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Contribution No. 3384 from the Laboratory of Inorganic Chemistry, Aristotelian University, Thessaloniki, Greece, and the Molecular Structure Center and Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Molecular Structure and Solution Dynamics of (η^5-C_5H_5)Ni(PPh_3)$S_2COC_2H_5$

CONSTANTINOS TSIPIS, GEORGE E. MANOUSSAKIS, D. P. KESSISSOGLOU, JOHN C. HUFFMAN, LARRY N. LEWIS, MARK A. ADAMS, and KENNETH G. CAULTON*

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The ^{1}H NMR spectrum of CpNi(PPh_3)S_2COR (R = Me, Et) exhibits a broad cyclopentadienyl resonance. As a preliminary to an understanding of this phenomenon, the crystal and molecular structure of the ethyl xanthate complex was determined at −170 °C. The complex contains a η^5-C_5H_5 ring and a monodentate xanthate ligand. A variable-temperature study of the ^{1}H NMR spectrum of the ethyl xanthate complex is consistent with equilibration of two inequivalent conformers about the Ni–S bond. Another phase of this motion causes equivalence of the two diastereotopic methylene protons in the isomer found in the crystalline state. At higher temperatures, the temperature dependence of the C_5H_5 chemical shift reverses direction, consistent with the intervention of a second dynamic process. Experiments with added triphenylphosphine show that this second process is phosphine dissociation. It is argued, on the basis of the crystal structure and observations on the complex CpNi[P(*n*-Bu)$_3$]S_2COEt, that the occurrence and spectropscopic detectability of these processes are specific to phosphines bearing aromatic rings, particularly P(C_6H_5)$_3$.

Introduction

In the course of a program of synthesis and spectral characterization of a series of xanthate complexes of the type (C_5H_5)Ni(PR_3)(S_2COR'), we have observed unusual proton NMR behavior for those compounds where R = C_6H_5 and R′ = CH_3 or C_2H_5. Specifically, we observed broad resonances for the C_5H_5 protons in $CDCl_3$ or $C_6D_5CD_3$ at 25 °C; other ligand resonances are sharp. Several explanations of this behavior are possible. One involves a bidentate xanthate ligand along with a η^3-, but fluxional, cyclopentadienyl ligand. A second possibility is that the xanthate ligand is monodentate; in this case, the origin of the NMR phenomenon is not immediately evident.

We report here the results of an X-ray study of CpNi(PPh_3)(S_2COEt) which definitively settles the question of its solid-state structure. This work, along with the results of a variable-temperature proton NMR study, has revealed the molecular basis for the unusual features observed in the room-temperature NMR spectrum.

Experimental Section

General Methods. The (π-cyclopentadienyl)(triphenylphosphine)nickel chloride was prepared according to Rausch et al.[1] All manipulations were carried out under an argon atmosphere with redistilled solvents.

(C_5H_5)Ni(PPh_3)$S_2COC_2H_5$. A 100-mL Schlenk tube was charged with 0.842 g (2.0 mmol) of $C_5H_5Ni(PPh_3)Cl$ and 25 mL of acetone and was cooled to −30 °C. To the resulting solution was added 0.320 g (2.0 mmol) of $KS_2COC_2H_5$ in 20 mL of acetone slowly with stirring, causing an immediate color change from purple to red-brown. After 0.5 h, the solution was allowed to warm to 25 °C, and the solvent was removed under vacuum. The resulting solid was treated with 50 mL of Et_2O, and the solution was filtered to remove KCl. Concentration of the filtrate to 5–10 mL yielded black-brown crystals, which were filtered and washed with small portions of petroleum ether (bp 40–60 °C) and dried under vacuum: yield 0.45 g (45%); mp 103–104 °C. Anal. Calcd for $C_{26}H_{25}OPS_2Ni$: C, 61.53; H, 4.93; S, 12.22; Ni, 11.63; mol wt 507. Found: C, 61.52; H, 5.06; S, 12.56; Ni, 11.69; mol wt 511. ^{1}H NMR ($CDCl_3$): δ 1.43 (t, CH_3, J = 7.0 Hz), 4.43 (q, CH_2, J = 7.0 Hz), 4.75 (br, C_5H_5), 7.45 (m, C_6H_5).

