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Isomerization of the Alkyl Ligand in $(Me_2NCS_2)Pd(PR_3)(alkyl)$ Complexes. Influences of Heteroatom Substituents in the Alkyl Group on the Alkyl Isomerization Equilibria and Stability of Alkylmetal Complexes

Daniel L. Reger,* David G. Garza, and Lukasz Lebioda

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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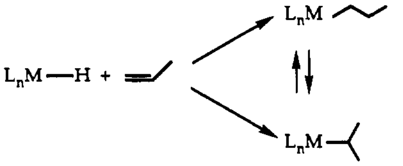
A series of complexes of unusually stable alkylpalladium complexes of the formula $(Me_2NCS_2)Pd(PR_3)(alkyl)$ (R = Me, Et) have been prepared from the reaction of $(Me_2NCS_2)Pd(PR_3)Cl$ and the appropriate alkyllithium or Grignard reagent. The substituted complexes $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CF_3)$ and $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CN)$ were prepared in similar reactions, and the isomer of the latter, $(Me_2NCS_2)Pd(PEt_3)(CH(CN)CH_3)$, was prepared from the low-temperature, in situ reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and CH_2CHCN. The reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ with $Li[C(CH_3)_3]CuCN$ gives a color change indicative of the formation of the alkylpalladium complex, but this *tert*-butyl compound decomposes above −40 °C with the formation of its isomer, $(Me_2NCS_2)Pd(PEt_3)(CH_2CH(CH_3)_2)$. With this one exception, all of these complexes are extremely stable, especially the substituted alkyl complexes, which can be heated over 100 °C in solution for extended periods without noticeable decomposition. Heating the unsubstituted isomers at 75 °C in solution leads to isomerization of the alkyl ligand. For example, heating either $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CH_3)$ or $(Me_2NCS_2)Pd(PEt_3)(CH(CH_3)_2)$ leads to a 10:1.0 equilibrium mixture, respectively, of the two. An equilibrium mixture of 10:1.0 is found for the other alkyl ligands studied. This 1.6 kcal/mol difference between the isomers is proposed to be the difference in energy between secondary versus primary alkylmetal complexes in the *absence of steric constraints* imposed by other ligands in the coordination sphere. At 120 °C, the primary isomer $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CN)$ isomerizes completely to the secondary isomer $(Me_2NCS_2)Pd(PEt_3)(CH(CN)CH_3)$, whereas $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CF_3)$ isomerizes to a 1:1 mixture with its secondary isomer. The alkyl ligand in $(Me_2NCS_2)Pd(PEt_3)(CH(CH_3)_2)$ exchanges with 1-hexene to yield an isomeric mixture of all three $(Me_2NCS_2)Pd(PEt_3)(hexyl)$ isomers. This reaction is only successful for monosubstituted alkenes. Kinetic studies of the alkyl isomerization reaction show that it is first order and that Lewis bases, especially added PEt_3, substantially slow the reaction. It has also been shown that the free and complexed PEt_3 exchange rapidly. The structure of $((CH_2)_4NCS_2)Pd(PEt_3)(CH(CN)CH_3)$ has been determined by X-ray crystallography. Crystal data: triclinic, $P\bar{1}$, $a = 11.865$ (3) Å, $b = 16.003$ (5) Å, $c = 10.060$ (3) Å, $\alpha = 93.45$ (3)°, $\beta = 91.27$ (3)°, $\gamma = 101.08$ (3)°, $V = 1870$ Å^3, $Z = 4$, $R_F = 4.1\%$, and $R_{wF} = 5.8\%$. There are no obvious structural features in the standard square planar geometry of this compound that indicate why the cyanide substituent stabilizes this branched isomer in favor of the linear isomer.

Introduction

Investigations into the synthesis and reactivity of alkylmetal complexes are central to the understanding of many processes catalyzed by transition metals.[1] In many important industrial processes, such as the hydroformylation reaction,[2] an alkylmetal intermediate is formed by the insertion of alkenes into a metal–hydride bond. This reaction can lead to isomeric mixtures of alkylmetal complexes (Scheme I) and products. The ultimate mixture of products that forms in a process that has an insertion step of this type may not be determined by the initial insertion regiochemistry of the alkene because the isomeric alkylmetal intermediates are generally in rapid equilibrium.[3] The isomerization of alkylmetal complexes is also important in the Du Pont adiponitrile process (nylon production).[1f]

Scheme I



While many important compounds have been produced for numerous years with this chemistry, fundamental information on the factors that control the isomerization reaction in Scheme I is lacking. Studies aimed at controlling the product mixtures that result from this reaction have been of the empirical type—modify the catalyst system and study the effects of the change. For example, using the initial catalyst for the hydroformylation reaction, $Co_2(CO)_8$, a 4:1 ratio of linear/branched products is obtained from propene. It is the linear compound that is desired for most commercial products. The ratio is improved to 7:1 by a Shell modification of the catalyst system that involves adding tributylphosphine to the reaction

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mixture. Recently, Union Carbide used a rhodium catalyst in the presence of triphenylphosphine to improve the ratio.[2] There have also been continuing efforts to understand the factors that control product mixtures in the adiponitrile process.[4]

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 $CpFeCO(PPh_3)$(*sec*-butyl) isomerizes completely to $CpFeCO(PPh_3)$(*n*-butyl) when heated at 65 °C in solution.[5] Thus, the primary isomer is more stable than the secondary isomer for these sterically hindered alkylmetal complexes, although we were able to demonstrate in one case that a secondary isomer stabilized by a cyanide substituent, $CpFeCO(PPh_3)(CH(CN)CH_3)$, was more stable than the corresponding primary isomer.[5b] A limited number of other alkyl isomerization reactions have been reported.[6-9] With one exception,[6b] these systems 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 recently reported the syntheses of unusually stable palladium(II)[10] and platinum(II)[11] derivatives of the formula $(Me_2NCS_2)M(PEt_3)$(alkyl). At elevated temperatures, alkyl isomers of these types equilibrate to their thermodynamic mixtures. The system is designed such that the isomerization reaction can be studied with minimal steric influences from ancillary ligands. Reported here are full results on the equilibration of a variety of $(Me_2NCS_2)Pd(PR_3)$(alkyl) (R = Me, Et) complexes. In addition to results with the isomers where alkyl = propyl, butyl, and hexyl, we have been able to prepare and study the heteronuclear substituted alkyls $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2X)$, where X = CN and CF_3. We also report mechanistic information on the isomerization reaction, alkyl ligand exchange reactions with free alkenes, and the solid-state structure of $[(CH_2)_4NCS_2)Pd(PEt_3)(CH(CN)CH_3)$. Preliminary results on these isomerization reactions have been reported.[12]

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. The ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on either a Bruker AM300 or AM500 spectrometer using a 5-mm broad band probe. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR chemical shifts are reported in ppm versus TMS, TMS, CF_3CO_2D, and H_3PO_4, respectively. All phosphorus and carbon spectra were run with proton decoupling. The triethylphosphine proton resonances are generally seen as a pentet (1:4:6:4:1) centered at 1.5 ppm (doublet of quartets for the CH_2 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 CH_3 resonance (J_{HP} = 16 Hz, J_{HH} = 8 Hz)) and are not listed for each individual complex. The $(R'_2NCS_2)Pd(PR_3)Cl$ (R′ = Me, R'_2 = $-(CH_2)_4-$; R = Me, Et) complexes were prepared via metathesis of the appropriate dichloro bis(phosphine)[8a] and bis(dithiocarbamato)[8b] complexes in refluxing toluene for 24 h. High-resolution mass spectra were run as solids on a VG 70SQ spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by Robertson Laboratory, Inc. Super-Hydride, *tert*-butyllithium, allylmagnesium chloride, and isobutyl-, *n*-hexyl-, *n*-propyl-, and isopropylmagnesium chloride were purchased from Aldrich Chemical Co. and were used as received. 1-Chloro-3,3,3-trifluoropropane was purchased from Narchem Corp. 3-Bromohexane was received as a mixture containing 30% 2-bromohexane from Lancaster Synthesis Inc.

