Improved One-Pot Synthesis of Mixed Methyl−Aryl Platinum(II) Diimine Complexes

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Summary: A general one-pot synthetic route for mixed methyl−aryl Pt(II) diimine complexes is described. Performing the alkylation in neat Me_2S instead of ether or THF greatly reduces the amount of comproportionation products otherwise formed, diminishes separation problems, and improves yields. Treatment of the intermediate methyl−aryl complexes $(Me_2S)_2Pt(Me)(Ar)$ with diimines (N−N) furnishes the methyl−aryl Pt(II) diimine complexes (N−N)Pt(Me)(Ar) in 76−84% yields. The Pt methyl−phenyl complex [p-Tol-N═C(Me)C(Me)═N-p-Tol]Pt(Me)(Ph) has been characterized by X-ray diffraction.

Introduction

The development of methods for direct, selective conversion of hydrocarbons to value-added products remains a challenge.[1−4] Seminal work by Garnett and Shilov demonstrated that Pt salts are able to activate otherwise unreactive aromatic and aliphatic C−H bonds and to mediate the hydrocarbon functionalization.[5−7] Studies on the aqueous K_2PtCl_4 system and on model systems have provided considerable mechanistic understanding of the process; our groups have made particularly effective use of model complexes $(N−N)PtR_2$, where N−N is a diimine ligand.[8,9]

Both aliphatic and aromatic C−H activations by cationic Pt(II) complexes have been studied extensively. A good deal of the mechanistic insight is obtained from studies on the reverse reaction, protonolysis of Pt hydrocarbyls. Hence, a convenient synthetic route to mixed alkyl−aryl Pt(II) model complexes would provide a valuable tool for comparisons of aliphatic and aromatic C−H activation reactivity. A substantial number of syntheses of mixed $L_2Pt(R')(R'')$ compounds have previously been attempted,[10−14] primarily to study competition between cleavage of alkyl vs aryl bonds in reactions with electrophiles[15] or in thermal decomposition.[16] A common feature of successful syntheses is that the ligand L used in the alkylation or arylation step (typically COD and PR_3) is not particularly labile and therefore not easily displaced by diimine ligands, rendering these compounds less suitable as intermediates in the synthesis of mixed Pt(II) alkyl−aryl diimine complexes.

One such compound, (N−N)Pt(Me)(Ph) (where N−N = Ar-N═C(Me)-C(Me)═NAr (**1**), Ar = 2,6-$Me_2C_6H_3$ (**1a**)) has been synthesized by making use of a more labile ligand, dimethyl sulfide, allowing for facile introduction of the desired diimine ligand. $(Me_2S)_2Pt(Me)(Ph)$ was prepared by reacting phenyllithium with $(Me_2S)_2Pt(Me)(Cl)$ in ether at −20 °C. This resulted in a complex mixture (most likely due to the presence of dinuclear Me_2S-bridged species in addition to the desired product). Subsequent reaction of this mixture with the diimine **1a** in toluene furnished the desired methyl−phenyl product (N−N)Pt(Me)(Ph) (**2a**) in 31% overall yield after separation from the diphenyl byproduct $(N−N)PtPh_2$ (**3a**) by flash chromatography.[17] However, attempts to synthesize analogous compounds with other diimine ligands yielded significant amounts of the undesired dimethyl and diphenyl byproducts, the latter being particularly difficult to separate from the desired product. In this work we show that a variety of methyl−phenyl and methyl−tolyl Pt(II) diimine complexes can be synthesized in a one-pot procedure by performing the arylation step in dimethyl sulfide as solvent, followed by addition of the diimine ligand. The formation of byproducts due to disproportionation of the intermediates (Scheme 1) is greatly suppressed in the presence of a large excess of dimethyl sulfide.

