Reactions of Indene and Indoles with Platinum Methyl Cations: Indene C−H Activation, Indole π versus Nitrogen Lone-Pair Coordination

Travis J. Williams, Jay A. Labinger,* and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

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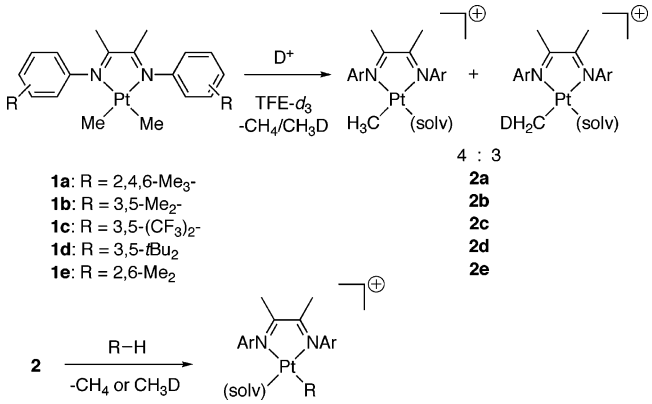
Reactions of indene and various substituted indoles with [(diimine)Pt^{II}(Me)(TFE)]$^+$ cations have been studied (diimine = ArN═C(Me)−C(Me)═NAr; TFE = 2,2,2-trifluoroethanol). Indene displaces the TFE ligand from platinum to form a stable π coordination complex that, upon heating, undergoes C−H activation with first-order kinetics, $\Delta H^{\ddagger}$= 29 kcal/mol, $\Delta S^{\ddagger}$ = 10 eu, and a kinetic isotope effect of 1.1 at 60 °C. Indoles also initially form coordination complexes through the C2═C3 olefin, but these undergo rearrangement to the corresponding *N*-bound complexes. The relative rates of initial coordination and rearrangement are affected by excess acid or methyl substitution on indole.

Introduction

Selective C−H bond activation is a potentially valuable approach to synthetic problems in areas ranging from fuels and bulk chemicals to fine chemicals and pharmaceutical synthesis.[1] Studies of C−H activation in our laboratory have focused on models of the Shilov system,[2] particularly [(diimine)Pt^{II}(Me)(solv)]$^+$ (**2**, diimine = ArN═C(Me)−C(Me)═NAr; solv = 2,2,2-trifluoroethanol (TFE), H_2O).[3] These cations are capable of activating a variety of carbon−hydrogen bonds.[4] Cations **2** can be generated by protonolysis of (diimine)$Pt^{II}Me_2$ species **1** in TFE with aqueous HBF_4[3,4a,b] or BX_3 (X = C_6F_5,[4c,d] F[5]), the latter producing H^+ by boron coordination to TFE.[4c] In deuterated solvent **2** is formed as a mixture of two isotopologues. Reaction of **2** with a C−H group then results in liberation of methane as a mixture of CH_4 and CH_3D along with the formation of a new alkyl or aryl platinum(II) complex [(diimine)Pt^{II}(R)(solv)]$^+$ (Scheme 1).[6]

The presence of donor heteroatoms (N, O, S, etc.) in the substrate might inhibit C−H activation because these heteroatoms tend to bind tightly to electrophilic metal centers and block C−H bond coordination. In the cases of methanol and dimethyl ether,[4e] stable complexes of the organic substrate with platinum are observed, but kinetics studies indicate that substrate−platinum binding is rapid and reversible and that rebinding (or rearrangement) of the substrate to a C−H bond-coordinated intermediate is rate-determining. Heteroatom binding can be used to advantage, however, in coordinatively directed cyclometalation reactions,[7] the basis of many synthetic methods. Several recent examples of these involving nitrogen-containing heterocycles have appeared.[8] Specifically regarding indole, a functionality found frequently in natural products and pharmaceutical agents, several groups have identified conditions for cyclization of indoles with pendent olefins,[9] and both Sames[10] and Sanford[11]

Scheme 1



* Corresponding authors. E-mail: bercaw@caltech.edu.

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(6) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739−740.

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(8) Some examples include: (a) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300−2301. (b) Desai, L. V.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9542−9543. (c) Tan, K. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 2685−2686. (d) Tan, K. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc*, **2002**, *124*, 13964−13965. (e) Dangel, B. D.; Godula, K.; Youn, S. W.; Sezen, B.; Sames, D. *J. Am. Chem. Soc.* **2002**, *124*,11856−11857.

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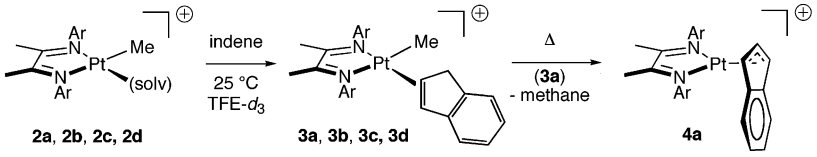
Scheme 2



have reported selective arylation of simple indoles via palladium-catalyzed C−H activation.

Prior literature reports of stable group 10 metal−indole complexes are few in number. Platinum-coordinated tryptophan and tryptamine derivatives have been studied,[12] but only a single platinum complex, *cis*-Pt(indole)$_2$Cl$_2$, having a neutral, simple L-type donor indole ligand[13] has been reported. Unfortunately, it was characterized only by elemental analysis and infrared, and neither offers insight into the binding of the indole ligand.[14] Moreover, although (1-indolyl)metal amides (functioning as X-type ligands) are common,[15] and indole−metal arene complexes have been described for several transition metals,[16] we are aware of no examples of transition metal complexes having indole C2═C3 olefin ligation.

The present work examines the reactions of indoles with cations **2**. Toward this end, we describe the reaction of these cations with indene, indole's hydrocarbon analogue, as well as with various methyl-substituted indoles. We find that indene forms a stable olefin coordination complex that undergoes C−H activation upon heating. Analogously, indoles initially form olefin coordination complexes, but rather than undergoing C−H activation, these complexes rearrange to stable *N*-bound 3*H*-indole species. We expect that C−H activation of nitrogen-containing unsaturated heterocycles is more likely to proceed from a metal−heterocycle π complex than an *N*-complex, so strategies to extend the lifetime of platinum(II)−indole π complexes have been pursued. We find that the rate of rearrangement of indole π complexes to *N*-complexes can be diminished by introducing steric bulk on the indole or by increasing [H$^+$].