(C_5H_5)Ni(PPh_3)S_2COCH_3. This complex was prepared as above by substituting KS_2COCH_3 for the ethyl salt: yield 0.51 g (52%); mp 107–108 °C. Anal. Calcd: C, 60.86; H, 4.66; S, 12.98; P, 6.28; Ni, 11.96; mol wt 493. Found: C, 60.58; H, 4.70; S, 13.02; P, 6.55; Ni, 11.60; mol wt 496. ^{1}H NMR ($CDCl_3$): δ 3.98 (s, CH_3), 4.72 (br, C_5H_5), 7.42 (m, C_6H_5). The mass spectrum showed ions due to $C_5H_5NiSCOCH_3^+$, $P(C_6H_5)_3^+$, and $SP(C_6H_5)_3^+$, as well as smaller fragments.

Both compounds are air stable and soluble in acetone, chloroform, CH_2Cl_2, C_6H_6, and Et_2O. They are only slightly soluble in petroleum ether and methanol and are insoluble in water. Both exhibit infrared absorptions which have been attributed to the R—O—C═S structure of a unidentate xanthate ligand.[2-6]

Table I. Crystal Data for (C_5H_5)Ni($S_2COC_2H_5$)[P(C_6H_5)$_3$]

empirical formula	$C_{26}H_{25}NiOPS_2$
cryst dimens	0.15 × 0.15 × 0.2 mm
space group	$P\bar{1}$
cell dimens (at −170 °C, 22 rflctns)	
a	14.710 (7) Å
b	9.566 (5) Å
c	9.777 (6) Å
α	116.53 (5)°
β	77.20 (6)°
γ	88.03 (5)°
molec/cell	2
vol	1186.23 Å^3
calcd density	1.42 g/cm^3
wavelength	0.710 69 Å
mol wt	507.29
linear abs coeff	10.721 cm^{-1}
tot no. of rflctns collected	3725
no. of unique intensities	3117
no. with $F > 0.0$	3038
no. with $F > \sigma(F)$	3026
no. with $F > 2.33\sigma(F)$	3004
final residuals	
R_F	0.078
R_{wF}	0.149
goodness of fit for last cycle	4.18
max Δ/σ for last cycle	0.29

Crystal Structure Determination. Unit cell dimensions and other parameters of the data collection appear in Table I. Intensity data were collected in the usual manner[7] at −170 °C in the range 4° ≤ 2θ ≤ 50° and were processed as described previously.[7] No absorption or extinction corrections were made. The structure was solved by direct methods (LSAM), and the heavy-atom positions were confirmed by Patterson techniques. Hydrogen atoms were poorly defined in difference maps and were therefore placed in calculated positions (B = 3.0 Å^2) for the final full-matrix refinement. The results of the structure determination are reported in Tables II–IV and Figures 1 and 2. Anisotropic B's and structure factors are available as supplementary material.

Distances and angles within the Ni$P(C_6H_5)_3$ unit are unexceptional. Carbon–carbon bond lengths within the phenyl rings are identical

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*To whom correspondence should be addressed at Indiana University.

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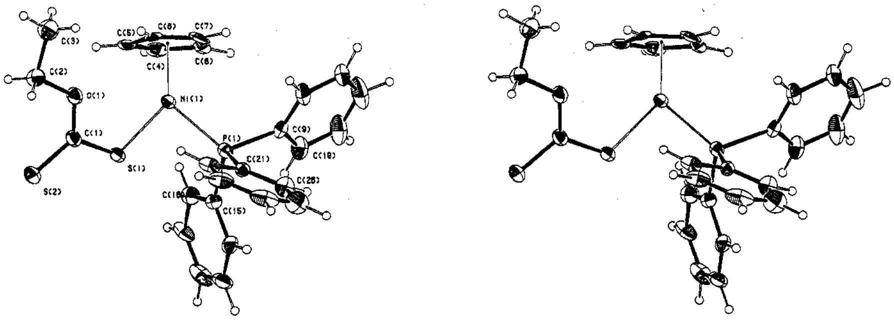

Figure 1. Stereoscopic drawing of the molecular structure of $(C_5H_5)Ni[P(C_6H_5)_3]S_2COC_2H_5$ viewed nearly perpendicular to the SNiP plane. Hydrogen atom thermal parameters have been artificially reduced.

