

## Tris(triazenido)thallium(III) Compounds

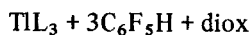
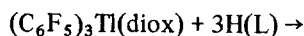
D. St. C. BLACK, V. C. DAVIS, G. B. DEACON and R. J. SCHULTZE

Chemistry Department, Monash University, Clayton, Vic. 3168, Australia

Received July 9, 1979

Recent failures to prepare tris(1,3-diorganotriazenido)thallium(III) complexes,  $\text{Tl}(\text{RN}_3\text{R}')_3$  ( $\text{R} = p\text{-MeC}_6\text{H}_4$ ;  $\text{R}' = p\text{-MeC}_6\text{H}_4$  or  $\text{Me}$ ) by reaction of thallic chloride with silver triazenes and by other methods was attributed to decomposition of the triazenido groups [1]. We now report the successful preparation of two stable tris(1,3-diorganotriazenido)thallium(III) complexes by a method which utilizes the powerful deprotonating ability of 1,4-dioxantris(pentafluorophenyl)thallium(III) [2].

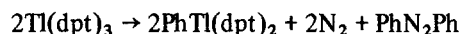
Reaction of  $(\text{C}_6\text{F}_5)_3\text{Tl}(\text{diox})$  ( $\text{diox} = 1,4\text{-dioxan}$ ) with 1,3-diphenyltriazene ( $\text{Hdpt}$ ) or 1-phenyl-3-(2'-pyridyl)triazene ( $\text{Hppt}$ ) in refluxing benzene under nitrogen resulted in elimination of pentafluorobenzene and formation of the corresponding tris(triazenido)thallium(III) derivative,  $\text{TlL}_3$  ( $\text{L} = \text{dpt}$  or  $\text{ppt}$ ).



Evaporation to low volume, addition of petrol, and slow crystallization gave analytically pure  $\text{Tl}(\text{dpt})_3$ , 57%, m.p. 157–158 °C, and  $\text{Tl}(\text{ppt})_3$ , 63%, m.p. 185–187 °C.

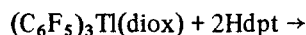
The infrared spectra of  $\text{Tl}(\text{dpt})_3$  and  $\text{Tl}(\text{ppt})_3$  show intense broad absorptions at 1343 and 1351  $\text{cm}^{-1}$  respectively, which are attributable to  $\nu_{\text{as}}(\text{NNN})$  of the coordinated triazenido ligands (cf. 1416  $\text{cm}^{-1}$  [3] and 1414  $\text{cm}^{-1}$  for  $\nu(\text{N}=\text{N})$  of the respective triazenes). In  $\text{Co}(\text{dpt})_3$ , which has six-coordinate cobalt and chelating triazenido groups [4],  $\nu_{\text{as}}(\text{NNN})$  gives a similar broad intense band at 1290  $\text{cm}^{-1}$  (this work). Both complexes are monomeric in benzene, consistent with bidentate triazenido ligands and six-coordinate thallium. Complex formation by the triazenes is accompanied by a ca. 20 nm shift of the near ultraviolet/visible maximum to longer wavelengths, attributable to the change from an  $\text{N}=\text{N}$  chromophore to the more extended  $\text{N}=\text{N}-\text{N}$  system.

The mass spectrum of  $\text{Tl}(\text{dpt})_3$  surprisingly shows clusters attributable to  $\text{PhTl}(\text{dpt})_2^+$ ,  $\text{Ph}_2\text{Tl}(\text{dpt})^+$ ,  $\text{PhTl}(\text{dpt})^+$  and  $\text{Ph}_2\text{Tl}^+$ , besides the more expected  $\text{Tl}(\text{dpt})^+$ . Formation of the first two can arise from thermal or electron impact induced rearrangements, e.g.



Similar features were not observed for  $\text{Tl}(\text{ppt})_3$ .

Reaction of  $(\text{C}_6\text{F}_5)_3\text{Tl}(\text{diox})$  with 1,3-diphenyltriazene in hot (not refluxing) benzene resulted in cleavage of two  $\text{C}_6\text{F}_5$  groups.



Addition of petrol and crystallization gave analytically pure  $\text{C}_6\text{F}_5\text{Tl}(\text{dpt})_2$ , 10%, m.p. 134 °C. The compound is monomeric in benzene and shows infrared and electronic spectral features similar to those of  $\text{Tl}(\text{dpt})_3$ , consistent with chelating 1,3-diphenyltriazenido groups and five-coordinate thallium. Two  $\text{C}_6\text{F}_5\text{Tl}$  groups, differing only very slightly in chemical shifts and coupling constants, were observed in the  $^{19}\text{F}$  n.m.r. spectrum. Possibly the complex has trigonal bipyramidal stereochemistry, and, in solution, exists in forms with the  $\text{C}_6\text{F}_5$  group both axial and equatorial, the rate of exchange being slow. The similarity of the coupling constants for the two groups rules out any equilibrium involving mono-(pentafluorophenyl)- and bis(pentafluorophenyl)-thallium(III) species [5].

## Acknowledgements

We are grateful to the Australian Research Grants Committee for support, and to Dr. B. F. Hoskins, University of Melbourne for a sample of  $\text{Co}(\text{dpt})_3$ .

## References

- 1 P. I. Van Vliet and K. Vrieze, *J. Organomet. Chem.*, **139**, 337 (1977).
- 2 G. B. Deacon, S. J. Faulks, B. M. Gatehouse and A. J. Jozsa, *Inorg. Chim. Acta*, **21**, L1 (1977).
- 3 R. Kübler, W. Lüttke and S. Weckherlin, *Z. Elektrochem. (Ber. Bunsenges. Phys. Chem.)*, **64**, 650 (1960).
- 4 M. Corbett and B. F. Hoskins, *Aust. J. Chem.*, **27**, 665 (1974).
- 5 G. B. Deacon, R. M. Slade and D. G. Vince, *J. Fluorine Chem.*, **11**, 37 (1978); G. B. Deacon and D. Tunaley, *Aust. J. Chem.*, **32**, 737 (1979).