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CO, Isocyanide, Alkene, and Alkyne Insertions into Platinaoxetane Pt−O Bonds

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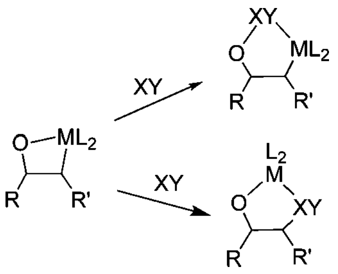
Platinaoxetanes $Pt(COD)(C_7H_{10}O)$ (**1**) and $Pt(PEt_3)_2(C_7H_{10}O)$ (**2**) undergo insertion of CO into their Pt−O bonds to afford $Pt(COD)(C(O)OC_7H_{10})$ (**3**) and $Pt(PEt_3)_2)(C(O)OC_7H_{10})$ (**4**), respectively. Complex **4** is also available from **3** and PEt_3. Platinaoxetanes $[Pt(COD)(C_7H_{10}O)Pt(COD)Cl)]^+$ (**5**) and $Pt(COD)(C_7H_{10}OBF_3)$ (**6**), with Lewis acids bonded to the platinaoxetane ring oxygen atom, give free norbornene when treated with CO. Treatment of **3** with $BF_3 \cdot Et_2O$ immediately gives **6**. Both types of platinaoxetanes are inert to CO_2. Treatment of **1** with tetracyanoethylene (TCNE) yields $Pt(COD)(TCNEOC_7H_{10})$ (**7**) by alkene insertion into the Pt−O bond, while **1** shows no reactivity with ethylene or isobutylene. Similarly **1** reacts with diethylacetylenedicarboxylate (DEAD) to give a rare alkyne M−O bond insertion product $Pt(COD)(DEADOC_7H_{10})$ (**8**) but is inert to diphenylacetylene. Reaction of **1** with isocyanide in a 1:3 molar ratio gives $Pt(Bu^tNC)_2(C_7H_{10}OBu^tNC)$ (**9**), a result of COD displacement by 2 isocyanides and insertion of another isocyanide into the Pt−O bond. Complex **3** was characterized by single-crystal X-ray crystallography.

Introduction

The insertion of small unsaturated molecules such as CO, olefins, and alkynes into transition metal−carbon bonds is a key step in a number of metal-catalyzed reactions and has received considerable interest for a long time.[1,2] Studies of similar insertions into late transition metal alkoxide linkage are more limited, although such reactions are also important in catalytic and stoichiometric reactions.[3−5] Both of these types of insertion reactions are possible with 1-metalla-2-oxacyclobutanes (metallaoxetanes[6]) as illustrated in Scheme 1. The involvement of metallaoxetanes in alkene oxidations,[7−13] epoxide reactions,[14−16] and other reactions[17−19] necessitates an understanding of their reaction chemistry. Metallaoxetanes also provide the opportunity for a direct comparison of the reactivity of M−C and M−O bonds with small molecules.

Scheme 1



The first metallaoxetanes $PtL_2(C_2(CN)_4O)$ ($L = AsPh_3, PPh_3$) show no reactivity with CO or CO_2 at room temperature.[14] Ruthenaoxetane $Ru(PMe_3)_4(OC(Me)(Ph)CH_2)$ undergoes CO insertion into the metal−carbon bond rather than the metal−oxygen bond.[18] In contrast, iridaoxetane $Cp^*Ir(PMe_3)(CH_2CMe_2O)$ undergoes CO_2 or *tert*-butyl isocyanide insertion into the metal−oxygen bond,[20] and $[(tpa)Rh(CH_2CH_2O)]^+$ (tpa = *N,N,N*-tri(2-pyridylmethyl)amine) inserts MeCN into the metal−oxygen bond but only on protonation of the rhodaoxetane oxygen atom.[21,22] (An aza-palladaoxetane or palladaazetidine does an intramolecular alkene Pd−C bond insertion on treatment with CuI.[23])

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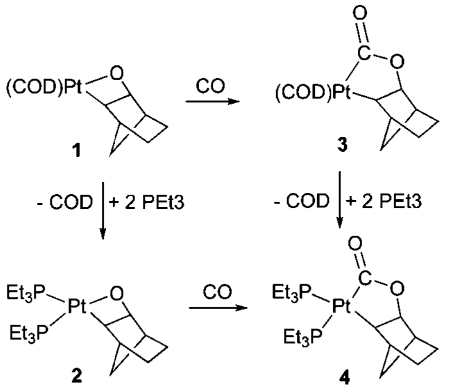
Scheme 2



Recently a family of platinaoxetanes has been synthesized and characterized by our group.[9,24,25] While unusual reversible alkene extrusion involving C−O bond cleavage was discovered,[25] we also began to explore insertion chemistry of the platinaoxetanes. Herein we report that the unsaturated molecules CO, *tert*-butyl isocyanide, and activated alkene and alkynes insert exclusively into the Pt−O bond of the platinaoxetanes.

Results

Carbon monoxide addition to a benzene solution of **1** at room temperature for 3 h leads to the complete loss of the most downfield ^{1}H NMR signal for **1** (broad singlet at 6.62 ppm), and a new doublet appears at 4.03 ppm. Evaporation of the solvent affords the white product Pt(COD)(C(O)OC$_7$H$_{10}$) (**3**) in 93% isolated yield (Scheme 2).

The infrared absorption for the inserted CO is observed at 1644 cm^{-1}, indicative of the presence of a C−O double bond. Table 1 gives selected NMR data and atom-numbering schemes. ^{1}H NMR spectra of **3** in C$_6$D$_6$ exhibit resonances for all 10 protons. Unlike precursor **1**, which shows only two widely spaced olefinic COD peaks, four distinct olefinic COD resonances without ^{195}Pt satellites are observed at 5.52, 5.33, 4.97, and 4.79 ppm for **3**. A doublet at 4.03 ppm with $J_{H-H} = 6.3$ Hz is assigned to the proton adjacent to the oxygen atom (H2). A doublet of doublets at 2.80 ppm with $J_{Pt-H} = 105$ Hz is assigned to the Pt-bonded CH (H1). A doublet at 2.66 ppm is assigned to H6, the bridgehead hydrogen atom adjacent to the Pt-bonded carbon atom. A broad singlet at 2.10 ppm with weaker coupling to ^{195}Pt (32 Hz) is assigned to H3, the bridgehead hydrogen atom adjacent to the oxygen-bonded carbon atom. ^{13}C NMR spectra show the expected 16-carbon resonances. A resonance at 180.5 ppm is assigned to the inserted CO. In contrast to precursor **1**, the chemical shifts for the four olefinic COD carbon atoms are very close at 109.0, 108.4, 107.7, and 106.8 ppm and are flanked by ^{195}Pt satellites with similar J_{Pt-C} (~50 Hz), indicating similar electron-donating groups *trans* to the COD ligand. This and the similarity of the olefinic COD proton resonances are consistent with CO insertion into the Pt−O bond of **1**. A ^{13}C peak at 60.4 ppm shows a large ^{13}C−^{195}Pt coupling of 853 Hz and is assigned to the Pt-bonded norbornene carbon atom C1. The oxygen-bonded norbornene carbon atom, C2, is found at 85.7 ppm with $J_{Pt-C} = 44$ Hz. The ^{195}Pt NMR resonance for **3** (−3820 in C$_6$D$_6$) is at a lower frequency than for **1** (−2891 ppm in C$_6$D$_6$).