Table II. Fractional Coordinates and Thermal Parameters[a] for $(C_5H_5)Ni(S_2COC_2H_5)[P(C_6H_5)_3]$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Ni	3407 (1)	3415 (1)	1220 (1)	16
S(1)	3066 (1)	5538 (2)	3538 (2)	20
S(2)	3195 (1)	6727 (2)	6822 (2)	24
P(1)	2055 (1)	3910 (2)	826 (2)	16
O(1)	3875 (4)	3834 (5)	4522 (5)	22
C(1)	3420 (5)	5258 (8)	4980 (8)	19
C(2)	4286 (5)	3552 (9)	5626 (8)	22
C(3)	4701 (6)	1848 (10)	4804 (10)	30
C(4)	4770 (5)	2793 (9)	−348 (9)	24
C(5)	4788 (5)	2609 (8)	997 (9)	23
C(6)	4213 (5)	1454 (8)	1041 (9)	23
C(7)	3831 (5)	985 (8)	−246 (9)	25
C(8)	4149 (5)	1826 (8)	−1094 (8)	20
C(9)	2001 (5)	2803 (8)	−1242 (8)	18
C(10)	1932 (6)	3579 (10)	−2143 (9)	28
C(11)	1966 (7)	2729 (12)	−3704 (10)	38
C(12)	2072 (7)	1111 (13)	−4419 (10)	45
C(13)	2099 (6)	330 (10)	−3502 (10)	36
C(14)	2055 (6)	1187 (9)	−1921 (10)	29
C(15)	1785 (5)	5967 (8)	1275 (8)	17
C(16)	859 (5)	6779 (9)	1886 (8)	23
C(17)	721 (6)	8308 (9)	2076 (9)	32
C(18)	1449 (7)	8998 (9)	1636 (9)	33
C(19)	2373 (6)	8200 (9)	1077 (9)	27
C(20)	2524 (5)	6685 (9)	907 (9)	24
C(21)	1015 (4)	3427 (8)	1905 (8)	15
C(22)	1085 (5)	3318 (8)	3249 (8)	22
C(23)	303 (5)	3005 (9)	4108 (9)	27
C(24)	−514 (6)	2770 (9)	3616 (10)	35
C(25)	−567 (6)	2873 (11)	2260 (11)	35
C(26)	236 (6)	3185 (10)	1396 (10)	31

[a] The isotropic thermal parameter listed for those atoms refined anisotropically is the isotropic equivalent.

within experimental error, as are the average values of each of the rings; the esd's based on a scatter formula are only about 50% larger than any individual esd, indicating the precision of those values. Within the cyclopentadienyl ring the C–C distances scatter by less than 3σ (average). The average angles within the five- and six-carbon rings are 108.0 and 120.0°, respectively. Cyclopentadienyl carbons deviate by less than 1.6σ from their least-squares plane. The ring midpoint, Ni, P(1), and S(1) deviate less than 0.01 Å from their least-squares plane, and the cyclopentadienyl ring makes an angle of 90.5° with this plane. The line Ni–M makes an angle of 89.9° with the cyclopentadienyl plane. The nickel–oxygen distance is greater than 3 Å. Intramolecular distances from nickel to the hydrogens on the ethyl and phenyl groups (with C–H fixed at 0.98 Å) all exceed 3.0 Å. All intermolecular contacts shorter than 3.0 Å involve at least one hydrogen atom; the shortest of these is a contact between two phenyl hydrogens (2.27 Å).

Results and Discussion

X-ray Structure Determination. The X-ray study establishes that the xanthate ligand in $CpNi(PPh_3)S_2COEt$ is monodentate in the solid state and that the cyclopentadienyl ligand is η^5 bonded. Discrete, coordinatively saturated (18-electron) molecules comprise the solid structure. While the Ni–C distances span a range of 0.036 Å (5σ), these variations appear

Table III. Bond Distances (Å) in $(C_5H_5)Ni(S_2COC_2H_5)[P(C_6H_5)_3]$

Ni	S(1)	2.197 (2)	C(9)	C(10)	1.398 (10)
Ni	P(1)	2.184 (2)	C(9)	C(14)	1.374 (11)
Ni	M[a]	1.717	C(10)	C(11)	1.359 (12)
Ni	C(4)	2.113 (7)	C(11)	C(12)	1.370 (14)
Ni	C(5)	2.077 (7)	C(12)	C(13)	1.406 (14)
Ni	C(6)	2.102 (7)	C(13)	C(14)	1.372 (12)
Ni	C(7)	2.091 (7)		av	1.380
Ni	C(8)	2.084 (7)	C(15)	C(16)	1.402 (10)
S(1)	S(2)	2.943 (3)	C(15)	C(20)	1.373 (11)
S(1)	C(1)	1.727 (7)	C(16)	C(17)	1.392 (11)
S(2)	C(1)	1.665 (7)	C(17)	C(18)	1.366 (13)
O(1)	C(1)	1.328 (8)	C(18)	C(19)	1.398 (12)
O(1)	C(2)	1.463 (8)	C(19)	C(20)	1.387 (11)
C(2)	C(3)	1.490 (11)		av	1.386
C(4)	C(5)	1.407 (11)	C(21)	C(22)	1.389 (10)
C(4)	C(8)	1.405 (11)	C(21)	C(26)	1.336 (11)
C(5)	C(6)	1.425 (11)	C(22)	C(23)	1.393 (10)
C(6)	C(7)	1.388 (11)	C(23)	C(24)	1.380 (13)
C(7)	C(8)	1.416 (11)	C(24)	C(25)	1.392 (13)
	av	1.408 (14)[b]	C(25)	C(26)	1.415 (12)
P(1)	C(9)	1.838 (7)		av	1.384
P(1)	C(15)	1.822 (7)	grand av = 1.383 (19)[b]		
P(1)	C(21)	1.854 (6)			
	av	1.838 (16)[b]			

