

Synthesis, Structure, and Reactivity of an Unusual Platinum Olefin Carbene Complex, $[(\eta^4\text{-cod})\text{Pt}\{\text{=C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{2-\kappa}\text{C},\kappa\text{N}\}]$

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The organolithium dimer $[\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]_2$ ($[\text{Li}_2\text{-1}]_2$) reacts with 2 equiv of $[\text{PtCl}_2(\text{cod})]$ (cod = 1,5-cyclooctadiene) in Et_2O solution to give the novel Pt–carbene complex $[(\eta^4\text{-cod})\text{Pt}\{\text{=C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{2-\kappa}\text{C},\kappa\text{N}\}]$ (**2**), which is characterized by a relatively long Pt–C(carbene) bond and relatively short Pt–C(olefin) interactions indicative of an electron-rich Pt center. Under oxygen- and moisture-free conditions, **2** is remarkably inert; the cod ligand is not displaced by either monodentate or bidentate phosphines, phosphine sulfide, phosphite, or pyridine at room temperature, nor is the four-membered C,N-chelate ring opened by these reagents. However, **2** reacts with the electrophiles MeOTf (OTf = trifluoromethanesulfonate) and CO_2 . In the former case, the uncoordinated N atom of **2** is methylated to form $[(\eta^4\text{-cod})\text{Pt}\{\text{=C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)(\text{Ph}_2\text{P}=\text{N}(\text{Me})\text{SiMe}_3)_{-\kappa}\text{C},\kappa\text{N}\}][\text{OTf}]$ (**3**). In the latter, initial nucleophilic attack by the uncoordinated N atom on CO_2 , followed by trimethylsilyl group migration from N to O, gives $[(\eta^4\text{-cod})\text{Pt}\{\text{=C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)(\text{Ph}_2\text{P}=\text{NC}(\text{O})\text{OSiMe}_3)_{-\kappa}\text{C},\kappa\text{N}\}]$ (**4**). Heating a benzene solution of **2** to 100 °C in a sealed tube for several hours, or to 60 °C for 10 min in the presence of H_2O , yields the ortho-metalated complex $[(\eta^4\text{-cod})\text{Pt}\{\text{CH}(\text{Ph}(\text{C}_6\text{H}_4)\text{P}=\text{NSiMe}_3)(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{-\kappa}\text{C},\kappa\text{C}'\}]$ (**5**), which is characterized by Pt–C distances that are in the typical range for Pt–C(alkyl) and Pt–C(arene) interactions. The diastereoselectivity of the ortho metalation is consistent with an oxidative addition (nucleophilic) reaction mechanism for the ortho metalation. In contrast to **2**, **5** displays typical cod substitution reactivity with chelating phosphines. The reaction between $[\text{Li}_2\text{-1}]_2$ and $[\text{PtCl}_2(\text{cod})]$ in C_6H_6 solution proceeds only very slowly and gives $[\text{Li}][\text{Pt}\{\text{CH}(\text{Ph}(\text{C}_6\text{H}_4)\text{P}=\text{NSiMe}_3)(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{-\kappa}\text{C},\kappa\text{C}'\}]\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{2-\kappa}\text{C},\kappa\text{N}\}]$ (**7**) in low yield.

Introduction

Some time ago, we^{1,2} and others³ reported the synthesis and characterization of the structurally unusual organolithium complex $[\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]_2$ ($[\text{Li}_2\text{-1}]_2$), which can be obtained by double deprotonation of the methylene C atom of $\text{CH}_2(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2$ ($\text{H}_2\text{-1}$)^{4,5} using alkyl- or aryllithium reagents. Recently, we have employed $[\text{Li}_2\text{-1}]_2$ and $\text{H}_2\text{-1}$ in the synthesis of a number of novel “pincer” carbene complexes of the group 4 metals^{6–10} and lanthanides,¹¹ as well as bridging carbene complexes of Cr¹² and Al.¹³ In all of these systems,

1 forms a carbene-like M–C bond stabilized by chelation of both N atoms to the metal. Structural studies show that the pincer carbene systems have short metal–carbon interactions indicative of M=C(carbene) double bonds and that there is a substantial ylidic character to the bonding within the framework of the ligand **1**. Single-point calculations at the density functional level for $[\text{Zr}(\text{CH}_2\text{Ph})_2\{\text{=C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_{2-\kappa}\text{C},\kappa\text{N},\kappa\text{N}\}]$ reveal an appreciable negative charge on the carbene C atom as well as positive charge on the P atoms,⁶ and indeed related group 4 chlorides (Scheme 1) behave like Schrock-type (nucleophilic) carbenes in that they undergo $[2 +$

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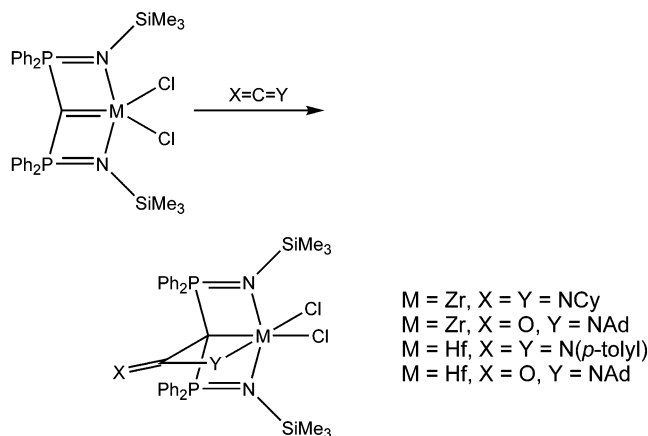
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Scheme 1. Reactions of Group 4 "Pincer" Carbenes with Isocyanates and Carbodiimides



2] cycloaddition reactions with isocyanates and carbodiimides.⁸

The recent report of the application of the N-heterocyclic carbene (NHC) complexes [Pt(η^4 -O(Me₂SiCH=CH₂)₂)(NHC)] to hydrosilylation catalysis^{14,15} provides impetus for investigation into the synthesis and reactivity of other types of Pt-carbene complexes, especially those involving chelating diolefins as ancillary ligands.

Herein, we report the first development of *late*-transition-metal chemistry incorporating **1**. We describe the synthesis and structural characterization of an intriguing Pt(II) compound, [(η^4 -cod)Pt{=C(Ph₂P=NSiMe₃)_{2- κ C, κ N}}] (**2**), and compare and contrast its bonding and reactivity with those of its early-transition-metal counterparts. Because the formally dianionic ligand **1** coordinates via a single four-membered C,N-chelate in **2**, the complex represents the first example we have encountered in the use of **1** that is not a classical "pincer" or bridging carbene, and indeed this and other factors yield novel reactivity patterns. We report the reactions of **2** with nucleophiles and electrophiles, including heteroallenes, and the synthesis, structural characterization, and preliminary reactivity studies of the ortho-metalated complex [(η^4 -cod)Pt{CH(Ph(C₆H₄)P=NSiMe₃)(Ph₂P=NSiMe₃)- κ C, κ C'}] (**5**).

Results and Discussion

Reaction of [Li₂-**1**]₂ with 2 equiv of [PtCl₂(η^4 -cod)] in Et₂O gives [(η^4 -cod)Pt{=C(Ph₂P=NSiMe₃)_{2- κ C, κ N}}] (**2**) as a red-orange crystalline powder in 50% isolated yield (Scheme 2). The analogous reaction conducted in C₆H₆ proceeds differently and will be discussed below. Attempts to prepare similar complexes starting from [PtCl₂(nitrile)₂] (nitrile = MeCN, PhCN) and *cis*-[PtCl₂(PPh₃)₂] have so far been unsuccessful.

An ORTEP representation of the molecular structure of **2** is shown in Figure 1; selected relevant bond lengths and angles are given in Table 1. The coordination environment around the Pt atom is a slightly distorted square plane. The ligand **1** adopts a κ C, κ N coordination mode in which one of the two N atoms of the ligand is involved in a four-membered chelate with Pt, and the

other is "dangling." The sum of the angles around the carbene C atom in **2** is 360°; C(1), P(1), P(2), and Pt form a perfect plane. Complexes that contain chelating C,N ligands where C is carbenic are relatively rare; other examples are the recently discovered Ru-aminocarbene complexes [RuCp(L)(=CPhNHpy- κ C, κ N)] [PF₆] (L = CH₃-CN, PMe₃; py = *o*-pyridyl)¹⁶ and the tris(pyrazolyl)-borate ruthenium carbenes derived from terminal alkynes and 2-aminopyridines.¹⁷

The Pt-C(carbene) distance in **2** is 2.021(5) Å, appreciably longer than those typically found for both NHC complexes of two- and four-coordinate Pt (1.93–1.97 Å)^{18–20} and Fischer carbene complexes of four-coordinate Pt (1.87–1.96 Å).^{21–26} Indeed, the Pt-C(carbene) distance in **2** is unusual in that it is more akin to those found for Fischer carbene complexes of five-²⁷ and six-coordinate²⁸ Pt (1.99–2.01 Å). Nevertheless, the Pt-C(carbene) bond in **2** is still shorter than typical Pt-C(alkyl) single bonds (2.07–2.15 Å).²⁹ Such partial multiple-bond character may be the result of π -electron delocalization within the ligand framework.