Results and Discussion

Reactions of Indene with Cations 2. Treatment of platinum cations **2** with 1 equiv of indene results in the formation of stable olefin complexes, **3** (Scheme 2). In each case, complexation is efficient and rapid. Exchange of coordinated indene with 1 equiv (15 mM) of added indene-d_3 under the same conditions is slower, with $k_{obs} \approx 5 \times 10^{-3}$ s^{-1}, $t_{1/2} \approx 1$ min (from McKay analysis).[17] The resulting products **3** can be characterized by NMR and electrospray MS methods. The ^{1}H NMR spectrum for **3a** is sharp at ambient temperature, and ^{195}Pt−H coupling constants of 74 and 79 Hz are observed for the C2 and C3 protons of indene. The C1 methylene protons appear as a pair of doublets ($^2J_{H-H}$ = 23 Hz) with weak ^{195}Pt satellites (J_{Pt-H} = 41 Hz). By contrast, ambient-temperature ^{1}H NMR spectra of **3b**, **3c**, and **3d** give broad signals for the C1, C2, and C3 indenyl C−H protons near 3.2, 6.5, and 5.6 ppm, respectively. In all cases, Pt−*CH$_3$* signals are shifted significantly upfield from the parent cation **2**: whereas **2** typically displays δ(Pt−*CH$_3$*) in the range 0.6−1.3 ppm, indene complexes **3** have δ(Pt−*CH$_3$*) between −0.8 and −0.3 ppm. This shift is similar to that for a previously reported η^2-benzene adduct, which has δ(Pt−*CH$_3$*) = −1.3 ppm at −33 °C.[4a] Upon gentle heating, complexes **3** react to form η^3-indenyl complex **4** and methane (Scheme 2). In the case of **3a**, the reaction is clean (>95% yield) as determined by ^{1}H NMR. By contrast, heating complexes **3b** and **3c** results in formation of a complex mixture of products, including **4**.

Scheme 3

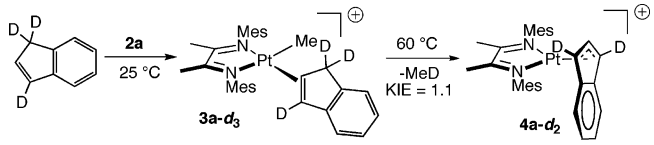


Table 1. First-Order Rate Constants for the Conversion of Indene π Complex 3a to η^3-Indenyl Complex 4a

entry	T (°C)	k (s^{-1})	$t_{(1/2)}$ (min)
1	50	3.38 (11) × 10^{-5}	342(11)
2	60	1.31 (9) × 10^{-4}	88.5(58)
3	70	4.60 (18) × 10^{-4}	25.1(10)
4	80	1.84 (10) × 10^{-3}	6.28(32)
5	90	5.10 (10) × 10^{-3}	2.28(38)

Mechanism of Indene Activation. First-order rate constants were measured for the conversion of indene complex **3a** to indenyl complex **4a** (Table 1). Importantly, two trials at 60 °C with 1 and 5 equiv of indene gave the same rate constants (1.24(9) × 10^{-4} and 1.37(9) × 10^{-4} s^{-1}) within error, indicating a zero-order rate dependence on [indene]. Activation parameters for the conversion of **3a** to **4a**, measured by Eyring analysis for kinetic runs conducted at temperatures ranging from 50 to 90 °C (Figure 1), are $\Delta H^{\ddagger} = 28.7 \pm 0.7$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 9.7 \pm 2.2$ eu.[18] A kinetic isotope effect was determined for the conversion of indene-d_3 to deuterated indenyl complex **4a**-d_2 (Scheme 3). 1,1,3-Trideuteroindene was prepared according to

(10) Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050−8057.

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(14) We believe that indole is bound through N1 as suggested by the authors, but is in the 3*H*-tautomer. ^{1}H NMR (300 MHz, dichloromethane-d_2) δ: 8.37 (s, J_{Pt-H} = 30 Hz, 2H, C2H), 8.58 (d, J_{Pt-H} = 8.2 Hz, 2H), 7.62−7.08 (m, 6H), 4.03 (s, 4H, C3−H2).

(15) For example: indole + Pt^0(PEt$_3$)$_4$ → *trans*-[(PEt$_3$)$_2$Pt^{II}(H)(1-indolyl)] + 2 PEt$_3$. Chantson, J. T.; Lotz, S. *J. Organomet. Chem.* **2004**, *689*, 1315−1324.

(16) [(η^6-C$_8$H$_7$N)ML$_n$] complexes are known for several metals. Common examples include ML$_n$ = Cr(CO)$_3$; see: Fischer, E. O.; Goodwin, H. A.; Kreiter, C. G.; Simmons, H. D.; Sonogashira, K.; Wild, S. B. *J. Organomet. Chem.* **1968**, *14*, 359−374. Nesmeyanov, A. N.; Ustynyuk, N. A.; Thoma, T.; Prostakov, N. S.; Soldatenkov, A. T.; Pleshakov, V. G.; Urga, K.; Ustynyuk, Y. A.; Trifonova, O. I.; Oprunenko, Y. F. *J. Organomet. Chem.* **1982**, 231, 5−24. ML$_n$ = CpRu$^+$, see: Moriarty, R. M.; Ku, Y. Y.; Gill, U. S. *Organometallics* **1988**, *7*, 660−665. Other examples include M = Mn^I, Co^{III}, Rh^I, Rh^{III}, Ir^I, and Ir^{III}. [(η^5-C$_8$H$_6$N)ML$_n$] complexes are known for ML$_n$ = Mn(CO)$_3^+$; see: Ji, L. N.; Kershner, D. L.; Rerek, M. E.; Basolo, F. *J. Organomet. Chem.* **1985**, *296*, 83−94. MLn = Cp*Ir^{2+}, see: White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654−1661. Other examples include M = Ti^{IV}, Mo^{II}, and Fe^{II}.

(17) Analyzed as in: Romeo, R.; Monsu, Scolaro, L.; Nastasi, N.; Arena, G. *Inorg. Chem.* **1996**, *35*, 5087−5096.

(18) Error determined by established methods. See: Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646−1655.

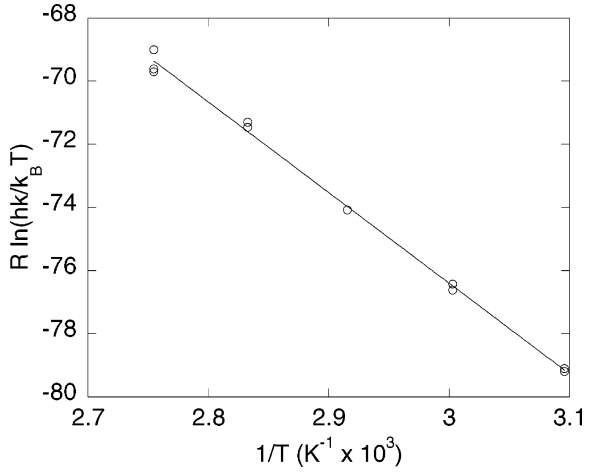
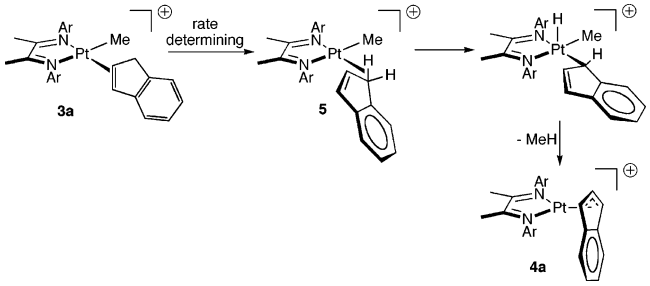


Figure 1. Eyring plot for the conversion of **3a** to **4a**.

