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Hemilability of P(X)N-type ligands (X = O, N–H): rollover cyclometalation and benzene C–H activation from (P(X)N)$PtMe_2$ complexes†‡

Margaret L. Scheuermann,[a] Kyle A. Grice,§[a] Matthew J. Ruppel,[a] Marta Roselló-Merino,[b] Werner Kaminsky[a] and Karen I. Goldberg*[a]

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The thermolyses of ($^{t\mathrm{Bu}}$P(O)N)$PtMe_2$ (**1**, $^{t\mathrm{Bu}}$P(O)N = (di-*tert*-butylphosphinito)pyridine) and ($^{t\mathrm{Bu}}$P(N–H)N)$PtMe_2$ (**3**, $^{t\mathrm{Bu}}$P(N–H)N = (di-*tert*-butylphosphino)-2-aminopyridine) in benzene-d_6 were investigated. With ($^{t\mathrm{Bu}}$P(O)N)$PtMe_2$, the product of a rollover cyclometalation of the pyridyl ring was observed in 80% yield along with formation of CH_4. In contrast, thermolysis of ($^{t\mathrm{Bu}}$P(N–H)N)$PtMe_2$ resulted in competing rollover cyclometalation and intermolecular benzene C–H activation with production of a mixture of CH_4 and CH_3D.

Introduction

Bidentate ligands bearing two different donor atoms have been widely employed in the field of catalysis.[1] They are often chosen for properties such as hemilability, tunability, and ability to support metal centers in multiple oxidation states. One such ligand motif that has recently gained prominence is the P(X)N-type ligand (Fig. 1; X = O, N–R, CH_2).[2–12] Complexes supported by such ligands have been shown to be competent catalysts for Suzuki–Miyaura reactions,[5,9,10] alkyl amine synthesis,[2,6] transfer hydrogenation,[3] methoxycarbonylation of olefins,[7] and arene coupling.[8] As with many bidentate ligands bearing two different donor atoms, P(X)N-type ligands can be hemilabile.[1] The hemilability of the ligand generates an open site allowing the metal center to engage in reaction pathways that might otherwise be inaccessible. Here we describe new Pt complexes with P(X)N-type ligands (X = O, N–H) and report rollover cyclometalation reactions at (P(X)N)$PtMe_2$ complexes (X = O, N–H). Intermolecular C–H activation was also observed for (P(N–H)N)$PtMe_2$. The reactivity observed for both complexes can be attributed to the hemilability of the P(X)N ligands.

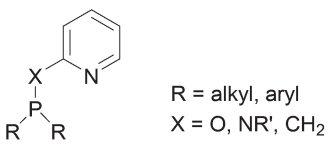

Fig. 1 P(X)N ligand motif.

Results and discussion

Synthesis, characterization, and thermolysis of ($^{t\mathrm{Bu}}$P(O)N)$PtMe_2$

The 2-(di-*tert*-butylphosphinito)pyridine ($^{t\mathrm{Bu}}$P(O)N) ligand was prepared using methods for the synthesis of structurally related molecules.[13,14] Unrefined ligand can be mixed directly with $[PtMe_2(SMe_2)]_2$[15] in toluene at room temperature to generate the Pt^{II} dimethyl complex, ($^{t\mathrm{Bu}}$P(O)N)$PtMe_2$ (**1**, $^{t\mathrm{Bu}}$P(O)N = (di-*tert*-butylphosphinito)pyridine, Fig. 2). Complex **1** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The ^{1}H NMR spectrum of **1** in C_6D_6 contains signals corresponding to two inequivalent Pt–Me groups at 1.65 ppm ($^2J_{\mathrm{Pt–H}}$ = 90 Hz, $^3J_{\mathrm{P–H}}$ = 6 Hz) and 1.36 ppm ($^2J_{\mathrm{Pt–H}}$ = 64 Hz, $^3J_{\mathrm{P–H}}$ = 7 Hz). The substantial difference in the $^2J_{\mathrm{Pt–H}}$ values is consistent with the methyl group resonating at 1.65 ppm being situated *trans* to the pyridine moiety of the $^{t\mathrm{Bu}}$P(O)N ligand and the methyl group resonating at 1.36 ppm being situated *trans* to the more strongly σ-donating phosphine.[16] The ^{31}P{^{1}H} NMR spectrum of **1** contains a singlet at 184.2 ppm ($^1J_{\mathrm{Pt–P}}$ = 2113 Hz), shifted downfield of the 153.3 ppm value measured for free $^{t\mathrm{Bu}}$P(O)N. Crystals of **1** were obtained from a toluene–ether solution at −35 °C and were analyzed by X-ray diffraction. The crystals were very small and of poor quality, causing a high mosaicity but still a molecular

[a]*Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195, USA. E-mail: goldberg@chem.washington.edu*
[b]*Departamento de Química Inorgánica, CSIC-Universidad de Sevilla, Instituto de Investigaciones Químicas, Avda. Américo Vespucio 49, 41092 Sevilla, Spain*
†Contributed in honor of the 80th birthday of Professor William C. Kaska in recognition of his tremendous contributions to the field.
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§Present address: Department of Chemistry, DePaul University, 1110 West Belden Avenue, Chicago, IL 60614, USA.