The intraligand distances of bound **1** merit discussion in this regard. Both of the P-C(carbene) lengths in **2**, particularly that of the endocyclic bond, are considerably shorter than that found for P-C(methylene) in H₂-**1**⁵ (1.697(5) (endo) and 1.721(5) (exo) vs 1.827(1) Å), while the P-N distances, again particularly that of the endocyclic bond, are appreciably longer (1.631(4) (endo) and 1.550(4) Å (exo) vs 1.539(2) Å). In addition, the Pt-N bond in **2** (2.092(4) Å) is shorter than those of the related Pt complexes [PtCl(PEt₃)₂CH(Ph₂P=N-*p*-tolyl)-(Ph₂PNH-*p*-tolyl)- κ C, κ N)] [PtCl₃(PEt₃)] (2.124(8) Å)³⁰ and [PtCl(PPhMe₂)₂CH(Ph₂P=N-*p*-tolyl)_{2- κ C, κ N}]] (2.132(4) Å)³¹ but identical in length with that of [PdCl₂(Me₃SiN=PEt₃)₂] (2.095 Å).³² This may reflect either partial double-bond character of the Pt-N bond or simply the

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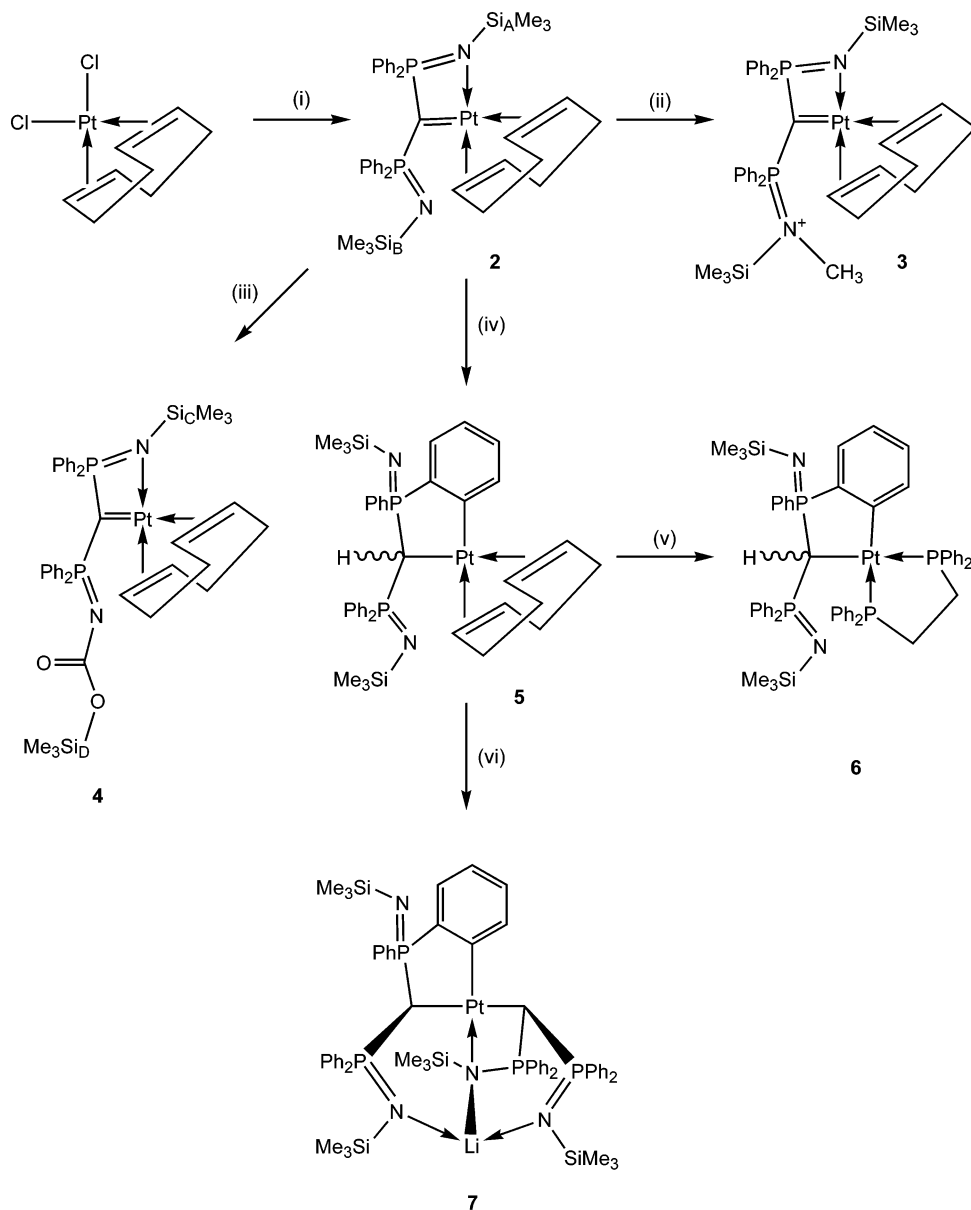
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Scheme 2. Synthesis and Reactions of the Pt–Carbene Complex $[(\eta^4\text{-cod})\text{Pt}\{\text{=C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C},\kappa\text{N}}]$ (2**)^a**



^a Labels for the trimethylsilyl groups in **2** and **4** are discussed in the text. Reactions were conducted at room temperature unless otherwise indicated. Reagents, solvents, and conditions: (i) $\frac{1}{2}$ $[\text{Li}_2\text{-1}]_2$, Et_2O ; (ii) MeOTf , Et_2O ; (iii) CO_2 (1 atm), hexanes; (iv) 100°C , 20 h, C_6H_6 , or 60°C , 10 min, C_6H_6 with 5 equiv of added H_2O ; (v) dppe , C_6H_6 ; (vi) LiH-1 , C_6H_6 , and also from $\text{PtCl}_2(\text{cod})$ and $\frac{1}{2}$ $[\text{Li}_2\text{-1}]_2$ in C_6H_6 over days (see Experimental Section).

strong Lewis basicity of silylated phosphineimines. We have previously postulated an electronically delocalized model to account for structural differences between $\text{H}_2\text{-1}$ and bound **1**.^{2–6} Despite the great differences in metallic electron density between **2** and the pincer carbene complexes $\text{MCl}_2(\text{1-}\kappa\text{C},\kappa\text{N},\kappa\text{N})$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$), the endocyclic P–N bond in **2** (1.631(4) Å) is remarkably similar to the average of those found in the group 4 complexes, which are 1.621(4),⁹ 1.630(6),⁹ and 1.637(5) Å,⁷ respectively. The endocyclic P–C bond length is also similar, but less so: viz., 1.697(5) Å vs 1.679(4), 1.666–(7) and 1.666(7) Å, respectively. These observations are consistent with our previous assertions of π -electron delocalization. In the case of **2** this is especially, but not exclusively, manifest within the four-membered C,N chelate. A more apt description of the bonding in **2** may be that given in Chart 1.

An asymmetrically bound η^4 -cod ligand is also present in **2**. There is considerable difference between the lengths of the Pt–C(olefin) bonds trans to the N-donor atom (C(2) and C(3), average 2.145(5) Å) and those trans to the carbene C atom (C(6) and C(7), average 2.212(5) Å), suggesting a higher trans influence for the latter donor atom. For reasons that are not immediately obvious, the olefinic C atoms C(2) and C(3) are bound symmetrically to the Pt center (Pt–C(2) = 2.142(5) Å, Pt–C(3) = 2.147(5) Å), while those of the other alkene are bound in a distinctly asymmetric fashion (Pt–C(6) = 2.200(5) Å, Pt–C(7) = 2.223(5) Å).