Scheme 4

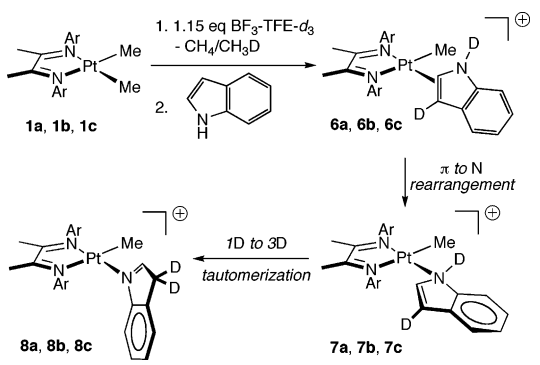


a previously reported procedure[19] and was complexed to **2a** as above. Conversion of **3a**-d_3 to **4a**-d_2 proceeded smoothly to afford a selectively deuterated product. Comparisons of measured rate constants for parallel runs gave a kinetic isotope effect of $k_H/k_D = 1.1$.

The small, positive value for $\Delta S^{\ddagger}$ and the small KIE are suggestive of an intramolecular **3a**-to-**4a** process *not* involving rate-determining C−H oxidative addition. A mechanistic scenario that is in accord with these features involves rate-determining rearrangement of π complex **3a** to C−H σ complex **5**, followed by more rapid C−H oxidative cleavage and reductive elimination of methane (Scheme 4). Analogous reaction of **2e** (solv = CF_3CD_2OD) with *p*-xylene was found to afford a mixture of products resulting from competitive aryl ($k_H/k_D \approx 4$) and benzylic ($k_H/k_D \approx 1$) C−H activation processes, the latter affording an η^3-benzylic product.[4c] Rearrangement of **3a** to **4a** thus resembles the benzylic activation process and suggests that benzylic C−H bond activation by **2e** also proceeds via an initially formed arene π complex that undergoes rate-determining rearrangement to a C−H σ complex, followed by C−H oxidative cleavage.

Reactions of Cations 2 with Indoles. Indole reacts rapidly with platinum cations **2**, ultimately to give *N*-complexation products **8** (Scheme 5). Analogously to reaction with indene, the initially formed adduct is a C2═C3 π complex **6**; however, *N*-ligation, likely via transient **7**, inhibits C−H activation, and tautomer **8** is the stable adduct that is generated.[20] Reaction of **2a** with indole at 40 °C begins with a buildup of **6a**-d_2 (^{1}H

Scheme 5



NMR), which converts to **8a** in minutes. H/D exchange of N1−H with solvent is rapid relative to complexation, but exchange of C3−H may occur before or after π complexation.[21] Although the participation of platinum in the H/D exchange cannot be excluded, this exchange is rapid in the presence of 0.2 mol % BF_3−TFE solution (not containing **1a**) and is complete in minutes at room temperature. NMR spectra are consistent with assignment of the 3D tautomer **8**: in all three complexes (**8a**, **8b**, **8c**) the ^{13}C signal for the C3 methylene carbon appears as a multiplet at ∼44 ppm, and the ^{1}H signal for the C2 hydrogen appears as a singlet with ^{195}Pt satellites ($J_{Pt-H} \approx 40$ Hz) at ∼8 ppm.

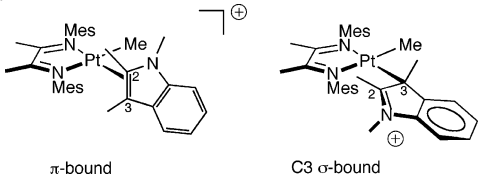
Reactions of methyl-substituted indoles were studied with cation **2a**. Reactions of **2a** with 1-methylindole and 2-methylindole proceed through the intermediacy of observable and more stable π complexes (**9**, **11**; Scheme 6).[22] ^{1}H NMR spectra for **9** and **11** share important features with indene complex **3a**: each shows a significantly upfield Pt−CH_3 chemical shift relative to cation **2a**. Upon rearrangement to the corresponding *N*-bound complexes **10** and **12**, the Pt−CH_3 signal returns downfield (Table 2). Other heterocycles (pyrrole, carbazole, benzofuran) did not afford clean results under these conditions; most notably, *N*-protected indoles gave rise to complex mixtures of products.[23]

(19) Yasuda, M.; Pak, C.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 502−507.

(20) Some [(3*H*-indole)ML_n] complexes are known for other metals. For examples of [Re] complexes, see: Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 3182−3193. For [Ir] see: Chen, S.; Noll, B. C.; Peslherbe, L.; Rakowski DuBois, M. *Organometallics* **1997**, *16*, 1089−1092.

(21) C3−H in **6a** can be observed at early stages of kinetic runs (δ = 5.95 ppm, J_{Pt-H} = 87 Hz (500 MHz)), but N1−H was never found for coordinated indole.

(22) A reviewer proposed an alternative C3 σ-bound structure for **6a**, **9**, and **11**, but we favor the π complexes as shown. The σ-bound structure is inconsistent with ^{1}H and ^{13}C chemical shifts for C3−H: δ C3−H = 5.4 and 6.0 for compounds **6a** and **11**, respectively, as identified by J_{Pt-H} and H/D exchange. This is more consistent with an sp^2 carbon center. Moreover, no ^{13}C signal is present in the 175−180 region of the spectrum of **11**, as would be needed for C2 in the σ-bound structure. It is likely, however, that the platinum center is more tightly associated with the more electron rich C3 side of the olefin. This is a possible explanation for the low J_{Pt-H} for C2 in **11**.



(23) Reactions of *N*-protected indoles (Ac, Tf, Ts) and benzofuran afforded complex mixtures of C−H activation products. Pyrrole, carbazole, and 3-methylindole afforded complex mixtures of coordination complexes of the general form [(diimine)Pt(Me)(C_nH_nN-d_n)]$^+$. Hydrogenated homologues of indene and indole also react with **2a**. Indane forms a mixture of C−H activation products, which includes an η^3-benzyl complex analogous to that obtained from ethylbenzene; see notes 4c,d. 2,3-Dihydroindole forms a stable *N*-bound coordination complex, which has ^{1}H NMR (300 MHz, TFE-d_3) δ: 7.21−7.14 (m, 3H), 7.07−7.06 (m, 4H), 6.89 (s, 1H), 3.47−3.30 (m, 2H), 2.87−2.75 (m, 1H), 2.58−2.47 (m, 1H), 2.33 (s, 3H), 2.30 (s, 6H), 2.17 (s, 3H), 2.17 (s, 3H), 1.93 (s, 3H), 1.80 (s, 3H), 1.75 (s, 3H), 0.53 (s, J_{Pt-H} = 76 Hz, 3H).

Scheme 6

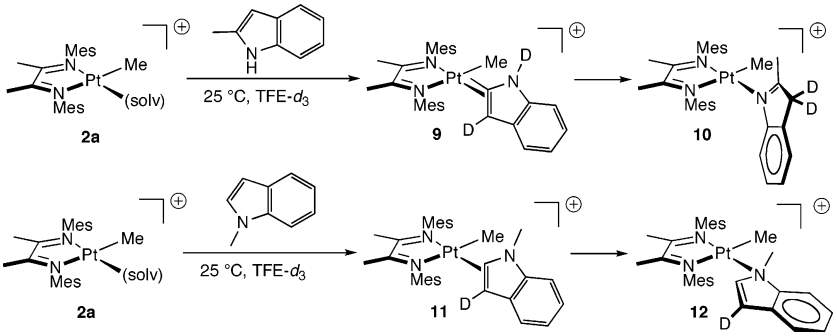


Table 2. NMR Data for Pt−*Me* Groups of TFE Adduct 2a, Indene π Complex 3a, and the π and *N*-Indole Adducts

complex	^{1}H δ^a (ppm)	^{13}C δ (ppm)	$J_{Pt-H}{}^b$ (Hz)
2a (TFE)[c]	+0.66	21.5	72
3a (indene)	−0.74	4.7	72
6a (indole π)	−1.02	−[d]	62[a]
8a (indole *N*)	0.74	−12.1	78
9	−0.75	−3.6	73
10	0.53	−13.7	78
11	−1.16	−3.0	73
12	0.26	−16.8	78

[a] Data recorded at 500 or 600 MHz. [b] Recorded at 300 MHz. [c] Notes 4b,c. [d] The lifetime of this species is too short to record ^{13}C NMR.

