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Influence of the size of the phosphine ligand on primary–secondary alkyl isomerization equilibria with $(Me_2NCS_2)Pt(PR_3)(alkyl)$ complexes

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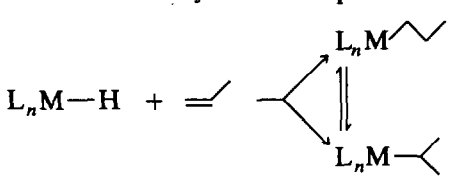
Abstract

The reactions of $(Me_2NCS_2)Pt(PR_3)Cl$ with Grignard or alkyl lithium reagents lead to the preparations of $(Me_2NCS_2)Pt(PR_3)(alkyl)$ (R = Me, Et, Ph, Cy, *o*-$CH_3C_6H_4$, C_6F_5) complexes. The reactions are successful at or below room temperature for R = Me, Et, Ph, but reactions with the starting chloride containing phosphines with larger cone angles need to be heated in refluxing Et_2O or THF. The alkylplatinum complexes are extremely stable, and can be heated in solution to 100°C without decomposition. At 120°C, the alkyl ligand undergoes a slow isomerization reaction that leads to a mixture of the linear and branched isomers. For example, heating either $(Me_2NCS_2)Pt(PMe_3)(\eta^1\text{-}CH_2CH_2CH_2CH_3)$ or $(Me_2NCS_2)Pt(PMe_3)(\eta^1\text{-}CH(CH_3)CH_2CH_3)$ in xylene produces a 9/1 mixture, respectively, of the two isomers. Similar equilibrium mixtures are observed for the analogous PEt_3 and PPh_3 complexes and also for complexes of all three ligands in which the alkyl ligand is a propyl substituent. The bulky phosphines where R is Cy and *o*-$CH_3C_6H_4$ shift the equilibria to favor the linear isomers, but some of the branched isomer is still observed at equilibrium. The solid state structure of $(Me_2NCS_2)Pt(PCy_3)$(sec-butyl) has been determined crystallographically. Crystal data: triclinic, $P\bar{1}$, $a = 9.288(3)$ Å, $b = 19.538(5)$ Å, $c = 8.854(3)$ Å, $\alpha = 99.76(2)°$, $\beta = 91.98(2)°$, $\gamma = 103.02(2)°$, $V = 1538$ Å^3, $Z = 2$, $R_F = 5.2\%$ and $R_{wF} = 6.4\%$. The steric influence of the bulky phosphine causes a substantial increase in the P–Pt–C(butyl) angle when compared to the structures of analogous complexes containing phosphine ligands with small cone angles.

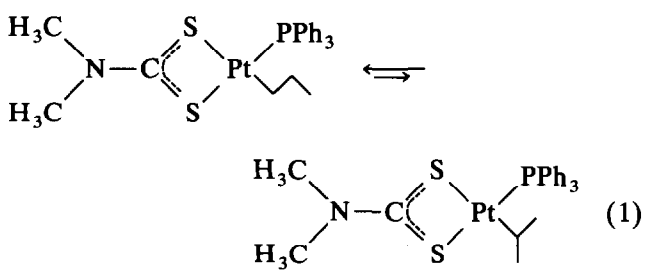
1. Introduction

The insertion of alkenes into metal–hydrogen bonds, a reaction that is important to many processes catalyzed by transition metals [1], can lead to isomeric mixtures of alkylmetal complexes (Scheme 1). The various isomers, which are generally in rapid equilibrium, can control the types of products produced in these reactions [2]. While a number of alkyl isomerization reactions of alkylmetal complexes have been reported [3–7], fundamental information on the factors that determine the bonding preferences is still lacking.



Scheme 1.

We have recently reported a series of new palladium and platinum complexes of the general formula $(R'_2NCS_2)M(PR_3)(alkyl)$ (R = Et, Ph; R' = Me, Et) that will undergo the alkyl isomerization, but that have minimal steric influences from the ancillary ligands. An example is shown in eqn. (1) [8].



(1)

At equilibrium, both isomers are observed in a ratio of 9/1 for platinum and 10/1 for the analogous palladium complexes. Also, the primary/secondary ratio of

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the equilibrium is not influenced by changing the phosphine ligand from PEt_3 to PPh_3 or the alkyl ligand from propyl to butyl. The solid state structures for the pair of isomers $[(CH_2)_4NCS_2]Pd(PEt_3)$(*n*-propyl) and $[(CH_2)_4NCS_2]Pd(PEt_3)$(isopropyl) have been determined by X-ray crystallography. These structures verify that there are no close contacts between the alkyl group and the ancillary ligands in either isomer [9]. The 9/1 to 10/1 equilibrium ratios represent an energy difference of 1.6 kcal mol^{-1} to 1.7 kcal mol^{-1}. We believe these values represent the energy differences in primary *vs.* secondary alkylmetal complexes for these metals in the absence of steric constraints imposed by other ligands in the coordination sphere.

Reported here are complete results of these studies in the platinum system. We report the syntheses of $(Me_2NCS_2)Pt(PR_3)$(alkyl) complexes where the R-group on the phosphine is varied to be methyl, ethyl, phenyl, cyclohexyl (Cy), *ortho*-tolyl, and pentafluorophenyl. We have determined the influences on the positions of the equilibrium reactions of introducing bulky phosphine ligands. The solid-state structure, as determined by X-ray crystallography, is reported for $(Me_2NCS_2)Pt(PCy_3)$ (sec-butyl).

