Synthesis of Extremely Stable Alkylpalladium Complexes of the Type (Me₂NCS₂)Pd(PEt₃)(alkyl). Crystal and Molecular Structures of the Isomers (C̄H₂CH₂CH₂CH₂N̄CS₂)Pd(PEt₃)(*n*-propyl) and (C̄H₂CH₂CH₂CH₂N̄CS₂)Pd(PEt₃)(isopropyl)

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The reaction of (R₂NCS₂)Pd(PEt₃)Cl (R = Me, R₂ = -(CH₂)₄-) with alkyllithium or Grignard reagents leads to the preparation of (R₂NCS₂)Pd(PEt₃)(alkyl) (alkyl = methyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl) complexes. These alkylpalladium complexes can be heated in solution at 60 °C without decomposition and thus appear to be the most thermally stable complexes containing an acyclic alkyl ligand with β-hydrogen atoms to be reported for this metal. The solid-state structures of (C̄H₂CH₂CH₂CH₂N̄CS₂)Pd(PEt₃)(*n*-propyl) (1) and (C̄H₂CH₂CH₂CH₂N̄CS₂)Pd(PEt₃)(isopropyl) (2) have been determined by X-ray crystallography. Crystal data: 1, monoclinic, $P2_1/n$, a = 8.227 (2) Å, b = 17.807 (4) Å, c = 13.299 (3) Å, β = 96.60 (2)°, V = 1948 Å³, Z = 4, R_F = 3.4%, and R_{wF} = 4.5%; 2, monoclinic, $P2_1/n$, a = 11.021 (3) Å, b = 17.836 (5) Å, c = 9.694 (3) Å, β = 94.81 (2)°, V = 1906 Å³, Z = 4, R_F = 2.8%, and R_{wF} = 3.5%. The square-planar geometry of each complex is very similar. The main difference in the two structures is the longer Pd–S distance trans to the alkyl ligand in 2 indicating a greater trans influence for the isopropyl ligand. There are minimal intramolecular steric contacts between the alkyl ligand and the ancillary ligands, even for the bulkier isopropyl ligand.

Introduction

The investigation of the synthesis and reactivity of alkylmetal complexes is central to the understanding of many processes catalyzed by transition metals.[1] An area of continuing interest to us has been the relative stability of various types of alkyl ligands σ bonded to a transition metal. We have investigated this relative stability by studying the position of alkyl isomerization reactions of alkylmetal complexes. For example, the complex CpFe-CO(PPh₃)(*sec*-butyl) isomerizes completely to CpFeCO-(PPh₃)(*n*-butyl) when heated in solution at 65 °C.[2] Thus, the primary isomer is more stable than the secondary isomer for these sterically hindered alkylmetal complexes. A number of other alkyl isomerization reactions have been reported also.[3-6] With one exception,[3b] the systems that have been studied previously have a significant contribution to the position of the isomerization reaction from the steric effects of the bulky ancillary ligands, an effect clearly favoring the primary isomers.

We have communicated results on a new series of palladium and platinum complexes of the general formula (R₂NCS₂)M(PR′₃)(alkyl) (R = Me, Et; R′ = Et, Ph) that will undergo the alkyl isomerization but that have minimal steric influences from the ancillary ligands. An exmple is shown in eq 1.[7] At equilibrium, both isomers are observed

$$(1)$$
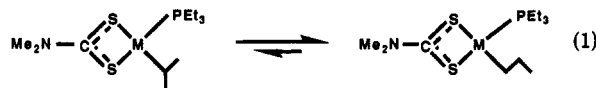
in a ratio of 9:1.0 for platinum and 10:1.0 for palladium. Also, the primary/secondary ratio of the equilibrium is not influenced by changing the phosphine ligand from PEt₃ to PPh₃ or the alkyl ligand from propyl to butyl.