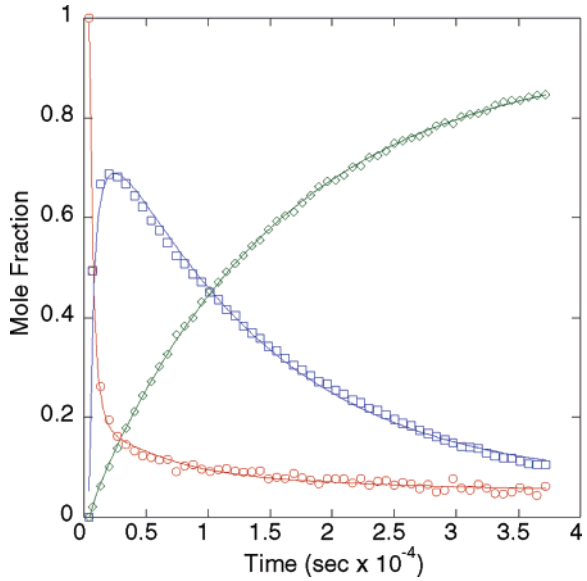


Figure 2. Formation of complex **9** from **2a** and its conversion to **10**. Cation **2a** (red ○) is treated with 1 equiv of 2-methylindole at 30 °C to form **9** (blue □), which rearranges to **10** (green ◇), k_{RAR} = 6.72(2) × 10^{-5} s^{-1} (**9** → **10**).

The mechanism of conversion of π-bound indole complexes to final *N*-bound complexes **8**, **10**, and **12** likely involves direct (intramolecular) slippage of platinum from the C2═C3 π bond to N1 because the rate of π to N1 conversion is independent of [indole]. Moreover, in a simple crossover experiment, a solution of the 2-methylindole adduct **9** (~90% conversion from **2a**) was treated with 1 equiv of 1-methylindole. Upon further reaction, a distribution of 81(1)% **9**, 10(1)% **10**, and 9(1)% **11** was observed, and finally a mixture containing 91(1)% **10** and 9(1)% **12** was observed. Thus little crossover is observed, excluding a mechanism involving indole displacement from the metal center.

Rearrangements of complexes **9** and **11** to complexes **10** and **12** are spontaneous at room temperature (also zero-order in indole). For the conversion of **2a** to **10** at 30 °C, the rate of rearrangement of **9** to **10** is close to the rate for the binding of 2-methylindole to cation **2a**, thus enabling NMR observation of all three species simultaneously in a single experiment (Figure 2). First-order rate constants for the rearrangements of π complexes **9** and **11** were measured at 40 °C in the presence of excess indole (Table 3). Strikingly, rearrangement of these π complexes requires hours at 40 °C, whereas *N*-ligated complexes **8** are fully formed at room temperature in only minutes, indicating that methylation of the indole in the 1 or 2 position substantially retards the rate of rearrangement of indole π complexes.

Table 3. First-Order Rate Constants for Rearrangement of π Complexes at 40 °C

entry	π complex	product	k (s^{-1})	$t_{1/2}$ (min)	
1	**6a**	**8a**	1.24(16) × 10^{-2}	0.94(12)	$\pi \rightarrow N$
2	**9**	**10**	3.05(7) × 10^{-4}	37.9(86)	$\pi \rightarrow N$
3	**11**	**12**	7.87(37) × 10^{-5}	147(71)	$\pi \rightarrow N$
4	**3a**	**4a**	8.4(6) × 10^{-6} [a]	1380(98)	C−H activation

[a] Extrapolated from Eyring plot.

Table 4. Acid Dependence of Rate Constant for Rearrangement of 6a[a]

entry	BF_3 (equiv)	k (s^{-1})	$t_{1/2}$ (min)
1	1.1	1.24(16) × 10^{-2}	0.94(12)
2	2.5	1.09(21) × 10^{-2}	1.09(19)
3	4.0	3.51(12) × 10^{-3}	3.29(11)
4[b]	5.0	1.48(5) × 10^{-4}	78.3(27)

[a] Conditions: BF_3 is added to **1a** in TFE; 5 equiv of indole in TFE is then injected. [b] Indole binding and tautomerization are slow relative to k_{RAR}.

The rate of rearrangement of indole π complex **6a** to *N*-ligated complex **8a** is significantly diminished by added acid. When **2a** is mixed with 1 equiv of indole in the presence of a small amount (15 mol %) of excess acid at room temperature, **6a** is completely converted to **8a** in minutes at room temperature, but conversion takes hours in the presence of 50 mol % excess acid. In a more systematic set of experiments, **2a** is prepared from **1a** with a variable excess of acid, then 5 equiv of indole is added, and reaction progress is monitored by NMR at 40 °C; apparent rate constants for rearrangement of **6a** are shown in Table 4. Only modest reductions of rate are observed up to about 3-fold excess acid, but when the excess acid becomes comparable to the amount of excess indole, the rate slows dramatically (entry 4). Under these conditions indole complexation to form **6a** is also slowed, to only approximately 3 times the rate of rearrangement (compared to at least 2 orders of magnitude faster in the absence of acid). Furthermore, the initial product of π to N1 rearrangement is *not* **8a** but a different *N*-adduct (presumably **7a**); the rate of tautomerization of the first-formed *N*-adduct to

the ultimate product **8a** is slow under these acidic conditions.[24] Thus protonation of the nitrogen lone pair slows both coordination of platinum to the C═C double bond and subsequent migration of platinum to nitrogen; the inhibition of [1D] to [3D] indole tautomerization suggests that it is mediated by free (unprotonated) indole.

Conclusions

The new indole complexes generated by addition of indole, 1-methylindole, and 2-methylindole to [(diimine)Pt(Me)(solv)]$^+$ cations are very rare examples of stable complexes of this class of heterocycle with late transition metals. The initial interaction is *not* with the nitrogen lone pair, but rather indole C2═C3 olefin ligation, the first examples of such complexation. Indene forms a more stable π complex with cation **2a** that undergoes subsequent activation of the indenyl C−H group in hours at 60 °C to afford methane and an η^3-indenyl adduct. By contrast, indole π complexes of cation **2a** rearrange to *N*-ligated species. The rate of rearrangement can be controlled by substitution of the indole or by added H$^+$. Presumably, productive C−H activation chemistry on the indole nucleus is more likely to proceed from a complex of the indole C2═C3 olefin rather than N1; therefore strategies to prevent the formation of apparently inert *N* complexes from the corresponding π complexes are of interest to the continued development of synthetic strategies for functionalization of indoles by metal-mediated C−H activation, although we have not yet achieved the latter. Progress toward these objectives is ongoing in our laboratories.