2. Experimental details

2.1. General procedure

All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or a Vacuum Atmosphere HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. The ^1H and ^{31}P NMR spectra were recorded at ambient temperature on either a Bruker AM-300 spectrometer or a Bruker AM-500 spectrometer using a 5 mm broad band probe. ^1H NMR chemical shifts are reported in parts per million *vs.* TMS. All ^{31}P NMR spectra were run with proton decoupling, and ^{31}P NMR chemical shifts are reported in ppm vs. H_3PO_4. Mass spectra were run on a VG 70SQ mass spectrometer. The clusters assigned to specific ions show the appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by Robertson Laboratory, Inc. Alkyllithium reagents and Grignard reagents were purchased from Aldrich Chemical Company and used as received. Trimethylphosphine also was purchased from Aldrich, and other phosphines were purchased from Strem Chemicals, Inc. $Pt(S_2CNMe_2)_2$ [10], $[Pt(Me_2NCS_2)Cl]_2$ [11], $(Et_2NCS_2)Pt(PEt_3)(\eta^1$-propyl) [8b], $(Et_2NCS_2)Pt(PEt_3)(\eta^1$-butyl) [8b] and $Pt(PR_3)_2Cl_2$ (R = Cy [12] *o*-tolyl [13] C_6F_5 [14], and Me [15]) were prepared by the literature methods.

2.2. Chloro(dimethyldithiocarbamato)(tricyclohexylphosphine)platinum(II) $(Me_2NCS_2)Pt(PCy_3)Cl$

2.2.1. Method A

$Pt(S_2CNMe_2)_2$ (0.42 g, 0.96 mmol) and $Pt(PCy_3)_2Cl_2$ (Cy = cyclohexyl, 0.78 g, 0.94 mmol) were combined in a 250 ml round bottomed flask, followed by the addition of CH_2ClCH_2Cl (100 ml). This mixture was heated at reflux for 72 h. The solution was filtered and the solvent was removed under vacuum. The residue was extracted with benzene, filtered and the solvent evaporated to yield a yellow solid (0.52 g, 0.82 mmol, 88%). ^1H NMR (δ, $CDCl_3$): 3.22, 3.20 (3, 3; s, s; -NMe_2); 1.24–2.08 (33, m, PCy_3). ^{31}P NMR (δ, $CDCl_3$): 18.80 (J(PPt) = 3546 Hz). The mass spectrum shows clusters at *m/e* 631 (M^+) and 594 (M^+–Cl). Anal. Calcd. for $C_{21}H_{39}ClNPPtS_2$: C, 39.96; H, 6.23; N, 2.22. Found: C, 39.95; H, 6.18; N, 2.12.

2.2.2. Method B

$[Pt(Me_2NCS_2)Cl]_2$ (1.59 g, 2.23 mmol) and PCy_3 (2.54 g, 9.06 mmol) were placed in a flask, followed by addition of toluene (80 ml). The mixture was stirred for several hours until all the yellow solid had dissolved. The solution was filtered, and the solvent was removed under vacuum. The yellow solid was washed with ethanol and recrystallized from CH_2Cl_2/hexane (1.65 g, 2.69 mmol, 60%).

2.3. (Dimethyldithiocarbamato)n-propyl(tricyclohexylphosphine)platinum(II) $(Me_2NCS_2)Pt(PCy_3)$ $(\eta^1$-$CH_2CH_2CH_3)$

$(Me_2NCS_2)Pt(PCy_3)Cl$ (0.10 g, 0.16 mmol) was dissolved in benzene (10 ml). Diethyl ether (20 ml) was added to the solution followed by n-propylmagnesium chloride (0.15 ml, 2.0 M, 0.30 mmol). The reaction mixture was heated at reflux for 1 h. The solvent was removed under vacuum. The residue was extracted with benzene (10 ml), filtered and the benzene evaporated to yield a yellow solid (0.090 g, 0.14 mmol, 88%). ^1H NMR (δ, $CDCl_3$): 3.25, 3.23 (3, 3; s, s; NMe_2); 1.16–1.98 (33, m, PCy_3); 0.88 (3, t, J(HH) = 7 Hz, $CH_2CH_2CH_3$); the resonances for the methylene hydrogen atoms of the propyl group could not be assigned because of overlap with the multiplet of the cyclohexyl group. ^{31}P NMR (δ, C_6D_6): 21.16 (J(PPt) = 4044 Hz). Anal. Calcd. for $C_{24}H_{46}NPPtS_2$: C, 45.12; H, 7.26. Found: C, 45.25; H, 7.09.

2.4. (Dimethyldithiocarbamato)isopropyl(tricyclohexylphosphine)platinum(II) $(Me_2NCS_2)Pt(PCy_3)(\eta^1$-$CH(CH_3)_2)$

This complex was prepared as indicated above for the n-propyl analog in 88% yield. ^1H NMR (δ, $CDCl_3$): (3.25, 3.22 3, 3; s, s; NMe_2); 1.08–1.98 (33, m, PCy_3);

1.14 (6, d, J(HH) = 7 Hz, $CH(CH_3)_2$); the resonance for the methine hydrogen atom could not be assigned. ^{31}P NMR (δ, C_6D_6): 20.77 (J(PPt) = 4182 Hz). Anal. Calcd. for $C_{24}H_{46}NPPtS_2$: C, 45.12; H, 7.26. Found: C, 45.42; H, 7.43.