Reported here is the synthesis and characterization of the palladium complexes (Me₂NCS₂)Pd(PEt₃)(alkyl). These complexes are the most thermally stable simple alkyl derivatives containing β-hydrogen atoms that have been prepared for this metal. We also report the solid-state structures as determined by X-ray crystallography for the isomers (C̄H₂CH₂CH₂CH₂N̄CS₂)Pd(PEt₃)(*n*-propyl) (1) and (C̄H₂CH₂CH₂CH₂N̄CS₂)Pd(PEt₃)(isopropyl) (2). These structures offer a unique opportunity to compare linear and branched isomers in complexes for which there is minimal steric crowding from the ancillary ligands on the metal.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere by using either standard Schlenk techniques or a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. The ¹H and ³¹P NMR spectra were recorded on either a Bruker AM-300 or a Bruker AM-500 spectrometer using a 5-mm broad-band probe. All spectra were recorded at ambient temperature. Proton chemical shifts are reported in ppm downfield from TMS. The triethylphosphine proton resonances are seen as a pentet (1:4:6:4:1) centered at 1.5 ppm (doublet of quartets for the CH₂ resonance (J_{HP} = 8 Hz, J_{HH} = 8 Hz)) and a pentet (1:2:2:2:1) centered at 0.9 ppm (doublet of triplets for the CH₃ resonance (J_{HP} = 16 Hz, J_{HH} = 8 Hz)) and are not listed for each individual complex.

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Phosphorus chemical shifts are reported in ppm downfield from H_3PO_4. All phosphorus spectra were run with proton decoupling. Elemental analyses were performed by Robertson Laboratories, Inc. $(R_2NCS_2)Pd(PEt_3)Cl$ (R = Me, R_2 = $-(CH_2)_4-$) was prepared via metathesis of the appropriate dichloro bis(phosphine)[8a] and bis(dithiocarbamato)[8b] complexes in refluxing toluene for 24 h. Alkyllithium reagents and Grignard reagents were purchased from Aldrich Chemical Co. and used as received.

(Dimethyldithiocarbamato)methyl(triethylphosphine)-palladium(II), $(Me_2NCS_2)Pd(PEt_3)Me$. $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.19 g, 0.50 mmol) was dissolved in THF (10 mL), and the solution was cooled to -78 °C. Methyllithium (0.55 mL, 1.0 M, 0.55 mmol) was added dropwise, and the mixture was allowed to warm to room temperature (1 h). The THF was removed under vacuum, and the solid was extracted with hexane (3 × 4 mL). The hexane solution was placed in a freezer at -30 °C overnight to yield pale yellow crystals (0.12 g, 0.33 mmol, 67%); mp = 85.5-87 °C. ¹H NMR (C_6D_6): δ 2.71, 2.69 (s, s; 3, 3; NCH_3); δ 0.83 (d; 3; J_{HP} = 4 Hz; $PdCH_3$). ³¹P NMR (C_6D_6): δ 25.5. Anal. Calcd for $C_{10}H_{24}NPPdS_2$: C, 33.37; H, 6.67. Found: C, 33.44; H, 6.67.

(Dimethyldithiocarbamato)-n-propyl(triethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PEt_3)(\eta^1-CH_2CH_2CH_3)$. $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.11 g, 0.29 mmol) was dissolved in THF (10 mL), and the solution was cooled to -78 °C. n-Propylmagnesium chloride (0.16 mL, 2.0 M, 0.32 mmol) was added dropwise, and the mixture was allowed to warm to room temperature (1 h). The THF was removed under vacuum, and the solid was extracted with hexane (3 × 4 mL). The hexane solution was placed in a freezer at -30 °C overnight to yield 0.070 g (0.18 mmol, 62%) of tan needles; mp = 75-77 °C. ¹H NMR (C_6D_6): δ 2.74, 2.72 (s, s; 3, 3; NCH_3); δ 2.09, 1.67 (m, m; 2, 2; $PdCH_2CH_2CH_3$); δ 1.34 (m; 3; $PdCH_2CH_2CH_3$). ³¹P NMR (C_6D_6): δ 24.4. Anal. Calcd for $C_{12}H_{28}NPPdS_2$: C, 37.16; H, 7.28. Found: C, 37.10; H, 7.20.

(Dimethyldithiocarbamato)isopropyl(triethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PEt_3)(\eta^1-CH(CH_3)_2)$. This complex was prepared as above for the n-propyl analogue in 62% yield; mp = 120-122 °C dec. ¹H NMR $(CDCl_3)$: δ 3.37, 3.33 (s, s; 3, 3; NCH_3); δ 1.9 (m; 1; $PdCH$); δ 1.2 (m; 6; $PdCH(CH_3)_2$). ³¹P NMR (C_6D_6): δ 23.6. Anal. Calcd for $C_{12}H_{28}NPPdS_2$: C, 37.16; H, 7.28. Found: C, 36.96; H, 7.19.

