

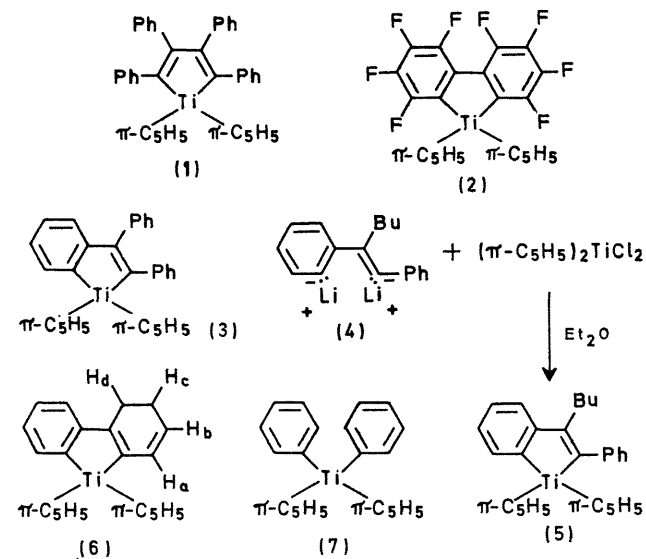
Preparation and Characterization of two new Titanium Metallo-cycles

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Summary The ^1H n.m.r. spectral properties and thermal stabilities of two new substituted titana-indene and titana-fluorene metallo-cycles are discussed.

THE structure of a titana-cyclopentadiene metallo-cycle (1)¹ and the preparation of titana-fluorene and titana-indene complexes (2)² and (3)³ have been reported. We now report the formation and characterization of two more titanium metallo-cycles.



Condensation of the n-butyl-lithium-tolane dilithium reagent (4)^{4,5} with titanocene dichloride in diethyl ether led to the formation in 16% yield of dark burgundy needles of titana-indene (5) (m.p. 143–146°, from pentane). Elemental analysis† and mass spectral data (M^+ , 412) confirmed the molecular formula, $\text{C}_{28}\text{H}_{28}\text{Ti}$.

The ^1H n.m.r. spectrum of (5)‡ had absorptions at τ 2.62–3.43 (aromatic, 8H, m), 3.77 (C_5H_5 , 10H, s), 4.02 (aromatic, 1H, d of t), 8.07, 8.73, and 9.22 (C_4H_9 , 9H, br t, br m, and apparent d, respectively). In this spectrum the unique aromatic proton (at τ 4.02) and the methylene group *alpha* to the metallo-cycle ring (at τ 8.07) are shifted upfield by +0.87 and +0.77 p.p.m., respectively, from their virtually constant positions in similar metallo-indene derivatives.⁴ This marked shielding probably arises from the localized anisotropic fields associated with the π -cyclopentadienyl rings of (5).

The reaction of 2,2'-dilithiobiphenyl⁶ with titanocene dichloride in diethyl ether afforded titana-fluorene (6) as bright red crystals (m.p. 143–144° from pentane) in 12% yield. The structural formulation for (6) is supported by elemental analysis and mass spectral data (M^+ , 330).

The ^1H n.m.r. spectrum of (6) shows a singlet (τ 3.76) for the two equivalent π -cyclopentadienyl rings and an ABCD pattern (first-order spin-spin interactions) for the aromatic protons. Resonances in the aromatic region of the spectrum were assigned as follows: τ 2.52 (H_a , 2H, d and t), 3.10 (H_b , 2H, triplet of doublets), 3.30 (H_c , 2H, triplet of doublets), and 4.12 (H_d , 2H, two t, $J_{ab} = J_{bc} = J_{cd} = 7.5$ Hz and $J_{ac} = J_{bd} = J_{ad} = 1.9$ Hz). The symmetry required by this splitting pattern supports the metallo-cyclic structural assignment for (6).§

Titana-fluorene (6), like its highly fluorinated analogue (2), is stable at ambient temperature even in the presence of air but bis-(π -cyclopentadienyl)bis-(σ -phenyl)titanium (7) must be stored at low temperature, preferably under nitrogen, to prevent decomposition.⁷ Such enhanced stabilities of metallo-cycles *vis à vis* their non-cyclic counterparts may be due to electronic factors associated with incorporation of the metal into an unsaturated ring system, or to the relative steric requirements of the metallo-cyclic ligand compared to two σ -aryl substituents. Studies to elucidate these factors are in progress.

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† Total elemental analyses were obtained on all new compounds.

‡ ^1H n.m.r. spectra were obtained in CDCl_3 solution using a Varian A-60 spectrometer (Me_4Si internal reference).

§ An A_2B_2 pattern would be expected for the aromatic protons if (6) had a (π -cyclobutadiene)titanium structure. For background on the structural controversy associated with complex (1), see refs. 1–4.

¹ M. E. Vol'pin, V. A. Dubovitskii, O. V. Nogina, and D. N. Kursanov, *Doklady Akad. Nauk S.S.S.R.*, 1963, **151**, 1100; *Chem. Abs.*, 1963, **59**, 14,012; G. W. Watt and F. O. Drummond, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 862; K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Japan*, 1966, **39**, 1178; F. W. Siegert and H. J. de Liefde Meijer, *Rec. Trav. chim.*, 1970, **89**, 764.

² S. C. Cohen and A. G. Massey, *J. Organometallic Chem.*, 1967, **10**, 471.

³ H. Masai, K. Sonogashira, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 750; J. Dvorak, R. J. O'Brien, and W. Santo, *Chem. Comm.*, 1970, 411.

⁴ M. D. Rausch and L. P. Klemann, *J. Amer. Chem. Soc.*, 1967, **89**, 5732.

⁵ J. E. Mulvaney and D. J. Newton, *J. Org. Chem.*, 1969, **34**, 1936.

⁶ H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.*, 1958, **80**, 1883.

⁷ L. Summers, R. H. Uloth, and A. Holmes, *J. Amer. Chem. Soc.*, 1955, **77**, 3604; M. D. Rausch and H. B. Gordon, unpublished results.