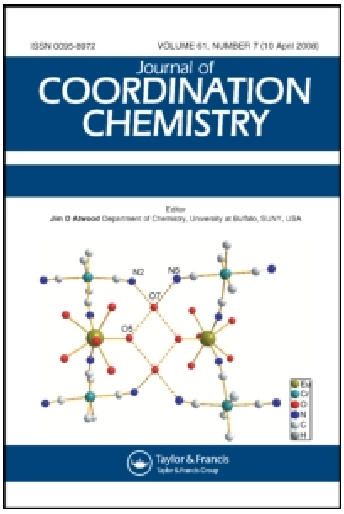

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

ADDUCT FORMATION BETWEEN BISCYCLOPENTADIENYL TITANIUMDIFLUORIDE AND BORON TRIFLUORIDE AND PHOSPHORUS PENTAFLUORIDE

H. C. Clark[a]; Alan Shaver[a]
[a] Department of Chemistry, University of Western Ontario, London, Ontario, Canada

To cite this Article Clark, H. C. and Shaver, Alan(1975) 'ADDUCT FORMATION BETWEEN BISCYCLOPENTADIENYL TITANIUMDIFLUORIDE AND BORON TRIFLUORIDE AND PHOSPHORUS PENTAFLUORIDE', Journal of Coordination Chemistry, 4: 4, 243 — 245

To link to this Article: DOI: 10.1080/00958977508075907

URL: http://dx.doi.org/10.1080/00958977508075907

J. Coord. Chem.
1975, Vol. 4, pp 243–245

ADDUCT FORMATION BETWEEN BISCYCLOPENTADIENYL TITANIUMDIFLUORIDE AND BORON TRIFLUORIDE AND PHOSPHORUS PENTAFLUORIDE

H. C. CLARK† and ALAN SHAVER

Department of Chemistry, University of Western Ontario, London, Ontario, Canada

(Received October 1, 1974; in final form January 24, 1975)

The reactions of organoplatinum cations have been investigated over the past few years in this laboratory.[1] As part of a general program, we recently tried to synthesize the biscyclopentadienyltitanium dication, Cp_2Ti^{2+} (where Cp = *pentahapto*cyclopentadienyl). Reaction of Cp_2TiCl_2 with two equivalents of $AgBF_4$ (or $AgPF_6$) in acetone gave, after filtering and evaporating the reaction solution, a red oil. Treatment of this red oil with methanol caused immediate precipitation of yellow Cp_2TiF_2. The isolation of Cp_2TiF_2 has been reported previously from reactions involving fluorine-containing reagents such as silver salts of CF_3S^-,[2] BF_4^-, PF_6^-, SbF_6^- and AsF_6^-.[3] Methanolysis of bis(cyclopentadienyl) (ethyl-3-ketobutyrato)titanium hexafluorophosphate also yields Cp_2TiF_2[4]. This sort of transfer of fluorine from counter-ion to metal has recently been observed in the reactions of metal bistetrafluoroborates ($M = Co^{2+}$, Ni^{2+} and Cu^{2+}) with triethylenediamine and quinuclidene[5] in refluxing tetrahydrofuran-dimethoxypropane azeotrope. The products in these cases were the metal difluorides and BF_3 adducts of the strong nitrogen bases. The phenomenon is not confined to transition metals. $(CH_3)_2SnF_2$ is formed in the reaction of $(CH_3)_2SnCl_2$ with two equivalents of $AgBF_4$ or $AgPF_6$ in methanol.[6]

It appears that this type of reaction may be quite common. However, in the case of these titanium BF_4 and PF_6 systems the reactions are not as straightforward as has been reported previously. Specifically, the intermediate red compounds, presumably BF_4 and PF_6 salts of Cp_2Ti^{2+}, have not been mentioned before. In addition we find that Cp_2TiF_2 in CH_2Cl_2 and liquid SO_2 reacts with BF_3 and PF_5 to regenerate these red compounds.

We have conducted some infrared and nmr spectroscopic studies and conductivity measurements on these compounds and solutions of them in liquid SO_2 and CH_2Cl_2. These data suggest the existence of the equilibria shown and

$$Cp_2TiF_2 + BF_3 \rightleftharpoons Cp_2TiF(BF_4)$$
$$Cp_2TiF(BF_4) + BF_3 \rightleftharpoons Cp_2Ti(BF_4)_2$$
$$Cp_2TiF_2 + PF_5 \rightleftharpoons Cp_2TiF(PF_6)$$
$$Cp_2TiF(PF_6) + PF_5 \rightleftharpoons Cp_2Ti(PF_6)_2$$

allow us to characterise partially the structure of the BF_4 and PF_6 species.

