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Reactivity of $CpTiCl_3$ toward $AgMF_6$: Identification and Stability of $CpTi(MF_6)_3$ (M = As, Sb)*

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For a long time Lewis acid adducts of titanocene-difluoride of the type $Cp_2Ti(LF)_2$ ($L = BF_3$, PF_5) were known to be unstable and non-existent in the solid state [1]. Recently we reported the preparation and characterization of $Cp_2Ti(SbF_6)_2$ (**1a**) [2] and also the X-ray structure of $Cp_2Ti(AsF_6)_2$ (**1b**) [3]. **1b** can be prepared either by reaction of Cp_2TiF_2 with the very powerful F^- acceptor AsF_5 (compared with PF_5) [4] or, more convenient, like **2** by reaction of Cp_2TiCl_2 with $AgAsF_6$ [3]. Surprisingly **1b** does not decompose (as expected) in the MS (60 °C) to Cp_2TiF_2 and AsF_5 but shows an intense peak due to $CpTiF_3^+$ [3]. Moreover, no evidence for Cp_2TiF_2 as a product of the thermal decomposition ($60\ ^{\circ}C \leqslant T \leqslant 300\ ^{\circ}C$) of **1b** could be found [3]. Our interest in the reactivity of $CpTiCl_3$ toward $AgMF_6$ (M = As, Sb) and AsF_5 derived from these observations. We were also interested in the stability and the decomposition behaviour of the products formed by those reactions. The results of our investigations are described in this paper and they may help to achieve further synthesis of more MF_6^- organometallic complexes (M = pnicogen) which are still in the very beginning of their discovery.

All techniques have been described in ref. 2. $CpTiCl_3$ was prepared according to ref. 5. $AgAsF_6$ (Alfa) and $AgSbF_6$ (Alfa) were used without further purification.

$CpTiCl_3$ reacts at −50 °C in SO_2 (l) spontaneously with three equivalents of $AgMF_6$ quantitatively according to eqn. (1), affording deep red solutions (AgCl, found by weight: 98%, As; 97%, Sb).

$$\text{CpTiCl}_3 + 3\ \text{AgMF}_6 \xrightarrow[-50\ ^{\circ}\text{C}]{\text{SO}_2\ (\text{l})} (\text{CpTi}^{3+}(\text{MF}_6^-)_3\text{solv.}) + 3\ \text{AgCl}\downarrow \qquad (1)$$

(M = As, **2**; Sb, **3**)

The new complexes **2** and **3** are, as far as we know, the first examples of mono(cyclopentadienyl)-titanium(IV) derivatives which contain a MF_6 unit (M = pnicogen). They can be regarded formally as Lewis acid (AsF_5, SbF_5) adducts of $CpTiF_3$. (NB, AsF_5 decomposes $CpTiCl_3$ in SO_2 solution within minutes with cleavage of the Cp–Ti bond [6].) While **2** and **3** decompose in solution at RT within some hours and even slowly at −50 °C, they are non-existent in the solid state (evaporating SO_2 at −20 °C). However, they seem to be stable when frozen in SO_2 at −196 °C. (Cp_2TiCl_2 is stable in SO_2 at RT for at least one week [6].) **2** and **3** were identified in solution by ^1H NMR spectroscopy (see Table I). The singlet resonance in the Cp region (quartet expected for three Ti–F bonds) and the low field shift, compared with $CpTiCl_3$, indicates dissociation of these complexes as shown in eqn. (1) and already discussed for **1b** [3], or rapid exchange (equality of all F atoms). The low field shift of **3** compared with **2** may be due to equilibria (*cf.* eqn. (2)) in solution and the appearance of $CpTi(Sb_2F_{11})_3$ [6]. In addition to the Cp singlet both **2** and **3** show a complex multiplet (7.2–7.8 ppm) due to unsaturated C_mH_n and therefore some decomposition with Ti–Cp bond breaking.

