

I. Experimental

General Methods. All reactions, except where indicated, were carried out in flame-dried glassware under a dry, oxygen-free argon atmosphere using standard Schlenk and drybox techniques. All solvents were either freshly distilled from sodium benzophenone (or P_2O_5 in the case of CH_2Cl_2) or deoxygenated then dried by passing them through a column of activated alumina under nitrogen¹. CD_2Cl_2 was purchased from Cambridge Isotope Laboratories, Inc. and dried over CaH_2 or P_4O_{10} . The CD_2Cl_2 was subjected to three freeze-pump-thaw cycles and vacuum transferred into glass Schlenk tubes fitted with high-vacuum Teflon plugs, and then stored under Ar. $CDCl_3$ was prepared by literature procedure.² Air sensitive complexes were handled in an argon filled glove box and stored under argon at $-30\text{ }^\circ\text{C}$. CP grade CO and C_2H_4 were purchased from National Welders Supply and used as received. ^{13}CO (99% ^{13}C) and $^{13}CH_2^{13}CH_2$ (99% ^{13}C) were purchased from Cambridge Isotope Laboratories, Inc. and used as received. Trimethylaluminum (2.0 M in toluene), 1,3-bis-(diphenylphosphino)propane and $Ni(acac)_2$ were purchased from Aldrich Chemicals and used as received. Elemental analyses were obtained from Atlantic Microlabs Inc., Norcross GA.

$H(OEt)_2BAR'_4$,³ and $CDCl_2F$ ² were synthesized using published methods.

Analytical Measurements. FT-IR experiments were recorded using a ReactIR 1000 from ASI Applied Systems fitted with a silicon-tipped (SiComp) probe inserted through a nylon adapter and O-ring seal into a 2-necked flask.

The 1H and ^{13}C NMR data attributed to the counterion BAR'_4 ($Ar' = 3,5-(CF_3)_2C_6H_3$) are consistent for all cationic complexes examined and are not included in

each compound characterized below. Full spectral details have been previously reported.⁴

Kinetic Measurements. Kinetics experiments were carried out under argon in NMR tubes equipped with septa. CDCl_2F was added to samples at $-78\text{ }^\circ\text{C}$ unless otherwise indicated, after which solids were dissolved at the lowest temperature possible. Kinetics experiments were carried out on a Bruker Avance 300 spectrometer. NMR probe temperatures were measured using a thermocouple.⁵

(dppp)NiMe₂, 1. $\text{Ni}(\text{acac})_2$ (2.64 g, 0.103 mmol) and 1,3-bis-(diphenylphosphino)propane (4.24 g, 0.103 mmol) were combined in a schlenk flask under argon atmosphere and slurried in Et_2O (60 mL) at $25\text{ }^\circ\text{C}$ for 1 h. The slurry became a light blue color. The slurry was cooled to $-50\text{ }^\circ\text{C}$ and 4.75 mL (2.0 M in toluene, 0.029 mmol based on Me) of AlMe_3 was added dropwise via syringe. The solution was allowed to warm slowly to $25\text{ }^\circ\text{C}$ and stir overnight. A yellow-brown slurry formed that upon filtration gave a canary-yellow solid. The solid was washed with Et_2O (3 x 20 mL) and dried in vacuo to yield 3.16 g (61 %) of **1**. The NMR spectra were consistent with that previously reported.⁶

In Situ Preparation of Cationic Nickel Complexes for IR Studies.

The standard procedure utilized for the generation of complex **2** for the purpose of characterizing CO derivatives by IR spectroscopy is as follows: $\text{dpppNi}(\text{CH}_3)_2$ (15.0 mg, 0.030 mmol) and $\text{H}(\text{OEt}_2)_2\text{BAr}'_4$ (30.0 mg, 0.030 mmol) were combined in a Schlenk tube fitted with a septum and cooled to $-80\text{ }^\circ\text{C}$. CH_2Cl_2 (2 mL) was added via syringe and the solution was stirred until homogeneous. This solution was then transferred via cannula to the two-necked IR flask cooled to $-80\text{ }^\circ\text{C}$. This solution of **2** was used to

generate complexes **4**, **5** and **6** by the same procedure as that described below for the NMR reactions. For complex **5** the temperature at which CO was introduced was -80 °C.

In Situ Preparation of Cationic Nickel Complexes for NMR Studies.

(dppp)NiCH₃(OEt₂)⁺(BAr'₄)⁻, 2[OEt₂]. dpppNi(CH₃)₂ (5.0 mg, 0.010 mmol) and H(OEt₂)₂BAr'₄ (10 mg, 0.010 mmol) were combined in an NMR tube fitted with a septum. The tube was cooled to -80 °C and 0.5 mL CD₂Cl₂ was added via syringe. The tube was agitated with slight warming to ensure complete dissolution and protonation. ¹H NMR (300 MHz, CD₂Cl₂, -80 °C) δ 7.30-7.73 (m, 20H, (C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 3.28 (br, 4H, O(CH₂CH₃)₂), 2.32 (br, 2H, PCH₂CH₂CH₂P), 2.20 (br, 2H, PCH₂CH₂CH₂P), 1.81 (br, 2H, PCH₂CH₂CH₂P), 1.10 (br, 6H, O(CH₂CH₃)₂), -0.08 (br, 3H, Ni-CH₃). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, -80 °C) δ [(C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂] 133.0 (d, ²J_{CP} = 11, *ortho*), 131.8 (d, ²J_{CP} = 10, *ortho'*), 131.3 (s, *meta*), 130.8 (s, *meta'*), 130.1 (s, *para*), 129.5 (s, *para*), 129.1 (d, ¹J_{CP} = 10, *ipso*), 128.7 (d, ¹J_{CP} = 9, *ipso'*), 67.7 (s, Ni-O(CH₂CH₃)₂), 27.1 (dd, ¹J_{CP} = 26, ³J_{CP} = 9, PCH₂CH₂CH₂P), 26.7 (d, ¹J_{CP} = 22, PCH₂CH₂CH₂P), 17.0 (s, PCH₂CH₂CH₂P), 14.4 (s, Ni-O(CH₂CH₃)₂) 8.4 (dd, ²J_{CPtrans} = 55, ²J_{CPcis} = 37, Ni-CH₃). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, -80 °C) δ 27.2 (d, ²J_{PP} = 30), 0.95 (d, ²J_{PP} = 30).

(dppp)NiCH₃(OH₂)⁺(BAr'₄)⁻, 2[OH₂]. A solution of (dppp)NiCH₃(OEt₂)⁺(BAr'₄)⁻ in CD₂Cl₂/CDCl₂F (50:50 v/v) was prepared similarly to that described above. To the solution at -80 °C was added 1 drop of degassed H₂O via syringe. The NMR tube was agitated to ensure thorough mixing. ¹H NMR (300 MHz, CD₂Cl₂/CDCl₂F, -80 °C) δ 7.4-7.6 (m, 20H, (C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 4.56 (br,

Ni-OH₂), 2.33 (br, 4H, PCH₂CH₂CH₂P), 1.69 (br, 2H, PCH₂CH₂CH₂P), -0.16 (br, 3H, Ni-CH₃). ³¹P{¹H} NMR (121 MHz, CDCl₂F, -80 °C) δ 31.9 (d, ²J_P = 37), 0.1 (d, ²J_{PP} = 37).