[a] M is the midpoint of the cyclopentadienyl ring. [b] Esd's on average values are calculated by using the scatter formula $\sigma(\mathrm{av}) = [\Sigma(d_i - \bar{d})^2/(N - 1)]^{1/2}$ where d_i is one of N individual values and $\bar{d}$ is their average.

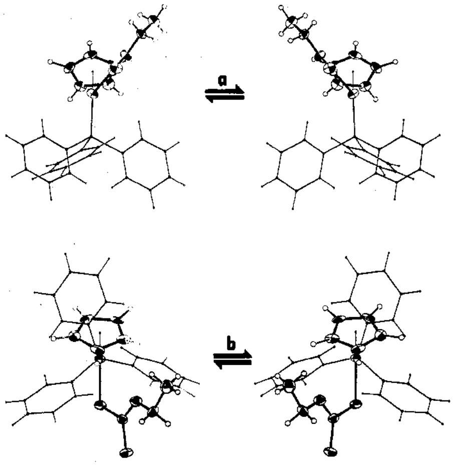

Figure 2. (a) Molecular structure of $CpNi(PPh_3)S_2COEt$ viewed down the Ni–S bond. The conformational process which interchanges the diastereotopic methylene protons is shown; note the concurrent rearrangement of the PPh_3 ligand. (b) The same process, viewed down the P–Ni bond, showing the placement of the cyclopentadienyl ring above the face of one phenyl ring.