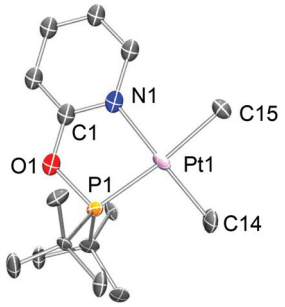


Fig. 2 POV-Ray[18] rendition of the ORTEP[19] of ($^{t\mathrm{Bu}}$P(O)N)PtMe$_2$, **1**, at the 50% level of probability with hydrogen atoms and full molecule disorder omitted for clarity. Selected bond lengths (Å) and angles (°): O1–C1 = 1.36(3), O1–P1 = 1.704(19), N1–Pt1 = 2.088(18), P1–Pt1 = 2.223(7), Pt1–C14 = 2.05(3), Pt1–C15 = 2.14(3); C1–O1–P1 = 116.9(16), C14–Pt1–C15 = 86.0(12), N1–Pt1–C15 = 92.9(10), C14–Pt1–P1 = 99.0(9), N1–Pt1–P1 = 82.1(6).

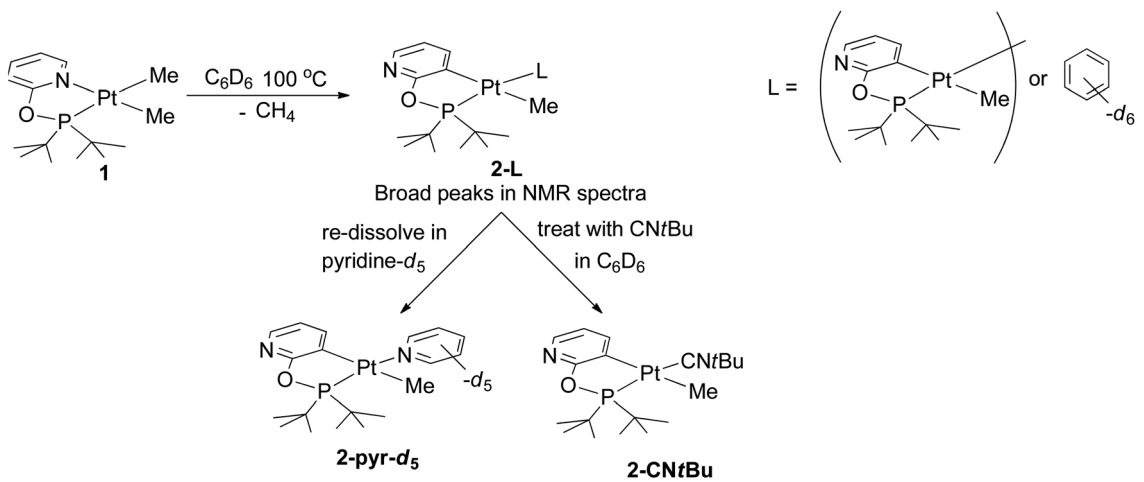
structure consistent with the NMR data was obtained (Fig. 2).[17] The crystals contained disordered molecules related by a mirror plane parallel to (0 1 0). The mirror plane is not part of the space group symmetry but is part of the point group, and thus, is inconsistent with twinning. A distinctive feature of this nearly square planar structure is the significant difference in the Pt–CH_3 bond lengths with values of 2.05(3) and 2.14(3) Å for the Pt–C bonds *trans* to nitrogen and phosphorus, respectively.

Upon heating a sample of **1** in C_6D_6 at 100 °C for four days, the NMR resonances of **1** disappeared and broad resonances corresponding to a new species, **2-L**, appeared along with a sharp singlet at 0.16 ppm consistent with the formation of CH_4 (Scheme 1).[20] The broad resonances that could be clearly identified were centered at 0.77 ppm ($\nu_{1/2}$ = ~90 Hz, Pt–Me), 1.45 ppm ($\nu_{1/2}$ = ~160 Hz, *t*Bu resonances having the appearance of a virtual triplet), and in the aromatic region centered at 6.48 and 7.99 ppm. Another aromatic feature appears to be centered under the benzene residual solvent resonance (7.16 ppm). Integration of the ^{1}H NMR resonances *versus* a hexamethylbenzene internal standard indicated that the new species, **2-L**, formed in *ca.* 80% yield. The solution remained clear and colorless throughout the thermolysis and a broad ^{31}P NMR resonance at approximately 159 ppm with coupling to Pt ($^1J_{\mathrm{Pt-P}}$ ~ 4400 Hz) indicated that the phosphine was still bound to Pt, although *trans* to a more weakly donating ligand than a Me group.[16]