The Pt–C(olefin) distances in **2** are shorter than average for other Pt–cod complexes (2.230 Å),²⁹ consistent with an electron-rich Pt center that strongly binds π -acceptor ligands such as olefins. These structural observations are in accord with the relative stability of

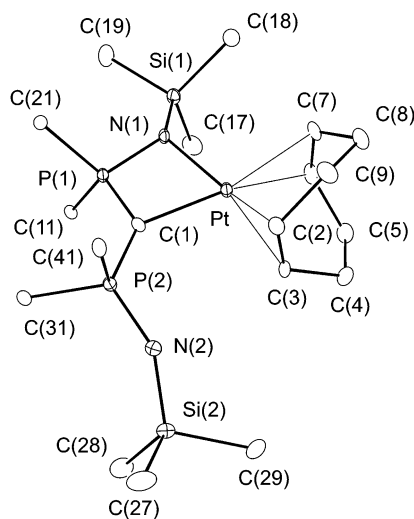
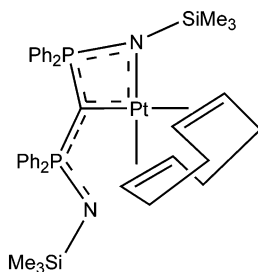


Figure 1. ORTEP representation (20% ellipsoids) of the molecular structure of **2**. Hydrogen atoms and all but the ipso carbon atoms of the phenyl rings have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2** with Estimated Standard Deviations in Parentheses

Pt–N(1)	2.092(4)	Pt–C(1)	2.021(5)
Pt–C(2)	2.142(5)	Pt–C(3)	2.147(5)
Pt–C(6)	2.200(5)	Pt–C(7)	2.223(5)
P(1)–N(1)	1.631(4)	P(1)–C(1)	1.697(5)
P(2)–N(2)	1.550(4)	P(2)–C(1)	1.721(5)
N(1)–Pt–C(1)	75.2(2)	Pt–N(1)–P(1)	93.0(2)
N(1)–P1–C(1)	97.9(2)	Pt–C(1)–P(2)	132.3(3)
P(1)–C1–P(2)	134.0(3)	N(2)–P(2)–C(1)	115.4(2)

Chart 1. Putative Electron Delocalization within **1** for Pt(cod)(1-κ C_κN) (**2**)



the cod ligand of **2** with respect to substitution by common bases (vide infra).

Assignment of an oxidation state to the Pt center in **2** is complicated in that although simple electron counting yields 18 electrons and a corresponding oxidation state of 0, the square-planar coordination geometry of the complex suggests Pt(II). Restricted Hartree–Fock calculations by Nakamura and Morokuma have found that the 18-electron carbene carbonyl complex *cis*-[Pt-(PH₃)₂(CO)(CH₂)] adopts a square-planar structure as its most stable coordination geometry, with the C–H bonds in the plane.³³ The stability of the square-planar structure over a tetrahedral one was attributed to CH₂–(π)–Pt(pπ) overlap, which constitutes the HOMO in this complex.³³ The square-planar geometry of **2** may likewise be the result of such an overlap. In light of these

calculations, we believe that **2** may represent a rare example of a square-planar, 18-electron Pt(II) complex, in which the ligand **1** bears a formal 2[−] charge. However, we cannot discount the possibility of neutral **1** coordinated to Pt(0).

NMR spectroscopic characterization reveals that the solid-state structure of **2** is likely retained in solution. As expected, there are two chemically inequivalent P atom environments (δ_P 65.5 (d, $^2J_{PP} = 67$ Hz, $^2J_{PPt} = 528$ Hz), -1.1 (d, $^2J_{PP} = 67$, $^2J_{PPt} = 0$ Hz)) as well as two correspondingly inequivalent SiMe₃ proton environments (δ_H -0.01 (s), 0.48 (s)). The upfield phosphorus resonance falls at a frequency similar to that of the two equivalent P atoms of H₂-**1** (δ_P -4.2), suggesting that this upfield doublet corresponds to the P atom of bound **1**, whose corresponding N atom is not coordinated to the metal center. In contrast to the upfield resonance for which P–Pt coupling is zero, the low-field signal has distinct ¹⁹⁵Pt ($I = 1/2$; 33.7% natural abundance) “satellites.” This suggests that the P–Pt coupling is mediated via the P=N–Pt rather than the P=C–Pt linkage. The ¹⁹⁵Pt{¹H} NMR spectrum is consistent with this, in that it shows a doublet (δ_{Pt} 1136, $^2J_{PtP} = 521$ Hz) and not the doublet of doublets that would arise from coupling to two inequivalent P atoms. In addition, a ³¹P TROESY experiment shows that the bound and free N atoms of **2** do not exchange chemically (during 0.4 s). This is likely due to the strong, partial-double Pt–N bond. Notably, the N atoms of the Pt–alkanide complexes [PtCl(PR₃)₂{CR'(Ph₂P=NR')₂-κ C,κ N}], reported by Elsevier and co-workers,³¹ are indeed in chemical exchange and become equivalent on the NMR time scale at 293 K. The strong Pt–N bond in our complexes has important ramifications for their chemistry.

Carbene complexes bearing coordinated olefins are particularly important in that they are probably implicated as intermediates in olefin metathesis catalytic cycles.³⁴ Compound **2** represents a rare example of a such a Pt–carbene complex. Two other Pt compounds in this category are the NHC–ethylene complex [PtCl₂–(η²-C₂H₄)(NHC)]¹⁸ (NHC = 1-ethyl-3-methylimidazol-2-ylidene), and the five-coordinate Fischer carbene–ethylene complex [(dmphen)PtCl(CHNMe₂)(η²-C₂H₄)]²⁷ (dmphen = 2,9-dimethylphenanthroline). To date, the only examples other than **2** of Pt carbene complexes bearing a chelating diolefin are the family of hydrosilylation catalysts supported by a range of NHCs, [Pt–(η⁴-O(Me₂SiCH=CH₂)₂)(NHC)].¹⁴

We have examined the reactivity of **2** with a number of substrates and have found that the complex is relatively inert under air- and moisture-free conditions. Contrary to our expectations, treatment of C₆D₆ solutions of **2** (typically 10 mg) either with 2 equiv of PPh₃, S=PPh₃, P(OEt)₃ or pyridine or with 1 equiv of 1,1'-bis(diphenylphosphino)ferrocene (dppf) or 1,2-bis(diphenylphosphino)ethane (dppe) at room temperature resulted neither in substitution of the cod ligand nor in opening of the four-membered C,N-chelate. Heating these solutions to 50–90 °C for periods of 2–5 h resulted in all cases (except that of dppe, vide infra) in complex mixtures whose NMR spectroscopic characteristics could not be reconciled with any of the anticipated substitu-

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tion products. No reaction was observed between **2** and ethylene, nor between **2** and H₂ at room temperature and 1 atm. However, prolonged heating of the H₂ reaction mixture in a sealed NMR tube (90 °C, 24 h) resulted in an orange solution (completely clear to visual inspection) containing cyclooctane and free H₂-**1**, the latter representing the only spectroscopically observable P-containing product. The fate of the Pt in this reaction remains to be determined. Similarly, heating **2** in the presence of excess H₂SiEt₂ also gave H₂-**1** as the single P-containing product.

Although unreactive toward nucleophiles, complex **2** reacts with strong electrophiles. Thus, treatment of an ethereal solution of **2** with 1 equiv of MeOSO₂CF₃ (MeOTf) cleanly affords the canary yellow N-methylated complex [Pt(η^4 -cod){=C(Ph₂P=NSiMe₃)(Ph₂P=N(Me)-SiMe₃)- κ C, κ N}][OTf] (**3**) which precipitates from solution. This species can be distinguished easily from the hypothetical carbene-methylated alternative [Pt(η^4 -cod){=C(Me)(Ph₂P=NSiMe₃)- κ C, κ N}][OTf] by ¹H NMR spectroscopy. The NMe protons of **3** give rise to a doublet (δ 3.19, ³J_{HP} = 14.4 Hz) arising from coupling to a single P atom, not to the doublet of doublets that would result from a methyl group coupling to two inequivalent P atoms in the hypothetical product. Other than a ~30 ppm downfield shift of the ³¹P resonance attributed to the dangling P=NSiMe₃ "arm" in **2**, and the presence of the doublet at δ 3.19 in the proton spectrum, there are no significant differences between the NMR spectra of **2** and **3**. This indicates that, aside from methylation of the uncoordinated N atom, the overall symmetry and topology of **3** are very similar to that of **2**. That is, the four-membered C,N chelate containing the P–C double bond is preserved, as is the η^4 -cod ligand.