(Dimethyldithiocarbamato)-n-butyl(triethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PEt_3)(\eta^1-CH_2CH_2CH_2CH_3)$. This complex was prepared as above for the n-propyl analogue in 80% yield; mp = 60-61 °C. ¹H NMR $(CDCl_3)$: δ 3.33, 3.29 (s, s; 3, 3; NCH_3); δ 1.5, 1.3 (m, m; 2, 4; $PdCH_2CH_2CH_2CH_3$); δ 0.81 (t; 3; $PdCH_2CH_2CH_2CH_3$; J_{HH} = 7 Hz). ³¹P NMR $(CDCl_3)$: δ 25.0. Anal. Calcd for $C_{13}H_{30}NPPdS_2$: C, 38.86; H, 7.52. Found: C, 39.02; H, 7.70.

(Dimethyldithiocarbamato)-sec-butyl(triethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PEt_3)(\eta^1-CH_2(CH_2CH_3)CH_3)$. This complex was prepared as above for the methyl analogue in 65% yield; mp = 123-124 °C dec. ¹H NMR $(CDCl_3)$: δ 3.34, 3.30 (s, s; 3, 3; NCH_3); δ 1.7, 1.1 (m, m; 3, 3; $PdCH(CH_2CH_3)CH_3$); δ 1.01 (t; 3; $PdCH(CH_2CH_3)CH_3$; J_{HH} = 7 Hz). ³¹P NMR $(CDCl_3)$: δ 23.2. Anal. Calcd for $C_{13}H_{30}NPPdS_2$: C, 38.86; H, 7.52. Found: C, 38.85; H, 7.67.

(Pyrrolidinecarbodithioato)-n-propyl(triethylphosphine)palladium(II), $(CH_2CH_2CH_2CH_2NCS_2)Pd(PEt_3)(\eta^1-CH_2CH_2CH_3)$ (1). This complex was prepared as above for the dimethyldithiocarbamato analogue from $(CH_2CH_2CH_2CH_2NCS_2)Pd(PEt_3)Cl$ and n-propylmagnesium chloride. In the purification procedure, the flask containing the hexane solution was placed in a room-temperature salt bath and the flask and bath were placed in a refrigerator (-5 °C) overnight to yield pale yellow prisms (0.059 g, 0.14 mmol, 59%) suitable for X-ray crystallography; mp = 130-131 °C dec. ¹H NMR (C_6D_6): δ 3.4 (m; 4; $CH_2CH_2CH_2CH_2N$); δ 2.1, 1.7 (m, q; 2, 2; $PdCH_2CH_2CH_3$); δ 1.4 (m; 3; $PdCH_2CH_2CH_3$); δ 1.0 (s (broad); 4; $CH_2CH_2CH_2CH_2N$). ³¹P NMR (C_6D_6): δ 24.6. Anal. Calcd for $C_{14}H_{30}NPPdS_2$: C, 40.61; H, 7.30. Found: C, 40.47; H, 7.35.

Table I. Crystallographic Data for the Structural Analysis of 1 and 2

	1	2
formula	$C_{14}H_{30}NPPdS_2$	$C_{14}H_{30}NPPdS_2$
mol wt	413.9	413.9
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	8.227 (2)	11.021 (3)
b, Å	17.807 (4)	17.836 (5)
c, Å	13.299 (3)	9.694 (3)
β, deg	96.60 (2)	94.81 (2)
V, Å³	1948	1906
Z	4	4
cryst size, mm	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.2
monochromator	graphite	
radiation (λ, Å)	Mo Kα (0.710 73)	
ρ_{calc}, g cm⁻¹	1.409	1.448
temp	ambient	
2θ range, deg	4-50 (+h,+k,±l)	
no. of rflns measd	3436	3465
no. of rflns obsd	3342	3277
linear abs coeff, cm⁻¹	12.27	12.49
transm factors		
max	1.336	1.220
min	0.780	0.862
av	0.996	0.993
decay cor		
max	1.081	1.082
av	1.036	1.040
R_F	0.034	0.028
R_{wF}	0.045	0.035

Table II. Positional Parameters for $(CH_2CH_2CH_2CH_2NCS_2)Pd(PEt_3)(n$-propyl) with Estimated Standard Deviations in Parentheses

