th, 1966

J. Organometal. Chem., 7 (1967) 525–528

Dicyclopentadienyltitanium(IV) halide species in acetone solutions

In a paper on the kinetics of dicyclopentadienyltitanium(IV) complexes Langford and Aplington[1] elude a proposal by Jensen[2,3] that such compounds are dimerized in acetone solution. Also, objections have been raised to the introduction of more intermediates despite the local inconsistencies in the parameters from different experiments[4]. Multicomponent mixtures are liable to great freedom in interpretation[5], and a global approach[6] in handling the experimental data is needed in order to bring such freedom under reasonable control.

This note is an attempt to mediate between the crowded model of Jensen and the simplified reaction scheme of Langford and Aplington[1], in which—after deduction of the influence of the water content—a single parameter should characterize the exchange of one ligand for another. We have used Jensen's data for the LiSCN/LiCl system, see Table 1, because for these ligands we may neglect the aquation effects, which seem to be competitive in case of LiBr.

J. Organometal. Chem., 7 (1967) 528–530

TABLE 1

THE RANGE OF THE EXPERIMENTAL DATA AT 25.0°

	[M]	*[LiSCN]*	*[LiCl]*	*time*	*Number of wavelengths*	*Number of observations*
		0.000247	0.001341			
Equilibrium	0.00005			6–8 hours	23	355
		0.001347	0.00001175			
$MCl_2 \rightarrow M(SCN)_2$	0.000025	0.005	(0.00005)	60–6900 sec	8	136
$M(SCN)_2 \rightarrow MCl_2$	0.0001	(0.0002)	0.05	60–1320 sec	7	119

Assuming the monomeric structure, MX_2, where M stands for the dicyclopentadienyltitanium(IV) ion, the following equations correspond to plausible thermodynamic conceptions,

$$-\frac{d}{dt}\begin{Bmatrix}[M(SCN)_2]\\ [M(SCN)Cl]\\ [MCl_2]\end{Bmatrix} =$$

$$\begin{Bmatrix} k_{12}[LiCl] & -k_{21}[LiSCN] & 0 \\ -k_{12}[LiCl] & k_{21}[LiSCN]+k_{23}[LiCl] & -k_{32}[LiSCN] \\ 0 & -k_{23}[LiCl] & k_{32}[LiSCN]\end{Bmatrix}\begin{Bmatrix}[M(SCN)_2]\\ [M(SCN)Cl]\\ [MCl_2]\end{Bmatrix}$$

which at equilibrium give:

$$\frac{[M(SCN)Cl][LiSCN]}{[M(SCN)_2][LiCl]} = k_{12}/k_{21} = K_1$$

$$\frac{[MCl_2][LiSCN]}{[M(SCN)Cl][LiCl]} = k_{23}/k_{32} = K_2$$

For each wavelength we had three molar extinction coefficients, which, including four rate constants, gave 73 parameters to reflect the 610 observations.

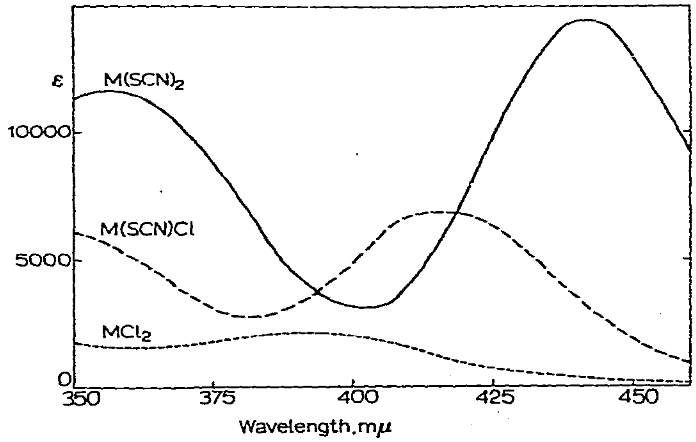

Fig. 1. Spectra of dicyclopentadienyltitanium(IV) halides.

Such simultaneous comparison of several experiments with models that are tied together by joint parameters was made possible by a framework program for the computer, GIER. The following is a report of the observations made with all data present.

First of all, the spectrum of the intermediate complex stood out very distinctly (see Fig. 1), intermediate in density as well as in wavelength.

Whereas k_{12} and k_{21} were so large that only their ratio could be estimated with any degree of certainty, k_{23} and k_{32} appeared to be the rate-determining parameters.

We found a rather anomalous ratio between the two equilibrium constants, obviously the reason for the failure of the previously used graphical method[7].

The noise level ($\sim$0.5% of maximal absorbancy) was nearly doubled when the kinetic experiments were added to the equilibrium experiments. On closer examination this strain, which we do not consider serious for the conclusion, is likely to reflect the fact, that 6–8 hours were insufficient for complete equilibration. Table 2 contains the information conditioned on the proposed model, which seems equally well adapted to the data and to basic ideas within spectroscopy and thermodynamics. However, we have only taken the given data into consideration, and the needs of a specific situation may call for a revision and for new directed experiments.

TABLE 2

PARAMETERS OF THE PROPOSED MODEL AT 25.0°

	Estimate	*Noise level*
k_{12}	(430) M^{-1} sec^{-1}	3000
k_{21}	(48) M^{-1} sec^{-1}	400
k_{23}	0.0419 M^{-1} sec^{-1}	0.0008
k_{32}	0.0630 M^{-1} sec^{-1}	0.0007
K_1	9.1	0.1
K_2	0.66	0.02

Departments of Inorganic Chemistry,
The Royal Danish School of Pharmacy,
and Regnecentralen, Inc.,
Copenhagen (Danmark)

ARNE JENSEN
ERIK JØRGENSEN

1 C. H. LANGFORD AND J. P. APLINGTON, *J. Organometal. Chem.*, 4 (1965) 271.
2 A. JENSEN, *Proc. 7th Intern. Conf. Coord. Chem., Stockholm*, Almqvist and Wiksell, Uppsala, 1962, 254.
3 A. JENSEN, *Udbytningsreaktioner for Biscyclopentadienyltitan(IV)komplekser* (with an English summary). Akademisk Forlag, Copenhagen, 1965.
4 E. JØRGENSEN, private communication.
5 E. JØRGENSEN AND J. BJERRUM, *Acta Chem. Scand.*, 13 (1959) 2075.
6 E. JØRGENSEN, *Proc. 7th Intern. Conf. Coord. Chem., Stockholm*, Almqvist and Wiksell, Uppsala, 1962, 208.
7 L. NEWMAN AND D. N. HUME, *J. Am. Chem. Soc.*, 79 (1957) 4571.

Received June 30th, 1966