(Dimethyldithiocarbamato)isobutyl(triethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}CH_2CH(CH_3)_2)$. $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.15 g, 0.39 mmol) was dissolved in THF (15 mL) and the solution cooled to −78 °C. Isobutylmagnesium chloride (0.39 mL, 0.78 mmol, 2.0 M) was added dropwise, and the solution was allowed to warm to room temperature (1 h). The THF was removed under vacuum, and the resulting solid was extracted with hexane (4 × 5 mL). The hexane solution was placed in a freezer overnight to yield pale yellow crystals (0.12 g, 0.30 mmol, 75%); mp = 74–75 °C. ^1H NMR (C_6D_6): δ 2.75, 2.73 (s, s; 3, 3; NCH_3); 2.3 (m; 1; $CH_2CH(CH_3)_2$; J_{HH} = 7 Hz); 1.6 (t; 2; $CH_2CH(CH_3)_2$; J_{HH} = 7 Hz, J_{HP} = 7 Hz); 1.4 (d; 6; $CH_2CH(CH_3)_2$; J_{HH} = 7 Hz). ^{31}P NMR (C_6D_6): δ 24.41. Anal. Calcd for $C_{13}H_{30}NPPdS_2$: C, 38.85; H, 7.52. Found: C, 38.80; H, 7.45.

Reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ and $Li[C(CH_3)_3]CuCN$. *tert*-Butyllithium (0.25 mL, 0.42 mmol, 1.7 M) was added to a stirring mixture of CuCN (0.36, 0.40 mmol) and THF (5 mL) at −78 °C. After 30 min the CuCN had dissolved, and this solution was transferred via cannula to a flask containing a THF (15 mL) solution at −78 °C of $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.15 g, 0.39 mmol). The addition resulted in a slight color change in the solution from yellow to orange. The solution was then placed in a cryogenic bath at −40 °C for 40 h during which time the solution gradually turned dark brown. The solution was warmed to room temperature, and the solvent was evaporated under vacuum. The resulting solid was extracted with hexane (4 × 5 mL). The hexane was evaporated to yield a pale yellow solid of $(Me_2NCS_2)Pd(PEt_3)(CH_2CH(CH_3)_2)$ (0.053 g, 0.13 mmol, 33%), as identified by ^1H and ^{31}P NMR.

(Dimethyldithiocarbamato)(1-hexyl)(triethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}CH_2CH_2CH_2CH_2CH_2CH_3)$. This complex was prepared as above for the isobutyl analog in 48% yield; mp = 41–43 °C. ^1H NMR (C_6D_6): δ 2.75, 2.73 (s, s; 3, 3; NCH_3); 2.0, 1.7, 1.5, 1.4 (p, m, m, m; 2, 4, 2, 2; CH_2's); 0.9 (t; 3; CH_3; J_{HH} = 7 Hz). ^{31}P NMR (C_6D_6): δ 24.43.

(Dimethyldithiocarbamato)(3-hexyl)(triethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_2CH_3)CH_2CH_2CH_3)$. This complex was prepared as above for the isobutyl analog in 56% yield. ^1H NMR (C_6D_6): δ 2.78, 2.75 (s, s; 3, 3; NCH_3); 2.0, 1.9, 1.6 (m, m, m; 2, 2, 2; CH_2's); 1.4, 0.9 (t, t; 3, 3; CH_3's; J_{HH} = 7 Hz); methine hydrogen resonance cannot be clearly assigned. ^{31}P NMR (C_6D_6): δ 21.34. (^{31}P NMR shows that the sample consists of about 30% of the 2-hexyl isomer: δ 22.55.) Anal. Calcd for $C_{15}H_{34}NPPdS_2$: C, 41.91; H, 7.97. Found: C, 41.51; H, 8.04.

(Dimethyldithiocarbamato)isopropyl(trimethylphosphine)palladium(II), $(Me_2NCS_2)Pd(PMe_3)(\eta^1\text{-}CH(CH_3)_2)$. $(Me_2NCS_2)Pd(PMe_3)Cl$ (0.15 g, 0.43 mmol) was dissolved in THF (15 mL) and the solution cooled to −78 °C. Isopropylmagnesium chloride (0.25 mL, 0.50 mmol, 2.0 M) was added dropwise, and the solution was allowed to warm to room temperature (2 h). The THF was removed under vacuum, and the resulting solid was extracted with benzene (3 × 4 mL). The benzene was evaporated to yield a yellow powder (0.10 g, 0.28 mmol; 65%); mp = 123–124 °C (dec). The analytical sample was

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further recrystallized from a toluene/hexane mixture. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.79, 2.76 (s, s; 3, 3; $\mathrm{NC}H_3$); 1.8 (m; 1; $\mathrm{PdC}H\mathrm{(CH_3)_2}$); 1.7 (d of d; 6; $\mathrm{PdCH(C}H_3\mathrm{)_2}$; J_{HH} = 6 Hz, J_{HP} = 2 Hz); 1.9 (d; 9; $\mathrm{PC}H_3$; J_{HP} = 9 Hz). ^{31}P NMR ($\mathrm{C_6D_6}$): δ −11.30. Anal. Calcd for $\mathrm{C_9H_{22}NPPdS_2}$: C, 31.26; H, 6.41. Found: C, 31.39; H, 6.47.

(Dimethyldithiocarbamato)-*n*-propyl(trimethylphosphine)palladium(II), ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PMe_3}$)(η^1-$\mathrm{CH_2CH_2CH_3}$). This complex was prepared as above for the isopropyl analog in 60% yield: mp = 120–122 °C (dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.74, 2.70 (s, s; 3, 3; $\mathrm{NC}H_3$); 2.1 (sextet; 2; $\mathrm{PdCH_2C}H_2\mathrm{CH_3}$; J_{HH} = 6 Hz); 1.7 (q; 2; $\mathrm{PdC}H_2\mathrm{CH_2CH_3}$; J_{HH} = 6 Hz, J_{HP} = 6 Hz); 1.3 (t; 3; $\mathrm{PdCH_2CH_2C}H_3$; J_{HH} = 6 Hz); 0.9 (d; 9; $\mathrm{PC}H_3$; J_{HP} = 9 Hz). ^{31}P NMR ($\mathrm{C_6D_6}$): δ −11.05.

(Dimethyldithiocarbamato)(1-cyanoethyl)(triethylphosphine)palladium(II), ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)(η^1-CH(CN)$\mathrm{CH_3}$). ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)Cl (0.20 g, 0.53 mmol) was dissolved in THF (15 mL) and the solution cooled to −78 °C. Super-Hydride (0.58 mL, 0.58 mmol, 1.0 M) was added dropwise to the above solution. Acrylonitrile (50 μL, 0.76 mmol) was added, and the solution was allowed to warm to room temperature (2 h). The THF was removed under vacuum, and the resulting solid was extracted with benzene. The benzene was evaporated to yield yellow crystals (0.18 g, 0.45 mmol, 86%); mp = 133–134 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.60, 2.56 (s, s; 3, 3; $\mathrm{NC}H_3$); 2.0 (pentet; 1; $\mathrm{PdC}H\mathrm{(CN)CH_3}$; J_{HH} = 7 Hz, J_{HP} = 7 Hz); 1.7 (d; 3; J_{HH} = 7 Hz), 1.4 (m; 6; $\mathrm{PC}H_2$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 21.99. IR spectrum (KBr, cm^{-1}): 2182 (CN). Anal. Calcd for $\mathrm{C_{12}H_{28}N_2PPdS_2}$: C, 36.14; H, 6.32. Found: C, 35.88; H, 6.35.