(dppp)Ni(CO)COCH₃⁺(BAr'₄)⁻, 4. (dppp)NiCH₃(OEt₂)⁺(BAr'₄)⁻ was prepared as above. The solution at -80 °C was purged with a gentle stream of CO for 3-5 minutes. The solution was next warmed to -20 °C and purged with a gentle stream of argon for 30 minutes. ¹H NMR (300 MHz, CD₂Cl₂, -90 °C) δ 7.15-7.74 (m, 20H, (C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 2.63 (br m, 2H, PCH₂CH₂CH₂P), 2.32 (br m, 2H, PCH₂CH₂CH₂P), 1.87 (br, 3H, Ni-COCH₃), 1.65 (br m, 2H, PCH₂CH₂CH₂P). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, -90 °C) δ 243.0 (d, ²J_{CP} = 48, Ni-COCH₃), 180.6 (dd, ²J_{CP} = 52, ²J_{CP} = 15, Ni-CO), 133.4, 132.5, 132.4, 132.0, 131.6, 131.0, 130.8, 129.9, 129.3, 129.1, 124.9, 124.3, 123.6 ((C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 39.0 (dd, ³J_{CP} = 26, ³J_{CP} = 14 Ni-COCH₃), 24.0 (d, ¹J_{CP} = 37, PCH₂CH₂CH₂P), 23.6 (d, ¹J_{CP} = 42, PCH₂CH₂CH₂P), 17.5 (s, PCH₂CH₂CH₂P). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, -80 °C) δ 3.13 (d, ²J_{PP} = 57), -1.28 (d, ²J_{PP} = 57). IR (CH₂Cl₂, -80 °C) ν_{CO} = 2082 cm⁻¹, ν_{acyl} = 1698 cm⁻¹.

(dppp)Ni(CO)₂COCH₃⁺(BAr'₄)⁻, 5. (dppp)NiCH₃(OEt₂)⁺(BAr'₄)⁻ was prepared as above. The solution at -140 °C was purged with a gentle stream of CO for ca. 2 minutes. ¹H NMR (400 MHz, CD₂Cl₂, -80 °C) δ 7.15-7.74 (m, 20H, (C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 2.59 (br m, 4H, PCH₂CH₂CH₂P), 2.20 (br, 3H, Ni-COCH₃), 1.92 (br m, 2H, PCH₂CH₂CH₂P). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, -90 °C) δ 219.1 (d, ²J_{CP} = 45, Ni-COCH₃), 183.8 (br, Ni-(CO)₂), 131.5, 129.2, 129.0 ((C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 46.5 (br d, Ni-COCH₃), 25.5 (br, PCH₂CH₂CH₂P), 17.0 (s, PCH₂CH₂CH₂P). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, -90 °C) δ 11.65 (d, ²J_{PP} = 85), -

0.19 (d, $^2J_{PP} = 85$). IR (CH_2Cl_2 , $-80\text{ }^\circ\text{C}$) $\nu_{\text{CO}(\text{sym})} = 2094\text{ cm}^{-1}$, $\nu_{\text{CO}(\text{asym})} = 2059\text{ cm}^{-1}$, $\nu_{\text{acyl}} = 1733\text{ cm}^{-1}$.

The ^{13}C labeled compound was made in an analogous manner in CDCl_2F using ^{13}CO . $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_2F , $-90\text{ }^\circ\text{C}$) δ 221.3 (br d, $^2J_{CP} = 45$, Ni-COCH₃), 184.5 (dd, $^2J_{CP} = 24$, $^2J_{CP} = 22$, Ni-(CO)₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_2F , $-110\text{ }^\circ\text{C}$) δ 11.8 (ddt, $^2J_{PP} = 85$, $^2J_{\text{PC}(\text{acyl})} = 45$, $^2J_{\text{PC}(\text{carbonyl})} = 22$), -1.25 (dtd, $^2J_{PP} = 85$, $^2J_{\text{PC}(\text{carbonyl})} = 24$, $^2J_{\text{PC}(\text{acyl})} = 5$).



was prepared as above. C_2H_4 (1.05 equiv.) was added via syringe to the solution at $-80\text{ }^\circ\text{C}$. The solution was allowed to warm to $-45\text{ }^\circ\text{C}$. The reaction was monitored with ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy until complete conversion to the chelate complex was observed. IR (CH_2Cl_2 , $-80\text{ }^\circ\text{C}$) $\nu_{\text{CO}} = 2045\text{ cm}^{-1}$. The chirality at Ni in complex **6** greatly complicated the ^1H spectrum as there are five sets of diastereotopic methylenes with the central methylene of the phosphine ligand being the only decipherable set as revealed by ^1H COSY (see ^1H data below). ^1H NMR (300 MHz, CD_2Cl_2 , $-85\text{ }^\circ\text{C}$) δ 6.9-8.1 (m, 20H, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$), 2.49-2.96 (m, 8H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ and $\text{NiCOCH}_2\text{CH}_2\text{COCH}_3$), 2.35 (s, 3H, $\text{NiCOCH}_2\text{CH}_2\text{COCH}_3$), 1.75 (br d, 1H, $^2J_{\text{HaHa}'} = 15$, $\text{PCH}_2\text{CHaHa}'\text{CH}_2\text{P}$), 1.32 (app. t, 1H, $\text{PCH}_2\text{CHaHa}'\text{CH}_2\text{P}$). $^1\text{H}\{\text{COSY}\}$ exposed $^2J_{\text{HH}}$ coupling between the resonances at δ 1.75 and 1.32 (see below for spectrum). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , $-85\text{ }^\circ\text{C}$) δ 241.2 (d, $^2J_{CP} = 58$, Ni-COCH₂CH₂COCH₃), 223.1 (s, Ni-COCH₂CH₂COCH₃), 180.1 (dd, $^2J_{CP} = 47$, $^2J_{CP} = 24$, Ni-(CO)), 124.7-133.8 ($(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$), 37.8 (s, Ni-COCH₂CH₂COCH₃), 37.6 (d, $^3J_{CP} = 28\text{ Hz}$,

Ni-COCH₂CH₂COCH₃), 31.6 (s, Ni-COCH₂CH₂COCH₃), 23.4 (d, ¹J_{CP} = 24 Hz, PCH₂CH₂CH₂P), 22.5 (d, ¹J_{CP} = 22 Hz, PCH₂CH₂CH₂P), 16.8 (s, PCH₂CH₂CH₂P). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, -85 °C) δ 9.38 (d, ²J_{PP} = 78), -5.50 (d, ²J_{PP} = 78).

The ¹³C labeled compound was made in an analogous manner using ¹³CO.

