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Seeking a Mechanistic Analogue of the Water−Gas Shift Reaction: Carboxamido Ligand Formation and Isocyanate Elimination from Complexes Containing the Tp′PtMe Fragment

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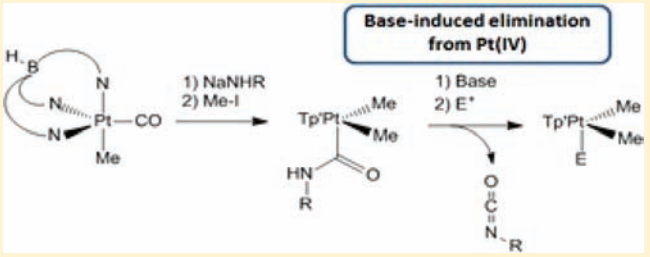
Supporting Information

ABSTRACT: A series of stable, isolable Tp′Pt(IV) carboxamido complexes of the type Tp′PtMe$_2$(C(O)NHR) (R = Et, ^{n}Pr, ^{i}Pr, ^{t}Bu, Bn, Ph) has been synthesized by addition of amide nucleophiles to the carbonyl ligand in Tp′Pt(Me)(CO) followed by trapping of the Pt(II) intermediate with methyl iodide as the methylating reagent. These compounds mimic elusive intermediates resulting from hydroxide addition to platinum-bound CO in the Water−Gas Shift Reaction (WGSR). Seeking parallels to WGSR chemistry, we find that deprotonation of the carboxamido NH initiates elimination and the isocyanate-derived products form; the resulting platinum fragment can be protonated to reoxidize the metal center and generate Tp′PtMe$_2$H, the synthetic precursor to Tp′Pt(Me)(CO). Mechanistic studies on the formation of and elimination from Tp′PtMe$_2$(C(O)NHR) suggest a stepwise process with deprotonation from a Pt(IV) species as the key step prompting elimination.

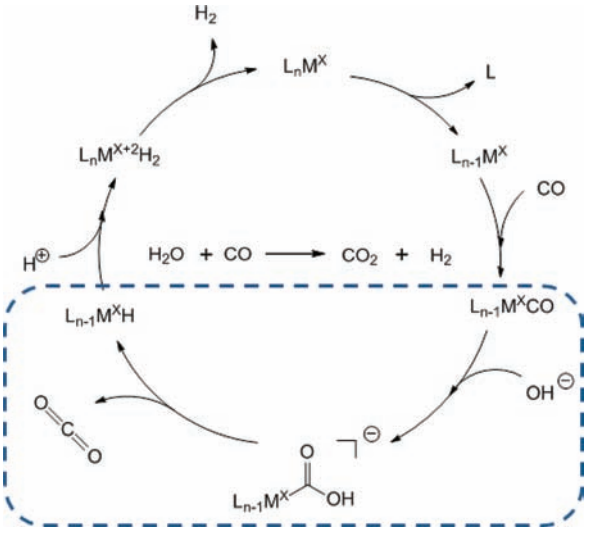


INTRODUCTION

In the face of ever-increasing global energy consumption, the search for suitable clean, renewable energy sources remains a significant challenge.[1−5] A hydrogen-based fuel economy is often discussed as a potential alternative solution to fossil fuels, and extensive research has focused on viable sources for hydrogen production, including biomass, hydrocarbons, and water.[1,6−11] Among this list, an attractive route for hydrogen formation is the Water−Gas Shift Reaction (WGSR), which converts water and carbon monoxide to hydrogen and carbon dioxide (Scheme 1).[1] Although thermodynamically favorable at standard temperature and pressures, harsher conditions are often utilized to facilitate rapid conversion to products.[12−14] The past few decades have seen advances in the utility of various transition metal complexes as catalysts for WGS chemistry. Ford[15,16] and King[17,18] identified $Ru_3(CO)_{12}$ and group 6 hexacarbonyl complexes, respectively, as homogeneous WGSR catalysts decades ago, and related systems led to substantial improvements over previous iron oxide heterogeneous systems and lowered the required reaction temperature to near 100 °C. Since then, a plethora of both hetero- and homogeneous transition metal complexes have been reported that demonstrate WGSR catalytic activity.[14,19−26] Despite these advances, no homogeneous catalytic WGSR system has been adapted on an industrial scale.[14,21,27,28]

In order to improve catalyst design, a thorough understanding of the WGSR mechanism is required. The generally accepted homogeneous-catalysis mechanism is shown in

Scheme 1. General Water−Gas Shift Reaction Mechanism



Scheme 1. This reactivity sequence is proposed to apply to $Fe(CO)_5$ and nitrogen-ligated systems, such as $Ru(bpy)_2Cl_2$ and Cp*Ir(bpy)Cl, where the metal−carbonyl linkage is activated for hydroxide addition to the carbon to form a metallacarboxylic acid (Scheme 1). Hydroxide addition is

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followed by loss of CO_2 and generation of a dihydride species in a sequence that appears to be metal−ligand system dependent.[1,19,20] Choudhury has proposed direct β-H elimination from $RuCl(CO_2H)(bpy)_2$ to release CO_2 and form a monohydride, which is subsequently protonated to give $[RuClH_2(bpy)_2]^+$.[20] However, in Ziessel's $[Cp^*Ir(bpy)Cl]^+$ system, a series of discrete deprotonation, decarboxylation, and protonation steps are hypothesized. Regardless of the decarboxylation mechanism, elimination of hydrogen from the dihydride complex completes the WGSR cycle.[19,28,29]

We have previously reported a Tp′Pt (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate, Figure 1) system that performs

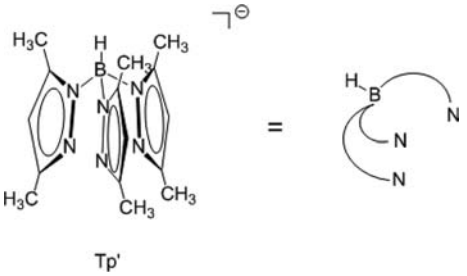
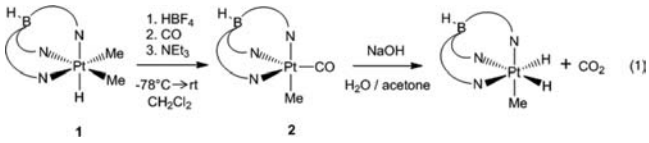
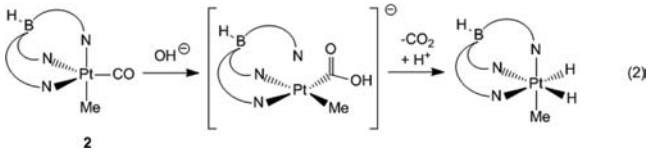


Figure 1. Tp′ ligand.

stepwise WGSR chemistry.[30−33] Low-temperature protonation or thermolysis of $Tp'PtMe_2H$ **1** in the presence of carbon monoxide induces methane loss to form the trapped product Tp′Pt(Me)(CO) **2**. Heating **2** in a basic water/acetone mixture generates $Tp'PtMeH_2$ in good yield (eq 1) and while the





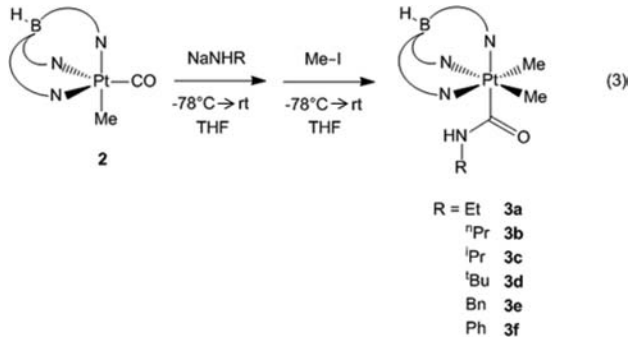
mechanism for this transformation (eq 2) is believed to follow the general WGSR cycle, details of the decarboxylation and protonation steps remain unclear.[34] These steps could proceed through any of the possibilities mentioned previously (vida supra). Repeating the reaction sequence with the platinum methyl dihydride complex (rather than the dimethyl hydride) produced $Tp'PtH_3$, from which elimination of hydrogen under CO occurs to complete a stepwise and stoichiometric WGSR.

