Alkene and Alkyne Insertion Reactions with the Unstable Palladium Hydride Complex $(Me_2NCS_2)Pd(PEt_3)H$ and Carbon Monoxide Insertion Reactions with $(Me_2NCS_2)Pd(PEt_3)(alkyl)$ Complexes

Daniel L. Reger* and David G. Garza

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

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The unstable complex $(Me_2NCS_2)Pd(PEt_3)H$ is prepared in situ at low temperature by the reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ and $LiHBEt_3$. The reaction of $(Me_2NCS_2)Pd(PEt_3)H$ with $CH_2{=}CHCN$ at low temperature gives $(Me_2NCS_2)Pd(PEt_3)(CH(CN)CH_3)$. The hydride reacts with $CH_3O_2CC{\equiv}CCO_2CH_3$ to produce both the *Z* and *E* isomers of $(Me_2NCS_2)Pd(PEt_3)$-$[(CH_3O_2C)C{=}C(CO_2CH_3)H]$ in a 4:1 ratio. A similar reaction with the unsymmetrical alkyne $CH_3O_2CC{\equiv}CCH_3$ yields all four possible insertion products. The insertion reaction with $HC{\equiv}CCH_2CH_2CH_3$ yields $(Me_2NCS_2)Pd(PEt_3)[(CH_3CH_2CH_2)C{=}CH_2]$ and (Me_2NCS_2)-$Pd(PEt_3)[(E)$-$(H)C{=}C(H)CH_2CH_2CH_3]$ in a 4:1 ratio. The complexes $(Me_2NCS_2)Pd(PEt_3)R$ (R = methyl, *n*-propyl, isopropyl) react with carbon monoxide to yield the respective acyl complexes, $(Me_2NCS_2)Pd(PEt_3)COR$. The isopropyl acyl complex will not decarbonylate or isomerize to the *n*-propyl derivative when heated in solution at 75 °C. $(Me_2NCS_2)Pd(PEt_3)COCH_3$ reacts with $CH_3O_2CC{\equiv}CCO_2CH_3$ to yield $(Me_2NCS_2)Pd(PEt_3)[(CH_3O_2C)C{=}C(COCH_3)CO_2$-$CH_3]$.

Introduction

One of the most important processes in the chemical industry is the hydroformylation reaction. In this reaction, an alkene, carbon monoxide, and hydrogen are converted into an aldehyde (eq 1). The reaction is carried out in the

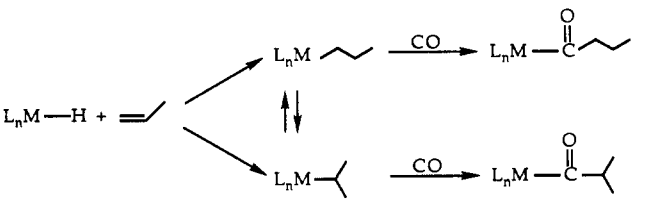
$$CH_3CH{=}CH_2 + CO + H_2 \xrightarrow{\text{cat.}} CH_3CH_2CH_2CHO + CH_3\underset{\displaystyle CHO}{\underset{|}{C}}HCH_3 \qquad (1)$$

presence of a homogeneous transition-metal catalyst. Ten billion pounds of aldehydes are produced yearly by this process.[1]

In this reaction, both linear and branched aldehydes are formed. The ratio of branched to linear aldehydes can be controlled by varying the catalyst and reaction conditions.[1]

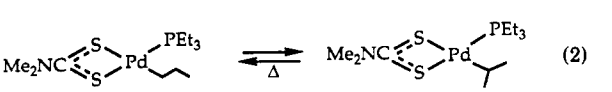
There are two important insertion steps in the hydroformylation reaction. The first is the insertion of the alkene into a metal-hydrogen bond. As shown in Scheme I, this can lead to either the branched or linear alkylmetal intermediate. The second is the insertion reaction of carbon monoxide into the metal-carbon bond formed in the first step. As shown, the ultimate product mixture[2] is not determined by the regiochemistry of the initial

Scheme I



insertion reaction of the alkene because the isomeric alkylmetal intermediates are in rapid equilibrium.[3] Thus, the ratio of isomeric products is determined by a combination of the alkyl isomerization and carbon monoxide insertion reactions.

