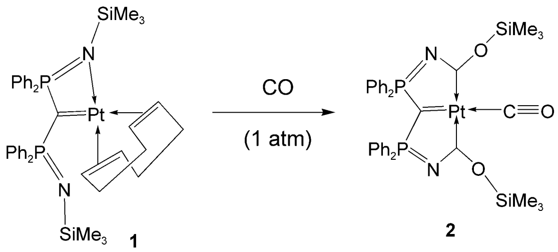
A Pt Tris(carbene) Pincer Complex

A Tris(carbene) Pincer Complex: Monomeric Platinum Carbonyl with Three Bound Carbene Centers**

*Guanyang Lin, Nathan D. Jones, Robert A. Gossage, Robert McDonald, and Ronald G. Cavell**

Transition-metal carbene complexes are currently the focus of intense research because of their wide-ranging application in olefin metathesis[1–3] and organic synthesis.[4] Since 1999, we have been developing a series of novel "pincer" carbene complexes of the group four metals[5–9] and lanthanides,[10,11] as well as a number of bimetallic Cr[12] and Al[13] compounds containing bridging carbenes. The latter species are very efficient transition-metal-free ethylene polymerization catalyst precursors when activated by only one equivalent of trityl borate.[14] These new pincer-type complexes incorporate N,C,N chelates or bridges, with the carbene C atom being substituted by two $Ph_2P{=}NSiMe_3$ groups.

Recently, we extended this chemistry to the late transition metals and reported the synthesis, characterization and some reactivity of a novel Pt–olefin–carbene complex, $[(\eta^4\text{-cod})Pt\{{=}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N\}]$ (**1**; cod = cycloocta-1,5-diene), in which only one of the N atoms is coordinated to the metal center.[15] Herein we report that **1** reacts with CO to give the remarkable compound $[(CO)Pt\{=C(Ph_2P=NCO\text{-}SiMe_3)_2\text{-}\kappa C, \kappa C', \kappa C''\}]$ (**2**) which contains a tridentate pincer ligand in which all three donors are carbenes (Scheme 1).



Scheme 1. The reaction of **1** with CO to give **2**.

The treatment of a pentane or hexanes suspension of **1** with 1 atm of CO gas at room temperature resulted in the rapid and quantitative conversion of **1** to **2**.[16] Interrogation of **2** by solution ^1H and $^{13}C\{^1H\}$ NMR and solid-state IR spectroscopies, mass spectrometry and elemental analysis revealed that **2** did not contain cod, and that it incorporated three molecules of CO, one of which was a terminal CO ligand and the other two had been chemically transformed and were related by a mirror plane.

An X-ray crystallographic study revealed the structure of **2** to be that shown in Figure 1.[17] The molecule contains a

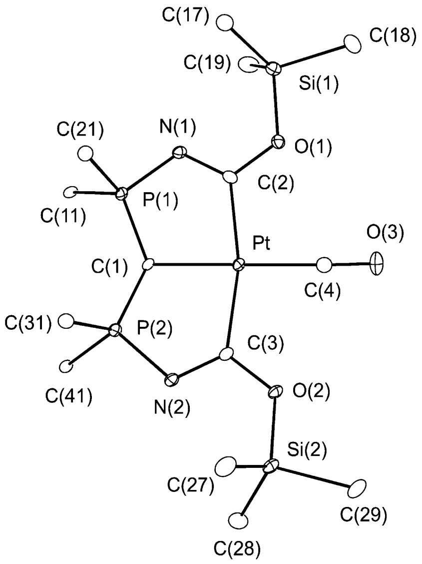


Figure 1. An ORTEP representation (ellipsoids set at the 20% probability level) of the molecular structure of **2**. Only the ipso carbon atoms of the phenyl rings are shown, and hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): Pt-C(1) 2.002(5), Pt-C(2) 2.059(6), Pt-C(3) 2.048(6), Pt-C(4) 1.868(6), C(4)-O(3) 1.139(7); P(1)-C(1)-P(2) 133.3(3), P(1)-C(1)-Pt 111.6(3), C(1)-Pt-C(4) 179.2(3), C(2)-Pt-C(3) 166.9(2).

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total of three CO fragments, consistent with the mass spectrometric and elemental analytical data, including one terminal CO ligand, as revealed by the IR and NMR spectroscopic data. The other two CO groups have been inserted into both of the N–Si bonds with concomitant formation of two Fischer-type N,O-carbenes. The good correspondence between the solid-state and solution data shows that the molecular structure as revealed by X-ray crystallography is essentially maintained in solution.

