Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Bidentate *N,O*-Prolinate Ruthenium benzylidene Catalyst Highly Active in RCM of Disubstituted Dienes

Joseph S. M. Samec and Robert H. Grubbs*

Contents

Materials and Methods

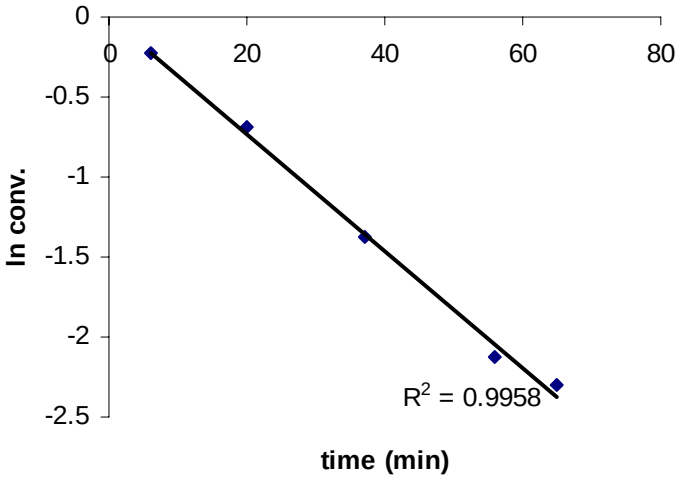
All reactions were conducted in oven-dried glassware under an argon atmosphere using standard glove-box or Schlenk techniques. Solvents were purified by passage through alumina.[1] Resonances for NMR spectra are reported relative to Me_4Si (δ 0.0) for ^1H and ^{13}C, and H_3PO_4 (δ 0.0) for ^{31}P. Spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. L-proline and Cu(I)oxide were purchased from Aldrich and used without prior purification. Catalyst **1** was obtained from Materia, Inc.

Experimental Procedures

Synthesis of $(PCy_3)(Pro)Cl_2Ru(CHPh)$ (5). A Schlenk flask was charged with $(PCy_3)_2Cl_2Ru(CHPh)$ (105 mg, 0.128 mmol), L-Proline (150 mg, 1.3 mmol), and Cu_2O (500 mg, 3 mmol) and flushed with argon. Methylene chloride (10 mL) was canula transferred and the reaction was stirred for 5h at RT under argon during which time a color change from purple to green was observed. The reaction mixture was filtered through a glass-frit and concentrated in vacuo. The resulting solid was purified via column chromatography (TSI silica) using a gradient of ether and ethyl acetate to give **5** (32 mg, 40%) as a green solid. ^1H NMR (300 MHz, CD_2Cl_2) δ 19.62 (d, *J* = 11.2 Hz 1H), 8.07 (m, *J* = 7.3 Hz 2H), 7.68 (m, *J* = 7.3 Hz 1H), 7.50 (m, *J* = 7.6 Hz 2H), 3.58 (m, 1H), 3.43 (m, 1H), 2.80 (m, 1H), 2.50 (m, 1H), 2.19 (q, *J* = 9.9 Hz 4H), 1.09-2.10 (aliphatic region 33 H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 305.0 (d, *J* = 14.5 Hz), 185.7, 155.8, 131.9, 131.4, 126.5, 62.4, 51.0, 36.2 (d, *J* = 20.6 Hz), 31.9, 31.5, 29.8, 28.5 27.1. ^{31}P NMR (121 MHz, CD_2Cl_2) δ 43.88. IR (CH_2Cl_2) ν = 3200, 2927, 2850, 1604, 1446 cm^{-1}. FAB-HRMS: *m/z* calcd for $C_{30}H_{47}NO_2PRuCl$ 621.2077 found 621.2015.