We have been interested in designing a system in which both the alkyl isomerization and carbon monoxide insertion reaction can be studied separately but in the same system in order to determine the nature of the steric and electronic factors controlling these reactions. To this end, we have recently reported the syntheses of unusually stable palladium(II)[4] and platinum(II)[5] derivatives of the formula $(Me_2NCS_2)M(PEt_3)(alkyl)$. At elevated temperatures, alkyl isomers of these types can be equilibrated to their thermodynamic mixtures (see eq 2 for the propyl case), allowing the investigation of the alkyl isomerization reaction.[4a]



(2)

As part of these investigations, we have studied in the palladium system both of the insertion reactions shown

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed; Interscience: New York, 1988; Chapter 28. (b) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (c) Tolman, C. A. *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 271-312. (d) Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 743 and references therein. (e) Collman, J. P.; Hegedus, L.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987. (f) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; Chapters 2-4. (g) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: London, 1981.

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(3) (a) Orchin, M. *Adv. Catalysis* **1966**, *16*, 1. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 2994. (c) Lazzaroni, R.; Uccello-Barretta, G.; Benetti, M. *Organometallics* **1989**, *8*, 2323.

(4) (a) Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1991**, *10*, 902. (b) Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1992**, *11*, 4285.

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in Scheme I. First, we have investigated the reactions of alkenes and alkynes with the unstable palladium hydride $(Me_2NCS_2)Pd(PEt_3)H$. Second, we report the facile insertion of carbon monoxide into the palladium–carbon bond of complexes of the type $(Me_2NCS_2)Pd(PEt_3)(alkyl)$ to yield the corresponding acyl complexes. Finally, we report the additional insertion reaction of a palladium acyl with dimethyl acetylenedicarboxylate.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or 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 and ^{31}P NMR spectra were recorded on either a Bruker AM300 or AM500 spectrometer using a 5-mm broad-band probe. ^1H and ^{31}P NMR chemical shifts are reported in ppm versus TMS and H_3PO_4, respectively. All phosphorus 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. $(Me_2NCS_2)Pd(PEt_3)Cl$ was prepared via metathesis of dichloro bis(triethylphosphine)[6a] and bis(dimethyldithiocarbamato)[6b] complexes in refluxing toluene for 24 h. $(Me_2NCS_2)Pd(PEt_3)(alkyl)$ complexes were prepared by published methods.[4] Elemental analyses were performed by Robertson Laboratory, Inc. Super-Hydride and dimethyl acetylenedicarboxylate were purchased from Aldrich Chemical Co. and used as received. Methyl 2-butynoate and 1-pentyne were purchased from Farchan Laboratories and were used as received.

$(Me_2NCS_2)Pd(PEt_3)H$ (1). $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.20 g, 0.53 mmol) was dissolved in THF (15 mL) and then cooled to −78 °C. Super-Hydride (0.58 mL, 0.58 mmol, 1.0 M) was added dropwise to the above solution, resulting in a color change in the solution to almost colorless. The sample for NMR was prepared by adding 1 equiv of Super-Hydride to a small amount of $(Me_2NCS_2)Pd(PEt_3)Cl$ in toluene-d_8 at −78 °C. ^1H NMR (C_7D_8, −75 °C; δ): 2.60, 2.55 (s, s; 3, 3; NCH_3); −11.7 (d; PdH; J_{HP} = 18 Hz).

Reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and Acrylonitrile. $(Me_2NCS_2)Pd(PEt_3)H$ (0.53 mmol) was generated in situ as above at −78 °C. Acrylonitrile (50 μL, 0.76 mmol) was added, and the solution was warmed 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 of $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$ (2) (0.18 g, 0.45 mmol, 86%): mp 133–134 °C. ^1H NMR (C_6D_6; δ): 2.60, 2.56 (s, s; 3, 3; NCH_3); 2.0 (pentet, 1; $CH(CN)$; J_{HH} = 7 Hz, J_{HP} = 7 Hz); 1.7 (d; 3; J_{HH} = 7 Hz; $CHCH_3$), 1.4 (m; 6; PCH_2). ^{31}P NMR (C_6D_6; δ): 21.99. IR spectrum (KBr, cm^{-1}): 2182 (CN). Anal. Calcd for $C_{12}H_{28}N_2PPdS_2$: C, 36.14; H, 6.32. Found: C, 35.88; H, 6.35.

Reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and $CH_3O_2CC{\equiv}CCO_2CH_3$. $(Me_2NCS_2)Pd(PEt_3)H$ (0.40 mmol) was generated in situ as above at −78 °C. Dimethyl acetylenedicarboxylate (54 μL, 0.40 mmol) was added, and the solution was warmed to room temperature (1 h). The solvent was removed under vacuum, and the solid was extracted with benzene (3 × 5 mL). A small amount of activated carbon was added, the solution was filtered, and the benzene was evaporated to yield a yellow solid (0.14 g, 0.29 mmol, 72%). Analysis of the spectral data showed the solid to be a 4:1 mixture of the *Z* and *E* isomers **3** and **4**, respectively.

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(Z)\text{-}(CH_3O_2C)C{=}C(CO_2CH_3)H]$ (3). This isomer was isolated free of **4** by recrystallization of the above mixture from toluene/hexane: mp 136–137 °C. ^1H NMR (C_6D_6; δ): 6.99 (s; 1; C=CH); 3.50 (s; 6; CH_3CO_2); 2.50, 2.42 (s, s; 3, 3; CH_3N). Anal. Calcd for $C_{15}H_{28}NO_4PPdS_2$: C, 36.93; H, 5.78. Found: C, 37.14; H, 5.68. ^{31}P NMR (C_6D_6): δ 20.79.

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(E)\text{-}(CH_3O_2C)C{=}C(H)CO_2CH_3]$ (4). ^1H NMR (C_6D_6; δ): 6.39 (s; 1; C=H); 3.64 (s; 6; CH_3CO_2); 2.60, 2.59 (s, s; 3, 3; CH_3N). ^{31}P NMR (C_6D_6; δ): 21.52.

Reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and $CH_3O_2CC{\equiv}CCH_3$. Methyl 2-butynoate was allowed to react with **1** as above for the acrylonitrile analogue to yield a yellow oil in 45% yield. Analysis of the spectral data showed this oil to be a mixture of complexes **5**, **6**, **7**, and **8** in a 4:1:1:1 ratio.

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(E)\text{-}(CH_3O_2C)C{=}C(H)CH_3]$ (5). A mixture of complexes **5** and **6** was isolated by recrystallization from toluene/hexane. ^1H NMR (C_6D_6; δ): 5.7 (q; 1,; C=CH; J_{HH} = 7 Hz); 3.59 (s; 3; CH_3CO_2); 2.50, 2.42 (s, s; 3, 3; CH_3N); 2.0 (d of d; 3; $C{=}C(H)CH_3$; J_{HH} = 7 Hz, J_{HP} = 1 Hz). Anal. (of the mixture) Calcd for $C_{14}H_{28}NO_2PPdS_2$: C, 37.88; H, 6.36. Found: C, 37.88; H, 6.16.

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(Z)\text{-}(CH_3O_2C)C{=}C(CH_3)H]$ (6). ^1H NMR (C_6D_6; δ): 6.6 (p; 1; C=CH; J_{HH} = 2 Hz, J_{HP} = 2 Hz); 3.51 (s; 3; CH_3CO_2); 3.2 (d; 3; $C{=}C(H)CH_3$; J_{HH} = 2 Hz); 2.50, 2.42 (s, s; 3, 3; CH_3N).

