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Syntheses of carbene and alkenyl derivatives of palladium. Solid-state structures of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ and $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6 \cdot Et_2O$

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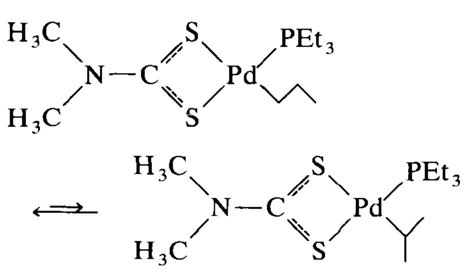
Abstract

The reaction of ${}^tBuNC$ and $(Me_2NCS_2)Pd(PEt_3)CH_3$ yields $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NC(CH_3)_3)CH_3]$. Reaction of this amino acyl complex with $[(CH_3)_3O]BF_4$ yields, after anion exchange, $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$. An analogous reaction with NH_4PF_6 yields $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6$. Both of these carbene complexes have been characterized crystallographically. Crystal data: $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ triclinic, $P\bar{1}$, $a = 12.253(12)$ Å, $b = 14.422(5)$ Å, $c = 11.564(5)$ Å, $\alpha = 97.38(3)°$, $\beta = 93.04(6)°$, $\gamma = 85.21(5)°$, $V = 2018$ Å^3, $Z = 2$, $T = 298$ K, $R(F) = 7.6\%$; $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6 \cdot Et_2O$ triclinic, $P\bar{1}$, $a = 12.844(2)$ Å, $b = 15.247(2)$ Å, $c = 8.312(2)$ Å, $\alpha = 105.60(1)°$, $\beta = 101.67(2)°$, $\gamma = 90.20(1)°$, $V = 1533$ Å^3, $Z = 2$, $T = 298$ K, $R(F) = 5.4\%$. In both complexes, the overall coordination geometry is approximately planar about both the palladium atom and carbene carbon atom, and these two planes are perpendicular. Reaction of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ with $LiCH_3$ results in deprotonation at the β-carbon yielding $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3){=}CH_2]$, and this reaction is reversed with $HBF_4 \cdot Et_2O$. The reaction of $LiC(OCH_2CH_3){=}CH_2$ with $(Me_2NCS_2)Pd(PEt_3)Cl$ yields $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(OCH_2CH_3){=}CH_2]$. This alkenyl complex reacts with BH_3 in ethanol to yield $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}CH(OCH_2CH_3)CH_3]$. $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(OCH_2CH_3){=}CH_2]$ also forms in the reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and $HC{\equiv}COCH_2CH_3$, along with both geometric isomers of $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}CH{=}CH(OCH_2CH_3)]$. Reaction of phenylacetylene and $(Me_2NCS_2)Pd(PEt_3)H$ yields mainly $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}C(Ph){=}CH_2)$ with small amounts of one of the other regioisomers present.

Keywords: Palladium; Carbene; Alkenyl derivatives; Dithiocarbamates

1. Introduction

We have recently reported a series of unusually stable alkylpalladium complexes of the formula $(Me_2NCS_2)Pd(PEt_3)(alkyl)$ (alkyl = methyl, ethyl, *n*-propyl, i-propyl, *n*-butyl, *sec*-butyl) [1]. These compounds are thermally stable to 60°C. Substitution of an electron-withdrawing substituent on the alkyl group increases the stability of the complexes. For example, $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)Me)$ can be heated to 100°C in solution for extended period without noticeable decomposition [2]. Of particular interest in this system is that the alkyl ligand undergoes an isomerization reaction upon warming to 75°C, shown in Eq. (1) for the propyl derivative [1].



(1)

The equilibrium favors the linear isomer (10:1 ratio) for the propyl and butyl derivatives, but introduction of electron-withdrawing groups in the alkyl chain shifts the equilibrium to favor the branched isomers [2]. We have also shown that $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-alkenyl})$

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complexes can be prepared by the reaction of alkynes with the unstable hydride complex $(Me_2NCS_2)Pd(PEt_3)H$ [3].

We report here efforts to explore further the chemistry of the $(Me_2NCS_2)Pd(PEt_3)$ system. It was of interest to determine if carbene or alkylidene complexes could be prepared, and, if prepared, whether they could be used for the syntheses of additional derivatives with substitution in the alkyl chain. The solid-state structures of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ and $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6 \cdot Et_2O$ are reported. We also report the syntheses of additional alkenyl derivatives in this system.

2. Experimental procedure

2.1. *General procedure*

All operations were carried out under a nitrogen atmosphere either using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 dry box. All solvents were dried, degassed and distilled prior to use. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer. The high-resolution mass spectra were analyzed as solids on a VG 70SQ spectrometer. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on either a Bruker AM300, AM400 or AM500 spectrometer using a 5-mm broad-band probe. ^1H, ^{13}C and ^{31}P NMR chemical shifts are reported in ppm vs. TMS, TMS and H_3PO_4 respectively. All phosphorus and carbon spectra were acquired with proton decoupling. The triethylphosphine proton resonances are generally seen as two multiplets having relative intensities of 1:4:6:4:1 (doublet of quartets centered near 1.7–1.6 ppm for the CH_2 groups) and 1:2:2:2:1 (doublet of triplets centered near 1.2–1.0 ppm for the CH_3 groups). $(Me_2NCS_2)Pd(PEt_3)Cl$ [1b], $(Me_2NCS_2)Pd(PEt_3)H$ [3], $(Me_2NCS_2)Pd(PEt_3)CH_3$ [1], and $LiC(OCH_2CH_3)$=CH_2 [4] were prepared according to literature methods. A standard stock solution of ^tBuNC (purchased from Aldrich) in hexanes was prepared with a concentration of 0.050 g ml^{-1}. A standard stock solution of $HC{\equiv}CPh$ (purchased from Aldrich) in THF was prepared with a concentration of 0.19 g ml^{-1}. A standard stock solution of $HC{\equiv}COCH_2CH_3$ (purchased from Aldrich) in THF was prepared with a concentration of 0.069 g ml^{-1}. $[(CH_3)_3O]BF_4$ was purchased from Lancaster. $NaBPh_4$, NH_4PF_6, $HBF_4 \cdot Et_2O$ (85% in diethyl ether), $LiCH_3$ (1.4 M in THF), $LiC(CH_3)_3$ (1.7 M in hexanes), $CH_3CH_2OCH{=}CH_2$, $LiHBEt_3$ (1.0 M in THF) and $BH_3 \cdot THF$ (1.0 M in THF) were purchased from Aldrich and used as received. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