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, -90 °C) δ 241.4 (br d, ²J_{CP} = 58, Ni-COCH₂CH₂COCH₃), 223.1 (s, Ni-COCH₂CH₂COCH₃), 179.9 (ddd, ²J_{CP} = 47, ²J_{CP} = 24, ²J_{CC} = 6, Ni-(CO)). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, -90 °C) δ 9.54 (ddd, ²J_{PP} = 78, ²J_{PC(acyl)} = 58, ²J_{PC(carbonyl)} = 24), -5.73 (ddd, ²J_{PP} = 78, ²J_{PC(carbonyl)} = 47, ²J_{PC(acyl)} = 11).

(dppp)NiCH₂CH₂COCH₃⁺(BAR'₄)⁻, 7. A solution of complex **6** was prepared as described above. Argon was purged through the solution for 20 minutes with warming to -15 °C. ¹H NMR (300 MHz, CD₂Cl₂, -60 °C) δ 7.37-7.59 (m, 20 H, (C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 2.78 (br, 2H, Ni-CH₂CH₂COCH₃), 2.33 (br 4H, PCH₂CH₂CH₂P), 2.24 (s, 3H, Ni-CH₂CH₂COCH₃), 1.79 (br, 2H, PCH₂CH₂CH₂P), 0.92 (Ni-CH₂CH₂COCH₃). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, -40 °C) δ 239.6 (d, ²J_{CP} = 14, Ni-CH₂CH₂COCH₃), 124.6-132.7 ((C₆H₅)₂PCH₂CH₂CH₂P(C₆H₅)₂), 51.0 (s, Ni-CH₂CH₂COCH₃), 29.4 (dd, ²J_{CP} = 56 Hz, ²J_{CP} = 26, Ni-CH₂CH₂COCH₃), 27.3 (s, Ni-CH₂CH₂COCH₃), 26.4 (br d, ¹J_{CP} = 28 Hz, PCH₂CH₂CH₂P), 25.5 (d, ¹J_{CP} = 25 Hz, PCH₂CH₂CH₂P), 18.2 (s, PCH₂CH₂CH₂P). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, -60 °C) δ 28.9 (d, ²J_{PP} = 40), -1.95 (d, ²J_{PP} = 40).

(dppp)NiCH₃(C₂H₄)⁺(BAR'₄)⁻, 8. A solution of (dppp)NiCH₃(OEt₂)⁺(BAR'₄)⁻ in CDCl₂F was prepared in a manner similar to that described above. The solution was cooled to -130 °C and C₂H₄ (ca. 25 equiv.) was added to the solution via syringe. ¹H

NMR (300 MHz, CDCl_2F , -105°C) δ 7.25-7.55 (m, 20H, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$), $\eta^2\text{-CH}_2\text{CH}_2$ was not observed due to fast exchange with non-coordinated ethylene (δ 5.4), 2.3-2.7 (br, 4H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$), 1.7-2.0 (br, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$), -0.01 (br, 3H, Ni- CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_2F , -105°C) δ 13.3 (d, $^2J_{\text{PP}} = 45$), 2.09 (d, $^2J_{\text{PP}} = 45$).

(dppp)NiCH₂CH₂- μ -H⁺(BAr'₄)⁻, 10. A solution of (dppp)NiCH₃(OEt₂)⁺(BAr'₄)⁻ in CDCl_2F was prepared in a manner similar to that described above. The solution was cooled to -130°C and C_2H_4 (ca. 30 equiv.) was added to the solution via syringe. The solution was warmed to -50°C where the loss of propylene and the formation of butenes was observed. ^1H NMR (300 MHz, CDCl_2F , -113°C) δ 7.24-7.47 (m, 20H, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$), 2.5 (br, 4H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$), 1.92 (br, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$), (resonance for Ni- CH_2CH_3 was obscured by free diethyl ether (δ 1.1)), -1.0 (br, 3H, Ni- CH_2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_2F , -113°C) δ 27.6 (br), 3.28 (br).

The ^{13}C labeled version was made in a similar manner using ca. 8 equiv. $^{13}\text{CH}_2^{13}\text{CH}_2$. ^1H NMR (300 MHz, CDCl_2F , -45°C) δ -1.0 (br d, $^1J_{\text{CH}} \sim 125$, 3H, Ni- CH_2CH_3). ^1H NMR (300 MHz, CDCl_2F , -113°C) δ -1.0 (br, 3H, Ni- CH_2CH_3). ^{13}C NMR (75 MHz, CDCl_2F , -113°C) δ 30.0 (br t, $^1J_{\text{CH}} = 160$, Ni- CH_2CH_3), 3.17 (dq, $^1J_{\text{CC}} = 32$, $^1J_{\text{CH}} = 124$, Ni- CH_2CH_3).

References

- 1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, 15, 1518.
- 2) Siegel, J. S.; Anet, F. A. L. *J. Org. Chem* **1988**, 53, 2629.

- 3) Brookhart, M.; Grant, B.; Volpe Jr., A. F. *Organometallics* **1992**, *11*, 3920.
4) LaPointe, A.; Brookhart, M. *Organometallics* **1998**, *17*, 1530.
5) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.
6) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265.

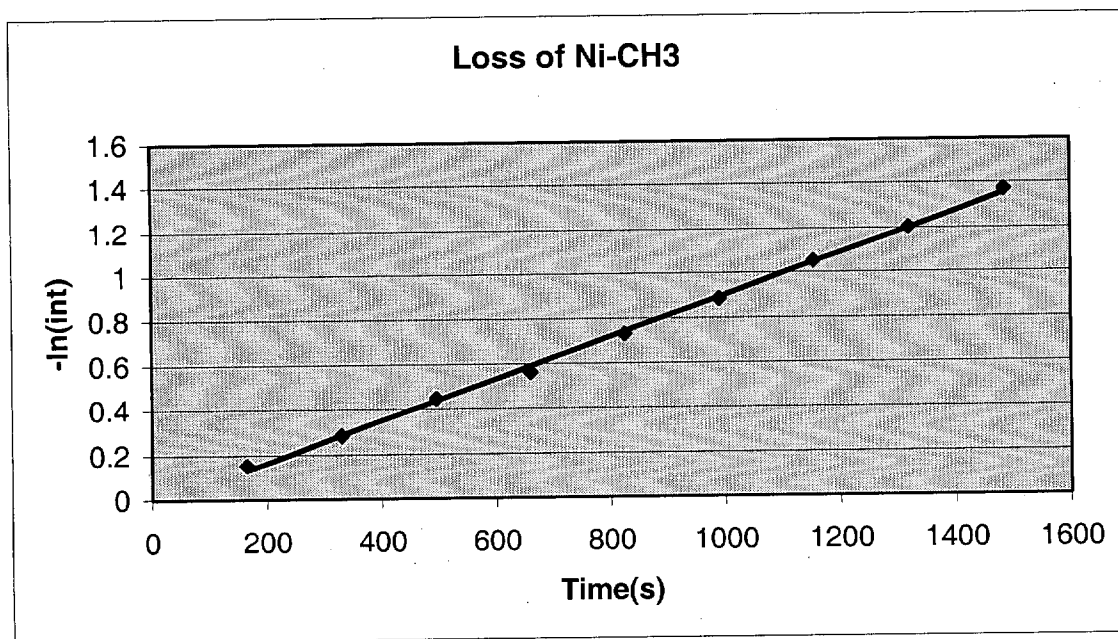
II. Kinetic Data

Kinetic Data for the migratory insertion of 8.