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(E)\text{-}(CH_3)C{=}C(H)CO_2CH_3]$ (7). ^1H NMR (C_6D_6; δ): 7.2 (q; 1; C=CH; J_{HH} = 1 Hz); 3.4 (s; 3; CO_2CH_3); 3.2 (d of d; 3; $(CH_3)C{=}C$; J_{HH} = 1 Hz, J_{HP} = 5 Hz); 2.53, 2.49 (s, s; 3, 3; CH_3N).

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(Z)\text{-}(CH_3)C{=}C(CO_2CH_3)H]$ (8). ^1H NMR (C_6D_6; δ): 7.6 (q; 1; C=CH; J_{HH} = 1 Hz); 3.4 (s; 3; CO_2CH_3); 2.48, 2.44 (s, s; 3, 3; CH_3N); 3.2 (d; 3; $(CH_3)C{=}C$; J_{HH} = 1 Hz).

Reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and $HC{\equiv}CCH_2CH_2CH_3$. 1-Pentyne was allowed to react with **1** as above for the acrylonitrile analogue to yield a yellow oil in 55% yield. Analysis of the spectral data showed the product to be a mixture of complexes **9** and **10** in a 4:1 ratio.

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(CH_3CH_2CH_2)C{=}CH_2]$ (9). ^1H NMR (C_6D_6; δ): 5.2 (sextet; 1; $C{=}CH$(cis to Pd); J_{HH} = 1 Hz, J_{HP} = 2 Hz); 5.7 (d of q; 1; $C{=}CH$(trans to Pd); J_{HH} = 1 Hz, J_{HP} = 5 Hz); 2.71, 2.67 (s, s; 3, 3; CH_3N); 2.6 (t of t; 2; $CH_2CH_2CH_3$; J_{HH} = 8 Hz; J_{HH} = 1 Hz); 2.0 (sextet; 2; $CH_2CH_2CH_3$; J_{HH} = 8 Hz); 1.1 (t; 3; $CH_2CH_2CH_3$; J_{HH} = 8 Hz).

$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}(E)\text{-}(H)C{=}C(H)CH_2CH_2CH_3]$ (10). ^1H NMR (C_6D_6; δ): 6.5 (d of d of t; 1; $PdCH$; J_{HH} = 15 Hz, J_{HP} = 12 Hz, J_{HH} = 1 Hz); 5.7 (d of t of d; 1; $PdC{=}CH$; J_{HH} = 15 Hz, J_{HH} = 8 Hz, J_{HP} = 5 Hz); 2.70, 2.65 (s, s; 3, 3; CH_3N); 2.2 (q; 2; $CH_2CH_2CH_3$; J_{HH} = 8 Hz); methyl and center methylene resonances on alkenyl ligand could not be distinguished.

$(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}COCH_3)$ (12). $Me_2NCS_2Pd(PEt_3)CH_3$ (0.20 g, 0.55 mmol) was dissolved in benzene (20 mL), and CO was slowly bubbled through the solution for 3 h. A small amount of activated carbon was added to the solution, the solution was filtered, and the benzene was removed under vacuum to yield yellow crystals (0.18 g, 0.46 mmol, 84% yield): mp 97–98 °C. ^1H NMR (C_6D_6; δ): 2.78, 2.76 (s, s; 3, 3; CH_3N); 2.52 (s; 3; $COCH_3$). ^{31}P NMR (C_6D_6; δ): 20.93. IR spectrum (ν_{CO}, cm^{-1}): 1650 (KBr), 1668 (benzene solution). Anal. Calcd for $C_{11}H_{24}NOPPdS_2$: C, 34.07; H, 6.24. Found: C, 34.35; H, 6.41.

$(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}COCH_2CH_2CH_3)$ (13). This complex is prepared as above for the methyl analogue in 96% yield in hexane: mp 59–61 °C. ^1H NMR (C_6D_6; δ): 3.0 (t; 2; $COCH_2CH_2CH_3$; J_{HH} = 7 Hz); 2.72, 2.66 (s, s; 3, 3; CH_3N); 1.8 (sextet; 2; $COCH_2CH_2CH_3$; J_{HH} = 7 Hz); 0.9 (t; 3; $COCH_2CH_2CH_3$; J_{HH} = 7 Hz). ^{31}P NMR (C_6D_6): δ 20.78. IR spectrum (KBr, cm^{-1}): 1650 (CO).