Crystals of **3** suitable for an X-ray diffraction study were obtained from toluene/hexane at −30 °C, and analysis of the data confirmed the proposed structure. A drawing of **3** is given in Figure 1. Crystallographic data are summarized in Table 2. Selected bond distances and bond angles are given in Table 3.

As suggested by the ^{1}H and ^{13}C NMR data, the four olefinic Pt−C distances, Pt1−C9, Pt1−C10, Pt1−C13, and Pt1−C14, are nearly identical, indicative of a similar *trans*-influence for the two carbon centers, C1 and C8, *trans* to the COD ligand. The Pt−C8 distance of 2.005(7) Å for the inserted CO carbon is slightly shorter than that of Pt−C1 (2.063(8) Å), consistent with the smaller radius of an sp^2-hybridized center. The O1−C8 bond distance of 1.215(9) Å is typical for a carbon−oxygen double bond. The C1−Pt−C8 angle of 82.1(3)° is much bigger than the corresponding angle in known platinaoxtanes (~70°),[9,14,15,24,25] indicating that the distortion of the square-planar Pt(II) geometry is much reduced. This may be attributed to the four-membered to five-membered ring expansion resulting from CO insertion. Similarly, the angles C2−C1−Pt and C1−C2−O2 (110.3(5)° and 112.9(6)°, respectively) have opened considerably from the corresponding angles (~93° and ~101°) in the platinaoxetanes. Similar angles are also present in Pt(IV) platinaoxetanes.[13]

Structurally characterized five-membered metallalactones similar to **3** are relatively rare.[26−34] The most closely related is the platinalactone Pt(PPh$_3$)$_2$(C(O)OCMe$_2$C(CH$_2$)) obtained by carbonylation of the alkyne complex Pt(PPh$_3$)$_2$(HOCMe$_2$-CCH).[35,36] This complex has a Pt−C(sp^2) bond in the ring rather than a Pt−C(sp^3) bond as in **3**. Nonetheless, the structures of the platinalactone rings are quite similar.

Phosphine-substituted platinaoxetane **2** also reacts with carbon monoxide (Scheme 2). Addition of CO to a benzene solution of **2** at room temperature gives the white insertion product Pt(PEt$_3$)$_2$)(C(O)OC$_7$H$_{10}$) (**4**) in 90% isolated yield. Complex **4** is also available from **3** by COD ligand displacement via addition of 2 molar equiv of PEt$_3$ (Scheme 2). Evidence that insertion has taken place into the Pt−O bond rather than the Pt−C bond of **2** is provided by NMR spectroscopy and by the formation of **4** from **3**.

The ^{31}P NMR spectrum of **4** in C$_6$D$_6$ shows two doublets flanked by ^{195}Pt satellites. The inequivalence of the phosphine ligands and the small P−P coupling of 9 Hz are consistent with

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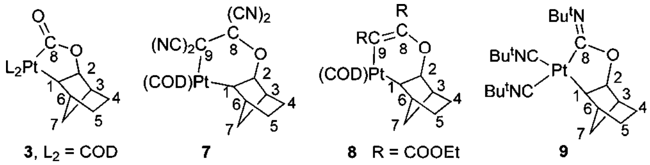
Table 1. Selected NMR Data and Atom-Numbering Scheme[a,b]



3, L_2 = COD **7** **8** R = COOEt **9**
4, L = PEt_3

	δ H2	δ H1	δ C2	δ C1	δ Pt
1[c]	5.99 (J_{PtH} = 60)	0.69 (br s, J_{PtH} = 66)	98.7	8.8	−2908
2[c]	6.92 (J_{PtH} = 40)	0.77 (m, J_{PtH} = 40.5)	100.1	8.2	−3883
3	4.03 (J_{HH} = 6.3)	2.80 (dd, J_{H-H} = 6.3, 2.1, J_{PtH} = 105)	85.7	60.4	−3820
4	4.24 (J_{HH} = 6.9)	2.63 (dd, J_{H-H} = 8.1, 1.5, J_{PtH} = 23)	84.6	56.7	−4564
7	4.29 (J_{HH} = 5.7)	2.08 (dd, J_{H-H} = 5.7, 2.1, J_{PtH} = 106)	85.7	50.4	−3895
8	3.63 (J_{HH} = 6.9)	2.40 (dd, J_{H-H} = 7.8, 1.8, J_{PtH} = 117)	82.8	51.2	−3937
9	4.46 (J_{HH} = 6.9)	3.03 (dd, J_{H-H} = 6.9, 2.4, J_{PtH} = 75)	89.5	52.3	−4337

[a] Shifts in ppm, coupling constants in Hz. [b] In C_6D_6. [c] From ref 24.

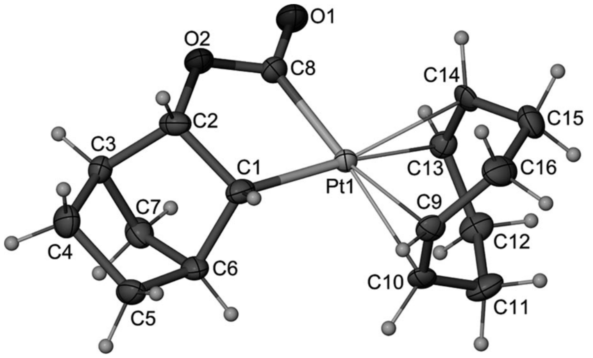


Figure 1. Drawing of the solid-state structure of Pt(COD)-($C(O)OC_7H_{10}$) (**3**).