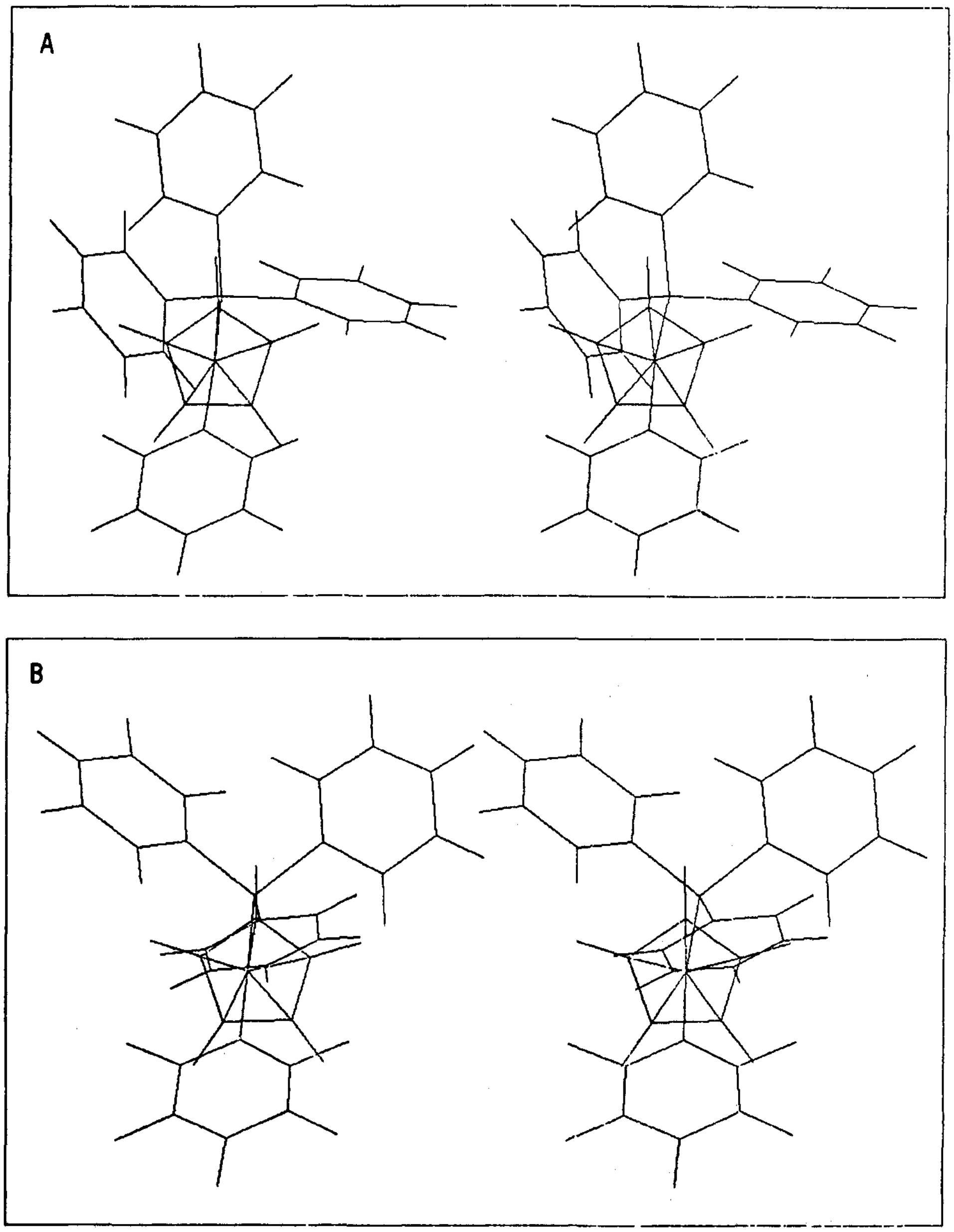

Figure 3. Stereoviews of the crystal structures of CpNi(PPh$_3$)C$_6$H$_5$ (A) and CpNi(PPh$_3$)C$_6$F$_5$ (B). These two structures differ primarily by a 60° rotation about the nickel–phosphorus bond.

to be random. There is no consistent pattern of "slipping" of this ring away from symmetrical metal–ring bonding. Likewise, the ring plane is not systematically tipped away from being perpendicular to a line from Ni to the ring midpoint. Both the average Ni–C distance and the observed variations are similar to those found in previous CpNi(PPh$_3$)R structures.[8-10] The Ni–P distance is longer (by as much as 0.046 Å) than that previously observed in other CpNi(PPh$_3$)R structures (R = CF$_3$, C$_6$F$_5$, C$_6$H$_5$). The angle at nickel between phosphorus and the variable ligand in CpNi(PPh$_3$)R compounds is 2–10° smaller in the xanthate in apparent response to the longer bond to sulfur.

Structural parameters of the monodentate xanthate ligand resemble those of others determined previously in M(S$_2$COEt)$_3^-$, with M = Cd,[11] Te,[12] and Sn(S$_2$COEt)$_n$ (n = 2[13] and 4[14]). All of these compounds, and the present one, share a rotational configuration about the S(coordinated)–C bond which places oxygen, not the second sulfur, in the nonbonded position nearest the metal. Since the Ni–O distance is clearly nonbonding, this conformation may be dictated by the smaller size of oxygen relative to sulfur. While the bond from carbon to the uncoordinated sulfur is clearly shorter than that to the other sulfur, these distances are neither as long (1.82 Å) nor as short (1.61 Å) as those in CH$_3$SH[15] or H$_2$CS,[16] respectively. The distance C(1)–O(1), 1.328 Å, while typical of those found in other monodentate xanthate ligands, is shorter than the corresponding distance to sp^2 carbon in methyl vinyl ether[17] [1.360 (3) Å]; taken together with the xanthate planarity and the 119.5° bond angle at O(1), significant C(1)–O(1) double-bond character is indicated. The CS lengthening and CO

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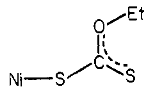
Table IV. Bond Angles (Deg) in (C_5H_5)Ni($S_2COC_2H_5$)[P(C_6H_5)$_3$]