2.2. *$(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NC(CH_3)_3)CH_3]$ (1)*

To a stirred solution of $(Me_2NCS_2)Pd(PEt_3)CH_3$ (0.25 g, 0.69 mmol) in benzene (10 ml) was added a slight excess of ^tBuNC in hexanes (1.2 ml, 0.72 mmol). After stirring 24 h at room temperature, the mixture was cannula-filtered and evaporated to dryness under vacuum, yielding a pale yellow powder (0.25 g, 0.56 mmol, 81%); m.p. = 148–152°C. ^1H NMR ($CDCl_3$): δ 3.31, 3.29 (s, s; 3, 3; $N(C\mathit{H}_3)_2$); 2.33 (s; 3; $C(N^tBu)C\mathit{H}_3$); 1.50 (s; 9; $NC(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 212.4 (s; $N\mathit{C}S_2$); 56.5 (d; $J(CP) = 2$ Hz; $\mathit{C}(CH_3)_3$); 39.2, 38.5 (s, s; $N(\mathit{C}H_3)_2$); 35.2 (d; $J(CP) = 13$ Hz; $PdC(N^tBu)\text{-}\mathit{C}H_3$); 32.2 (s; $C(\mathit{C}H_3)_3$); 18.0 (d; $J(CP) = 24$ Hz; $P(\mathit{C}H_2CH_3)_3$); 8.5 (s; $P(CH_2\mathit{C}H_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 17.0. IR (benzene): 1630 cm^{-1} (CN). Anal. Found: C, 40.56; H, 7.49; N, 6.26. $C_{15}H_{33}N_2PPdS_2$. Calc.: C, 40.67; H, 7.51; N, 6.32.

2.3. *$\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)\text{-}CH_3]\}BPh_4$ (2)*

A solid mixture of **1** (0.20 g, 0.45 mmol) and $(CH_3)_3OBF_4$ (0.07 g, 0.47 mmol) was treated with CH_2Cl_2 (10 ml) and allowed to stir at room temperature for 30 min or until dissolution of the $(CH_3)_3OBF_4$. The resulting orange solution was cannula-transferred onto excess solid $NaBPh_4$ (0.31 g, 0.91 mmol) and left to stir for 2 h at room temperature. The CH_2Cl_2 solution was then filtered via cannula and concentrated to a dark orange oil. This oil was triturated with CH_3OH (5 ml), yielding a pale yellow powder that was isolated (0.23 g; 0.30 mmol; 66%) after removing the CH_3OH extract by cannula filtration and washing with several portions of Et_2O (3 × 3 ml). Crystallization from a 50/50 mixture of CH_2Cl_2/Et_2O (4 ml) at −20°C yielded pale yellow crystals (0.16 g; 0.21 mmol; 46%); m.p. = 153–155°C. ^1H NMR ($CDCl_3$): δ 7.42, 7.04, 6.88 (m, t, t; 8, 8, 4; $C_6\mathit{H}_5$); 3.17, 3.15 (s, s; 3, 3; $N(C\mathit{H}_3)_2$); 2.54 (s; 3; $NC\mathit{H}_3^tBu$); 2.35 (d; 3; $J(HP) = 1$ Hz; $C(NCH_3^tBu)C\mathit{H}_3$); 1.62 (s; 9; $C(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 237.4 (d; $J(CP) = 9$ Hz; $\mathit{C}(NCH_3^tBu)CH_3$); 207.2 (s; $N\mathit{C}S_2$); 164.2, (q; $J(CB) = 49$ Hz; *ipso-C* of $B(C_6H_5)_4$); 136.3, 125.6, 121.7 (*o*, *m* and *p-C* of $B(\mathit{C}_6H_5)_4$); 67.2 (s; $\mathit{C}(CH_3)_3$); 38.8, 38.4 (s, s; $N(\mathit{C}H_3)_2$); 33.57 (d; $J(CP) = 3.2$ Hz; $C(NCH_3^tBu)\mathit{C}H_3$); 29.59 (s; $N\mathit{C}H_3^tBu$); 29.26 (s; $C(\mathit{C}H_3)_3$); 17.14 (d; $J(CP) = 27.0$ Hz; $P(\mathit{C}H_2CH_3)_3$); 8.16 (d; $J(CP) = 9.7$ Hz; $P(CH_2\mathit{C}H_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.8. IR (CH_2Cl_2); 1543 cm^{-1} (CN). A fast-atom-bombardment mass spectrum shows a cluster centered at *m/e* 457 (M^+). Anal. Found: C, 61.26; H, 7.33; N, 3.57. $C_{40}H_{56}BN_2PPdS_2$. Calc.: C, 61.82; H, 7.26; N, 3.60.

2.4. $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}$-$PF_6$ (3)

A solid mixture of **1** (0.20 g, 0.45 mmol) and NH_4PF_6 (0.07 g, 0.43 mmol) was dissolved in CH_2Cl_2 (10 ml) and allowed to stir at room temperature for 12 h. The reaction solution was then concentrated to saturation (about 1 ml) and treated with an equal volume of Et_2O. Colorless crystals were obtained by cooling overnight at −20°C (0.14 g; 0.24 mmol; 53%); m.p. = 162–165°C. ^1H NMR ($CDCl_3$): δ 9.5 (s; 1; NH^tBu); 3.26, 3.25 (s, s; 3, 3; $N(CH_3)_2$); 2.66 (d; 3; J(HP) = 1 Hz; $C(NH^tBu)CH_3$); 1.63 (s; 9; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 238.3 (d; J(CP) = 11 Hz; $C(NH^tBu)CH_3$); 207.70 (s; NCS_2); 66.17 (s; $C(CH_3)_3$); 39.04, 38.85 (s, s; $N(CH_3)_2$); 36.44 (d; J(CP) = 2.2 Hz; $C(NH^tBu)CH_3$); 29.75 (s; $C(CH_3)_3$); 17.16 (d; J(CP) = 27.6 Hz; $P(CH_2CH_3)_3$); 8.58 (d; J(CP) = 2.3 Hz; $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.6 (s; $P(CH_2CH_3)_3$); −144.2 (m; J(PF) = 287 Hz; PF_6). IR (CH_2Cl_2); 1543 cm^{-1} (CN). Anal. Found: C, 31.07; H, 5.75; N, 4.69. $C_{15}H_{34}F_6N_2P_2PdS_2$. Calc.: C, 30.59; H, 5.82; N, 4.76.

