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CYCLOOCTATETRAENECYCLOPENTADIENYLTITANIUM IODIDES

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Summary

The synthesis and some of the properties of the new complexes $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)TiI$ and $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)TiI_3$ are described.

Müller [1] has described the cycloheptatrienylcyclopentadienylvanadium cation, $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)V^+$. This ion is assumed to be present in the compound $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)VI_3$. The monoiodide, $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)VI$ could not be isolated.

We have investigated the reaction (in ether solution) of iodine with $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti$ [2], which is isoelectronic with $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)V$ [3]. (In both complexes the metal atom achieves a 17-electron configuration.) This reaction resulted in the isolation of either the monoiodide, $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)TiI$, or the triiodide, $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)TiI_3$, depending on the relative proportions of the reactants.

The complexes are thermally stable and not sensitive to air; in water, however, rapid decomposition occurs. On treatment of the monoiodide with KCNS or C_6H_5Li the original complex $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti$ was reformed. No reaction was observed with $NaClO_4$ or $NaBF_4$.

The IR spectra of the complexes (Fig. 1) indicate that a $h^8\text{-}C_8H_8$ and a $h^5\text{-}C_5H_5$ ligand are present in the molecules. The presence of these ligands is supported by mass spectroscopy. In the mass spectra (200°C) no peaks corresponding to the parent ions, $C_{13}H_{13}TiI^+$ and $C_{13}H_{13}TiI_3^+$, were observed, nor were peaks of iodine-containing organic ions. The spectra were superpositions of the spectra of $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti$ and $(h^5\text{-}C_5H_5)TiI_3$. The latter may arise from the original compounds by thermal decomposition in the mass spectrometer (at lower temperatures only the triiodide gave a spectrum; this spectrum, however, was mainly that of iodine). The absence of iodine-containing organic ions indicates that in the complexes iodine is not bound to the cyclic ligands.

In view of the foregoing we assume that the compounds are made up of ions $[(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti^+, I^-$ or $I_3^-]$, similar to the complex $(h^7\text{-}C_7H_7)(h^5\text{-}C_5H_5)V^+I_3^-$.

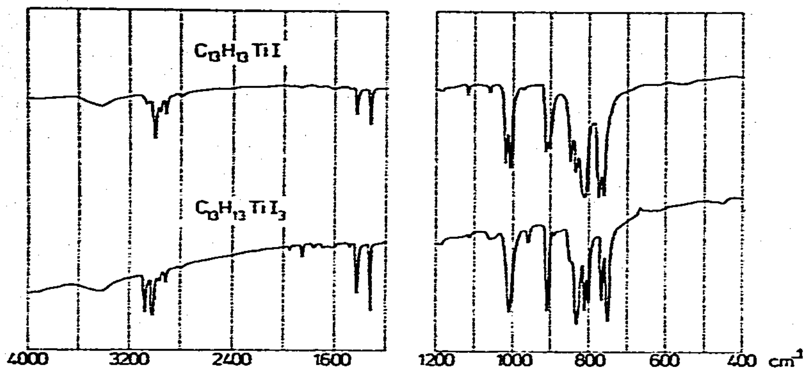

Fig. 1. IR spectra of $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)TiI$ and $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)TiI_3$ in KBr.

This could not be established definitely since no suitable solvent could be found for performing NMR spectra or conductivity studies.

Experimental

To a well-stirred suspension of $(h^8\text{-}C_8H_8)(h^5\text{-}C_5H_5)Ti$ (2.17 g, 10 mmol) in 100 ml of ether, 5, 10 or 15 mmol of iodine in ether were added dropwise. After stirring for two hours the supernatant liquid was removed by filtration. The residue was washed thoroughly with pentane and dried under reduced pressure. Starting from 5 mmol of I_2, yellow $C_{13}H_{13}TiI$ was formed; use of 15 mmol of I_2 gave the brownish-yellow compound $C_{13}H_{13}TiI_3$, and use of 10 mmol of I_2 gave a 1/1 mixture of the two compounds. The yields were 100%. ($C_{13}H_{13}TiI$: found, C, 45.48, 45.38; H, 3.89, 3.92; Ti, 13.92, 13.82; I, 36.85, 36.83; calcd.: C, 45.38; H, 3.81; Ti, 13.92; I, 36.88%. $C_{13}H_{13}TiI_3$: found, C, 26.17, 25.94; H, 2.16, 2.33; Ti, 8.03, 7.97; I, 63.07, 62.77; calcd.: C, 26.12; H, 2.19; Ti, 8.01; I, 63.68%.)

Acknowledgements

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References

1 J. Müller, P. Göser and P. Laubereau, J. Organometal. Chem., 14 (1968) P7.
2 H.O. van Oven and H.J. de Liefde Meijer, J. Organometal. Chem., 19 (1969) 373.
3 R.B. King and F.G.A. Stone, J. Amer. Chem. Soc., 81 (1959) 5263.