The carbene complex **2** reacts in a related manner with CO₂. Treatment of a hexanes suspension of **2** with 1 atm CO₂ at room temperature results in a slow orange to yellow transformation of the slurry. Elemental analysis data of the product are consistent with the formulation of the adduct, **2**·CO₂, and on the basis of the following spectroscopic and experimental evidence, as well as the knowledge of the higher affinity of Si for O than for N (799 vs 470 kJ mol⁻¹ bond energies, respectively, for the gaseous diatomic molecules³⁵), we have formulated this compound as [Pt(η^4 -cod){=C(Ph₂P=NSiMe₃)(Ph₂P=NC(O)OSiMe₃)- κ C, κ N}]} (**4**). The product results from insertion of CO₂ into the N–Si bond via initial nucleophilic attack on CO₂ by the uncoordinated N atom of **2**, followed by trimethylsilyl group migration from N to O. Such migration is a well-known phenomenon. It has been observed previously by us in reactions of Me₃SiNP(Ph₂)CH₂PPh₂ and ReO₃(OSiMe₃)₃³⁶ by Gerlach and Arnold in VO(N(SiMe₃)₂)₂ complexes,³⁷ by Schrock et al. in reactions of CO with Mo and W tri-(amido)amine complexes,³⁸ and by Veith and co-workers in the synthesis of polycyclic compounds containing N and Ge.³⁹

Like those of **2** and **3**, the ³¹P{¹H} NMR spectrum of **4** (under 1 atm of CO₂) consists of two doublets (δ_P 17.45 (d, ²J_{PP} = 67.2 Hz), 78.38 (d, ²J_{PP} = 67.2 Hz, ²J_{PPt} = 340 Hz)). The downfield resonance lies in the typical range for a P atom involved in a four-membered C,N chelate in these systems (65–80 ppm) and displays the characteristic two-bond P–Pt coupling (300–550 Hz) which results from the P=N–Pt linkage (vide supra). Furthermore, just as the reaction of **2** and MeOTf causes a dramatic downfield shift of the doublet attributed to the uncoordinated P=N group of **2** ($\Delta\delta$ = 33.4), so reaction with CO₂ effects a similar change ($\Delta\delta$ = 18.6). Further evidence for the participation of the uncoordinated N atom in the reaction of **2** and CO₂ comes from the fact that **3** does not react with 1 atm of CO₂, presumably on account of the fact that its "dangling", methylated N atom is no longer available for nucleophilic attack. Evidence for N-to-O migration of the trimethylsilyl group in the reaction of **2** with CO₂ is derived from ²⁹Si NMR spectroscopy. Given their relative similarities to data for H₂-**1** (δ_{Si} –11.59 (d, ²J_{SiP} = 19.2 Hz)),⁴⁰ the two resonances in **2** (δ_{Si} –19.1 (d, Si_A, ²J_{SiP} = 22.3 Hz), 5.2 (dd, Si_B, ²J_{SiP} = 26.1, ⁴J_{SiP} = 24.3)) may be assigned as in [Pt(η^4 -cod){=C(Ph₂P=NSi_BMe₃)(Ph₂P=NSi_AMe₃)- κ C, κ N}]}], where the italicized elements represent those that are bound to Pt. (It remains unclear as to why Si_B couples to both P atoms, whereas Si_A couples only to one of them. It is possible that the four-membered chelate has an effect on the Si–P coupling similar to the effect it appears to have on the P–Pt coupling.) It is expected that an N-to-O migration of the trimethylsilyl group should cause both a marked effect on the chemical shift of its Si atom and dramatically reduce the Si–P coupling. This is, in fact, exactly what is observed in the ²⁹Si NMR spectrum of **4**, i.e., [Pt(η^4 -cod){=C(Ph₂P=NSi_CMe₃)(Ph₂P=NC(O)OSi_DMe₃)- κ C, κ N}]} (δ_{Si} 21.49 (s, Si_C), 13.33 (d, Si_D, ²J_{SiP} = 22.3 Hz)) (Scheme 2).

In contrast to our findings, Elsevier and co-workers observed aza-Wittig reactivity between related complexes and CO₂.³¹ The difference between Elsevier's system and ours most probably derives from the absence in their systems of a N–Si bond. The expected product of an aza-Wittig reaction between **2** and CO₂, TMS–N=C=O, was not observed in this work.

Early-transition-metal pincer carbene complexes react with other heteroallenes such as isocyanates (e.g., AdN=C=O) and carbodiimides (e.g., Cy₂N=C=NCy₂) to form [2 + 2] cycloaddition products in which bonds are formed between the (more electronegative) heteroatom and the metal and between the carbene C atom and the central heteroallene C atom.⁸ In contrast to this, neither of the two heteroallenes above react with **2** at room temperature.

In the absence of added substrates, heating **2** (sealed tube, benzene, 100 °C, 20 h) results in ortho metalation of one of the phenyl rings and rearrangement, possibly through a Pt(IV)–hydride intermediate, to give [η^4 -cod]Pt{CH(Ph(C₆H₄))P=NSiMe₃)(Ph₂P=NSiMe₃)- κ C, κ C'} (**5**). Efforts to observe the intermediate by NMR spectroscopy have not yet been successful, nor have attempts to abstract the hydride with [Ph₃C][BF₄].

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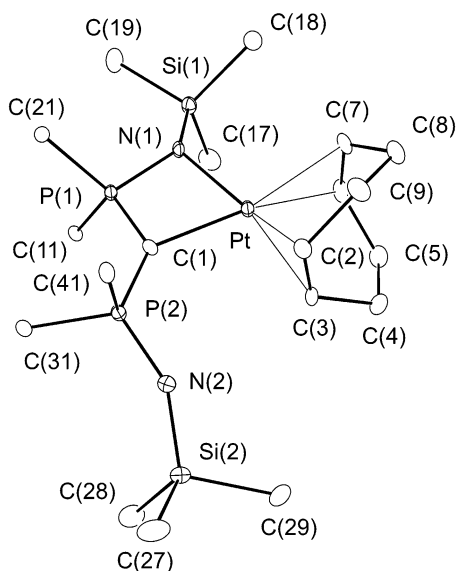


Figure 2. ORTEP representation (20% ellipsoids) of the molecular structure of **5**. For every phenyl ring except the ortho-metallated one, only the ipso carbon atom is shown. Except for H(1), the hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **5 with Estimated Standard Deviations in Parentheses**

Pt–C(1)	2.098(6)	Pt–C(12)	2.029(5)
Pt–C(2)	2.202(6)	Pt–C(3)	2.201(6)
Pt–C(6)	2.265(5)	Pt–C(7)	2.255(5)
P(1)–C(1)	1.822(6)	P(1)–N(1)	1.535(5)
P(2)–C(1)	1.805(6)	P(2)–N(2)	1.546(5)
C(1)–Pt–C(12)	85.2(2)	N(1)–P(1)–C(1)	118.0(3)
P(1)–C(1)–P(2)	119.7(3)	C(1)–P(1)–C(11)	99.0(3)
N(2)–P(2)–C(1)	112.0(3)	Pt–C(1)–P(1)	103.9(3)

An ORTEP representation of the molecular structure of **5** is shown in Figure 2; selected bond lengths and angles appear in Table 2. The coordination environment is essentially square planar, as expected, but in this case the bond lengths and angles are typical for Pt–alkyls and Pt–arenes. In addition, **5** does not display the kind of charge delocalization found in **2**. Thus, the P–C(H) bonds in **5** (average 1.814(6) Å) are similar to those found in H₂-**1** (1.827(1) Å), as are the P=N lengths (average 1.541(5) vs 1.539(2) Å for H₂-**1**). The bond distances between Pt and the olefinic C atoms trans to C(H) (C(2) and C(3), average 2.201(6) Å) in **5** are more similar to those found trans to C(carbene) in **2** (average 2.212(5) Å) than to those between Pt and the other olefinic C atoms, i.e., trans to C(phenyl), which are considerably longer (C(6) and C(7), average 2.600(5) Å).

The ortho-metallated complex **5** possesses two stereogenic centers, C(1) and P(1). Shown in Figure 2 is the *S,S* enantiomer; because the space group of this structure is centrosymmetric (*P2₁/n*), the opposite enantiomer is also present in equal abundance in the unit cell. Absent, however, are the *R,S* diastereomers. These observations, together with solution NMR data (vide infra), are consistent with diastereoselective formation of **5**.

The ³¹P{¹H} NMR spectrum of **5** shows the solution structure of the complex to be consistent with the solid-state structure. It consists of two closely separated doublets and their associated Pt satellites (δ_P 9.61 (d,

²*J*_{PP} = 5.91 Hz, ²*J*_{PPt} = 200 Hz), 9.27 (d, ²*J*_{PP} = 5.91 Hz, ²*J*_{PPt} = 125 Hz)), indicating two chemically inequivalent yet similar P atoms, as expected. Both P atoms in **5** show two-bond coupling to Pt, unlike those in **2**, but the magnitude of this coupling is lower than for the parent complex. As expected, the ¹⁹⁵Pt{¹H} NMR spectrum shows a doublet of doublets (δ_{Pt} 872) with the anticipated coupling constants.