Results and Discussion

Preparations. A closer examination of the synthesis of **2a** revealed that the reaction yields significant amounts of the Pt(II) diphenyl (**3a**) and dimethyl (**4a**) byproducts. Furthermore, varying reaction conditions and the ligand used showed that the product distribution largely depends on reaction times, workup procedure, and diimine ligand.[18] The chromatographic separation of the methyl−phenyl product from the dimethyl and diphenyl byproducts is not always trivial, depending on the ligand used. Because of these problems, a method was sought to reduce the formation of byproducts in the first place.

It is a possibility that the byproducts **3a** and **4a** are formed by disproportionation of the $(Me_2S)_2Pt(Me)(Ph)$ intermediate prior to coordination of the diimine. If so, it is expected that

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Scheme 1

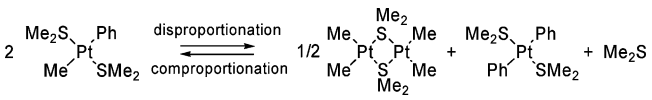
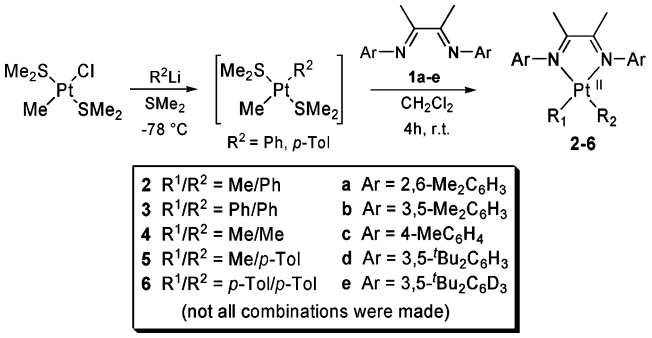


Table 1. ^{1}H NMR Product Distribution of 2a, 3a, and 4a in Test Reactions[a]

temp (°C)	solvent	product distribn **2a**:**3a**:**4a** (%)
−20	Et_2O	70:12:18
−20	Et_2O, 10 equiv Me_2S	77:10:14
−20	Me_2S	90:4:6
−78	Me_2S	99:1:0

[a] See experimental part for details.

Scheme 2



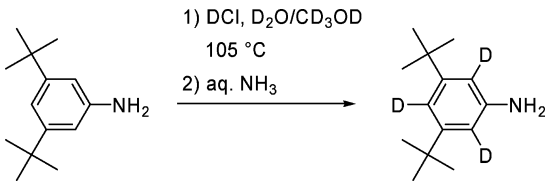
comproportionation of $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and $(Me_2S)_2PtPh_2$ will produce $(Me_2S)_2Pt(Me)(Ph)$ (Scheme 1). To test this, $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and $(Me_2S)_2PtPh_2$ were added to an NMR tube and dissolved in CD_2Cl_2. An immediate reaction took place, yielding a mixture of dimethyl, diphenyl, and methyl−phenyl complexes. NMR spectra recorded 20 h later showed virtually no change in the product distribution. A similar experiment was performed, but this time Me_2S was added to the CD_2Cl_2 before the reactants were dissolved. The ^{1}H NMR spectrum recorded immediately after mixing showed that, in the tube containing Me_2S, the dinuclear $Pt_2Me_4(\mu\text{-}SMe_2)_2$ was split up to form the corresponding mononuclear species $(Me_2S)_2PtMe_2$ and, most important, no comproportionation products were observed. These observations suggest that the comproportionation mechanism involves dissociation of Me_2S and that the disproportionation of $(Me_2S)_2Pt(Me)(Ph)$ could hence be inhibited by the addition of Me_2S.