To explore the identity of **2-L**, the volatiles were removed *in vacuo* and the sample was redissolved in pyridine-d_5. The ^{1}H NMR spectrum of the sample in pyridine-d_5 revealed a single major species with sharp resonances. A single Pt–Me resonance at 0.53 ppm with a $^2J_{\mathrm{Pt-H}}$ value of 46 Hz was observed. This small coupling constant suggests a more strongly donating *trans* ligand than a pyridine moiety or a phosphine. Of note, the $^1J_{\mathrm{Pt-P}}$ value remains large, 4272 Hz, suggesting that the phosphine remains *trans* to a weakly coordinating ligand. Similarly large $^1J_{\mathrm{Pt-P}}$ values have been observed in other Pt$^{\mathrm{II}}$ species with phosphine and pyridyl moieties *trans* to one another, albeit in cationic complexes.[21] A COSY experiment in pyridine-d_5 confirmed the presence of three and only three aromatic protons in the molecule. This observation suggested the possibility that a rollover cyclometalation cleaving an aromatic C–H bond could have occurred.

In benzene-d_6, the open site that would be generated by rollover cyclometalation and methane loss from **1** is likely filled by a pyridyl moiety in the ligand backbone of another molecule resulting in oligomeric species[22] or possibly by η^2-benzene as was reported by Brookhart, Templeton, and coworkers for a similar Pt$^{\mathrm{II}}$ system.[23] In contrast, dissolution of the material in the donor solvent pyridine-d_5 leads to coordination of pyridine solvent forming the distinct monometallic species, ($^{t\mathrm{Bu}}$P(O)C)PtMe(pyr-d_5), **2-pyr-d_5**. Efforts to isolate crystalline samples of **2-L** and **2-pyr-d_5** were not successful.

An isolable species, ($^{t\mathrm{Bu}}$P(O)C)PtMe(CN*t*Bu) (**2-CN*t*Bu**) was formed in approximately 80% yield based on starting **1** (^{1}H NMR integration) upon addition of *tert*-butylisonitrile (*ca.* 1 equiv.) to a solution of the thermolysis product, **2-L**, in benzene. The ^{1}H NMR spectrum of **2-CN*t*Bu** features three



Scheme 1 Thermolysis of (P(O)N)PtMe$_2$, **1**, and generation of **2-pyr-d_5** and **2-CN*t*Bu**.

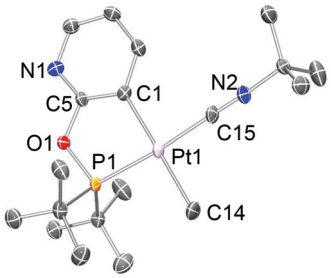


Fig. 3 POV-Ray[18] rendition of the ORTEP[19] of **2-CN*t*Bu** at the 50% level of probability with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1–C15 = 1.975(6), Pt1–C1 = 2.066(6), Pt1–C14 = 2.122(6), Pt1–P1 = 2.2363(14), P1–O1 = 1.642(4), O1–C5 = 1.389 (7); C15–Pt1–C1 = 94.6(2), C15–Pt1–C14 = 86.3(3), C1–Pt1–P1 = 80.68 (16), C14–Pt1–P1 = 98.41(19), C5–O1–P1 = 116.0(3).

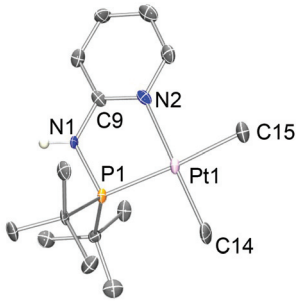


Fig. 4 POV-Ray[18] rendition of the ORTEP[19] of ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$, **3**, at the 50% level of probability with C–H hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1–C14 = 2.041(5), Pt1–C15 = 2.112(5), Pt1–N2 = 2.131(4), Pt1–P1 = 2.2411(13), P1–N1 = 1.705(4), N1–C9 = 1.382(6); C14–Pt1–C15 = 85.5(2), C15–Pt1–N2 = 94.56(18), C14–Pt1–P1 = 97.54(15), N2–Pt1–P1 = 82.44(11), N1–P1–Pt1 = 101.08(14), C9–N1–P1 = 120.5(3).

aromatic protons and a single Pt–Me resonance at 1.08 ppm ($^2J_{\mathrm{Pt-H}}$ = 54 Hz). This $^2J_{\mathrm{Pt-H}}$ value is consistent with a Pt–Me group situated *trans* to a strongly sigma-donating sp^2 aryl carbon.[16,24] The ^{31}P NMR resonance for **2-CN*t*Bu** at 155 ppm has a $^1J_{\mathrm{Pt-P}}$ value of 3452 Hz, consistent with CN*t*Bu being a stronger *trans* donor than pyridine.[25]

X-ray quality crystals of **2-CN*t*Bu** were obtained by slow evaporation of a benzene–ether solution in an N_2 atmosphere.[17] The X-ray structure (Fig. 3) obtained confirms the stereochemical assignment made based on the NMR coupling constants. The Pt–C bond *trans* to the aryl ligand has a bond length of 2.122(6) Å.