$$T = 177.5 \text{ K}$$

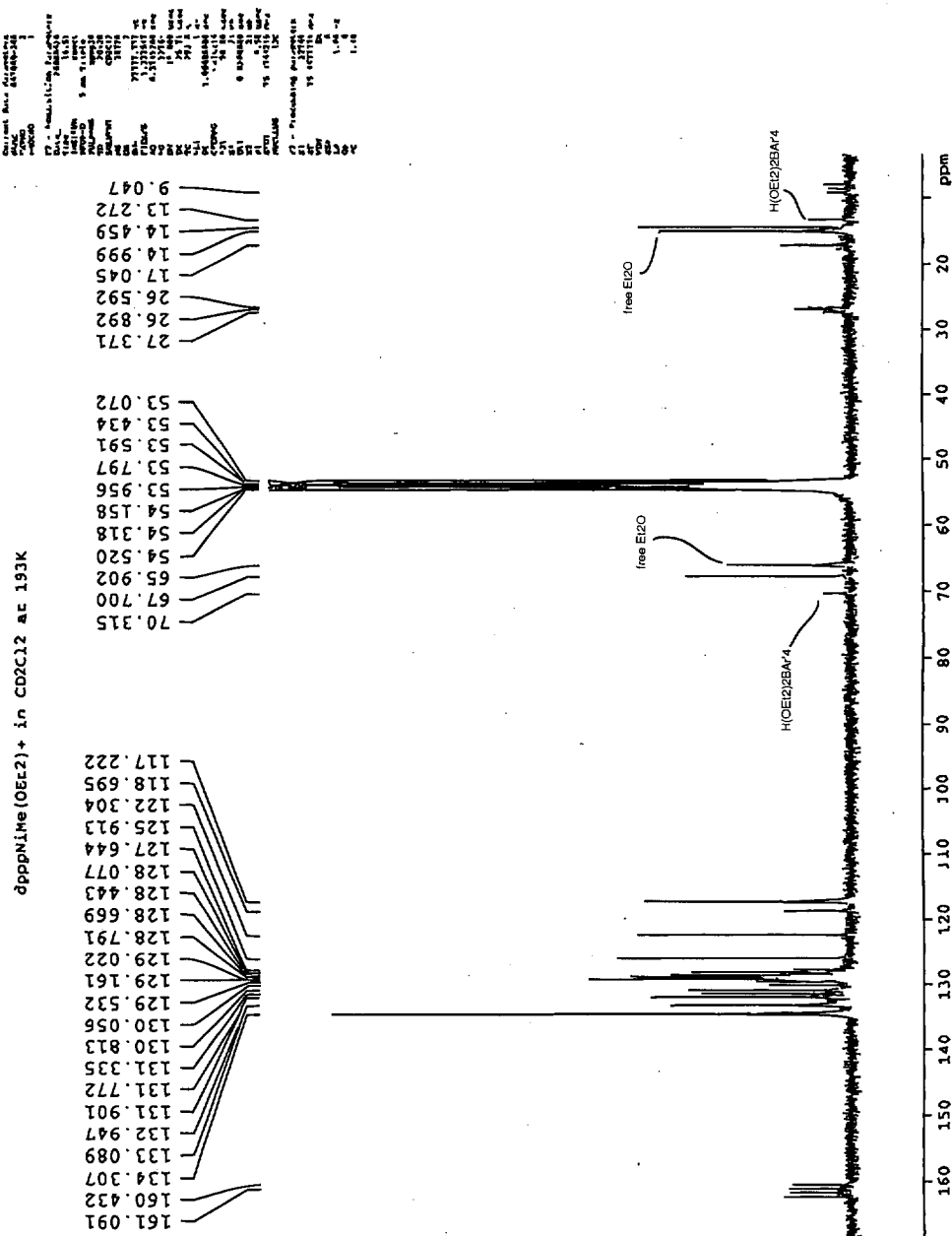
$$k = 9.3 \times 10^{-4} \text{ s}^{-1}$$