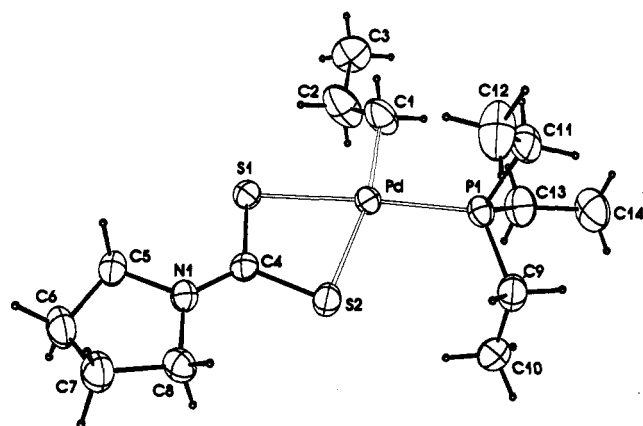| atom	x	y	z	B, Å²
Pd	0.22922 (5)	0.09026 (2)	0.23276 (3)	5.117 (8)
S1	0.2566 (2)	-0.01739 (7)	0.1293 (1)	5.87 (3)
S2	0.1831 (2)	0.13383 (8)	0.0606 (1)	6.71 (4)
P1	0.2114 (2)	0.19823 (8)	0.3171 (1)	5.69 (3)
N1	0.2329 (5)	0.0225 (2)	-0.9656 (3)	5.33 (9)
C1	0.286 (1)	0.0352 (4)	0.3674 (5)	10.9 (2)
C2	0.225 (1)	-0.0358 (5)	0.3814 (6)	13.3 (3)
C3	0.258 (1)	-0.0775 (4)	0.4766 (6)	11.0 (2)
C4	0.2244 (5)	0.0435 (3)	0.0278 (4)	5.1 (1)
C5	0.2696 (7)	-0.0545 (3)	-0.2090 (5)	8.7 (2)
C6	0.2438 (8)	-0.0490 (4)	-0.2090 (5)	8.7 (2)
C7	0.2591 (8)	0.0306 (4)	-0.2386 (5)	8.6 (2)
C8	0.2042 (8)	0.0740 (3)	-0.1528 (4)	6.9 (1)
C9	0.1388 (9)	0.2775 (3)	0.2398 (5)	7.9 (2)
C10	-0.0402 (9)	0.2711 (4)	0.1946 (6)	9.8 (2)
C11	0.4061 (8)	0.2311 (4)	0.3805 (5)	9.1 (2)
C12	0.5374 (9)	0.2328 (4)	0.3134 (7)	13.6 (2)
C13	0.0800 (9)	0.1960 (4)	0.4195 (5)	9.5 (2)
C14	0.072 (1)	0.2662 (5)	0.4788 (6)	12.1 (2)

(Pyrrolidinecarbodithioato)isopropyl(triethylphosphine)palladium(II), $(CH_2CH_2CH_2CH_2NCS_2)Pd(PEt_3)(\eta^1-CH(CH_3)_2$ (2). This complex was prepared as above for the n-propyl analogue in a 40% yield of yellow crystals; mp = 130-132 °C dec. ¹H NMR (C_6D_6): δ 3.5 (m; 4; $CH_2CH_2CH_2CH_2N$); δ 1.98 (doublet of septets; 1; $PdCH(CH_3)_2$); δ 1.72 (d of d; 6; $PdCH(CH_3)_2$; J_{HH} = 7 Hz, J_{PH} = 2 Hz); δ 1.1 (m; 4; $CH_2CH_2CH_2CH_2N$). ³¹P NMR (C_6D_6): δ 23.8. Anal. Calcd for $C_{14}H_{30}NPPdS_2$: C, 40.61; H, 7.30. Found: C, 40.67; H, 6.91.

Crystallographic Analysis of 1 and 2. Yellow prismatic crystals of both 1 and 2 were mounted in a thin-walled capillary tube on a CAD-4 diffractometer. The unit cells were determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analyses are listed in Table I. Data were collected in the ω/2θ scan mode with 0.7° + (0.35 tan θ)° scan range. The structure was solved by the heavy-atom method and refined by using SDP.[9] Hydrogen atoms were placed

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(9) Frenz, B. A. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1983.

Table III. Positional Parameters for (CH₂CH₂CH₂CH₂NCS₂)Pd(PEt₃)(isopropyl) with Estimated Standard Deviations in Parentheses