S(1)	Ni	P(1)	91.7 (1)
M^a	Ni	P(1)	132.0
M^a	Ni	S(1)	136.3
Ni	S(1)	C(1)	113.7 (2)
Ni	P(1)	C(9)	114.3 (2)
Ni	P(1)	C(15)	112.1 (2)
Ni	P(1)	C(21)	116.2 (2)
C(9)	P(1)	C(15)	103.4 (3)
C(9)	P(1)	C(21)	102.2 (3)
C(15)	P(1)	C(21)	107.4 (3)
C(1)	O(1)	C(2)	119.5 (5)
S(1)	C(1)	S(2)	120.4 (4)
S(1)	C(1)	O(1)	116.3 (5)
S(2)	C(1)	O(1)	123.4 (5)
O(1)	C(2)	C(3)	106.8 (6)
C(5)	C(4)	C(8)	107.7 (6)
C(4)	C(5)	C(6)	108.6 (6)
C(5)	C(6)	C(7)	106.7 (7)
C(6)	C(7)	C(8)	109.5 (7)
C(4)	C(8)	C(7)	107.4 (6)
P(1)	C(9)	C(10)	120.9 (6)
P(1)	C(9)	C(14)	119.4 (5)
C(10)	C(9)	C(14)	119.7 (7)
C(9)	C(10)	C(11)	120.0 (8)
C(10)	C(11)	C(12)	120.9 (8)
C(11)	C(12)	C(13)	119.2 (8)
C(12)	C(13)	C(14)	119.9 (8)
C(9)	C(14)	C(13)	120.1 (8)
P(1)	C(15)	C(16)	122.3 (5)
P(1)	C(15)	C(20)	117.2 (5)
C(16)	C(15)	C(20)	120.3 (7)
C(15)	C(16)	C(17)	117.9 (7)
C(16)	C(17)	C(18)	122.0 (8)
C(17)	C(18)	C(19)	119.6 (7)
C(18)	C(19)	C(20)	119.0 (7)
C(15)	C(20)	C(19)	121.0 (7)
P(1)	C(21)	C(22)	117.3 (5)
P(1)	C(21)	C(26)	120.9 (5)
C(22)	C(21)	C(26)	121.8 (6)
C(21)	C(22)	C(23)	118.4 (7)
C(22)	C(23)	C(24)	120.9 (7)
C(23)	C(24)	C(25)	119.8 (7)
C(24)	C(25)	C(26)	118.6 (8)
C(21)	C(26)	C(25)	120.5 (7)

^{a} C_5H_5 ring midpoint.

shortening are consistent with the following delocalized structure:



The rotational configuration about the Ni–S bond (Figure 2a) is that found about the Ni–C bond in CpNi(PPh_3)CF_3[10] and involves a staggered relationship of the Cp ring and the xanthate (or F). In addition, these two compounds [and CpNi(PPh_3)C_6H_5, Figure 3A] share the same rotational conformation about the Ni–P bond (Figure 2b). This configuration staggers two phenyl rings with respect to the Ni–S (or Ni–CF_3) bond. As a result, one phenyl ring approximately eclipses the Cp ring; in particular, the cyclopentadienyl ring lies over the face of this phenyl ring. This has significant consequences for the ^{1}H NMR spectrum.

^{1}H NMR Studies. The proton NMR spectrum (100 and 220 MHz) of CpNi(PPh_3)S_2COEt in $CDCl_3$ at probe temperature shows a typical ethyl pattern and a complex phenyl resonance; these integrate to the expected 15:2:3 ratio, reading toward high field.

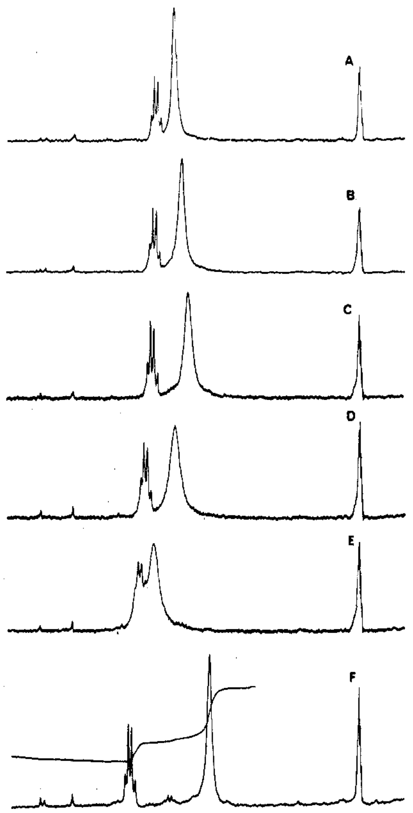
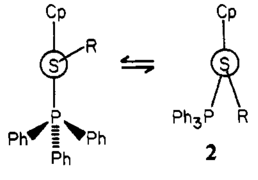


Figure 4. ^{1}H NMR spectra of the methylene and C_5H_5 protons of (C_5H_5)Ni[P(C_6H_5)$_3$]$S_2COCH_2CH_3$ in toluene-d_8 at various temperatures. The multiplet at far right is due to $C_6D_5CHD_2$: (A) 80 °C, (B) 70 °C, (C) 56 °C, (D) 29 °C, (E) 19 °C. Spectrum F is for the same sample as E (and at 19 °C), after addition of 2.2 equiv of PPh_3.