2.5. $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)$=$CH_2]$ (4)

To a stirred solution of **2** (0.20 g; 0.26 mmol) in THF (7 ml) at −78°C was added $LiCH_3$ (0.20 ml; 0.28 mmol). The reaction mixture was slowly warmed to room temperature and allowed to stir for 1 h. The THF was removed under vacuum and the yellow solid mixture extracted with hexanes (3 × 5 ml). After cannula filtration, the combined extracts were concentrated to saturation (about 2 ml). Yellow crystals resulted upon cooling overnight in the freezer at −20°C (0.08 g; 0.2 mmol; 70%); m.p. = 107–108°C. ^1H NMR (C_6D_6): δ 4.95 (s; 1; *cis*-CH_2); 4.91 (d; 1; J(HP) = 5 Hz; *trans*-CH_2); 3.05 (s; 3; N^tBuCH_3); 2.65 (s; 6; $N(CH_3)_2$); 1.58 (s; 9; $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 213.2 (s; NCS_2); 164.5 (d; J(CP) = 3 Hz; $C(N(CH_3^tBu)$=$CH_2)$; 95.2 (d; J(CP) = 5 Hz; $C(N(CH_3^tBu)$=$CH_2)$; 55.1 (s; $NC(CH_3)_3$); 38.5 (s; $N(CH_3)^tBu$); 38.3, 38.2 (s, s; $N(CH_3)_2$); 28.9 (s; $C(CH_3)_3$); 16.1 (d; J(CP) = 25 Hz; $P(CH_2CH_3)_3$); 8.2 (s; $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 19.71. Anal. Found: C, 41.85; H, 7.64; N, 5.96. $C_{16}H_{35}N_2PPdS_2$. Calc.: C, 42.05; H, 7.72; N, 6.13.

2.6. Reaction of $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C$-$(CH_3)_3)$=$CH_2]$ with HBF_4

4 (0.036 g; 0.079 mmol) was dissolved in CH_2Cl_2 (5 ml) and the solution was treated with HBF_4 (10 ml; 0.082 mmol) and allowed to stir 2 h before cannula-transferring onto solid $NaBPh_4$ (0.054 g; 0.16 mmol). The resulting mixture was stirred overnight (12 h) and **2** (identified by its ^1H NMR spectrum) was isolated (0.045 g; 0.058 mmol; 73 %) as above.

2.7. $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}C{\equiv}CPh)$ (5)

$(Me_2NCS_2)Pd(PEt_3)Cl$ (0.15 g; 0.39 mmol) and $LiC{\equiv}CPh$ (0.069; 0.56 mmol) were charged in separate flasks and each was dissolved in THF (5 ml). The resulting solutions were both cooled to −78°C and combined by slowly cannula-transferring the acetylide onto the Pd(II) halide, whereupon a bright yellow solution resulted. This reaction mixture was slowly brought to room temperature and allowed to stir 2 h before removal of the THF under vacuum. The remaining yellow oil was extracted with toluene (2 × 3 ml) and cannula-filtered. The filtrate was treated with an equal volume of hexanes. An unidentified yellow powder was obtained by cooling overnight at −20°C. After filtering, the filtrate was treated with additional hexanes (5 ml) and the solvent mixture was cooled at −20°C for several hours. Tan crystals precipitated (0.045 g; 0.10 mmol; 26%); m.p. = 99–100°C. ^1H NMR (C_6D_6): δ 7.60, 7.09, 6.97 (d, t, t; 2, 2, 1; C_6H_5); 2.49, 2.43 (s, s; 3, 3; $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 131.6, 129.3, 128.3, 125.4 (s, s, s, s; C_6H_5); 107.1, 101.7 (s, d; J(CP) = 26 Hz; $C{\equiv}C$); 37.8, 37.3 (s, s; $N(CH_3)_2$); 17.6 (d; J(CP) = 29 Hz; $P(CH_2CH_3)_3$); 8.5 (d; J(CP) = 2 Hz; $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 26.73. The high-resolution mass spectrum shows M^+ (m/e): calc. for $C_{17}H_{26}NP^{108}PdS_2$, 447.0269; found, 447.0283. Allowing $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}C{\equiv}CPh)$ to stand in solution leads to the precipitation of $(Me_2NCS_2)_2Pd$. Filtration and evaporation of the solvent yields *trans*-$(PEt_3)_2Pd(\eta^1\text{-}C{\equiv}CPh)_2$. ^1H NMR (C_6D_6): δ 7.58, 7.15, 7.01 (d, t, t; 2, 2, 1; C_6H_5); 1.89 (m; 6; $P(CH_2CH_3)_3$); 1.11 (m; 9; $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 131.2, 128.9, 128.3, 125.5 (s, s, s, s; C_6H_5); 111.5 (t; J(CP) = 17 Hz; $C{\equiv}CPh$); 111.2 (t; J(CP) = 3 Hz; $C{\equiv}CPh$); 17.6 (t; $P(CH_2CH_3)_3$; J(CP) = 14.4 Hz); $P(CH_2CH_3)_3$); 9.0 (s; $P(CH_2CH_3)_3$). A low-resolution mass spectrum shows a cluster centered at M^+ (m/e): 544. This complex has been briefly reported previously, but without full spectral characterization [5].

2.8. $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(OCH_2CH_3)$=$CH_2]$ (6)