Experimental Section

General Considerations. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using a Varian Inova 500 or 600 or Mercury 300 spectrometer. The data are reported by chemical shift (ppm) from tetramethylsilane, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet; dt, double triplet; br, broad), coupling constants (Hz), and integration. All ^{13}C NMR data were collected proton-decoupled (^{13}C{^{1}H}), except for those for **4a**, as specified. Mass spectra were acquired on a Finnigan LCQ ion trap or Agilent 5973 Network mass selective detector and were obtained by peak matching. All reactions were carried out under an atmosphere of nitrogen in glassware that had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Tris(pentafluorophenyl)borane [B(C_6F_5)$_3$] was purified by sublimation (90 °C, 0.5 Torr). 2,2,2-Trifluoroethanol-d_3 (TFE-d_3) was dried over 3 Å molecular sieves for at least 5 days and then vacuum distilled onto B(C_6F_5)$_3$. After 6 h, the trifluoroethanol-d_3 was vacuum distilled and stored in a Teflon needle-valved vessel. Boron trifluoride was purified according to Brown's procedure[25] and stored as a solution in TFE-d_3. The platinum dimethyl complexes were synthesized following earlier reported procedures, as noted. 2,2,2-Trifluoroethanol-d_3, B(C_6F_5)$_3$, and platinum dimethyl complexes were stored in a Vacuum Atmospheres dinitrogen atmosphere drybox.

Indene Complex 3a. Platinum dimethyl complex **1a**[4a] (19.2 μmol, 10.5 mg) was weighed out in an oven-dried 4 mL vial in the drybox. TFE-d_3 (700 μL) and BF_3 (0.477 M in TFE-d_3, 18 μmol, 38 μL) were then added, and the suspension was stirred until it became a homogeneous orange solution. Indene (19.2 μmol, 2.24 mg, 2.25 μL) was added, and the solution was transferred to an oven-dried J-Young NMR tube. After incubation at room temperature (24 h in this case) the solution was analyzed by NMR and found to contain **3a** in >95% yield.

^{1}H NMR (600 MHz, TFE-d_3) δ: 7.51 (dt, J_{H-H} = 6.8 Hz (doublet), 1.5 Hz (triplet), 1H), 7.26−7.23 (m, 3H), 7.15 (s, 1H), 7.10 (s, 1H), 6.99 (s, 1H), 6.96 (s, 1H), 6.16 (d, J_{H-H} = 4 Hz, J_{Pt-H} = 79 Hz, 1H), 5.24 (apparent t, $J_{H-H} \approx$ 6.4 Hz, J_{Pt-H} = 74 Hz, 1H), 3.30 (d, J_{H-H} = 23 Hz, J_{Pt-H} = 41 Hz, 1H), 3.07 (d, J_{H-H} = 23 Hz, J_{Pt}−H = 38 Hz, 1H), 2.32 (s, 6H), 2.25 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 1.97 (s, 3H), −0.74 (s, J_{Pt-H} = 53 Hz, 3H). ^{13}C NMR (150 MHz, TFE-d_3) δ: 185.6, 178.7, 148.4, 142.7, 141.5, 141.0, 140.9, 139.7, 131.8, 131.6, 131.0, 131.0, 130.8, 130.5, 130.4, 129.5, 129.2, 128.9, 126.2, 125.5, 103.1, 92.4, 40.7, 21.1, 21.1, 20.4, 20.2, 17.9, 17.9, 17.9, 17.8, 4.7. FTIR (neat): 2920 (w), 1476 (w), 1384 (w), 1237 (w), 1180 (m), 1160 (m), 1051 (s), 847 (w), 766 (w), 718 (w) cm^{-1}. FAB$^+$ MS, calcd for $C_{32}H_{40}N_2Pt$ ([M + H]$^+$): 647.2840, found 647.2822. Calcd for $C_{31}H_{36}N_2Pt$ ([M − Me]$^+$): 631.2526, found 631.2302.

Indene complex **3a**-d_3 was prepared as above. ^{1}H NMR (500 MHz, TFE-d_3) matches the data above, except that signals at δ = 6.16, 3.30, and 3.07 ppm are absent.

Indene Complexes 3b, 3c, and 3d. Complexes **3b**, **3c**, and **3d** were prepared by direct analogy to complex **3a** above, starting from platinum dimethyl species **1b**, **1d**,[4a] and **1c**.[3] **3b**: ^{1}H NMR (300 MHz, TFE-d_3) δ: 7.51 (d, 7.23 Hz, 1H), 7.29−7.19 (m, 3H), 7.02 (br s, 2H), 6.57 (br s, 4H), 6.46 (br s, 1H), 5.64 (br s, 1H), 3.20 (br s, 2H), 2.32 (br s, 12H), 2.07 (br s, 6H), −0.59 (s, J_{PtH-H} = 71 Hz, 3H). **3c**: ^{1}H NMR (300 MHz, TFE-d_3) δ: 7.96 (s, 2H), 7.56−7.52 (m, 1H), 7.53 (s, 4H), 7.29−7.11 (m, 3H), 6.53 (s, 1H), 5.68 (s, 1H), 3.22 (s, 2H), 2.12 (s, 6H), −0.34 (s, J_{Pt-H} = 69 Hz, 3H). **3d**: ^{1}H NMR (300 MHz, TFE-d_3) δ: 7.52−7.47 (m, 3H), 7.31−7.20 (m, 3H), 6.84 (br s, 4H), 6.33 (br s, 1H), 5.54 (br s, 1H), 3.13 (br s, 2H), 2.11 (br s, 6H), 1.33 (br s, 36H), −0.66 (s, J_{Pt-H} = 69 Hz, 3H).

Eyring Analysis for the Conversion of 3a to 4a. 3a was prepared as a solution in TFE-d_3 as described above, with the exception that 2.50 equiv of B(C_6F_5)$_3$ was used as the acid source. Conversion and rate were then recorded as described in the main text.

Indenyl Complex 4a. The solution of **3a** prepared above was heated in its J-Young tube to the temperature and time described in the main text.

^{1}H NMR (500 MHz, TFE-d_3) δ: 7.12−7.10 (m, 6H), 6.79 (dd J_{H-H} = 5.7, 3.1 Hz, ~3H), 5.01 (s,[26] 2H), 2.40 (s, 6H), 2.12 (s, 6H), 1.97 (s, 12H). ^{13}C NMR (150 MHz, TFE-d_3) δ: 172.6 (2C), 147.6 (2C), 140.8 (2C), 134.6, 131.2 (4C), 129.9 (4C), 129.3 (4C), 120.0 (2C), 71.6 (J_{Pt-C} = 130 Hz, 2C), 21.2 (2C), 18.0 (2C), 17.6 (4C). ^{13}C NMR (125 MHz, not {1H}, TFE-d_3) δ: 172.5 (s, 2C), 147.6 (s, 2C), 140.8 (d, J_{C-H} = 6 Hz, 2C), 134.6, 132−130 (m, $J_{1,C-H} \approx$ 150 Hz, 2C), 131.2 (d, J_{C-H} = 152 Hz, 2C), 129.9 (d, J_{C-H} = 154 Hz, 4C), 129.3 (s, 4C), 120.0 (d, J_{C-H} = 163 Hz, 2C), 71.6 (d, J_{C-H} = 181 Hz, 2C), 21.2 (q, J_{C-H} = 126 Hz, 2C), 18.0 (q, J_{C-H} = 132 Hz, 2C), 17.6 (q, J_{C-H} = 126 Hz, 4C). FTIR (neat): 2919 (w), 1476 (w), 1331 (w), 1385, 1244 (w), 1182 (m), 1157 (m), 1054 (s), 851, 754 (w) cm^{-1}. FAB$^+$ MS, calcd for $C_{31}H_{36}N_2Pt$ ([M + H]$^+$): 631.2526, found 631.2530 l. ^{2}H NMR (76.7 MHz, TFE-h_3) for this compound is shown in the Supporting Information.