The overall symmetry of **5** is lower than that of **2**. This is particularly manifest in its ¹H NMR spectrum, which shows four multiplets (and their associated Pt satellites) due to the olefinic protons of coordinated cod. The methine proton of the ortho-metallated ligand gives rise to a distinctive doublet of doublets (δ_H 3.88 (dd, ²*J*_{PP} = 13.6 Hz, ²*J*_{PP} = 16.0 Hz, ²*J*_{PPt} = 96 Hz)). The presence of diastereomers, which would be manifest in a complete second set of peaks, was not observed in either the ¹H or the ³¹P{¹H} solution NMR spectra of **5**.

The transformation of **2** to **5** requires an ortho metalation, a 1,2-H shift, and dissociation of the bound N atom. Although the ordering of these steps is uncertain, it is likely to be one of the phenyl rings associated with a “dangling” rather than with a bound Ph₂P=NSiMe₃ group that undergoes the metalation reaction: rotation about the P–C(carbene) bond of the former group would bring the ortho phenyl C atoms close to the Pt center. The crystal structure of **2** reveals, on the other hand, that the Pt–C(ortho phenyl) distances for the bound (endocyclic) Ph₂P=NSiMe₃ group are 4.158 and 4.401 Å, probably too distant for metalation without dissociation of the N atom.

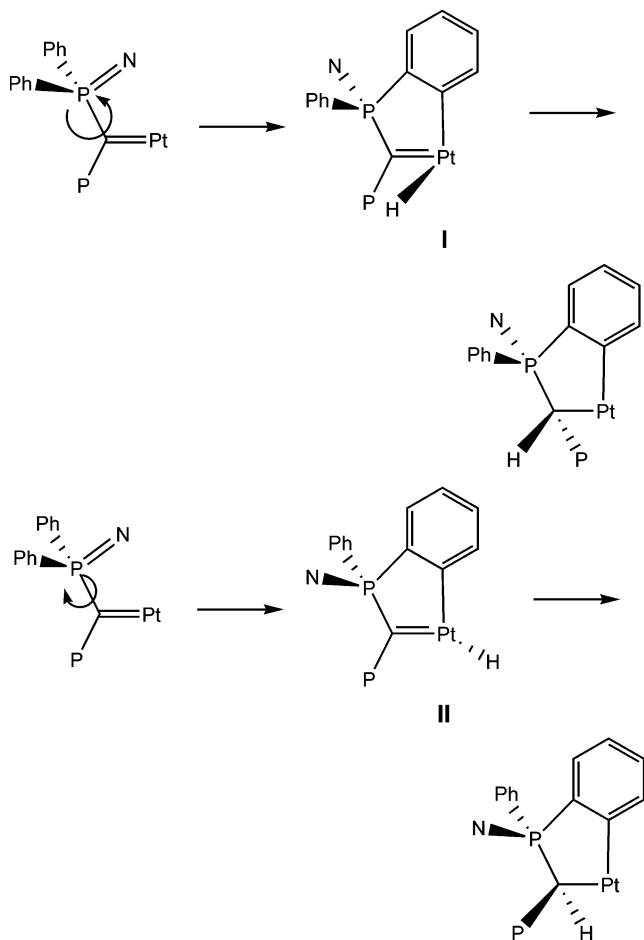
Without saying whether dissociation of the coordinated N atom occurs before or after the ortho-metalation event, we lean toward an oxidative addition, or nucleophilic, pathway for the cyclometalation reaction, even though we have been unable to detect a Pt–hydride intermediate. This is because the ortho metalation proceeds diastereoselectively, generating two stereocenters whose relative absolute configurations are fixed. Thus, if the absolute configuration at the stereogenic P atom in **5** is *R*, the configuration at the formerly carbene C atom will also be *R*, and vice versa. This is consistent with the two degenerate oxidative addition pathways shown in Scheme 3. Hydride **I**, which results from an anticlockwise rotation about the P–C(carbene) bond, is *R* at P and will give rise to *R,R*-**5** by proton transfer from Pt to the carbene C atom. Conversely, hydride **II**, which results from clockwise rotation, is *S* at P and will give rise to *S,S*-**5**. If the mechanism were electrophilic, and H⁺ rather than coordinated hydride resulted from the C–H activation, it would seem unlikely, even with the participation of the available N bases in **2**, that the carbene C atom would be protonated with perfect facial selectivity. This observation is in accord with the idea that C–H activations at Pt(II) typically proceed by nucleophilic pathways.⁴¹

Coordinative unsaturation in square-planar complexes is known to be an important prerequisite for cyclometalation, as has been demonstrated by Whitesides and co-workers in C–H activation reactions involving bis(neopentyl) complexes of Pt(II).⁴² It is

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Scheme 3. Degenerative Oxidative Addition, Hydride Transfer Pathways in the Transformation of **2 to **5****



possible that in our case the rate-limiting step in the conversion of **2** to **5** is dissociation of the coordinated N atom; the fact that NMR measurements show that the N atoms of **2** are not in chemical exchange is consistent with the hypothesis that the coordinated N atom is tightly bound, as is the fact that the C,N chelate of **2** is not opened by a variety of reagents (vide supra). Following dissociation, oxidative addition to the three-coordinate intermediate gives a Pt hydride which rapidly decomposes to **5**.

The transformation of **2** to **5** is promoted by adventitious water. Heating of a very dry C_6D_6 solution of **2** to 60 °C for 14 h gave no conversion to **5**, as determined by NMR spectroscopy. However, in the presence of 5 equiv of H_2O , conversion was complete within 10 min at this temperature. It is possible that slow transformation at higher temperature (100 °C) results either from water that becomes available via desorption from glass surfaces or through a thermal route in which water is not involved.

The accelerating effect of water on ortho-metalation reactions has been observed previously by Rourke and co-workers.⁴³ These researchers observed that the rate of the second cycloplatination of 2,6-diphenylpyridine in $[(o-C_6H_4)py(o-C_6H_5)-\kappa C, \kappa N]PtCl(CO)]$ was enhanced by addition of water or base. They attributed this

phenomenon to the thermodynamic requirement for eliminated HCl to be ionized, but because there is no such elimination in our case, this rationale cannot be applied here. The dependence of rate of cyclometalation reactions on solvent has also been observed by Simpson and co-workers in the reactions of *cis*- $[PtCl_2(dmsO)_2]$ and tertiary ferrocenylamines in $CHCl_3$ or acetone vs MeOH or H_2O .⁴⁴

In our case, it seems possible that H_2O may increase the propensity for dissociation of the bound N atom in **2** by competing for the coordination sphere of the metal, while it itself remains only weakly bound. This may accelerate the ortho-metalation process by increasing the concentration of coordinatively unsaturated Pt centers. Further exploration of this system is currently under way.

Although **2** does not react with dppe at room temperature, heating a benzene solution of the two compounds to 100 °C for several hours results in the slow consumption of **2** to give, not the expected product $[Pt(dppe)\{=C(Ph_2P=NSiMe_3)_{2-\kappa C, \kappa N}\}]$, but rather the ortho-metalated complex $[Pt(dppe)\{CH(Ph(C_6H_4)P=NSiMe_3)-(Ph_2P=NSiMe_3)-\kappa C, \kappa C'\}]$ (**6**). This must result from slow formation of **5**, which subsequently reacts quickly with dppe to form **6**. Indeed, periodic monitoring of the high-temperature reaction between **2** and dppe by NMR spectroscopy (at room temperature) does not reveal **5** but instead shows unreacted **2** and the final product **6**. This product is characterized by four chemically inequivalent P atoms, two of which show the anticipated single-bond P–Pt coupling and two of which show two-bond coupling. Complex **6** can also be made rationally, of course, by reacting isolated **5** with a stoichiometric quantity of dppe.

When the reaction between $[Li_2-1]_2$ and $[PtCl_2(\eta^4-cod)]$ was conducted in C_6H_6 as opposed to Et_2O , a very different product from **2**, $[Li][Pt\{CH(Ph(C_6H_4)P=NSiMe_3)(Ph_2P=NSiMe_3)-\kappa C, \kappa C'\}\{CH(Ph_2P=NSiMe_3)_{2-\kappa C, \kappa N}\}]$ (**7**), was isolated in low yield. This complex may be thought of as the product of the reaction between **5** and LiH-1, in which [H-1][−] forms a four-membered C,N chelate with the metal center and the overall negative charge on the Pt complex is balanced by Li^+ , which remains coordinated to three of the four N atoms (Scheme 2).

An ORTEP representation of the molecular structure of **7** is shown in Figure 3; selected bond distances and angles are given in Table 3. The Pt–C(1) and Pt–C(12) bond lengths in **7** are almost exactly the same as the corresponding distances in **5**.