$(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}COCH(CH_3)_2)$ (14). This complex is prepared as above for the methyl analogue in 90% yield in hexane: mp 54–56 °C. ^1H NMR (C_6D_6; δ): 3.1 (septet; 1; $COCH(CH_3)_2$; J_{HH} = 7 Hz); 2.69, 2.65 (s, s; 3, 3; CH_3N); 1.3 (d; 6; $COCH(CH_3)_2$; J_{HH} = 7 Hz). ^{31}P NMR (C_6D_6; δ): 21.29. IR spectrum (KBr, cm^{-1}): 1650 (CO).

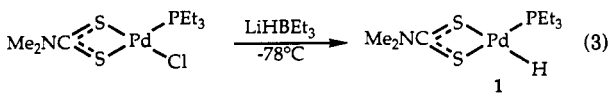
$(Me_2NCS_2)Pd(PEt_3)[(CH_3O_2C)C{=}C(COCH_3)CO_2CH_3]$ (15). Compound **12** (0.050 g, 0.13 mmol) was dissolved in benzene (5 mL), and $CH_3O_2CC{\equiv}CCO_2CH_3$ (16 μL, 0.13 mmol) was added.

(6) (a) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publishers: London, 1973; p 458. (b) Alison, I. M. C.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1973**, 254.

The solution was stirred for 1 h, and the benzene was removed by vacuum to yield a yellow solid (0.069 g, 0.13 mmol, 100%): mp 153–155 °C dec. ^{1}H NMR (C_6D_6; δ): 3.7, 3.3 (s, s; 3, 3; CO_2CH_3); 2.9 (s; 3; $COCH_3$); 2.42, 2.40 (s, s; 3, 3; NCH_3). ^{31}P NMR (C_6D_6; δ): 22.38. IR spectrum (ν_{CO}, cm^{-1}): 1721, 1701, 1664 (benzene solution). Anal. Calcd for $C_{17}H_{30}NO_5PPdS_2$: C, 38.53; H, 5.71. Found: C, 38.98; H, 5.64.

Results

Synthesis of the Palladium–Hydride Complex. The palladium–hydride complex $(Me_2NCS_2)Pd(PEt_3)H$ is prepared by the reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ with $LiHBEt_3$ (Super-Hydride) (eq 3). The hydride complex



(3)

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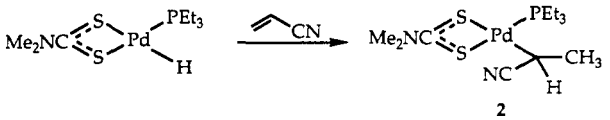
can also be prepared from other reagents such as $Li(s\text{-}Bu)_3BH$ or sodium cyanoborohydride, but the reaction with Super-Hydride proved superior. The palladium–hydride complex decomposes above −25 °C and thus cannot be isolated. However, at −75 °C the hydride resonance is observed by ^{1}H NMR at −11.7 ppm with J_{HP} = 18 Hz.

Hydropalladation of Alkenes and Alkynes. While the hydride complex itself could not be isolated, the products of reactions between the hydride and a variety of unsaturated substrates, initiated at −78 °C, can be isolated. The reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and acrylonitrile, CH_2=CH(CN), affords complex **2** in 86% yield (eq 4). Only the branched isomer (with palladium