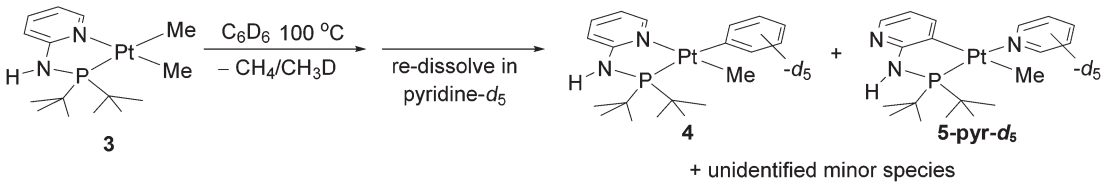
The crystal structure of **2-CN*t*Bu** clearly illustrates that rollover cyclometalation of the pyridine moiety has taken place. This is similar to the reported rollover cyclometalation chemistry of various (bpy)PtR$_2$ complexes (bpy = bipyridine or bipyridine derivative; R = Me or Ph).[22,26,27] Notably, when the thermolysis of (bpy)PtPh$_2$ was performed in the presence of a suitable trapping ligand, discrete molecular species formed. However in the absence of such a ligand, oligomeric or polymeric species were reported.[22] The observation of rollover cyclometalation from **1** is unusual as there are in general few examples of C–H activation at phosphine ligated Pt centers.[28,29] Rollover cyclometalation at other metals with a phosphine ligand present are known.[30,31]

Synthesis and thermolysis of ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$

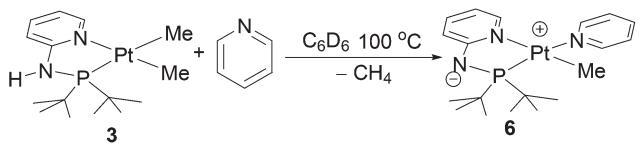
The chemistry of the related bifunctional P(N–H)N ligand on platinum was also examined. The $^{t\mathrm{Bu}}$P(N–H)N ligand ($^{t\mathrm{Bu}}$P(N–H)N = (di-*tert*-butylphosphino)-2-aminopyridine)[32] was combined with [PtMe$_2$(SMe$_2$)]$_2$[15] in toluene at room temperature to generate ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$ (**3**). Complex **3** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. As was seen with the related ($^{t\mathrm{Bu}}$P(O)N)PtMe$_2$ complex **1**, the ^{1}H NMR spectrum of **3** contains two inequivalent Pt–Me resonances with very different $^2J_{\mathrm{Pt-H}}$ values, 88 Hz and 65 Hz for the Pt–Me groups *trans* to the pyridyl and phosphine moieties respectively. Notably, these values are very close to those of **1** (90 and 64 Hz, respectively). The ^{31}P NMR spectrum of **3** contains a single peak at 105.3 ppm with a $^1J_{\mathrm{Pt-P}}$ value of 2080 Hz. X-ray quality crystals of **3** were obtained by slow evaporation of a toluene solution in an N_2 atmosphere (Fig. 4).

When a benzene-d_6 solution of **3** was thermolyzed at 100 °C, complete disappearance of the starting material was observed over four days. Well-resolved resonances corresponding to a new species appeared in the ^{1}H NMR spectrum, however spectroscopic yields of this new species were typically limited to *ca.* 30% (integration *vs.* hexamethylbenzene internal standard). In contrast to the thermolysis of **1** where CH_4 was the only isotopologue of methane observed, in the thermolysis of **3**, both CH_4 and CH_3D were observed (typically in a ratio of ~1 : 1), the CH_3D being consistent with cleavage of C–D bonds of the C_6D_6 solvent. In the aromatic region of the ^{1}H NMR spectrum of the ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$ thermolysis product mixture in benzene-d_6, four resonances were observed indicating that the formation of this product did not involve a rollover cyclometalation. This product displayed a single Pt–Me resonance in the ^{1}H NMR spectrum, 1.60 ($^2J_{\mathrm{Pt-H}}$ = 88 Hz) and a ^{31}P resonance at 102.2 ($^1J_{\mathrm{Pt-P}}$ = 1980 Hz). These data suggest a species with a single Pt–Me group located *trans* to the weakly donating pyridyl and a phosphorus donor *trans* to a strong ligand. Upon repeating the thermolysis in benzene-h_6, followed by spectroscopic characterization of the product in benzene-d_6, the product was identified as ($^{t\mathrm{Bu}}$P(N–H)N)PtMePh (**4**, Scheme 2), wherein a phenyl group is located *trans* to phosphorus. Thus, rather than rollover cyclometalation with C–H activation of the bidentate ligand, intermolecular C–H(D) activation of a benzene solvent molecule takes place to produce **4(-*d*$_5$)**.