In order to gain further mechanistic insight into nucleophilic attack on the carbonyl ligand and CO_2 loss (Scheme 1, highlighted) for this Tp′Pt system we have sought to synthesize stable, isolable analogs of the putative metallacarboxylic acid intermediate. Recently, we reported the synthesis of Tp′Pt isonitrile complexes, which are isoelectronic with the platinum carbonyl complex **2**.[35] Attack at the isonitrile carbon by methyl lithium and subsequent protonation resulted in isolable Pt(IV) iminoacyl products, and presumably these reactions are analogous to hydroxide attack on the CO ligand of **2**.

With this reactivity in mind, we decided to revisit the metal−carbonyl system using N-based nucleophiles in order to address whether similar isolable addition products can be generated or if they remain elusive due to rapid isocyanate elimination in analogy to the result of hydroxide attack on the carbonyl carbon of this same platinum complex. Here we report the synthesis of a series of isolable Pt(IV) carboxamido complexes and subsequent base-induced elimination to form isocyanate-derived products. These reactions may be relevant to the water-gas shift reaction mediated by similar platinum complexes.

RESULTS AND DISCUSSION

Synthesis of Carboxamido Pt(IV) Complexes. Paralleling previously reported syntheses of Tp′Pt(Me)(CO) **2** carbonyl addition products, we sought to generate analogous carboxamido complexes using amide ion nucleophiles. A series of deprotonated primary amines were added to a THF solution of **2** at −78 °C and warmed to room temperature. The resulting anionic Pt(II) fragment, $[Tp'PtMeC(O)NHR]^-$, was trapped with methyl iodide to form air- and moisture-stable Pt(IV) dimethyl complexes of the type $Tp'PtMe_2(C(O)NHR)$ (R = Et (**3a**), ^{n}Pr (**3b**), ^{i}Pr (**3c**), ^{t}Bu (**3d**), Bn (**3e**), Ph (**3f**)) (eq 3).



The crude reaction mixtures were chromatographed on alumina to afford the target carboxamido platinum products in moderate to good isolated yields (55−75%). Note that isocyanate elimination did not take place.

The Tp′ signals of carboxamido complexes **3a**−**f** display a 2:1 ratio in the ^{1}H NMR spectrum, indicating the presence of a mirror plane and C_s symmetry. The methyl signals resonate at ∼1.4 ppm with 72 Hz two-bond coupling, which is compatible with other reported Pt(IV) methyl complexes.[36−40] In the benzyl carboxamido complex **3e**, the two methylene protons appear as a doublet (due to vicinal coupling to the NH protons) with platinum satellites, thus exhibiting four-bond platinum−hydrogen coupling across the amide moiety. In the ^{13}C NMR spectrum, the platinum-bound carbonyl resonates at ∼150 ppm with a large one-bond ^{195}Pt−^{13}C coupling ranging from 1041 to 1170 Hz. Each compound displays a strong C═O stretching band in the infrared spectrum at ca. 1650 cm^{-1} and a weaker B−H stretching band at 2556 cm^{-1} in solution. Literature reports indicate that B−H stretches below 2500 cm^{-1} are indicative of a κ^2 binding mode for the Tp′ ligand, while stretches above 2500 cm^{-1} suggest κ^3 coordination.[32,41] The B−H stretches obtained for the carboxamido complexes therefore reflect κ^3 binding.

Slow diffusion of hexanes into a methylene chloride solution of benzyl complex **3e** produced clear, colorless rectangular crystals that were suitable for X-ray crystallography. The crystal structure of **3e**, shown in Figure 2, displays an octahedral

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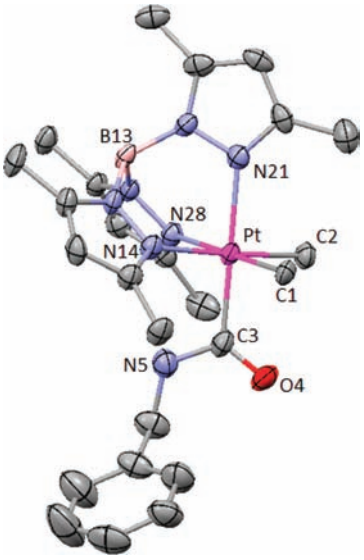

Figure 2. X-ray structure of Tp′PtMe$_2$(C(O)NHBn) **3e**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

geometry and confirms a κ^3 coordination mode for the Tp′ ligand. Selected bond distances and angles are presented in Table 1. The platinum methyl bond lengths of 2.071 Å and 2.081 Å are consistent with previously reported values for Pt−C distances in Tp′PtMe$_2$H[42] and TpPtMe$_2$OH.[43] The platinum−nitrogen distances trans to the methyl groups are similar in value, averaging 2.160 Å, while the stronger trans influence carboxamido ligand lengthens the apical platinum−nitrogen bond slightly by ∼0.023 Å. The three carboxamido C−X bond lengths (Pt−C3, 2.024(8)Å; C3−N5, 1.365(10); C3−O4, 1.213(9)) are compatible with other reported Group 10 metal-bound carboxamido complexes.[44−47] The platinum carbonyl is situated between the platinum methyls with a C1−Pt−C3−O4 torsional angle of 39.4°, so it lies near the molecular mirror plane, bisecting the two methyl groups.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3e

Bond Lengths			
Pt−C1	2.071(3)	Pt−N14	2.155(5)
Pt−C2	2.081(7)	Pt−N21	2.183(6)
Pt−C3	2.024(8)	Pt−N28	2.165(6)
C3−O4	1.213(9)	C3−N5	1.365(10)
Bond Angles			
C1−Pt−C2	89.1(3)	N14−Pt−N28	87.4(2)
Pt−C3−O4	124.2(6)	O4−C3−N5	120.9(7)
Pt−C3−N5	114.8(5)	C1−Pt−C3−O4	39.4(7)

In ^{13}C NMR spectra of **3a−f**, the platinum methyl signal was particularly broad relative to the other peaks, which suggested a dynamic process exchanging two distinct platinum methyl environments was occurring at room temperature. Cooling the carboxamido complexes to 200 K and recording the ^{1}H NMR spectrum revealed the presence of two isomers, which we believe to be rotamers. Figure 3 shows the NH signal of the *tert*-butyl complex **3d** as the solution is cooled to 200 K. For **3a−e**, the coalescence temperature for the NH signal was in the range of 225−235 K. For this series of carboxamido complexes,

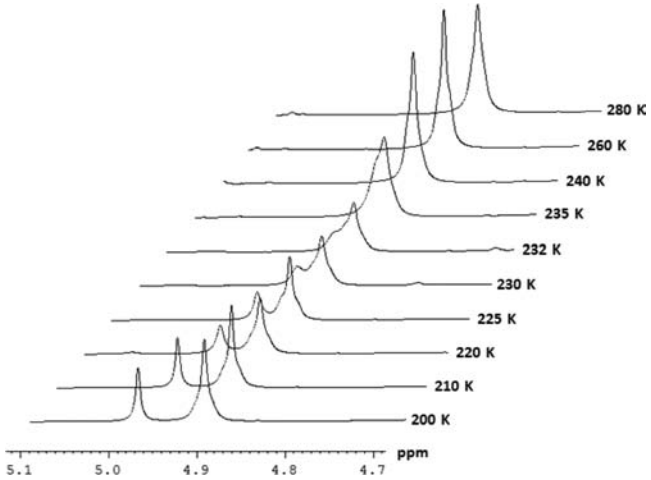

Figure 3. Variable-temperature ^{1}H NMR study of rotation in **3d**.

the ratio of major:minor isomers at low temperature (∼200 K) ranged from 1.2:1 to 2.2:1, with the ^{t}Bu adduct, not surprisingly, displaying the greatest energy difference between the two rotamers.