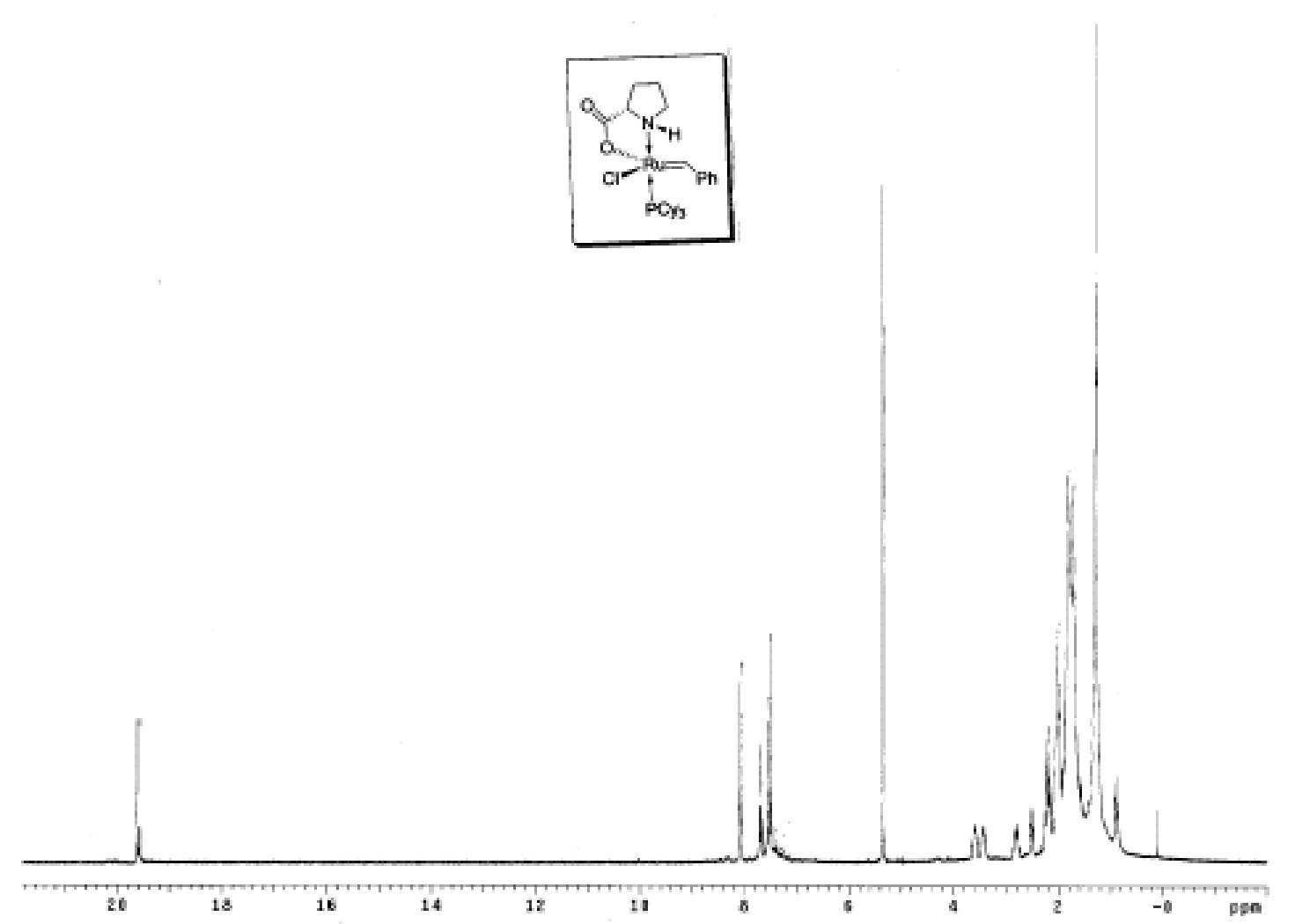
Kinetics. The reactions were carried out using a standardized procedure recently reported by us.[2] All reactions were repeated at least once. From this data also the reaction-order was determined by plotting ln conversion vs time. As can be seen in Figure 1, the reaction follows first-order kinetics over 4 half-lives.

Figure 1. First order determination of catalyst **5** in the RCM of diethyldiallyl malonate.