These results encouraged us to see what effect added Me_2S could have in the arylation of $(Me_2S)_2Pt(Me)(Cl)$. The best yields of the desired mixed alkyl−aryl products relative to the dimethyl and diaryl products were obtained by performing the reaction in neat Me_2S at −78 °C, as summarized in Table 1. Preparative-scale reactions were tested for a range of diimine ligands (Scheme 2). Excess lithium reagents were quenched by addition of *tert*-butyl bromide. A dichloromethane solution of the diimine ligand was added before the reaction mixture was warmed to room temperature and solvents were removed. The residue was redissolved in dichloromethane, filtered through Celite, and stirred for 4 h. Final workup involved rapid filtration through a short pad of basic alumina to remove traces of LiCl.[19] The mixed alkyl−aryl complexes **2a**−**c** and **5d**,**e** were obtained in 97−99% purity by ^{1}H NMR and in isolated yields of 76−84% (Scheme 2, Table 2). Chromatography was attempted with both basic alumina and silica gel. Decomposition of the products on the column can by minimized by addition of 1% triethylamine to the eluent. However, the separation is rather poor and any separation obtained might just as well be a result of the solubility trends in the eluent: **5d** > **6d** > **4d**.[20]

Table 2. ^{1}H NMR Product Distribution in Isolated Compounds

	isolated yield (%)	product distribn (%)
2a:**3a**:**4a**	78	99:1:0
2b:**3b**:**4b**	84	99:1:0
2c:**3c**:**4c**	80	99:1:0
5d:**6d**:**4d**	76	97:2:1

Scheme 3



A possible mechanism for the intermolecular transfer of methyl and phenyl ligands between the two Pt centers would be a metathesis-type reaction (intermolecular transfer of a methyl and/or phenyl group), with or without accompanying dissociation of Me_2S. Some examples of comproportionation and disproportionation of Pt(II) complexes are already known. Suzaki et al. report disproportionation of $(COD)Pt(Ph)(CH_2COMe)$ and comproportionation of $(COD)Pt(CH_2COMe)_2$ and $(COD)PtPh_2$, which supposedly proceed via an intermediate with bridging phenyl and acetonyl ligands.[21] Scott and Puddephatt investigated the comproportionation of $(Me_2S)_2PtCl_2$ and $(Me_2S)_2PtMe_2$.[22] This reaction proceeds by dissociation of Me_2S, leaving the coordinatively unsaturated intermediate $(Me_2S)PtMe_2$ (often referred to as a T-shaped, three-coordinate species). Two major pathways are outlined, involving either a bridging Me_2S or a bridging Cl followed by an oxidative addition/reductive elimination sequence or an S_E2 type reaction.

The observed inhibition of disproportionation of $(Me_2S)_2Pt(Me)(Ph)$ by Me_2S suggests that the major pathway of disproportionation involves dissociation of Me_2S, leading to a three-coordinate species as suggested by Scott and Puddephatt, followed by disproportionation, leading to the formation of $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and $(Me_2S)_2PtPh_2$. The fact that small amounts of Pt(II) dimethyl and diaryl byproducts are formed even when the reaction is performed in neat Me_2S might indicate that there also exists a nondissociative pathway for the disproportionation of $(Me_2S)_2Pt(Me)(Ph)$ and$(Me_2S)_2Pt(Me)(p\text{-}Tol)$, but this pathway must be less favorable energetically compared to the dissociative one.

Compound **2e**, a partially deuterated (at the diimine aryl groups) analogue of **2d**, was also prepared. The deuterated ligand **1e** was obtained from a deuterated aniline precursor which was prepared by heating 3,5-di-*tert*-butylaniline with DCl in D_2O (Scheme 3).[23] CD_3OD was added to increase the solubility of the formed anilinium chloride. Aqueous basic workup afforded the deuterated aniline.

Characterization. All new compounds were characterized by ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectra of the mixed alkyl−aryl complexes show a double set of signals from the

(18) It should be noted that if $(Me_2S)_2Pt(Me)(Cl)$ contains impurities of $(Me_2S)_2PtCl_2$, this will yield the corresponding $(Me_2S)_2PtAr_2$ after arylation.