To determine the identity of the major rotamer and to verify the nature of the observed dynamic process in **3a−f**, the NOESY NMR spectrum of isopropyl carboxamido **3c** was recorded at 185 K (Figure 4). An off-diagonal crosspeak correlates the *major* NH signal with the major *Tp′ methyl* signal, indicating a through-space NOE as a result of the NHR group bisecting the Tp′ pyrazolyl nitrogens with the carbonyl positioned between the platinum methyl groups, as was evident in the crystal structure of benzyl carboxamido **3e**. Conversely, an NOE is observed correlating the *minor* NH signal and the minor *platinum methyl* resonance.

Independent studies performed by Angelici[47,48] and Kessler[49] found dynamic processes for secondary dimethyl carboxamido complexes, [L$_n$M]C(O)NMe$_2$ (M = Mo, W, Pt, Pd) that were due to hindered rotation about the C−N bond. Many of these complexes had high C−N rotation barriers, as indicated by T_c values above 100 °C, with some exceeding 200 °C (473K) to equate the two ^{1}H NMR methyl signals. The low temperature NOE data presented here along with the dramatic difference in coalescence temperatures strongly suggest that the two rotamers in this work result from restricted rotation about the Pt−C bond and *not* the C−N bond. A 180° rotation about the Pt−C bond is required to achieve the second rotamer as demonstrated in the Newman projection in Figure 5.

We sought to generate analogous Tp′Pt secondary carboxamido complexes and further compare the coalescence temperatures and energy barriers associated with Pt−C and C−N rotation. The addition of dimethyl amide anion to **2** and subsequent methylation produced the secondary carboxamido complex Tp′PtMe$_2$(C(O)NMe$_2$) **3g** (eq 3). At room temperature, the methyl signals on the carboxamido ligand are inequivalent. Unlike the primary carboxamido complexes, the ^{13}C NMR spectrum of **3g** displays a sharp PtMe signal. Cooling to 205 K or warming to 365 K did not produce a significant change in the ^{1}H NMR spectrum. We believe that the added substituent on the carboxamido ligand has significantly increased the barrier for Pt−C rotation and that only one rotamer is populated. In accord with Angelici's and Kessler's findings, the coalescence temperature for C−N rotation must be >365 K (92 °C).

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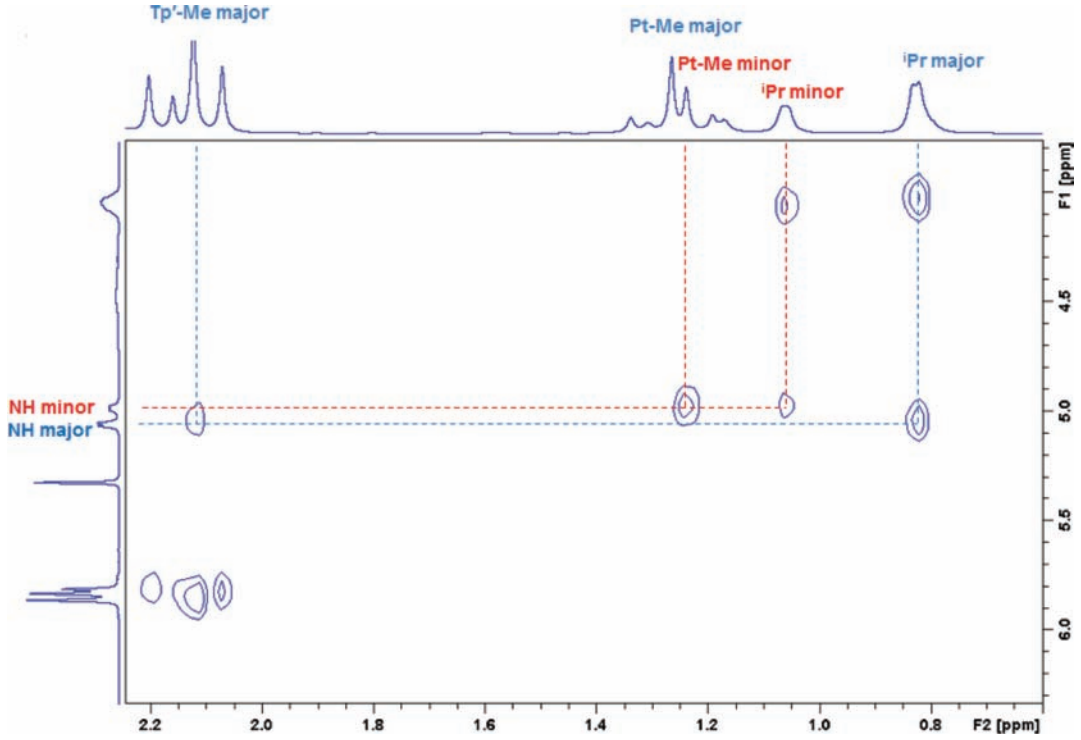


Figure 4. NOESY NMR spectrum of **3c** at 185 K.

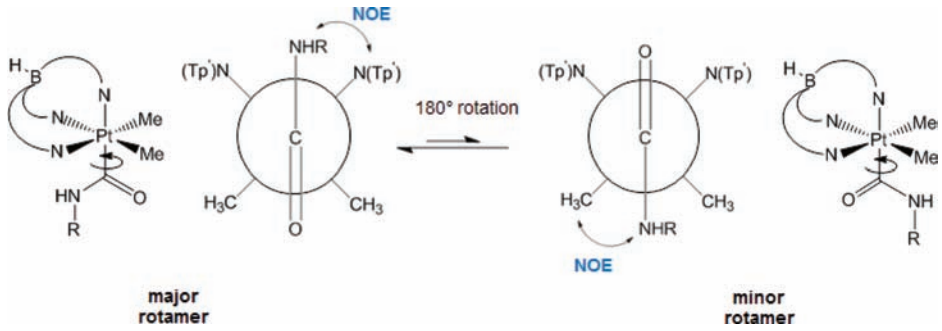
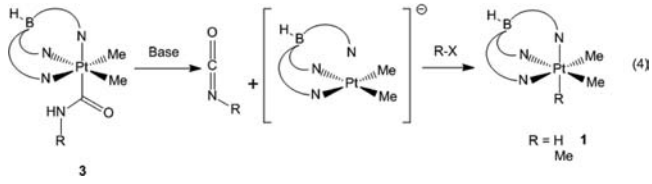


Figure 5. Newman projection of **3c** as viewed down the carbonyl carbon−platinum bond, with the platinum atom in the rear.

Elimination Reactions. After hydroxide addition to the metal carbonyl in the WGSR mechanism, decarboxylation of the resulting metallacarboxylic acid liberates CO_2 from the metal center. In a parallel mechanism, we postulated that deprotonation of the platinum carboxamido NH may prompt isocyanate elimination and leave a reactive anionic Pt(II) fragment that could be trapped by an electrophile. Indeed, the addition of a strong base, such as lithium diisopropyl amide (LDA) or sodium methoxide, to a dimethyl sulfoxide (DMSO) solution of a carboxamido complex resulted in quantitative conversion to the anionic dimethyl complex $[Tp'PtMe_2]^-$ as assessed by ^1H NMR. A series of bases with various strengths was added to the benzyl carboxamido complex **3e** and the pK_a range for the NH proton in DMSO was determined to be 18.0−23.5 and is in good agreement with previously reported pK_a values for organic amide NH protons.[50]

Subsequent methylation or protonation of the $[Tp'PtMe_2]^-$ species using methyl iodide or $HBF_4{\cdot}Et_2O$ resulted in the trimethyl complex, $Tp'PtMe_3$, or the dimethyl hydride complex $Tp'PtMe_2H$ **1**, respectively (eq 4). Both the ^1H and ^{13}C NMR data of these metal products match literature values.[42,51]