atom	x	y	z	B, Å²
Pd	0.21259 (3)	0.16101 (2)	0.22542 (4)	3.752 (6)
S1	0.1007 (1)	0.06039 (7)	0.3183 (1)	4.78 (3)
S2	0.0308 (1)	0.14344 (7)	0.0673 (1)	4.44 (3)
P1	0.3015 (1)	0.25665 (7)	0.1229 (1)	4.39 (3)
N1	-0.1030 (3)	0.0329 (2)	0.1573 (4)	3.80 (8)
C1	0.3006 (6)	0.1869 (4)	0.5170 (6)	7.5 (2)
C2	0.3511 (5)	0.1612 (3)	0.3840 (5)	5.5 (1)
C3	0.4061 (6)	0.0829 (4)	0.3974 (8)	9.4 (2)
C4	-0.0033 (4)	0.0736 (2)	0.1793 (4)	3.59 (9)
C5	-0.1390 (5)	-0.0271 (3)	0.2496 (5)	5.2 (1)
C6	-0.2717 (5)	-0.0369 (4)	0.2059 (6)	7.7 (2)
C7	-0.2911 (5)	-0.0134 (3)	0.0593 (6)	6.3 (1)
C8	-0.1932 (4)	0.0444 (3)	0.0396 (5)	4.4 (1)
C9	0.2912 (5)	0.3457 (3)	0.2102 (6)	6.2 (1)
C10	0.1616 (6)	0.3710 (4)	0.2229 (7)	8.4 (2)
C11	0.2309 (5)	0.2719 (3)	-0.0521 (5)	6.5 (1)
C12	0.2788 (7)	0.3357 (4)	-0.1350 (7)	11.3 (2)
C13	0.4648 (5)	0.2515 (4)	0.1030 (7)	7.1 (2)
C14	0.4999 (6)	0.1791 (5)	0.035 (1)	12.3 (2)

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for (CH₂CH₂CH₂CH₂NCS₂)Pd(PEt₃)(n-propyl) (1) and (CH₂CH₂CH₂CH₂NCS₂)Pd(PEt₃)(isopropyl) (2) with Estimated Standard Deviations in Parentheses

	1		2
Bond Distances			
Pd-C1	2.048 (5)	Pd-C2	2.074 (4)
Pd-P1	2.238 (1)	Pd-P1	2.241 (1)
Pd-S1	2.384 (2)	Pd-S1	2.395 (1)
Pd-S2	2.406 (1)	Pd-S2	2.439 (1)
S1-C4	1.727 (4)	S1-C4	1.710 (4)
S2-C4	1.710 (4)	S2-C4	1.714 (4)
N1-C4	1.306 (4)	N1-C4	1.320 (5)
N1-C5	1.473 (5)	N1-C5	1.472 (5)
N1-C8	1.476 (5)	N1-C8	1.463 (5)
C1-C2	1.377 (7)	C1-C2	1.517 (7)
C2-C3	1.467 (8)	C2-C3	1.525 (7)
Bond Angles			
S1-Pd-S2	74.02 (4)	S1-Pd-S2	73.63 (4)
S1-Pd-P1	174.24 (5)	S1-Pd-P1	174.30 (4)
S1-Pd-C1	95.3 (2)	S1-Pd-C2	95.3 (1)
S2-Pd-P1	100.85 (4)	S2-Pd-P1	100.71 (4)
S2-Pd-C1	169.0 (2)	S2-Pd-C2	168.9 (1)
P1-Pd-C1	89.7 (2)	P1-Pd-C2	90.4 (1)
Pd-C1-C2	120.5 (4)	Pd-C2-C1	109.3 (3)
		Pd-C2-C3	108.9 (3)
Pd-S1-C4	86.1 (1)	Pd-S1-C4	86.2 (1)
Pd-S2-C4	85.7 (1)	Pd-S2-C4	84.7 (1)
C1-C2-C3	123.1 (6)	C1-C2-C3	112.1 (5)
S1-C4-S2	114.0 (2)	S1-C4-S2	115.5 (2)
S1-C4-N1	123.0 (3)	S1-C4-N1	123.1 (3)
S2-C4-N1	123.0 (4)	S2-C4-N1	121.4 (3)
Pd-P1-C9	114.9 (2)	Pd-P1-C9	114.4 (2)
Pd-P1-C11	113.8 (2)	Pd-P1-C11	110.9 (2)
Pd-P1-C11	115.6 (2)	Pd-P1-C13	118.6 (2)

**Figure 1.** ORTEP drawing of [CH₂CH₂CH₂CH₂NCS₂]Pd-(PEt₃)(n-propyl)

in calculated positions and not refined. Full-matrix least-squares refinements were carried out with weights $w = (\sigma^2(F) + 0.0004F^2)^{-1}$ for reflections with $I > 3\sigma(I)$, where $\sigma(I)$ was derived from counting statistics. Absorption correction were by the method of Walker and Stuart.[10] Table II shows atomic parameters for 1, and Table III, those for 2.