(Pyrrolidinecarbodithioato)(1-cyanoethyl)(triethylphosphine)palladium(II), ($\overline{\mathrm{CH_2CH_2CH_2CH_2N}}\mathrm{CS_2}$)Pd($\mathrm{PEt_3}$)($\eta^1$-CH(CN)$\mathrm{CH_3}$). This complex can be prepared as above for the dimethyldithiocarbamato analogue in 80% yield; mp = 116–119 °C. Crystals suitable for X-ray crystallography were grown in a U-tube by slow gaseous diffusion of hexane into a toluene solution of the complex over a 2-week period. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 3.3 (m; 4; $\mathrm{C}H_2\mathrm{CH_2CH_2C}H_2\mathrm{N}$); 2.0 (pentet; 1; $\mathrm{PdC}H\mathrm{(CN)CH_3}$; J_{HH} = 7 Hz, J_{HP} = 7 Hz); 1.7 (d; 3; $\mathrm{PdCH(CN)C}H_3$; J_{HH} = 7 Hz); 1.0 (m; 4; $\mathrm{CH_2C}H_2\mathrm{C}H_2\mathrm{CH_2N}$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 22.12. Anal. Calcd for $\mathrm{C_{14}H_{27}N_2PPdS_2}$: C, 39.58; H, 6.40. Found: C, 39.81; H, 6.57.

(Dimethyldithiocarbamato)(2-cyanoethyl)(triethylphosphine)palladium(II), ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)(η^1-$\mathrm{CH_2CH_2CN}$). ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)Cl (0.15 g, 0.39 mmol) was dissolved in THF (15 mL), and the solution was cooled to −78 °C. $\mathrm{IZnCH_2CH_2CN}$[13] (1.5 mL, 0.45 mmol, 0.3 M) was added, and the solution was allowed to warm to room temperature (1 h). The solvent was removed under vacuum, and the solid was extracted with benzene (3 × 3 mL). The benzene solution was washed with $\mathrm{H_2O}$, dried over $\mathrm{MgSO_4}$, and filtered. The benzene was evaporated to yield yellow crystals (0.12 g, 0.30 mmol, 78%); mp = 104–106 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.67, 2.65 (s, s; 3, 3; $\mathrm{NC}H_3$); 2.55 (t; 2; $\mathrm{PdCH_2C}H_2\mathrm{CN}$; J_{HH} = 8 Hz); 1.4 (quartet; 2; $\mathrm{PdC}H_2\mathrm{CH_2CN}$; J_{HH} = 8 Hz, J_{HP} = 8 Hz). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 24.10. IR spectrum (KBr, cm^{-1}): 2231 (CN). The high resolution mass spectrum shows M$^+$ (*m/e*): calcd for $\mathrm{C_{12}H_{25}N_2P^{106}PdS_2}$, 398.0232; found, 398.0223.

(Dimethyldithiocarbamato)(2-(trifluoromethyl)ethyl)(triethylphosphine)palladium(II), ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)(η^1-$\mathrm{CH_2CH_2CF_3}$). ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)Cl (0.15 g, 0.39 mmol) was dissolved in THF (15 mL), and then the solution was cooled to −78 °C. $\mathrm{ClMgCH_2CH_2CF_3}$ (0.50 mL, 0.50 mmol, 1.0 M) was added, and the solution was allowed to warm to room temperature (1 h). The solvent was removed under vacuum, and the solid was extracted with hexane (4 × 5 mL). The hexane was evaporated to yield pale yellow crystals (0.16 g, 0.36 mmol, 92%); mp = 109–110 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.8, (m; 2; $\mathrm{CH_2C}H_2\mathrm{CF_3}$); 2.64, 2.61 (s, s; 3, 3; $\mathrm{NC}H_3$); 1.5 (m; 2; $\mathrm{C}H_2\mathrm{CH_2CF_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$) ($\delta$): 212.1 (s; $\mathrm{NCS_2}$); 128 (quartet; $\mathrm{CH_2CH_2}C\mathrm{F_3}$; $^1J_{\mathrm{CF}}$ = 278 Hz); 38.7, 38.5 (s, s; $\mathrm{NCH_3}$); 37 (quartet; $\mathrm{CH_2}C\mathrm{H_2CF_3}$; $^2J_{\mathrm{CF}}$ = 27 Hz); 16 (d; $\mathrm{P}C\mathrm{H_2CH_3}$; $^1J_{\mathrm{CP}}$ = 26 Hz); 8.2 (s; $\mathrm{PCH_2}C\mathrm{H_3}$); 1.4 (d; $C\mathrm{H_2CH_2CF_3}$; $^2J_{\mathrm{CP}}$ = 9 Hz). ^{19}F NMR ($\mathrm{C_6D_6}$): δ 8.4 (t; $^3J_{\mathrm{FH}}$ = 11 Hz). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 24.05. Anal. Calcd for $\mathrm{C_{12}H_{25}F_3NPPdS_2}$: C, 32.62; H, 5.70. Found: C, 32.90; H, 5.90.

Isomerization of ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)(η^1-$\mathrm{CH_2CH_2CF_3}$). Heating ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)($\mathrm{CH_2CH_2CF_3}$) in toluene solution in a sealed NMR tube at 120 °C for 48 h leads to a equal mixture (the ratio does not change upon further heating) of the starting material and its isomer ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)(CH($\mathrm{CF_3}$)$\mathrm{CH_3}$), as characterized by the following NMR data. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.60, 2.57 (s, s; 3, 3; $\mathrm{NC}H_3$); 2.2 (m; 1; $\mathrm{C}H\mathrm{(CF_3)CH_3}$); 1.7 (d; 3; $\mathrm{CH(CF_3)C}H_3$; J_{HH} = 7 Hz). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 212, (s; $\mathrm{NCS_2}$); 135 (q; $\mathrm{CH(}C\mathrm{F_3)CH_3}$; $^1J_{\mathrm{CF}}$ = 280 Hz); 38.22, 38.20 (s, s; $\mathrm{NCH_3}$); 20.5 (q of d; $C\mathrm{H(CF_3)CH_3}$; $^2J_{\mathrm{CF}}$ = 28 Hz, $^2J_{\mathrm{CP}}$ = 8 Hz); 16.8 (q; $\mathrm{CH(CF_3)}C\mathrm{H_3}$; $^3J_{\mathrm{CF}}$ = 6 Hz); 15.5 (d; $\mathrm{P}C\mathrm{H_2CH_3}$; $^1J_{\mathrm{CP}}$ = 26 Hz); 8.2 (s; $\mathrm{PCH_2}C\mathrm{H_3}$). ^{19}F NMR ($\mathrm{C_6D_6}$): δ 17.8 (d; $\mathrm{CH(C}F_3\mathrm{)CH_3}$; J_{FH} = 13 Hz). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 22.35.