Upon removal of the benzene solvent from the thermolysis product mixture of **3** *in vacuo* and redissolution of the residue in pyridine-d_5, a ^{1}H NMR spectrum revealed well-resolved resonances corresponding to two significant species. A COSY experiment revealed that one of the species contained four coupled aromatic protons, consistent with ($^{t\mathrm{Bu}}$P(N–H)N)PtMePh, **4**, while the other species had only three aromatic protons



Scheme 2 Thermolysis of (P(N–H)N)PtMe$_2$ in C_6D_6.



Scheme 3 Thermolysis of **3** in the presence of pyridine.

as would be expected if a rollover cyclometalation had occurred. This second species which forms competitively with **4** is suggested to be (^{tBu}P(N–H)C)PtMe(pyr-d_5), **5-pyr-d_5**. The formation of **5-pyr-d_5** is in analogy with the chemistry observed above with formation of the related **2-pyr-d_5** from the similar reaction of **1**. Typical yields for **5-pyr-d_5** were low (*ca.* 15%) which complicated efforts to obtain full characterization. In addition, with the N–H substituted ligand rather than the O-substituted ligand, efforts to find a trapping reagent analogous to the isonitrile (*vide supra*) that allowed for isolation and thorough characterization of the rollover cyclometalation product were not successful.

When the thermolysis of **3** was carried out in the presence of pyridine (5–50 equiv. or neat pyridine-d_5) as a trapping ligand, a high yield (>80%) of a single product was obtained (Scheme 3). In these reactions CH_4 was produced as a single isotopologue but neither inter- nor intramolecular C–H activation was observed.

The ^{1}H NMR spectrum is consistent with a species having a single Pt–Me group and all four aromatic C–H bonds intact. The ^{31}P NMR spectrum has a single resonance at 86.4 ppm ($^1J_{Pt-H}$ = 3921) suggesting a phosphine with a weakly donating *trans* ligand. Most notable however was that no N–H resonance was observed in the ^{1}H NMR spectrum of the product. Crystals of this new species were obtained by slow evaporation of a solution of dichloromethane (in air using benchtop solvent) and the product was shown to be (^{tBu}P(N)N)PtMe(pyr) by X-ray crystallography (**6**, Fig. 5). No pyridinium was detected spectroscopically and the crystal structure contained no anions. Disordered CH_2Cl_2 was uniquely identified from electron density maxima, bond-distances, and free site-occupancy fit to test correctness of element type assignment. A water molecule was located in the crystal lattice near the formally anionic nitrogen atom (N3···O1 = 2.880(8)). The water is disordered and two of the hydrogen atom sites on the water, H1b and H1o, are at fractional occupancies, consist with H_2O rather than H_3O^+. Water was refined with a rigid model, leaving H–H distances and O–H distances fixed, but allowing free rotation of the

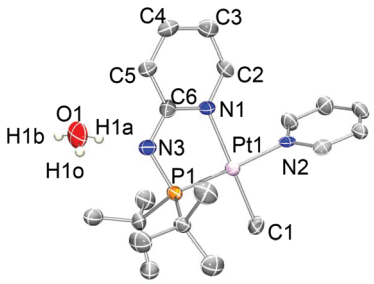


Fig. 5 POV-Ray[18] rendition of the ORTEP[19] of (^{tBu}P(N)N)PtMe(pyr), **6**, at the 50% level of probability with hydrogen atoms (except those on H_2O) and co-crystallized dichloromethane omitted for clarity. The sites for H1b and H1o are at 50% occupancy. Selected bond lengths (Å) and angles (°): Pt1–C1 = 2.061(9), Pt1–N2 = 2.097(6), Pt1–N1 = 2.106(7), Pt1–P1 = 2.202(2), P1–N3 = 1.680(7), N3–C6 = 1.348(10), C2–C3 = 1.377(12), C3–C4 = 1.385(11), C4–C5 = 1.381(11), C5–C6 = 1.420(11), N3···O1 = 2.880(8), N3···H1a = 2.097(16); C1–Pt1–N2 = 84.2(3), N2–Pt1–N1 = 95.3(2), C1–Pt1–P1 = 99.4(2), N1–Pt1–P1 = 81.22(16), C6–N3–P1 = 115.9(5).

water, which lead to the observation of a possible hydrogen bond interaction. This interaction between H1a and N3 could serve to stabilize the formally anionic charge through hydrogen bonding.