Indenyl complex **4a**-d_2 was prepared as above. ^{1}H NMR (500 MHz, TFE-d_3) matches the data above, except that the signal at δ = 5.01 ppm is absent. FAB$^+$ MS, calcd for $C_{31}H_{34}{}^2H_2N_2Pt$ ([M-d_2 + H]$^+$): 633.2652, and for $C_{31}H_{32}{}^2H_3N_2Pt$ ([M-d_3]$^+$): 633.2637,

(24) Rate constants for this experiment were determined by modeling [**6a**] as an intermediate in a scheme of consecutive reactions. For the reaction scheme

$$\mathbf{2a} + \text{indole (excess)} \xrightarrow{k_{binding}} \mathbf{6a} \xrightarrow{k_{RAR}} \text{products}$$

[**6a**]/[**6a**]$_o$ = ($k_{binding}$/($k_{binding}$ + k_{RAR}))($e^{-k_{binding}t}$ − $e^{-k_{RAR}t}$). See: Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987.

(25) Brown, H. C.; Johannesen, R. B. *J. Am. Chem. Soc.* **1953**, *75*, 16−20.

(26) Observed J_{Pt-H} = 22 Hz for this signal in a spectrum acquired at 300 MHz.

found 633.2631. ^{2}H NMR (76.7 MHz, TFE-h_3) for this compound is shown in the Supporting Information.

Indole π-Complex 6a. Complex **6a** is observed as an intermediate in kinetic runs (Table 4, entry 4). ^{1}H NMR (500 MHz, TFE-d_3) δ: 7.62 (s, 1H), 7.60 (d, J_{H-H} = 7.8 Hz, 1H), 7.25−7.22 (m, 2H), 7.17 (t, J_{H-H} = 8.0 Hz, 1H), 7.14 (s, 1H), 7.01 (s, 1H), 6.97 (s, 1H), 6.94 (s, 1H), 5.40 (s, J_{H-H} = 94 Hz, ∼0H),[27] 2.39 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H), 1.83 (s, 3H), 1.81 (s, 3H), −1.02 (s, J_{Pt-H} = 62 Hz, 3H).

Indole *N*-Complex 8a. Platinum dimethyl complex **1a**[4a] (46.6 μmol, 25.4 mg) was weighed out in an oven-dried 4 mL vial in the drybox. TFE-d_3 (350 μL) and BF_3 (0.455 M in TFE-d_3, 53.5 μmol, 118 μL) were then added, and the suspension was stirred until it became a homogeneous orange solution. Indole (47 μmol, 5.5 mg) was added, and the solution was transferred, rinsing with TFE-d_3 (350 μL), to an oven-dried J-Young NMR tube. The solution was analyzed by NMR and found to contain **8a** in >95% yield.

^{1}H NMR (500 MHz, TFE-d_3) δ: 7.89 (s, J_{Pt-H} = 34 Hz, 1H), 7.73 (d, J_{H-H} = 7.3 Hz, 1H), 7.40−7.35 (m, 3H), 7.12 (s, 1H), 7.09 (s, 1H), 6.97 (s, 1H), 6.50 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H), 1.88 (s, 3H), 1.87 (s, 3H), 1.80 (s, 3H), 0.61 (s, J_{Pt-H} = 73 Hz, 3H). ^{13}C NMR (125 MHz, TFE-d_3) δ: 182.1, 175.6, 175.1, 153.9, 142.7, 140.9, 140.4, 139.8, 134.5, 130.9, 130.9, 130.8, 130.7, 130.6, 130.5, 130.1, 130.0, 129.3, 128.9, 125.8, 122.3, ∼44 (m, 1C), 21.1, 20.8, 20.0, 19.5, 17.9, 17.8 (2C), 17.7, −12.1. FTIR (neat): 2921 (m), 2094 (w), 1474 (m), 1449 (m), 1382 (m), 1313 (m), 1240 (m), 1184 (s), 1128 (s), 1069 (s), 1018 (s), 852 (m), 818 (m), 769 (m), 644 (m), 534 (m) cm^{-1}. FAB$^+$ MS, calcd for $C_{31}H_{35}N_3Pt^2H_2$ ([M − H]$^+$): 649.2839, found 649.2847.

Indole Complex 8b. Platinum dimethyl complex **1b**[4a] (32.5 μmol, 16.8 mg) was weighed out in an oven-dried 4 mL vial in the drybox. TFE-d_3 (700 μL) and BF_3 (0.478 M in TFE-d_3, 37.3 μmol, 78.1 μL) were then added, and the suspension was stirred until it became a homogeneous orange solution. Indole (33 μmol, 3.8 mg) was added, and the solution was transferred to an oven-dried screw-capped NMR tube. The solution was analyzed by NMR and found to contain **8b** in >95% yield.

^{1}H NMR (500 MHz, TFE-d_3) δ: 8.01 (s, J_{Pt-H} = 36 Hz, 1H), 7.87 (d, J_{H-H} = 7.9 Hz, 1H), 7.46−7.41 (m, 2H), 7.38−7.35 (m, 1H), 7.06 (s, 1H), 6.75 (s, 1H), 6.71 (s, 1H), 6.66 (s, 1H), 6.49 (s, br, 1H), 6.06 (s, br, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.25 (s, br, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.69 (s, 3H), 0.74 (s, J_{Pt-H} = 73 Hz, 3H). ^{13}C NMR (125 MHz, TFE-d_3) δ: 182.3, 174.6, 175.1, 153.9, 147.8, 145.7, 141.9, 141.8, 141.9−141.5 (m, br, 2C), 134.5, 131.2, 130.5, 130.2, 129.4, 125.9, 122.7, 121.0, 121.0, 120.7 (br, 1C), 119.5 (br, 1C), ∼44 (m, 1C), 21.6, 21.5, 21.2, 21.9−21.8 (m, 2C), −11.3. FTIR (neat): 3014 (w), 2921 (w), 2875 (w), 1609 (w), 1593 (w), 1468 (w), 1453 (w), 1384 (w), 1308 (w), 1185 (m), 1130 (m), 1060 (s), 863 (w), 771 (w), 685 (w) cm^{-1}. FAB$^+$ MS, calcd for $C_{29}H_{31}N_3Pt^2H_2$ ([M − H]$^+$): 620.2448, found 620.2459.

Indole Complex 8c. Platinum dimethyl complex **1c**[3] (36.0 μmol, 26.4 mg) was weighed out in an oven-dried 4 mL vial in the drybox. TFE-d_3 (700 μL) and BF_3 (0.478 M in TFE-d_3, 41.4 μmol, 86.6 μL) were then added, and the suspension was stirred until it became a homogeneous orange solution. Indole (36 μmol, 9.2 mg) was added, and the solution was transferred to an oven-dried screw-capped NMR tube. The solution was analyzed by NMR and found to contain **8c** in >95% yield.