Although the platinum product was easily identified by NMR spectroscopy, the putative isocyanate product remained elusive regardless of the carboxamido complex starting material employed. The tell-tale signature of an isocyanate is the ^{13}C NMR chemical shift of the central carbon, which is typically near 120 ppm, but it is often difficult to identify due to its weak intensity.[52−54] To assist in identification of the organic product, the ^{13}C-labeled $Tp'PtMe_2(^{13}C(O)NHEt)$ complex was prepared. Addition of LDA to this ^{13}C-labeled carboxamido complex in DMSO-d_6 followed by addition of methyl iodide revealed several label-derived signals between 166 and 168 ppm, which is attributed to the formation of urea derivatives from the isocyanate reacting with LDA, diisopropyl amine, and methyl iodide in the reaction milieu (eq 5). It is well established

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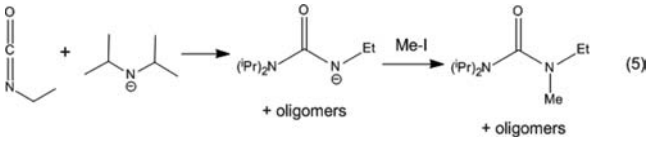
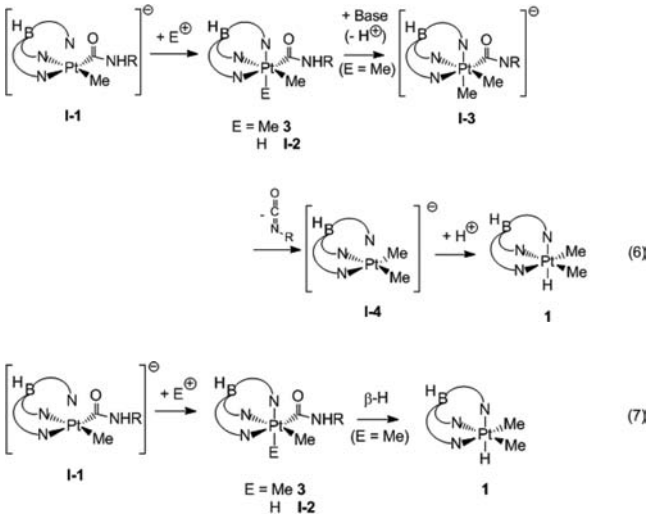


(5)

that this chemical shift range is typical for amide and urea carbonyl carbons.[55,56] This reactivity reflects the susceptibility of the electrophilic isocyanate carbon toward nucleophilic attack[57−59] and indeed, treating ethyl isocyanate with LDA followed by methyl iodide produced a mixture of products giving rise to several carbonyl ^{13}C NMR signals in this range. Attempts to promote isocyanate elimination using non-nucleophilic bases such as NaH, Hünig's base, or 1,8-bis(dimethylamino)naphthalene (proton sponge) proved unsuccessful.

Mechanistic Studies. The conversion of Tp′Pt(Me)(CO) **2** to carboxamido complex **3** and subsequent elimination to form Tp′PtMe$_2$H or Tp′PtMe$_3$ mimics the general WGSR scheme (Scheme 1). Investigation of the mechanism for these amine-based reactions may provide insight into the WGSR sequence. After nucleophilic attack on the CO ligand with an amide nucleophile, a series of protonation, deprotonation, and elimination steps or a direct β-H elimination must occur to generate isocyanate and a Pt(IV) species. Various combinations of these steps result in five possible mechanisms stemming from the [Tp′Pt(Me)C(O)NHR]$^-$ anion **I-1**, as outlined in eqs 6−10. In the first two pathways (eqs 6 and 7), methylation of

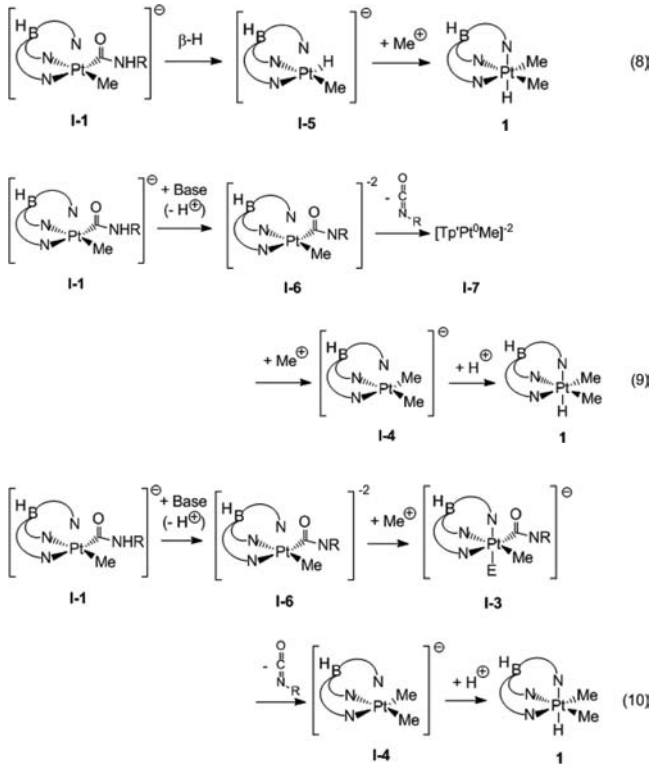


(6)

(7)

the anion results in a six-coordinate neutral Pt(IV) carboxamido **3**. Deprotonation of the NH proton prompts isocyanate elimination, and the resulting four-coordinate Pt(II) dimethyl anion ***I*-4** is protonated to generate Tp′PtMe$_2$H **1** (eq 6). Alternatively, direct β-H elimination from **3** could produce **1** in one step (eq 7).

A third possibility is that β-H elimination occurs first from **I-1** to form the Pt(II) methyl hydride anion **I-5** which forms **1** upon methylation (eq 8). The final two pathways stem from deprotonation of **I-1** to form the Pt(II) dianion, [Tp′Pt(Me)(C(O)NR]$^{-2}$ **I-6**. Loss of isocyanate from **I-6** would result in a Pt(0) dianion **I-7** and subsequent methylation and protonation would produce **1** (eq 9). Lastly, methylation of **I-6** would generate the [Tp′PtMe$_2$(C(O)NR]$^{-1}$ anion **I-3** which could lose isocyanate to form [Tp′PtMe$_2$]$^-$ ***I*-4** and then protonation would lead to **1** (eq 10).



(8)

(9)

(10)

We first explored the possibility of deprotonation of the [Tp′Pt(Me)(C(O)NHR]$^-$ anion by adding excess strong base. Tp′Pt(Me)(CO) was treated with a THF solution containing 1.25 equiv of the benzyl amide anion, HNBn$^-$. An extra equivalent of LDA was added to the mixture and stirred for 30 min before methylation. The resulting product was Pt(IV) benzyl carboxamido **3e**, revealing that additional base does not promote further reactivity, and also suggesting that deprotonation of the anion is not a feasible mechanistic possibility. In light of this result, neither eq 9 nor eq 10 is an attractive mechanism for the elimination of isocyanate and conversion to Tp′PtMe$_2$H.

Direct β-H elimination from **I-1** does not appear to be an attractive mechanism either, since such a pathway would imply that the Pt(IV) dimethyl hydride forms upon methylation without going through a carboxamido Pt(IV) complex, while in the amide addition reaction, we have shown that the Pt(IV) carboxamido complex forms when methylation occurs.