$LiC(OEt)$=CH_2 was generated in situ as described by Baldwin et al. [4]. A typical reaction involved treating a THF (5 ml) solution of ethyl vinyl ether (2 ml; 21 mmol) with Li^tBu (0.38 ml; 0.64 mmol) dropwise at −78°C. This reaction mixture was gradually warmed until the initial bright yellow color disappeared (about 5 min) and then immediately cooled again to −78°C. After stirring 1 h at this temperature, the lithium reagent was cannula-transferred onto a THF (5 ml) solution of $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.20 g; 0.53 mmol) previously cooled at −78°C. The resulting bright orange reaction mixture was slowly brought to room temperature and allowed to stir 0.5 h before removing the THF under vacuum. A bright yellow-orange oil remained. This oil was extracted with hexanes (3 × 5 ml) and cannula-filtered. A bright yellow powder was obtained upon evaporation of the hexanes (0.15 g; 0.36 mmol; 68%); m.p. = 79–80°C. ^{1}H NMR (C_7D_8): δ 4.82 (s; 1; *cis*-CH_2); 4.32 (d; 1; J(HP) = 1 Hz; *trans*-CH_2); 3.95 (q; 2; J(HH) = 7 Hz; OCH_2CH$_3$); 2.67, 2.62 (s, s; 3, 3; N(CH_3)$_2$); 1.22 (t; 3; J(HH) = 7 Hz; OCH$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 89.7 (s; =CH$_2$); 64.5 (s; OCH$_2$CH$_3$); 38.6, 38.0 (s, s; N(CH$_3$)$_2$); 23.0 (s; OCH$_2$$CH_3$); 16.6 (d; J(CP) = 26 Hz; P(CH$_2$CH$_3$)$_3$); 8.3 (s; P(CH$_2$$CH_3$)$_3$); the quaternary carbons were not observed. ^{31}P{^{1}H} NMR (C_6D_6): δ 22.56. Anal. Found: C, 37.21; H, 6.38; N, 3.37. $C_{13}H_{28}NOPPdS_2$. Calc.: C, 37.59; H, 6.80; N, 3.37.

2.9. $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}CH(OCH_2CH_3)CH_3]$ (7)

To a stirred solution of **6** (0.10 g; 0.24 mmol) in oxygen-free ethanol (8 ml) was added $BH_3 \cdot THF$ (0.5 ml, 0.5 mmol). After stirring several minutes, the solution darkened and an unidentified white solid precipitated. This brown mixture was allowed to stir 12 h, cannula-filtered and the ethanol removed under vacuum. The remaining dark oil was extracted with hexanes (2 × 5 ml) and cannula-filtered. The filtrate was evaporated to dryness providing a pale yellow solid (0.060 g; 0.10 mmol; 60%); m.p. = 85–86°C. ^{1}H NMR (C_6D_6): δ 4.43 (dq; 1; J(HP) = 15.1 Hz; J(HH) = 6.0 Hz; CH(OEt)CH$_3$); 4.37, 3.55 (dq, dq; 1, 1; J(HH) = 8.9 Hz; J(HH) = 7.0 Hz; OCH_2CH$_3$); 2.79, 2.76 (s, s; 3, 3; N(CH_3)$_2$); 2.03 (dd; 3; J(HH) = 6.0 Hz; J(HP) = 3.4 Hz; CH(OEt)CH_3); 1.37 (m; 9; P(CH_2CH$_3$)$_3$ and OCH$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 166.54 (s; NCS$_2$); 78.34 (s; CH(OEt)CH$_3$); 66.61 (s; OCH$_2$CH$_3$); 39.57, 39.44 (s, s; N(CH$_3$)$_2$); 25.84 (s; CH(OEt)CH$_3$); 16.09 (s; OCH$_2$$CH_3$); 15.70 (d; J(HP) = 24 Hz; P(CH$_2$CH$_3$)$_3$); 8.26 (s; P(CH$_2$$CH_3$)$_3$). ^{31}P{^{1}H} NMR ($C_6D_6$): δ 21.51. Anal. Found: C, 37.80; H, 7.27; N, 3.23. $C_{13}H_{30}NOPPdS_2$. Calc.: C, 37.36; H, 7.24; N, 3.35.

2.10. Reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and $HC{\equiv}CPh$

$(Me_2NCS_2)Pd(PEt_3)H$ was prepared in situ as described previously [3]. A typical reaction involved treating a THF (8 ml) solution of $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.15 g; 0.39 mmol) with $LiHBEt_3$ (0.40 ml; 0.40 mmol) at −78°C. The resulting reaction mixture was stirred at this temperature for 15 min before addition of a slight excess of $HC{\equiv}CPh$ in THF (0.26 ml; 0.47 mmol). After stirring for 30 min at −78°C, the reaction mixture was gradually warmed to room temperature and stirred an additional 30 min before removing the THF under vacuum. The remaining dark yellow oil was extracted with (2 × 5 ml) of hexanes and cannula-filtered. Removal of the hexanes provided a yellow oil. Analysis of the spectral data showed a mixture of two isomers (5 : 1 ratio). Only spectroscopic data of the major isomer are reported here. ^{1}H NMR (C_6D_6): δ 8.04, 7.22, 7.09 (d, t, d; 2, 2, 1; C$_6$$H_5$); 6.15 (dd; 1; ^2J(HH) = 0.8 Hz, ^4J(HP) = 3.1 Hz; trans-CH_2); 5.59 (s, 1, *cis*-CH_2); 2.67, 2.60 (s, s; 3, 3; N(CH_3)$_2$). ^{31}P NMR (C_6D_6): δ 20.11.

2.11. Reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and $HC{\equiv}COEt$:

$(Me_2NCS_2)Pd(PEt_3)H$ was prepared in situ as described above, and treated with a slight excess of $HC{\equiv}COEt$ in THF (0.48 ml; 0.47 mmol). After stirring for 30 min at −78°C, the reaction mixture was gradually warmed to room temperature and stirred an additional 30 min before removing the THF under vacuum. The remaining dark yellow oil was extracted with hexanes (2 × 5 ml) and cannula-filtered. Removal of the hexanes provided a yellow oil. Analysis of the spectral

Table 1
Crystallographic data for the structural analyses

	2	**3**
Formula	$C_{40}H_{56}PdBN_2PS_2$	$C_{19}H_{44}F_6N_2OP_2PdS_2$
Mol.wt.	777.22	663.05
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no 2)	$P\bar{1}$ (no 2)
a (Å)	12.253(12)	12.844(2)
b (Å)	14.422(5)	15.247(2)
c (Å)	11.564(5)	8.312(2)
α (deg)	97.38(3)	105.60(1)
β (deg)	93.04(6)	101.67(2)
γ (deg)	85.21(5)	90.20(1)
V (Å^3)	2018	1533
Z	2	2
Crystal size (mm)	0.08 × 0.25 × 0.36	0.30 × 0.26 × 0.14
Monochromator	Graphite crystal	Graphite crystal
Radiation wavelength (Å)	Mo K (0.71073)	Mo K (0.71073)
Temperature	ambient	ambient
2θ range (deg)	4–46 (±h, ±k, +l)	4–46 (±h, ±k, +l)
No. of reflections measured	5919	4589
No. of reflections observed	5591	2760
Linear abs coeff (cm^{-1})	6.2	8.8
Transmission factors		
max.	95.981	
min.	85.944	
R_F	0.076	0.054
R_{wF}	0.111	0.060

data showed a mixture of three isomers, **6** and both isomers of $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}CH{=}CH(OCH_2CH_3)]$ in a 2/1/1 ratio, as characterized by ^1H and ^{31}P NMR.