(19) LiCl has a considerable solubility in methylene chloride. This is evidenced by yields in excess of 100% after evaporation only.

(20) The R_f values from a TLC plate eluted with 1:2 Et_2O/hexane were all around 0.43−0.46 for **5d**, **6d**, and **4d**.

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Table 3. Selected ^{1}H NMR Data for the Pt(II) Methyl−Aryl Compounds

	^{1}H NMR, δ[a]		
compd	Pt−*Me* ($^2J(^{195}$Pt−H))	N=C*Me*	Ar *Me* or Ar C*Me*$_3$
2a[b]	0.75 (87.8)	1.41, 1.52	2.10, 2.25
2b	0.92 (87.5)	1.66, 1.72	2.11, 2.39
2c	0.94 (87.6)	1.63, 1.71	2.27, 2.44
5d	0.92 (86)	1.67, 1.72	1.19, 1.38

[a] Dichloromethane-d_2. [b] Data from ref 17.

Table 4. Crystal Data and Structure Refinement Details for 2c

empirical formula	$C_{25}H_{25}N_2Pt$
formula wt	548.56
temp	105(2) K
wavelength	0.71073
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	$a = 26.9672(7)$ Å
	$b = 8.8779(2)$ Å
	$c = 18.9608(5)$ Å
	$\beta = 107.046(1)°$
vol, Z	4340.0(2) Å^3
density (calcd)	1.679 Mg/m^3
abs coeff	6.478 mm^{-1}
F(000)	2136
cryst size	0.25 × 0.20 × 0.15 mm
θ range for data	2.15−35.02°
no. of rflns collected	86 453
no. of indep rflns	19 007
refinement method	least-squares against F^2 using all rflns
data/param ratio	37
goodness of fit on F^2	1.19
final R indices ($I > 2\sigma(I)$)	0.050
R indices (all data)	0.062
$\Delta\rho$(max)	4.4
$\Delta\rho$(min)	−3.8

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Molecule A of the Crystal Structure of 2c

	Distances		
Pt(1A)−N(1A)	2.085	N(1A)−C(1A)	1.300
Pt(1A)−N(2A)	2.122	N(1A)−C(5A)	1.439
Pt(1A)−C(19A)	2.043	N(2A)−C(2A)	1.303
Pt(1A)−C(20A)	2.012	N(2A)−C(12A)	1.425
	Angles		
Pt(1A)−N(1A)−C(1A)	117.86	N(1A)−Pt(1A)−N(2A)	75.96
Pt(1A)−N(1A)−C(5A)	124.12	C(19A)−Pt(1A)−N(1A)	96.37
Pt(1A)−N(2A)−C(2A)	116.25	C(20A)−Pt(1A)−N(2A)	99.86
Pt(1A)−N(2A)−C(12A)	124.69	C(19A)−Pt(1A)−C(20A)	87.85

nonequivalent halves of the diimine ligand (selected data are shown in Table 3).

X-ray-quality crystals of **2c** were grown by slow evaporation from an ether solution. Details of the structure determination are given in the Experimental Section. Table 4 lists experimental and crystallographic data, and selected bond distances and angles for molecule **A** are given in Table 5. The asymmetric unit contained the two nearly identical molecules **A** and **B**. Figure 1 shows an ORTEP drawing of molecule **A** of **2c**. The diimine N-aryl rings are twisted relative to the coordination plane by Pt−N−C(ipso)−C(ortho) dihedral angles of 60.5/81.7° and 68.5/80.3° for **A** and **B**, respectively. The chelate rings in **A** and **B** are almost perfectly planar, the sum of the four cis L−Pt−L′ angles around Pt being 360.0 and 360.3°, respectively. The Pt(1)−N(2) bond trans to Pt-Me is 0.03 Å (average) longer than the Pt(1)−N(1) bond trans to Pt−Ph, presumably reflecting a slightly greater trans influence of the methyl group compared to the phenyl group. Although the diimine N-aryl rings are twisted out of the coordination plane in the solid state for **2c**, the aryl rings presumably rotate freely in solution for **2b**,**c** and **5d**. However, the methyl groups in the 2,6-positions of the N-aryl groups in **2a** would present a barrier toward this rotation. The angles between the coordination plane and the aryl rings in **2c** (61−82°) span a greater range than the corresponding angles in related (N−N)Pt^{II} diphenyl complexes (66−71 and 79−88°, respectively, for complexes without and with methyl groups in the 2,6-positions of the diimine N-aryl rings).[24] The upfield shift of Pt−*Me* and N=C*Me* in **2a** compared to the signals in **2b**,**c** and **5d** could be a result of different conformational preferences and consequential interligand aromatic ring-current effects of the 2,6-substituted ligand (**2a**) compared with the 3,5- and 4-substituted ligands.