The sharp ^{1}H NMR methylene quartet in CpNi(PPh_3)S_2COEt contradicts the finding that these two protons are inequivalent in the solid state. The NMR equivalence of these diastereotopic protons indicates that *partial* rotation about the Ni–S bond (Figure 2) occurs rapidly at 25 °C.

In contrast, the cyclopentadienyl protons appear as a broadened peak at δ 4.75 ($CDCl_3$); $\nu_{1/2}$ = 11 Hz on the 220-MHz spectrometer (sample temperature 16 °C) and 6 Hz at 28 °C on a 100-MHz spectrometer. This same selective broadening is observed in the ^{1}H NMR spectrum of CpNi(PPh_3)S_2COMe.[18]

It is proposed that the line broadening is caused by an intermediate rate for the conformational equilibrium shown in eq 1. We attempted to observe sharp signals for conformers



1 2 (1)

R = C(S)OEt

(isomers) **1** and **2** directly by low-temperature ^{1}H NMR. At −35 °C in $CDCl_3$ (100 MHz) the C_5H_5 protons are indeed sharp,[19,20] but only one such resonance is observed; the methylene proton signal remains sharp. Thus, while the rate process (eq 1) has been slowed, the accompanying equilibrium shift has depopulated one isomer to the point where it is no

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(18) Assuming free rotation of the C_5H_5 ring, the conformational process shown in Figure 2 does not produce broadening of the ring-proton signal.

(19) This confirms the idea that the broadening is not really unresolved coupling to phosphorus. Such coupling has never been reported for CpNi(PR_3)X molecules; in CpNi(PPh_3)CN, an upper limit on *J*(PH) may be set at 0.2 Hz.[20]

(20) Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *96*, 99.

longer spectroscopically detectable. The altered equilibrium populations are evident in the reversible temperature dependence of the chemical shifts, however. The Cp resonance moves upfield 0.37 ppm on warming of the sample from −35 to +25 °C. In this temperature region, the methylene and methyl protons move only −0.08 and +0.06 ppm, respectively.

To complete our characterization of equilibrium 1, we extended our ^{1}H NMR measurements into the elevated-temperature region; it was anticipated that the C_5H_5 signal would sharpen and reach a constant chemical shift as the mole fractions of **1** and **2** approach 0.5. The spectra in Figure 4 (toluene solvent), which are reversible in temperature, continue to show an upfield shift of the C_5H_5 protons as the temperature rises, along with the expected line narrowing.[21] However, above 56 °C, this narrowing ceases, and the C_5H_5 chemical shift begins to move *slowly downfield*. This reversal of shift direction is clear evidence for the intervention of a second dynamic process which produces a new species whose cyclopentadienyl resonance is downfield of that of both conformers **1** and **2**. Moreover, both the later (i.e., higher temperature) appearance of this process and the reduced rate of chemical shift dependence are characteristic of a process of larger ΔG than that characteristic of eq 1.

We have established that this high-temperature process is phosphine dissociation (eq 2). Thus (Figure 4), addition of

$$\mathrm{CpNi(PPh_3)S_2COEt} \rightleftharpoons \mathrm{CpNiS_2COEt} + \mathrm{PPh_3} \quad (2)$$

2.2 equiv of PPh_3 to a toluene solution of $CpNi(PPh_3)S_2COEt$ at 16 °C causes the C_5H_5 resonance to *narrow* and *move upfield* 0.54 ppm (Figure 4E,F). This confirms the downfield chemical shift position of the high-temperature species, $CpNiS_2COEt$, deduced above and also establishes that the line broadening contains contributions from the processes in both eq 1 and eq 2.