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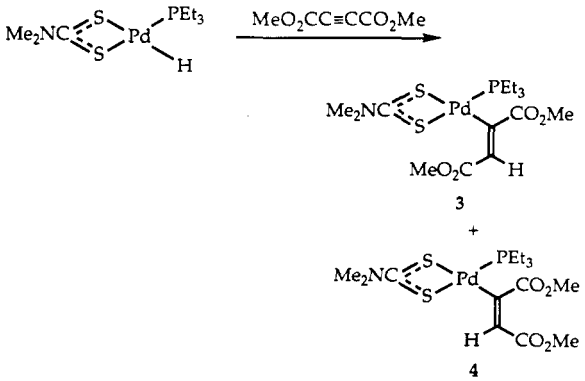
(4)

bound to the central carbon atom) is formed in this reaction; none of the linear isomer is observed. It was hoped that similar insertion reactions with substituted alkenes would be a route to the synthesis of a variety of substituted palladium–alkyl complexes. Unfortunately, the reaction is not successful for allene, 1,4-butadiene, styrene, 1-hexene, and allyl methyl ether. Only the reaction with acrylonitrile was found to yield an isolable product.

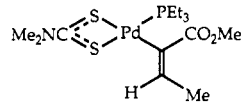
The hydride complex was also found to react with a variety of alkynes. Dimethyl acetylenedicarboxylate undergoes hydropalladation to give a 4:1 mixture of complexes **3** and **4**, respectively (eq 5). Complex **3** can be separated



(5)

from the mixture by fractional recrystallization. Determination of reaction stereochemistry is based on H–H coupling constants and ^{1}H chemical shift values.[7] It has been demonstrated that a hydrogen cis to palladium in an alkenyl complex is typically shifted about 1 ppm upfield from a hydrogen trans to the metal.[8] In the present case, the vinylic hydrogen for complex **3** resonates at δ 7.0, while the vinylic hydrogen in **4** resonates at δ 6.4.

Methyl 2-butynoate undergoes hydropalladation to give all four possible isomers (stereoisomeric pairs of two regioisomers), complexes **5**, **6**, **7**, and **8**, in a 4:1:1:1 ratio. Complexes **5** and **6** can be separated from complexes **7** and **8** by fractional recrystallization. Complexes **5** and **6**



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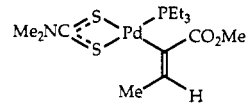

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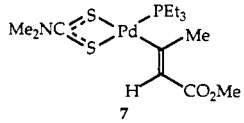

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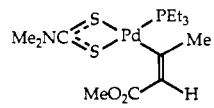

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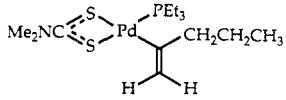
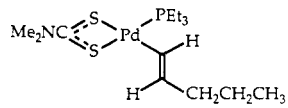
represent a stereoisomeric pair in which palladium is bound to the alkenyl carbon atom bearing the electron-withdrawing ester group. The vinylic hydrogen in **5** resonates at δ 5.7 and shows strong coupling to the geminal methyl group (J = 7 Hz). The vinylic hydrogen in **6** resonates at δ 6.6 and shows coupling to the geminal methyl group (J = 2 Hz) and to phosphorus across the double bond (J = 2 Hz). Likewise, complexes **7** and **8** represent the other stereoisomeric pair. Complexes **7** and **8** both show weak allylic coupling to the methyl group (J = 1 Hz) and resonate at δ 7.2 and 7.6, respectively.

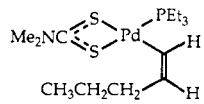
Hydropalladation of 1-pentyne gives mainly two of the three possible isomers, complexes **9** and **10**. The ^{1}H NMR spectrum also shows evidence of a small amount (<5%) of complex **11**. The products are obtained in a 4:1 ratio



9



10

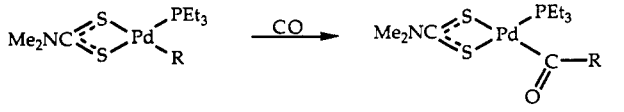


11

favoring complex **9**. The vinylic hydrogen atoms in **9** resonate at δ 5.2 for the hydrogen cis to palladium and at δ 5.7 for the hydrogen trans to the metal. Both hydrogen atoms show allylic coupling to the methylene and geminal coupling to one another (J = 1 Hz). The vinylic hydrogens in **10** resonate at δ 6.5 for the hydrogen geminal to the palladium and at δ 6.0 for the hydrogen cis to the metal. These two hydrogen atoms show strong trans coupling to one another (J = 15 Hz). Attempted hydropalladation of 3-hexyne did not afford isolable products.