We sought to observe the postulated anionic **I-1** intermediate by ^1H NMR spectroscopy in order to monitor any possible Pt−H resonances. Access to the Pt(II) carboxamido anion for NMR experiments allowed us to probe several important reaction steps. Performing the benzyl amide addition to Tp′Pt(Me)(CO) **2** in THF-d_8 produces the C_1-symmetric anion [Tp′Pt(Me)(C(O)NHR]$^-$ in 85% conversion as assessed by ^1H NMR. The Tp′ ligand displays three distinct resonances for the methine protons and six unique Tp′ methyl resonances. The Pt methyl signal shifts upfield relative to the Tp′Pt(Me)-(CO) starting material and resonates at 0.4 ppm ($^2J_{Pt-H}$ = 81 Hz). The C_1 symmetry of the intermediate is also reflected in the diastereotopic methylene protons of the benzyl linkage in the carboxamido ligand, with each proton resonating as a doublet of doublets as a result of coupling to the NH proton as well as geminal coupling to each other. The ^1H NMR spectrum does not exhibit a detectable Pt hydride signal, and the anion

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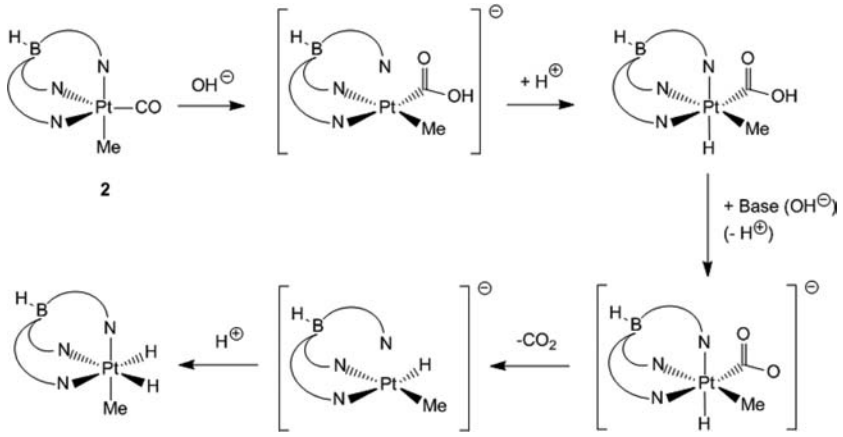
Scheme 2. Proposed Mechanism for the Conversion of Tp′Pt(Me)(CO) 2 to Tp′PtMeH$_2$

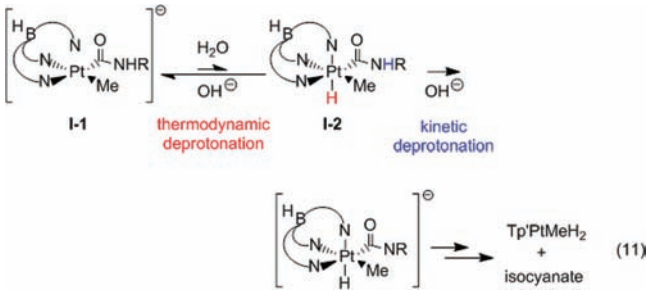


does not exhibit any further reactivity until the introduction of methyl iodide to produce **3e**.

Consistent with the formation and isolation of carboxamido complex **3**, oxidation to Pt(IV) appears to be a requirement enroute to isocyanate elimination and formation of **1**. Given the stability of the carboxamido complexes over a period of weeks, direct β-H elimination is an unattractive mechanistic route (eq 7). Rather, deprotonation-initiated elimination of isocyanate from Pt(IV) remains as the most plausible mechanistic pathway (eq 6). Presumably, the WGS chemistry observed from Tp′Pt(Me)(CO) proceeds in a similar manner and tracks the steps shown in eq 6 as depicted in Scheme 2. Hydroxide attack at CO produces a metallacarboxylic acid anion, analogous to **I-1**. In the presence of water, the anion is protonated at platinum to oxidize the metal center to Pt(IV). Hydroxide ion in solution then deprotonates the carboxylic acid, which prompts elimination of carbon dioxide to leave a Pt(II) methyl hydride anion in the penultimate step. Finally, protonation of this anion generates Tp′PtMeH$_2$.

A crucial difference between the WGS reaction conditions and the amide work presented here is the lack of an electrophilic oxidation source after nucleophilic addition to the CO ligand in the latter scenario. Under WGSR conditions (aqueous base), the presence of both a base (OH^-) and a proton source allows for a complete cascade from Tp′Pt(Me)-(CO) **2** to Tp′PtMeH$_2$. Would the addition of water to the benzyl anion [Tp′Pt(Me)(C(O)NHBn]$^-$ **I-1** prompt a similar cascade without isolation of a Pt(IV) species before elimination? Addition of 3 equiv of water to a mixture of **I-1** and benzyl amide (0.5 equiv) did not result in consumption of **I-1**. After 9 more equivalents (12 equiv total) of water were added, a minute Pt−H signal appeared in the ^{1}H NMR spectrum. The chemical shift and the one-bond coupling constant are consistent with data for Tp′PtMeH$_2$.[30] In contrast to the water addition experiment, the addition of glacial acetic acid cleanly and completely protonates **I-1** and converts it to Tp′Pt(Me)(H)(C(O)NHBn **I-2**, the methyl hydride analogue of the dimethyl carboxamido complex **3e**. Similar to **I-1**, hydride **I-2** displays C_1 symmetry by ^{1}H NMR with unique Tp′ methine and methyl signals. The Pt(IV) methyl signal appears at 1.26 ppm ($^2J_{Pt-H}$ = 69 Hz) and the hydride resonates at −19.8 ppm ($^1J_{Pt-H}$ = 1372 Hz).

Why were we able to produce the methyl hydride carboxamido complex, but the analogous WGS-related Tp′Pt-(Me)(H)(COOH) remains elusive? The key difference stems from the dramatically different pK_a values for the carboxylic acid OH vs the carboxamido NH. In the amide case, the NH is *less* acidic than the PtH and the thermodynamically favored deprotonation site is the Pt−H, resulting in regeneration of **I-1** (eq 11). However, the kinetically favored acidic site may well be the NH proton, which is accessible in spite of the steric bulk surrounding the six-coordinate metal center. Furthermore, the reorganization energy for metal-based deprotonation to form a Pt(II) species is likely to be higher than the energy required for the restructuring that would accompany deprotonation at nitrogen. Deprotonation of the NH proton of the Pt(IV) species prompts elimination of the isocyanate molecule and formation of an anionic Pt(II) fragment that upon subsequent protonation accounts for the observed Tp′PtMeH$_2$. Under acidic conditions, the metal center is protonated to form the Pt(IV) hydride **I-2**, but the acetate anion is not a sufficiently strong base to deprotonate the NH proton and induce isocyanate elimination.



On the other hand, the OH of the metallacarboxylic acid in the WGSR is *more* acidic than the corresponding Pt−H. In the presence of water, the [Tp′Pt(Me)(COOH)]$^-$ anion is likely protonated to form Tp′Pt(Me)(H)(COOH). Here, the carboxylic acid is the preferred deprotonation site which prompts carbon dioxide loss and presumably forms a Pt(II) anion intermediate. Subsequent protonation by water would account for the direct conversion to Tp′PtMeH$_2$.

SUMMARY

A series of stable, isolable Tp′Pt(IV) carboxamido complexes has been synthesized via amide ion attack on the neutral platinum carbonyl precursor, Tp′Pt(Me)(CO), and subsequent methylation. Such reactivity mirrors hydroxide attack on the same carbonyl moiety in the water−gas shift reaction. Unlike

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the WGSR case where CO_2 elimination is rapid, elimination of an organic isocyanate does *not* spontaneously follow nucleophilic addition. This reluctance to eliminate O=C=NR is presumably due to the higher amide pK_a, which shuts down proton transfer to the metal center and inhibits access to the Pt(IV) intermediate on the road to elimination. The high barrier to elimination allows isolation of analogues to WGSR intermediate along the reaction coordinate. Low-temperature ^{1}H and NOESY NMR data of the carboxamido complexes reveal a dynamic process that reflects restricted rotation about the Pt−$C_{carboxamido}$ bond. Addition of a strong base promotes isocyanate elimination and subsequent protonation at platinum regenerates Tp′PtMe$_2$H.

EXPERIMENTAL SECTION

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk and drybox techniques. Nitrogen was purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. Methylene chloride, tetrahydrofuran, hexanes, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[60] All other chemicals were used as received without further purification. Alumina column chromatography was conducted with 80−200 mesh alumina.