Table 2. Crystal Data and Structure Refinement Details for 3[a]

formula	$C_{16}H_{22}O_2Pt$	V, Å^3	2786.9(5)
fw	441.43	Z	8
space group	*C*2/*c*	d_{calc}, g/cm^3	2.104
a, Å	20.776(2)	μ, mm^{-1}	10.065
b, Å	13.8500(14)	R1[b], wR2[c]	0.0375, 0.0800
c, Å	11.4466(12)	Gof	1.092
β, deg	122.2070(10)	*T*	−100 °C

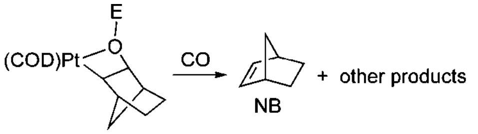
[a] λ = 0.71073 Å (Mo). [b] $R1 = (\sum||F_o| - |F_c||)/\sum F_o$. [c] $wR2 = [(\sum w(||F_o| - |F_c||)^2)/\sum wF_o^2]^{1/2}$; $w = 4F_o^2/(\sum F_o^2)^2$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3

Pt1−C8	2.005(7)	Pt1−C9	2.262(7)
Pt1−C1	2.063(8)	Pt1−C10	2.303(7)
O1−C8	1.215(9)	Pt1−C13	2.259(7)
O2−C8	1.354(9)	Pt1−C14	2.275(6)
O2−C2	1.450(9)	C2−C1	1.542(10)
C8−Pt1−C1	82.1(3)	O2−C8−Pt1	117.0(5)
C8−O2−C2	116.8(6)	O2−C2−C1	112.9(6)
O1−C8−O2	116.1(6)	C2−C1−Pt1	110.3(5)
O1−C8−Pt1	126.7(6)	O2−C2−C3	109.9(6)

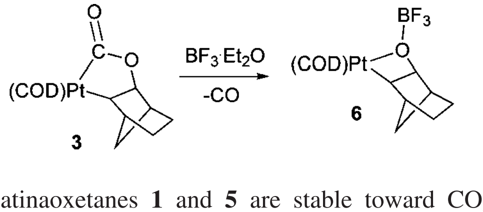
the *cis*-phosphine geometry at the Pt centers. The upfield doublet at 5.49 ppm shows J_{P-Pt} = 1985 Hz, only ca. 130 Hz greater than the downfield doublet at 18.57 ppm (J_{P-Pt} = 1856 Hz). The disappearance of the P atom signal with the large Pt−P coupling constant *trans* to the weakly donating oxygen atom in **2** and the small Pt−P coupling constants for both P atoms in **4** suggest that both P atoms are *trans* to more or less equally donating carbon atoms in **4** and that the CO has inserted into the Pt−O bond of **2**. The ^{195}Pt NMR spectrum of **4** in C_6D_6 shows a triplet at −4564 ppm with J_{P-Pt} = 1959 Hz, further confirming coupling between the Pt center and two similar phosphine ligands. The ^{13}C NMR spectrum displays a resonance for the inserted CO as a doublet of doublets at 195.0 ppm (J_{P-C} = 150 and 7.5 Hz) and a resonance for the Pt-bonded norbornyl carbon atom (C1) as a doublet of doublets at 56.7 ppm (J_{P-C} = 77.0 and 5.3 Hz). Three other norbornene carbons (C3, C5, C7) also exhibit coupling to the ^{31}P nuclei of the phosphine ligands. The signal for the oxygen-bonded carbon atom (C2) of the norbornyl unit is found at 84.6 ppm flanked by satellites with a small ^{13}C−^{195}Pt coupling of 9.8 Hz but with no ^{31}P−^{13}C coupling. ^{1}H NMR spectra of **4** in C_6D_6 show all 10 norbornyl proton peaks in addition to the resonances for the phosphine ligands. A doublet at 4.24 ppm with J_{H-H} = 6.9 Hz is assigned to H2, and a doublet of doublets with satellites (J_{Pt-H} = 23 Hz) at 2.63 ppm is assigned to H1. Finally, a C=O stretching absorption is observed at 1642 cm^{-1} in the infrared spectrum of **4**.

In contrast to **1** and **2**, addition of 1 equiv of CO to platinaoxetane **5** in CD_2Cl_2 results in (COD)$PtCl_2$ and free norbornene (NB) (eq 1). Presumably, CO_2 and the fragments “(COD)Pt^{2+}” and “(COD)Pt” are also formed, although the fate of these fragments is unknown. No CO insertion product is observed. Excess CO and **5** gives a black precipitate (assumed to be finely divided Pt metal), free COD, norbornene, and presumably CO_2. Similarly, addition of CO to **6** in C_6D_6 gives norbornene with CO_2, BF_3, and “(COD)Pt” as presumed additional products (eq 1). To examine the stability of an insertion product, **3** was treated with $BF_3 \cdot Et_2O$ (eq 2). Complex **6** was immediately produced (presumably along with CO), indicating that the CO insertion product of **6** is unstable.



(1)

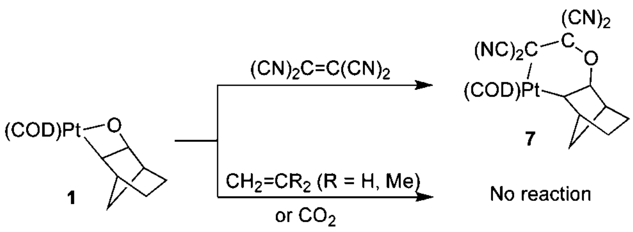
5, E = $[Pt(COD)Cl]^+$
6, E = BF_3



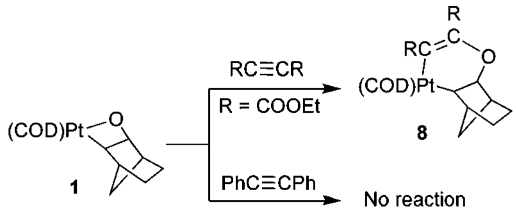
(2)

Platinaoxetanes **1** and **5** are stable toward CO_2. When a solution of **1** or **5** is exposed to 1 atm of CO_2 at room temperature for 48 h, no evidence for CO_2 insertion or any other reaction is observed by ^{1}H NMR spectroscopy. Since **1** also