$$\Delta G^\ddagger = 12.7 \text{ kcal/mol}$$



S 10

III. Representative NMR and IR spectra: $^{13}\text{C}\{^1\text{H}\}$ spectrum of $2[\text{OEt}_2]$

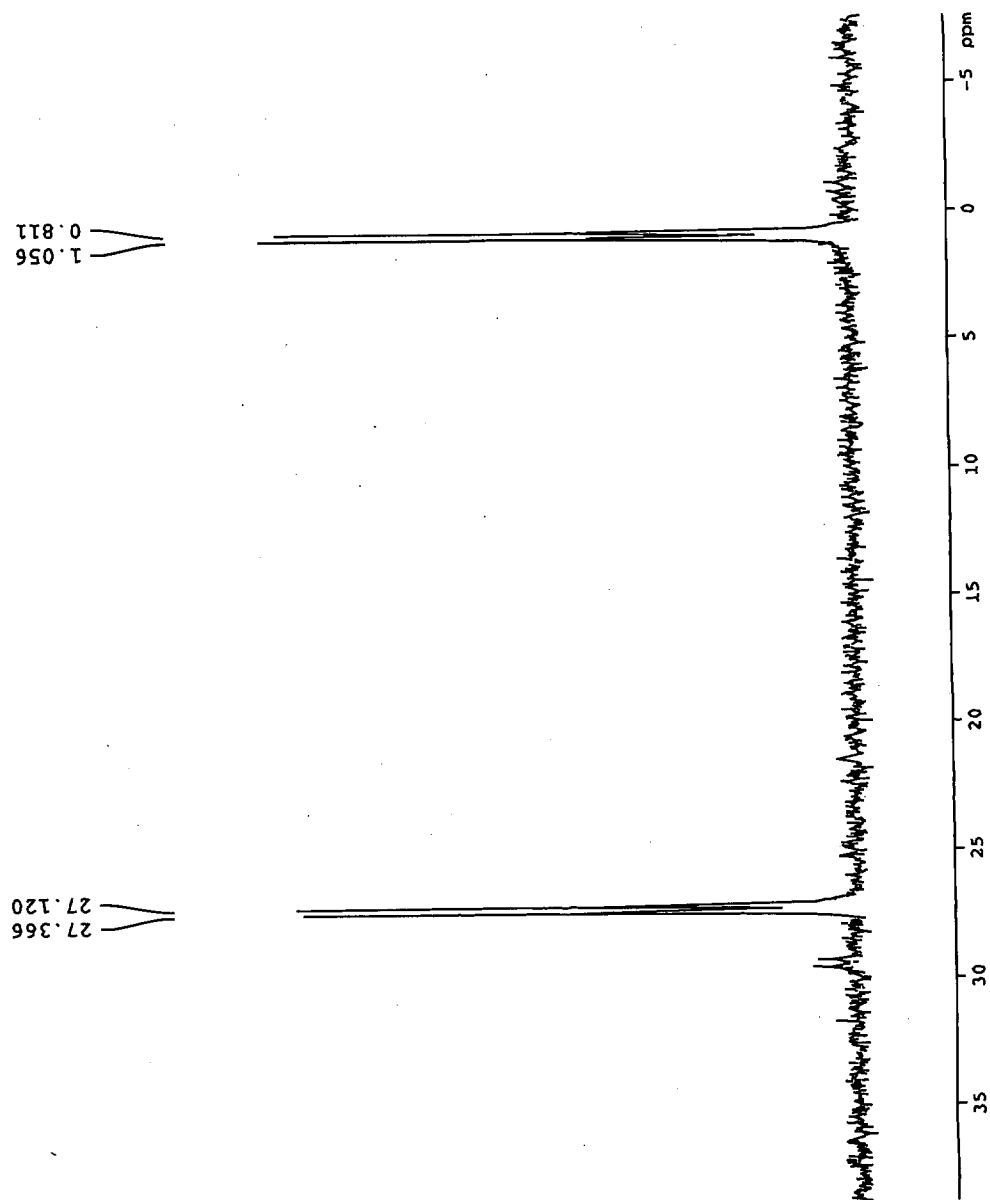


10

S11

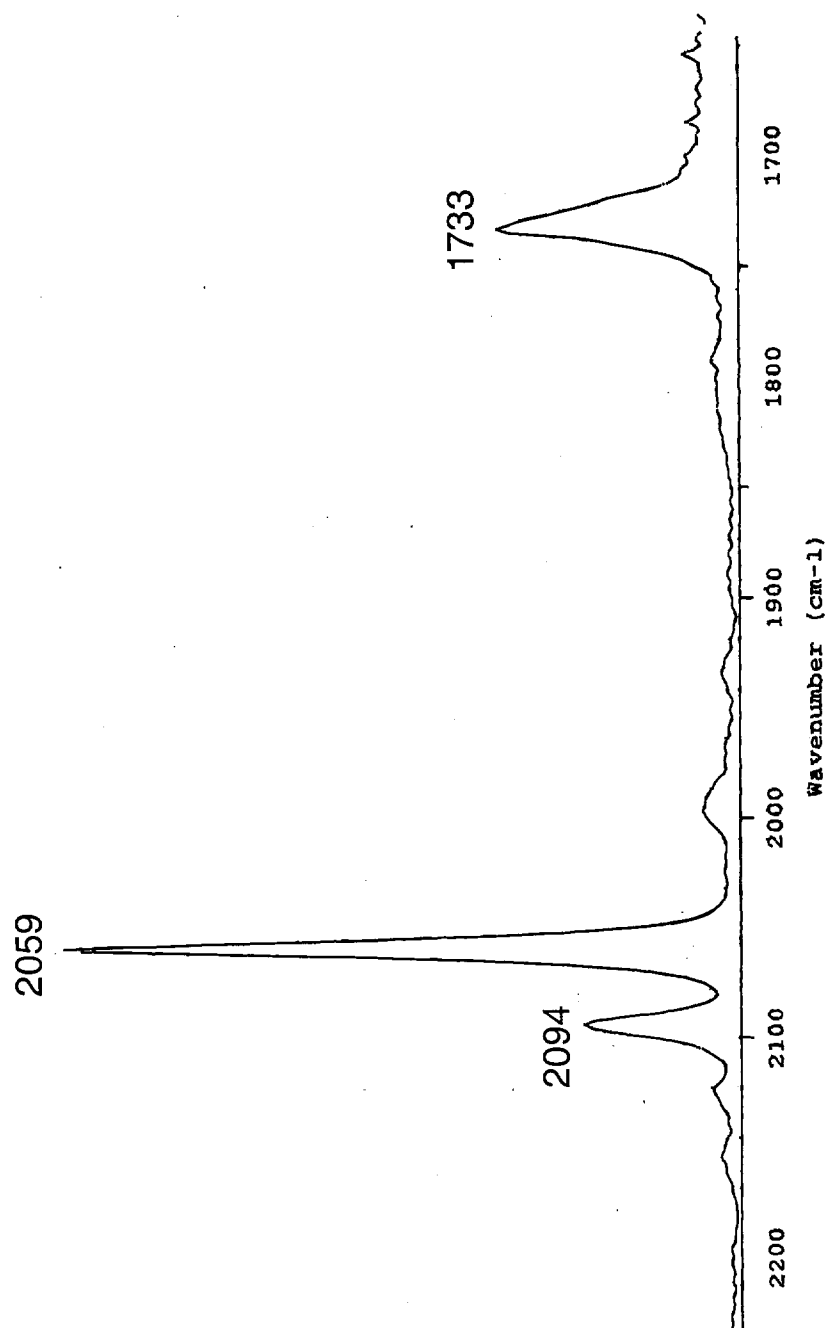
$^3\text{P}\{^1\text{H}\}$ spectrum of $2[\text{OEt}_2]$

$\delta\text{ppmNiMe}_2 + \text{H}(\text{OEt}_2)2\text{BAr}'_4$ at 193K in CD_2Cl_2