RESULTS AND DISCUSSION

A molar conductance of 0.051 $ohm^{-1}\ cm^2$ was found for Cp_2TiF_2 in CH_2Cl_2, as expected for a non-electrolyte. On the other hand BF_3 and PF_5 react with CH_2Cl_2. In both cases the conductance of the 2×10^{-3} M solutions increased rapidly with time and did not reach an equilibrium value within ½ hr. The PF_5 solution turned a distinct brown colour and its molar conductance was in excess of 20 $ohm^{-1}\ cm^2$ and increasing when the solution was discarded. However, in the presence of Cp_2TiF_2 these reactions are inhibited. Very stable readings of 1.09 $ohm^{-1}\ cm^2$ and 0.651 $ohm^{-1}\ cm^2$ were obtained for 1×10^{-3} M solutions of $Cp_2Ti(BF_4)_2$ and $Cp_2Ti(PF_6)_2$ respectively. These values indicate a strong interaction between the complex and two equivalents of BF_3 or PF_5. As a check on the experiment the conductance of a 1×10^{-3} M solution of $[CpFe(CO)_2P(C_6H_5)_3]PF_6$ was measured in CH_2Cl_2. The molar conductance was 36.2 $ohm^{-1}\ cm^2$. Molar conductance values greater than 20 $ohm^{-1}\ cm^2$ have been reported for 1:1 electrolytes in CH_2Cl_2[7]. We conclude that the complexes do not dissociate into ions in CH_2Cl_2. Hence, either the reaction between Cp_2TiF_2 and BF_3 or PF_5 does not form an ionic product [i.e. $(Cp_2Ti^{2+})(BF_4^-)_2$ $(Cp_2Ti^{2+})(PF_6^-)_2$] or the ionic products that are formed, exist as very tightly bound ion pairs. The

---

†Author to whom correspondence should be addressed.

cation Cp_2Ti^{2+} would be coordinatively unsaturated (in contrast to $CpFe(CO)_2P(C_6H_5)_3^+$) so that structures with BF_4 and PF_6 groups coordinated to the titanium can be envisioned. Such structures might not undergo ionic dissociation in weakly polar ChH_2Cl_2 solution.

The infrared spectra of the products obtained as oils via the reaction of Cp_2TiCl_2 with $AgBF_4$ and $AgPF_6$ were the same as those of the products obtained via the reaction of Cp_2TiF_2 with BF_3 and PF_5 respectively in liquid SO_2. The spectra consist of bands due to BF_4 and PF_6 superimposed on the bands from Cp_2TiF_2 except for one very significant difference. In the spectrum of Cp_2TiF_2 bands at 564 and 539 cm^{-1} have been assigned to titanium–fluorine symmetric and asymmetric stretching modes respectively.[8] These bands are quite strong and are unchanged when a sample of Cp_2TiF_2, which has been dissolved in liquid SO_2 and recovered, is used. However, these Ti–F bands are completely absent from the spectra of $Cp_2Ti(BF_4)_2$ and $Cp_2Ti(PF_6)_2$ and no new bands down to 300 cm^{-1} are observed. The disappearance of the Ti–F bands in both $Cp_2Ti(BF_4)_2$ and $Cp_2Ti(PF_6)_2$ seems to argue convincingly that both titanium–fluorine terminal bonds are not present. This does not rule out the possibility that titanium–fluorine–boron (phosphorus) bridge bonds are present.

While no bands due to BF_3 and PF_5 were observed,[9] the bands due to BF_4 and PF_6 were not split as might be expected if the high symmetry of these counter-ions was reduced due to coordination.[10] However, since the spectra were run on oils small splittings might not have been resolved.

The ^1H nmr spectrum of Cp_2TiF_2 consists of a triplet in the Cp region.[2,11] The coupling to the fluorine nuclei is about 2 Hz. When the spectrum is run in $BF_3[O(C_2H_5)_2]_2$, however, this coupling is lost and a single sharp line is observed. The same singlet is observed when Cp_2TiF_2 is treated with stoichiometric amounts of BF_3 and PF_5 in liquid SO_2. Cp_2TiF_2 in liquid SO_2 still shows a triplet pattern. It is of interest to note that removal of the coupling occurs for the samples with one quivalent of BF_3 and PF_5 as well as those containing two and four equivalents. The ^{19}F nmr spectrum of Cp_2TiF_2 is a complex multiplet due to coupling with the ten cyclopentadienyl protons. In $BF_3[(OC_2H_5)_2]_2$ this resonance is not observed and only a broad band due to $BF_3[O(C_2H_5)_2]_2$ is recorded. The resonance due to the fluorine atoms of Cp_2TiF_2 is observed in liquid SO_2. But in the presence of one, two or four equivalents of BF_3 or PF_5 in liquid SO_2 this resonance is not found. Only resonances assigned to BF_3 or PF_5 are observed.