The changes in the ligand bond lengths between **3** and **6** are subtle, all less than 0.04 Å. Kirchner[33] previously reported crystal structures for [(^{BINOL}P(N–H)N(N–H)P)Fe(MeCN)$_3$]2[BF_4],[34] (^{BINOL}P(N–H)N(N–H)P = (*N*,*N*′-bis(*S*-dinaphtho[2,1-*d*:1′2′-*f*][1,3,2]-dioxaphosphepine)-2,6-diaminopyridine) and its mono-deprotonated analogue [(^{BINOL}P(N)N(N–H)P)Fe(MeCN)$_3$][BF_4].[35] Notably the changes in bond lengths upon deprotonation were also approximately 0.05 Å or less. The differences in bond lengths observed in the structures of [(^{Ph}P(N–H)N)$_2$Pt]2Cl,[36] and its twice deprotonated analogue (^{Ph}P(N)N)$_2$Pt,[37] were all 0.07 Å or less.[38]

The formation of **6** is notable because it represents the formal coupling of an N–H proton in the ligand backbone with a methyl group bound to the metal center. The microscopic reverse of this reaction would be a net C–H activation reaction that is reminiscent of H_2 activation by Noyori type hydrogenation catalysts with nitrogen on the ligand receiving a proton.[39] Mechanistic investigations of the formation of **6** are in progress and preliminary results indicate that the added pyridine is involved in mediating the reaction; formation of **6** was qualitatively faster with increasing pyridine concentration and fastest in neat pyridine-d_5.

Summary

New organometallic Pt complexes with bidentate ligands bearing two different donor atoms were prepared and their thermolyses were explored. The hemilability of the ligand appears to play a significant role in the reactivity observed. Dissociation of the pyridyl ring in ($^{t\mathrm{Bu}}$P(O)N)PtMe$_2$, **1**, leads primarily to rollover cyclometalation, with the formation of **2-L** (where L is benzene solvent or the pyridine N of another rollover product molecule). Complex **2-L** is effectively trapped by *tert*-butylisonitrile allowing isolation and characterization of **2-CN*t*Bu**. In the case of ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$, **3**, inter- and intramolecular C–H activations appear to be competitive with both activation of benzene solvent, to yield the methyl phenyl derivative **4** and rollover cyclometalation to yield a $^{t\mathrm{Bu}}$P(N–H)C analog of **2-L**. Thus the subtle change from an O atom linker to a NH linker in the backbone of the bidentate ligand significantly changes the selectivity of the C–H activation reaction. In addition, thermolysis of the ($^{t\mathrm{Bu}}$P(N–H)N) ligated **3** in the presence of pyridine allowed for the isolation of complex **6**, the product of an unusual coupling of the proton on the N of the ligand backbone with a Pt–Me group. Studies of the effects of varying the linker group (atoms and linker lengths), the substituents on the nitrogen, and the substituents on the phosphorus in these P(X)N ligands are ongoing in our laboratory in order to provide insight for the development of catalytic systems involving C–H bond activation.

Experimental

General conditions

Unless otherwise specified, all manipulations were carried out in a nitrogen-filled glovebox, using a Schlenk line, or using a high vacuum manifold. Glassware was oven-dried prior to use. Dichloromethane and THF were dried by passage through activated alumina columns under argon. Benzene, toluene, and pentane were dried by passage through columns containing activated alumina and Q5 reactant, a supported copper oxygen scavenger, under argon.[40] C_6D_6 was vacuum transferred from sodium/benzophenone ketyl. Pyridine-d_5 was vacuum transferred from CaH_2. Tetramethylenediamine and triethylamine were dried over CaH_2 and distilled prior to use. $[PtMe_2(SMe_2)]_2$ was prepared according to a literature procedure.[15] All other reagents were obtained from commercial vendors and used as received. NMR spectra were recorded on Bruker AV300, DRX500, AV500, AV700, or AV800 spectrometers and were referenced to the residual protiated solvent signal. Data from HMQC and HMBC experiments were used in the assignment of ^{13}C NMR resonances. Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br = broad.

Synthetic procedures

Synthesis of $^{t\mathrm{Bu}}$P(O)N. The preparation of $^{t\mathrm{Bu}}$P(O)N is based on the reported synthesis of a related molecule.[14] In a Schlenk flask, hydroxypyridine (1.11 g, 11.7 mmol) was dissolved in 30 mL THF. To this solution was added tetramethylenediamine (1.5 mL, 10 mmol) and triethylamine (1.0 mL, 11 mmol). The solution was cooled in an ice water bath and di-*tert*-butylphosphine (2.0 mL, 11 mmol) was added. The flask was fitted with a reflux condenser and heated at reflux for four hours, then cooled to room temperature. The volatiles were removed *in vacuo* and the residue was extracted with several portions of benzene (~50 mL total). The benzene extracts were collected and filtered. The volatiles were removed *in vacuo* to give a pale yellow oil. Yield: 1.9 g, 7.9 mmol, 74%. The crude material was used without further purification. ^{1}H NMR (C_6D_6, 500 MHz, 298 K) δ 8.12 (m, 1H), 7.07 (m, 1H), 6.73 (d, 1H), 6.43 (m, 1H), 1.19 (d, 18H, $^3J_{\mathrm{P-H}}$ = 11 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 298 K) δ 148.5, 139.1, 118.1, 112.6, 35.9 (d, $^1J_{\mathrm{P-C}}$ = 29 Hz), 28.1 (d, $^2J_{\mathrm{P-C}}$ = 16 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 298 K) δ 153.3.

