

1-METHYLALLYL(CYCLOOCTATETRAENE)TITANIUM

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SUMMARY

The complex 1-methylallyl(cyclooctatetraene)titanium has been prepared by the reaction of cyclooctatetraenetitanium chloride and 1-methylallylmagnesium bromide. The IR spectrum shows the vibrations of the h^8 -C₈H₈ ligand and of a π -bonded methylallyl group. The mass spectrum is also discussed.

π -Allyl complexes of titanium, $(h^5-C_5H_5)_2TiR$, in which R = h^3 -allyl or substituted allyl, have been reported by Martin *et al.*¹. In the course of our investigations on cyclooctatetraene complexes of titanium the compound 1-methylallyl(cyclooctatetraene)titanium, $(h^3-C_3H_4CH_3)Ti(h^8-C_8H_8)$, was isolated. The complex, obtained by reaction of $[h^8-C_8H_8TiCl]_2$ ² with 1-methylallylmagnesium bromide, CH₃C₃H₄MgBr, is sensitive to air and moisture. Differential thermal analysis (heating rate 2.5°/min) shows the compound to decompose at about 110°. The paramagnetic complex is soluble in common organic solvents.

The infrared spectrum of the compound indicates that the C₈H₈ ligand is symmetrically bonded to the metal atom, the normal vibrations of an h^8 -C₈H₈ group appearing in the usual ranges. Evidence for π -bonding of the 1-methylallyl group is found in the absorption band at 1500 cm⁻¹ (compare¹ $(h^5-C_5H_5)_2Ti(h^3-C_3H_4CH_3)$: 1533 cm⁻¹). The following features were observed in the mass spectrum of the compound: the parent ion, C₈H₈TiC₄H₇⁺ ($m/e=207$, $I=100$) breaks down by elimination of C₂H₄ giving the ion C₈H₈TiC₂H₃⁺ ($m/e=179$, $I=12$). Degradation of this ion occurs via two pathways. In the first route C₂H₃ is lost giving the ion C₈H₈Ti⁺ ($m/e=152$, $I=95$), which in turn loses C₂H₂ to give the ion C₆H₆Ti⁺ ($m/e=126$, $I=36$). In the second pathway the ion C₈H₈TiC₂H₃⁺ loses C₂H₂ giving the ion C₆H₆TiC₂H₃⁺ ($m/e=153$, $I=95$) which in turn loses C₂H₃ to give the ion C₆H₆Ti⁺ again. This fragmentation is in agreement with the degradation of other titanium complexes containing an h^8 -C₈H₈ or an h^3 -1-methylallyl group, for instance $(h^8-C_8H_8)Ti(h^5-C_5H_5)$ ³, $[h^8-C_8H_8TiCl]_2$ ⁴ and $(h^5-C_5H_5)_2Ti(h^3-C_3H_4CH_3)$ ⁴.

Other ions observed in the mass spectrum are:

C₅H₅Ti⁺ ($m/e=113$, $I=46$), C₄H₃Ti⁺ ($m/e=99$, $I=14$)

C₄H₂Ti⁺ ($m/e=98$, $I=15$), C₃H₃Ti⁺ ($m/e=87$, $I=19$)

C₃H₂Ti⁺ ($m/e=86$, $I=8$), C₃H Ti⁺ ($m/e=85$, $I=8$)

C₂H₃Ti⁺ ($m/e=75$, $I=9$), C₂H₂Ti⁺ ($m/e=74$, $I=17$)

C₂H Ti⁺ ($m/e=73$, $I=30$), Ti⁺ ($m/e=48$, $I=45$)

and purely organic ions with rather high intensities.

EXPERIMENTAL

To a cooled (-80°) suspension of $[\text{C}_8\text{H}_8\text{TiCl}]_2^*$ (1.41 g, 3.76 mmoles) in 125 ml of ether, 10.0 ml of a 0.75 M solution of $\text{CH}_3\text{C}_3\text{H}_4\text{MgBr}$ in ether were added in the course of 30 min. The reaction mixture was allowed to warm slowly to 0° . The original grass-green colour of the suspension gradually changed to brownish-green. After stirring for 4 h the solvent was removed under reduced pressure. Recrystallization from n-pentane gave brownish-green crystals of $(h^8\text{-C}_8\text{H}_8)\text{Ti}(h^3\text{-C}_3\text{H}_4\text{CH}_3)$; the yield was 0.78 g (3.76 mmoles, 50%). (Found: C, 69.70, 70.18; H, 7.65, 7.53; Ti, 22.71, 22.88. $\text{C}_{12}\text{H}_{15}\text{Ti}$ calcd.: C, 69.61; H, 7.30; Ti, 23.09%).

All experiments were carried out in an atmosphere of purified nitrogen and the temperature was kept below 0° . The mass spectrum of the complex was run on an AEI MS 9 mass spectrometer. No ions were observed at m/e values above that of the parent ion, $\text{C}_{12}\text{H}_{15}\text{Ti}^+$. The Ti-containing ions showed the normal isotopic distribution of Ti; only ions with ^{48}Ti are given. The intensities I are uncorrected.

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* This complex was prepared by reaction of TiCl_3 with one mole of $\text{K}_2\text{C}_8\text{H}_8$ in tetrahydrofuran⁴.