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Laboratories and Demonstrations

An Inorganic Experiment:

An Application of Second Order ^{31}P NMR Computer Simulation

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This experiment is designed for senior undergraduate and graduate students. They prepare a nickel organophosphorus ylide complex using the Schlenk technique and then investigate the effect of field strength and coupling constants on the second order ^{31}P NMR spectrum.

Organophosphine ligands… constitute one of the few series of ligands in which electronic and steric properties can be altered in a systematic and predictable way…

Introduction

Organophosphine ligands have a lone pair on the central atom that can be donated to a transition metal. Different types of phosphine ligands can form a variety of transition metal complexes. Organophosphine ligands are important because they constitute one of the few series of ligands in which electronic and steric properties can be altered in a systematic and predictable way over a wide range by varying organic R groups [1, 2]. Various effects

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of these ligands, such as electronic effects and angle effects on the ^{31}P NMR spectra, have been well studied [3].

The appearance of a second-order NMR spectrum is field dependent. When the magnitude of the separation between two peaks in the NMR, expressed in Hz, is of the same order of magnitude as the coupling constant, second-order spectra result. The use of computer simulation to analyze second-order NMR spectra has played an important role in scientific research [4–6]. Computational programs, such as LAOCOON [7, 8] and RACCOON [9], can be used to analyze experimental spectra that exhibit second-order effects. The chemical shifts and coupling constants of a complicated second-order NMR spectrum may not be readily available, but they can be determined by theoretically fitting the second-order spectrum until the calculated spectrum is identical to the experimental spectrum. The computer program we used for this experiment is LAOCOON PC, developed by J. S. Thrasher [7].

Experimental Section

Materials and Physical Measurements

Syntheses were carried out under a nitrogen atmosphere using the Schlenk technique or a glove box. Solvents (diethyl ether, toluene, tetrahydrofuran) were reagent grade and were distilled from the appropriate drying agents. All solvents were deoxygenated with nitrogen gas prior to use. The following chemicals: CH_2Br_2, $NaNH_2$ and bis(diphenylphosphino)methane (dppm), were used as received from Aldrich Chemical Company. $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) was purchased from Strem Chemicals and was used as received.

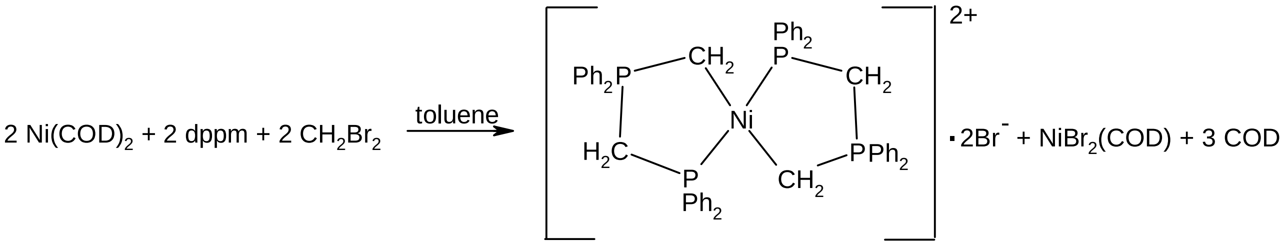
Bis(1,5-cyclooctadiene)nickel (0), dibromomethane, toluene (anhydrous), diethyl ether, and tetrahydrofuran

Hazard: All of these chemicals are highly flammable and harmful if inhaled. Handle them in the fume-hood. Wear gloves and avoid contact with eyes. $NaNH_2$ *is toxic and reacts violently with water. It may produce a highly explosive mixture when limited water absorption takes place. Disposal: bis(1,5-cyclooctadiene)nickel (0) should be properly disposed of in the solid waste. It will react with air to form nickel oxide. Dibromomethane and toluene (anhydrous), should be properly disposed of in the organic solvents waste. Burn in a chemical incinerator equipped with an afterburner and scrubber for final disposal.*

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian 200 and Gemini 200 spectrometers. ^1H NMR was measured against internal $(CH_3)_4Si$ and $^{31}P\{^1H\}$ chemical shifts were reported relative to 85% H_3PO_4.