2.12. Crystallographic analysis of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ and $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6$

A yellow crystal of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ and a colorless crystal of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6 \cdot Et_2O$ were each grown by slow diffusion of ethyl ether into saturated methylene chloride solutions. Both were mounted in thin-wall capillary tubes 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 1. Data were collected in the ω–2θ scan mode with a $0.8° + (0.35 \tan \theta)°$ scan range. The structures were solved by the heavy atom method and refined by using MoLEN [6]. All hydrogen atoms were included in the structure factor calculations and are not refined. Full matrix least-squares refinements were carried out for reflections with $I > 3\sigma(I)$, where $\sigma(I)$ was derived from counting statistics. Absorption corrections were performed on $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ by the method of Walker and Stuart using a gaussian function [7]. Atomic positions are shown in Tables 2 and 3.

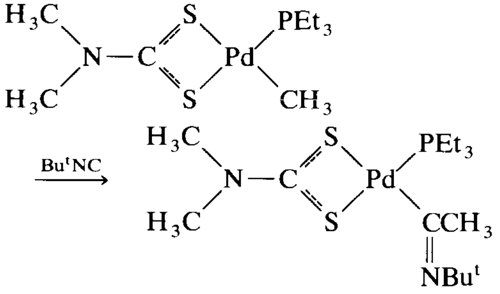
Table 2
Positional parameters for $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ with estimated standard deviations in parentheses and equivalent isotropic temperature factors

Atom	*x*	*y*	*z*	*B* (Å^2)
Pd	0.0903(1)	0.29578(9)	0.2225(1)	3.43(2)
S1	0.0314(3)	0.3163(3)	0.4155(3)	4.30(9)
S2	−0.0513(4)	0.4164(3)	0.2261(4)	5.3(1)
P1	0.1326(4)	0.3074(3)	0.0344(4)	5.3(1)
N1	−0.140(1)	0.445(1)	0.436(1)	4.9(3)
N2	0.1989(9)	0.1074(9)	0.255(1)	4.1(3)
C2	−0.219(1)	0.515(1)	0.395(2)	7.3(5)
C3	−0.147(1)	0.429(1)	0.558(2)	6.1(5)
C4	0.007(2)	0.295(1)	−0.063(2)	7.1(6)
C5	0.014(2)	0.309(2)	−0.182(2)	10.4(8)
C6	0.168(2)	0.424(1)	0.024(2)	7.7(6)
C7	0.250(2)	0.461(2)	0.108(2)	10.8(7)
C8	0.245(2)	0.235(2)	−0.034(2)	8.6(6)
C9	0.233(2)	0.135(2)	−0.058(2)	10.3(7)
C10	0.205(1)	0.196(1)	0.250(1)	4.1(3)
C11	0.314(1)	0.234(1)	0.288(2)	6.2(5)
C12	0.097(1)	0.047(1)	0.226(1)	4.8(4)
C13	0.003(1)	0.108(1)	0.165(1)	4.5(4)
C14	0.055(2)	0.032(1)	0.343(2)	6.8(5)
C15	0.124(2)	−0.035(1)	0.149(2)	6.4(5)
C16	0.296(1)	0.041(1)	0.292(2)	5.7(4)
C17	0.460(1)	0.417(1)	−0.163(1)	5.2(4)
C18	0.433(2)	0.505(1)	−0.145(2)	6.3(5)
C19	0.461(2)	0.571(1)	−0.223(2)	6.0(5)
C20	0.514(1)	0.527(1)	−0.324(2)	5.3(4)
C21	0.539(1)	0.433(1)	−0.343(1)	4.8(4)
C22	0.512(1)	0.367(1)	−0.266(1)	4.7(4)
C23	0.717(2)	0.243(1)	0.014(2)	5.9(5)
C24	0.673(1)	0.270(1)	−0.097(1)	5.1(4)
C25	0.588(1)	0.223(1)	−0.157(1)	4.1(4)
C26	0.549(1)	0.150(1)	−0.107(1)	5.4(4)
C27	0.593(2)	0.121(2)	0.002(2)	7.0(5)
C28	0.677(2)	0.177(2)	0.063(1)	6.7(5)
C29	0.427(1)	0.200(1)	−0.328(1)	4.3(4)
C30	0.437(1)	0.106(1)	−0.361(2)	5.3(4)
C31	0.349(2)	0.048(2)	−0.394(2)	7.4(6)
C32	0.244(2)	0.098(2)	−0.400(2)	7.7(6)
C33	0.231(1)	0.193(2)	−0.375(2)	6.6(5)
C34	0.324(1)	0.250(2)	−0.336(1)	5.8(5)
C35	0.627(1)	0.231(1)	−0.389(1)	3.9(3)
C36	0.587(1)	0.233(2)	−0.508(1)	5.7(5)
C37	0.656(2)	0.218(2)	−0.602(2)	6.2(5)
C38	0.769(2)	0.189(1)	−0.579(2)	6.6(5)
C39	0.814(2)	0.177(1)	−0.468(2)	5.7(5)
C40	0.739(1)	0.204(1)	−0.371(2)	5.0(4)
B1	0.538(1)	0.260(1)	−0.283(2)	4.1(4)

3. Results and discussion

3.1. Carbene complexes

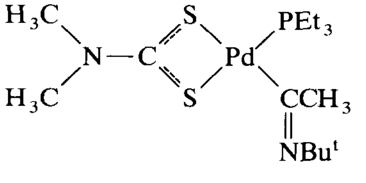
The reaction of ^tBuNC and $(Me_2NCS_2)Pd(PEt_3)CH_3$ occurs readily at room temperature to afford $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NC(CH_3)_3)CH_3]$ (**1**) in 81% yield (Eq. (2)).