^{1}H NMR (500 MHz, TFE-d_3) δ: 8.27 (s, J_{Pt-H} ≈ 40 Hz, 1H), 8.02 (s, 1H), 7.78 (d, J_{H-H} = 8.5 Hz, 1H), 7.73 (s, 1H), 7.68 (s, 1H), 7.55 (S, 1H), 7.45−7.27 (m, 5H), 2.04 (s, 3H), 2.03 (s, 3H), 0.76 (s, J_{Pt-H} ≈ 60 Hz, 3H). ^{13}C NMR (125 MHz, TFE-d_3) δ: 184.5, 177.7, 175.6 (m, 1C), 152.9 (m, 1C), 148.5, 147.0, 136.1−134.1 (m, apparent 4C), 134.1, 130.7, 129.4, 126.2, 124.6 (apparent 2C), 124−122 (m, apparent 4C), 122.3 (q, J_{C-F} = 227 Hz), 122.0, ∼44 (m, 1C), 21.9, 20.5, −9.4. Three CF_3 quartets cannot be identified because of coincidences with the solvent CF_3; each has δ ≈ 126 ppm, J_{C-F} ≈ 280 Hz. FTIR (neat): 3065 (w), 2932 (w), 2882 (w), 1622 (w), 1460 (m), 1373 (s), 1281 (s), 1182 (s), 1141 (s), 1067 (m), 903 (m), 848 (w), 771 (w), 705 (w), 684 (m) cm^{-1}. FAB$^+$ MS, calcd for $C_{29}H_{19}F_{12}N_3Pt^2H_2$ ([M − H]$^+$): 836.1317, found 836.1333.

2-Methylindole-π-complex 9. Platinum dimethyl complex **1a**[4a] (33.4 μmol, 18.2 mg) was weighed out in an oven-dried 4 mL vial in the drybox. TFE-d_3 (700 μL) and BF_3 (0.455 M in TFE-d_3, 38.4 μmol, 84.3 μL) were then added, and the suspension was stirred until it became a homogeneous orange solution. 2-Methylindole (33 μmol, 4.4 mg) was added, and the solution was transferred to an oven-dried screw-capped NMR tube. The solution was analyzed by NMR and found to contain **9** in >95% yield.

^{1}H NMR (500 MHz, TFE-d_3) δ: 7.35 (d, J_{H-H} = 7.5 Hz, 1H), 7.29 (d, J_{H-H} = 7.5 Hz, 1H), 7.25 (s, 1H), 7.20−7.14 (m, 3H), 6.97 (s, 1H), 6.90 (s, 1H), 2.53 (s, 3H), 2.43 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H), 2.10 (s, 3H), 1.90 (s, 3H), 1.83 (s, 3H), 1.63 (s, 3H), −0.75 (s, J_{Pt-H} = 67, 3H). ^{13}C NMR (125 MHz, TFE-d_3) δ: 178.0, 176.8, 143.3, 142.7, 141.9, 141.5, 140.2, 139.7, 131.5, 131.4, 130.7, 130.6, 130.5, 130.4, 130.1, 129.4, 126.7, 126.1, 123.9, 114.1, 21.1, 21.0, 20.2, 19.9, 18.1, 18.0, 17.5 (2C), −3.6. (3 C cannot be uniquely identified because of dispersity in the aryl region and the transitory nature of **9**.) FTIR (neat): 2918 (w), 1612 (w), 1505 (w), 1479 (w), 1458 (w), 1383 (w), 1329 (w), 1238 (m), 1157 (m), 1059 (s), 848 (w), 742 (m), 571 (w), 534 (w) cm^{-1}. **9** is not sufficiently long-lived for HRMS.

2-Methylindole-*N*-complex 10. The crude solution of **9** prepared above was incubated at room temperature for 50 h to give **10** in >95% yield.

^{1}H NMR (500 MHz, TFE-d_3) δ: 7.74 (d, J_{H-H} = 7.8 Hz, 1H), 7.32 (d, J_{H-H} = 7.9 Hz, 1H), 7.29−7.27 (m, 2H), 7.11 (s, 1H), 7.10 (s, 1H), 6.87 (s, 1H), 6.44 (s, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H), 2.12 (s, 3H), 1.86 (s, 3H), 1.85 (s, 3H), 1.83 (s, 3H), 0.53 (s, J_{Pt-H} = 74, 3H). ^{13}C NMR (125 MHz, TFE-d_3) δ: 186.0, 181.7, 175.8, 154.9, 142.8, 142.0, 140.3, 139.6, 135.0, 130.9, 130.7, 130.4, 129.9, 128.9, 128.8, 128.7, 122.5, 121.6, 121.1, 121.0, 112.4, ∼45 (m, 1C), 22.1, 21.1, 20.8, 20.1, 19.5, 18.4, 17.9, 17.8, 13.5, −13.7. FTIR (neat): 3512 (br, w), 3399 (br, w), 2921 (br, w), 1613 (w), 1573 (w), 1476 (m), 1456 (m), 1384 (m), 1316 (m), 1240 (m), 1187 (s), 1130 (s), 1069 (s), 852 (w), 756 (w), 646 (w), 535 (w) cm^{-1}. FAB$^+$ MS, calcd for $C_{32}H_{38}N_3Pt^2H_2$ ([M]$^+$): 663.2996, found 663.2980.

1-Methylindole-π-complex 11. Platinum dimethyl complex **1a**[4a] (46.9 μmol, 25.6 mg) was weighed out in an oven-dried 4 mL vial in the drybox. TFE-d_3 (700 μL) and BF_3 (0.455 M in TFE-d_3, 54 μmol, 119 μL) were then added, and the suspension was stirred until it became a homogeneous orange solution. 1-Methylindole (46.9 μmol, 6.16 mg, 6.00 μL) was added, and the solution was transferred to an oven-dried screw-capped NMR tube. The solution was analyzed by NMR and found to contain **11** in >95% yield.

^{1}H NMR (500 MHz, TFE-d_3) δ: 7.57 (d, J_{H-H} = 8.7 Hz, 1H), 7.50 (s, J_{Pt-H} = 49 Hz, 1H), 7.28 (t, J_{H-H} = 7.8 Hz, 1H), 7.22−7.17 (m, 2H), 7.16 (s, 1H), 7.07 (s, 1H), 6.97 (s, 1H), 6.91 (s, 1H), 5.95 (s, J_{H-H} = 88 Hz, ∼0H),[27] 3.65 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H), 2.24 (s, 6H), 2.14 (s, 3H), 2.00 (s, 3H), 1.86 (s, 3H), 1.80 (s, 3H), −1.16 (s, J_{Pt-H} = 70 Hz, 3H). ^{13}C NMR (125 MHz, TFE-d_3) δ: 179.4, 177.1, 144.9, 142.6, 141.5, 140.4, 140.1, 137.3, 131.7, 131.5, 130.8, 130.7, 130.6, 130.2, 130.1, 129.8, 125.2, 125.0, 128.9, 128.3, 111.9, 34.2, 21.1, 21.0, 20.0, 19.8, 18.0, 17.7 (2C), 17.6, −3.0. Because of dispersion in the 130 ppm region, 1C cannot be located. FTIR (neat): 2919 (w), 1477 (w), 1454 (w), 1383 (w), 1327 (w), 1238 (w), 1184 (m), 1128 (m), 1054 (s), 847 (w), 753 (w), 679 (w) cm^{-1}. FAB$^+$ MS, calcd for $C_{32}H_{39}N_3Pt^2H_1$ ([M]$^+$): 662.2933, found 662.2932.

