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Search for ^{13}C equilibrium isotope effects in dicyclopentadienyltricarbonyldirhodium

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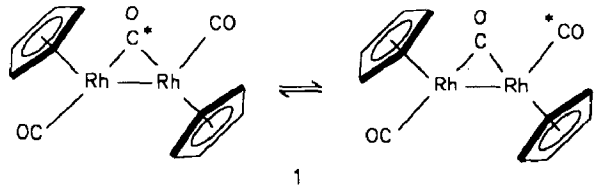
Abstract

The interchange of the carbonyl groups in dicyclopentadienyltricarbonyldirhodium $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ (**1**) has been investigated by the method of isotopic perturbation of equilibrium. Neither direct integration of the signals of terminal and bridged CO carbons in the ^{13}C NMR spectrum at 193 K nor measurement of the ^{13}C chemical shift of the averaged CO signal in the spectrum at 298 K at different grades of ^{13}CO enrichment indicated an isotopic perturbation. It is concluded that a ^{13}C equilibrium isotope effect for the carbonyl groups in **1** is either nonexistent, or is too small to be detected by the method employed.

Introduction

Isotopic perturbation of equilibrium is now an established method of investigating the bonding situation in fluxional compounds [1]. So far mainly the deuterium isotope has been used. For organometallic compounds, ^{13}C isotope effects involving the carbonyl groups could possibly widen the scope of the method and provide new information on the dynamic character of metal carbonyl bonds. Only a few systems with ^{13}C equilibrium isotope effects are known. For example, a primary ^{13}C equilibrium isotope effect has been observed in rearrangement of the 2,3-dimethyl-2-[2-^{13}C]butyl cation [2]. Booth and Everett [3] failed to detect a ^{13}C equilibrium isotope effect in [^{13}C-1-methyl]-*cis*-1,4-dimethylcyclohexane. They commented on the difficulty in measuring the small equilibrium isotope effects induced by ^{13}C substitution.

We have tried to detect a ^{13}C equilibrium isotope effect on the well known fast carbonyl exchange in dicyclopentadienyltricarbonyldirhodium (**1**).



1

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Complex **1** seemed to be a good candidate for such a study since it shows a fast exchange process of terminal and bridged carbonyl ligands. At 298 K the ^{13}C NMR spectrum in the carbonyl region shows only a sharp triplet, at 203.8 ppm with $^{1}J(C-Rh) = 43$ Hz, reflecting the rapid intermolecular site exchange between the carbonyl groups [4]. At 193 K the exchange is slow and separate resonances for terminal and bridged CO groups can be detected. A doublet appears at 193.1 ppm, with $^{1}J(C-Rh) = 83$ Hz, for the terminal CO groups, and a triplet at 231.8 ppm with $^{1}J(C-Rh) = 45$ Hz for the bridging CO group.

When ^{12}CO and ^{13}CO are allowed to equilibrate among two sites having different bonding situations, the heavier isotope tends to accumulate in the position with the "stiffer bond" [1]. A substitution with ^{13}CO should therefore lead to higher concentration of ^{13}CO in the terminal position in **1**. Qualitative theoretical calculations [5] predicted a change in the position of the degenerate equilibrium by about 1% after isotopic substitution with ^{13}C. With a chemical shift difference of 40 ppm between the terminal and bridged CO resonance a measurable isotope effect was expected.

Results

We tried to determine a ^{13}C equilibrium isotope effect in the ^{13}CO enriched complex **1** by two methods. First the integral ratio of terminal and bridged CO groups was investigated in the region of slow exchange on the NMR time scale. The integrals should differ from the statistical ratio, 2/1, if an equilibrium isotope effect exists.

The ^{13}C NMR spectra of 20–80% ^{13}CO enriched complexes were recorded at 193 K with long relaxation delays ($> 5 \cdot T_1$) by use of the inverse gated pulse sequence [6]. Relaxation measurements at room temperature for the averaged CO signal gave T_1 values of 15 ± 2 s.

Within the accuracy of the integral measurements the ratio of terminal and bridged carbonyl group was 2/1. Nevertheless some asymmetry was detected, slightly more ^{13}CO being present at the terminal position. No dependence on the level of ^{13}CO enrichment was determined. Moreover the integral ratio showed no significant temperature dependence in the range 193 to 203 K.

Since the integral measurement was inconclusive, we next examined the chemical shift of **1** in the region of fast exchange on the NMR time scale. If the ^{13}CO group prefers the terminal position the chemical shift of the averaged CO signal should be different from that for the unlabelled compound, since the chemical shift of the CO signal is given by the average of the shifts of the terminal and bridged carbonyl groups weighted for their concentrations. The presence of more ^{13}CO in the terminal position should therefore result in a downfield shift of the averaged CO signal.

To determine probable small chemical shift differences in samples with different ^{13}CO enrichments a special technique was used. The samples were put in concentric NMR tubes. Susceptibility effects were checked by interchanging the samples from the inner and outer tube. However, no shift difference in samples with different degrees of ^{13}CO enrichment could be detected.

Conclusions

Although theoretical prediction, based on the different binding sites for CO in **1** and on the large chemical shift difference is in favour of experimental detectibility of ^{13}C equilibrium isotope effects, we were not able to observe them. Research is in progress to apply this method for compounds which are even better suited for this purpose.

Experimental

The spectra were recorded on a Bruker AM-400 equipped with an Aspect 3000 computer. **1** was prepared by the published procedure [7]. Stirring of a CH_2Cl_2 solution of the complex for 5 up to 36 h under an excess of 99% ^{13}C-enriched carbon monoxide gave **1** with its carbonyl ligands 20 to 80% labelled.

Acknowledgements

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