Inorganica Chimica Acta, 37 (1979) L528
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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

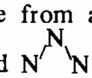
Received July 9, 1979

Recent failures to prepare tris(1,3-diorganotriazenido)thallium(III) complexes, $Tl(RN_3R')_3$ (R = p-MeC_6H_4; R' = p-MeC_6H_4 or Me) by reaction of thallic chloride with silver triazenides 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 $(C_6F_5)_3Tl(diox)$ (diox = 1,4-dioxan) with 1,3-diphenyltriazene (Hdpt) or 1-phenyl-3-(2'-pyridyl)triazene (Hppt) in refluxing benzene under nitrogen resulted in elimination of pentafluorobenzene and formation of the corresponding tris(triazenido)thallium(III) derivative, TlL_3 (L = dpt or ppt).

$$(C_6F_5)_3Tl(diox) + 3H(L) \rightarrow TlL_3 + 3C_6F_5H + diox$$

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

The infrared spectra of $Tl(dpt)_3$ and $Tl(ppt)_3$ show intense broad absorptions at 1343 and 1351 cm^{-1} respectively, which are attributable to $\nu_{as}(NNN)$ of the coordinated triazenide ligands (*cf.* 1416 cm^{-1} [3] and 1414 cm^{-1} for $\nu(N{=}N)$ of the respective triazenes). In $Co(dpt)_3$, which has six-coordinate cobalt and chelating triazenido groups [4], $\nu_{as}(NNN)$ gives a similar broad intense band at 1290 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 N=N chromophore to the more extended  $\overset{N}{N\quad N}$ system.

The mass spectrum of $Tl(dpt)_3$ surprisingly shows clusters attributable to $PhTl(dpt)_2^+$, $Ph_2Tl(dpt)^+$, $PhTl(dpt)^+$ and Ph_2Tl^+, besides the more expected $Tl(dpt)^+$. Formation of the first two can arise from thermal or electron impact induced rearrangements, *e.g.*

$$2Tl(dpt)_3 \rightarrow 2PhTl(dpt)_2 + 2N_2 + PhN_2Ph$$

Similar features were not observed for $Tl(ppt)_3$.

Reaction of $(C_6F_5)_3Tl(diox)$ with 1,3-diphenyltriazene in hot (not refluxing) benzene resulted in cleavage of two C_6F_5 groups.

$$(C_6F_5)_3Tl(diox) + 2Hdpt \rightarrow 2C_6F_5H + C_6F_5Tl(dpt)_2 + diox$$

Addition of petrol and crystallization gave analytically pure $C_6F_5Tl(dpt)_2$, 10%, m.p. 134 °C. The compound is monomeric in benzene and shows infrared and electronic spectral features similar to those of $Tl(dpt)_3$, consistent with chelating 1,3-diphenyltriazenido groups and five-coordinate thallium. Two C_6F_5Tl groups, differing only very slightly in chemical shifts and coupling constants, were observed in the ^{19}F n.m.r. spectrum. Possibly the complex has trigonal bipyramidal stereochemistry, and, in solution, exists in forms with the C_6F_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 $Co(dpt)_3$.

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