Preparation of $[Ni(CH_2PPh_2CH_2PPh_2)_2]Br_2$ *and* $Ni(CH_2PPh_2CHPPh_2)_2$

The nickel phosphorus ylide complex, $Ni(CH_2PPh_2CHPPh_2)_2$ (Ph = C_6H_5), can be prepared by a two step procedure. The first step is to prepare $[Ni(CH_2PPh_2CH_2PPh_2)_2]Br_2$ (**1**). Complex **1** was prepared by addition of 2 equiv of dppm (0.279 g) to 2 equiv of $Ni(COD)_2$ (0.20 g) at -15 °C in toluene, followed by addition of 2 equiv of CH_2Br_2 (0.051 mL) by syringe. Some yellow precipitate was observed after the mixture was kept stirring for 20 min. The reaction mixture was stirred for another 20 min. The precipitate formed was then filtered, washed with diethyl ether, and dried under vacuum to obtain 0.360 g of **1** in yields approaching the theoretical limit of 50% based on $Ni(COD)_2$ (1 equiv of $Ni(COD)_2$ is oxidized by CH_2Br_2).



The $^{31}P\{^1H\}$ NMR spectrum of **1** in DMSO-d_6 consists of two triplets centered at 47.87 and 32.31 ppm with $J_{AB} \approx J_{AB}' = 56.5$ Hz. The ^1H NMR spectrum reveals both types of methylenes. The ylide protons are observed at $\delta = 1.38$ ppm (m, 4H), and the normal methylene protons appear as a pseudotriplet at $\delta = 4.40$ ppm (4H). The structure of **1** can be found in reference [4].

One methylene proton of each chelating ylide ligand of complex **1** can be reversibly deprotonated. To a THF solution of **1**, 2.5 equiv of $NaNH_2$ was added. The suspension was stirred at room temperature for 12 hr. The yellow solution (almost homogeneous) was filtered to obtain a small amount of white solid (NaBr). The filtrate was then dried under vacuum to obtain the neutral complex $Ni(CH_2PPh_2CHPPh_2)_2$ (**2)** in 85% yield [^1H NMR (CD_2Cl_2): $\delta = 0.85$ ppm (m, 2H), $\delta = 1.4$ ppm (t, 1H), 7.0–7.9 ppm (m, 20H)]. The $^{31}P\{^1H\}$ NMR spectra of **2** in THF-d_8 at 80.96 MHz and 36.43 MHz are shown in Figure 1.