2.5. (Dimethyldithiocarbamato)sec-butyl(tricyclohexylphosphine)platinum(II) $(Me_2NCS_2)Pt(PCy_3)(\eta^1\text{-}CH(CH_3)CH_2CH_3)$

$(Me_2NCS_2)Pt(PCy_3)Cl$ (0.10 g, 0.16 mmol) was dissolved in THF (20 ml). Sec-butylmagnesium chloride (0.30 ml, 2.0 M, 0.60 mmol) was added, and the mixture was heated at reflux for 3 h. Acetone (2 ml) was added to consume excess sec-butylmagnesium chloride. The solvent was removed under vacuum. The residue was extracted with hexane, filtered and the hexane evaporated to yield a yellow solid (0.050 g, 0.080 mmol, 50%). ^1H NMR (δ, C_6D_6): 2.57, 2.53 (3, 3; s, s; NMe_2); 1.17–2.10 (33, m, PCy_3); 1.40 (3, t, J(HH) = 7 Hz, $CH(CH_3)CH_2CH_3$); the other hydrogen atoms of sec-butyl group could not be assigned. ^{31}P NMR (δ, C_6D_6): 20.05 (J(PPt) = 4193 Hz). Anal. Calcd. for $C_{25}H_{48}NPPtS_2$: C, 45.99; H, 7.41. Found: C, 46.05; H, 7.33.

2.6. (Dimethyldithiocarbamato)n-butyl(tricyclohexylphosphine)platinum(II) $(Me_2NCS_2)Pt(PCy_3)(\eta^1\text{-}CH_2CH_2CH_2CH_3)$

$(Me_2NCS_2)Pt(PCy_3)Cl$ (0.10 g, 0.16 mmol) was dissolved in THF (10 ml). The solution was cooled to −78°C and butyllithium (0.10 ml, 2.5 M, 0.25 mmol) was added. The mixture was allowed to warm up to room temperature (3 h). The solvent was removed under vacuum. The residue was extracted with benzene (10 ml), filtered and the benzene evaporated to yield a yellow solid (0.070 g, 0.14 mmol, 87%). The analytical sample was recrystallized from toluene–hexane. ^1H NMR (δ, C_6D_6): 2.56, 2.55 (3, 3; s, s; NMe_2); 1.16 (3, t, J(HH) = 7 Hz, $CH_2CH_2CH_2CH_3$); the resonances for the other butyl group hydrogen atoms could not be assigned. ^{31}P NMR (δ, C_6H_6): 21.11 (J(PPt) = 4046 Hz). Anal. Calcd. for $C_{25}H_{48}NPPtS_2$: C, 45.99; H, 7.41. Found: C, 46.27; H, 7.61.

2.7. Chloro(dimethyldithiocarbamato)(tri-o-tolylphosphine)platinum(II) $(Me_2NCS_2)Pt[P(o\text{-}CH_3C_6H_4)_3]Cl$

$Pt[P(o\text{-}CH_3C_6H_4)_3]_2Cl_2$ (1.49 g, 1.70 mmol) and $Pt(S_2CNMe_2)_2$ (0.89 g, 2.0 mmol) were combined in a round bottomed flask. Xylenes (200 ml) were added and the reaction mixture was heated at reflux for 4 d. The solution was filtered and the solvent was removed under vacuum. The yellow solid was recrystallized from CH_2Cl_2–hexane (30 ml) (1.15 g, 1.76 mmol, 52%). ^1H NMR (δ, $CDCl_3$): 6.87–7.35 (12, m, C_6H_4); 3.25, 3.23 (3, 3; s, s; NMe_2); 3.26, 3.20 (4.5, 4.5; s, s; $CH_3C_6H_4$). ^{31}P NMR (δ, $CDCl_3$): 24.23 (J(PPt) = 3971 Hz). The high resolution mass spectrum shows M^+, m/e: calcd. for $C_{24}H_{27}ClNP^{194}PtS_2$, 654.0659; found, 654.0675. Anal. Calcd. for $C_{24}H_{27}ClNPPtS_2$: C, 44.00; H, 4.15. Found: C, 44.35; H, 4.28.

2.8. (Dimethyldithiocarbamato)n-propyl(tri-o-tolylphosphine)platinum(II) $(Me_2NCS_2)Pt[P(o\text{-}CH_3C_6H_4)_3](\eta^1\text{-}CH_2CH_2CH_3)$

$(Me_2NCS_2)Pt[P(o\text{-}CH_3C_6H_4)_3]Cl$ (0.10 g, 0.15 mmol was dissolved in THF (10 ml). Propylmagnesium chloride (0.10 ml, 2.0 M, 0.20 mmol) was added. The mixture was heated at reflux for 6 h. The solvent was removed under vacuum. The residue was extracted with benzene (10 ml), filtered and the benzene evaporated to yield a yellow solid. NMR analysis indicated that the desired product was contaminated by the starting material (*ca.* 50%) and free $P(o\text{-}CH_3C_6H_4)_3$ (*ca.* 15%). The phosphine can be removed by washing with ethanol, but a number of attempted purification methods failed to remove the starting material impurity. ^1H NMR (δ, C_6D_6): 6.73–7.39 (m, $CH_3C_6H_4$); 2.37, 2.43, 2.44, 2.47 (all singlets, NMe_2 and $CH_3C_6H_4$); 0.97 (t, J(HH) = 7 Hz, $CH_2CH_2CH_3$). ^{31}P NMR (δ, C_6D_6): 17.75 (J(PPt) = 4162 Hz). The high resolution mass spectrum shows M^+, m/e: calcd. for $C_{27}H_{34}NP^{194}PtS_2$, 661.1497; found, 661.1510.

2.9. (Dimethyldithiocarbamato)isopropyl(tri-o-tolylphosphine)platinum(II) $(Me_2NCS_2)Pt[P(o\text{-}CH_3C_6H_4)_3](\eta^1\text{-}CH(CH_3)_2)$

This complex was prepared as indicated above for the n-propyl analog using isopropylmagnesium chloride. The desired product was contaminated with starting material (*ca.* 20%) that could not be separated. ^1H NMR (δ, C_6D_6): 6.75–7.39 (m, $CH_3C_6H_4$); 2.41, 2.44, 2.45, 2.49 (all singlets, NMe_2 and $CH_3C_6H_4$); 0.97 (t, J(HH) = 7 Hz, $CH(CH_3)_2$). ^{31}P NMR (δ, C_6D_6): 18.48 (J(PPt) = 4287 Hz).