In addition to the appearance of C_mH_n (^1H NMR), owing to the decomposition process, HF (IR) and TiF_4 (MS) could be identified as final products after pumping off the SO_2. This indicates a very similar behaviour as observed for the thermal decomposition of **1**, although in the case of **2** and **3** this reaction takes place already at low temperature and the compounds are non-existent in the solid phase. Presumably fluorine transfer is the first step in the decomposition sequence due to the very strong Ti(IV)–F bond (585 kJ/mol) [7], which is even stronger than the As(V)–F bond (406 kJ/mol) [8]. This can be simulated by a thermodynamic cycle (eqn. (3)), describing the reaction of $CpTiCl_3$ with AsF_5 ($CpTiF_3$ and MF_5 may be somehow in equilibrium with **2** and **3**, and for the thermodynamic

TABLE I. ^1H NMR Data[a]

Complex	δ (ppm)	Reference
Cp_2TiCl_2	6.65s	3
$Cp_2Ti(SbF_6)_2$ (**1a**)	7.25s	2
$Cp_2Ti(AsF_6)_2$ (**1b**)	7.30s	3
$CpTiCl_3$	7.23s	this work
$CpTi(AsF_6)_3$ (**2**)	8.52s	this work
$CpTi(SbF_6)_3$ (**3**)[b]	8.80s	this work

[a] SO_2 solution, 20 °C, reference TMS. [b] Due to $CpTi(Sb_2F_{11})_3$ in solution (*cf.* eqn. (2)).

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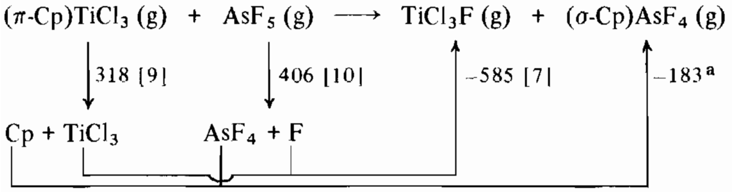
estimations it does not matter whether $CpTiF_3$ is used or $CpTiCl_3$; see eqn. (2).

$$CpTi(MF_6)_3 \rightleftharpoons CpTiF_3 + 3\,MF_5 \qquad (2)$$



(3)

[a] (σ-Cp)–As(V) bond energy (BE) estimated as CH_3–As(V) BE, calculated from CH_3–As(III) BE (229 kJ/mol) [11] minus 20% due to ν(As(III)–C): 568 cm^{-1} [12] and ν_{eq}(As(V)–C): 519 cm^{-1} [13].

The heat of reaction (3) can be estimated as $\Delta H_{(3)} = -44$ kJ/mol. In a similar way the heat of reaction (4) was estimated to $\Delta H_{(4)} = -92$ kJ/mol (BE, Cp–Ti in Cp_2TiCl_2:269 kJ/mol) [14] (gaseous state).

$$(\pi\text{-}Cp)_2TiCl_2 + AsF_5 \longrightarrow (\pi\text{-}Cp)TiCl_2F + (\sigma\text{-}Cp)AsF_4 \qquad (4)$$

It seems likely that some of the bond strength estimate data may either have some experimental error or be slightly inaccurate. However, only the trend in thermodynamics should be shown and the experimental results fit this thermodynamic analysis. It is obvious that eqns. (3) and (4) only represent the first decomposition step as $CpAsF_4$ cannot exist as a stable compound. The summarized decomposition reactions of **1b** and **2** are given in eqns. (5) and (6), where 'C_mH_n' is represented by $C_{10}H_8$ (naphthalene). It has to be mentioned that the kind of organic carbonhydride does not make any difference to the large $\Delta H_{(5)}$ and $\Delta H_{(6)}$ numbers as its $\Delta H_f{}^{\circ}$ value is small, compared with those of inorganic halogen compounds. The $\Delta H_{298}{}^{\circ}$ values (kJ/mol) are given in brackets after the phase symbol.