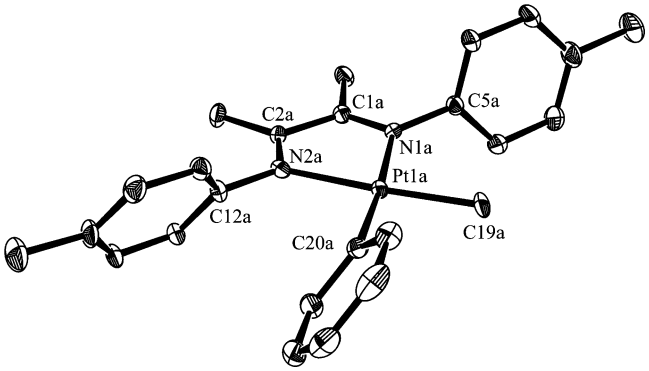

Figure 1. ORTEP drawing of compound **2c** (molecule A) with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Conclusion. Mixed diimine Pt(II) alkyl−aryl complexes have been synthesized in a convenient one-pot procedure by performing the arylation at low temperature with Me_2S as the solvent. This procedure suppresses the formation of dimethyl and diphenyl byproducts.

Experimental Section

General Considerations. Me_2S was dried by stirring with a Na dispersion in mineral oil (Aldrich), vacuum-distilled, and stored over activated 4 Å molecular sieves.[25] All other reagents were used as received. Phenyllithium in cyclohexane/ether was purchased from Aldrich and standardized by titration with 1,3-diphenyl-2-propanone tosylhydrazone.[26] Basic alumina was purchased from Panreac. *cis*/*trans*-$(Me_2S)_2$Pt(Me)(Cl)[27] and the diimine ligands[28] **1a**−**d** were synthesized as previously described.

NMR spectra were recorded on Bruker 300 and 500 instruments (300.13 and 500.13 MHz for ^{1}H). Chemical shifts (δ) are reported in ppm relative to C*H*DCl_2 at δ 5.32, C*H*Cl_3 at δ 7.24, or C_6HD_5 at δ 7.15 for ^{1}H and relative to *C*D_2Cl_2 at δ 53.8 for ^{13}C. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium (Kronach, Germany).

Test Reactions: [ArN=C(Me)C(Me)=NAr]Pt(Me)(Ph), Ar = 2,6-$Me_2C_6H_3$ (2a). Small-scale test reactions were done to determine relative product distributions. In a typical reaction, $(Me_2S)_2$Pt(Me)(Cl) (40 μmol) and a stirring bar were added to a 5 mL round-bottomed flask, which was fitted with a septum and flushed with nitrogen. Dry solvent was added, and the flask was cooled (see Table 1 for details). PhLi (40 μmol) was added by dropwise addition to the stirred suspension. After 20 min a few drops of aqueous 2 M NH_4Cl were added to quench excess lithium reagents. Diimine ligand **1a** (40 μmol) dissolved in toluene (4 mL) was added, and the reaction mixture was gradually warmed to room temperature and stirred overnight. Evaporation yielded a residue which was dissolved in CD_2Cl_2 and analyzed by ^{1}H NMR.