Results

The starting materials for the preparation of the alkylpalladium complexes, (R₂NCS₂)Pd(PEt₃)Cl (R = Me, R₂ = -(CH₂)₄-), are prepared in high yield from an exchange reaction of the bis(phosphine) and bis(dithiocarbamato) complexes (eq 2). This chloride reacts with

$$Pd(PEt_3)_2Cl_2 + Pd(R_2NCS_2)_2 \longrightarrow 2[R_2NCS_2]Pd(PEt_3)Cl \quad (2)$$

alkyllithium or Grignard reagents to produce the alkylpalladium complexes in good yield (eq 3). In general, the
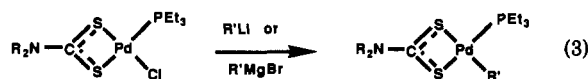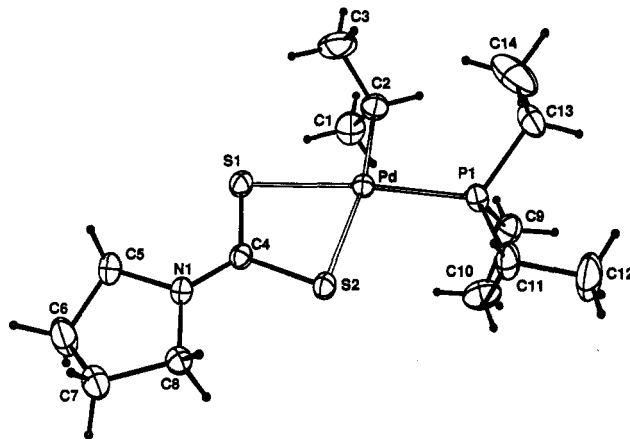

R' = Me, n-propyl, isopropyl, n-butyl, sec-butyl

reactions proceed better with the Grignard reagents but are very clean for both reagents. Yields are comparable for both the linear and branched alkyls with isolated yields reflecting the solubility properties.

(10) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

Figure 2. ORTEP drawing of [CH₂CH₂CH₂CH₂NCS₂]Pd-(PEt₃)(isopropyl)

The new alkylpalladium complexes are soluble in hexane and other common organic solvents. The solids only slowly decompose in air, but decomposition in solution is rapid in air. The complexes can be heated in degassed toluene at 60 °C for extended periods without noticeable decomposition. At 75 °C, slow decomposition is noted as well as the isomerization reaction shown in eq 1.

Molecular Structures of 1 and 2. In order to definitively characterize a pair of linear and branched isomers that undergo the alkyl isomerization reaction, the solid-state structures of the isomers (CH₂CH₂CH₂CH₂NCS₂)-Pd(PEt₃)(η^1-CH₂CH₂CH₃) (1) and (CH₂CH₂CH₂CH₂N-CS₂)Pd(PEt₃)(η^1-CH(CH₃)₂) (2) have been determined crystallographically. The pyrrolidine group of the dithiocarbamate ligand aids in the formation of crystallographic quality crystals.
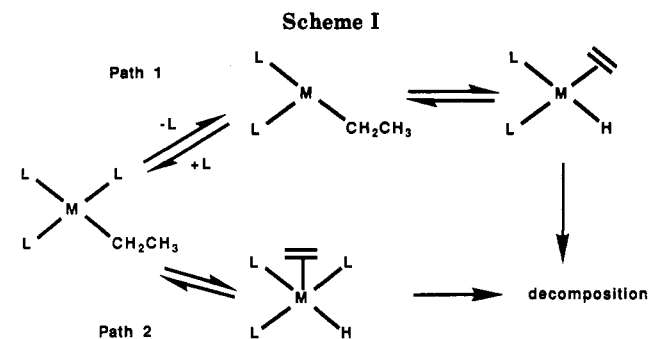
ORTEP drawings of 1 and 2 are shown in Figures 1 and 2, and bond distances and angles are shown in Table IV. Both complexes are four-coordinated with no close intermolecular contacts. The overall structures of the two complexes are very similar. The basic geometry about palladium is square planar. The largest deviation from the Pd and donor atoms plane is in 1, where the palladium atom is 0.0441 (4) Å out of the least-squares plane. For 2, the palladium atom is only 0.018 (3) Å out of this plane. The S1–Pd–S2 bond angle is, as expected,[11] restricted by the chelate ring to 74.02 (4) and 73.63 (4)° in 1 and 2, respectively. This causes the S2–Pd–P1 angle to open to 100.85 (4)° for 1 and 100.71 (4)° for 2 and the S1–Pd–C angle to open to 95.3 (2)° for each structure. The remaining angle in the square plane, P1–Pd–C, is nearly 90° for both structures.