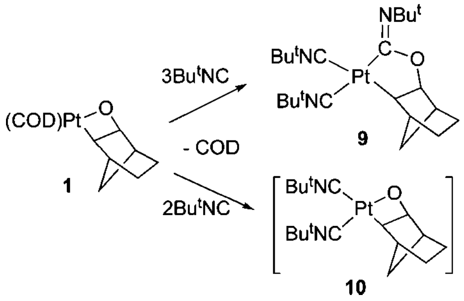
Scheme 3



Scheme 4



Scheme 5



shows no reactivity with ethylene, isobutylene, and norbornene, we turned our attention to more electrophilic reagents. Treatment of **1** with 1 equiv of tetracyanoethylene (TCNE) in C_6D_6 at room temperature gives insertion product $Pt(COD)(TCNEOC_7H_{10})$ (**7**) (Scheme 3). The ^1H NMR spectrum of **7** displays a doublet at 4.29 ppm with $J_{H-H} = 5.7$ Hz, which is similar to the H2 peak in the spectrum of **3** (doublet at 4.03 with $J_{H-H} = 6.3$ Hz) and **4** (doublet at 4.24 ppm with $J_{H-H} = 6.9$ Hz), suggesting TCNE insertion into the Pt−O bond. The Pt-bonded CH (H1) appears as a doublet of doublets with satellites at 2.08 ppm due to coupling to H3 and H6 and ^{195}Pt ($J_{Pt-H} = 106$ Hz). Two doublets at 2.19 and 2.66 ppm are assigned to H3 and H6, respectively. Four nonoverlapping COD olefinic protons are observed at 5.52, 5.33, 4.97, and 4.79 ppm with satellites. The C≡N stretching absorption is observed at 2224 cm^{-1} in the infrared spectrum, and resonances at 116.2, 114.7, 113.2, and 112.5 ppm in the ^{13}C NMR spectrum are assigned to CN units. The Pt-bonded norbornene carbon atom (C1) and oxygen-bonded norbornene carbon (C2) are found at 50.4 and 85.7 ppm, respectively. The two ethylene carbon atoms of TCNE are found at 69.6 ppm (oxygen-bonded, C8) and 26.8 ppm (Pt-bonded, C9). The resonances (113.1, 112.6, 102.1, 101.2) are assigned to the four COD olefinic carbon atoms. The ^{195}Pt NMR resonance for **7** (−3895 ppm in C_6D_6) is ∼100 ppm to lower frequency than that for **1** (−2891 ppm in C_6D_6) and is similar to that for **3** (−3820 ppm in C_6D_6).

Complex **7** is not stable in solution. When a solution of **7** in C_6D_6 solution is kept overnight at room temperature, a black precipitate forms and trace amounts of COD and free norbornene are detected by ^1H NMR spectroscopy. The amount of these decomposition products increases with time.

Although **1** shows no reactivity with an equamolar amount of PhC≡CPh even at 75 °C for 4 h (toluene), there is a reaction with the activated alkyne diethylacetylenedicarboxylate (DEAD). Reaction occurs (∼20 h) slowly in CH_2Cl_2 or C_6D_6 at room temperature to give the Pt−O insertion product $Pt(COD)(DEADOC_7H_{10})$ (**8**) (Scheme 4), isolated as a pale yellow solid in 85% yield. The presence of the DEAD ligand is confirmed by IR absorption bands at 1707 cm^{-1} (carboxylate) and 1435 cm^{-1} (C=C), ^{13}C NMR carbonyl (174.4, 164.1 ppm) and olefinic (143.7, 141.4 ppm) resonances, and ethyl group resonances in the ^1H and ^{13}C NMR spectra. The H1 resonance is found as a doublet of doublets with satellites in the ^1H NMR spectrum. The large $^1H-^{195}Pt$ coupling constant of ∼117 Hz suggests that the Pt−C1 bond is retained. The oxygen-bonded CH (H2) resonance at 6.62 ppm for starting complex **1** is replaced by a new doublet at 3.63 ppm similar to the oxygen-bonded CH (H2) peaks in insertion products **3**, **4**, **7**, and **8**, indicating that insertion into the Pt−O bond has again occurred. The COD olefinic protons *trans* to the norbornene carbon atom (C1) appear at 5.76 and 5.53 ppm with no satellites. Although not equivalent, the remaining COD olefinic protons are found as a single multiplet at 4.62 ppm with satellites ($J_{Pt-H} = 46$ Hz). The ^{195}Pt NMR resonance of **8** in C_6D_6 is found at −3937 ppm.

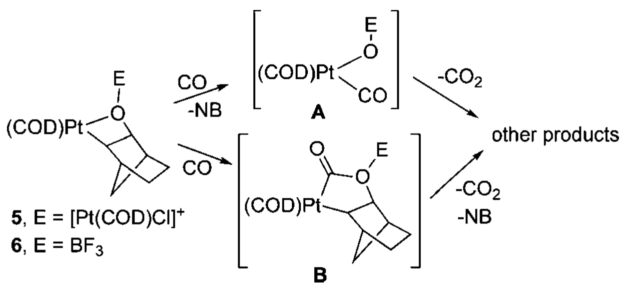
Treatment of **1** with 3 equiv of *tert*-butyl isocyanide leads to the immediate formation of a new, pale brown product and free COD. After removal of COD, the product is isolated in 89% yield and characterized as $(Bu^tNC)_2Pt(C_7H_{10}OBu^tNC)$ (**9**) (Scheme 5), the product of isocyanide substitution at the metal center and isocyanide insertion into the metal−oxygen bond. The infrared absorption for coordinated Bu^{t}NC is observed at 2714 cm^{-1} and for inserted Bu^{t}NC at 1573 cm^{-1}. The ^{13}C NMR spectrum exhibits a resonance at 54.9 ppm with $J_{Pt-C} = 57.4$ Hz for the inserted Bu^{t}NC and one at 180.8 ppm for the coordinated Bu^{t}NC. The oxygen-bonded norbornylene carbon (C2) is observed at 89.5 ppm. Similar to other insertion products, the H2 resonance is observed as a doublet at 4.46 ppm and the H1 resonance as a doublet of doublets at 3.03 ppm with $J_{Pt-H} \approx 75$ Hz in the ^1H NMR spectrum. The ^{195}Pt NMR resonance of **9** in C_6D_6 is found at −4337.