Synthesis of ($^{t\mathrm{Bu}}$P(O)N)PtMe$_2$ (1). A solution of unrefined $^{t\mathrm{Bu}}$P(O)N (130 mg, 0.54 mmol) in 5 mL toluene was added to $[PtMe_2(SMe_2)]_2$ (*ca*. 150 mg, 0.26 mmol). The reaction mixture was stirred for 15 minutes at room temperature and then the volatiles were removed *in vacuo*. The residue was dissolved in minimal toluene (approx. 3 mL), filtered through a 0.2 μm PTFE syringe filter, and recrystallized from a toluene–ether mixture at −35 °C yielding crystalline ($^{t\mathrm{Bu}}$P(O)N)PtMe$_2$ (113 mg, 0.24 mmol, 46%). ^{1}H NMR (C_6D_6, 500 MHz, 298 K) δ 8.84 (d, 1H, $^3J_{\mathrm{Pt-H}}$ < 24 Hz),[41] 6.88 (t, 1H), 6.47 (d, 1H), 6.07 (m, 1H), 1.65 (d, 3H, $^3J_{\mathrm{P-H}}$ = 6 Hz, $^2J_{\mathrm{Pt-H}}$ = 90 Hz), 1.36 (d, 3H, $^3J_{\mathrm{P-H}}$ = 7 Hz, $^2J_{\mathrm{Pt-H}}$ = 64 Hz), 1.21 (d, 18H, $^2J_{\mathrm{P-H}}$ = 14 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 298 K) δ 166.8 (d, $^2J_{\mathrm{P-C}}$ = 4 Hz, $^2J_{\mathrm{Pt-C}}$ = 15 Hz), 146.4 (d, $^3J_{\mathrm{P-C}}$ = 3 Hz, $^2J_{\mathrm{Pt-C}}$ = 16 Hz), 139.4, 118.6 ($^4J_{\mathrm{Pt-C}}$ = 14 Hz), 110.6 (d, $^3J_{\mathrm{P-C}}$ = 4 Hz), 40.2 (d, $^1J_{\mathrm{P-C}}$ = 9 Hz, $^2J_{\mathrm{Pt-C}}$ = 45 Hz), 27.7 (d, $^2J_{\mathrm{P-C}}$ = 6 Hz, $^3J_{\mathrm{Pt-C}}$ < 19 Hz),[41] 17.0 (d, $^2J_{\mathrm{P-C}}$ = 115 Hz, $^1J_{\mathrm{Pt-C}}$ = 665 Hz), −22.8 (d, $^2J_{\mathrm{P-C}}$ = 4 Hz, $^1J_{\mathrm{Pt-C}}$ = 760 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 298 K) δ 184.2 ($^1J_{\mathrm{Pt-P}}$ = 2113 Hz). Anal. Calcd For $C_{15}H_{28}NOPPt$: C, 38.79; H, 6.08: N, 3.02. Found: C, 38.89; H, 6.09; N, 3.04.

Synthesis of $^{t\mathrm{Bu}}$P(N–H)N. The preparation of $^{t\mathrm{Bu}}$P(N–H)N is based on the reported synthesis of a related molecule.[32] A Schlenk flask was charged with 2-aminopyridine (1.56 g, 16.6 mmol) in THF (40 mL). The solution was cooled in a dry ice/acetone bath and *n*-butyllithium (~2.5 M hexanes, 7.8 mL, 20 mmol) was added by syringe. The solution was stirred for one hour then chloro-di-*tert*-butylphosphine (3.5 mL, 18 mmol) was added and the mixture was allowed to warm to room temperature. After 45 minutes the volatiles were removed *in vacuo*. The residue was extracted with pentane and the extracts were filtered through a 0.2 μm PTFE syringe filter and again the solvent was removed *in vacuo*. The resulting material was suspended in acetonitrile and stirred overnight. The resulting white solid $^{t\mathrm{Bu}}$P(N–H)N was collected on a medium frit (1.55 g, 6.5 mmol, 46%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) δ 8.02 (d, 1H), 7.44 (t(d), 1H), 7.15 (d(d), 1H), 6.62 (t, 1H), 5.02 (s-br, 1H), 1.14 (d, 18H, $^3J_{\mathrm{P-H}}$ = 12 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 298 K) δ 161.3 (d, $^2J_{\mathrm{P-C}}$ = 21 Hz), 148.1, 137.7, 114.4, 109.2 (d, $^3J_{\mathrm{P-C}}$ = 18 Hz), 34.2 (d, $^1J_{\mathrm{P-C}}$ = 19), 28.3 (d, $^2J_{\mathrm{P-C}}$ = 16). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 298 K) δ 59.7.

