

SYNTHESIS OF NOVEL SUBSTITUTED CYCLOPENTADIENES AND THEIR EARLY TRANSITION METAL COMPLEXES

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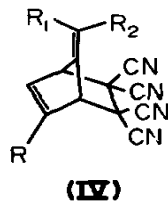
Abstract:

Synthesis of two substituted cyclopentadienes, 1,3-bis(1-methylcyclohexyl) cyclopentadiene, Cp'H and [2-methyl-2-(2-pyridyl)ethyl]cyclopentadiene, Cp''H from fulvene intermediates is reported. These are readily converted to their early transition metal complexes Cp'W(CO)₃Me, Cp''Mo(CO)₃Me, Cp''W(CO)₃Me and [Cp''Ti(O)Cl · CH₂Cl₂]₂. The X-ray crystal structure of the titanium compound shows that the nitrogen of the pyridine cyclopentadienyl substituent is coordinated to the titanium.

Article:

The search for synthetic routes to 1,3-cyclopentadienes with a variety of substitution patterns is an area of great current interest. We report here on the synthesis of some novel substituted 1,3-cyclopentadienes (as mixtures of double bond isomers) and their early transition metal complexes.

Regioselective routes to isomeric 1,3-dialkylcyclopentadienes are limited but we have recently developed high yield regioselective syntheses using fulvene intermediates.¹ For example, 1,3- bis(1-methylcyclohexyl)-cyclopentadiene (I, Cp'H) may be obtained via (1-methylcyclohexyl)-6,6-pentamethylenefulvene (III) (Fig. 1). The regio selectivity of the synthesis of III is confirmed by isolation of its Diels-Alder adduct with tetracyanoethylene, which yields only IV, which is identified by its ¹H NMR spectrum.



The cyclopentadiene, Cp'H, can readily be converted into its transition metal complexes, e.g. [Cp'W(CO)₃Me] (V) (Fig. 1). The solution IR spectrum of this compound is solvent dependent. In hexane, for example, it shows three stretches at 2010, 1925 and 1890 cm⁻¹ whereas in chloroform it shows four stretches at 2005, 1920, 1870 and 1820 cm⁻¹. This may be due to varying proportions of rotomers in different solvents, perhaps indicating that the steric bulk of the 1-methylcyclohexyl substituents causes an appreciable barrier to rotation. Similar effects have been observed with other cyclopentadienyl complexes.^{2,4} Further studies are underway.

1,3-Cyclopentadienes with substituents containing potential chelating donor atoms should provide organometallic complexes with interesting properties. As an example, [2-methyl-2-(2-pyridyl)ethyl]cyclopentadiene (VII, Cp''H) can be obtained in 52% yield from 6-methyl-6-(2-pyridyl)-fulvene (VI) eq. (1)



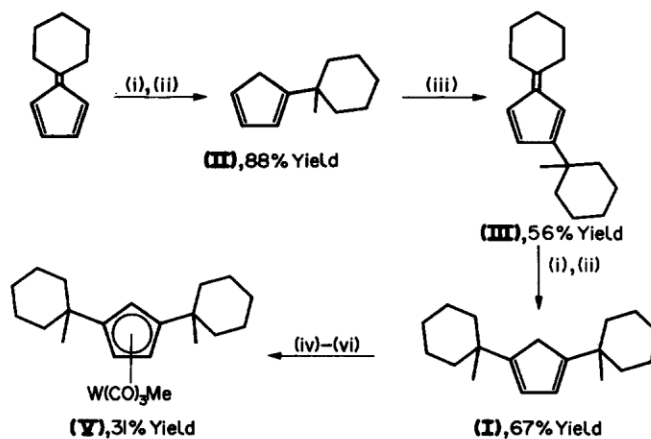


Fig. 1. Synthesis of [1,3-bis(1-methylcyclohexyl)ethylcyclohexyl]cyclopentadienyl]tricarbonylmethyltungsten (**V**). Reaction conditions (i) MeLi; (ii) H₂O, H⁺; (iii) cyclohexanone, pyrrolidine, methanol; (iv) BuLi; (v) (C₂H₅CN)₃W(CO)₃; (vi) MeI.

The cyclopentadiene, Cp''H, can be converted to the metal complexes [Cp''M(CO)₃Me] (**VIII**, M = Mo; **IX**, M = W). The carbonyl stretches of those complexes are similar to those of the unsubstituted cyclopentadienyl complexes [**VIII**, (CO) 2020, 1940 cm⁻¹ (hexane), **IX** (CO) 2020, 1920 cm⁻¹ (CHCl₃)], indicating no coordination of the nitrogen, as this would be expected to give stretches at lower wavenumbers. Neither thermolysis in refluxing octane or UV irradiation caused changes in the spectra that could be interpreted as chelation of the pyridine moiety or as insertion of carbon monoxide into the metal methyl bond.