Reducing the amount of added *tert*-butyl isocyanide to 2 molar equiv and monitoring the reaction by ^1H NMR spectroscopy in C_6D_6 shows the formation of free COD and a new complex. The new complex shows a doublet with satellites at 6.91 ppm with $J_{H-H} = 5.1$ Hz and $J_{Pt-H} = 49.2$ Hz, typical for the oxygen-bonded carbon proton (H2) of norbornyl platinaoxetanes. Two equal intensity singlets at 0.86 and 0.64 ppm are assigned to coordinated Bu^{t}NC. This and the integration ratio of the doublet and two singlets of 1:9:9 reasonably identify the new product as the platinaoxetane $(Bu^tNC)_2Pt(C_7H_{10}O)$ (**10**) (Scheme 5). Attempts to isolate **10** were unsuccessful. Vacuum removal of the volatiles for the reaction mixture left a white residue, which when redissolved in C_6D_6, gave an ^1H NMR spectrum that showed the disappearance of the above peaks.

Discussion

Our observation of CO insertion into the Pt−O bonds of **1** and **2** is consistent with known chemistry of related systems. CO insertion into the Pt−O bond of platinum(II) alkoxides has been reported, and when both a Pt−O and a Pt−C bond are present, insertion into the Pt−O bond is exclusively observed.[37−41] DFT computational studies on the model complexes $Pt(Me)(OMe)(PH_3)_2$ and $Pt(Me)(OMe)(H_2PCH_2CH_2PH_2)$ show that for a CO migratory insertion pathway there is both a thermodynamic and a kinetic preference for reaction at the Pt−O

Scheme 6



rather than the Pt−C bond.[42,43] The stronger C−O bond formed in the carbonyl-alkoxide product compared to the C−C bond of the alternative acyl species is a key driving force. These preferences evidently remain in effect for **1** and **2**.

An alternative to migratory insertion, suggested by data for Ir(I) alkoxo complexes, involves displacement of RO^- by CO, followed by nucleophilic attack of RO^- on the coordinated CO.[44,45] While migratory insertion is supported by the above-mentioned DFT studies and by data for Pt(dppe)(Me)(OMe),[40] the ring strain in **1** and **2** could shift the reaction in the direction of the anion displacement mechanism. While we have no data to support or refute this possibility for CO insertion, we do find that the alkyne insertion rate of **2** changes very little from benzene to methylene chloride. A large increase would be expected if formation of ionic species was involved in this insertion, although transient coordination of a trace Lewis acid to the platinaoxetane oxygen atom could moderate this effect.

The CO reactions of platinaoxetanes **5** and **6** (eq 1) contrast sharply with those of **1** and **2**, indicating that coordination of a Lewis acid (E = $Pt(COD)Cl^+$ or BF_3) to the platinaoxetane oxygen atom greatly affects reactivity. Two possible pathways for norbornene (NB) formation in these reactions are illustrated in Scheme 6. The first goes through intermediate **A** by norbornene extrusion and coordination of CO, probably catalyzed by traces of a Lewis acid. A similar process is involved in the alkene exchange of **5** and **6**, where the norbornene unit of **5** and **6** is replaced with another alkene.[25] Intermediate **A** would then go on to products by coupling of the coordinated CO with the OE group. The second pathway, through platinalactone intermediate **B**, is based on the observed CO insertions of **1** and **2** to give platinalactones **3** and **4**. BF_3 addition to **3** should also form **B** (E = BF_3), ultimately yielding the same products as the reaction of **6** with CO. The second pathway is eliminated by the outcome of the reaction of **3** with BF_3. This reaction should produce intermediate **B**, which would eliminate CO_2, giving the same products as the reaction of **6** with CO. Instead, CO elimination and formation of **6** are observed. Complex **6** then slowly reacts with the liberated CO via **A**.

The reaction of **1** with Bu^tNC follows a somewhat different course from that of CO. It is likely that the insertion follows a similar mechanism to that of CO, but evidently the strong bonding ability of Bu^tNC results first in displacement of COD and then follows the insertion into the Pt−O bond. This sequence is evident from the observation of the Bu^tNC-ligated platinaoxetane **10** (Scheme 5). There is only one other report of isocyanide insertion into a metallaoxetane.[20]

Despite its strained ring, the alkene reaction chemistry of **1** is comparable to that reported for acyclic analogues. Tetrafluoroethylene inserts into the Pt−O bond of Pt(dppe)(Me)(OMe) to give $Pt(dppe)(Me)(CF_2CF_2OMe)$.[39,46] Dimethyl maleate undergoes *syn* addition to the Pt−OH bond of *cis*-$Pt(PPh_3)_2(OH)(Me)$ to afford *cis*-$Pt(PPh_3)_2(Me)(CH(CO_2Me)CH(OH)(CO_2Me))$.[47,48] No reactivity is observed with simple alkenes. Apparently, alkene insertion into Pt−O bonds is limited to those alkenes bearing strongly electron-withdrawing groups (F, CN, CO_2Me). What can be considered an exception to this was recently reported for the complex $Pt(dpms)(OH)(C_2H_4)$ (dpms = di(2-pyridyl)methanesulfonate).[13] Although the coordinated ethylene does not insert into the Pt−OH bond, cyclooctene and norbornene displace the ethylene and add to the Pt−OH bond, giving protonated platinaoxetanes. Similarly, the formation of platinacycle **5** from the $[Pt_4(COD)_4(O)_2Cl_2]^{2+}$ and norbornene can be considered an insertion, but the mechanism of this reaction is not obvious and is currently under investigation.[9]

The reaction of **1** with diethylacetylenedicarboxylate (DEAD) appears to be the first example of simple alkyne insertion into a Pt−O bond. Alkyne insertions into M−O bonds are rare, with examples for Rh,[49] Ir,[49,50] and Mn, Re, and Mo.[51] Such reactions could be important in alkyne hydration catalyzed by Pt and other metals.[52] Complex **1** shows no reactivity with diphenylacetylene, indicating that like in alkene insertion activation of the alkyne with electron-withdrawing groups is required. Even with DEAD the reaction rate is much slower than the alkene insertions.

Conclusions

As with the acyclic counterparts, insertion reactions of the platinaoxetanes **1** and **2** occur exclusively at the Pt−O bond. Although we have no mechanistic information on the reactions, they probably occur by migratory insertion as is thought for the acyclic complexes. While CO and Bu^tNC insert readily, alkenes and alkynes insert only if they are activated with electron-withdrawing groups, indicating that ring strain in the platinaoxetanes does little to activate the complexes. Coordination of a Lewis acid to the platinaoxetane ring oxygen atom dramatically alters reactivity such that C−O bond cleavage dominates and insertion products are not observed.