Preparative Scale: [ArN=C(Me)C(Me)=NAr]Pt(Me)(Ph), Ar = 3,5-$Me_2C_6H_3$ (2b). In a typical reaction, $(Me_2S)_2$Pt(Me)(Cl)

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(25) Attemps to store Me_2S over Na/benzophenone resulted in slow formation of gas bubbles. These were not analyzed further.

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(202.1 mg, 0.546 mmol) and a magnetic stirring bar was added to a 25 mL round-bottomed flask fitted with a septum and flushed with nitrogen. Dry Me_2S (4 mL) was added with a syringe and the mixture cooled to −78 °C, causing the starting material to form a fine precipitate. PhLi (0.469 mL, 1.34 M, 0.628 mmol, 1.15 equiv) was added by dropwise addition to the stirred suspension. After the complete addition of PhLi the formed precipitate disappeared, leaving a clear solution. The solution was stirred overnight and excess lithium reagent quenched by addition of *tert*-butyl bromide (127 μL, 1.092 mmol, 2 equiv). The diimine ligand **1b** (159.0 mg, 0.546 mmol) dissolved in CH_2Cl_2 (3 mL) was added, the mixture was taken up to room temperature, and all solvents were evaporated on a vacuum line with a cold trap (*stench!* glassware cleaned with household bleach). The residue was dissolved in CH_2Cl_2, upon which a deep red complex immediately was formed, filtered through a short pad of Celite, and stirred for 4 h at room temperature. Filtration through a plug of basic alumina and evaporation of the solvent yielded a deep purple residue which was washed several times with pentane. Drying under vacuum yielded **2b** (265.0 mg, 84% yield) as a deep purple powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.92 (s, 3H, Pt−CH_3, $^2J_{Pt-H}$ = 87.5 Hz), 1.66 (s, 3H, N=CCH_3), 1.72 (s, 3H, N=CCH_3), 2.12 (s, 6H, Ar CH_3), 2.39 (s, 6H, Ar CH_3), 6.33 (br s, 2H, Ar *H*), 6.68 (br s, 3H, Ar *H*), 6.50−6.83 (m, 5H, Pt−(C_6H_5)), 6.96 (br s, 1H, Ar *H*). ^{13}C NMR (75 MHz): δ −11.9 (Pt−CH_3, $^1J_{Pt-C}$ = 807 Hz), 20.8 (overlapping Ar Me and N=CCH_3), 21.17 (N=CCH_3), 119.2 (6 Hz), 120.2 (7 Hz), 120.8 (12 Hz), 125.5 (Roth H, $^3J_{Pt-H}$ = 78 Hz), 127.3, 127.9, 137.4 (31 Hz), 137.9 (Ar CH_3), 138.8 (Ar CH_3), 145.8 (ipso), 146.6 (ipso), 147.3 (ipso), 170.1 (N=CCH_3), 173.1 (N=CCH_3). Anal. Calcd for $C_{27}H_{32}N_2Pt$: C, 55.95; H, 5.56; N, 4.83. Found: C, 56.09; H, 5.26; N, 4.92.

[ArN=C(Me)C(Me)=NAr]Pt(Me)(Ph), Ar = 2,6-$Me_2C_6H_3$ (2a). 2a was synthesized and worked up in a manner similar to that for **2b** (see above) from $(Me_2S)_2$Pt(Me)(Cl) (52.6 mg, 0.142 mmol, 1 equiv) and **1a** (41.5 mg, 0.142 mmol, 1 equiv), yielding **2a** (64.6 mg, 78% yield) as a deep purple powder. The recorded ^{1}H NMR spectrum was in accordance with published data.[10]

