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Notes

Synthesis of a Platinum(II) Bis(trimethylsilyl)amido Complex: A Better Starting Material for the Cyclometalation of Pincer Ligands

Athimoolam Arunachalampillai, Magnus T. Johnson, and Ola F. Wendt*

Organic Chemistry, Department of Chemistry, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

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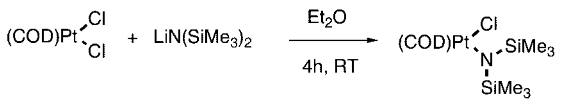
Summary: Treatment of [(COD)PtCl$_2$] with LiN(SiMe$_3$)$_2$ gives [COD]PtClN(SiMe$_3$)$_2$ in high yield. This product was fully characterized, including an X-ray structure. From a number of examples it is shown to be a very convenient starting material for the preparation of PXP platinum pincer complexes, giving excellent yields of the cyclometalated product under mild conditions.

PXP pincer complexes of late transition metals have attracted much attention since their first discovery in 1976.[1] The PXP backbone not only gives oxidative stability but also provides a high thermal stability to the complex. Thus, iridium complexes of PCP ligands have shown thermal stability up to 250 °C during the dehydrogenation of alkanes,[2] and similar palladium complexes have also shown a high stability in cross-coupling reactions, although most authors agree that it is highly reactive decomposition products that are responsible for the catalytic activity.[3] Platinum pincer complexes have been applied as SO$_2$-triggered switches,[4] biomarkers,[5] and catalysts for the hydroamination of acrylonitrile[6] and have also been used for the insertion of CO$_2$,[7] but in general the applications of platinum complexes are fewer than those of Ir, Rh, and Pd. One possible reason for this is that a convenient precursor has not been available. The most easily accessible precursor for this reaction is [COD]PtCl$_2$, but it has poor solubility in most organic solvents and usually requires the use of an external base and high temperature. Typically triethylamine in xylene has been used.[8] The use of [COD]PtMeCl gives cyclometalation under much milder conditions, but on the other hand, it can only be obtained through a long synthetic route (diiodination, dimethylation, and chlorination with acetyl chloride).[9] In our hands it sometimes also gives poor yields and often [COD]PtMe$_2$ as an impurity. Also, *cis*-PtCl$_2$(PPh$_3$)$_2$ has been used, giving moderate yields in the cyclometalation of phosphines, whereas the use of PtCl$_2$(SEt$_2$)$_2$ gave excellent yields in the cyclometalation of phosphinites.[10] Another possibility, which is widely used in the organometallic chemistry of f-block metals, would be the use of a monodentate amido ligand, but such examples are unusual for platinum(II), probably due to the hard−soft mismatch. Here we report the synthesis, characterization, and cyclometalation reactivity of the new compound [COD]PtClN(SiMe$_3$)$_2$ (**1**), which can be used as a very convenient starting material for the preparation of PXP pincer complexes. The choice of the ligand N(SiMe$_3$)$_2$ was dictated by the fact that the trimethylsilyl group prevents β-elimination and facilitates a high solubility and the amide functionality provides an internal base.

Compound **1** was synthesized on a preparative scale (up to 5.0 g) by mixing [COD]PtCl$_2$ and 1 equiv of LiN(SiMe$_3$) in ether at room temperature (eq 1).



(1)

The reaction is complete after 4 h at room temperature, and filtration and recrystallization from hot hexane gave the product in 84% isolated yield. The compound was fully characterized by ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis. The presence of the trimethylsilyl group makes the complex soluble in any of the common organic solvents such as hexane, ether, benzene, and toluene, and it was stored under nitrogen for several months without any sign of decomposition. Attempts to displace the second chloride using an excess of lithium

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* To whom correspondence should be addressed. E-mail: ola.wendt@organic.lu.se.