2.10. Chloro(dimethyldithiocarbamato)[tris(pentafluorophenyl)phosphine]platinum(II) $(Me_2NCS_2)Pt[P(C_6F_5)_3]Cl$

This complex was prepared as indicated above for the tri-*o*-tolylphosphine analog in 56% yield. ^1H NMR (δ, $CDCl_3$): 3.25, 3.21 (s, s, NMe_2). ^{31}P NMR (δ, C_6D_6): −36.67 (J(PPt) = 3830 Hz). The mass spectrum shows clusters at m/e 883 (M^+) and 846 (M^+-Cl). Anal. Calcd. for $C_{21}H_6ClF_{15}NPPtS_2$: C, 28.87; H, 0.69. Found: C, 28.54; H, 0.87.

2.11. (Dimethyldithiocarbamato)n-propyl[tris(pentafluorophenyl)phosphine]platinum(II) $(Me_2NCS_2)Pt[P(C_6F_5)_3](\eta^1\text{-}CH_2CH_2CH_3)$

$(Me_2NCS_2)Pt[P(C_6F_5)_3]Cl$ (0.10 g, 0.11 mmol) was dissolved in THF (10 ml). The solution was cooled

down to −78°C. Propylmagnesium chloride (0.15 ml, 2.0 M, 0.30 mmol) was added. The mixture was allowed to warm up to room temperature (2 h). The solvent was removed under vacuum. The residue was extracted with benzene (10 ml), filtered and the benzene evaporated to yield a yellow solid (0.050 g, 0.056 mmol, 51%). ^{1}H NMR (δ, C_6D_6): 2.37, 2.34 (3,3; s, s, NMe_2); 0.87 (t, 3, $CH_2CH_2CH_3$, J(HH) = 7 Hz). ^{31}P NMR (δ, C_6D_6) −12.55 ($J_{(PPt)}$ = 4313 Hz). Anal. Calcd. for $C_{24}H_{13}F_{15}NPPtS_2$: C, 32.36; H, 1.47. Found: C, 32.57; H, 1.34.

2.12. Chloro(dimethyldithiocarbamato)(trimethylphosphine)platinum (II) $(Me_2NCS_2)Pt(PMe_3)Cl$

This complex was prepared as indicated above for the tri-*o*-tolylphosphine analog in 89% yield. The analytical sample was recrystallized from CH_2Cl_2–hexane. ^{1}H NMR (δ, $CDCl_3$): 3.25, 3.22 (3, 3; s, s; NMe_2); 1.53 (9, d, J(HP) = 11 Hz (J(HPt) = 36 Hz), PMe_3). ^{31}P NMR (δ, $CDCl_3$): −26.03 (J(PPt) = 3500 Hz). Anal. Calcd. for $C_6H_{15}ClNPPtS_2$: C, 16.88; H, 3.54. Found: C, 16.94; H, 3.37.

2.13. (Dimethyldithiocarbamato)n-butyl(trimethylphosphine)platinum(II) $(Me_2NCS_2)Pt(PMe_3)(\eta^1$-$CH_2CH_2$-$CH_2CH_3)$

$(Me_2NCS_2)Pt(PMe_3)Cl$ (0.10 g, 0.23 mmol) was dissolved in THF (10 ml). The solution was cooled to −78°C, followed by addition of butyllithium (0.20 ml, 1.6 M, 0.32 mmol). The mixture was allowed to warm up to room temperature (2 h). The solvent was removed under vacuum. The residue was extracted with benzene (10 ml), filtered and the benzene evaporated to yield a yellow solid (0.090 g, 0.20 mmol, 87%). The analytical sample was recrystallized from toluene-hexane. ^{1}H NMR (δ, C_6D_6): 2.59, 2.53 (3, 3; s, s; NMe_2); 2.09–1.96 (2, m, $CH_2CH_2CH_2CH_3$); 1.84–1.67 (4, m, $CH_2CH_2CH_2CH_3$); 1.13 (3, t, J(HH) = 7 Hz, $CH_2CH_2CH_2CH_3$); 1.05 (9, d, J(HP) = 10 Hz (J(HPt) = 42 Hz), PMe_3). ^{31}P NMR (δ, C_6D_6): −28.26 (J(PPt) = 4036 Hz). Anal. Calcd. for $C_{10}H_{24}NPPtS_2$: C, 26.78; H, 5.39. Found: C, 27.09; H, 5.41.

2.14. Dimethyldithiocarbamato)sec-butyl(trimethylphosphine)platinum(II) $(Me_2NCS_2)Pt(PMe_3)(\eta^1$-$CH(CH_3)$ $CH_2CH_3)$

This complex was prepared as indicated above for the n-butyl analog in 78% yield. The analytical sample was recrystallized from toluene–hexane. ^{1}H NMR (δ, C_6D_6): 2.64, 2.57 (3, 3, s, s; NMe_2); 2.1 (2, m, CH_2); 2.0 (1, m CH); 1.72 (3, d, J(HH) = 5 Hz, $CH(CH_3)$ CH_2CH_3); 1.43 (3, t, J(HH) = 7 Hz, $CH(CH_3)CH_2$-CH_3); 1.06 (9, d, J(HP) = 10 Hz (J(HPt) = 43 Hz), PMe_3). ^{31}P NMR (C_6D_6): δ −27.77 (J(PPt) = 4186 Hz). Anal. Calcd. for $C_{10}H_{24}NPPtS_2$: C, 26.78; H, 5.39. Found: C, 26.97; H, 5.59.