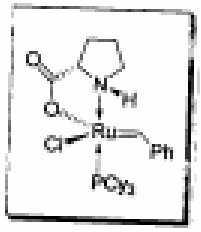


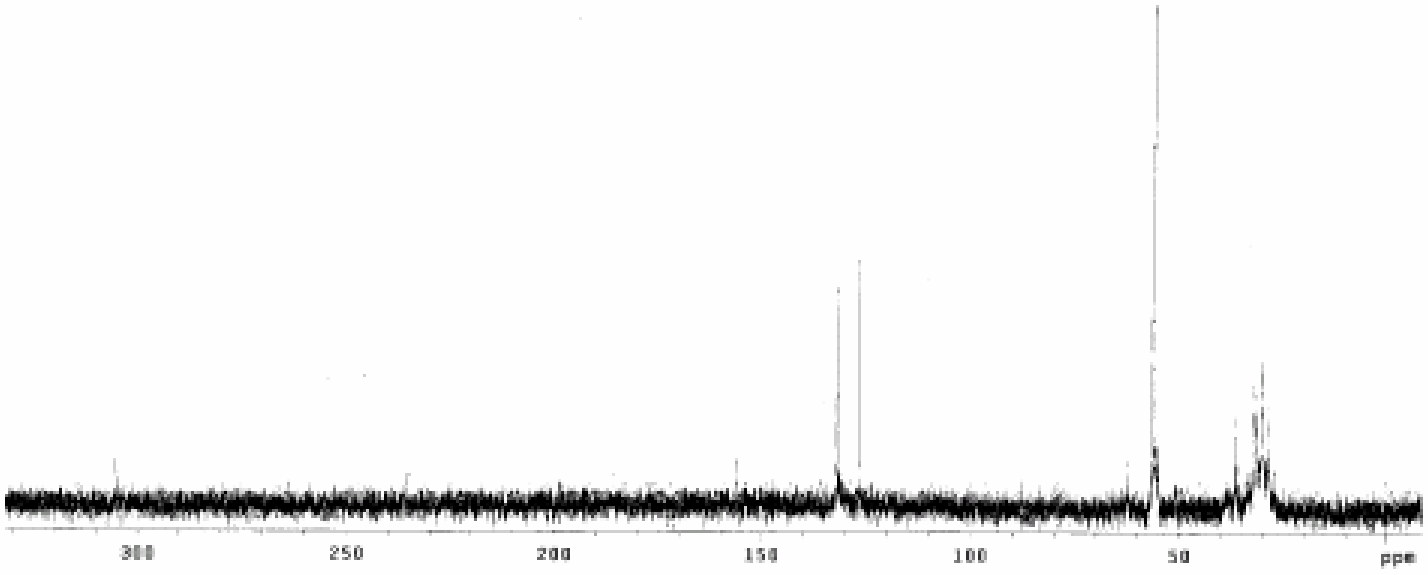
RCM of disubstituted olefines in Table 1. Catalyst **5** (2mM, 0.75 mL) was added to a screw-cap NMR tube inside a drybox. The substrate was added via syringe outside the box and the NMR-tube was directly inserted into a pre-warmed spectrometer (30 °C). The reactions were followed by ^{1}H NMR, monitoring known signals of the starting material and the product, to above 95% conversion.