(Dimethyldithiocarbamato)(2-propenyl)(triethylphosphine)palladium(II), ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)(η^1-C($\mathrm{CH_3}$)=$\mathrm{CH_2}$). *tert*-Butyllithium (0.47 mL, 1.7 M, 0.80 mmol) was added dropwise to a solution of 2-bromopropene (40 μL, 0.44 mmol) in THF (5 mL) at −78 °C.[14] This solution was transferred via cannula to a solution of ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)Cl (0.15 g, 0.39 mmol) dissolved in THF (15 mL) at −78 °C. The solution was allowed to warm to room temperature (1 h), and the solvent was removed under vacuum. The resulting solid was extracted with hexane (3 × 5 mL), and this solution was placed in a freezer overnight to yield tan crystals (0.082 g, 0.22 mmol, 55%); mp = 120–122 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 5.6, 5.0 (m, m; 1, 1; $\mathrm{Pd(CH_3)C{=}C}H_2$); 2.70, 2.64 (s, s; 3, 3; $\mathrm{NC}H_3$); 2.4 (t; 3; $\mathrm{Pd(C}H_3\mathrm{)C{=}CH_2}$; J_{HH} = 1 Hz). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 21.07. Anal. Calcd for $\mathrm{C_{12}H_{26}NPPdS_2}$: C, 37.35; H, 6.79. Found: C, 37.33; H, 6.68.

(Dimethyldithiocarbamato)allyl(triethylphosphine)palladium(II), ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)($\mathrm{CH_2CHCH_2}$). This complex can be prepared as above for the isobutyl analogue in 60% yield. ^{1}H NMR ($\mathrm{C_6D_6}$, 297 K) (δ): (pentet; 1; $\mathrm{Pd(CH_2C}H\mathrm{CH_2)}$); 5.0, 2.4 (s (broad), s (broad); 2, 2; $\mathrm{Pd(C}H_2\mathrm{CHC}H_2\mathrm{)}$; 2.74 (s; 6; $\mathrm{NC}H_3$). ^{1}H NMR (toluene-d_8, 223 K): δ 6.7 (sextet; 1; $\mathrm{PdCH_2C}H\mathrm{{=}CH_2}$; J_{HH} = 15 Hz, J_{HH} = 8 Hz); 5.2 (d of d; 1; $\mathrm{PdCH_2CH{=}C}H$(trans to H); J_{HH} = 15 Hz, J_{HH} = 1 Hz); 5.1 (d of d; 1; $\mathrm{PdCH_2CH{=}C}H$ (cis to H); J_{HH} = 8 Hz, J_{HH} = 1 Hz); 2.6 (s; 6; $\mathrm{NC}H_3$); 2.6 (m; 2; $\mathrm{PdC}H_2\mathrm{CH{=}CH_2}$). ^{31}P NMR ($\mathrm{C_6D_6}$, 297 K): δ 23.3 (broad).

Isomerization Reactions. Isomerization reactions were monitored in toluene-d_8 solutions. A sample in an NMR tube was heated in a constant-temperature bath and its spectrum run at specified intervals until the equilibrium had been clearly established. For the values in Table IV, a typical isomerization procedure was to dissolve 0.010 g of the palladium alkyl complex in 1.0 mL of toluene and freeze–thaw–degas the solution, which was then sealed under vacuum in a glass tube and heated. After equilibration, the toluene was removed under vacuum and the composition of the sample was then analyzed by ^{1}H and ^{31}P NMR.

Crystallographic Analysis of (($\mathrm{CH_2}$)$_4$$\mathrm{NCS_2}$)Pd($\mathrm{PEt_3}$)($\eta^1$-CH(CN)$\mathrm{CH_3}$). A yellow prismatic crystal of (($\mathrm{CH_2}$)$_4$$\mathrm{NCS_2}$)Pd($\mathrm{PEt_3}$)(CH(CN)$\mathrm{CH_3}$) was mounted in a thin-walled capillary tube on a CAD-4 diffractometer. The unit cell dimensions 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 $\omega/2\theta$ scan mode with 0.7° + (0.35 tan θ)° scan range. The structure was solved by the heavy-atom method using SDP and refined by SHELX-76.[15] Hydrogen atoms were placed in calculated positions and were 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 corrections were by the method of Walker and Stuart.[16] Tables II and III show atomic parameters for the two forms of the molecule.

Results

Syntheses of Complexes. The unsubstituted alkyl complexes ($\mathrm{Me_2NCS_2}$)Pd($\mathrm{PEt_3}$)(alkyl) are prepared by the

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[14] Negishi, E. I.; Swanson, D. R.; Rousset, C. J. *J. Org. Chem.* **1990**, *55*, 5406.

[15] (a) Frenz, B. A. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1983. (b) Shedrick, G. M. *Shelx-76 A program for Crystal Structure Determination*; Cambridge University Press: Cambridge, England, 1976.

[16] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

Table I. Crystallographic Data for the Structural Analysis of $(\overline{CH_2CH_2CH_2CH_2N}CS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$ (1)

formula	$C_{14}H_{27}N_2PPdS_2$
mol wt	424.9
cryst system	triclinic
space group	$P\bar{1}$
a, Å	11.865 (3)
b, Å	16.003 (5)
c, Å	10.060 (3)
α, deg	93.45 (3)
β, deg	91.27 (3)
γ, deg	101.08 (3)
V, Å^3	1870
Z	4
cryst size, mm	0.3 × 0.3 × 0.3
monochromator	graphite
radiation (λ, Å)	Mo Kα (0.71073)
temp	ambient
2θ range, deg	4–50 ($+h$, $\pm k$, $\pm l$)
no. of rflns measd	6891
no. of rflns obsd	6543
linear abs coeff, cm^{-1}	12.7
transm factors	
max	1.123
min	0.906
decay corr	
max	1.038
av	1.018
R_F	0.041
R_{wF}	0.0584

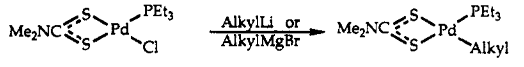
Table II. Fractional Atomic Coordinates for Form A of $(\overline{CH_2CH_2CH_2CH_2N}CS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$ with Esd's in Parentheses and Equivalent Isotropic Temperature Factors

	x/a	y/b	z/c	B, Å^2
Pd(1A)	0.4109 (0)	0.2012 (0)	1.1574 (0)	3.67
S(1A)	0.2955 (1)	0.0711 (1)	1.0672 (1)	4.87
S(2A)	0.5120 (1)	0.1571 (1)	0.9722 (1)	4.34
C(4A)	0.3971 (4)	0.0740 (3)	0.9475 (4)	3.86
N(1A)	0.3853 (3)	0.0175 (2)	0.8444 (4)	4.29
C(5A)	0.2880 (4)	−0.0538 (3)	0.8235 (5)	5.02
C(6A)	0.3006 (7)	−0.0849 (5)	0.6837 (7)	8.20
C(7A)	0.4175 (6)	−0.0594 (4)	0.6504 (6)	6.97
C(8A)	0.4673 (5)	0.0205 (3)	0.7372 (5)	5.12
P(1A)	0.5276 (1)	0.3266 (1)	1.2208 (1)	4.40
C(9A)	0.6351 (5)	0.3639 (4)	1.0981 (7)	6.37
C(10A)	0.5875 (6)	0.3842 (4)	0.9692 (7)	7.14
C(11A)	0.4503 (5)	0.4143 (3)	1.2512 (6)	5.25
C(12A)	0.5222 (6)	0.5012 (3)	1.2921 (7)	6.86
C(13A)	0.6204 (5)	0.3285 (4)	1.3695 (7)	6.48
C(14A)	0.5612 (7)	0.3015 (5)	1.4924 (7)	7.70
C(1A)	0.1819 (5)	0.2274 (4)	1.2485 (6)	6.19
C(2A)	0.2974 (4)	0.2178 (3)	1.3085 (5)	4.79
C(3A)	0.2921 (5)	0.1447 (4)	1.3863 (5)	5.30
N(2A)	0.2904 (5)	0.0849 (4)	1.4459 (5)	7.67