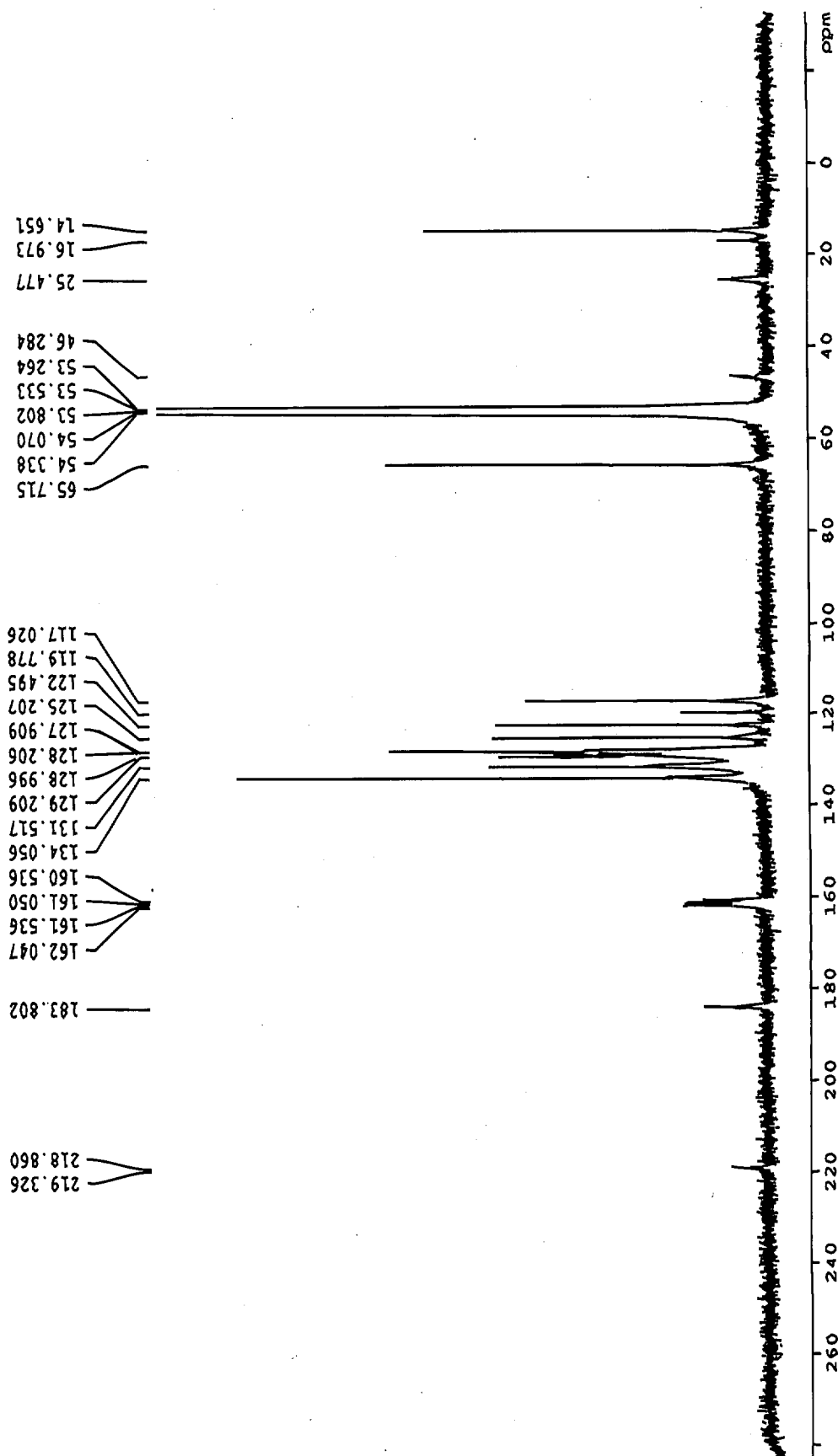


S 12

IR spectrum of **5** generated from unlabeled CO.



S 13

 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** generated from unlabeled CO δ ppm Ni(CO)₂COMe⁺ in CD₂Cl₂ at 183 K

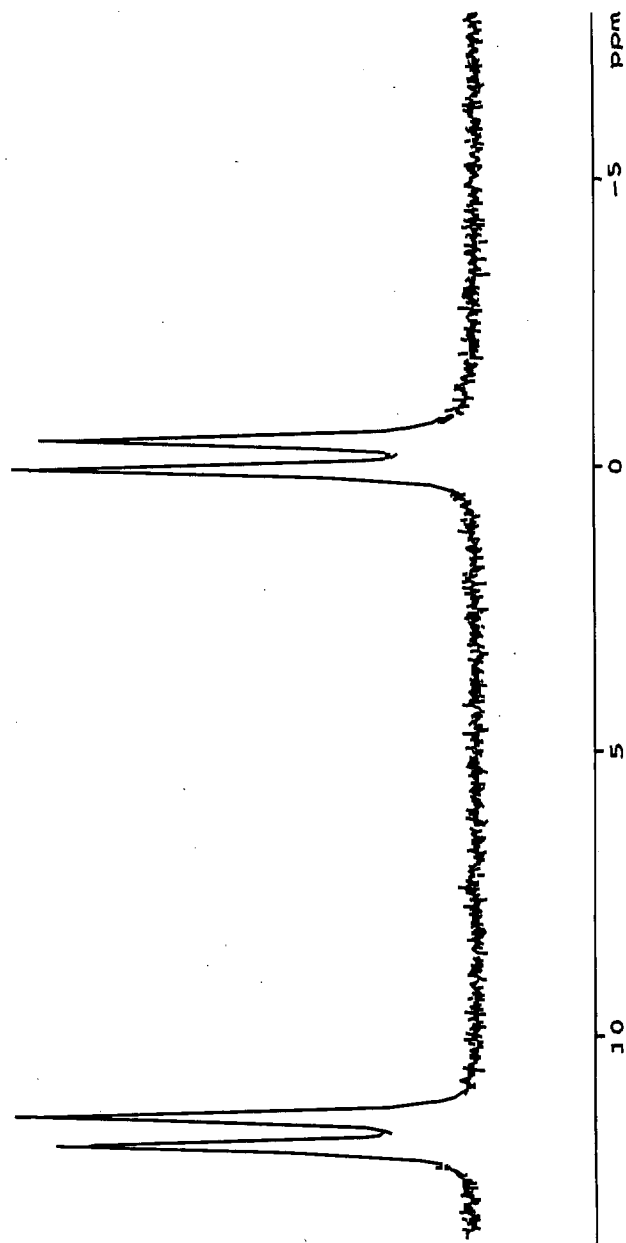
S 14

$^3\text{P}\{^1\text{H}\}$ NMR spectrum of **5** generated from unlabeled CO.

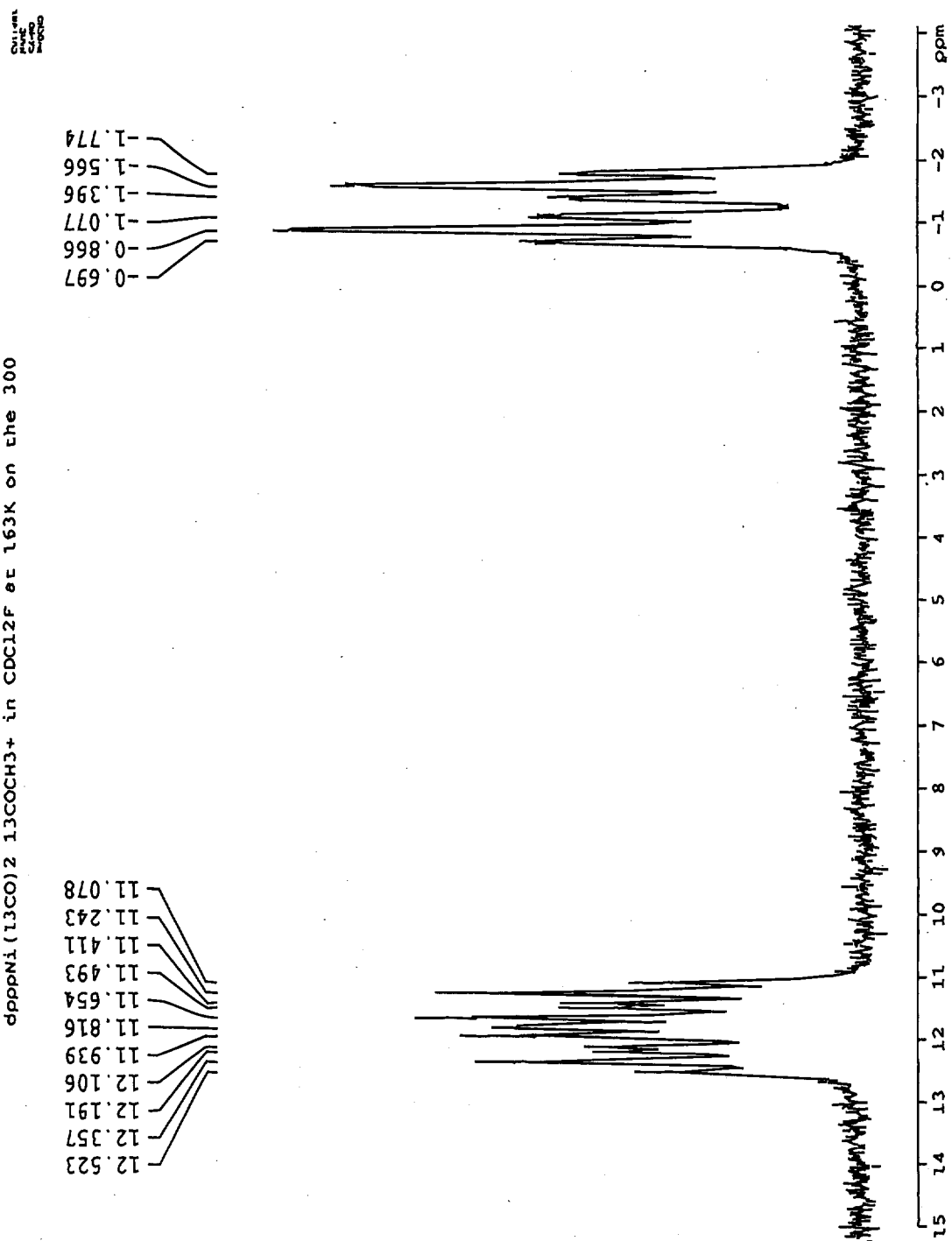
$\delta_{\text{ppm}}(\text{CO})_2\text{COME}$ in CD_2Cl_2 at 183K

