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CARBON-13 NMR STUDY OF AN INTERMEDIATE COMPLEX IN HYDROESTERIFICATION OF OLEFINS

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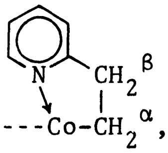
Reaction of a new hydroesterification catalyst $H_2Co_3Py_5(CO)_9$ with 2-vinylpyridine yielded an alkylcobalt complex  $\text{---Co-CH}_2^{\alpha}$ (with CH_2^{β}), which is considered to be an intermediate complex in the hydroesterification of 2-vinylpyridine. The ^{13}C-NMR parameters of the α- and β-methylene groups were δ=60.0 ppm (J_{C-H}=147 Hz) and 37.4 ppm (132 Hz), respectively.

Cobalt carbonyl catalyzed hydroesterification of olefins with carbon monoxide and an alcohol generally proceeds under milder conditions in the presence of pyridine.[1)] For example, hydroesterification of 1-decene proceeds under an extremely mild condition (80°C and P_{CO}=20 kg/cm^2) when $Co_2(CO)_8$ and pyridine are added in a molar ratio of 1:4 to the reaction mixture. A new type of cobalt carbonyl-pyridine complex catalyst was isolated from the cooled reaction product. Elemental analysis of the catalyst agreed with the chemical composition of $H_2Co_3Py_5(CO)_9$ (m.p. 41°C).[2)] This compound is also obtainable by the direct reaction of $Co_2(CO)_8$ with pyridine in *n*-pentane under a mixed gas pressure of 20-50 kg/cm^2 (CO/H_2=1-19) at 100°C for a few hours. Figure 1 is the IR spectrum of the catalyst, which shows the stretching vibrations of two kinds of carbonyl groups; i.e., 2010 and 1890 cm^{-1}.

The present investigation is aimed at the ^{13}C-NMR study of the intermediate complex produced by the stoichiometric reaction of $H_2Co_3Py_5(CO)_9$ with 2-vinylpyridine at room temperature. As a test olefin, was 2-vinylpyridine selected, since it easily dissolves the solid catalyst, and also the reaction between them takes place readily at room temperature.

All of the experimental steps were operated under argon. Freshly prepared orange-yellow crystals of $H_2Co_3Py_5(CO)_9$ and freshly distilled 2-vinylpyridine were mixed at a molar ratio of 1:1. The reddish brown solution thus obtained was subjected to the ^{13}C-NMR measurement using C_6D_6 as the internal standard (δ=128.0 ppm).[3)]

Figure 2 depicts the proton noise decoupled ^{13}C-NMR spectra of 2-vinylpyridine and of the reaction system (1:1) 2-vinylpyridine-$H_2Co_3Py_5(CO)_9$. As compared with the

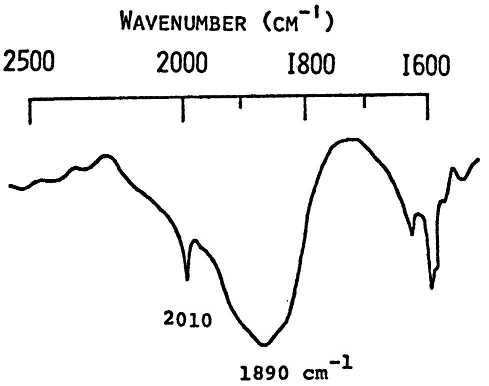
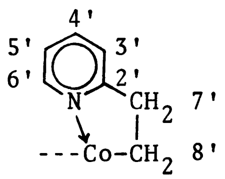
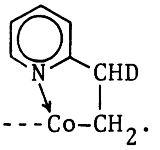


Fig. 1. IR spectrum of a new catalyst $H_2Co_3Py_5(CO)_9$, where Py is an abbreviation of C_5H_5N (pyridine).

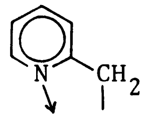
spectrum of 2-vinylpyridine, two pronounced new peaks (peak number 7' and 8') appeared in a higher magnetic field on the latter spectrum. Simultaneously, three peaks due to "free" pyridine (Py_α, Py_β and Py_γ) came out, which demonstrates that some of the coordinated pyridine molecules were released from the original complex upon reaction with 2-vinylpyridine. Figure 2(b') shows a part of the non-spin decoupled ^{13}C-NMR spectrum of the system (1:1) 2-vinylpyridine-$H_2Co_3Py_5(CO)_9$. It is clear that both peak 7' and 8' in Fig. 2(b) split into triplets as a result of the spin-spin coupling between ^{13}C and ^{1}H nuclei. This fact suggests that these two peaks are of methylene groups. Therefore, we supposed that this newly obtained complex should possess a five-membered ring structure:



The ^{13}C chemical shifts and ^{13}C-^{1}H coupling constants of the two methylene groups (7' and 8') were δ=37.4 ppm (J_{C-H}=132 Hz) and 60.0 ppm (147 Hz), respectively. The former is typical one of the methylene group of ordinary alkanes,[4] while the latter must be located at the α-position relative to the cobalt atom. Further, proton noise decoupled and non-spin decoupled ^{13}C-NMR spectra were measured of the system 2-vinylpyridine-$D_2Co_3(d_5\text{-}Py)_5(CO)_9$. As expected, those spectra were of the corresponding structure:



The following two experimental facts prove that this is not an acyl- but alkylcobalt complex; 1) the IR spectrum of the reaction mixture displayed no stretching vibration of acyl group in the region of 1700-1800 cm^{-1}. 2) The ester expected to be derived from an acylcobalt complex was not detected upon treating the reaction mixture with methanol in the absence of carbon monoxide.