Table III. Fractional Atomic Coordinates for Form B of $(\overline{CH_2CH_2CH_2CH_2N}CS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$ with Esd's in Parentheses and Equivalent Isotropic Temperature Factors

	x/a	y/b	z/c	B, Å^2
Pd(1B)	1.0776 (0)	0.2750 (0)	0.6768 (0)	3.87
S(1B)	1.1821 (1)	0.3911 (1)	0.5631 (1)	5.14
S(2B)	0.9505 (1)	0.2993 (1)	0.5029 (1)	4.57
C(4B)	1.0598 (4)	0.3792 (3)	0.4618 (4)	3.90
N(1B)	1.0521 (3)	0.4262 (2)	0.3621 (4)	4.38
C(5B)	1.1458 (5)	0.4936 (4)	0.3218 (6)	5.81
C(6B)	1.0900 (6)	0.5308 (4)	0.2086 (6)	6.82
C(7B)	0.9867 (6)	0.4682 (5)	0.1604 (6)	7.07
C(8B)	0.9479 (5)	0.4186 (4)	0.2775 (5)	5.33
P(1B)	0.9716 (1)	0.1588 (1)	0.7563 (1)	5.77
C(9B)	0.8292 (6)	0.1279 (5)	0.6794 (8)	8.55
C(10B)	0.7521 (6)	0.1834 (6)	0.7074 (10)	9.71
C(11B)	1.0456 (8)	0.0646 (4)	0.7106 (11)	10.65
C(12B)	0.9976 (9)	−0.0141 (9)	0.7369 (14)	14.75
C(13B)	0.9567 (6)	0.1524 (5)	0.9331 (7)	7.98
C(14B)	0.9324 (7)	0.2307 (6)	1.0054 (8)	9.65
C(1B)	1.3173 (5)	0.2554 (4)	0.7392 (6)	6.60
C(2B)	1.2109 (5)	0.2675 (3)	0.8138 (5)	5.10
C(3B)	1.2291 (5)	0.3452 (4)	0.8935 (5)	5.25
N(2B)	1.2413 (5)	0.4086 (4)	0.9602 (6)	7.65

reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ and alkyllithium or Grignard reagents (eq 1). The $(Me_2NCS_2)Pd(PMe_3)$-



(1)

Alkyl = Me, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, 1-hexyl, 3-hexyl

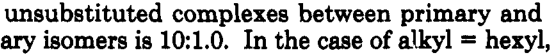
(propyl) derivatives were also prepared by reaction with the Grignard reagents. The new alkylpalladium complexes are soluble in hexane and other common organic solvents. The solids only decompose slowly in air, but decomposition in solution is rapid in air. The complexes can be heated in degassed toluene at 60 °C for extended periods without noticeable decomposition. At 75 °C, slow decomposition is noted as well as isomerization of the alkyl ligand (vide infra).

Although mixing $(Me_2NCS_2)Pd(PR_3)Cl$ and either $LiC(CH_3)_3$ or $(CH_3)_3CMgCl$ at −78 °C leads to immediate decomposition (formation of palladium metal), the cuprate reagent $Li[C(CH_3)_3]CuCN$ gives a color change indicative of the formation of the alkylpalladium complex. This compound decomposes above −40 °C, but the formation of $(Me_2NCS_2)Pd(PEt_3)(C(CH_3)_3)$ is indicated by the isolation of its isomer, $(Me_2NCS_2)Pd(PEt_3)(CH_2CH(CH_3)_2)$, from this reaction in 33% yield. In order to show that the formation of this isobutyl complex was not a result of isomerization of the cuprate, we quenched the cuprate with PhCOCl and isolated $PhCOMe_3$ in high yield.

The substituted alkyl complex $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CN)$ was prepared in a similar reaction using the zinc reagent $IZnCH_2CH_2CN$.[13] Its branched isomer, $(Me_2NCS_2)Pd(PEt_3)(CH(CN)CH_3)$, is prepared from the reaction of the hydride complex $(Me_2NCS_2)Pd(PEt_3)H$ (generated in situ at −78 °C) and $CH_2{=}CHCN$. None of the linear isomer is formed in this reaction. Complete discussion of this insertion chemistry will be reported separately.[11b] For the trifluoromethyl-substituted complexes, the linear isomer $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CF_3)$ is prepared from the Grignard reagent as in eq 1. The branched isomer, $(Me_2NCS_2)Pd(PEt_3)(CH(CF_3)CH_3)$, was not prepared directly but was definitively characterized in solution by multinuclear NMR as a mixture with the linear isomer after partial isomerization.

These alkylpalladium complexes substituted with the electron-withdrawing –CN and $-CF_3$ groups are extremely stable. They can be heated at 120 °C in solution for extended periods with little decomposition. They are also stable in air as solids but slowly decompose in solutions exposed to air.

Isomerization Studies. The alkyl complexes undergo a slow isomerization reaction ($t_{1/2}$ of 5 h) of the alkyl ligand when dissolved in aromatic hydrocarbons at 75 °C (eq 2 shows the propyl case).



(2)

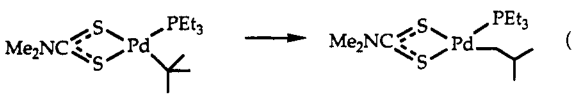
As shown in Table IV, the equilibrium ratios for all of the unsubstituted complexes between primary and secondary isomers is 10:1.0. In the case of alkyl = hexyl, the 3-hexyl isomer is slightly less stable than the 2-hexyl isomer. For all of these pairs of isomers, the equilibrium positions were verified starting from each individual isomer.

Table IV. Equilibria Positions of Isomerization Reactions

isomer group[a]	isomer ratio	temp, °C
$[Pd](CH_2CH_2CH_3):[Pd](CH(CH_3)_2)$	10:1	75
$[Pd](CH_2CH_2CH_2CH_3:[Pd](CH(CH_3)CH_2CH_3)$	10:1	75
[Pd](1-hexyl):[Pd](2-hexyl):[Pd](3-hexyl)	10:1:0.7	75
$[Pd](CH_2CH(CH_3)_2:[Pd](C(CH_3)_3)$	infinite	−40
$(dtc)Pd(PMe_3)(CH_2CH_2CH_3):(dtc)Pd(PMe_3)(CH(CH_3)_2)$	10:1	75
$[Pd](CH(CN)CH_3):[Pd](CH_2CH_2CN)$	infinite	120
$[Pd](CH(CF_3)CH_3):[Pd](CH_2CH_2CF_3)$	1:1	120

[a] $[Pd] = (Me_2NCS_2)Pd(PEt_3)$; $(dtc) = Me_2NCS_2$.

The tertiary isomer, $(Me_2NCS_2)Pd(PEt_3)(C(CH_3)_3)$, is unstable and decomposes if solutions are warmed above −40 °C. If the solutions are warmed to −40 °C and held at this temperature for 40 h, this complex isomerizes to the isomeric primary complex, $(Me_2NCS_2)Pd(PEt_3)(CH_2CH(CH_3)_2)$ (eq 3).