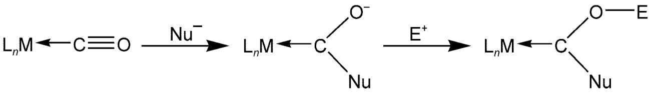
The bond angles surrounding C(1), C(2) and C(3) range from 111.6(3)° to 133.3(3)° and the sums of the angles around these centers are 356.8(3)°, 360.0(4)° and 359.9(4)°, respectively, suggesting sp^2 hybridization at these carbon atoms. The Pt–C(1) bond length (2.002(5) Å) is significantly shorter than those of Pt–C(2) and Pt–C(3) (2.059(6) and 2.048(6) Å, respectively), and slightly shorter than the corresponding bond length found in **1** (2.021(5) Å).[15] All of these lengths are significantly longer than those typically found for both N-heterocyclic carbene complexes of two- and four-coordinate Pt centers (1.93–1.97 Å),[18–20] and the Fischer carbene complexes of four-coordinate Pt centers (1.87–1.96 Å).[21–25] Indeed, the Pt–C(1) bond length in **2** is unusual in that it is more akin to those found for Fischer carbene complexes of five-[26] and six-coordinate[27] Pt centers (1.99–2.01 Å). Nevertheless, all of the the Pt–C(carbene) bonds in **2** are shorter than typical Pt–C(alkyl) single bonds (2.07–2.15 Å).[28]

It is interesting to note that the Pt–C(4) (carbonyl) bond in **2** (1.868(6) Å) is significantly shorter than those found in typical four-coordinate Pt^{II}-carbonyl complexes, for example, those in *cis*-[PtCl$_2$(CO)$_2$] are 1.901(5) and 1.893(5) Å.[29] In addition, the C(4)–O(3) distance in **2** (1.139(7) Å) is longer than the corresponding lengths in *cis*-[PtCl$_2$(CO)$_2$] (1.110(7) and 1.121(6) Å), and its $\tilde{\nu}$(C≡O) is much lower (2038 *vs.* 2170 and 2128 cm^{-1}, respectively). In contrast, these distances in **2** are comparable to those found in Pt(0) carbonyl complexes, for example, [Pt(CO)(PPh$_3$)$_3$] has Pt–C bond lengths of 1.86(3)[30] and 1.84(2)[31] Å (two polymorphs) and corresponding C–O distances of 1.12(4) and 1.13(3) Å. The comparative data suggest that the metal center in **2** is appreciably electron rich, as we have suggested previously for the Pt center in **1**,[15] and that there is significant π-backbonding to the terminal CO ligand. Given that Pt^{II}- and Pd^{II}-CO bonds have been considered repeatedly to be almost pure σ-type interactions,[29,32] a zero oxidation state of the Pt center in **2** is possible, and **2**, as drawn, is an 18-electron species. However, its square-planar coordination geometry strongly suggests a 16-electron Pt^{II} configuration.

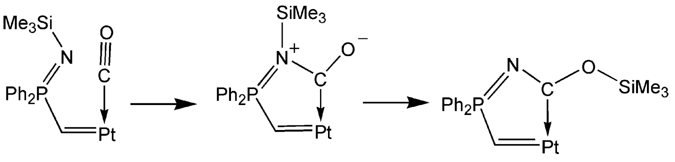
The apparent electron-count/coordination geometry discrepancy may be resolved either by describing **2** in terms of 16-electron resonance structures incorporating two Pt–C covalent bonds and one Pt–C dative bond, or by reference to restricted Hartree-Fock calculations by Nakamura and Morokuma. These researchers have found that their 18-electron carbene carbonyl model complex *cis*-[Pt(PH$_3$)$_2$(CO)(CH$_2$)] adopts a square-planar structure as its most stable coordination geometry, with the C–H bonds in the plane.[33] They attribute the stability of the square-planar structure over a tetrahedral one to CH$_2$(π)-Pt(pπ) overlap, which constitutes the HOMO in their complex. Carbene complex **2** may likewise be an 18-electron Pt^{II} compound whose square-planar geometry is the result of such an overlap.

Phosphorus substituted carbene (P,P-carbene) metal complexes are rare. In addition to compounds developed by us, only a few examples have been reported previously, and almost all of these are based on the carbodiphosphoranes R$_3$P=C=PR$_3$ (R=Me,[34] Ph[35]). Apart from **1** and **2**, only three structurally characterised Group 10 P,P-carbene complexes have so far appeared in the literature: [(OC)$_n$Ni{=C(PPh$_3$)$_2$}] (n = 2, 3)[36] and [Pd(μ-Cl)$_2$Pt{=C(PPh$_2$)$_2$}]$_\infty$.[37] Other examples of Ph$_3$P=C=PPh$_3$ complexes of Pt have been characterized spectroscopically.[38,39] Aside from **2**, we are not aware of any Group 10 complexes bearing P,P- as well as classical Fischer carbene ligands.

Fischer carbene complexes are typically made from metal-carbonyl or metal-isonitrile complexes by the stepwise addition of a strong nucleophile and an electrophile according to Scheme 2.[2] It is therefore reasonable to postulate that the reaction of CO with **1** to generate **2** may proceed analogously, with the mechanism containing steps that are outlined in Scheme 3 (only the crucial atoms are shown). Nucleophilic attack on a coordinated CO ligand by the N-atom of a “dangling” Ph$_2$P=NSiMe$_3$ group, and subsequent N-to-O trimethylsilyl migration generates an N,O-carbene. This sequence of steps must occur on both “sides” of the molecule to generate the final product.



