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Fast olefin site interchange of cycloocta-1,5-diene in a Rh^{I} square planar derivative

E. Rotondo *, G. Battaglia, C.G. Arena and F. Faraone

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Salita Sperone, 31, Villaggio S. Agata, 98100 Messina (Italy)

Abstract

Rapid exchange between non-equivalent sites causes collapse of the olefinic double bonds resonances in the ^{1}H NMR spectrum of [Rh(COD)(Ph_2PPy)Cl] [COD = cycloocta-1,5-diene; (PPh_2Py) = 2-(diphenylphosphino)pyridine], **1**, below room temperature. A fast equilibrium between the square planar **1** and a pentacoordinated trigonal bipyramid TBP, formed by chelation of the pyridine nitrogen to the metal, accounts for the low activation energy of the process; Rh-cycloocta-1,5-diene pentacoordinates, in fact, are known to undergo readily a Berry pseudorotation that leads to interchange of axial and equatorial sites in the TBP. NMR data for the analogous square planar complex [Rh(COD)(PPh_3)Cl], **2**, show that in the absence of intramolecular pathways for pentacoordination the activation energy for the double bond interconversion is much higher.

Introduction

A number of asymmetric cyclic diolefin complexes of rhodium(I) and iridium(I) have temperature-dependent ^{1}H NMR spectra indicating exchange of olefinic protons between non-equivalent sites. The activation energy of the process depends on the configuration of the substrate; thus the interchange takes place intramolecularly below room temperature for many TBP pentacoordinates while high temperature and/or intermolecular exchange are required for square planar species. We present below NMR evidence for a surprisingly fast olefin site intramolecular exchange in the square planar complex [Rh(COD)(Ph_2PPy)Cl], **1**, a recently synthesized short-bite metal ligand whose reactivity has been throughly investigated in our laboratory [1]. The NMR data for **1** are compared with those for the structurally very similar Rh(COD)(PPh_3)Cl, **2**, in order to shed light on the scrambling process.

Results and discussion

In chloroform complex **1** is square planar. The absence of a permanent interaction between the nitrogen of Ph_2PPy and the metal in this substrate can be inferred from the 6-H frequency resonance of the pyridine ring (8.72 ppm). Coordination of the nitrogen causes a large shift of this resonance, which in the free Ph_2PPy appears

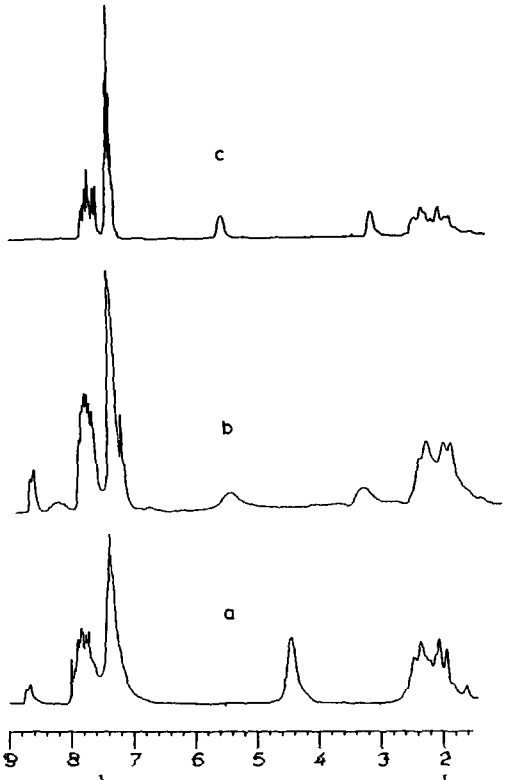
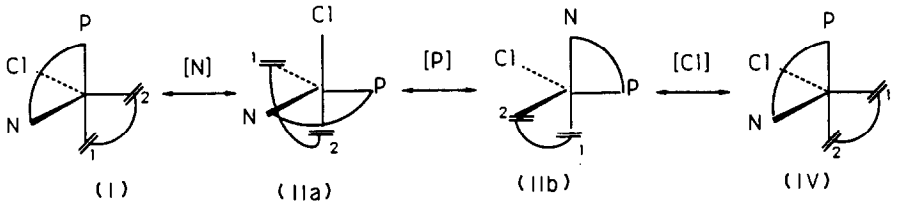


Fig. 1. (a) ^{1}H NMR spectrum of **1** at 303 K. (b) ^{1}H NMR spectrum of **1** at 240 K. (c) ^{1}H NMR spectrum of **2** at 303 K.

at 8.73 ppm, well separated from the signals from the remaining aromatic protons [1,2]. The square planar configuration of **1** is also supported by the similarity of the electronic spectra in the *d–d* transition region and by the $^{31}P\{^1H\}$ NMR spectra of the two complexes (*vide infra*).

The ^{1}H NMR spectrum of **1** at 303 K shows dynamic behaviour; thus the vinyl protons of COD appears as a single unresolved multiplet centred at 4.42 ppm (Fig. 1a). Complex **2**, under the same conditions, shows two well separated resonances at 5.58 and 3.14 ppm, attributable to the double bond protons *trans* to phosphine and chloride, respectively. The collapse of the vinylic protons in a single resonance must be related to some kind of rapid interconversion of the double bonds. The process can be frozen by lowering the temperature at 240 K when the non-equivalence of the double bond protons of **1** is clearly shown (Fig. 1b). In the case of **2**, the resonances from the vinyl protons broaden but are still separated at the boiling point of chloroform; coalescence is reached in toluene at 370 K.