(7) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981.
(8) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961.

CO Insertion Reactions. The palladium alkyl complexes, prepared by published methods,[4] undergo facile insertion of carbon monoxide in solution at room temperature (eq 6) to give the corresponding acyls. The

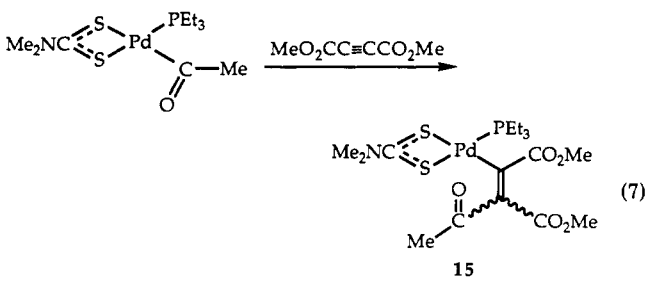


(6)

R = methyl, n-propyl, isopropyl

reaction proceeds much slower in THF. If left under a CO atmosphere overnight, the acyl complexes decompose, yielding bright magenta solutions. It did not prove possible to characterize products from these solutions. The palladium alkenyl complex **3** and the cyano-substituted complex **2** did not undergo CO insertion under these conditions. The isopropyl acyl complex, when heated in a sealed NMR tube in toluene at 75 °C for 12 h, shows no sign of decarbonylation or isomerization to the *n*-propyl alkyl or acyl isomers.

Reaction of $(Me_2NCS_2)Pd(PEt_3)COCH_3$ and $CH_3O_2CC{\equiv}CCO_2CH_3$. The methyl acyl complex **12** reacts readily with dimethyl acetylenedicarboxylate to yield a single isomer of undefined stereochemistry (eq 7). If more



(7)

15

than 1 equiv of the alkyne is used, the solution immediately turns orange-red, from which no product could be characterized. Complex **12** did not react under similar conditions with methyl 2-butynoate, 1-pentyne, or acrylonitrile, and when heated or exposed to an excess of these reagents, it gave complicated mixtures.

Discussion

While the palladium hydride complex **1** cannot be isolated, it can be identified at low temperature by the characteristic upfield ^1H NMR chemical shift for a metal hydride. This resonance also shows coupling to the phosphorus atom of the PEt_3 ligand. The hydride complex is also characterized by its extensive insertion chemistry with alkynes and acrylonitrile. It decomposes in solution at ca. −25 °C. This lack of stability is characteristic of most palladium hydrides, although a few exceptions bearing exceptionally bulky phosphines, such as *trans*-$PdHCl(PBz_3)_2$[9] and [*trans*-$Pd(H)(H_2O)(PCy_3)_2]^+$,[10] have been isolated.

The hydropalladation reactions with alkynes did not prove to be selective. In general, hydrometalation reactions of alkynes yield cis insertion products by a mechanism involving a concerted, four-center, cyclic transition state.[11] Clearly, additional reaction pathways must be operative in the chemistry of **1**. It has also been shown that hydrometalation of alkynes activated by electron-withdrawing substituents can proceed by an electron-transfer mechanism to yield trans insertion products.[8] In studies conducted by Clark et al., reactions of alkynes with *trans*-$PtH_2(PR_3)$ provided only the trans insertion products.[8] It was demonstrated that an electron-transfer mechanism in these insertions reactions is responsible for the trans nature of the products. Clark has also shown that the regioselectivity of these hydroplatination reactions with unsymmetrical alkynes may vary depending on the hydride used in the reaction.[12] For example, *trans*-$PtXH(PEt_3)_2$ (X = Cl, NO_3) complexes react to yield alkenyl products in which the platinum exclusively bonds to the carbon atom bearing the electron-withdrawing group. However, complexes of the type *trans*-$[PtH(solvent)(PEt_3)_2]PF_6$ react to give products in which the platinum atom bonds exclusively to the alkenyl carbon atom away from the electron-withdrawing group.