Experimental Section

General Procedures. Experiments were performed under a dinitrogen atmosphere in a Vacuum Atmosphere Corporation drybox. Solvents were dried by standard techniques and stored under

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dinitrogen over 4 Å molecular sieves or sodium metal. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Complexes **1**, **2**, **5**, and **6** were synthesized by literature procedures.[9,24,25] NMR spectra were recorded on Bruker AMX-250, -300, or -500 spectrometers at ambient probe temperatures. NMR data are given in ppm relative to TMS (referenced to protio solvent signals) for ^{1}H and ^{13}C spectra or relative to external standards for ^{195}Pt (K_2PtCl_4/D_2O, −1624 ppm), ^{31}P (H_3PO_4, 0 ppm), and ^{19}F ($CFCl_3$, 0 ppm). IR samples were prepared by evaporation of a CH_2Cl_2 solution onto a NaCl plate. Elemental analyses (inert atmosphere) were provided by Desert Analytics, Inc.

Pt(COD)(C(O)OC$_7$H$_{10}$) (3). CO (0.63 mL, 0.028 mmol) was injected into an agitated 0.5 mL C_6D_6 solution of **1** (8.0 mg, 0.019 mmol) in a screw-cap 5 mm NMR tube. After 3 h, 0.5 mL of hexane was added. A trace amount of precipitate was removed by filtration. Evaporation of the filtrate gave white product **3**. Colorless single crystals for the X-ray analysis were grown from toluene/hexane at −30 °C. Yield: 7.9 mg, 93%. Anal. Calcd (found) for $C_{16}H_{22}O_2Pt$: C, 43.53 (43.25); H, 5.02 (5.20). IR (cm^{-1}): 1664 (ν_{CO}). ^{1}H NMR (300 MHz, C_6D_6): 5.52 (m, 1H, COD CH), 5.33 (m, 1H, COD CH), 4.97 (m, 1H, COD CH), 4.79 (m, 1H, COD CH), 4.03 (d, $J_{H-H} = 6.3$ Hz, 1H, CH-2), 2.80 (dd, $J_{H-H} = 6.3$ Hz, $J_{H-H} = 2.1$ Hz, $J_{Pt-H} = 105$ Hz, 1H, CH-1), 2.66 (d, $J_{H-H} = 3.9$ Hz, 1H, CH-6), 2.10 (br, s, $J_{Pt-H} = 32$ Hz, 1H, CH-3), 1.71 (m, 1H, C*H*H-7), 1.69 (m, overlapping with C*H*H-7, 8H, COD CH$_2$), 1.42 (m, 1H, C*H*H-4), 1.39 (m, 1H, C*H*H-5′), 0.98 (m, 1H, C*H*H-5′), 0.95 (br, s, 1H, C*H*H-4′), 0.92 (br, s, 1H, C*H*H-7′). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): 180.5 (CO), 109.0 ($J_{Pt-C} = 45.3$ Hz, COD CH), 108.4 ($J_{Pt-C} = 54.3$ Hz, COD CH), 107.7 ($J_{Pt-C} = 45.3$ Hz, COD CH), 106.8 ($J_{Pt-C} = 51.3$ Hz, COD CH), 85.7 ($J_{Pt-C} = 43.8$ Hz, C-2), 60.4 ($J_{Pt-C} = 852.8$ Hz, C-1), 43.9 ($J_{Pt-C} = 17.4$ Hz, C-3), 42.2 (C-6), 35.6 ($J_{Pt-C} = 17.4$ Hz, C-7), 31.3 ($J_{Pt-C} = 68.7$ Hz, C-5), 29.9, 28.7, 28.6 and 27.5 (COD CH$_2$), 24.2 (C-4). ^{195}Pt NMR (64 MHz, C_6D_6): −3820.

Pt(PEt$_3$)$_2$(C(O)OC$_7$H$_{10}$) (4). CO (0.44 mL, 0.020 mmol) was injected into an agitated 0.5 mL C_6D_6 solution of **2** (9.8 mg, 0.018 mmol) in a 5 mm screw-cap NMR tube. After 90 min, the solvent was evaporated to give product **4**, which was washed with cold hexane and dried *in vacuo*. The solid was dissolved in minimum toluene, excess hexane was added, and the mixture was kept at −40 °C for 1 day. The resulting white precipitate was collected, washed with cold hexane, and dried *in vacuo*. Yield: 9.3 mg, 90%. Anal. Calcd (found) for $C_{20}H_{40}O_2P_2Pt$: C, 42.18 (42.80); H, 7.08 (7.22). IR (cm^{-1}) 1642 (ν_{CO}). ^{1}H NMR (300 MHz, C_6D_6): 4.24 (d, $J_{H-H} = 6.9$ Hz, 1H, CH-2), 2.82 (d, $J_{H-H} = 4.5$ Hz, 1H, CH-6), 2.63 (dd with satellites, $J_{H-H} = 6.9$ Hz, $J_{H-H} = 1.5$ Hz, $J_{Pt-H} = 23$ Hz, 1H, CH-1), 2.30 (br s with satellites, $J_{Pt-H} = 28$ Hz, 1H, CH-3), 1.96 (m, 1H, C*H*H-7), 1.89 (m, 6H, PCH$_2$Me), 1.61 (m, 1H, C*H*H-5), 1.58 (m, 1H, C*H*H-4′), 1.45 (m, 6H, PCH$_2$Me), 1.22 (m, 1H, C*H*H-5′), 1.05 (m, 1H, C*H*H-4′), 1.04 (m, 1H, C*H*H-7′), 0.86 (m, 18H, −CH$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): 195.0 (dd, $J_{P-C} = 150$ Hz, 7.5 Hz, CO), 84.6 ($J_{Pt-C} = 9.8$ Hz, C-2), 56.7 (dd, $J_{P-C} = 77.0$ Hz, 5.3 Hz, C-1), 44.0 ($J_{P-C} = 2$ Hz, C-3), 43.1 (C-6), 35.1 ($J_{Pt-C} = 12.8$ Hz, C-7), 32.3 ($J_{P-C} = 7.5$ Hz, C-5), 24.2 (C-4), 16.4 (dd with satellites, $J_{P-C} = 27.2$ Hz, 2 Hz, $J_{Pt-C} = 19.6$ Hz, $P\underline{C}H_2CH_3$), 15.5 (d with satellites, $J_{P-C} = 24.9$ Hz, $J_{Pt-C} = 15.8$ Hz, $P\underline{C}H_2CH_3$), 8.63 ($J_{Pt-C} = 20.4$, $PCH_2\underline{C}H_3$), 8.10 ($J_{Pt-C} = 19.6$ Hz, $PCH_2\underline{C}H_3$). ^{31}P NMR (101 MHz, C_6D_6): 18.57 (d with satellites, $J_{P-P} = 8.8$ Hz, $J_{Pt-P} = 1855$ Hz), 5.49 (d with satellites, $J_{P-P} = 8.8$ Hz, $J_{Pt-P} = 1985$ Hz). ^{195}Pt NMR (64 MHz, C_6D_6): −4564 (t, $J_{Pt-P1} \approx J_{Pt-P2} = 1959$ Hz).