However, chelation of the pyridine nitrogen did occur in the [2-methyl-2-(2-pyridyl)ethylcyclopentadienyl]-chlorotitanoxane dimer (**X**). This compound was prepared from the reaction between 1,1'-bis(2-methyl-2-(2-pyridyl)ethyl)magnesocene and titanium tetrachloride, followed by recrystallization with wet dichloromethane [eq. (2)].

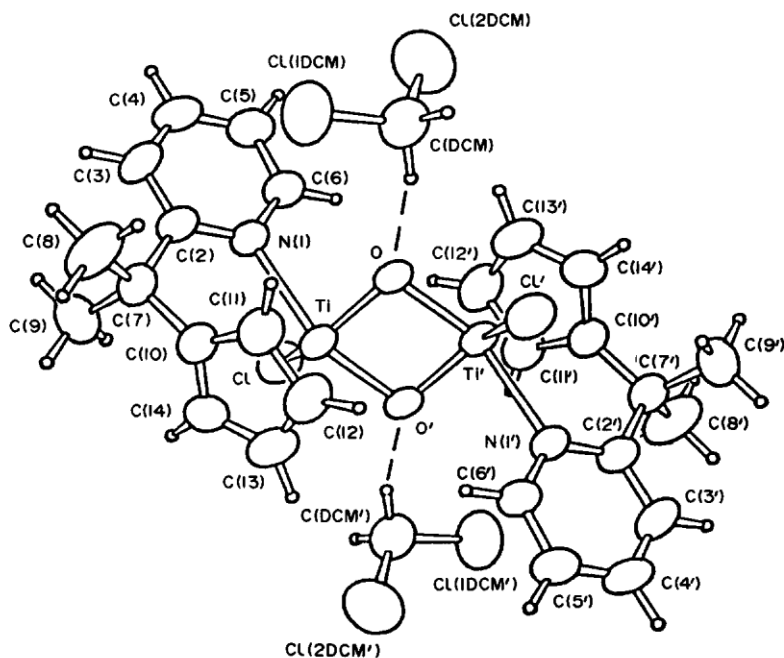
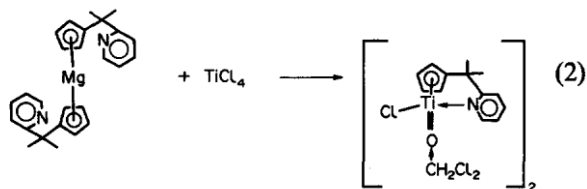


Fig. 2. Structure, solid-state conformation and atom-numbering scheme for **X**: small circles denote hydrogen atoms. Selected bond distances (Å): Ti—N, 2.297(3); Ti—O, 1.791(3); Ti—O', 1.910(2); Ti—Ti', 2.801(1).



The X-ray crystal structure confirmed X as the product. The crystal structure and ORTEP diagram are shown (Fig. 2).^{*} The titanium centre is coordinated to both the cyclopentadienyl ring, as well as the nitrogen atom, with a Ti—N bond distance of 2.297 Å.

Polytitanoxanes are known,⁵ however, this is the first example of a dimeric product. Previous complexes exist as trimers and tetramers. This change in structure is presumed to be due to the internal chelation of the nitrogen atom occupying the coordination site normally used in forming a Ti—O bond in trimeric and tetrameric complexes. The high oxidation state of titanium and electronegative oxygen atoms aid in the internal coordination of the nitrogen atoms in this complex.

Note:

*Crystal data of X : C₁₂H₁₁C1NOTi • CH₂Cl₂]₂, *M* = 737.10, triclinic space group *P* $\bar{1}$ (*C*_i¹, *a* = 10.188(3), *b* = 10.385(2), *c* = 8.410(3) Å, α = 101.78(2), β = 92.76(2), γ = 68.51(2)°, *V* = 810.16 Å³, *Z* = 1, *D*_{*c*} = 1.511 g cm⁻³, μ (Cu-*K* α) = 91.4 cm⁻¹, 2884 non-equivalent reflections, 2014 retained [*I* > 3.0 σ (*I*)], *R* = 0.046, *R*_w = 0.054. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

REFERENCES

1. T. J. Clark, MS thesis, University of North Carolina at Greensboro (1988).
2. R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta* 1973, 7, 153.
3. P. Hackett, P. S. O'Neill and A. R. Manning, *J. Chem. Soc., Dalton Trans.* 1974, 1625.
4. S. Luthra, MS thesis, University of North Carolina at Greensboro (1986).
5. P. C. Wailes, R. S. P. Coutts and H. Weigold, *Organometallic Chemistry of Titanium, Zirconium and Hafnium*, 1st edn, p. 43. Academic Press, New York (1974).