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Preparation and Reactivity of the Platinum(0) Anion $[(Me_2NCS_2)Pt(PEt_3)]^-$

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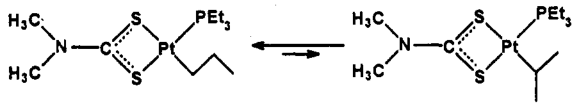
Summary: The first monometallic anionic complex of platinum(0), $[(Me_2NCS_2)Pt(PEt_3)]^-$, has been prepared from the reaction of butyllithium or lithium diisopropylamide and $(Me_2NCS_2)Pt(PEt_3)H$. The anion decomposes in solutions warmed above 0 °C, but its ^{31}P NMR spectrum can be observed at −41 °C. By proper manipulation of the reaction conditions, the anion reacts successfully with triphenyltin chloride, methyl iodide, or iodine to yield $(Me_2NCS_2)Pt(PEt_3)SnPh_3$, $(Me_2NCS_2)Pt(PEt_3)Me$, and $(Me_2NCS_2)Pt(PEt_3)I$, respectively.

Introduction

We are interested in the syntheses of alkylmetal complexes of the type $(Me_2NCS_2)Pt(PEt_3)(alkyl)$.[1] These complexes are important because they can be used to study isomerization reactions of the alkyl ligands, reactions of considerable importance in many processes catalyzed by transition metals.[2] For example, heating xylene solutions of either the *n*-propyl or isopropyl derivative at 120 °C for 1 week leads to the establishment of a 9/1 ratio of the *n*-propyl/isopropyl complexes (eq 1).[3,4]



(1)

The preparations of the alkylplatinum complexes have been carried out by the reaction of $(Me_2NCS_2)Pt(PEt_3)Cl$ and the appropriate alkyllithium or Grignard reagents.[1] An alternate route to alkylmetal complexes is the reaction of organometallic anions with alkyl halides.[5] One method to prepare these anions is the deprotonation of metal hydride complexes.[6] We report here the in situ generation of $[(Me_2NCS_2)Pt(PEt_3)]^-$ from the stable hydride complex $(Me_2NCS_2)Pt(PEt_3)H$ and its reactions with a variety of electrophiles.

Experimental Section

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. ^1H NMR chemical shifts are reported in ppm versus TMS. All ^{31}P NMR spectra were run with proton decoupling, and ^{31}P NMR chemical shifts are reported in ppm versus H_3PO_4. Elemental analyses were performed by Robertson Laboratory, Inc. All chemicals were purchased from Aldrich Chemical Co. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) and $HN[CH(CH_3)_2]_2$ were distilled from CaH_2. Methyl iodide was distilled from P_2O_5. Butyllithium was used as received. $(Me_2NCS_2)Pt(PEt_3)H$ was prepared by using the published method.[1]

(Dimethyldithiocarbamato)(triethylphosphine)(triphenylstannyl)platinum(II) $(Me_2NCS_2)Pt(PEt_3)(SnPh_3)$. $(Me_2NCS_2)Pt(PEt_3)H$ (0.080 g, 0.18 mmol) was dissolved in THF (10 mL) and cooled to −78 °C. Butyllithium (0.14 mL, 1.6 M, 0.22 mmol) was added. The reaction mixture was stirred for 2 h. A THF (10 mL) solution of Ph_3SnCl (0.11 g, 0.28 mmol) was added at −78 °C. The mixture was allowed to warm to room temperature (3 h) and stirred for an additional 2 h. The solvent was removed under vacuum. The residue was extracted with benzene (10 mL), the extract was filtered, and the benzene was evaporated. Recrystallization from toluene/hexane yielded the title compound (0.091 g, 0.12 mmol, 67%). ^1H NMR (C_6D_6): δ 8.10 (m, 6, *m*-C_6H_5); 7.31–7.19 (m, 9, *o*-, *p*-C_6H_5); 2.34, 2.11 (s, s; 3, 3; $N(CH_3)_2$); 1.45 (d of q, 6, PCH_2CH_3, $J_{HH} = 7.6$ Hz, $J_{HP} = 25$ Hz); 0.84 (d of t, 9, PCH_2CH_3, $J_{HH} = 7.6$ Hz, $J_{HP} = 17$ Hz). ^{31}P NMR (C_6D_6): δ 7.03 ($J_{PPt} = 3498$ Hz, $J_{PSn} = 174$ Hz). Anal. Calcd for $C_{27}H_{36}NPPtS_2Sn$: C, 41.39; H, 4.63. Found: C, 41.24; H, 4.50.

(Dimethyldithiocarbamato)iodo(triethylphosphine)platinum(II) $(Me_2NCS_2)Pt(PEt_3)I$. $(Me_2NCS_2)Pt(PEt_3)H$ (0.10 g, 0.23 mmol) was dissolved in THF (8 mL) and cooled to −78 °C. Lithium diisopropylamide (LDA) (0.23 mmol, freshly prepared from $HN[CH(CH_3)_2]_2$ and butyllithium in 5 mL of THF) was added dropwise at −78 °C. The mixture was stirred for 30 min. I_2 (0.070 g, 0.28 mmol) was added as a THF solution (10 mL, −78 °C). The mixture was warmed to room temperature (2 h) and stirred overnight. The solvent was removed under vacuum. The residue was extracted with benzene (10 mL), and the extract was filtered out and washed with dilute $Na_2S_2O_3$(aq) solution. The benzene was removed under vacuum, and the resulting solid recrystallized from toluene/hexane to yield a yellow solid (0.080 g, 0.14 mmol, 61%). ^1H NMR ($CDCl_3$): δ 3.21, 3.17 (s, s; 3, 3; $N(CH_3)_2$); 1.94 (d of q, 6, PCH_2CH_3, $J_{HH} = 7.6$ Hz, $J_{HP} = 25$ Hz); 1.13 (d of t, 9, PCH_2CH_3, $J_{HH} = 7.6$ Hz, $J_{HP} = 17$ Hz). ^{31}P NMR ($CDCl_{3'}$): δ 3.95 ($J_{PPt} = 3427$ Hz). Anal. Calcd for $C_9H_{21}INPPtS_2$: C, 19.29; H, 3.78. Found: C, 19.00; H, 3.60.