$$\begin{aligned} &Cp_2TiCl_2\,(s, -385)\,[14] + 2AsF_5\,(g, -1236)\,[8] \longrightarrow \\ &\quad TiCl_2F_2\,(g, -1156)\,[7] + C_{10}H_8\,(s, +61)\,[15] \\ &\quad + 2AsF_3\,(l, -956)\,[7] \\ &\quad + 2HF\,(g, -271)\,[7] \qquad (5) \end{aligned}$$

$$\begin{aligned} &2CpTiCl_3\,(s, -608)\,[9] + 2AsF_5\,(g) \longrightarrow \\ &\quad 2TiCl_3F\,(g, -958)\,[7] + C_{10}H_8\,(s) \\ &\quad + 2AsF_3\,(l) + 2HF\,(g) \qquad (6) \end{aligned}$$

Both reactions (5) and (6) are strongly exothermic, $\Delta H_{(5)} = -692$ kJ/mol and $\Delta H_{(6)} = -621$ kJ/mol, and they have nearly the same heat of reaction.

From these results it can be concluded that **1a**, **1b**, **2** and **3** are thermodynamically unstable with respect to decomposition reactions involving fluorine transfer to the transition metal. In all cases this fluorination of the Ti centre was observed in the experiment. Whereas the titanocene (Cp_2Ti) derivatives **1a** and **1b** are kinetically stabilized and existent as pure compounds in solution and even in the solid state, the mono-Cp complexes **2** and **3** decompose rapidly even at low temperature and are not yet known as solids. The kinetic stability of **1** may be explained by the higher activation barrier involving titanocene metallocene fragments because of the steric protection of the Ti centre by the bulky Cp rings.

References

1 H. C. Clark and A. Shaver, *J. Coord. Chem., 4,* 243 (1975).
2 T. Klapötke, *Polyhedron, 7,* 1221 (1988).
3 T. Klapötke and U. Thewalt, *J. Organomet. Chem.,* in press.
4 T. E. Mallouk, G. L. Rosenthal, G. Müller, R. Brusasco and N. Bartlett, *Inorg. Chem., 23,* 3167 (1984).
5 R. D. Gorisch, *J. Am. Chem. Soc., 80,* 4744 (1958).
6 T. Klapötke, unpublished results.
7 D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry', 2nd edn., Cambridge University Press, Cambridge, 1982, Appendix.
8 I. Barin, O. Knackle and O. Kubaschewski, 'Thermochemical Properties of Inorganic Substances', Springer, New York, 1977, Supplement.
9 V. I. Tel'noi, I. B. Rabinovich, V. D. Tikhonov, V. N. Latyaeva, L. I. Vyshinskaya and G. A. Razuvaev, *Dokl. Akad. Nauk. SSSR, 174,* 1374 (1967); *Dokl. Chem. Proc. Acad. Sci. USSR, 174,* 467 (1967).
10 J. E. Huheey, 'Inorganic Chemistry', 3rd edn., Harper Int. SI Edition, Cambridge/Philadelphia/San Francisco/London/Mexico City/Sao Paulo/Sydney, 1983, Appendix.
11 C. Elschenbroich and A. Salzer, 'Organometallchemie', B. G. Teubner, Stuttgart, 1986, p. 19.
12 J. D. Smith, 'Comprehensive Inorganic Chemistry', Vol. 2, Pergamon, Oxford/New York/Toronto/Sydney/Braunschweig, 1973, p. 624.
13 K.-H. Mitschke and H. Schmidbaur, *Chem. Ber., 106,* 3645 (1973).
14 V. I. Tel'noi and I. B. Rabinovich, *Russ. Chem. Rev., 46,* 689 (1977).
15 R. C. Weast, 'Handbook of Chemistry and Physics', 54 edn., CRC Press, Cleveland, Ohio, 1973/74, D-246.