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX400, AVANCE400, or AMX300 spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. Elemental analyses were performed by Robertson Microlit Laboratories of Madison, NJ. High-resolution mass spectra were recorded on a Bruker BioTOF II ESI-TOF mass spectrometer. Mass spectral data are reported for the most abundant platinum isotope. Tp′PtMe$_2$H **1** and Tp′Pt(Me)(CO) **2** were synthesized using published procedures.[33,42]

Synthesis of Tp′PtMe$_2$(C(O)NHR) Complexes. *General Method.* A Schlenk flask containing 50 mg (0.47 mmol, 1.25 equiv) of LDA in 10 mL THF was cooled to −78 °C, and amine (0.66 mmol, 1.75 equiv) was added slowly. The amide solution was allowed to warm to room temperature and was cannula transferred to a Schlenk flask containing 200 mg (0.37 mmol, 1 equiv) of **2** in 10 mL of THF at −78 °C. After stirring at room temperature for 30 min, 48 μL (0.75 mmol, 2 equiv) of methyl iodide was added at −78 °C. The solution was stirred at room temperature for 30 min, and the solvent was removed *in vacuo*. Impurities were removed on an alumina column with 1:1 hexanes/CH_2Cl_2 before the product was eluted with 1:3 THF/CH_2Cl_2. Removal of solvent resulted in a pale-yellow powder.

*Tp′PtMe$_2$(C(O)NHCH$_2$CH$_3$) (**3a**).* The general method above was performed using 0.33 mL (0.66 mmol, 1.75 equiv) of a 2.0 M THF solution of ethylamine to yield 144 mg (0.242 mmol, 64.8%) of pure **3a**. ^{1}H NMR (δ, CD_2Cl_2, 298 K): 5.85 (s, 2H, Tp′CH), 5.80 (s, 1H, Tp′CH), 5.15 (t, 1H, NH), 3.21 (m, 2H, NCH_2CH$_3$), 2.37, 2.17 (s, 6H each, Tp′CH$_3$), 2.37, 2.28 (s, 3H each, Tp′CH$_3$), 1.41 (s, 6H, Pt-Me, $^2J_{Pt,H}$ = 72 Hz), 0.98 (t, 3H, NCH$_2$CH$_3$). ^{13}C NMR (δ, CD_2Cl_2, 298 K): 151.5 (C=O, $^1J_{Pt,C}$ = 1071 Hz), 150.6, 149.9, 144.4, 144.3 (Tp′CCH$_3$), 108.0, 107.5 (Tp′CH), 35.8 (NCH$_2$CH$_3$), 15.2 (NCH$_2$CH$_3$), 13.8, 13.1, 12.9, 12.8 (Tp′CH$_3$), −7.4 (Pt-CH$_3$, $^1J_{Pt,C}$ = 689 Hz). IR(KBr): ν_{N-H} = 3453 cm^{-1}, ν_{B-H} = 2557 cm^{-1}, $\nu_{C=O}$ = 1637 cm^{-1}. HRMS (ESI) *m*/*z* Calc.: 727.1620 (M + Cs$^+$). Found: 727.1613. Anal. Calcd for $C_{20}H_{34}BN_7OPt$: C, 40.41; H, 5.77; N, 16.49. Found: C, 40.68; H, 5.64; N, 16.21.

*Tp′PtMe$_2$(C(O)NHCH$_2$CH$_2$CH$_3$) (**3b**).* The general method above was performed using 54 μL (0.66 mmol, 1.75 equiv) of propylamine to yield 170 mg (0.28 mmol, 74.8%) of pure **3b**. ^{1}H NMR (δ, CD_2Cl_2, 298 K): 5.85 (s, 2H, Tp′CH), 5.81 (s, 1H, Tp′CH), 5.22 (bt, 1H, NH), 3.13 (m, 2H, NCH_2CH$_2$CH$_3$), 2.39, 2.17 (s, 6H each, Tp′CH$_3$), 2.37, 2.28 (s, 3H each, Tp′CH$_3$), 1.42 (s, 6H, Pt-Me, $^2J_{Pt,H}$ = 72 Hz), 1.37 (m, 2H, NCH$_2$CH_2CH$_3$), 0.83 (t, 3H, NCH$_2$CH$_2$CH_3). ^{13}C NMR (δ, CD_2Cl_2, 298 K): 152.2 (C=O, $^1J_{Pt,C}$ = 1079 Hz), 150.6, 149.9, 144.5, 144.4 (Tp′CCH$_3$), 108.0, 107.5 (Tp′CH), 43.1 (NCH$_2$CH$_2$CH$_3$), 23.3 (NCH$_2$CH$_2$CH$_3$), 13.9, 13.1, 12.9, 12.8 (Tp′CH$_3$), 11.6 (NCH$_2$CH$_2$CH$_3$), −7.5 (Pt-CH$_3$, $^1J_{Pt,C}$ = 694 Hz). IR(CH_2Cl_2 solution): ν_{N-H} = 3441 cm^{-1}, ν_{B-H} = 2556 cm^{-1}, $\nu_{C=O}$ = 1620 cm^{-1}. HRMS (ESI) *m*/*z* Calc: 741.1777 (M + Cs$^+$). Found: 741.1746. Anal. Calcd for $C_{21}H_{36}BN_7OPt$: C, 41.45; H, 5.96; N, 16.11. Found: C, 41.54; H, 5.75; N, 15.85.

*Tp′PtMe$_2$(C(O)NHCH(CH$_3$)$_2$) (**3c**).* The general method above was performed using 56 μL (0.66 mmol, 1.75 equiv) of isopropylamine to yield 171 mg (0.28 mmol, 75.2%) of pure **3c**. ^{1}H NMR (δ, CD_2Cl_2, 298 K): 5.84 (s, 2H, Tp′CH), 5.80 (s, 1H, Tp′CH), 4.92 (bd, 1H, N*H*), 4.06 (m, 1H, NC*H*(CH$_3$)$_2$), 2.38, 2.18 (s, 6H each, Tp′CH$_3$), 2.36, 2.23 (s, 3H each, Tp′CH$_3$), 1.40 (s, 6H, Pt-Me, $^2J_{Pt,H}$ = 71 Hz), 1.01 (d, 6H, NCH(CH_3)$_2$). ^{13}C NMR (δ, CD_2Cl_2, 298 K): 150.3 (C=O, $^1J_{Pt,C}$ = 1063 Hz), 150.5, 149.8, 144.4, 144.3 (Tp′CCH$_3$), 107.9, 107.5 (Tp′CH), 42.4 (NCH(CH$_3$)$_2$), 22.9 (NCH(CH$_3$)$_2$), 14.0, 13.1, 13.0, 12.8 (Tp′CH$_3$), −7.7 (Pt-CH$_3$, $^1J_{Pt,C}$ = 697 Hz). IR(CH_2Cl_2 solution): ν_{N-H} = 3432 cm^{-1}, ν_{B-H} = 2556 cm^{-1}, $\nu_{C=O}$ = 1622 cm^{-1}. HRMS (ESI) *m*/*z* Calc.: 741.1777 (M + Cs$^+$). Found: 741.1781. Anal. Calcd for $C_{21}H_{36}BN_7OPt$: C, 41.45; H, 5.96; N, 16.11. Found: C, 41.51; H, 5.59; N, 15.73.