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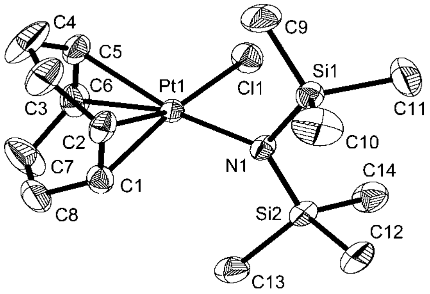
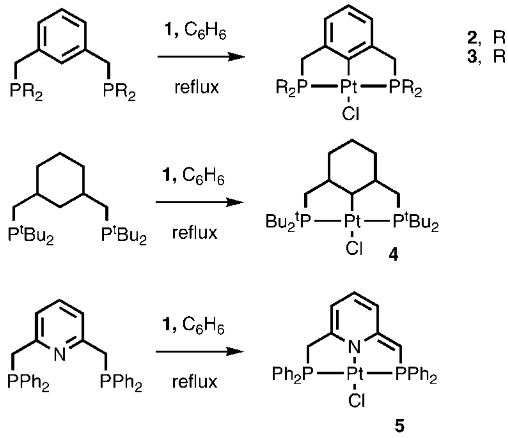


Figure 1. DIAMOND drawing of complex **1**. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt1−N(1) = 2.045(3), Pt1−(av C1, C2) = 2.155(4), Pt1−(av C5, C6) = 2.201(4) Å, Pt1−Cl1 = 2.3224(11); (av C1, C2)−Pt1−(av C5, C6) = 86.81, N1−Pt1−Cl1 = 91.27(9).

Scheme 1



hexamethyldisilazide and/or reaction at elevated temperature were unsuccessful, and the monosubstituted product was always obtained.

A ^{1}H NMR spectrum of **1** in C_6D_6 shows that there is a single resonance for the trimethylsilyl protons at 0.55 ppm, and the corresponding ^{13}C NMR signal appears at 6.26 ppm. The vinylic protons of the cyclooctadiene appear as multiplets with platinum satellites at 4.68 and 5.0 ppm, indicating that the COD is coordinated with little fluxionality. The $^{2}J_{Pt-H}$ coupling constants are different. Thus, the vinylic protons trans to chlorine have a coupling constant of 68.5 Hz, whereas that of the protons trans to the amido group is 53.0 Hz. The corresponding ^{13}C NMR signals appear at 101.37 and 94.19 ppm with the $^{1}J_{Pt-C}$ value trans to the chlorine being 182.2 Hz and that trans to amido group being 105.6 Hz. Taken together, this supports a higher trans influence for the amido group.

Compound **1** gave crystals suitable for X-ray diffraction, and this confirmed the molecular structure as given in Figure 1. The structure shows the expected mononuclear pseudo-square-planar platinum in which the chlorine and amido groups are cis to each other and the complexes are packed with dispersion forces, with the only noteworthy intermolecular contact being a weak hydrogen bond between chlorine and a COD C−H bond of an adjacent molecule. The relative trans influence obtained from the coupling constants was confirmed by the XRD, with the Pt−C bond trans to chlorine being 0.046 Å shorter than that trans to nitrogen.

To probe the ability of **1** to induce cyclometalation without any external base, it was reacted with various PXP ligands in C_6D_6 at reflux temperature (cf. Scheme 1). The reactions were monitored using either ^{31}P NMR or ^{1}H NMR (appearance of $HN(SiMe_3)_2$). A unique product formation was observed in all cases when the reaction was run in deuterated benzene, and there is no visible formation of any other product. The reactions were also performed on a preparative scale with reaction times and yields as reported in Table 1. In the preparation of **5** the reaction proceeds also at room temperature, but a longer reaction time is needed. All products are known compounds, and their NMR spectra were compared with those reported in the literature. The byproducts of the reactions are cyclooctadiene and hexamethyldisilazane, and these can easily be washed out with hexane. The presence of impurities such as LiCl and KCl in the ligand (usually during the preparation) should be avoided, since this prolongs the reaction times.

Table 1. Cyclometalation Reactions as Shown in Scheme 1 using 1 as Precursor[a]

entry	product	*t*/h	isolated yield/%
1	**2**	2	92
2[b]	**3**	6	96
3	**4**	1.5	98
4	**5**	0.5	97

[a] All reactions were performed at 80 °C in benzene. [b] The reaction time was not optimized.

In conclusion, we have described the convenient synthesis of compound **1**, which is a very useful starting material for the high-yield synthesis of platinum pincer complexes.

Experimental Section

General Procedures and Materials. All experiments were carried out under an atmosphere of nitrogen in a glovebox or using standard Schlenk or high-vacuum-line techniques.[11] All nondeuterated solvents were vacuum-transferred from sodium/benzophenone ketyl directly to the reaction vessel. Benzene-d_6 was dried over sodium/benzophenone ketyl and vacuum-transferred directly to a J. Young NMR tube. All the other commercially available reagents were purchased from Sigma Aldrich and used as received. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in benzene-d_6 on a Varian Unity INOVA 500 spectrometer operating at 499.77 MHz (^{1}H). $(COD)PtCl_2$[12] and all PXP ligands were prepared according to reported procedures.[8b,13,14] Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H and ^{13}C NMR) or H_3PO_4 as reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, v = virtual. Elemental analyses were performed by H. Kolbe, Mülheim an der Ruhr, Germany.