In contrast to the reaction between $[Li_2-1]_2$ and $[PtCl_2(\eta^4-cod)]$ in Et_2O solution, in which the deep orange color of the product, **2**, begins to form within minutes, the corresponding reaction in C_6H_6 is slow. Indeed, in situ NMR spectroscopic analysis of the reaction mixture after 2 h at room temperature reveals no formation of **2**. After 20 h, both **2** and **5** are apparent, in addition to unreacted $[Li_2-1]_2$ and traces of H_2-1 . After this mixture had been stirred at room temperature for a total of 5 days and then heated to 100 °C for 20 h, a 22% yield of **7** was recovered after recrystallization (see Experimental Section).

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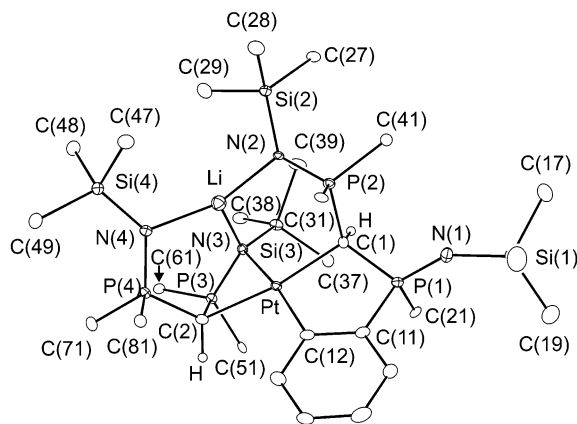


Figure 3. ORTEP representation (20% ellipsoids) of the molecular structure of **7**. For every phenyl ring except the ortho-metalated one, only the ipso carbon atom is shown. Except for H(1) and H(2), the hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **7 with Estimated Standard Deviations in Parentheses**

Pt–C(1)	2.091(7)	Pt–C(12)	2.000(8)
Pt–C(2)	2.155(7)	Pt–N(3)	2.256(6)
Li–N(2)	2.073(16)	Li–N(3)	2.212(16)
Li–N(4)	2.074(16)		
C(1)–Pt–C(12)	86.0(3)	N(3)–Pt–C(2)	73.4(2)
C(1)–Pt–C(2)	171.1(3)	N(3)–Pt–C(12)	168.8(3)
N(2)–Li–N(3)	111.4(7)	N(3)–Li–N(4)	105.6(7)
N(2)–Li–N(4)	141.9(8)		

The product distribution after 20 h is likely due (i) to the presence of adventitious water, which both promotes the ortho metalation of **2** and also reacts with $[\text{Li}_2\text{-1}]_2$ to give $\text{H}_2\text{-1}$, and (ii) to the fact that the reaction between $[\text{Li}_2\text{-1}]_2$ and $[\text{PtCl}_2(\eta^4\text{-cod})]$ in benzene is sluggish, presumably on account of the stability of the fomer cluster in donor-free solvent, and the conversion of **2** to **5** therefore occurs at a rate comparable to the formation of **2**. The resulting simultaneous presence of both **5** and $[\text{Li}_2\text{-1}]_2$ in the reaction mixture is the condition that ultimately must give rise to the formation of **7**. The methanide LiH-1 , which is formed, presumably, either by partial hydrolysis of $[\text{Li}_2\text{-1}]_2$ or by disproportionation of $[\text{Li}_2\text{-1}]_2$ and $\text{H}_2\text{-1}$, reacts with **5** to give **7**. This is consistent with our observation that the cod ligand of **5** is substitutionally labile, whereas that of **2** is not. To confirm these hypotheses, the reaction between isolated **5** and LiH-1 was performed and followed in situ by NMR spectroscopy; it did indeed give **7**.

Conclusion

In all our previous investigations, we have found the formally dianionic ligand **1** to coordinate through its carbene C atom as well as both N atoms, either as a "pincer" or a bridging carbene, and the question has arisen as to whether the N donors were necessary to stabilize the complexes. In the case of **2**, we have now shown that only one coordinated N atom is necessary in the case of Pt. Indeed, the reactivity of **2** is dominated by the uncoordinated N atom; reactions with electrophiles demonstrate that this center is more nucleophilic than the carbene C atom. The substitutional inertness of the cod ligand in **2** and the short Pt–C(olefin)

distances in this complex are indicative of an electron-rich Pt center. Correspondingly, the low nucleophilicity of the carbene C atom is consistent with its electron deficiency. We believe that the carbene complex **2** may be an example of a square-planar 18-electron Pt(II) metal center bonded to 12^- . In contrast, the ortho-metalated complex **5** behaves typically for 16-electron Pt(II) complexes; its cod ligand is readily substituted by chelating phosphines in the usual fashion. Investigation into the use of **2** and **5** in other reactions is currently under way.

Experimental Section

General Considerations. All manipulations were performed either in an Ar-filled glovebox or under an Ar or N_2 atmosphere using standard Schlenk techniques. Solvents were dried over appropriate drying agents and degassed by three freeze–pump–thaw cycles prior to use. The organolithium compounds $[\text{Li}_2\text{-1}]_2$ ¹ and LiH-1 ⁴⁵ were prepared according to a minor modification of our published procedures. The precursor $[\text{PtCl}_2(\text{cod})]$ was made by the method of Whitesides and co-workers;⁴⁶ other transition-metal precursors were purchased from commercial sources. Unless otherwise indicated, NMR spectra were recorded at ambient temperature using C_6D_6 solutions of the complexes on a Varian i400 spectrometer (161.9 MHz for ^{31}P , 100.6 MHz for ^{13}C , 79.5 MHz for ^{29}Si , 85.7 MHz for ^{195}Pt) and referenced to residual solvent proton (^1H), solvent carbon (^{13}C), external TMS (^{29}Si : δ 0.00), external $\text{P}(\text{OMe})_3$ (^{31}P , δ 141.00 vs external 85% H_3PO_4), or external 10% aqueous H_2PtCl_6 (^{195}Pt , δ 4522). All J values are given in Hz; abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet, and p = pseudo. Elemental analyses were performed by Ms. Darlene Mahlow of the University of Alberta Chemistry Department. IR spectra were recorded using KBr pellets on a Bomem MB100 instrument and are reported in cm^{-1} ; abbreviations used are s = strong, m = medium, and w = weak.

Syntheses. $[\text{Pt}(\eta^4\text{-cod})\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C},\kappa\text{N}\}]$ (**2**). To an Et_2O suspension (35 mL) of $[\text{Li}_2\text{-1}]_2$ (0.86 g, 0.75 mmol) was added $[\text{PtCl}_2(\text{cod})]$ (0.55 g, 1.5 mmol) as a solid in a single portion at room temperature. The resulting milky yellow suspension was stirred at room temperature for a period of 24 h, over which time the mixture turned a deep red. The solids were removed by centrifugation, and the red organic portion was reduced in vacuo to approximately 5 mL. This mixture was cooled to -18°C overnight, and red crystals (0.27 g) of **2** formed. The supernatant was decanted, further reduced, and cooled again to obtain a second crop (0.27 g) of **2**. Repeating this procedure allowed for the isolation of further two portions of **2** (combined weight 0.083 g); the overall yield of **2** was 0.62 g (49%). In the solid state, **2** is stable to air for short periods of time. Anal. Calcd for $\text{C}_{39}\text{H}_{50}\text{N}_2\text{P}_2\text{PtSi}_2$: C, 54.5; H, 5.9; N, 3.3. Found: C, 54.1; H, 5.9; N, 3.3. ^1H NMR: δ -0.01 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.48 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.53 (m, 4H, cod CH_2), 2.03 (m, 4H, cod CH_2), 4.93 (m, 2H, cod CH , $^2J_{\text{HPt}} = 48$), 5.88 (m, 2H, cod CH , $^2J_{\text{HPt}} = 72$), 7.03 (m, 6H, Ph H), 7.16 (m, 8H, Ph H), 7.81 (m, 8H, Ph H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 4.3 (d, $\text{Si}(\text{CH}_3)_3$, $^3J_{\text{CP}} = 3.3$), 5.1 (d, $\text{Si}(\text{CH}_3)_3$, $^3J_{\text{CP}} = 2.6$), 29.5 (s, cod CH_2), 31.7 (s, cod CH_2), 49.2 (dd, PCP, $^1J_{\text{CP}} = 134$, $^1J_{\text{CP}} = 84$), 84.7 (s, cod CH , $^1J_{\text{CPt}} = 167$), 91.4 (s, cod CH , $^1J_{\text{CPt}} = 84$), 127.2–132.7 (m, Ph C), 138.0–143.8 (m, Ph C). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ -1.1 (d, $^2J_{\text{PP}} = 67$, $^2J_{\text{PPt}} = 0$), 65.5 (d, $^2J_{\text{PP}} = 67$, $^2J_{\text{PPt}} = 530$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (toluene- d_8): δ -19.1 (d, $^2J_{\text{SiP}} = 22$), 5.2 (dd, $^2J_{\text{SiP}} = 26$, $^4J_{\text{SiP}} = 24$). $^{195}\text{Pt}\{^1\text{H}\}$ NMR: δ 1136 (d, $^2J_{\text{PtP}} = 520$). Crystals