Pt(COD)(TCNEOC$_7$H$_{10}$) (7). TCNE (2.5 mg, 0.020 mmol) in minimum C_6D_6 was added to an agitated 0.5 mL C_6D_6 solution of **1** (8.1 mg, 0.020 mmol). The solution gradually changed from colorless to yellow. After about 5 min, the solution was reduced to half its original volume, and then excess hexane was added to precipitate a yellow solid. The supernatant was carefully decanted off the solid, which was dried and extracted with 1 mL of C_6H_6. Evaporation of the C_6H_6 gave product **7**. Yield: 7.6 mg, 72%. Attempts to purify **7** by recrystallization resulted in decomposition, and an analytically pure sample could not be obtained (3 attempts). Anal. Calcd (found) for $C_{21}H_{22}N_4OPt$: C, 46.58 (26.90, 42.70, 36.07); H, 4.10 (2.30, 4.90, 3.55). IR (cm^{-1}): 2224 (ν_{CN}). ^{1}H NMR (300 MHz, C_6D_6): 5.39 (m with satellites, $J_{Pt-H} = 37$ Hz, 1H, COD CH's), 5.00 (m with satellites, $J_{Pt-H} = 67$ Hz, 1H, COD CH), 4.46 (m with satellites, $J_{Pt-H} \approx 48$ Hz, 1H, COD CH), 4.37 (m, 1H, COD CH) 4.29 (d, $J_{H-H} = 5.7$ Hz, 1H, CH-2), 2.19 (d, $J_{H-H} = 4.5$ Hz, 1H, CH-3), 2.08 (dd with satellites, $J_{H-H} = 5.7$ Hz, $J_{H-H} = 2.1$ Hz, $J_{Pt-H} = 106$ Hz, 1H, CH-1), 1.66 (d, $J_{H-H} = 2.1$ Hz, 1H, CH-6), 1.78 (m) and 1.35 (m, overlapping with C*H*H-7, 8H, COD CH$_2$), 1.40 (d, $J_{H-H} = 9.5$ Hz, 1H, C*H*H-7), 1.14 (m, 1H, C*H*H-5), 1.11 (m, 1H, C*H*H-4′), 0.73 (d, $J_{H-H} = 9.0$ Hz, 1H, C*H*H-7′), 0.81 (m, 1H, C*H*H-5′), 0.71 (m, 1H, C*H*H-4′). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): 116.2, 114.7, 113.1 and 112.5 (CN), 113.1, 112.6, 102.1 and 101.2 (COD CH's), 85.7 (C-2), 69.6 (C-8), 50.4 (C-1), 43.3 (C-3), 36.7 (C-6), 35.8 (C-7), 31.7 (C-5), 31.1, 29.8, 28.1, and 26.5 (COD CH$_2$), 26.8 (C-9), 23.8 (C-4). ^{195}Pt NMR (64 MHz, C_6D_6): −3895. (See the Supporting Information for copies of the ^{1}H and ^{13}C NMR spectra.)

Pt(COD)(DEADOC$_7$H$_{10}$) (8). Diethylacetylenedicarboxylate (3.1 μL, 0.019 mmol) was added to an agitated 0.5 mL C_6D_6 solution of **1** (7.9 mg, 0.019 mmol). The solution slowly changed from colorless to pale yellow and then yellow. After standing the mixture overnight, all volatiles were removed *in vacuo* to give yellow product **8**, which was washed with a small amount of cold hexane and dried *in vacuo*. Yield: 9.5 mg, 85%. Anal. Calcd (found) for $C_{23}H_{32}\ O_5Pt$: C, 47.24 (46.58); H, 5.53 (5.55). IR (cm^{-1}): 1707 (ν_{CO}), 1435 ($\nu_{C=C}$). ^{1}H NMR (300 MHz, C_6D_6): 5.76 (m, 1H, COD CH), 5.53 (m, 1H, COD CH), 4.62 (m with satellites, $J_{Pt-H} \approx 46$ Hz, 2H, COD CH), 4.33 (m, 2H, CH$_2$Me), 4.10 (m, 2H, CH$_2$Me), 3.63 (d, $J_{H-H} = 6.9$ Hz, 1H, CH-2), 2.89 (d, $J_{H-H} = 7.2$ Hz, 1H, CH-3), 2.40 (dd with satellites, $J_{H-H} = 7.8$ Hz, $J_{H-H} = 1.8$ Hz, $J_{Pt-H} \approx 117$ Hz, 1H, CH-1), 2.13 (m, $J_{Pt-H} \approx 36$ Hz, 1H, CH-6), 2.01 (d, $J_{H-H} = 9.0$ Hz, 1H, CH-7), 1.49 (m, 1H, C*H*H-4), 1.43 (m, 1H, C*H*H-5′), 1.20 (t, $J_{H-H} = 7.2$ Hz, 6H, CH$_3$), 1.07 (d, $J_{H-H} = 7.2$ Hz, 1H, C*H*H-5′), 1.03 (t, $J_{H-H} = 7.2$ Hz, 6H, CH$_3$), 1.01 (m, overlapping with CH$_3$ peak, 1H, C*H*H-4′), 0.85 (m, 1H, C*H*H-7′). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): 174.4 and 164.1 (COO), 143.7 and 141.4 (C═C), 105.4, 104.5, 100.3, and 100.0 (COD CH's), 82.8 (C-2), 60.6 and 60.2 ($O\underline{C}H_2Me$), 51.2 (C-1), 44.3 (C-3), 41.7 (C-6), 36.01 (C-7), 32.4 (C-5), 30.2, 29.7, 28.9, and 28.4 (COD CH2), 26.3 (C-4), 14.5 and 14.4 (Me). ^{195}Pt NMR (64 MHz, C_6D_6): −3937.