2.15. (Dimethyldithiocarbamato)n-propyl(trimethylphosphine)platinum(II) $(Me_2NCS_2)Pt(PMe_3)(\eta^1$-$CH_2CH_2$-$CH_3)$

$(Me_2NCS_2)Pt(PMe_3)Cl$ (0.10 g, 0.23 mmol) was dissolved in THF (10 ml). The solution was cooled to −78°C. Propylmagnesium chloride (0.30 ml, 2.0 M, 0.60 mmol) was added. The mixture was allowed to warm up to room temperature (2 h). The solvent was removed under vacuum. The residue was extracted with benzene (10 ml), filtered and the benzene evaporated to yield a yellow solid (0.080 g, 0.18 mmol, 76%). ^{1}H NMR (δ, C_6D_6): 2.58, 2.51 (3, 3; s, s; NMe_2); 2.10 (2, m, $CH_2CH_2CH_3$); 1.76 (2, m, $CH_2CH_2CH_3$); 1.36 (3, t, J(HH) = 7 Hz, $CH_2CH_2CH_3$); 1.04 (9, d, J(HP) = 10 Hz (J(HPt) = 43 Hz), PMe_3). ^{31}P NMR (δ, C_6D_6): −28.22 (J(PPt) = 4035 Hz). Anal. Calcd. for $C_9H_{22}NPPtS_2$: C, 24.88; H, 5.10. Found: C, 25.05; H, 5.21.

2.16. (Dimethyldithiocarbamato)isopropyl(trimethylphosphine)platinum(II) $(Me_2NCS_2)Pt(PMe_3)(\eta^1$-$CH$-$(CH_3)_2)$

This complex was prepared as indicated above for the n-propyl analog in 76% yield. ^{1}H NMR (δ, C_6D_6): 2.61, 2.55 (3, 3; s, s; NMe_2); 1.74 (6, d, J(HH) = 6 Hz, $CH(CH_3)_2$); 1.03 (9, d, J(HP) = 10 Hz (J(HPt) = 44 Hz), PMe_3). ^{31}P NMR (δ, C_6D_6): −27.42 (J(PPt) = 4187 Hz). Anal. Calcd. for $C_9H_{22}NPPtS_2$: C, 24.88; H, 5.10. Found: C, 25.26; H, 4.88.

2.17. (Dimethyldithiocarbamato)n-propyl(triphenylphosphine)platinum(II) $(Me_2NCS_2)Pt(PPh_3)(\eta^1$-$CH_2CH_2$-$CH_3)$

$(Me_2NCS_2)Pt(PPh_3)Cl$ (0.10 g, 0.16 mmol) was dissolved in THF (10 ml). The solution was cooled to −78°C, and n-propylmagnesium chloride (0.10 ml, 2.0 M, 0.20 mmol) was added dropwise. The mixture was allowed to warm to room temperature (1 h), the THF was removed under vacuum, and the remaining solid was extracted with benzene (2 × 4 ml). The benzene was removed under vacuum to yield 0.048 g (0.077 mmol, 48%) of a yellow powder. ^{1}H NMR (δ, $CDCl_3$): 7.6, 7.4 (m, m; 6, 9; $P(C_6H_5)_3$); 3.28, 3.18 (s, s; 3, 3; NCH_3); 1.4 (m; 2; $PtCH_2CH_2CH_3$); 1.2 (d of t; 2; $PtCH_2CH_2CH_3$; J(PtH) = 35 Hz, J(PH) = 9 Hz, J(HH) = 6 Hz); 0.69 (t; 3; $PtCH_2CH_2CH_3$; J(HH) = 7 Hz). ^{31}P NMR (δ, $CDCl_3$): 21.38 (J(PPt) = 4245 Hz). Anal. Calcd. for $C_{24}H_{28}NPPtS_2$: C, 46.44; H, 4.55. Found: C, 45.92; H, 4.97. The high resolution mass spectrum shows M^+, m/e: calcd. for $C_{24}H_{28}NP^{194}PtS_2$, 619.1028; found, 619.1033.

2.18. (Dimethyldithiocarbamato)isopropyl(triphenylphosphine)platinum(II) (Me_2NCS_2)Pt(PPh_3)(η^1-CH(CH_3)$_2$)

This complex was prepared as above for the n-propyl analog in 36% yield. ^{1}H NMR (δ, $CDCl_3$): 7.6, 7.4 (m, m; 6, 9; P(C_6H_5)$_3$); 3.30, 3.20 (s, s; 3, 3; NCH_3); 1.7 (m; 1; PtCH(CH_3)$_2$); 1.0 (d; 6; PtCH(CH_3)$_2$; J(PtH) = 54 Hz, J(HH) = 7 Hz). ^{31}P NMR (δ, $CDCl_3$): 21.16 (J(PPt) = 4380). The high resolution mass spectrum shows M^+, m/e: calcd. for $C_{24}H_{28}NP^{194}PtS_2$, 619.1028; found, 619.1048.

2.19. Isomerization

The alkylplatinum complexes were dissolved in xylenes (containing 20% xylenes-d_{10}). This solution was placed in an NMR tube and degassed by freeze–thaw pumping sequences. The tube was sealed and placed in a 120°C bath until equilibrium was established (as monitored by ^{31}P NMR). Typical times needed to establish the equilibria are a week. The positions of the equilibria were determined by ^{31}P NMR spectroscopy. The resonance for each isomer had baseline separation and the pulsing sequence was carefully checked for saturation. The digital resolution was 0.031 Hz/point. It is estimated that the reported equilibria ratios have an error of ±3%.