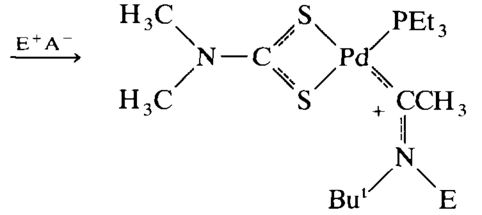
(2)

1

Multiple insertion of ^tBuNC was not observed, even in the presence of excess ^tBuNC. Complex **1** is hydrocarbon-soluble and only slowly decomposes in solution when exposed to air. The reaction of **1** with $[(CH_3)_3O]BF_4$ in CH_2Cl_2 resulted in the formation of the corresponding amino-carbene complex $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BF_4$, isolated after anion exchange as $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}BPh_4$ (**2**; Eq. (3)).



1



(3)

$E = CH_3$, $A = BPh_4$ for **2**
$E = H$, $A = PF_6$ for **3**

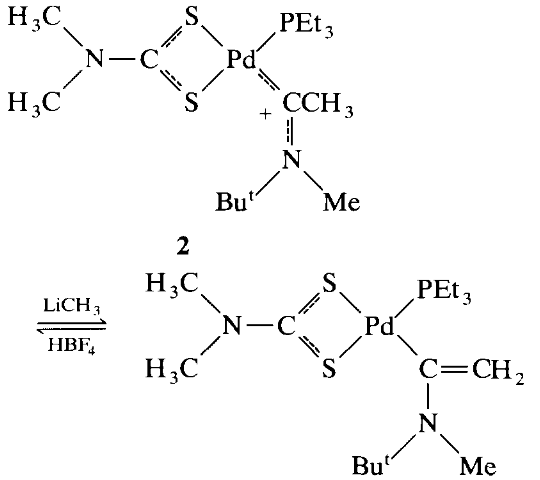
An analogous reaction of **1** and NH_4PF_6 yields $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6$ (**3**). Both complexes are moderately air-stable as solids and in solution. As anticipated, the C=N stretching vibration in the IR is lowered upon protonation or alkylation. Characteristic carbene carbon atom resonances at 237.4 ppm for **2** and 238.3 ppm for **3** are observed in the ^{13}C NMR spectra [8]. A nickel analog of **3** has been previously reported by a similar reaction [9].

In contrast to these results with the aminoacyl derivative **1**, it has not proven possible to isolate cationic carbene complexes starting with $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(O)CH_3]$ [3]. Attempted alkylation or protonation of the acyl ligand did not yield characterizable new products.

Attempts to reduce **2** with several hydride sources ($LiBEt_3H$, K-selectride, $NaB(OMe)_3H$, NaH) were not successful. Reaction of **2** with $LiCH_3$ results in deprotonation at the β-carbon providing the alkenylpalladium complex $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)=CH_2]$ (**4**; Eq. (4)).

Table 3
Positional parameters for $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6 \cdot Et_2O$ with estimated standard deviations in parentheses and equivalent isotropic temperature factors

Atom	x	y	z	B (Å^2)
Pd	0.78253(6)	0.78076(5)	0.9574(1)	3.44(1)
S1	0.8836(2)	0.9205(2)	1.0406(4)	5.43(7)
S2	0.6645(2)	0.8925(2)	1.0485(4)	5.59(7)
P1	0.6603(2)	0.6597(2)	0.8718(3)	3.91(6)
N1	0.7668(8)	1.0578(6)	1.158(1)	6.5(3)
N2	0.9792(6)	0.6786(5)	0.966(1)	4.3(2)
C1	0.7703(9)	0.9695(6)	1.093(1)	5.5(3)
C2	0.861(1)	1.1200(8)	1.194(2)	10.0(5)
C3	0.670(1)	1.0965(8)	1.207(2)	9.2(4)
C4	0.7102(8)	0.5474(6)	0.859(1)	4.7(3)
C5	0.626(1)	0.4686(7)	0.797(2)	6.9(4)
C6	0.5797(9)	0.6492(7)	0.660(1)	5.6(3)
C7	0.534(1)	0.7327(8)	0.630(2)	7.4(4)
C8	0.5662(8)	0.6721(8)	1.010(1)	5.6(3)
C9	0.616(1)	0.6783(9)	1.192(1)	7.5(3)
C10	0.8991(7)	0.7052(6)	0.877(1)	3.6(2)
C11	0.8947(8)	0.6827(8)	0.688(1)	5.2(3)
C12	1.0175(8)	0.6911(7)	1.153(1)	4.8(3)
C13	0.930(1)	0.707(1)	1.246(2)	9.1(5)
C14	1.068(1)	0.6056(9)	1.173(2)	11.2(5)
C15	1.099(1)	0.769(1)	1.216(2)	11.7(6)
C16	0.756(2)	−0.055(1)	0.579(3)	14.2(8)
C17	0.628(2)	0.056(2)	0.693(3)	16.5(9)
C18	0.596(2)	0.141(2)	0.724(3)	16.9(9)
C19	0.857(2)	−0.050(1)	0.549(2)	12.4(7)
O	0.715(1)	0.0356(8)	0.625(2)	16.1(5)
F1	0.810(1)	0.4695(8)	0.465(1)	19.1(6)
F2	0.8546(8)	0.3463(8)	0.329(2)	19.2(6)
F3	0.679(1)	0.4587(8)	0.251(2)	22.8(6)
F4	0.706(1)	0.3531(9)	0.377(2)	19.6(4)
F5	0.832(1)	0.4572(9)	0.221(2)	20.1(4)
F6	0.723(2)	0.337(1)	0.138(2)	21.9(7)



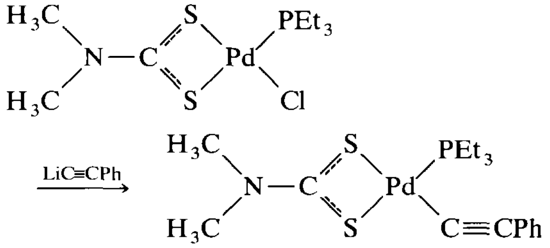
2

4

(4)

Eq. (4) is reversible. The reaction of **4** with $HBF_4 \cdot Et_2O$ results in the nearly quantitative isolation of **2**. As expected, addition of one equivalent of $LiCH_3$ to **3** results in deprotonation at the amino nitrogen, providing the aminoacyl **1**.

In an attempt to prepare an alkylidene complex, $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}C{\equiv}CPh)$ (**5**) was prepared in good yield from the reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ and $LiC{\equiv}CPh$ (Eq. 5).