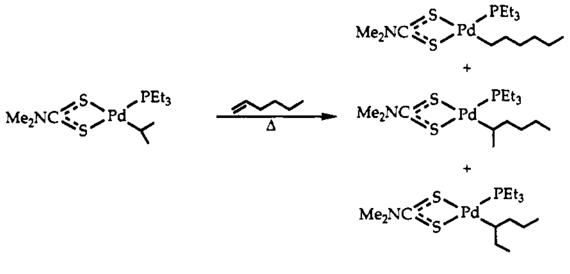


(3)

The primary isomer $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CN)$ isomerizes completely to the secondary isomer $(Me_2NCS_2)Pd(PEt_3)(CH(CN)CH_3)$. For the isomerization reaction to take place at a rate comparable to that for the alkyl complexes, the solutions need to be heated at 120 °C. $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CF_3)$ isomerizes to its secondary isomer at this temperature, but the equilibrium position is a 1:1 mixture.

The isomeric pair $(Me_2NCS_2)Pd(PEt_3)(CH_2CH{=}CH_2)$ and $(Me_2NCS_2)Pd(PEt_3)(C({=}CH_2)CH_3)$ were also prepared, but heating at 75 °C leads only to decomposition; no isomerization was observed. The σ-allyl complex is fluxional at room temperature, with the ^1H NMR signals for the allyl group freezing out at −50 °C.

Alkyl Exchange Reactions. Heating $(Me_2NCS_2)Pd(PEt_3)(CH(CH_3)_2)$ in 1-hexene at 75 °C leads to the slow replacement of the propyl group to form an isomeric mixture of $(Me_2NCS_2)Pd(PEt_3)$(hexyl) complexes (eq 4).



(4)

As the reaction proceeds, isomerization of $(Me_2NCS_2)Pd(PEt_3)(CH(CH_3)_2)$ to $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CH_3)$ is also noted. The presence of 1-hexene stabilizes the alkylpalladium complexes to thermal decomposition. These exchange reactions show no apparent decomposition over the 100 h at 75 °C needed for the exchange reaction to take place. Under similar conditions, the unsubstituted alkyl complexes in toluene show appreciable decomposition.

This exchange reaction is only successful for monosubstituted alkenes. No exchange is observed with 2-hexene, 2,4,4-trimethyl-1-pentene, cyclohexene, or cyclopentene under similar conditions. Also, the stabilizing effect of the alkylpalladium complexes noted for 1-hexene is not observed with these alkenes. Attempts to exchange the alkyl ligand with alkenes or alkynes bearing electron-withdrawing groups, such as CH_2CHCN or $CH_3C{\equiv}CCO_2Me$, leads to rapid polymerization of the alkene or alkyne. Partial exchange was noted with 1-pentyne, but the reaction is not synthetically useful.

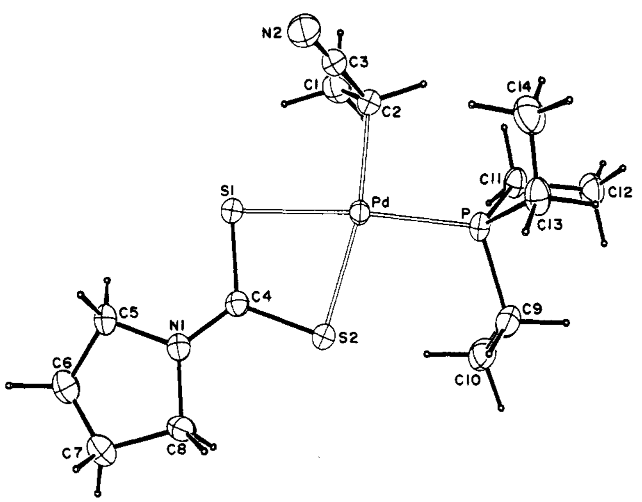


Figure 1. ORTEP drawing of $(\overline{CH_2CH_2CH_2CH_2N}CS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$ (form A).

Kinetics of Isomerization Reaction. The kinetics of the isomerization reaction of $(Me_2NCS_2)Pd(PEt_3)(CH(CH_3)_2)$ was studied by ^{31}P NMR in toluene-d_8. At 75 °C, the reaction is first order with $k = 4.3 \times 10^{-5}$ s^{-1} ($t_{1/2} = 5$ h). Sample decomposition of approximately 1%/h was noted in the kinetic run, and the data were analyzed after 4 half-lives. It was not possible to study the rate of reaction as a function of temperature. At higher temperatures, even 80 °C, extensive decomposition takes place. At 60 °C the reaction is too slow to monitor effectively, and even at 70 °C the half-life of the reaction is over 20 h.

The rate of the isomerization reaction is similar in toluene and (trifluoromethyl)benzene. In THF or CH_3CN the reaction is appreciably slower, as is the rate of decomposition. Addition of 1 equiv of PEt_3 to a toluene solution stops the isomerization and decomposition reactions at 75 °C completely.

Phosphine Exchange Reactions. At −79 °C, separate sharp resonances are observed in the ^{31}P NMR spectrum of a mixture of PEt_3 and $(Me_2NCS_2)Pd(PEt_3)(CH(CH_3)_2)$. At higher temperatures line broadening is observed indicating exchange of the phosphine ligand. Analysis of these spectra over the temperature range of −79 to 11 °C using a standard Eyring plot yields the activation parameters $\Delta H^* = 4.4$ kcal/mol and $\Delta S^* = -30$ eu. The barrier to exchange for $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CH_3)$ is lower and a limiting low-temperature spectrum was not observed at −93 °C.

Phosphine exchange is also rapid between the alkylpalladium complexes. Thus, an NMR spectrum run immediately on a sample prepared by addition of toluene-d_8 to a mixture of $(Me_2NCS_2)Pd(PMe_3)(CH_2CH_2CH_3)$ and $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CH_2CH_3)$ showed the presence of an equal mixture of these two compounds and $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CH_3)$ and $(Me_2NCS_2)Pd(PMe_3)(CH_2CH_2CH_2CH_3)$.

X-ray Crystal Structure of $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$. The structure of $((CH_2)_4NCS_2)Pd(PEt_3)(CH(CN)CH_3)$ has been determined crystallographically. There are two independent, but similar, molecules in the unit cell. An ORTEP drawing of form A is shown in Figure 1, and bond distances and angles are shown in Table V. Also shown in Table V, for comparison, are the analogous bond distances and angles for $((CH_2)_4NCS_2)Pd(PEt_3)(CH(CH_3)_2)$, the structure of

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for $(CH_2CH_2CH_2CH_2NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$ (A and B) and $(CH_2CH_2CH_2CH_2NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$ with Esd's in Parentheses

