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Tris(triazenido)thallium(III) Compounds

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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 ν_{as}(NNN) of the coordinated triazenide ligands (*cf.* 1416 cm^{-1} [3] and 1414 cm^{-1} for ν(N=N) of the respective triazenes). In $Co(dpt)_3$, which has six-coordinate cobalt and chelating triazenido groups [4], ν_{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 N⟨N⟩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].

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