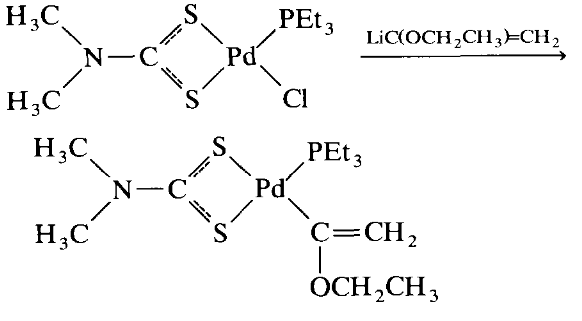
5

(5)

Complex **5** is air-stable and is soluble in aromatic and halocarbon solvents, but not hydrocarbons. A number of attempts to convert **5** into a cationic alkylidene using electrophilic reagents were unsuccessful. Complex **5** readily decomposes to disproportionation products $Pd[(CH_3)_2NCS_2]_2$ and $Pd(PEt_3)_2(\eta^1\text{-}C{\equiv}CPh)_2$ during purification procedures.

3.2. Alkenyl complexes

The reaction of $LiC(OCH_2CH_3)=CH_2$ with $(Me_2NCS_2)Pd(PEt_3)Cl$ in THF at −78°C affords the complex $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(OCH_2CH_3){=}CH_2]$ (**6**; Eq. (6)) in good yield.

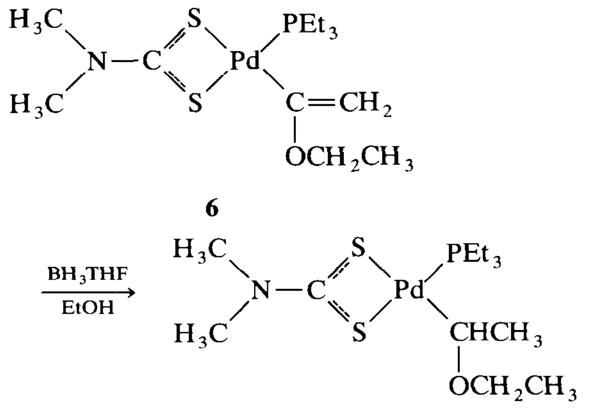


6

(6)

In contrast to **4**, complex **6** could not be protonated at the β-vinyl carbon to yield an ethoxy-carbene. Given the inability to prepare the same type of complex from the reaction of $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(O)CH_3]$ and $(CH_3)_3OBF_4$, it appears that the expected alkoxy-carbene complexes from these two reactions, $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(OR)CH_3]\}^+$, are unstable. The increased stability of the amino-carbene complexes reflects the greater ability of the less electronegative nitrogen, when compared to oxygen, to act as a π-donor to the empty p-orbital of the carbene carbon atom [10].

The reaction of **6** with BH_3 in ethanol yields the saturated complex $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}CH(OCH_2CH_3)CH_3]$ (**7**; Eq. (7)).



7

(7)

Assignments of the complex ^1H NMR spectrum for **7** were aided by a COSY 2-D experiment.

In contrast to other alkyl complexes in this system, it did not prove possible to find a condition that would lead to the isomerization of the alkyl ligand in **7** [1,2]. Heating in solution below 70°C does not lead to the observation of the other possible isomer, $(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}CH_2CH_2(OCH_2CH_3)]$, and higher temperatures cause decomposition.

Surprisingly, it did not prove possible to hydrogenate the double bond of the aminoalkene complex **4**. The BH_3/ethanol conditions or other high-pressure hydrogenation reactions lead to re-isolation of unreacted starting material.

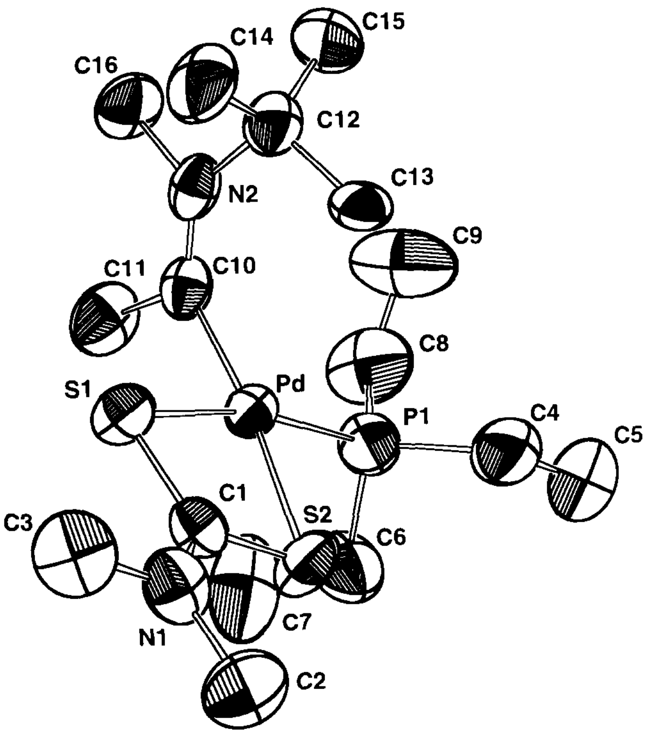
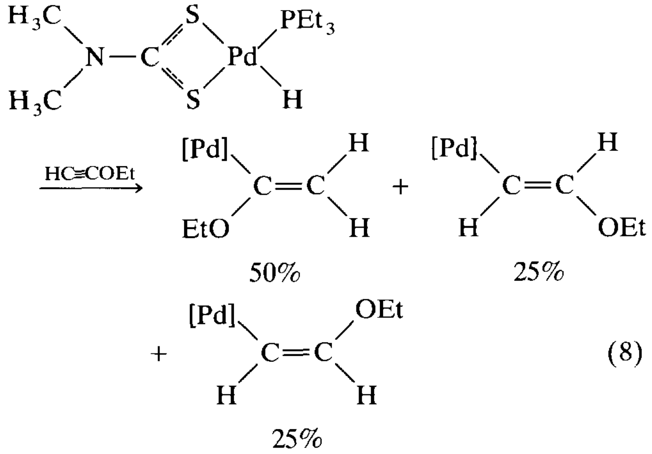


Fig. 1. ORTEP drawing of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(N(CH_3)C(CH_3)_3)CH_3]\}^+$.

The low-temperature reaction of $(Me_2NCS_2)Pd(PEt_3)H$ and $HC{\equiv}COCH_2CH_3$ yields all three possible insertion isomers (Eq. (8)).