(Dimethyldithiocarbamato)methyl(triethylphosphine)platinum(II) $(Me_2NCS_2)Pt(PEt_3)CH_3$. $(Me_2NCS_2)Pt(PEt_3)H$ (0.10 g, 0.23 mmol) was dissolved in THF (8 mL) and cooled to −78 °C. TMEDA (0.045 mL, 0.035 g, 0.30 mmol) and butyllithium (0.20 mL, 1.6 M, 0.32 mmol) were added. The mixture was stirred

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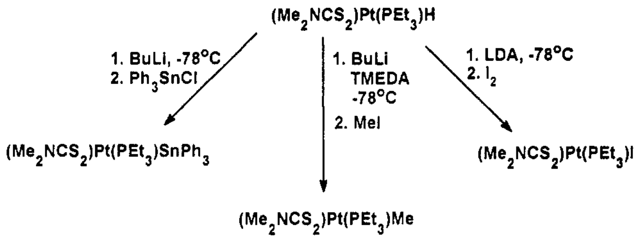
Scheme 1



for 30 min. Methyl iodide (0.031 mL, 0.071 g, 0.50 mmol) was added. The mixture was allowed to warm to room temperature (2 h) and stirred overnight. The solvent was removed under vacuum. The residue was extracted with benzene (10 mL), the extract was filtered, and the benzene was evaporated. Recrystallization from toluene/hexane yielded a yellow solid, shown by ^{1}H and ^{31}P NMR spectroscopy to be a pure sample of (Me$_2$NCS$_2$)Pt(PEt$_3$)CH$_3$[1] (0.072 g, 0.16 mm, 70%).

^{31}P NMR Spectrum of [(Me$_2$NCS$_2$)Pt(PEt$_3$)]$^-$. (Me$_2$NCS$_2$)Pt(PEt$_3$)H (0.010 g, 0.023 mmol) was placed in a NMR tube. Approximately 1 mL of toluene-d_8 was added. The solution was cooled to −78 °C. Butyllithium (0.05 mL, 1.6 M, 0.08 mmol) was added via a syringe. After 30 min, the tube was placed into an NMR spectrometer in which the probe had been cooled to −41 °C and the ^{31}P NMR spectrum was recorded. The spectrum showed a broad peak at 14.99 ppm with J_{PPt} = 2115 Hz. This signal disappears when this sample is warmed to room temperature.

Results and Discussion

The reaction of (Me$_2$NCS$_2$)Pt(PEt$_3$)H and butyllithium in THF at −78 °C leads to a color change indicative of formation of the desired anion. Addition of Ph$_3$SnCl, the reagent established by Ellis as the best choice for trapping unstable organometallic anions,[7] leads to the isolation of (Me$_2$NCS$_2$)Pt(PEt$_3$)SnPh$_3$ in good yield (Scheme 1). Ph$_3$SnCl must be added to the cooled solution of the anion. None of the desired product is isolated if the anion solution is allowed to warm before addition of Ph$_3$SnCl.

An analogous reaction with methyl iodide yields (Me$_2$NCS$_2$)Pt(PEt$_3$)Me, but also a considerable amount (15–40%) of (Me$_2$NCS$_2$)Pt(PEt$_3$)I is formed. Following the results of Crocco and Gladysz,[6] we found that addition of TMEDA to the deprotonation reaction prevents the formation of this byproduct.

Reaction of the anion and I$_2$ produces (Me$_2$NCS$_2$)Pt(PEt$_3$)I, but this product is contaminated with (Me$_2$NCS$_2$)Pt(PEt$_3$)(butyl). This byproduct presumably arises from the reaction of the platinum anion with butyl iodide, formed from excess butyllithium and iodine. To circumvent this problem the hydride can be deprotonated with LDA followed by addition of the I$_2$ to yield exclusively (Me$_2$NCS$_2$)Pt(PEt$_3$)I. Thus, by proper manipulation of the reaction conditions, the anion reacts successfully with a variety of different types of electrophiles.

Although attempts to isolate [(Me$_2$NCS$_2$)Pt(PEt$_3$)]$^-$ have failed, its ^{31}P NMR spectrum could be observed at −41 °C. The chemical shift of the anion is not very different from the starting hydride, but the phosphorus–platinum coupling constant drops from 3606 to 2115 Hz. In the ^{1}H NMR spectrum run on this sample at −41 °C, the uniquely shifted hydride resonance of the starting material at δ −15 has completely disappeared and no new hydride resonances are observed. The [(Me$_2$NCS$_2$)Pt(PEt$_3$)]$^-$ anion, formally a d^{10} complex, appears to be the *first monometallic anionic derivative of platinum(0) to be reported.* Nast has reported the preparation of K$_2$Pt(C≡CR)$_2$, an insoluble powder that is likely to be oligomeric.[8] It is possible that with [(Me$_2$NCS$_2$)Pt(PEt$_3$)]$^-$ some type of association also takes place, but it remains soluble in THF at low temperatures.

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