11.919
11.403

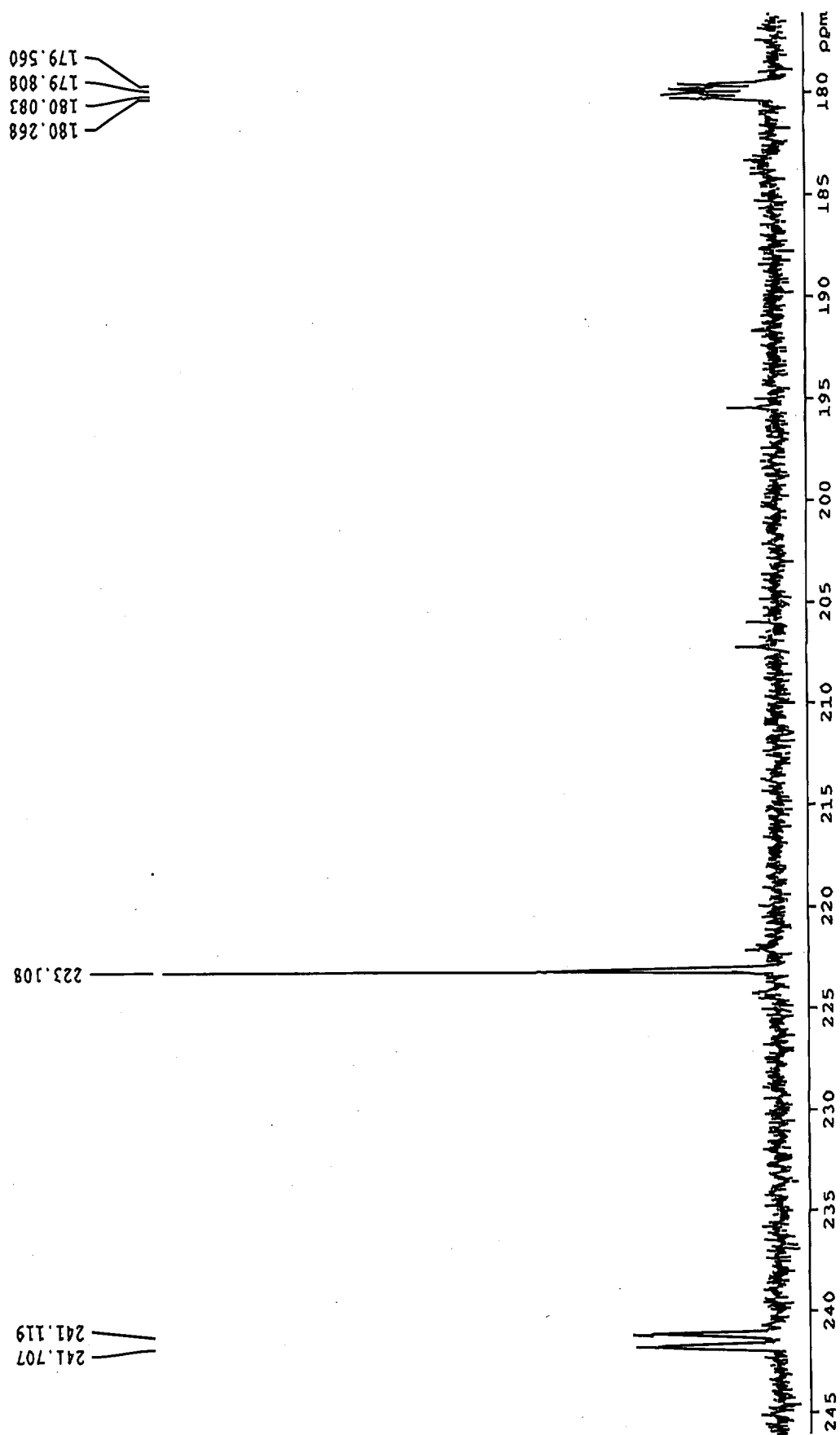
0.070
-0.452



S15

 $^3\text{P}\{^1\text{H}\}$ spectrum of **5** generated using ^{13}CO .dpppNi(^{13}CO) $_2$ $^{13}\text{COCH}_3$ in CDCl_2F at 163K on the 300