(8)

The main product (about 50%) is **6**, the regioisomer formed from the insertion taking place such as to locate the ethoxy substituent adjacent to the metal. Both geometric isomers of the other regioisomer form in about equal amounts (25% each as characterized in the mixture by NMR). Hydrogenation of this mixture resulted in the conversion of **6** into **7**, as observed for pure **6**, but no hydrogenation of the β-isomers was observed.

An analogous insertion reaction with phenylacetylene and $(Me_2NCS_2)Pd(PEt_3)H$ yields mainly $(Me_2NCS_2)Pd(PEt_3)(\eta^1\text{-}C(Ph){=}CH_2)$ with small amounts of one of the other regioisomers present. Attempted hydrogenation of this mixture resulted in the re-isolation of the starting mixture of alkenyl complexes.

3.3. X-Ray structural analyses

The structure of **2** has been solved crystallographically. An ORTEP diagram is provided in Fig. 1, and bond distances and angles are shown in Table 4. The overall coordination geometry for **2** is approximately square planar about the palladium atom (sum of four angles about Pd is 359.9°). The Pd–C(carbene) bond distance of 1.97(1) Å is considerably shorter than expected from the sum of the σ-covalent radii (2.05 Å) [11], and 0.10 Å shorter than in the alkyl complex $[(CH_2)_4NCS_2]Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$ [1b]. This palladium–carbene bond distance is comparable to those in other palladium(II) carbene complexes (1.95–2.02 Å) [12]. The carbene carbon is nearly coplanar with the three atoms bonded to it (sum of three angles about C10 is 359.7°), and this plane is nearly parallel to the planar arrangement about N2 (C16–N2–C10–Pd torsion angle = −172.8°). The C10–N2 bond distance of 1.30 Å is again comparable to other reported palladium(II) carbene complexes (1.31–1.34 Å) [12a–12e]. The short C–N bond length and parallel arrangement of the planar geometry about each of these atoms clearly points to substantial pπ–pπ interaction between the amino nitrogen atom and the carbene carbon atom [12a–12e].

Table 4
Selected bond distances and bond angles for $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NC(CH_3)_3CH_3)CH_3]\}BPh_4$ and $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}PF_6 \cdot Et_2O$ with estimated standard deviations in parentheses

Bond distances (Å)	2	3
Pd–S1	2.357(4)	2.352(3)
Pd–S2	2.351(5)	2.358(3)
Pd–P1	2.292(5)	2.280(3)
Pd–C10	1.97(1)	2.004(9)
C10–N2	1.30(2)	1.28(1)
C10–C11	1.51(2)	1.50(1)
N2–C12	1.58(2)	1.49(1)
N2–C16	1.54(2)	
Bond angle (deg)	**2**	**3**
S1–Pd–S2	75.2(2)	74.8(1)
S1–Pd–P1	168.0(2)	170.3(1)
S1–Pd–C10	94.4(4)	95.1(3)
S2–Pd–P1	93.9(2)	96.2(1)
S2–Pd–C10	169.6(4)	169.4(3)
P1–Pd–C10	96.4(4)	93.7(3)
N2–C10–C11	116.0(1)	116.2(9)
N1–C10–Pd	131.0(1)	128.5(8)
C11–C10–Pd	113.0(1)	115.1(7)
C10–N2–C16	124.0(1)	
C12–N2–C16	108.0(1)	
C10–N2–C12	129.0(1)	133.6(9)

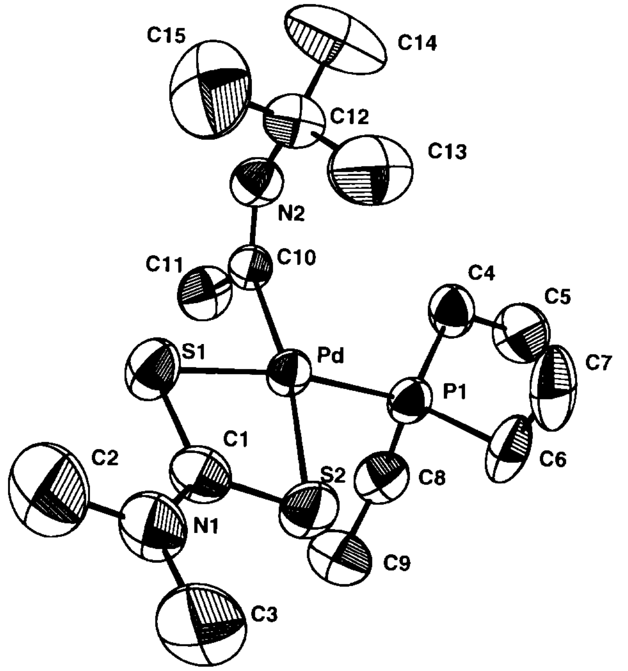


Fig. 2. ORTEP drawing of $\{(Me_2NCS_2)Pd(PEt_3)[\eta^1\text{-}C(NHC(CH_3)_3)CH_3]\}^+$.

The plane about the carbene carbon atom is nearly perpendicular to the square plane about the palladium atom (S2–Pd–C10–N2 torsion angle = 84.7°). This type of orientation is observed in the other palladium–carbene complexes [12a–12d]. The bulky *tert*-butyl substituent is oriented cis with respect to the palladium atom.

The palladium–sulfur bond distances are nearly equivalent (2.357(4) Å and 2.351(5) Å), suggesting that the Pd–C(carbene) bond exerts a similar trans influence as the Pd–P bond. Even though the Pd–C(carbene) bond distance is 0.10 Å *shorter* than the Pd–C(sp^3) bond in $[(CH_2)_4NCS_2]Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$ [1b], the latter exerts a greater trans influence. The Pd–S bond distance trans to the isopropyl ligand is 2.439(1) Å while the Pd–S bond trans to the phosphine is 2.395(1) Å, comparable to those in **2**. It has been noted previously for platinum(II) carbene complexes that the trans influence of a carbene ligand is similar to a phosphine ligand [10a,13].

The structure of **3** has also been solved crystallographically. An ORTEP diagram is provided in Fig. 2, and bond distances and angles are shown in Table 4. This complex crystallizes similarly in the $P\bar{1}$ space group, and the structures are very similar. As observed with **2**, the *tert*-butyl substituent is oriented cis with respect to the palladium atom.

4. Supplementary material available

Tables of complete bond distances, angles, anisotropic thermal parameters and positional parameters of H atoms are available from the authors.

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