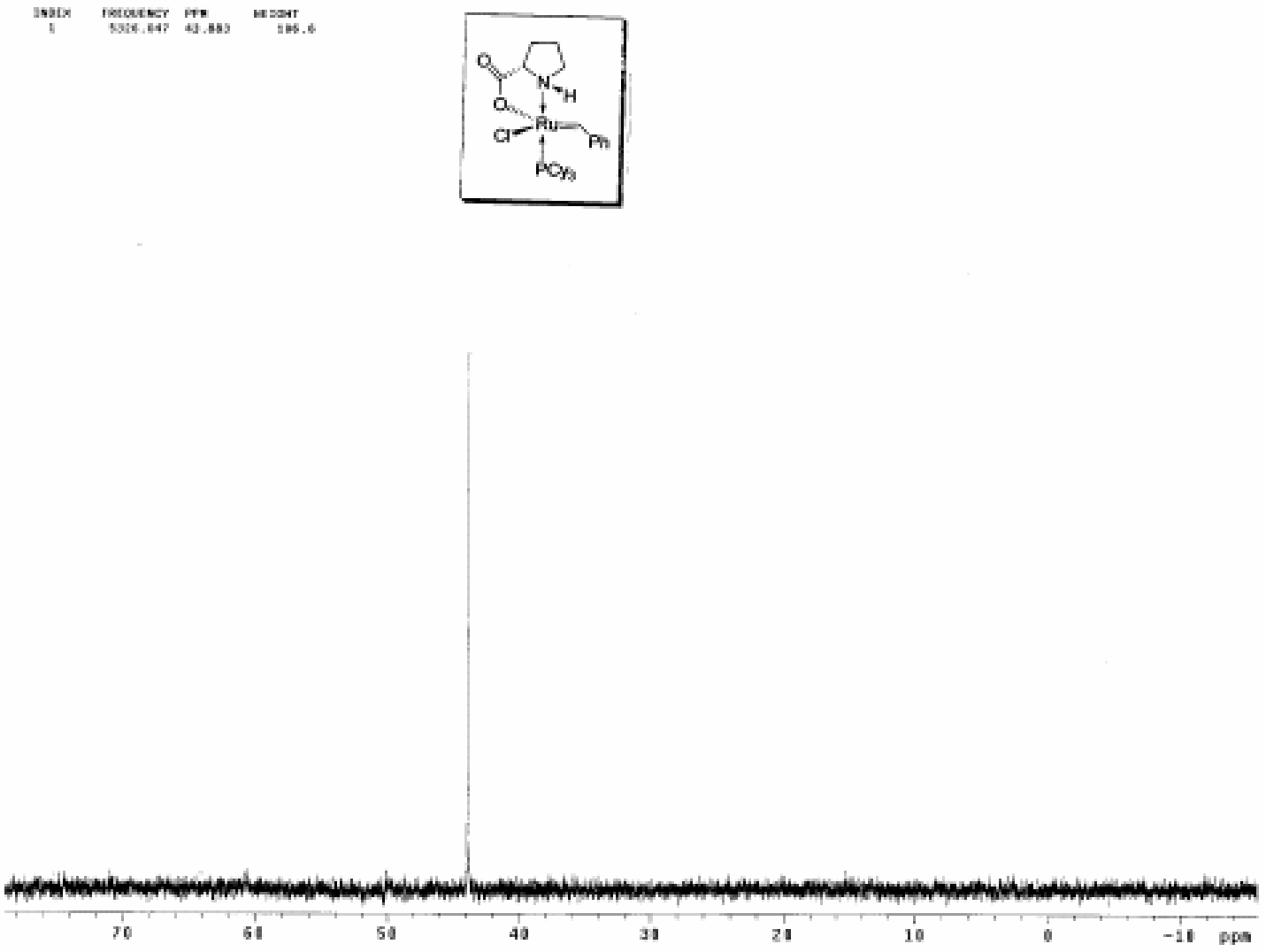
[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, **15**, 518.
[2] T. Ritter, A. Hejl, A. G. Wenzel, T. W. Funk, R. H. Grubbs, *Organometallics,* 2006, **25**, 5740.