All of the results obtained in this study ensured that a new "stable" alkylcobalt complex with the structure  is obtained from the system 2-vinylpyridine-$H_2Co_3Py_5(CO)_9$ at room temperature. The above results are also consistent with the results of the catalytic hydroesterification of 2-vinylpyridine, where methyl 3-(2-pyridyl)propionate is "selectively" produced.[5] An analogous "stable" five-membered chelate ring complex of cobalt, σ-bonded with carbon and coordinated by amine-nitro-

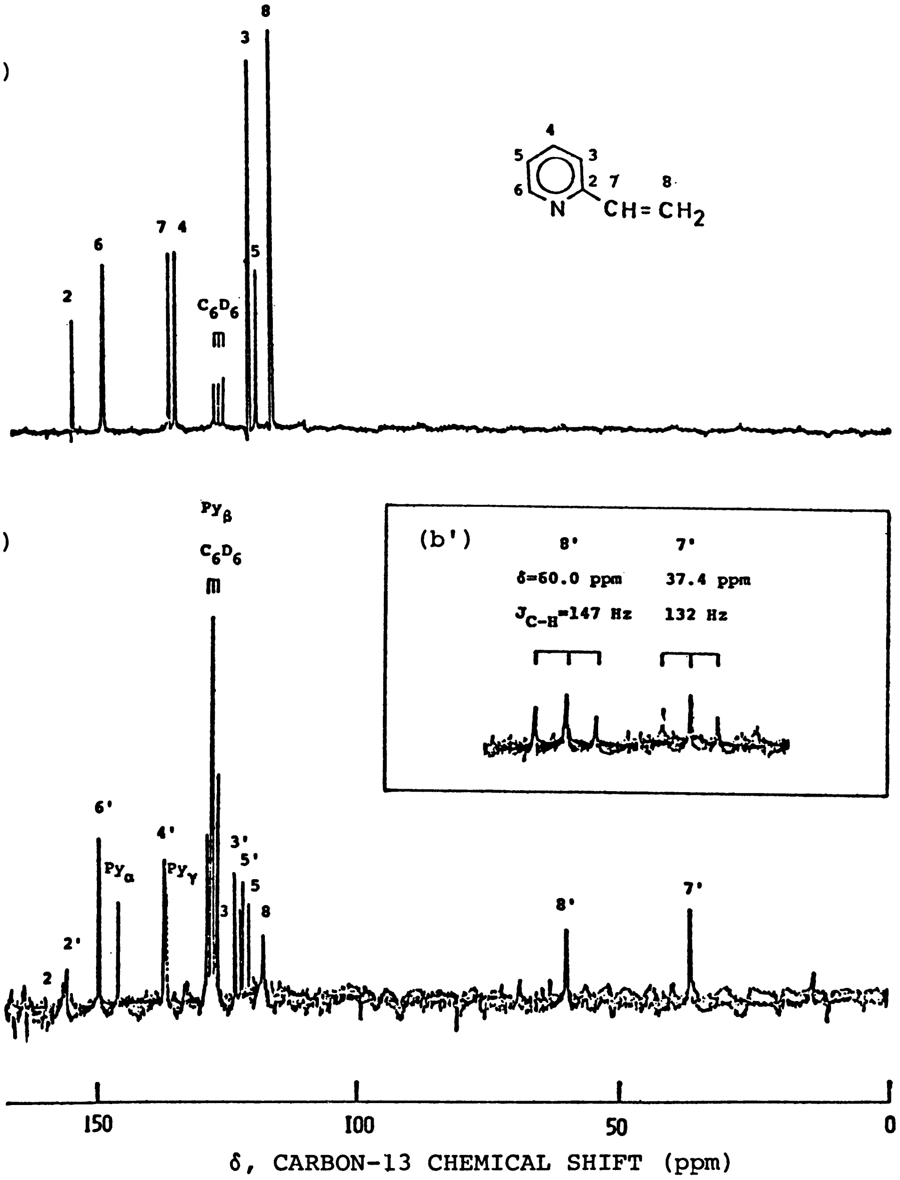
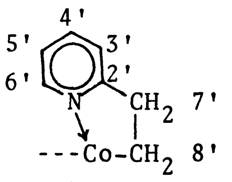
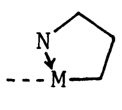


Fig. 2. Proton noise decoupled ^{13}C-NMR spectra of (a) 2-vinylpyridine and (b) (1:1) 2-vinylpyridine-$H_2Co_3Py_5(CO)_9$. The spectrum of (b') is the non-spin decoupled data of (b). The assignment of the new peaks in (b) and (b') is as follows:



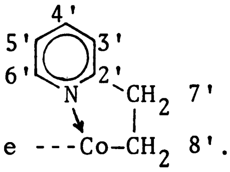
gen, has been reported.6) Furthermore, there are reports on the similar complexes of other metals, represented as:



(M = Cr, Mn, Fe, Pd and Pt).7)

Table 1 summarizes the ^{13}C chemical shift and ^{13}C-^{1}H coupling constant of each carbon atom of the alkylcobalt complex obtained in this study.

Table 1. Carbon-13 chemical shift (δ) and ^{13}C-^{1}H coupling constant (J_{C-H}) of an alkylcobalt complex with the structure ---Co-CH_2 8'.



Number of carbon atom	(ppm)	J_{C-H}(Hz)
2'	154.5	0
3'	123.4	162
4'	136.7	164
5'	122.1	165
6'	149.0	175
7'	37.4	132
8'	60.0	147

Acknowledgement

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