We have previously reported that the platinum analogue of **1**, $(Me_2NCS_2)Pt(PEt_3)H$, reacts with $CH_3O_2CC{\equiv}CCO_2CH_3$ to yield a mixture of cis and trans insertion products.[5] This platinum hydride is stable at room temperature, and the reaction with this highly activated alkyne required 40 h. The hydropalladation reactions reported here with $(Me_2NCS_2)Pd(PEt_3)H$ must take place rapidly below −25 °C, the decomposition temperature of the hydride, and are not selective. The wide variety of isomers generated by these hydropalladation reactions may be due in part to the very low steric hindrance around the palladium center. The ancillary ligands in the complexes of this system have minimal steric bulk.[4] The reactions have at least a partial electron-transfer component, and the low steric demands of the palladium intermediate allow products to form without steric directing effects. In contrast, the hydrozirconation[13] and hydrostannation[14] of terminal alkynes such as 1-hexyne are selective, with the metal bonding to the terminal carbon atom, which is the least hindered site. In the system studied here, hydropalladation of 1-pentyne leads to a mixture of regioisomers but favors insertion with palladium bound to the more hindered internal carbon.

The hydropalladation of acrylonitrile yields a single product, **2**. Regiochemistry of this type with acrylonitrile has been observed in other systems.[15] In other studies, we have shown that **2** is the thermodynamically more stable product.[4b] The other possible product, $(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CN)$ (prepared independently[4b]), will isomerize completely to complex **2** when heated at 120 °C.[4b]

The alkylpalladium complexes in this system react readily with carbon monoxide at 1 atm of pressure and room temperature to yield the corresponding acyls. The α-cyano-substituted complex **2** and the alkenyl complex **3** do not react with carbon monoxide under these conditions.

Although we have shown that the two propyl isomers will equilibrate at 75 °C (eq 2), the insertion reactions proceed with no isomerization of the alkyl group. Also, heating the isopropyl acyl complex **14** at 75 °C does not

(9) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371.
(10) Leoni, P.; Sommovigo, M.; Pasquali, M.; Midollini, S.; Braga, D.; Sabatino, P. *Organometallics* **1991**, *10*, 1038.
(11) Reference 1e, p 383.
(12) Attig, T. G.; Clark, H. C.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 189.
(13) Schwartz, J.; Blackburn, T. F.; Hart, D. W. *J. Am. Chem. Soc.* **1975**, *97*, 679.
(14) Leusink, A. J.; Budding, H. A. *J. Organomet. Chem.* **1968**, *11*, 533.
(15) Halpern, J.; Wong, L. *J. Am. Chem. Soc.* **1968**, *90*, 6665.

lead to isomerization of the propyl group. This result indicates that the carbon monoxide insertion reacton is not reversible under the same conditions needed for the alkyl isomerization reaction. This is in contrast to the report by Sens et al., who have shown that $[(PPh_3)_2Pd(NCCH_3)(COR)]^+$ complexes isomerize at ambient temperatures.[16] For example, $[(PPh_3)_2Pd(NCCH_3)(CO\text{-}i\text{-}Pr)]^+$ isomerizes to a 5.1:1.0 mixture of $[(PPh_3)_2Pd(NCCH_3)(CO\text{-}n\text{-}Pr)]^+$ and $[(PPh_3)_2Pd(NCCH_3)(CO\text{-}i\text{-}Pr)]^+$.

Finally, the acyl complex **12** will react with dimethyl acetylenedicarboxylate to yield **15**. This reaction yields a single product. Unfortunately, it did not prove possible to assign the stereochemistry of the product.

(16) Sen, A.; Brumbaugh, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 803.

In conclusion, we have shown that a variety of insertion reactions are possible in this system. The reactions include insertion chemistry with palladium–hydride, –alkyl, and –acyl derivatives.

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