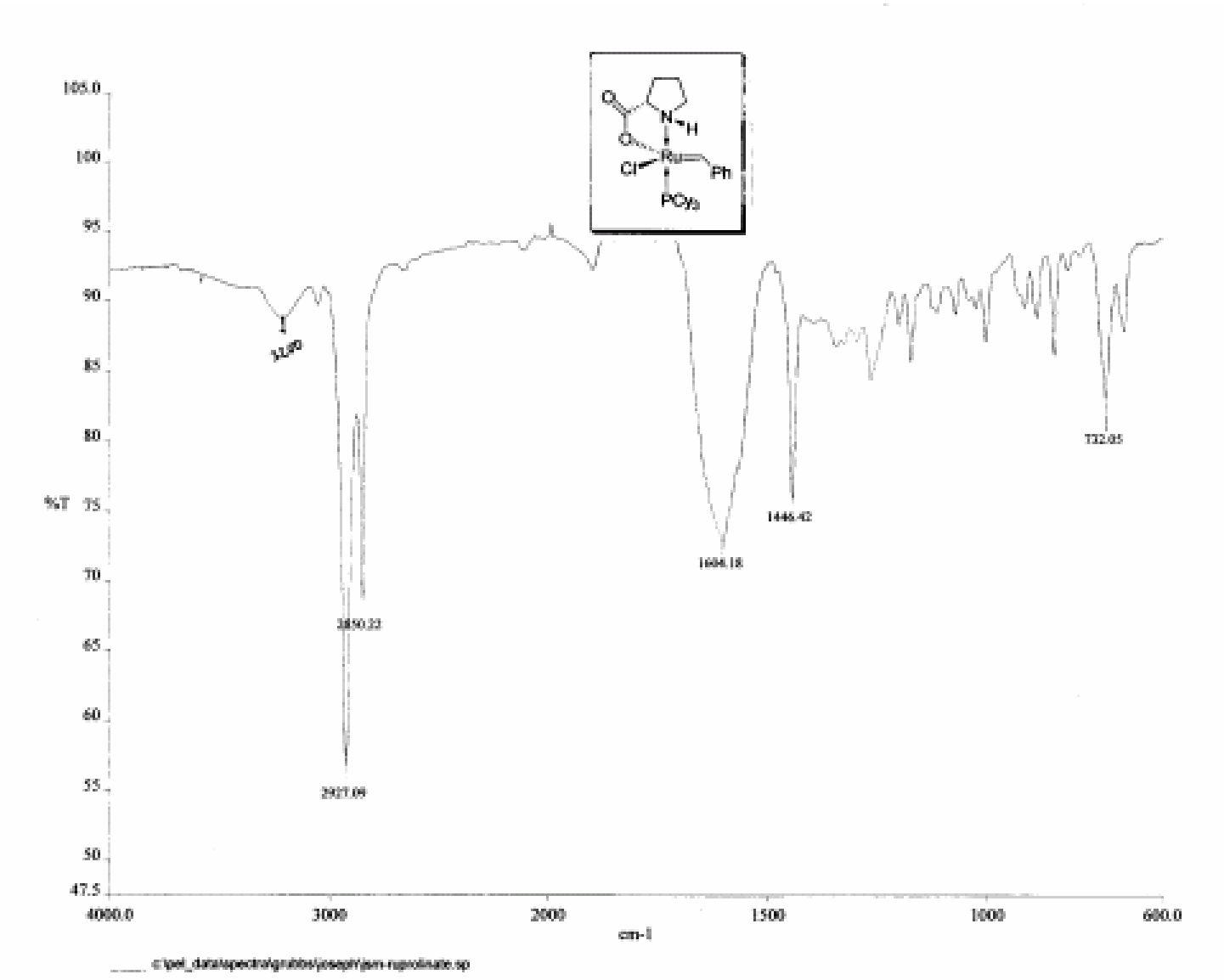


INDEX	FREQUENCY	PPM	HEIGHT
1	23910.328	395.179	8.3
2	22595.670	364.568	7.4
3	11796.868	194.866	7.8
4	9943.465	131.872	38.1
5	9808.849	132.355	19.6
6	9536.818	128.688	63.6
7	4784.359	62.351	7.5
8	4248.888	56.359	32.8
9	4221.419	55.986	63.5
10	4193.953	55.621	88.0
11	4167.250	55.267	59.3
12	4139.784	54.903	32.3
13	2748.553	36.366	13.2
14	2728.717	36.083	15.5
15	2486.456	32.577	6.4
16	2484.860	31.856	21.6
17	2372.816	31.969	19.5
18	2252.272	29.870	25.3
19	2198.838	28.514	17.4
20	2047.961	27.168	6.1









CALTECH
9/15/2006

Page 1

File: 091506-12 Date Run: 09-15-2006 (13:45:26)
Sample: m/z 585/621 HR FAB NOE
Instrument: JEOL MSRoute Ionization mode: FAB+
Joseph Samec

Scan: 9-18 Base: m/z 621; 8.3%FS TIC: 3701645

Selected Isotopes : C H $N_{1-2}O_{1-3}P_{1-2}Ru_1Cl_{0-2}$ Error Limit : 10 ppm

Measured Mass	% Base	Formula	Calculated Mass	Error
621.2015	100.0%	$C_{38}H_{47}NO_2PRuCl$	621.2077	-10.0

Scan: 9-18 Base: m/z 621; 8.3%FS TIC: 3701645