The Pd–C1 bond distance in 1 of 2.048 (5) Å is in the range typically found for a C(sp^3)–Pd σ bond.[12] The Pd–S2 bond distance trans to the alkyl ligand is longer (2.406 (1) Å) than the cis Pd–S1 distance (2.384 (1) Å). This difference reflects the greater trans influence of the Pd–C σ bond. In the branched alkyl isomer 2, the Pd–C2 bond distance is 2.074 (4) Å. The trans influence of the branched alkyl ligand is *greater* than the linear isomer as indicated by the 2.439 (1) Å Pd–S2 bond length, which is 0.033 Å longer than the analogous distance in 1. The nearly identical Pd–P1 distances in the two structures supports the contention that this Pd–S2 difference is meaningful. The Pd–S1 distance is also slightly longer in 2 by 0.011 Å, but the difference between the Pd–S1 and Pd–S2 distances is greater in 2 (0.044 Å) than in 1 (0.022 Å), again reflecting the greater trans influence of the isopropyl ligand.

An important reason to determine these two structures is to confirm the contention made from our equilibrium studies[7a] that the ancillary ligands do not have a significant steric influence on the alkyl ligand, even for a secondary alkyl ligand as in 2. This point is also important to the comparison of the Pd–C bond lengths in the two structures made above. There are no close intramolecular contacts between the alkyl ligand and any other atoms in either structure. The S1···C1 and P1···C1 distances in 1 are 3.284 (5) and 3.024 (5) Å, and the analogous S1···C2 and P1···C2 distances for 2 are 3.311 (5) and 3.062 (5) Å. In both structures, the β-carbon atoms of the alkyl ligand are rotated toward the adjacent sulfur atom, S1, and straddle the square plane of the metal and donor atoms. In 1, the S1Pd–C1C2 torsion angle is –41.1 (7)° and the analogous S1Pd–C2C1 and S1Pd–C2C3 torsion angles in 2 are –67.4 (4) and 55.4 (4)°. The distance in 1 from the β-carbon, C2, to S1 is 3.407 (6) Å, and from the two β-carbon atoms in 2 these distances are 3.598 (6) Å for C1 and 3.413 (6) Å for C3. All contacts in both isomers between the alkyl ligand and the ethyl groups on the PEt₃ ligand are greater than 3.58 Å.

In the structure of 1, the Pd–C1–C2 and C1–C2–C3 angles are large at 120.5 (4) and 123.1 (6)° and the C1–C2 and C2–C3 bond distances short (normal C(sp^3)–C(sp^3) bond length is 1.54 Å) at 1.377 (7) and 1.447 (8) Å. These values probably reflect disorder of the propyl ligand, as indicated by the large thermal factors for C1 and C2. In contrast, the isopropyl ligand in 2 has normal Pd–C–C bond angles of 109.3 (3) and 108.9 (3)°, a C1–C2–C3 angle

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Scheme I

of 112.1 (5)°, C–C bond lengths of 1.517 (7) and 1.525 (7) Å, and lower thermal factors for the carbon atoms of the isopropyl ligand.

Discussion

The (R₂NCS₂)Pd(PEt₃)(alkyl) derivatives reported here appear to be the most thermally stable complexes containing an acyclic alkyl ligand with β-hydrogen atoms to be reported for this metal. For comparison, the complexes *cis-* and *trans*-[Pd(Et)₂(PMe₂Ph)₂] decompose in solution at room temperature and are too unstable for microanalysis.[13] Pd(DPPE)(Et)₂ decomposes rapidly in solution by 60 °C.[14] CpPd(PPh₃)(butyl) decomposes in solution at 35 °C, and CpPd(PPh₃)(CH₂CH₂CH(COMe)₂), at 50 °C.[15] Given the large number of less stable alkylpalladium phosphine complexes, it is clear that the stability of these new complexes can be attributed to the dithiocarbamate ligand. It is well recognized that sulfur forms strong bonds with the "soft" palladium(II) center, and this stability, in comparison to oxygen, has been suggested to arise from back-bonding from the metal to the sulfur donor atoms.[16]

Stability for alkylmetal complex containing β-hydrogen atoms is believed to be related to kinetic factors.[1] These types of complexes decompose by a β-elimination process, a reaction that is generally a low-energy process for palladium(II). Two β-elimination mechanisms have been proposed for square-planar palladium and platinum alkyls (Scheme I): (1) dissociation of ligand (generally a phosphine ligand) followed by β-elimination from the 14-electron, three-coordinate intermediate;[17] (2) direct β-elimination from the 16-electron complex to yield a five-coordinate intermediate.[18]

While we do not, at present, know the mechanism of decomposition of these complexes, the dithiocarbamate ligand could stabilize either the 14-electron intermediate or the 16-electron ground state with respect to the β-elimination reaction by partially filling the empty palla-

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dium orbitals by π *donation* of electron density from the sulfur atoms to palladium. Thus, the sulfur donor ligands may stabilize palladium alkyls because of the formation of strong S–Pd bonds and the donation of electron density to empty palladium orbitals blocking the β-elimination process.