[ArN=C(Me)C(Me)=NAr]Pt(Me)(Ph), Ar = 4-MeC_6H_4 (2c). 2c was synthesized and worked up in a similar manner from $(Me_2S)_2$Pt(Me)(Cl) (53.5 mg, 0.144 mmol) and **1c** (38.2 mg, 0.144 mmol), yielding **2c** (63.8 mg, 80%) as a deep purple powder. X-ray-quality crystals were grown by slow evaporation from a diethyl ether solution. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.94 (s, 3H, Pt−CH_3, $^1J_{Pt-H}$ = 87.6 Hz), 1.63 (s, 3H, N=CCH_3), 1.71 (s, 3H, N=CCH_3), 2.29 (s, 3H, Ar CH_3), 2.45 (s, 3H, Ar CH_3), 6.51−6.86 (m, 7H), 6.67 (d, 4H, ^3J = 8.2 Hz), 7.34 (d, 2H, ^3J = 8.0 Hz). ^{13}C NMR (75 MHz): δ −10.7 (Pt−CH_3, $^1J_{Pt-C}$ = 810 Hz), 21.0, 21.12, 21.14, 21.2, 121.0, 121.8, 122.4, 126.0 (J_{Pt-H} = 82 Hz), 128.8, 129.7, 136.2, 136.5, 138.0 (J_{Pt-C} = 32 Hz), 145.0, 145.2, 145.4, 171.0, 173.8. Anal. Calcd for $C_{25}H_{28}N_2Pt$: C, 54.44; H, 5.12; N, 5.08. Found: C, 54.51; H, 5.10; N, 5.08.

[ArN=C(Me)C(Me)=NAr]Pt(Me)(*p*-Tol), Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$ (5d). Butyllithium (103.3 μL, 1.6 M in hexane, 0.165 mmol, 1.15 equiv) was added by dropwise addition to 4-iodotoluene (37.6 mg, 0.172 mmol, 1.2 equiv) dissolved in 1 mL of anhydrous Me_2S under nitrogen, and the mixture was stirred for 15 min at −78 °C and then for 15 min at ambient temperature. The solution of *p*-tolyllithium was cooled to −78 °C again and transferred via cannula to **4** (53.2 mg, 0.143 mmol, 1 equiv) dissolved in 1 mL of anhydrous Me_2S, and this mixture was stirred overnight at −78 °C. Quenching, reaction with diimine ligand **1c** (66.2 mg, 0.143 mmol), and workup as described above yielded **5d** (100.3 mg, 76%) as a deep purple powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.92 (3H, s, $^2J_{Pt-H}$ = 86 Hz), 1.19 (18H, s, C(CH_3)$_3$), 1.38 (18H, s, C(CH_3)$_3$), 1.67 (3H, s, N=CCH_3), 1.72 (3H, s, N=CCH_3), 2.04 (3H, s, (C_6H_4)CH_3), 6.38−6.40 (2H, m), 6.44−6.60 (4H, m (incl $^3J_{Pt-H,ortho}$ = 65 Hz), 6.89 (2H, d, J = 1.7 Hz), 7.11 (1H, br t, J = 3.4 Hz), 7.35 (1H, br t, J = 3.4 Hz). ^{1}H NMR (300 MHz, C_6D_6): δ 0.81 (3H, s, N=CCH_3), 0.88 (3H, s, N=CCH_3), 1.27 (18H, s, C(CH_3)$_3$), 1.32 (18H, s, C(CH_3)$_3$), 2.04 (3H, s, $^2J_{Pt-H}$ = 87 Hz), 2.27 (3H, s, (C_6H_4)CH_3), 6.78−6.83 (4H, m), 7.06 (2H, d, J = 1.7 Hz), 7.25−7.46 (4H, m). ^{13}C NMR (75 MHz, CD_2Cl_2): δ −10.6 (J_{Pt-C} = 807 Hz), 20.7, 21.11, 21.14, 31.3, 31.5, 35.0, 35.4, 116.5, 116.9, 120.3, 120.5, 127.0 (J_{Pt-C} = 78 Hz), 129.7, 137.5 (J_{Pt-C} = 30 Hz), 140.5, 147.0, 147.2, 151.3, 152.0, 170.4, 173.2. Anal. Calcd for $C_{40}H_{58}N_2Pt$: C, 63.05; H, 7.67; N, 3.68. Found: C, 63.44; H, 7.61; N, 3.68.