	A	B	isopropyl
	Bond Distances		
Pd–C(2)	2.091 (4)	2.100 (5)	2.074 (4)
Pd–P(1)	2.256 (1)	2.237 (1)	2.241 (1)
Pd–S(1)	2.378 (1)	2.394 (1)	2.395 (1)
Pd–S(2)	2.382 (1)	2.382 (1)	2.439 (1)
S(1)–C(4)	1.719 (4)	1.728 (4)	1.710 (4)
S(2)–C(4)	1.714 (4)	1.714 (4)	1.714 (4)
N(1)–C(4)	1.321 (6)	1.301 (6)	1.320 (5)
N(1)–C(5)	1.460 (5)	1.475 (6)	1.472 (5)
N(1)–C(8)	1.465 (6)	1.467 (6)	1.463 (5)
C(1)–C(2)	1.524 (6)	1.521 (7)	1.517 (7)
C(2)–C(3)	1.438 (7)	1.416 (7)	1.525 (7)
C(3)–N(2)	1.157 (8)	1.165 (8)	
	Bond Angles		
S(1)–Pd–S(2)	74.6 (0)	74.4 (0)	73.63 (4)
S(1)–Pd–P(1)	173.8 (0)	172.4 (0)	174.30 (4)
S(1)–Pd–C(2)	93.8 (1)	96.1 (1)	95.3 (1)
S(2)–Pd–P(1)	99.9 (0)	99.8 (0)	100.71 (4)
S(2)–Pd–C(2)	168.4 (1)	170.4 (0)	168.9 (1)
P(1)–Pd–C(2)	91.6 (1)	89.5 (1)	90.4 (1)
Pd–C(2)–C(1)	110.2 (3)	109.6 (3)	109.3 (3)
Pd–C(2)–C(3)	105.1 (3)	105.5 (3)	108.9 (3)
Pd–S(1)–C(4)	85.5 (1)	85.4 (1)	86.2 (1)
Pd–S(2)–C(4)	85.5 (1)	86.1 (1)	84.7 (1)
C(1)–C(2)–C(3)	114.2 (4)	112.3 (4)	112.1 (5)
S(1)–C(4)–S(2)	114.3 (2)	114.1 (2)	115.5 (2)
S(1)–C(4)–N(1)	122.2 (3)	122.8 (3)	123.1 (3)
S(2)–C(4)–N(1)	123.5 (3)	123.1 (3)	121.4 (3)
Pd–P(1)–C(9)	113.8 (2)	114.0 (2)	114.4 (2)
Pd–P(1)–C(11)	113.3 (2)	107.2 (3)	110.9 (2)
Pd–P(1)–C(13)	116.8 (2)	119.9 (2)	118.6 (2)

which was reported previously.[10]

Overall, the complexes are four-coordinate with no close intermolecular contacts. The basic geometry about palladium is square planar. In molecule A, the largest deviation from the Pd and donor atoms plane is S(1), which is 0.0303 (4) Å out of the least-squares plane. The S(1)–Pd–S(2) bond angle is, as expected,[17] restricted by the chelate ring to 74.6 (0)°. This causes the S(2)–Pd–P angle to open to 99.9 (0)° and the S(1)–Pd–C(2) angle to open to 93.8 (1)°. The remaining angle in the square plane, P–Pd–C(2), is 91.6 (1)°.

The two independent molecules differ by the arrangement of the ethyl groups in the PEt_3 ligand. In comparison to the molecule A shown in Figure 1, in form B the C(9), C(10) ethyl group is rotated up and the C(13), C(14) group is rotated toward the S(2) corner of the plane. These differing orientations do impact on the coordination sphere. In A the Pd–P distance (2.256 (1) Å) is 0.019 Å longer than in B (2.237 (1) Å), and the Pd–S(1) distance trans to this bond is 0.016 Å shorter. Also, the P–Pd–C(2) bond angle in A is larger by 2.1° and the S(1)–Pd–C(2) angle is smaller by 2.3°. Thus, the orientation in A seems to place some steric constraints between the PEt_3 ligand and the cyanoethyl ligand, which are relieved by a lengthening of the Pd–P bond and an opening of the P–Pd–C(2) angle. Lengthening of the Pd–P bond in A causes a shortening of the trans Pd–S(1) distance.

The Pd–C(2) bond distance is 2.091 (4) Å in A and 2.100 (5) in B, within the range typically found for a $C(sp^3)$–Pd σ bond.[17] The Pd–S(2) bond distance trans to the alkyl ligand is the same in both structures (2.382 (1) Å), but as noted above the cis Pd–S(1) distance is 0.016 shorter in B. Given the greater trans influence expected for the Pd–C σ bond versus a Pd–P bond, the Pd–S(1) distance would be expected to be noticeably longer than the Pd–S(2) distance. This expected trend was observed in both $((CH_2)_4NCS_2)Pd(PEt_3)$(propyl) structures but is not observed in the two cyanoalkyl molecules.

The overall structure of $((CH_2)_4NCS_2)Pd(PEt_3)(CH(CN)CH_3)$ is similar to that of $((CH_2)_4NCS_2)Pd(PEt_3)(CH(CH_3)_2)$, but the metal–ligand bond distances differ somewhat. The Pd–C(2) bond distance is 0.017 and 0.026 Å longer, and the Pd–S(2) bond distance is 0.058 Å shorter in the cyanide-substituted complexes. For comparison, the alkylmetal complexes studied most extensively by crystallographic means are the cobaloximes, analogs of the B_{12} coenzyme.[19] It has been found that the Co–C bond distances for similar complexes are *shorter* for alkyl ligands bearing electron-withdrawing groups. For the cases analogous to the results presented here, two pairs of isopropyl/cyanoethyl complexes with the same ancillary ligands, the cyanoethyl ethyl bond distance was shorter by 0.032 and 0.14 Å.[20]

Discussion

The $(R_2NCS_2)Pd(PEt_3)$(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*-$[Pd(Et)_2(PMe_2Ph)_2]$ decompose in solution at room temperature and are too unstable for microanalysis.[21] $CpPd(PPh_3)$(butyl) decomposes in solution at 35 °C, and $CpPd(PPh_3)(CH_2CH_2CH(COMe)_2)$ does so at 50 °C.[22] In fact, the low thermal stability of alkylpalladium complexes with β-hydrogen atoms has been extensively exploited in organic synthesis.[23] While the alkylpalladium complexes are very stable, substitution of an electron-withdrawing substituent at either the α- or β-position on the alkyl group dramatically increases the stability. These cyanide- and trifluoromethyl-substituted complexes can be heated above 100 °C in solution without apparent decomposition.

In solution at elevated temperatures, the alkyl complexes undergo a slow isomerization reaction ($t_{1/2}$ of ca. 5 h at 75 °C) of the alkyl ligand. For the alkylpalladium complexes, the position of the equilibrium (Table IV) is the same, 10:1.0, primary/secondary for alkyl = propyl, butyl, and hexyl, and is also not changed if the phosphine is varied from PEt_3 to PMe_3. Only in the case of the 3-hexyl isomer is the ratio slightly higher. As expected, the isomer with the metal bonded to a primary carbon is favored, but substantial amounts of the secondary isomer are present

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in the equilibrium mixtures.

The 10:1.0 ratio at 75 °C corresponds to a free energy difference of 1.6 kcal/mol. We believe that this represents the difference in energy between primary versus secondary alkylmetal complexes in the *absence of steric constraints* imposed by other ligands in the coordination sphere. The lack of steric crowding by the ancillary ligands has been verified crystallographically by the determination of the structures of both isomers of (($(CH_2)_4NCS_2$)Pd(PEt_3)(propyl).[10] In these structures, there are minimal intramolecular steric contacts between the alkyl ligand and the ancillary ligands, even for the bulkier isopropyl ligand. Also, in the analogous platinum complexes, similar equilibrium ratios of alkyl isomers are observed for more bulky phosphines, such as PPh_3, and changes in the isomerization equilibrium positions are not observed until the phosphine is very bulky (PCy_3).[24]

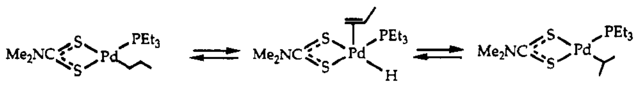
Other estimates of the differences in energies for linear versus branched alkylmetal isomers that contain both steric and electronic contributions are generally at least 5 kcal/mol.[25] For comparison, the energy difference in a C–H bond for primary versus secondary carbon atoms is ca. 3 kcal/mol.[26] The lower value for the transition metal complexes may simply reflect the longer M–C bond distances.