The crystal structures of the isomers 1 and 2 offer a unique opportunity to compare the bonding of a linear and branched alkyl ligand in a metal complex in which there is *minimal steric influences from the ancillary ligand.* The most important conclusion that can be made from the two structures is that they are very similar; changing from a primary to a secondary alkyl ligand has only a small structural effect. It is known that primary alkyls are generally much easier to prepare in most transition-metal systems.[1] For the $(R_2NCS_2)M(PEt_3)$(alkyl) (M = Pd, Pt) complexes, the ease of preparation and thermal stability of the primary and secondary isomers are very similar. Thus, we conclude that in other systems the primary alkyl isomers are generally easier to prepare because steric crowding from the ancillary ligands destabilizes secondary alkylmetal complexes.

Another interesting feature of the structures is the greater trans influence of the isopropyl ligand compared to the n-propyl ligand. For comparison, the alkylmetal complexes studied most extensively by crystallographic means are the cobaloximes, analogues of the B_{12} coenzyme.[19] Although this octahedral system has important steric interactions that influence the alkyl ligands, parallel to our observations, it has been found that the Co–X bond trans to the alkyl is longer for an isopropyl than an analogous ethyl derivative.[19]

Supplementary Material Available: Tables of positional parameters of H atoms and anisotropic thermal parameters (6 pages); listings of structure factor amplitudes (44 pages). Ordering information is given on any current masthead page.

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Organometallic Oxides: Preparation and Properties of the Tetrahedral (T_d) Cubane [(η-C5(CH3)5)Cr(μ3-O)]4 and Comparison with the D_2 [(η-C5H5)Cr(μ3-O)]4 and D_{2d} [(η-C5H4CH3)Cr(μ3-O)]4

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The cubane [(η-C5(CH3)5)Cr(μ3-O)]4 (3) was prepared by the reaction between (η-C5(CH3)5)2Cr (4) and N_2O (1:1 molar ratio) in toluene at 80 °C. The structures of 3 and 4 have been determined by X-ray diffraction. 3: M_r = 813.0, triclinic, $P\bar{1}$, a = 10.876 (2) Å, b = 10.923 (2) Å, c = 18.105 (2) Å, α = 83.75 (1)°, β = 83.89 (1)°, γ = 66.86 (1)°, Z = 2, R = 0.060, R_w = 0.080 for 4121 observed reflections and 463 refined parameters. 4: M_r = 322.45, orthorhombic, *Ccmm*, a = 8.6857 (5) Å, b = 14.7842 (8) Å, c = 29.2031 (15) Å, Z = 8, R = 0.079, R_w = 0.092 for 816 observed reflections and 100 parameters. 3 has T_d symmetry, the six Cr–Cr distances averaging 2.834 (2), and the Cr–O distances, 1.945 (5) Å. The Cr–O–Cr angles average 93.5 (2); the O–Cr–O angles, 86.4 (2)°. 3 is antiferromagnetic, the magnetic moment increasing from 1.10 at 4.5 to 1.94 μ_B at 84.5 K; at 295 K the moment was 3.74 μ_B. The physical and chemical properties of 3 are compared to those of [(η-C5H5)Cr(μ3-O)]4 (1), which has D_2 symmetry, and to [(η-C5H4CH3)Cr(μ3-O)]4, which has D_{2d} symmetry. It is concluded that the η-C5R5 ring does not influence the [Cr(μ3-O)]4 core. Whereas 1 lost all η-C5H5 ligands rapidly on treatment with O_2, 3 was essentially inert to it.

Introduction

In previous papers we have discussed the preparation[1,2] and physical properties[3] of the cubane [(η-C5H5)Cr(μ3-O)]4

(1). This intriguing cluster, which was the first cubane prepared (in 1960), though it was not then recognized as such,[4] has a markedly distorted (D_2) structure, with three pairs of Cr–Cr distances, the pairs averaging 2.8960 (5),

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