3,5-Di-*tert*-butyl-2,4,6-trideuterioaniline. The following is a modification of a published procedure.[23] A glass bomb was fitted with a magnetic stirring bar, filled with 3,5-di-*tert*-butylaniline (0.530 g, 2.584 mmol), DCl (0.5 mL), D_2O (1.0 mL), and CD_3OD (0.5 mL), frozen, and evacuated on a vacuum line. The bomb was heated to 105 °C for 3 days. All solvents were evaporated, and new DCl (0.5 mL), D_2O (1.0 mL) and CD_3OD (0.5 mL) were added. After freezing and evacuation the bomb was heated for another 5 days. After evaporation the process was repeated one more time with heating for another 5 days. The reaction mixture was quenched by addition of 2 M NH_4OH to pH 10 and extracted with diethyl ether (3 × 20 mL). The organic phase was washed with water and dried with $MgSO_4$. Evaporation yielded the product (0.509 g, 95%) as an off-white solid. The degree of deuteration by ^{1}H NMR was ∼98% in both para and ortho positions. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (18H, s), 3.56 (2H, br s).

[ArN=C(Me)C(Me)=NAr]Pt(Me)(*p*-Tol), Ar = 3,5-^{t}Bu$_2$C$_6$D$_3$ (5e). 5e was synthesized as described above from *p*-tolyllithium, $(Me_2S)_2$Pt(Me)(Cl) (193 mg, 0.5224 mmol), and diimine **1e** (243.8 mg, 0.5224 mmol), yielding **5e** (282.1 mg, 70%) as a deep purple solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.92 (3H, s, $^2J_{Pt-H}$ = 87 Hz, Pt−CH_3), 1.19 (18H, s, C(CH_3)$_3$), 1.38 (18H, s, C(CH_3)$_3$), 1.67 (3H, s, N=CCH_3), 1.72 (3H, s, N=CCH_3), 2.04 (3H, s, (C_6H_4)-CH_3), 6.39 (2H, "d", $^3J_{H-H}$ = 8.1 Hz, *m-H*), 6.52 (2H, "d", $^3J_{H-H}$ = 8.1 Hz, $^3J_{Pt-H}$ = 65 Hz, *o-H*); due to incomplete deuteration of the ligand peaks are also seen at δ 6.89 (s), 7.11 (s), and 7.35 (s).

X-ray Crystallographic Structure Determination of 2c. Crystals of **2c** were grown by slow evaporation from a diethyl ether solution. Single-crystal X-ray data were collected at 105 K with a Bruker Smart 1k CCD diffractometer, integrated, and processed with Saint.[29] Analytical absorption correction was carried out using Xprep[29] followed by Sadabs.[30] The structure was solved in space group $P2_1/c$ with two crystallographically independent molecules in the asymmetric unit and refined with Shelxtl[31] to a final R factor of 0.05 with data (>99% completeness) extending to 2θ = 70° (Mo Kα radiation). All non-hydrogen atoms were refined anisotropically, while all H atoms were kept in idealized positions, refining a single C−H distance for all H atoms connected to the same C atom. U_{iso} values for the H atoms were fixed at $1.2U_{eq}$ (−CH− and $-CH_2-$) and $1.5U_{eq}$ ($-CH_3$) of the parent C atom. Experimental data, crystal data, and refinement results are summarized in Table 4.

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Supporting Information Available: Crystal structure data for **2c** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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