*Tp′PtMe$_2$(C(O)NH^{t}Bu) (**3d**).* The general method above was performed using 69 μL (0.66 mmol, 1.75 equiv) of *tert*-butylamine to yield 132 mg (0.21 mmol, 56.8%) of pure **3e**. ^{1}H NMR (δ, CD_2Cl_2, 298 K): 5.83 (s, 2H, Tp′CH), 5.80 (s, 1H, Tp′CH), 4.93 (s, 1H, NH), 2.37, 2.22 (s, 6H each, Tp′CH$_3$), 2.36, 2.26 (s, 3H each, Tp′CH$_3$), 1.37 (s, 6H, Pt-Me, $^2J_{Pt,H}$ = 71 Hz), 1.28 (s, 9H, ^{t}Bu). ^{13}C NMR (δ, CD_2Cl_2, 298 K): 149.0 (C=O, $^1J_{Pt,C}$ = 1041 Hz), 150.2, 149.7, 144.3, 144.0 (Tp′CCH$_3$), 107.8, 107.4 (Tp′CH), 51.9 (*C*(CH$_3$)$_3$), 28.8 (C(*C*H$_3$)$_3$), 14.1, 13.0, 12.9, 12.8 (Tp′CH$_3$), −8.8 (Pt-CH$_3$). IR(CH_2Cl_2): ν_{N-H} = 3457 cm^{-1}, ν_{B-H} = 2556 cm^{-1}, $\nu_{C=O}$ = 1632 cm^{-1}. HRMS (ESI) *m*/*z* Calc: 755.1933 (M + Cs$^+$). Found: 755.1921. Anal. Calcd for $C_{22}H_{38}BN_7OPt$: C, 42.45; H, 6.15; N, 15.75. Found: C, 42.68; H, 6.03; N, 14.27.

*Tp′PtMe$_2$(C(O)NHCH$_2$Ph) (**3e**).* The general method above was performed using 74 μL (0.66 mmol, 1.75 equiv.) of benzylamine to yield 180 mg (0.27 mmol, 73.4%) of pure **3d**. X-ray quality crystals were formed by slow diffusion of hexanes into a methylene chloride solution of **3d** at 0 °C. ^{1}H NMR (δ, CD_2Cl_2, 298 K): 7.25 (m, 5H, Ph), 5.79 (s, 2H, Tp′CH), 5.76 (s, 1H, Tp′CH), 5.51 (bt, 1H, NH), 4.40 (d, 2H, CH_2Ph), 2.37, 2.09 (s, 6H each, Tp′CH$_3$), 2.36, 2.30 (s, 3H each, Tp′CH$_3$), 1.52 (s, 6H, Pt-Me, $^2J_{Pt,H}$ = 72 Hz). ^{13}C NMR (δ, CD_2Cl_2, 298 K): 152.2 (C=O, $^1J_{Pt,C}$ = 1169 Hz), 150.3, 149.7, 143.8, 143.3 (Tp′CCH$_3$), 138.6 (*ipso*-Ph), 129.7, 128.0, 126.9 (Ph), 108.0, 107.1 (Tp′CH), 52.2 (NCH$_2$Ph, $^3J_{Pt,C}$ = 18 Hz), 13.1, 13.0, 12.8, 12.7 (Tp′CH$_3$), −3.0 (Pt-CH$_3$, $^1J_{Pt,C}$ = 679 Hz). IR(KBr): ν_{N-H} = 3445 cm^{-1}, ν_{B-H} = 2557 cm^{-1}, $\nu_{C=O}$ = 1630 cm^{-1}. HRMS (ESI) *m*/*z* Calc: 657.2800 (M + H$^+$). Found: 657.2793. Anal. Calcd for $C_{25}H_{36}BN_7OPt$: C, 45.74; H, 5.53; N, 14.94. Found: C, 45.48; H, 5.36; N, 14.66.

*Tp′PtMe$_2$(C(O)NHPh) (**3f**).* The general method above was performed using 60 μL (0.655 mmol, 1.75 equiv) of aniline to yield 135 mg (0.210 mmol, 55.0%) of pure **3f**. ^{1}H NMR (δ, CD_2Cl_2, 298 K): 7.27 (m, 2H, *o*-Ph), 7.23 (t, 1H, *p*-Ph), 6.99 (s, 2H, *m*-Ph), 6.94 (bs, 1H, NH), 5.89 (s, 2H, Tp′CH), 5.85 (s, 1H, Tp′CH), 2.43, 2.19 (s, 6H each, Tp′CH$_3$), 2.41, 2.34 (s, 3H each, Tp′CH$_3$), 1.54 (s, 6H, Pt-Me, $^2J_{Pt,H}$ = 72 Hz). ^{13}C NMR (δ, CD_2Cl_2, 298 K): 151.1 (C=O, $^1J_{Pt,C}$ = 1117 Hz), 150.8, 150.0, 144.8, 144.6 (Tp′CCH$_3$), 139.9 (*ipso*-Ph, $^3J_{Pt,C}$ = 48 Hz), 128.9, 123.8, 119.3 (Ph), 108.3, 107.8 (Tp′CH), 13.7, 13.2, 13.0, 12.9 (Tp′CH$_3$), −6.3 (Pt-CH$_3$, $^1J_{Pt,C}$ = 681 Hz). IR(CH_2Cl_2 solution): ν_{N-H} = 3418 cm^{-1}, ν_{B-H} = 2556 cm^{-1}, $\nu_{C=O}$ = 1657 cm^{-1}. HRMS (ESI) *m*/*z* Calc: 775.1620 (M + Cs$^+$). Found: 775.1594. Anal. Calcd for $C_{24}H_{34}BN_7OPt$: C, 44.87; H, 5.33; N, 15.26. Found: C, 44.62; H, 5.20; N, 14.98.

*Tp′PtMe$_2$(C(O)NMe$_2$) (**3g**).* The general method above was performed using 326 μL (0.655 mmol, 1.75 equiv) of a 2 M dimethylamine in THF solution to yield 103 mg (0.173 mmol, 46%) of pure **3g**. ^{1}H NMR (δ, $C_2D_2Cl_4$, 298 K): 5.72 (s, 2H, Tp′CH), 5.71 (s, 1H, Tp′CH), 2.76, 1.66 (s, 3H each, NMe$_2$), 2.31, 2.01 (s, 6H each, Tp′CH$_3$), 2.27, 2.25 (s, 3H each, Tp′CH$_3$), 1.45 (s, 6H, Pt-Me, $^2J_{Pt,H}$ = 73 Hz). ^{13}C NMR (δ, $C_2D_2Cl_4$, 298 K): 152.0 (C=O), 150.0, 149.4,

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143.9, 143.4 (Tp′CCH_3), 107.7, 107.0 (Tp′CH), 37.4, 36.4 (NMe_2), 13.1, 13.1, 12.8, 12.8 (Tp′CH_3), −3.4 (Pt-CH_3, $^1J_{Pt,C}$ = 683 Hz).

*In Situ generation of [Na][Tp′Pt(Me)(C(O)NHBn)] (**I-1**).* In a glovebox, a 5-mL rbf was charged with LDA (6 mg, 0.058 mmol) and covered with a septum. THF-d_8 (0.7 mL) was added through the septum, and the flask was cooled to −78 °C in a dry ice/isopropanol bath. Benzyl amine (9 μL, 0.082 mmol) was added, and the pink solution was stirred for 5 min. An NMR tube was charged with Tp′Pt(Me)(CO) (25 mg, 0.046 mmol). A septum was placed on top, and the tube was purged with nitrogen. The purged NMR tube was cooled to −78 °C, and the amide solution was syringed through the septum. The tube was shaken to induce mixing, and the solution became yellow upon warming to room temperature. **I-1** was produced in 85% conversion by ^{1}H NMR. ^{1}H NMR (δ, THF-d_8 298 K): 7.29−7.22 (m, 5H, Ph), 6.32 (br t, 1H, NH), 5.84, 5.72, 5.70 (s, 1H each, Tp′CH), 4.35, 4.20 (dd, 1H each, CH_2), 2.36, 2.30, 2.22, 2.08, 2.03, 1.78 (s, 3H each, Tp′-CH_3), 0.36 (s, 3H, $^2J_{Pt-H}$ = 82 Hz, Pt-CH_3).

*In Situ Generation of Tp′Pt(Me)(H)(C(O)NHR) (**I-2**).* An NMR tube sample containing **I-1** (0.046 mmol) in THF-d_8 was treated with glacial acetic acid (5 μL, 0.092 mmol). ^{1}H NMR (δ, THF-d_8, 298 K): 7.20−7.09 (m, 5H, Ph), 6.42 (br t, 1H, NH), 5.71, 5.67 (s, 2H, 1H, Tp′CH), 2.32, 2.28, 2.27, 2.14, 2.05, 1.93 (s, 3H, Tp′-CH_3), 1.26 (s, 3H, $^2J_{Pt-H}$ = 69 Hz, Pt-CH_3), −19.76 (s, 1H, $^1J_{Pt-H}$ = 1372 Hz).