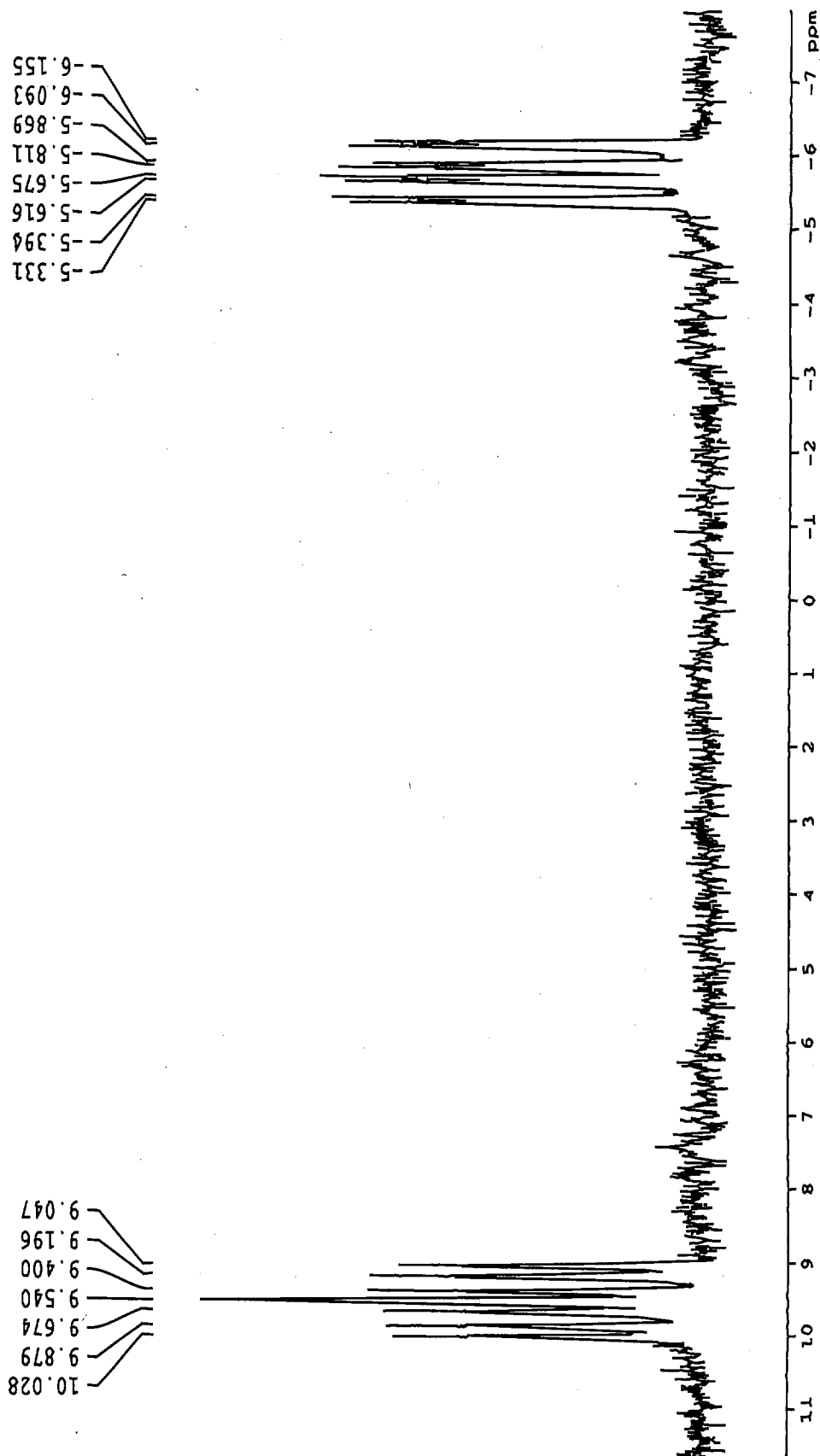
$^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of **6** generated from ^{13}CO .



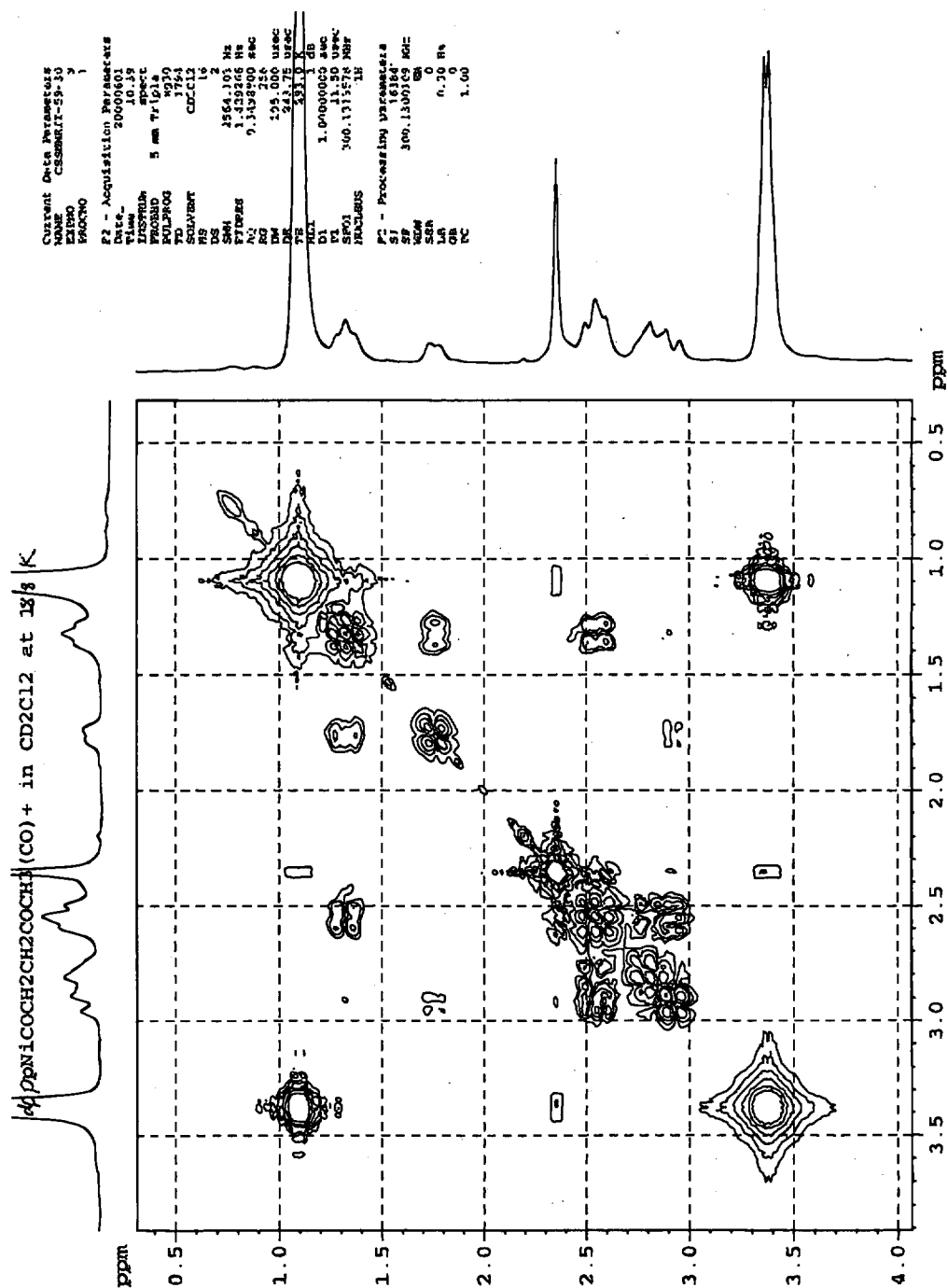
S 17

$^3\text{P}\{^1\text{H}\}$ NMR spectrum of **6** generated from ^{13}CO .

after insert ^{13}CO and ethylene at 183K



S 18

¹H COSY of complex 6.

S 19

^{13}C NMR spectrum of 7.

$\text{dpppNi}(\text{CH}_2\text{CH}_2\text{COCH}_3)_2$ in CH_2Cl_2 at 233K