(27) This signal (C3−H) is rapidly deuterated under the reaction conditions, but can be observed at the beginning of a kinetics run.

1-Methylindole-*N*-complex 12. The crude solution of **11** prepared above was incubated at room temperature for 2 days, then heated to 40 °C for 4 h to give **12** in ~78% yield by NMR. ^{1}H NMR (500 MHz, TFE-d_3) δ: 7.32 (t, J_{H-H} = 7.6 Hz, 1H), 7.28 (d, J_{H-H} = 7.4 Hz, 1H), 7.22 (t, J_{H-H} = 7.4 Hz, 1H), 7.19 (d, J_{H-H} = 8.4 Hz, 1H), 7.08 (s, 1H), 7.07 (s, 1H), 6.91 (s, 1H), 6.69 (s, 1H), 3.83 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.85 (s, 3H), 0.26 (s, J_{Pt-H} = 77 Hz, 3H). ^{13}C NMR (125 MHz, TFE-d_3) δ: 180.1, 176.3, 148.4, 144.6, 142.0, 139.9, 139.7, 137.0, 136.9, 130.9, 130.7, 130.7, 130.4, 130.2, 129.3, 128.8, 128.8, 128.6, 127.6, 125.6, 125.5, 112.7, 39.9 (J_{Pt-C} = 81 Hz), 21.1, 20.7, 20.0, 19.8, 17.9, 17.9, 17.9, 17.8, −16.8. FTIR (neat): 2923 (m, br), 2100 (w), 1609 (w), 1515 (m), 1463 (s), 1384 (m), 1312 (m), 1238 (m), 1186 (s), 1130 (s), 1069 (s, br), 860 (w), 818 (w), 759 (m), 646 (w), 535 (w) cm^{-1}. FAB$^+$ MS, calcd for $C_{32}H_{39}N_3Pt^2H$ ([M]$^+$): 662.2933, found 663.2939.

Crossover Experiment between 9 and 1-Methylindole. Platinum dimethyl complex **1a** (22.4 μmol, 12.2 mg) was weighed out in an oven-dried screw-capped NMR tube in the drybox. TFE-d_3 (511 μL) and BF_3 (0.477 M in TFE-d_3, 24.6 μmol, 51.6 μL) were then added. The suspension was removed from the drybox and sonicated until it became a homogeneous orange solution. The reaction was then thermally equilibrated to 30 °C in a Varian mercury 300 MHz NMR, and 2-methylindole (0.183 M in TFE-d_3, 22.4 μmol, 122 μL) was then injected. [**9**] was monitored and reached a maximum in ca. 2 min, at which time conversion of **2a** to **9** was ~90% complete. The tube was then removed from the instrument, 1-methylindole (2.93 mg, 22.4 μmol, 2.86 μL) was injected, and the sample was reinserted (~30 s.) An initial ratio of 81(1)% **9**, 10(1)% **10**, 9(1)% **11** was observed with 0(1)% **2a**. Kinetic data were recorded for 9.7 h. After an additional 2 days at RT, **9** was completely converted to **10** ($k_{RAR} = 9.1(3) \times 10^{-5}$ s^{-1}), and **11** was completely converted to **12**. A ratio of 91(1)% **10** to 9(1)% **12** was observed.

Conversion of 6a to 8a at High [H$^+$]. Platinum dimethyl complex **1a** (22.7 μmol, 12.4 mg) was weighed out in a 1 mL graduated cylinder in the drybox. BF_3 (0.477 M in TFE-d_3, 56.8 μmol, 119 μL) and TFE-d_3 (to make 1.00 mL) were then added. A 480 μL portion of this solution (10.9 μmol Pt, 2.5 equiv of BF_3) was then distributed into each of two screw-capped NMR tubes. Separately, indole (14.5 mg, 124 μmol), BF_3 (0.477 M in TFE-d_3, 62.0 μmol, 130 μL), and TFE-d_3 (356 μL) were mixed in a 10 mL culture tube. Then 220 μL of this solution (5 equiv of indole to Pt, 2.5 equiv of BF_3 to Pt) was then distributed into each of two 1 mL syringes. The NMR tubes and syringes were removed from the drybox. One NMR tube was then thermally equilibrated to 40 °C in a Varian Inova 500 MHz NMR spectrometer. It was then ejected, and the content of 1 syringe was added to the NMR tube (to make 10.9 μmol of Pt, 5 equiv of BF_3, 5 equiv of indole, and 700 μL of TFE-d_3). The tube was shaken and reinserted. After rapid reshimming, kinetic data were recorded for 7.5 h. A second trial was then conducted with the other NMR tube and syringe. Reaction progress was monitored by NMR. Rate constants for this experiment are $k_{binding} = 5.35 \times 10^{-4}$ s^{-1} and $k_{RAR} = 1.44 \times 10^{-4}$ s^{-1}, where $k_{binding}$ is the pseudo-first-order rate constant for the binding of indole to **2a**.[24]

Comment Regarding H/D Exchange and Methane Isotopologues Formed in the Conversion of 3 to 4. In the conversion of **3a** to **4a** the methane that is formed is 65% CH_4, 35% CH_3D due to D$^+$ incorporation in the formation of **2a** from **1a**. A distribution of 53% CH_4, 47% CH_3D is observed in the conversion of **3a**-d_3 to **4a**-d_2. ^{2}H NMR spectra of **4a** and **4a**-d_2 were recorded to track ^{2}H incorporation in these compounds (see Supporting Information). ^{2}H incorporation is observed in C2−H (6.8 ppm) in both **4a** and **4a**-d_2. Little ^{2}H incorporation is observed in C1,3−H (5.0 ppm) in **4a**. As expected, ^{2}H is observed in this signal in **4a**-d_2. A small amount of H/D exchange with solvent is observed in the diimine backbone (2.4 ppm), but none is observed in the mesityl methyl groups. Accordingly, the high level of CH_4 relative to CH_3D observed in the formation of **4a**-d_2 is attributed to some H/D exchange with C2−H in the indenyl fragment prior to methane liberation and a low level of decomposition of the diimine ligand.

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Note Added in Proof. A preliminary X-ray structure for **8a** has recently been obtained. This is a preliminary, low-resolution structure from a poorly diffracting crystal. Connectivity is unambiguous although distance and angle measurements have large errors. These data, CCDC 628218, can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available: Spectral data for the crossover experiment between **9** and 1-methylindole, spectral and kinetic data for the conversion of **6a** to **8a** in the presence of excess acid, ^{2}H NMR spectra for **4a** and **4a**-d_2, and graphical ^{1}H NMR spectra for **3a**, **3a**-d_3, **4a**, **4a**-d_2, **8a**, **8b**, **8c**, **9**, **10**, **11**, and **12** are available free of charge via the Internet at http://pubs.acs.org.

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