Inorganica Chimica Acta, 21 (1977) L6

π-Cyclopentadienyl(butadiene)iridium(I)

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(Received November 10, 1976)

The reactivity of some butadiene complexes of transition metals has been studied [1–4]. In this communication we report the synthesis and protonation studies of the π-cyclopentadienyl(butadiene) iridium(I) complex.

The title compound was synthesized by reaction of chlorobis(butadiene)iridium(I) with thallium(I) cyclopentadienide. The proton nmr spectrum of the compound was similar to that of other butadiene complexes and may be interpreted in terms of an $A_2B_2X_2$ system, showing resonances ($CDCl_3$) at τ 5.21, 7.41, 10.14(C_4H_6) and 4.80(π-C_5H_5).

The complex was protonated by addition of an equimolecular quantity of trifluoroacetic acid to a solution in $CDCl_3$. The proton nmr spectrum of the resulting species was comparable with the previously documented antimethallyl iron [3] and rhodium [4] cations, showing resonances at τ 4.47(s, π-C_5H_5), 4.75(m, H^2 + H^1_{outer}), 5.38(dm, H^3, J(H^3, CH_3 = 6Hz), 7.58(dd, H^1_{inner}, J(H^1_{inner}, H^2)= 10Hz, J_{gem} = 1Hz), 9.21(d, CH_3, J(CH_3, H^3) = 6Hz).

Addition of an equimolecular quantity of deuterated trifluoroacetic acid to the π-cyclopentadienyl(butadiene)iridium(I) complex produced a deuterium incorporated antimethallyl cation in which the relative intensities of the resonances attributed to H^1 and CH_3 remained constant (1:3), although their intensities had decreased in relation to the absorption of π-C_5H_5 at τ 4.74, according to the added deuterium.

These results may be interpreted postulating that protonation occurs initially at the metal to produce a metal protonated cation of very short life-time, and the proton is rapidly transferred to the terminal carbon atoms generating antimethallyl cations in equilibrium. This equilibrium is sufficiently rapid to average the added deuterium between the terminal carbon atoms although slow enough to allow resolution of the individual methallyl complexes. No changes are observed when the spectrum was recorded at low temperatures.

Experimental

A suspension of chlorobis(butadiene)iridium(I) [5] was shaken with an equimolecular quantity of thallium(I) cyclopentadienide for two hours. The suspension was filtered and the solvent was removed *in vacuo* from the filtrate. Chromatography of the crude product on alumina (TLC) with petroleum ether (40–60 °C) as eluent developed a colourless band of the product, which was purified by sublimation (60 °C, 0.5 mm Hg), to yield the pure product, π-cyclopentadienyl(butadiene)iridium(I) (m.p. 109 °C). *Anal.* Calcd for $C_9C_{11}Ir$: C, 34.73; H, 3.54. Found: C, 34.46; H, 3.66%. The mass spectrum showed the molecular peaks at m/e 312($C_9H_{11}Ir^{193}$) and 310($C_9H_{11}Ir^{191}$).

Proton nmr spectra were obtained by dissolution of the complex in $CDCl_3$ and addition of an equimolecular quantity of trifluoroacetic acid.

Acknowledgments

The author wishes to thank the Juan March Foundation for financial support and Prof. Dr. J. Lewis (University of Cambridge) in whose laboratory this work has been carried out.

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