Pt(Bu^{t}NC)$_2$(C$_7$H$_{10}$OBu^{t}NC) (9). Bu^{t}NC (3.3 μL, 0.029 mmol) was added to an agitated 0.5 mL C_6D_6 solution of **1** (4.0 mg, 0.0097 mmol). After 5 min, the volatiles were removed *in vacuo*. The resulting oily residue was redissolved in toluene, and the mixture was evaporated to dryness and left *in vacuo* for 2 h. This procedure was repeated for two or three times until residual COD and Bu^{t}NC were eliminated and pale brown solid product **9** was obtained. Yield: 4.8 mg, 89%. Anal. Calcd (found) for $C_{22}H_{37}N_3OPt$: C, 47.64 (47.20); H, 6.72 (7.22). IR (cm^{-1}): 2714 (ν_{CN}), 1573 ($\nu_{C=N}$). ^{1}H NMR (300 MHz, C_6D_6): 4.46 (d, $J_{H-H} = 6.9$ Hz, 1H, CH-2), 3.03 (dd with satellites, $J_{H-H} = 6.9$ Hz, $J_{H-H} = 2.4$ Hz, $J_{Pt-H} \approx 75$ Hz, 1H, CH-1), 2.74 (d, $J_{H-H} = 4.5$ Hz, 1H, CH-3), 2.58 (br s with satellites, $J_{Pt-H} \approx 29$ Hz, 1H, CH-6), 2.24 (d, $J_{H-H} = 9.0$ Hz, 1H, C*H*H-7), 1.62 (m, 1H, C*H*H-4), 1.54 (m, 1H, C*H*H-5′), 1.31 (m, 1H, C*H*H-5′), 1.21 (m, 1H, C*H*H-4′), 1.14 (m, 1H, C*H*H-7′), 1.83 (s, 9H, CH$_3$), 1.06 (s, 9H, CH$_3$), 0.79 (s, 9H, CH$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): 180.8 (CN), 89.5 ($J_{Pt-C} = 37.7$ Hz, C-2), 54.9 ($J_{Pt-C} = 57.4$ Hz, Pt-CN), 52.3 (C-1), 44.7 (C-3), 43.5 (C-6), 35.6 (C-7), 32.2 (C-5), 24.7 (C-4), 56.6 and 56.2 (CMe$_3$), 32.0, 29.6, and 29.5 (Me). ^{195}Pt NMR (64 MHz, C_6D_6): −4337.

Attempted Isolation of Pt(Bu^{t}NC)$_2$(C$_7$H$_{10}$O) (10). Bu^{t}NC (2.8 μL, 0.029 mmol) was added to an agitated 0.5 mL C_6D_6 solution of **1** (5.0 mg, 0.0015 mmol). The ^{1}H NMR spectrum of the mixture showed, in addition to free COD at 5.57 and 2.21 ppm, peaks at 6.91 (d with satellites, $J_{H-H} = 5.1$ Hz, $J_{Pt-H} = 49.2$ Hz, 1H), 3.56 (m, 1H), 2.44 (br s, 1H), 1.63 (d, $J_{H-H} = 5.1$ Hz, 2H), 1.40 (m, 1H), 0.99 (m, 4H), 0.86 (s, 9H), and 0.64 (s, 9H). The volatiles were removed *in vacuo*, the resulting oily residue was redissolved in toluene, and the mixture was evaporated to dryness and left *in vacuo* for 2 h. This procedure was repeated two or three times until residual COD was eliminated. A ^{1}H NMR spectrum of the resulting white solid in C_6D_6 gave a new set of peaks with the distinctive CH peak at 6.91 ppm for **10** absent and new major peaks at 1.86, 1.64, 1.20, 1.06 1.01, 0.96, 0.89, and 0.77 ppm.

Attempted Reactions of 1. CO$_2$. CO_2 (0.71 mL, 0.013 mmol) was injected into an agitated 0.5 mL C_6D_6 solution of **1** (3.3 mg, 0.0080 mmol) in a 5 mm screw-cap NMR tube. The reaction was monitored by NMR spectroscopy, and no reaction was observed after two days. **CH$_2$=CH$_2$ or CH$_2$=CMe$_2$.** A medium-walled 5 mm NMR tube was charged with a solution of **1** (3.9 mg, 0.0087 mmol) in 0.5 mL of C_6D_6, and then it was connected to a vacuum line, immersed into liquid nitrogen, and evacuated. $CH_2{=}CH_2$ or $CH_2{=}CMe_2$ gas at atmospheric pressure (5 mL, 0.22 mmol at 25 °C) was added by vacuum transfer, and then the NMR tube was flame-sealed and allowed to warm to room temperature. The reaction was monitored by NMR spectroscopy. No reaction was observed after three days. **PhCCPh**. PhCCPh (1.8 mg, 0.010 mmol) was added to an agitated solution of **1** (4.3 mg, 0.010 mmol) in 0.5 mL of toluene-*d*$_8$. The reaction was monitored by ^{1}H NMR spectroscopy. No reaction was observed after two days at room temperature and then after 4 h at 75 °C.

Reaction of 6 with CO. CO (0.28 mL, 0.013 mmol) was injected into a screw-cap NMR tube containing a solution of **6** (6.0 mg, 0.013 mmol) in 0.6 mL of C_6D_6. After 1.5 h a black precipitate appeared on the NMR tube walls and free NB was observed. After 4 h about half the NB was released from **6** and after 11 h all NB was released as determined by NMR integration.

Reaction of 5 with CO. CO (0.26 mL, 0.012 mmol) was injected into a solution of **5** (11 mg, 0.012 mmol) in 0.6 mL of CD_2Cl_2 in a screw-cap NMR tube,. After 1.5 h the reaction was completed and the products CODPtCl$_2$ and free NB were identified by ^{1}H NMR spectroscopy. With 4 equiv of CO, the reaction was completed in 10 min. A black precipitate, COD, and NB were observed.

Reaction of 6 with TCNE. TCNE (1.4 mg, 0.011 mg) was added to a solution of **6** (5.2 mg, 0.011 mmol) in 0.5 mL of CD_2Cl_2. After 5 h no reaction was observed and another 3 equiv of TCNE was added. The reaction was immediately completed, and free NB was observed.

Reaction of 3 with BF$_3$. $BF_3 \cdot Et_2O$ (1.3 μL, 0.011 mmol) was added to an agitated solution of **3** (5.0 mg, 0.011 mmol) in 0.6 mL of C_6D_6. ^{1}H and ^{195}Pt NMR spectra showed immediate formation of **6** in nearly quantitative yield. After 15 min a precipitate appeared on the NMR tube walls and free NB was observed. The precipitate and free NB increase with time. After 32 h the reaction was complete.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for Pt(COD)(TCNEOC$_7$H$_{10}$) (**7**) and details of the crystal structure determination (cif file). This material is available free of charge via the Internet at http://pubs.acs.org.

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