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Table 4. Crystallographic Data for 2, 5, and 7 with Estimated Standard Deviations in Parentheses

	2	5	7
A. Crystal Data			
mol formula	C ₃₉ H ₅₀ N ₂ P ₂ PtSi ₂	C ₃₉ H ₅₀ N ₂ P ₂ PtSi ₂	C ₆₂ H ₇₇ LiN ₄ P ₄ PtSi ₄
mol wt	860.02	860.02	1316.55
cryst dims (mm)	0.25 × 0.15 × 0.15	0.32 × 0.18 × 0.06	0.25 × 0.08 × 0.05
cryst syst	orthorhombic	monoclinic	monoclinic
space group	<i>Pbca</i> (No. 61)	<i>P2₁/n</i> (No. 14)	<i>P2₁/n</i> (No. 14)
<i>a</i> (Å)	18.840(3)	11.1730(12)	14.5678(16)
<i>b</i> (Å)	24.212(4)	20.393(2)	23.722(3)
<i>c</i> (Å)	16.866(3)	16.7965(18)	18.762(2)
α (deg)	90	90	90
β (deg)	90	97.709(2)	98.823(2)
γ (deg)	90	90	90
<i>V</i> (Å ³)	7693(2)	3792.5(7)	6407.1(12)
<i>Z</i>	8	4	4
ρ _{calcd} (g cm ⁻³)	1.485	1.506	1.365
μ (mm ⁻¹)	3.822	3.877	2.405
B. Data Collection and Refinement			
diffractometer	Bruker PLATFORM/SMART 1000 CCD		
radiation (λ (Å))	graphite-monochromated Mo Kα (0.710 73)		
temp (K)	193		
total no. of data collected	48 592	22 819	39 411
index ranges	-23 ≤ <i>h</i> ≤ 23 -30 ≤ <i>k</i> ≤ 30 -19 ≤ <i>l</i> ≤ 21	-13 ≤ <i>h</i> ≤ 13 -24 ≤ <i>k</i> ≤ 25 -20 ≤ <i>l</i> ≤ 20	-18 ≤ <i>h</i> ≤ 18 -29 ≤ <i>k</i> ≤ 28 -23 ≤ <i>l</i> ≤ 23
no. of indep rflns (<i>R</i> _{int})	7910 (0.1139)	7701 (0.0754)	13059 (0.1668)
no. of data (<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²))/restraints/params	7910/0/415	7701/0/415	13059/0/680
goodness of fit (<i>S</i> ²) (<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²))	0.920	1.001	0.938
<i>R</i> ₁ ^b (<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²))	0.0385	0.0408	0.0567
<i>wR</i> ₂ ^c (<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²))	0.0943	0.0881	0.1174
largest diff peak and hole (e Å ⁻³)	2.876 and -1.761	2.592 and -0.693	1.988 and -0.710

^a *S* = [Σ*w*(*F*_o² - *F*_c²)/(*n* - *p*)]^{1/2} (*n* = number of data; *p* = number of parameters varied; *w* = [σ²(*F*_o²) + (*A*₀*P*²)]⁻¹ where *P* = [Max(*F*_o², 0) + 2*F*_c²/3] and *A*₀ = 0.0481 (2), 0.0356 (5), 0.0354 (7). ^b *R*₁ = Σ||*F*_o|| - |*F*_c||/Σ||*F*_o||. ^c *wR*₂ = [Σ*w*(*F*_o² - *F*_c²)/Σ*w*(*F*_o²)]^{1/2}.

suitable for X-ray diffraction analysis were obtained directly from the initial crop of **2**.

[Pt(η⁴-cod){=C(Ph₂P=N(Me)SiMe₃)(Ph₂P=NSiMe₃)}-κC,κN][OTf] (3). To an orange Et₂O (4 mL) solution containing **2** (0.076 g, 0.088 mmol) was added neat MeOTf (10.5 μL, 0.093 mmol) in a single portion by microliter syringe. Within seconds, a canary yellow precipitate formed. This was isolated by centrifugation, washed with Et₂O (2 × 3 mL), and dried in vacuo. Yield: 0.064 g (71%). Anal. Calcd for C₄₁H₅₃N₂F₃O₃P₂-PtSSi₂: C, 48.1; H, 5.2; N, 2.7. Found: C, 47.9; H, 5.4; N, 2.6. ¹H NMR (THF-*d*₆): δ -0.17 (s, 9H, Si(CH₃)₃), -0.10 (s, 9H, Si(CH₃)₃), 2.15 (m, 4H, cod CH₂), 2.37 (m, 2H, cod CH₂), 2.53 (m, 2H, cod CH₂), 3.19 (d, 3H, NCH₃, ³*J*_{HP} = 14), 4.34 (m, 2H, cod CH, ²*J*_{HPt} = 58), 5.54 (m, 2H, cod CH, ²*J*_{HPt} = 42), 7.30–7.65 (m, 20H, Ph *H*). ¹³C{¹H} NMR (THF-*d*₆): δ -0.8 (s, Si(CH₃)₃), 2.9 (d, Si(CH₃)₃, ³*J*_{CP} = 3.5), 28.3 (s, cod CH₂), 30.5 (s, cod CH₂), 31.0 (s, NCH₃), 86.8 (s, cod CH, ¹*J*_{Cpt} = 160), 97.6 (s, cod CH, ¹*J*_{Cpt} not observed), 128–132 (m, Ph *C*, Ph CH). The carbene C atom was not observed. ³¹P{¹H} NMR (THF-*d*₆): δ 33.3 (d, ²*J*_{PP} = 63, ²*J*_{Ppt} = 0), 68.6 (d, ²*J*_{PP} = 63, ²*J*_{Ppt} = 510).

[Pt(η⁴-cod){=C(Ph₂P=NSiMe₃)(Ph₂P=NC(O)OSiMe₃)}-κC,κN] (4). An orange slurry of **2** (0.035 g, 0.041 mmol) in hexanes (5 mL) in a round-bottomed flask capped with a Kontes valve was degassed by two freeze–pump–thaw cycles, and then 1 atm of CO₂ gas was admitted. After 0.5 h of stirring, the suspension had changed color from orange to yellow. The yellow solid was isolated by centrifugation and dried in vacuo. Yield: 0.030 g (82%). Anal. Calcd for C₄₀H₅₀N₂O₂P₂PtSi₂: C, 53.1; H, 5.6; N, 3.1. Found: C, 52.7; H, 5.4; N, 3.0. ¹H NMR (under 1 atm of CO₂): δ 0.02 (s, 9H, Si(CH₃)₃), 0.52 (s, 9H, Si(CH₃)₃), 1.42 (m, 4H, cod CH₂), 1.82 (br m, 4H, cod CH₂), 5.72 (br m, 4H, cod CH, ²*J*_{HPt} = 56), 6.90 (m, 6H, Ph *H*), 7.05 (m, 6H, Ph *H*), 7.95 (m, 8H, Ph *H*). ¹³C{¹H} NMR: δ -0.1 (s, Si(CH₃)₃), 1.2 (s, Si(CH₃)₃), 29.1 (s, cod CH₂), 31.6 (s, cod CH₂), 88.3 (s, cod CH), 96.7 (s, cod CH), 127–134 (m, Ph CH), 137.6 (d, Ph *C*, ¹*J*_{CP} = 100). The PCP and NC(O)O C atoms were not observed. ³¹P{¹H} NMR (under 1 atm of CO₂): δ 17.5 (d, ²*J*_{PP}

= 67, ²*J*_{Ppt} = 0), 78.4 (br d, ²*J*_{PP} = 67 Hz, ²*J*_{Ppt} = 340). ²⁹Si NMR (toluene-*d*₈): δ 21.5 (s, OSi), 13.3 (d, NSi, ²*J*_{SiP} = 22).