TABLE 1. Crystallographic data for the structural analysis of (Me_2NCS_2)Pt(PCy_3)(η^1-CH(CH_3)CH_2CH_3)

Formula	$C_{25}H_{48}NPPtS_2$
FW	652.86
Color and habit	Yellow prismatic
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.288(3)
b (Å)	19.538(5)
c (Å)	8.854(3)
α (°)	99.76(2)
β (°)	91.98(2)
γ (°)	103.02(2)
V (Å^3)	1538
Z	2
Crystal dimensions (mm)	0.36×0.34×0.08
d_{calcd} (g cm^{-1})	1.397
Monochromator	Graphite
Radiation (Å)	Mo Kα, (λ = 0.71073)
Temperature	Ambient
Scan	$\omega/2\theta$
2θ range (°)	4–46 ($\pm h$, $\pm k$, $+l$)
No. rflns. meas.	4453
No. rflns. obsd.	4303
Linear abs coeff (cm^{-1})	47.6
Transmission factors	
max	0.6670
min	0.2179
av	0.5516
Decay correction	
max	1.038
av	1.018
R	0.052
R_w	0.064

TABLE 2. Fractional atomic coordinates for (Me_2NCS_2)Pt(PCy_3)-(η^1-CH(CH_3)CH_2CH_3) with e.s.d.s in parentheses and equivalent isotropic temperature factors

Atom	x	y	z	B (Å^2)
Pt	0.1685(0)	0.2174(0)	0.0453(0)	3.37
S(1)	0.1505(3)	0.1158(2)	0.1710(3)	4.62
S(2)	−0.0845(3)	0.1498(1)	0.0025(3)	4.11
P	0.1398(3)	0.3051(1)	−0.0866(3)	3.19
N	−0.1293(10)	0.0374(4)	0.1580(10)	4.68
C(1)	0.3961(18)	0.2937(10)	0.3024(16)	8.06
C(2)	0.3914(13)	0.2615(7)	0.1282(14)	6.00
C(3)	0.4862(15)	0.2106(8)	0.1246(19)	7.54
C(4)	0.5026(16)	0.1824(8)	−0.0459(18)	7.24
C(5)	−0.0334(12)	0.0923(5)	0.1151(11)	3.91
C(6)	−0.2871(15)	0.0237(7)	0.1126(17)	6.79
C(7)	−0.0828(17)	−0.0111(6)	0.2516(14)	6.26
C(11)	0.0142(10)	0.2644(5)	−0.2553(10)	3.35
C(12)	0.0652(13)	0.2071(6)	−0.3587(12)	4.72
C(13)	−0.0574(14)	0.1622(6)	−0.4649(13)	5.22
C(14)	−0.1271(14)	0.2080(9)	−0.5629(13)	7.27
C(15)	−0.1611(12)	0.2670(6)	−0.4690(11)	4.82
C(16)	−0.0475(13)	0.3108(6)	−0.3563(12)	4.90
C(21)	0.3104(11)	0.3656(5)	−0.1447(11)	3.73
C(22)	0.2867(13)	0.4327(6)	−0.2077(14)	5.25
C(23)	0.4331(14)	0.4800(7)	−0.2378(15)	5.87
C(24)	0.5221(14)	0.4414(7)	−0.3415(14)	5.83
C(25)	0.5493(13)	0.3759(8)	−0.2760(15)	6.41
C(26)	0.3961(12)	0.3269(6)	−0.2538(13)	4.59
C(31)	0.0428(10)	0.3672(5)	0.0160(10)	3.38
C(32)	0.1343(12)	0.4056(7)	0.1601(13)	5.58
C(33)	0.0572(14)	0.4606(8)	0.2458(14)	6.09
C(34)	−0.0968(14)	0.4246(6)	0.2828(13)	5.19
C(35)	−0.1873(12)	0.3861(6)	0.1387(14)	5.49
C(36)	−0.1138(12)	0.3316(5)	0.0584(13)	4.63
C(1P)	0.4579(21)	0.0664(10)	0.5152(21)	9.21
C(2P)	0.6008(21)	−0.0122(11)	0.5991(21)	9.70
C(3P)	0.5709(22)	0.0497(11)	0.6198(22)	9.73

2.20. Crystallographic analysis of (Me_2NCS_2)Pt(PCy_3)-(η^1-CH(CH_3)CH_2CH_3)

A yellow prismatic crystal of (Me_2NCS_2)Pt(PCy_3)-(η^1-CH(CH_3)CH_2CH_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 analysis are listed in Table 1. Attempts to refine the structure in the noncentrosymmetric space group $P1$ were not successful due to a large correlation between parameters. 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 [16]. Hydrogen atoms were placed in calculated positions and not

refined. Full-matrix least-squares refinements were carried out with weights $w = (\sigma^2(F) + 0.0004F^2)^{-1}$ for reflections with $I > 3\sigma(I)$ where $\sigma(I)$ was derived from counting statistics. Absorption corrections were by the analytical method. Far from the major, metallorganic molecule, and close to the center of symmetry, three peaks were observed in the difference Fourier map. These peaks were assigned as carbon atoms and they refined to respectable temperature factors, about 10 Å^2. Chemical analysis of the crystals is not consistent with incorporation of half an equivalent of hexane, but partial incorporation of solvent hexane is possible. It also appears that C15, one of the carbon atoms of a cyclohexyl moiety, is disordered. The highest peak in the final difference map, 1.8 e Å^{-3}, was located close to this atom but it could not be interpreted as a simple chair-boat conformational equilibrium. It is equally likely that the peak is a result of errors in the absorption correction and the approximations in the treatment of the possible lattice solvent molecule. Table 2 shows atomic parameters for the molecule.