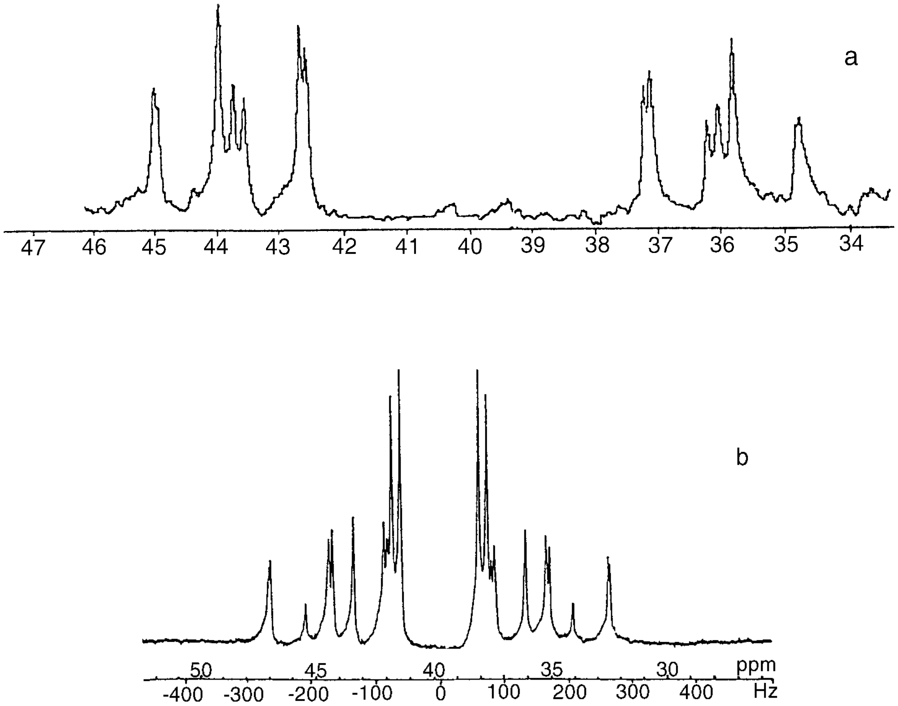
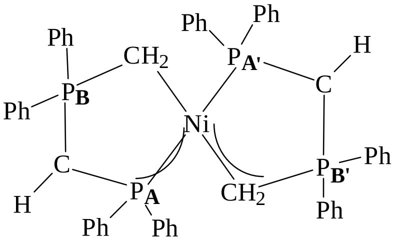


FIGURE 1. EXPERIMENTAL $^{31}P\{^{1}H\}$ NMR SPECTRA OF **2** AT (a) 80.96 MHz AND (b) 36.43 MHZ. (Figure 1b by permission of Angewandte Chemie International Edition and H. Schmidbaur.)

Complex **2** was first reported by Schmidbaur and coworkers by the addition of two equivalents of $Na[CH_2PPh_2CHPPh_2]$ to $NiCl_2(PMe_3)_2$. The detailed procedures can be found in the literature [5].

Computer Simulation

The software LAOCOON PC or RACCOON can be run on an IBM or IBM-compatible PC (XT or better). The program can run 2–7 nuclei with spin 1/2. The operating frequency is in MHz but the chemical shifts may be given in either ppm or Hz units. The coupling constants of the $^{31}P\{^{1}H\}$ NMR spectra of $Ni(CH_2PPh_2CHPPh_2)_2$ are $^{2}J_{P_AP_{A'}}$ = 271.7 Hz, $^{2}J_{P_AP_B} = {}^{2}J_{P_{A'}P_{B'}}$ = 155.9 Hz, $^{3}J_{P_AP_{B'}} = {}^{3}J_{P_{A'}P_B}$ = 34.7 Hz and $^{4}J_{P_BP_{B'}}$ = 0.2 Hz. The structure of complex **2** is shown below:



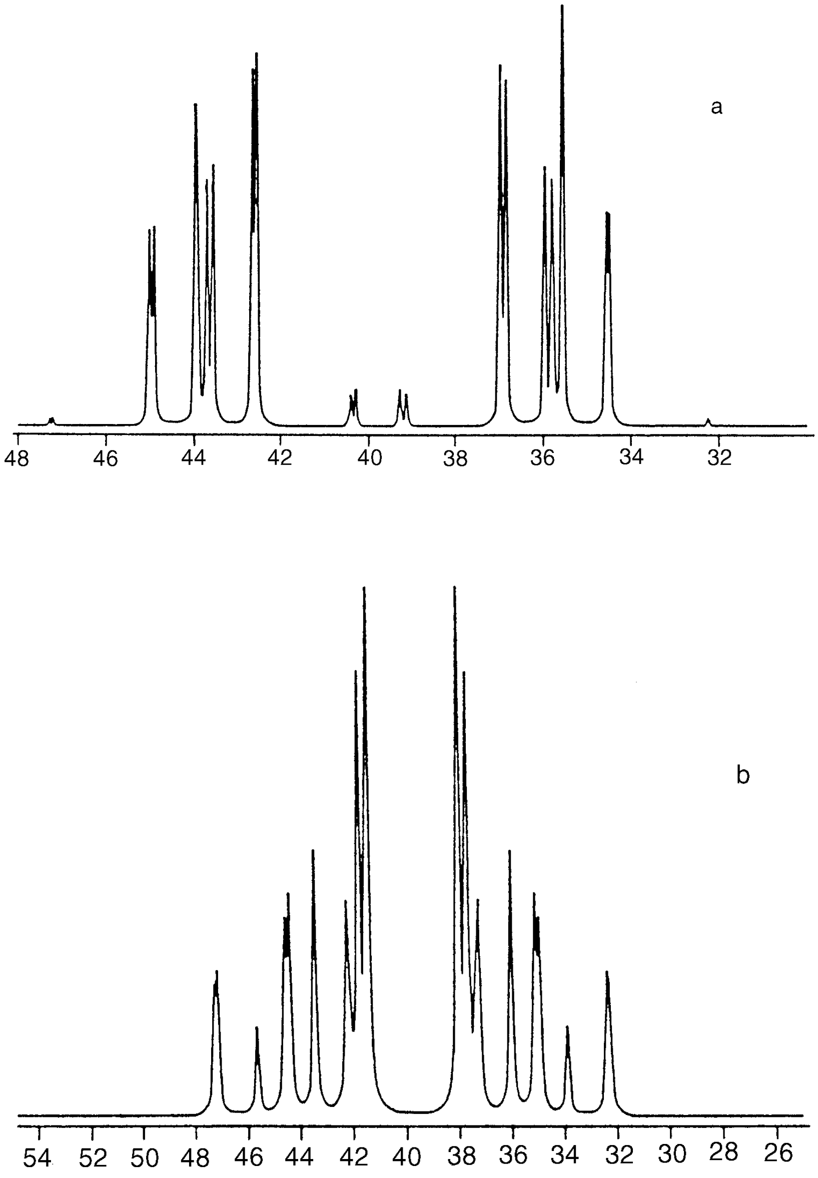


FIGURE 2. $^{31}P\{^1H\}$ NMR SPECTRA OF **2** CALCULATED BY RACCOON BASED ON (a) 80.96 MHz AND (b) 36.43 MHZ.

Both LAOCOON PC and RACCOON operate in a similar way. The parameters needed to calculate the simulation spectra are the number of nuclei, operating frequency, chemical shifts, intensity, line width, and coupling constants. The calculation takes about one minute on any PC (Intel 286 or better). Figure 2 shows the calculated NMR spectra of $Ni(CH_2PPh_2CHPPh_2)_2$ at 36.4 MHz and 81.0 MHz. The program window and the parameters used to calculate the spectrum at 81.0 MHz are given in Table 1. The operating frequencies can be changed in order to calculate different field strength NMR spectra.

TABLE 1. RACCOON program window and the parameters to calculate the spectrum at 81.0 MHz

Title of spectrum:

Number of Nuclei (2 to 7) = 4
Operating frequency = 81.0 MHz
Min. chemical shift = 30.00 δ
Maximum chemical shift = 50.00 δ
Minimum intensity = 0.020
Line width = 0.50 Hz

Chemical Shifts (δ)
W_A = 45.20
$W_{A'}$ = 45.20
W_B = 37.30
$W_{B'}$ = 37.30

Coupling constants (Hz)

	$P_{A'}$	P_B	$P_{B'}$
J_{P_AY}	271.70	155.90	34.70
$J_{P_{A'}Y}$		34.20	155.90
J_{P_BY}			0.20

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7. LAOCOON PC is commercially available ($75.00) from J. S. Thrasher, Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487.

8. Hinze, S.; Gong, J. K. *J. Chem. Inf. Comput. Sci*. **1995**, *35*, 451.

9. RACCOON is a program similar to LAOCOON PC written by Dr. Paul F. Schatz at the University of Wisconsin at Madison.