*In Situ Generation of [Li][Tp′PtMe$_2$] (**I4**).* In a glovebox, an NMR tube was charged with carboxamido complex **3a** (15 mg, 0.025 mmol) and excess LDA (7 mg, 0.065 mmol). DMSO-d_6 (0.5 mL) was added to the sample, and a septum was placed on top of the tube. Quantitative conversion from **3a** to **I4** was observed by ^{1}H NMR. ^{1}H NMR (δ, DMSO-d_6, 298 K): 5.78, 5.42 (s, 2H, 1H, Tp′CH), 2.51, 2.17 (s, 6H each, Tp′-CH_3), 1.99, 1.57 (s, 3H each, Tp′-CH_3), 0.07 (s, 6H, $^2J_{Pt-H}$ = 85 Hz, Pt-CH_3).). ^{13}C NMR (δ, DMSO-d_6, 298 K): 146.1, 144.5, 143.3, 141.9 (Tp′CCH_3), 105.2, 104.0 (Tp′CH), 14.0, 13.9, 13.6, 10.7 (Tp′CH_3), −20.7 (Pt-CH_3).

*Structural Data for **3e**.* Crystals were obtained from CH_2Cl_2/hexanes; $C_{25}H_{36}BN_7OPt$, M = 656.51; triclinic, space group $P\bar{1}$; Z = 2; a = 8.1004(3) Å, b = 9.5201(3) Å, c = 18.1022(7) Å; α = 78.606(2)°, β = 77.336(3)°, γ = 77.100(2)°; U = 1311.34(8) Å^3; D_c = 1.663 Mg/cm^3; T = 100(2) K; θ range = 4.82° to 69.70°; Reflections collected = 12697; Independent reflections = 4414; data were collected on a Bruker-AXS SMART Apect-II diffractometer. Goodness-of-fit = 1.198.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Representative ^{1}H and ^{13}C NMR spectra. Elimination and ^{13}C labeling studies data. CIF file for structures **3e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022.
(2) Lewis, N. S.; Nocera, D. G. *Proc. Nat. Acad. Sci. U.S.A.* **2006**, *103*, 15729.
(3) Eisenberg, R.; Nocera, D. G. *Inorg. Chem.* **2005**, *44*, 6799.
(4) Okkerse, C.; van Bekkum, H. *Green Chem.* **1999**, *1*, 107.
(5) Periana, R. A.; Bhalla, G.; Tenn, W. J.; Young, K. J. H.; Liu, X. Y.; Mironov, O.; Jones, C. J.; Ziatdinov, V. R. *J. Mol. Catal. A: Chem.* **2004**, *220*, 7.
(6) Cortright, R. D.; Davda, R. R.; Dumesic, J. A. *Nature* **2002**, *418*, 964.
(7) Forsberg, C. W. *Int. J. Hydrogen Energy* **2003**, *28*, 1073.
(8) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. *Science* **2003**, *300*, 2075.
(9) Deluga, G. A.; Salge, J. R.; Schmidt, L. D.; Verykios, X. E. *Science* **2004**, *303*, 993.
(10) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044.
(11) Sayama, K.; Nomura, A.; Zou, Z.; Abe, R.; Abe, Y.; Arakawa, H. *Chem. Commun.* **2003**, *23*, 2908.
(12) Rhodes, C.; Hutchings, G. J.; Ward, A. M. *Catal. Today* **1995**, *23*, 43.
(13) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice Hall: Upper Saddle River, NJ, 1997.
(14) Laine, R. M.; Crawford, E. J. *J. Mol. Catal.* **1988**, *44*, 357.
(15) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 252.
(16) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.
(17) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D. *J. Am. Chem. Soc.* **1978**, *100*, 2925.
(18) King, R. B. *J. Organomet. Chem.* **1999**, *586*, 2.
(19) Ziessel, R. *J. Am. Chem. Soc.* **1993**, *115*, 118.
(20) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885.
(21) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.
(22) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637.
(23) Rodriguez, J. A. *Catal. Today* **2011**, *160*, 3.
(24) Ratnasamy, C.; Wagner, J. P. *Catal. Rev.* **2009**, *51*, 325.
(25) Chen, C.-S.; Lin, J.-H.; Lai, T.-W. *Chem. Commun.* **2008**, 4983.
(26) Radhakrishnan, R.; Willigan, R. R.; Dardas, Z.; Vanderspurt, T. H. *Appl. Catal., B* **2006**, *66*, 23.
(27) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1735.
(28) Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 844.
(29) Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1988**, 16.
(30) Reinartz, S.; Baik, M.-H.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **2001**, *40*, 4726.
(31) West, N. M.; Templeton, J. L. *Can. J. Chem.* **2009**, *87*, 288.
(32) West, N. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 2059.
(33) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854.
(34) Haskel, A.; Keinan, E. *Organometallics* **1999**, *18*, 4677.
(35) Engelman, K. L.; White, P. S.; Templeton, J. L. *Organometallics* **2010**, *29*, 4943.
(36) Abo-Amer, A.; Puddephatt, R. J. *Inorg. Chem. Commun.* **2011**, *14*, 111.
(37) Reinartz, S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2002**, *21*, 247.
(38) Scollard, J. D.; Day, M.; Labinger, J. A.; Bercaw, J. E. *Helv. Chim. Acta* **2001**, *84*, 3247.
(39) Engelman, K. L.; White, P. S.; Templeton, J. L. *Inorg. Chim. Acta* **2009**, *362*, 4461.
(40) Frauhiger, B. E.; White, P. S.; Templeton, J. L. *Organometallics* **2012**, *31*, 225.
(41) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Morooka, Y. *Organometallics* **1997**, *16*, 4121.
(42) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684.

(43) Canty, A. J.; Fritsche, S. D.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *490*, C18.
(44) Aresta, M.; Giannoccaro, P.; Tommasi, I.; Dibenedetto, A.; Lanfredi, A. M. M.; Ugozzoli, F. *Organometallics* **2011**, *19*, 3879.
(45) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1991**, *10*, 175.
(46) Huang, T.-M.; You, Y.-J.; Yang, C.-S.; Tzeng, W.-H.; Chen, J.-T.; Cheng, M.-C.; Wang, Y. *Organometallics* **1991**, *10*, 1020.
(47) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.
(48) Green, C. R.; Angelici, R. J. *Inorg. Chem.* **1972**, *11*, 2095.
(49) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.
(50) Bordwell, F. G.; Ji, G. Z. *J. Am. Chem. Soc.* **1991**, *113*, 8398.
(51) Roth, S.; Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1990**, *29*, 3345.
(52) DeCoste, J. B.; Doetschman, D. C.; Lahr, M. J.; Kanyi, C. W.; Schulte, J. T. *Microporous Mesoporous Mater.* **2011**, *139*, 110.
(53) Charalambides, Y. C.; Moratti, S. C. *Synth. Commun.* **2007**, *37*, 1037.
(54) Fleischel, O.; Gimenez-Arnau, E.; Lepoittevin, J.-P. *Chem. Res. Toxicol.* **2009**, *22*, 1106.
(55) Friebol, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; J. Wiley & Sons: Weinheim, 2005.
(56) Hesse, M. *Spectroscopic Methods in Organic Chemistry*; G. Thieme: New York, 1997.
(57) Wirpsza, Z. *Polyurethanes: Chemistry, Technology, and Applications*; Ellis Horwood: London, 1993.
(58) Woods, G. *The ICI Polyurethanes Book*; ICI and Wiley: New York, 1987.
(59) Satchell, D. P. N.; Satchell, R. S. *Chem. Rev. Soc.* **1975**, *4*, 231.
(60) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.