In the $^{13}C\{^1H\}$ NMR spectrum of **1** the CH_2 carbons of cyclooctadiene give rise to a singlet at 31.1 ppm and the olefinic carbons to a broad signal centered at 88 ppm. Complex **2** shows two resonances for the CH_2 carbons at 29.2 and 33.3 ppm; the olefinic carbons *trans* to the chloride and phosphorus respectively give a doublet at 71.1 ppm (^1J(RhC) = 13.9 Hz) and a doublet of doublets at 105.4 ppm (^1J(RhC) = 12.3, ^2J(CP) = 7.0 Hz).

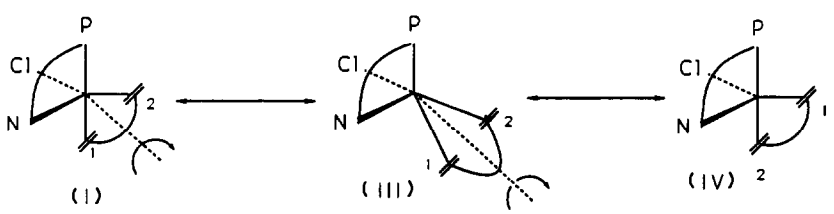


Scheme 1. $\widehat{P\,N}$ = 2-(diphenylphosphino)pyridine.

The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** are very similar; at room temperature they show a sharp doublet at 29.7 ppm (^1J(RhP) = 150.2 Hz) and 30.6 ppm (^1J(RhP) = 150.3 Hz), respectively. The chemical shifts are consistent with the absence of permanent nitrogen coordination in **1**; a large shift toward lower frequency would be expected for the resonance of a donor phosphorus in a four-membered ring [3].

The preservation of RhP couplings means that the fast scrambling of the olefin site in **1** cannot take place through dissociative or intermolecular mechanisms involving Rh–P bond breaking. Mechanisms involving displacement of the olefin by the pyridinic nitrogen would lead to the collapse of the *endo* and *exo* methylene protons resonances of the cyclooctadiene. It is noteworthy, that whereas the $^{13}C\{^1H\}$ NMR spectrum of **1** shows a single collapsed resonance for the CH_2 carbons of cyclooctadiene, the ^1H NMR spectrum shows two separate sets of resonances for the *endo* and *exo* methylene protons. The rapid interconversion of the double bonds can be accounted for in terms of a fast equilibrium between the square planar **1** and small amounts of a pentacoordinate TBP formed by chelation of the pyridine nitrogen. Pentacoordination should promote the scrambling of the non equivalent double bonds; it is well known that Rh-cyclooctadiene pentacoordinates readily undergo a Berry pseudorotation which results in interchange between axial and equatorial sites of the TBP. In our case the interchange can be accomplished by three reversibile and sequential pseudorotations with [N], [Cl], and [P] successively as pivots (Scheme 1).

An simpler alternative mechanism involves ligand interchange between two sites within the trigonal-bipyramidal structure, one axial and one equatorial, with the other ligands as spectators. The actual physical motion depicted is a twist of the diene about a pseudo-twofold axis perpendicular to the plane containing the double bonds (Scheme 2). The intervening structure III has been interpreted either as a transition state in which the relative dispositions of the remaining donor atoms P,N and Cl remains unchanged, or as an intermediate in which the ligands have relaxed somewhat to an approximately square pyramidal geometry [4].



Scheme 2. $\widehat{P\,N}$ = 2-(diphenylphosphino)pyridine.

The latter mechanism, with III as an intermediate, is more appropriate in the present case; a key role in the process must be played by the geometrical constraints induced by the coordination of the pyridine nitrogen atom with conseguent formation of a fourmembered chelate ring. The small P–Rh–N angle [70.4° in an analogous complex of 2-(diphenylphosphino)pyridine chelating Rh^{I} [5]] favours TBP structures with the nitrogen (the entering ligand in the chelation process) equatorial and the phosphorus axial. Pseudorotation requires a TBP intermediate (IIa) with both phosphorus and nitrogen atoms of the chelated ligand equatorial; this configuration involves a spanning P–Rh–N angle of 120°, far removed from the ideal chelation geometry. Thus I is the most stable configuration for the TBP, and the relatively high energy barrier towards development of a different geometry in the pentacoordinated species makes twisting of the diene about the pseudo-twofold axis (Scheme 2) more likely than pseudorotation.

The absence of intramolecular pathways for pentacoordination in complex **2** accounts for the different rates of olefin site interchange in the two substrates.

Experimental

Unless otherwise specified the NMR spectra, were recorded in $CDCl_3$ at 303 K on a WP 80-SY Bruker spectrometer. TMS was used as internal reference for ^{1}H and ^{13}C and H_3PO_4 85% as the external reference for ^{31}P spectra.

Complexes **1** and **2** were prepared as previously described [1].

Acknowledgement

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