[Pt(η⁴-cod){CH(Ph(C₆H₄)P=NSiMe₃)(Ph₂P=NSiMe₃)-κC,κC} (5). A C₆D₆ solution of **2** (0.091 g, 0.106 mmol) was sealed in an NMR tube that was subsequently immersed in a 100 °C oil bath for 20 h. The solvent was then removed in vacuo to give a pale yellow free-flowing powder that was recrystallized from Et₂O. Yield: 0.069 g (76%). Anal. Calcd for C₃₉H₅₀N₂P₂PtSi₂: C, 54.5; H, 5.9; N, 3.3. Found: C, 54.1; H, 5.9; N, 3.1. ¹H NMR: δ 0.18 (s, 9H, Si(CH₃)₃), 0.22 (s, 9H, Si(CH₃)₃), 1.00 (m, 1H, cod CH₂), 1.16 (m, 1H, cod CH₂), 1.36 (m, 2H, cod CH₂), 1.54 (m, 1H, cod CH₂), 1.95 (m, 1H, cod CH₂), 2.10 (m, 1H, cod CH₂), 2.61 (m, 1H, cod CH₂), 4.00 (dd, 1H, PCHP, ²*J*_{HP} = 13, ²*J*_{HP} = 16, ²*J*_{HPt} = 96), 4.20 (m, 1H, cod CH, ²*J*_{HPt} = 38), 4.45 (m, 1H, cod CH, ²*J*_{HPt} = 48), 4.70 (m, 1H, cod CH, ²*J*_{HPt} = 48), 6.68 (m, 1H, cod CH, ²*J*_{HPt} = 36), 6.80–8.25 (m, 19H, Ph *H*). ¹³C{¹H} NMR: δ 4.4 (d, Si(CH₃)₃, ³*J*_{CP} = 2.9), 4.6 (d, Si(CH₃)₃, ³*J*_{CP} = 3.4), 27.9 (s, cod CH₂), 28.3 (s, cod CH₂), 30.3 (s, cod CH₂), 30.7 (s, cod CH₂), 51.3 (dd, Pt-CH, ¹*J*_{CP} = 57, ¹*J*_{CP} = 67), 96.4 (s, cod CH, ¹*J*_{Cpt} = 97), 98.4 (s, cod CH, ¹*J*_{Cpt} = 97), 106.6 (s, cod CH, ¹*J*_{Cpt} = 42), 106.8 (s, cod CH, ¹*J*_{Cpt} = 48), 125–134 (m, Ph *C* and Ph CH). ³¹P{¹H} NMR (CD₂-Cl₂): δ 9.6 (d, ²*J*_{PP} = 5.9, ²*J*_{Ppt} = 200), 9.3 (d, ²*J*_{PP} = 5.9, ²*J*_{Ppt} = 130). ¹⁹⁵Pt{¹H} NMR: δ 872 (dd, ²*J*_{PtP} = 130, ²*J*_{PtP} = 200). Crystals suitable for X-ray diffraction were grown at -18 °C from a THF solution of **5** that had been layered with hexanes.

[Pt(dppe){CH(Ph(C₆H₄)P=NSiMe₃)(Ph₂P=NSiMe₃)-κC,κC} (6). To a combination of **5** (0.090 g, 0.105 mmol) and dppe (0.042 g, 0.105 mmol) was added C₆H₆ (3 mL), and the pale yellow solution was stirred for 3 h. The volume of the solution was reduced to ca. 0.5 mL in vacuo, and hexanes (10 mL) was added to give an off-white precipitate that was separated from the solution by centrifugation. The solution was placed in a -18 °C refrigerator for several days, and a pale yellow precipitate deposited. The supernatant liquid was removed, and the solid was dried in vacuo. Yield: 0.050 g (43%). Anal. Calcd for C₅₇H₆₄N₂P₄PtSi₂: C, 59.4; H, 5.6; N, 2.4.

Found: C, 59.8; H, 5.7; N, 2.4. ^1H NMR: δ -0.12 (s, 9H, Si(CH₃)₃), $^2J_{\text{HSi}} = 6$), 0.04 (s, 9H, Si(CH₃)₃), $^2J_{\text{HSi}} = 6$), 1.04 (m, 1H, CH₂), 1.43 (m, 1H, CH₂), 1.64 (m, 1H, CH₂), 1.73 (m, 1H, CH₂), 4.15 (m, 1H, Pt-CH), $^2J_{\text{HPt}} = 85$), 6.54–8.10 (m, 20H, Ph H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 4.5 (d, Si(CH₃)₃), $^3J_{\text{CP}} = 2.9$), 4.6 (d, Si(CH₃)₃), $^3J_{\text{CP}} = 3.8$), 23.0 (s, CH₂), 31.9 (s, CH₂), 124–136 (m, Ph C and Ph CH). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 14.41 (d, $^{2/3}J_{\text{PP}} = 13$, $^2J_{\text{PPt}} = 100$), 15.39 (dd, $^2J_{\text{PP}} = 10$, $^2J_{\text{PP}} = 31$, $^2J_{\text{PPt}} = 160$), 41.05 (appears as a pt, but must be a dd with two almost identical coupling constants: $^{2/3}J_{\text{PP}} \approx 13$, $^{2/3}J_{\text{PP}} \approx 13$, $^1J_{\text{PPt}} = 2670$), 43.70 (d, $^2J_{\text{PP}} = 31$, $^1J_{\text{PPt}} = 1800$).

**[Li][Pt{CH(Ph)(C₆H₄)P=NSiMe₃}(Ph₂P=NSiMe₃)-κC,κC'}-
{CH(Ph₂P=NSiMe₃)₂-κC,κN}] (7).** To a combination of [PtCl₂-(cod)] (0.17 g, 0.46 mmol) and [Li₂-1]₂ (0.26 g, 0.23 mmol) was added C₆H₆ (20 mL) to give a yellow solution that was stirred at ambient temperature for 5 days and then at 100 °C for 20 h. The solvent was removed in vacuo to give an oily brown residue that was extracted with hexanes (2 × 10 mL). The combined extracts were concentrated and cooled to -20 °C. Colorless X-ray diffraction quality crystals deposited. The supernatant liquid was decanted, and the crystals were washed with precooled hexanes and dried under vacuum. Yield: 0.078 g (26%). Anal. Calcd for C₆₂H₇₇N₄LiP₄PtSi₄: C, 56.6; H, 5.9; N, 4.3. Found: C, 55.7; H, 6.0; N, 4.0. ^1H NMR: δ -0.18 (s, 9H, Si(CH₃)₃), 0.25 (s, 9H, Si(CH₃)₃), 0.31 (s, 9H, Si(CH₃)₃), 0.44 (s, 9H, Si(CH₃)₃), 2.36 (m, 1H, PCHP), 4.38 (dd, 1H, PCHP), $^2J_{\text{HP}} = 20$, $^2J_{\text{HP}} = 16$), 6.42–9.42 (m, 39H, Ph H). ^{13}C NMR (CD₂Cl₂): δ 3.9 (d, Si(CH₃)₃), $^3J_{\text{CP}} = 2.4$), 4.5 (d, Si(CH₃)₃), $^3J_{\text{CP}} = 4.5$), 5.0 (d, Si(CH₃)₃), $^2J_{\text{CP}} = 4.1$), 5.4 (d, Si(CH₃)₃), $^2J_{\text{CP}} = 4.4$), 15.0 (dd, Pt-CH), $^1J_{\text{CP}} = 50$, $^1J_{\text{CP}} = 80$), 122–146 (m, Ph C, Ph CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ 16.4 (s, $^2J_{\text{PPt}} = 160$), 22.9 (m, $^2J_{\text{PPt}} = 76$), 24.8 (d, $^2J_{\text{PP}} = 5.0$, $^2J_{\text{PPt}} = 100$), 30.2 (d, $^2J_{\text{PP}} = 5.0$, $^2J_{\text{PPt}} = 270$).

Crystallography. A summary of crystallographic data for **2**, **5**, and **7** appears in Table 4. Details are given in the Supporting Information. Crystals of the three complexes were grown as outlined in their respective synthetic sections. In all cases, data were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer⁴⁷ using Mo K α radiation at 193 K. Unit cell parameters were obtained from a least-squares

refinement of the setting angles of 7006 (**2**), 7635 (**5**), and 4139 (**7**) reflections from the data collection. The space groups were determined to be *Pbca* (No. 61), *P2₁/n* (No. 14), and *P2₁/n* (No. 14), respectively. The data were corrected for absorption through use of a multiscan procedure (SADABS).

The structures of **2**, **5**, and **7** were solved using automated Patterson location of the heavy metal atoms and structure expansion using the DIRDIF-96⁴⁸ program. Refinement was completed using the program SHELXL-93.⁴⁹ Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons. The final model for **2** was refined to values of $R_1(F) = 0.0385$ (for 5439 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0943$ (for all 7910 independent data), that of **5** was refined to values of $R_1(F) = 0.0408$ (for 5356 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0881$ (for all 7701 independent data), and finally that of **7** was refined to $R_1(F) = 0.0567$ (for 7482 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1174$ (for all independent data).

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Supporting Information Available: Tables giving crystallographic data for **2**, **5**, and **7**; these data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(47) Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

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