One equivalent of BF_3 or PF_5 relaxes the coupling from both fluorine atoms to the Cp protons. At room temperature then the complexes $Cp_2TiF(BF_4)$ and $Cp_2TiF(PF_6)$ must undergo catalyzed fluorine exchange. The spectra of the samples containing four equivalents (excess) of BF_3 and PF_5 show only one band due to BF_3 and PF_5 respectively. The BF_4 and PF_6 groups in the complexes $Cp_2Ti(BF_4)_2$ and $Cp_2Ti(PF_6)_2$ must rapidly (with respect to the nmr time scale) exchange with free BF_3 and PF_5 in solution.[12]

How does the above data relate to the reactions and structures of the Cp_2TiF_2–BF_3 (and PF_5) systems? It seems reasonable that the red oils resulting from the reactions of Cp_2TiCl_2 with $AgBF_4$ and $AgPF_6$ are the same as those resulting from the reaction of Cp_2TiF_2 with BF_3 and PF_5 respectively. Their infrared spectra are the same (respectively) and they all form Cp_2TiF_2 when treated with methanol. The data suggest the existence of the equilibria shown above. In CH_2Cl_2 and liquid SO_2 these equilibria lie well to the right while in methanol they lie to the left. The interactions of Cp_2TiF_2 with BF_3 and PF_5 are analogous to those between MF_5 and SbF_5[13] (M = Nb and Ta) and between $(CH_3)_{3-n}$-SiF_n(n = 1,2) and SbF_5[14]. Similar interactions probably occur between Cp_2TiF_2 and TiF_4 and $SnCl_4$[15]. Transition metal halides have been shown to possess Lewis base qualities[16] where it has been assumed that the metal–halide bond is not broken in the complexes formed. We conclude the following about the structures of the complexes $Cp_2Ti(BF_4)_2$ and $Cp_2Ti(PF_6)_2$:

1) Simple Ti–F terminal bonds are not present. It is reasonable to assume however that the titanium atom is in close association with fluorine atoms since these complexes decompose to give Cp_2TiF_2 so easily.

2) The complexes do not exist as ionizable salts in CH_2Cl_2 [i.e. (Cp_2Ti^{2+})-$(BF_4^-)_2$ and $(Cp_2Ti^{2+})(PF_6^-)_2$]. This follows from the conductance measurements.

3) The distinction therefore needs to be made between the behavior of Cp_2TiF_2 as a Lewis base with the coordination of two BF_3 or PF_5 groups, and the behavior of Cp_2Ti^{2+} as an acid with coordination of two BF_4^- or PF_6^- groups. Our infrared data do not support coordinated counterions since splitting of degenerate vibration was not observed (this does not rule out such coordination however). On the other

hand the nmr and infrared data suggests that the Cp_2TiF_2 species does not maintain its integrity. The original fluorine atoms on titanium exchange with the fluorine atoms on boron and phosphorus. It is probable that the truth lies somewhere between the two extremes and the problem of describing the structures is the same as has been found in discussing those of similar derivatives of main group organometallic cations (i.e. one of semantics).[17]

ACKNOWLEDGEMENTS

The financial assistance of the National Research Council of Canada is gratefully acknowledged and also the award of a National Research Council of Canada post-Doctoral Fellowship to A.S. We thank Professor P. A. W. Dean for his interest and helpful discussions, and Mrs. Heather Schroeder for obtaining the nmr spectra.

REFERENCES

1. M. H. Chisholm and H. C. Clark, *Accounts Chem. Res.*, 6, 202 (1973).
2. R. B. King and N. Welcman, *Inorg. Chem.*, 8, 2540 (1969).
3. G. Doyle and R. S. Tobias, *Inorg. Chem.*, 6, 1111 (1967).
4. D. A. White, *J. Inorg. Nucl. Chem.*, 33, 691 (1971).
5. T. R. Musgrave and T. S. Lin, *J. Coord. Chem.*, **2**, 323 (1973).
6. H. C. Clark and R. G. Goel, *J. Organometal. Chem.*, 7, 263 (1967).
7. P. Uguagliati, G. Deganello, L. Busetto, U. Belluco, *Inorg. Chem.*, 8, 1625 (1969).
8. P. M. Druce, B. M. Kingston, M. F. Lappert, R. C. Srivastava, M. J. Frazer and W. E. Newton, *J. Chem. Soc.*, A, 2814 (1969).
9. K. Nakamoto *Infrared spectra of Inorganic and Coordination compounds*, 2nd ed. New York, Wiley-Interscience (1970).

10.a) S. Buffagni, L. M. Vallarino and J. V. Quagliano *Inorg. Chem.*, 3, 671 (1964).
  b) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 1020 (1963).

11. A. N. Nesmeyanov, O. V. Nogina, E. I. Fedin, V. A. Dubovitskii, B. A. Kvasov and P. V. Petrovskii, *Dokl. Adad. Nauk. S.S.S.R.*, **205**, 857 (1972).
12. S. Brownstein, *Can. J. Chem.*, **47**, 605 (1969).
13. P. A. W. Dean and R. J. Gillespie, *Can. J. Chem.*, **49**, 1736 (1971).
14. G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 4942 (1971).
15. P. A. W. Dean and A. Shaver, unpublished observations.

16.a) M. Pankowski, B. Demerseman, G. Bouquet and M. Bigorgne, *J. Organometal. Chem.*, **35**, 155 (1972).
  b) T. J. Marks, J. Kristoff, A. Alich, D. F. Shriver, *J. Organometal. Chem.*, **33**, C35 (1971).

17. H. C. Clark in *New Pathways in Inorganic Chemistry*, E. A. V. Ebsworth, A. G. Maddock, A. G. Sharpe (eds.). Cambridge University Press, 1968.