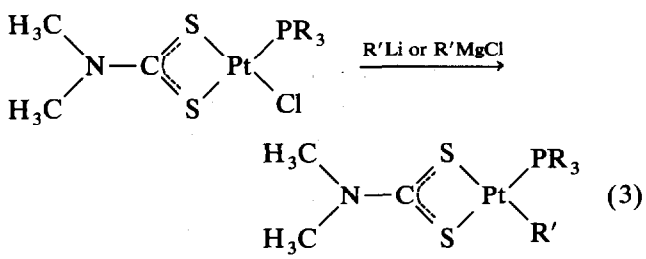
3. Results and discussion

3.1. Syntheses of complexes

The $(Me_2NCS_2)Pt(PR_3)Cl$ starting materials for the syntheses of alkyl metal complexes are prepared in high (R = Me, Cy) to moderate (R = Ph, *o*-$CH_3C_6H_4$, C_6F_5) yield from an exchange reaction of the bisphosphine and bisdithiocarbamate complexes (eqn. (2)).

$$Pt(PR_3)_2Cl_2 + Pt(Me_2NCS_2)_2 \longrightarrow 2(Me_2NCS_2)Pt(PR_3)Cl \quad (2)$$

As reported earlier [8b] for $(Et_2NCS_2)Pt(PEt_3)$(alkyl) complexes, the $(Me_2NCS_2)Pt(PR_3)$(alkyl) (R = Me, Ph) complexes form readily at or below ambient temperature in reactions of $(Me_2NCS_2)Pt(PR_3)Cl$ with Grignard or alkyllithium reagents.



(3)

In contrast, reactions of $(Me_2NCS_2)Pt(PCy_3)Cl$ with n-propyl and isopropyl magnesium chloride need to be heated in refluxing Et_2O and reactions with sec-butyl magnesium chloride in refluxing THF in order to go to completion. Alkyllithium reagents were only successful for n-butyllithium.

Reactions of $(Me_2NCS_2)Pt[P(o\text{-}CH_3C_6H_4)_3]Cl$ with Grignard or alkyllithium reagents could not be driven to completion. In the most successful preparations using n-propyl and isopropyl magnesium chloride, substantial (20–50%) amounts of the starting material remained. We were unable to separate the starting chloride from the desired propyl products. Starting with $(Me_2NCS_2)Pt[P(C_6F_5)_3]Cl$, the only alkyl complex that could be isolated was $(Me_2NCS_2)Pt[P(C_6F_5)_3]$(n-propyl). We were unable to directly prepare $(Me_2NCS_2)Pt[P(C_6F_5)_3]$(isopropyl) and attempts to form it in isomerization reactions of $(Me_2NCS_2)Pt[C_6F_5)_3]$(n-propyl) lead to decomposition.

3.2. Isomerization studies

Heating these alkylplatinum complexes in xylene solution for a number of days at 120°C leads to the establishment of an equilibrium between the linear and branched isomers, Table 3. In all cases reported in the Table, both the linear and branched isomers were separately prepared and the equilibrium position established starting with each isomer. For the $(Me_2NCS_2)Pt[P(o\text{-}CH_3C_6H_4)_3]$(propyl) complexes, isomerization results reported in the Table were carried out with samples of these complexes contaminated with $(Me_2NCS_2)Pt[P(o\text{-}CH_3C_6H_4)_3]Cl$. We feel that the chloride impurity does not influence the equilibrium position. To support this contention, we have demonstrated that addition of $(Et_2NCS_2)Pt(PEt_3)Cl$ to $(Et_2NCS_2)Pt(PEt_3)$(propyl) complexes does not change the equilibrium position.

TABLE 3. Isomerization of $(Me_2NCS_2)Pt(PR_3)$(alkyl): positions of equilibria

R	Alkyl	Ratio primary:secondary
Methyl	n-Propyl	12:1
Methyl	iso-Propyl	12:1
Methyl	n-Butyl	9:1
Methyl	sec-Butyl	9:1
Ethyl [a]	n-Propyl	9:1
Ethyl [a]	iso-Propyl	9:1
Ethyl [a]	n-Butyl	9:1
Ethyl [a]	sec-Butyl	9:1
Phenyl	n-Propyl	9:1
Phenyl	iso-Propyl	9:1
Cyclohexyl	n-Propyl	14:1
Cyclohexyl	iso-Propyl	14:1
Cyclohexyl	n-Butyl	25:1
Cyclohexyl	sec-Butyl	25:1
o-Tolyl	n-Propyl	12:1
o-Tolyl	iso-Propyl	12:1

[a] The positions of equilibria are determined from $(Et_2NCS_2)Pt(PEt_3)$(alkyl) complexes.

For the phosphines PMe_3, PEt_3 and PPh_3, the positions of the equilibria, primary/secondary, are essentially constant at 9/1. The one exception is the $(Me_2NCS_2)Pt(PMe_3)$(propyl) pair where the position is 12/1. The 9/1 ratios represent an energy difference between the isomers of 1.7 kcal mol^{-1}. As argued previously, this value represents the energy differences in primary *vs.* secondary alkylmetal complexes for these metals in the absence of steric constraints imposed by other ligands in the coordination sphere.