Substitution of a cyanide substituent on the alkyl ligand dramatically impacts on the relative stability of the linear versus branched isomers. This result was anticipated from our earlier results that showed that CpFeCO(PPh_3)(CH_2CH_2CN) also completely isomerizes to CpFeCO(PPh_3)(CH(CN)Me).[5b] We had previously attributed the stability of the branched isomer to the electronic stabilization of the metal–carbon bond by the electron-withdrawing cyanide group and suggested that the stability of primary versus secondary alkyl isomers may be partially explained by a destabilizing effect of the electron-donating alkyl substituents. To test this premise, we prepared (Me_2NCS_2)Pd(PEt_3)($CH_2CH_2CF_3$) and were surprised to find a 1.0:1.0 equilibrium mixture of isomers.

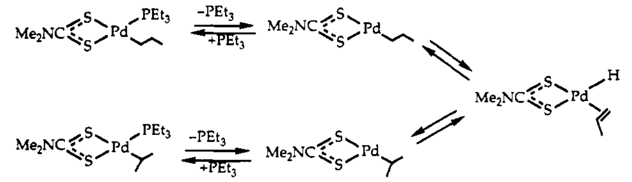
Although similar in electron-withdrawing ability,[27] the CN and CF_3 substituents have two major differences. First, the cyanide group has π bonding and antibonding orbitals that could interact with metal orbitals. Such an interaction is indicated in the infrared spectra where the α-cyano isomer has a ν(CN) sketching frequency 50 cm^{-1} lower than observed for the β-isomer and for nitriles in general.[28]

The structure of (($(CH_2)_4NCS_2$)Pd(PEt_3)(CH(CN)CH_3) was determined crystallographically in order to ascertain if any unusual interactions caused by the cyanide group could be observed. In fact, there is nothing in the structure that indicates any unusual effects of the cyanide substituent. The Pd–C bond distance is actually ca. 0.02 Å longer than in (($(CH_2)_4NCS_2$)Pd(PEt_3)($CH(CH_3)_2$), and the trans influence, as measured by the trans Pd–S bond distance, is lower than in the isopropyl complex. The CN and Me groups are in their sterically least hindered positions, rotated away from the phosphine ligand straddling the plane formed by the palladium atom and its donor atoms (the S(1)Pd–C(2)C (1 or 3) torsion angles are the same, 61 and −62°).

Scheme II



Scheme III



The second possible difference of the CF_3 group is steric; it is clearly larger than the CN substituent. It is hard to assess steric effects in the absence of a structure of (Me_2NCS_2)Pd(PEt_3)(CH(CF_3)CH_3) (we can only prepare this isomer as a mixture with (Me_2NCS_2)Pd(PEt_3)($CH_2CH_2CF_3$)). The CF_3 group is only slightly larger than a CH_3 group,[29] and steric effects seem to be minimal for (($(CH_2)_4NCS_2$)Pd(PEt_3)($CH(CH_3)_2$). Investigations of additional (Me_2NCS_2)Pd(PEt_3)(CH_2CH_2X) complexes are needed, but their syntheses have proven difficult. An important point that has been determined by these studies is that a *cyanide substituent has a dramatic effect* on the relative stability of alkylmetal isomers.

Mechanism of Isomerization Reaction. Two mechanisms are reasonable for the alkyl isomerization reactions, Schemes II and III. Note that a third mechanism, a dissociative mechanism similar to that shown in Scheme III in which the dithiocarbamate ligand becomes monohapto, is also possible. We favor the dissociative mechanism shown based on the favorable energy imparted by the chelate effect. The two are not distinguishable by the data, and the discussion is equally valid for both.

The alkyl isomerization reaction certainly takes place through a β-elimination–reinsertion process as shown in both schemes, but the important question is whether ligand dissociation is necessary before the β-elimination. At issue is whether the η^2-alkene–hydride intermediate is four- or five-coordinate. As studied most completely for β-elimination–reductive elimination reactions with $(PR_3)_2PtR_2$ complexes, the mechanism in Scheme III in which a phosphine dissociates prior to β-elimination is generally favored.[30] Calculations also support this mechanism.[31] Scheme II is supported by recent reports of β-elimination reactions for metals in this group that are believed to take place through five-coordinate intermediates[32] and by the fact that a number of five-coordinate η^2-alkene complexes have been isolated.[33]

We believe that the dissociative mechanism in Scheme III is correct. The best evidence supporting the dissociative mechanism is the inhibition of the isomerization reaction by added phosphine. Free phosphine would push the dissociation equilibria in Scheme III to the left, inhibiting the reaction. A similar reaction with other Lewis bases

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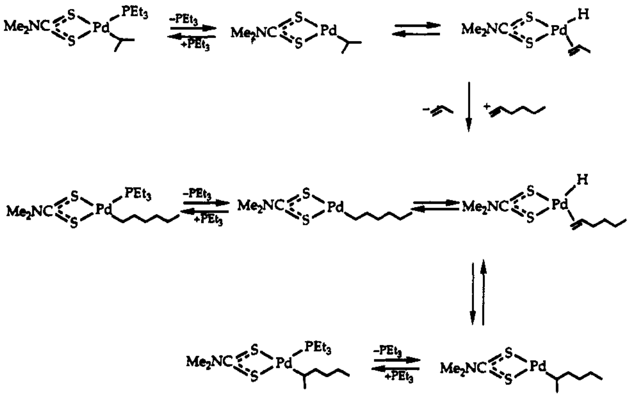
Scheme IV



would explain the rate retardation observed in donor solvents. Added phosphine would only affect Scheme II if it reacted with the starting alkyl complex forming a substantial amount of a five-coordinate complex. In low-temperature spectra of an equimolar mixture of $(Me_2NCS_2)Pd(PEt_3)(CH(CH_3)_2)$ and PEt_3, only the resonances for complexed and free phosphine are observed; there is no additional resonance for a five-coordinate complex.

Exchange Reaction. Additional support for the dissociative reaction pathway is the alkyl exchange reaction using 1-hexene (eq 4). As shown in Scheme IV, a mechanism involving exchange with the four-coordinate η^2-alkene–hydride intermediate in Scheme III is reasonable for this reaction. The exchange will only take place at the temperature needed for the isomerization reaction, indicating a common intermediate for the two reactions. The exchange step could be associative or it could proceed with the hexene capturing the three-coordinate hydride formed from dissociation of propene. We favor the latter on the basis of three observations. First, the exchange reaction is slower than the isomerization reaction of the starting material. If associative exchange was operative, given the high concentration of 1-hexene, one might expect the opposite result. Second, the alkyl solutions are much more stable with respect to decomposition in 1-hexene. We have assumed that the intermediate that leads to decomposition is the three-coordinate hydride formed by dissociation of the alkene from the η^2-alkene–hydride intermediate. In the presence of 1-hexene, this three-coordinate intermediate is trapped before it can decompose, leading to the exchange products. In fact, the rate of the exchange is similar to the rate of the decomposition reaction. Third, the isomerization reactions of the cyanide- and trifluoro-substituted complexes take place at higher temperatures. In these cases, the four-coordinate η^2-alkene–hydride intermediate must also be stabilized. It is known that electron-withdrawing substituents stabilize η^2-alkene complexes.[34] Thus, these alkenes would be less likely to dissociate, preventing decomposition by the dissociative route.

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Supplementary Material Available: Tables of positional parameters of H atoms and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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