Scheme 2. The formation of carbene complexes by the stepwise addition of a nucleophile and electrophile to a metal carbonyl.



Scheme 3. Postulated mechanism for the formation of **2**.

Because **1** may also be drawn in one resonance form as an alkyl amido complex, insertion of CO into the Pt–N bond is also possible in the formation of **2**. However, because such insertions are rare (though not unprecedented) for late transition-metal amides[40,41] and because **1** does not behave like a typical complex in this class (the Pt–N bond is not hydrolyzed, for example), we favor the route outlined in Scheme 3.

The first step in this proposed mechanism has precedence in reports of intramolecular attack by Ru-coordinated 2-amino[42] or 2-acetamido pyridine[43] on the α-carbon atom of a vinylidene ligand, and in those describing the ring-closing of W-, Mo-, Cr- and Fe-coordinated 2-hydroxyphenyl isonitrile by attack of the hydroxy group on the bound C-atom in the same ligand.[44–46] In all of these cases, Fischer carbenes ultimately result by N-to-C or O-to-N proton transfer, respectively.

Literature precedence for the second step is found in our own observations of N-to-O trimethylsilyl migration reactions,[47] as well as those of other groups.[48–50] Of particular relevance to this system is our recent finding that the reaction of **1** with CO_2 produced $[Pt(\eta^4\text{-cod})\{=C(Ph_2P{=}NSiMe_3)(Ph_2P{=}NC(O)OSiMe_3)\}\text{-}\kappa C,\kappa N\}]$.[15]

To the best of our knowledge, **2** represents the first example of a tris(carbene) pincer complex, although the homoleptic Fischer carbene complex $[Pt\{C(N(H)CH_3)_2\}_4]^{2+}$ has long been known.[51] We are aware neither of other instances in which a carbene complex is thought to be generated in the first step by intramolecular attack on coordinated CO (rather than on vinylidene[42,43] or isonitrile[44–46]), nor have we found instances of trimethylsilyl as opposed to proton migration as the second step in the carbene formation process. We are currently investigating the onward reactivity of **2**.

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[16] A suspension of **1** (62 mg, 0.072 mmol) in pentane was solidified at liquid N_2 temperature in an Schlenk flask. The flask was evacuated, allowed to warm to room temperature and filled with 1 atm of CO gas. The red orange suspension of **1** became green after 15 min of stirring. Centrifugation gave a crystalline solid, which was washed with pentane (2 × 5 mL) and dried under vacuum. Yield: 53 mg (88 %). A ^{13}C-enriched sample of **2** was made in exactly the same manner by using ^{13}CO gas. Elemental anal calcd (%) for $C_{34}H_{38}N_2O_3P_2PtSi_2$: C 48.85, H 4.58, N 3.35; found: C 48.92, H 4.46, N 3.25. ^1H NMR $[D_8]THF$): 0.22 (s, 18 H, $Si(CH_3)_3$), 7.19 (m, 8 H, *o*-Ph-*H*), 7.37 ppm (m, 12 H, *m*- and *p*-Ph-*H*). $^{31}P\{^1H\}$ ($[D_8]THF$): 46.9 ppm (s, $^2J_{PPt} = 35$ Hz). $^{13}C\{^1H\}$ NMR ($[D_8]THF$, ^{13}C-enriched): 1.1 (s, $Si(CH_3)_3$), 128.8 (m, Ph-*C*), 131.6 (m, Ph-*C*), 132.5 (m, Ph-*C*), 133.8 (m, Ph-*C*), 177.3 (s, *C*O, $^1J_{CPt} = 1370$ Hz, $^2J_{CC} = 0$ Hz), 207.1 ppm (apparent (second-order) triplet, N*C*O, $^2J_{CP} = 39$ Hz, $^2J_{CC} = 0$ Hz (both derived by simulation), $^1J_{CPt} = 871$ Hz). FTIR (KBr pellet) :$\nu = 2038$ (CH_2Cl_2); 2038 cm^{-1} . MS (EI, *m/z*): 836.1 ($[M]^+$, 21.2 %), 820.8 ($[M\text{-}CH_3]^+$, 10.8 %), 807.6 ($[M\text{-}CO]^+$, 68.8 %), 779.8 ($[M\text{-}2\,CO]^+$, 100.0 %), 751.4 ($[M\text{-}3\,CO]^+$, 15.2 %).

[17] Crystallographic data for **2**: triclinic, space group $P\bar{1}$(No. 2), $a = 12.3685(7)$, $b = 13.1635(7)$, $c = 13.1789(7)$ Å, $\alpha = 118.2869(10)$, $\beta = 108.3633(11)$, $\gamma = 93.0971(11)^\circ$, $V = 1739.37(16)$ Å^3, $Z = 2$. The structure was solved by direct methods and refined by full-matrix least-squares procedures: $R_1 = 0.0405$ $[F_0^2 \geqq 2\sigma F_0^2]$ and $wR_2 = 0.0951$ $[F_0^2 \geqq -3\sigma F_0^2]$. Extra details about the structure of **2** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-204403 . These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+ 44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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