The $(Me_2NCS_2)Pt(PR_3)$(alkyl) (R = C_6F_5, *o*-tolyl, Cy) complexes were prepared in order to introduce steric constraints from the other ligands. The most useful results were obtained with the PCy_3 complexes. With this ligand, the equilibrium position changes to 14/1 for the propyl pair and to 25/1 for the butyl pair. Clearly, the shifts in the positions of the equilibria reflect steric changes in the phosphine ligand. As expected, the impact is greater in the butyl system than the propyl system. Bennett *et al.* have previously shown a similar result in an iridium system [4b]. While bulky ligands are able to shift the equilibrium positions in favor of the linear isomers in this system, even with phosphines with very large cone angles, some of the branched isomer is observed. These results contrast most other systems in which alkyl isomerization studies have generally found that the linear isomer forms exclusively [3–7]. Thus, even with a sterically bulky phosphine in the coordination sphere, these square planar complexes have overall low steric constraints on the alkyl ligands.

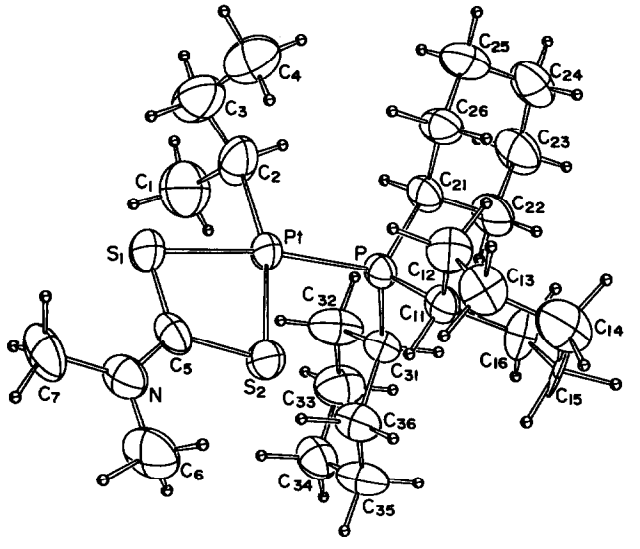


Fig. 1. ORTEP drawing of $(Me_2NCS_2)Pt(PCy_3)$(sec-butyl).

3.3. *X-ray structure of* $(Me_2NCS_2)Pt(PCy_3)$*(sec-butyl)*

In order to directly observe the steric impact of the bulky tricyclohexylphosphine ligand on the sec-butyl ligand, the solid state structure of $(Me_2NCS_2)Pt(PCy_3)$ (sec-butyl) was determined crystallographically. An ORTEP drawing of the molecule is shown in Fig. 1 and bond distances and angles are shown in Table 4. The complex is four coordinate with no close intermolecular contacts. The overall structure of the complex is similar to the structures of $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH_2CH_2CH_3)$, $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$ [9] and $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CN)CH_3)$ [17] determined earlier. For comparison, the bond distances and angles of $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$ are also shown in Table 4 (the two metals in the +2 oxidation state have essentially the same covalent radii [18]). As expected, the basic geometry about the platinum atom is square planar. The methyl and ethyl substituents on the butyl ligand are oriented away from the phosphine ligand and basically straddle

TABLE 4. Selected bond distances (Å) and bond angles (°) for $(Me_2NCS_2)Pt(PCy_3)(\eta^1\text{-}CH(CH_3)CH_2CH_3)$ and $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$ with e.s.d.s in parentheses

	M = Pt	M = Pd
Bond distances		
M–C(2)	2.108(9)	2.074(4)
M–P	2.288(2)	2.241(1)
M–S(1)	2.412(3)	2.395(1)
M–S(2)	2.404(2)	2.439(1)
S(1)–C(5)	1.698(9)	1.710(4)
S(2)–C(5)	1.752(9)	1.714(4)
N–C(5)	1.35(1)	1.320(5)
N–C(6)	1.46(1)	1.472(5)
N–C(7)	1.48(1)	1.463(5)
C(1)–C(2)	1.56(2)	1.517(7)
C(2)–C(3)	1.47(2)	1.525(7)
C(3)–C(4)	1.54(2)	
Bond angles		
S(1)–M–S(2)	72.9(1)	73.63(4)
S(1)–M–P	169.4(1)	174.30(4)
S(1)–M–C(2)	93.1(3)	95.3(1)
S(2)–M–P	96.4(1)	100.71(4)
S(2)–M–C(2)	165.3(3)	168.9(1)
P–M–C(2)	97.5(3)	90.4(1)
M–C(2)–C(1)	108.6(8)	109.3(3)
M–C(2)–C(3)	115.8(8)	108.9(3)
M–S(1)–C(5)	87.9(3)	86.2(1)
M–S(2)–C(5)	86.9(3)	84.7(1)
C(1)–C(2)–C(3)	103.5(9)	112.1(5)
C(2)–C(3)–C(4)	107.1(1)	
S(1)–C(5)–S(2)	112.1(5)	115.5(2)
S(1)–C(5)–N	123.6(7)	123.1(3)
S(2)–C(5)–N	124.2(7)	121.4(3)
M–P–C(11)	108.4(3)	110.9(2)
M–P–C(21)	119.1(3)	118.6(2)
M–P–C(31)	113.1(3)	114.4(2)

the square plane. The S1Pt–C2C1 and S1Pt–C2C3 torsion angles are −75.8° and 42.4°, respectively.

Although the effects are not dramatic, the large cone angle of the tricyclohexylphosphine ligand impacts on the structure. The major change is that the P–Pt–C2 angle increases from 90.4(1)° in the palladium complex to 97.5(3)°. This increase presumably arises from steric interaction between the sec-butyl and phosphine ligands. To compensate for this increase, the P–Pt–S2 angle decreases by 4.3° and the C2–Pt–S1 angle decreases by 2.2°.

4. Supplementary material available

Tables of positional parameters of H atoms, anisotropic thermal parameters and observed and calculated structural factors are available from the authors.

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