We feel that we are correct in associating the kinetic processes with the xanthate ligand since the effect is entirely lacking in $CpNi(PPh_3)CN$,[20] where the anionic ligand has axial symmetry and is sterically compact. More properly, we feel that eq 1 is made observable by and is possibly due to the interaction of xanthate rotation with the bulky and magnetically anisotropic PPh_3 ligand. As is evident from the above discussion, the ring-proton chemical shifts in the two conformers must be significantly different to make eq 1 detectable by proton NMR. An enforced rotation about the Ni–P bond (with accompanying rotation about the P–C bonds) as the xanthate rotates between **1** and **2** provides a mechanism for creating such disparate Cp ring chemical shifts; it is the interaction of the phenyl ring with the C_5H_5 ring which makes both eq 1 and eq 2 detectable. To see that this is wholly plausible, one need only examine the known structures of $CpNi(PPh_3)C_6H_5$[9] (Figure 3A) and $CpNi(PPh_3)C_6F_5$[8] (Figure 3B). In **1** and in Figure 3A, the C_5H_5 protons reside above the face of one phenyl ring and are influenced by the associated ring current. In $CpNi(PPh_3)C_6F_5$ (Figure 3B), a rotation of 60° about the Ni–P bond relative to Figure 3A minimizes the cyclopentadienyl/phenyl separation. Thus, if conformer **2** has the PPh_3 orientation of $CpNi(PPh_3)C_6F_5$, its C_5H_5 chemical shift will differ significantly from that of **1**. The absence of aromatic rings in $CpNiS_2COEt$ should produce a substantial downfield displacement of the C_5H_5 chemical shift, as is observed. It has been observed,[22] without comment, that the benzyl protons of $CpFeCO(PR_3)(CH_2Ph)$ are well-resolved (0.8 ppm) when R = Ph but unresolved for R = CH_2Ph and OPh. Hindered rotation about the Ni–C(benzyl) bond has been observed in $CpNi(PPh_3)CH_2Ph$.[23]

The dramatic influence of aromatic molecules on the cyclopentadienyl ring proton chemical shift is also evident on comparison of the spectra of $CpNi(PPh_3)S_2COEt$ in $CDCl_3$ and $C_6D_5CD_3$. The Cp ring resonance is upfield of the xanthate methylene resonance in toluene (Figure 4), while the reverse is true in $CDCl_3$. The Cp, methyl, and methylene chemical shifts change by 0.85, 0.27, and 0.35 ppm on going to toluene as solvent at constant temperature (29 °C). The upfield shift of the ring protons is consistent with a face-to-face alignment of the Cp and toluene rings.

The claim that our ability to perceive (i.e., spectroscopically resolve) these kinetic processes is due to intramolecular aromatic-induced shifts is subject to further test. Addition of excess tri-*n*-butylphosphine to a toluene solution of $CpNi(PPh_3)S_2COEt$ at 25 °C (eq 3) immediately produces a new

$$\mathrm{CpNi(PPh_3)S_2COEt} + \mathrm{P}(n\text{-Bu})_3 \rightarrow \mathrm{CpNi[P}(n\text{-Bu})_3]\mathrm{S_2COEt} + \mathrm{PPh_3} \quad (3)$$

5:2:3 ^{1}H NMR intensity pattern due to C_5H_5, CH_2, and CH_3 protons; none of the triphenylphosphine complex remains. The C_5H_5 resonance of the resultant complex (eq 3) is sharp and occurs at δ 5.11, or 0.9 ppm *down*field from that of the PPh_3 complex. Thus, $CpNi[P(n\text{-}Bu)_3]S_2COEt$ gives no evidence for phosphine dissociation or conformational equilibration.

Conclusion

Complexes of the form $CpNi(PPh_3)X$ are particularly suitable for detailed NMR observation of conformational (eq 1) and dissociative (eq 2) processes. The triphenylphosphine ligand is sufficiently bulky that it causes hindered (and probably coupled) internal rotation and also promotes phosphine dissociation. At the same time, intramolecular ring currents created by the aryl rings on the phosphine magnify normally small differences in the chemical shifts of the equilibrating species, making these processes more readily detectable. The observation of similar phenomena in $CpFeCO(PPh_3)CH_2Ph$[22,24] indicates that this may be a rather general characteristic of the $CpML_n(PPh_3)X$ molecular class.

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Registry No. $(C_5H_5)Ni(PPh_3)S_2COC_2H_5$, 73193-01-8; $(C_5H_5)Ni(PPh_3)S_2COCH_3$, 73178-93-5; $(C_5H_5)Ni(PPh_3)Cl$, 31904-79-7; $(C_5H_5)Ni[P(n\text{-}Bu)_3]S_2COC_2H_5$, 52247-33-3.

Supplementary Material Available: Listings of calculated and observed structure factors and anisotropic thermal parameters (30 pages). Ordering information is given on any current masthead page.

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