Preparation of [COD]PtClN(SiMe$_3$)$_2$ (1). To a suspension of $[COD]PtCl_2$ (5.0 g, 13.4 mmol) in ether (40 mL) was added a solution of 1 M $LiN(SiMe_3)_2$ (13.4 mL, 13.4 mmol) in hexane over a period of 10 min. The mixture was stirred for 4 h and filtered. Evaporation of the ethereal solution afforded a yellow solid, which was dissolved in hot hexane. Cooling the hexane solution to room temperature led to the formation of yellow crystals of $[COD]PtClN(SiMe_3)_2$, and more crystals were obtained upon cooling in the refrigerator. Decantation and drying in vacuo afforded 5.60 g (84%) of **1**. Anal. Calcd for $C_{14}H_{34}ClNPtSi_2$: C, 33.69; H, 6.06; N, 2.81. Found: C, 33.70; H, 6.15; N, 2.76. ^{1}H NMR (C_6H_6; δ, ppm): 0.55

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(s, 18H, $-\mathrm{SiMe_3}$), 1.15 (m, 2H, COD), 1.66 (m, 2H, COD), 1.80 (m, 4H, COD), 4.68 (m, 2H, $J_{\mathrm{Pt-H}} = 68.5$ Hz, vinylic), 5.0 (m, 2H, $J_{\mathrm{Pt-H}} = 53.0$ Hz, vinylic). ^{13}C NMR (C_6H_6; δ, ppm): 101.37 (s, $J_{\mathrm{Pt-C}} = 105.6$ Hz, vinylic), 94.19 (s, $J_{\mathrm{Pt-C}} = 182.2$ Hz, vinylic), 29.83 and 28.64 (s, CH_2, COD), 6.26 (s, CH_3, $-\mathrm{SiMe_3}$).

General Procedure for the Cyclometalation Reaction. To a stirred solution of the ligand in benzene was added an equimolar amount of $[\mathrm{COD}]\mathrm{PtClN(SiMe_3)_2}$, and the mixture was stirred at reflux temperature for the time specified in Table 1. The completion of the reaction was checked by either ^{31}P NMR or ^{1}H NMR spectroscopy. The benzene was evaporated, and the solid was washed thoroughly first with hexane and finally with a small amount of ether and dried under vacuum. The isolated yields of the reaction are listed in Table 1. The identity and purity were established by NMR spectroscopy and compared with those reported in the literature.[1a,10,12,15] NMR data for **5** (C_6D_6): ^{1}H, δ 2.96 (dd, 2H, CH_2), 4.14 (t, 1H, C═C*H*−P), 5.40 (t, 1H, pyr *H*), 6.43 (d, 2H, pyr H), 6.84 (m, 6H, Ar H), 6.98 (m, 2H, Ar H), 7.02 (m, 4H, Ar H), 7.64 (m, 4H, Ar H), 8.12 (m, 4H, Ar H); ^{31}P, δ 17.66 and 17.68 (s, $J_{\mathrm{P-Pt}} = 2618$ Hz).

X-ray Crystallography. Intensity data were collected at 293 K with an Oxford Diffraction Xcalibur 3 system using ω-scans and Mo Kα radiation ($\lambda = 0.710\,73$ Å).[16] CCD data were extracted and integrated using Crysalis RED.[17] The structure was solved using direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1.[18] Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. All crystallographic data are available in CIF format. Crystal data: $C_{14}H_{30}ClNPtSi_2$, $M_r = 499.11$, monoclinic, $a = 8.5130(3)$ Å, $b = 9.2430(3)$ Å, $c = 25.0060(9)$ Å, $\beta = 97.385(4)°$, $V = 1951.29(12)$ Å^3, space group $P2_1/n$, $Z = 4$, 19 410 reflections measured, 6728 unique reflections ($R_{\mathrm{int}} = 0.0361$), which were used in all calculations. The final $R_w(F^2)$ value was 0.0724 (all data), and the $R(F)$ value was 0.0291 ($I > 2\sigma(I)$) using 178 parameters. The CCDC reference number is 692530.

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Supporting Information Available: A CIF file giving full crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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