Synthesis of ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$ (3). A flask was charged with $^{t\mathrm{Bu}}$P(N–H)N (251 mg, 1.05 mmol) and crude [PtMe$_2$(SMe$_2$)]$_2$ (290 mg, 0.51 mmol). Toluene (5 mL) was added and the reaction mixture was stirred for approximately an hour during which time the solution became pale yellow and a white solid formed. The reaction mixture was then diluted with toluene (approx. 10 mL) until the white solid dissolved and was subsequently filtered through a 0.2 μm PTFE syringe filter. The solution was layered with pentane and stored at −35 °C resulting in crystalline ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$ (191 mg, 0.41 mmol, 40%). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K) δ 8.96 (d, 1H, $^2J_{\mathrm{Pt–H}}$ < 25 Hz),[41] 6.88 (t, 1H), 6.00 (t, 1H), 5.95 (d, 1H), 4.58 (s-br, 1H), 1.68 (d, 3H, $^3J_{\mathrm{P–H}}$ = 7 Hz, $^2J_{\mathrm{Pt–H}}$ = 88 Hz), 1.41 (d, 3H, $^3J_{\mathrm{P–H}}$ = 7 Hz, $^2J_{\mathrm{Pt–H}}$ = 65 Hz), 1.12 (d, 18H, $^2J_{\mathrm{P–H}}$ = 14 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 176 MHz, 298 K) δ 162.9 (d, $^2J_{\mathrm{P–C}}$ = 12 Hz), 147.2 (d, $^3J_{\mathrm{P–C}}$ = 2 Hz, $^2J_{\mathrm{Pt–C}}$ < 14 Hz),[41] 137.4, 115.4 (s, $^4J_{\mathrm{Pt–C}}$ = 14 Hz), 109.2 (d, $^3J_{\mathrm{P–C}}$ = 5 Hz), 38.2 (d, $^1J_{\mathrm{P–C}}$ = 12 Hz, $^2J_{\mathrm{Pt–C}}$ = 37 Hz), 28.4 (d, $^2J_{\mathrm{P–C}}$ = 5 Hz, $^3J_{\mathrm{Pt–C}}$ < 19 Hz),[41] 16.9 (d, $^2J_{\mathrm{P–C}}$ = 113 Hz, $^1J_{\mathrm{Pt–C}}$ = 683 Hz), −23.4 (d, $^2J_{\mathrm{P–C}}$ = 4 Hz, $^1J_{\mathrm{Pt–C}}$ = 748 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz, 298 K) δ 105.3 ($^1J_{\mathrm{Pt–P}}$ = 2080 Hz). Anal. Calcd For C$_{15}$H$_{29}$N$_2$PPt: C, 38.87; H, 6.31: N, 6.04. Found: C, 38.81; H, 6.33; N, 6.10.

Thermolyses and characterization of thermolyses products

Thermolysis of ($^{t\mathrm{Bu}}$P(O)N)PtMe$_2$ (1) in C$_6$D$_6$ to generate ($^{t\mathrm{Bu}}$P(O)C)PtMe(L) (2-L). In a typical experiment, a medium-walled NMR tube fitted with a ground glass joint was charged with (P(O)N)PtMe$_2$ (2.0–20.0 mg, 0.0043–0.043 mmol) and hexamethylbenzene internal standard. C$_6$D$_6$ (~0.4 mL) was added by vacuum transfer, the tube was flame sealed, and an initial ^{1}H NMR spectrum was recorded. The tube was then submerged in an oil bath at 100 °C for four days, monitored daily by ^{1}H NMR spectroscopy. There was no visual change in the appearance of the solution during heating and the rollover cyclometalation product **2-L** formed in approximately 80% yield (^{1}H NMR integration *vs.* hexamethylbenzene internal standard). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K) δ 7.99 (br), 6.48 (br), 1.45 (m, br), 0.77 (br), 0.16 (s, CH$_4$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz, 298 K) δ 159 (br, $^1J_{\mathrm{Pt–P}}$ = ~4400 Hz).

Generation of ($^{t\mathrm{Bu}}$P(O)C)PtMe(pyr-*d*$_5$) (2-pyr-*d*$_5$). The volatiles from a solution of **2-L** in C$_6$D$_6$ (prepared as described above) were removed *in vacuo* and pyridine-*d*$_5$ was added by vacuum transfer. ^{1}H NMR (pyridine-*d*$_5$, 500 MHz, 298 K) δ 8.22 (d, 1H), 7.07 (d, 1H), 6.76 (t, 1H), 1.44 (d, 18H, $^3J_{\mathrm{P–H}}$ = 15 Hz), 0.53 (s, $^2J_{\mathrm{P–H}}$ = 46 Hz).[42] ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz, 298 K) δ 147.5 ($^1J_{\mathrm{Pt–P}}$ = 4272 Hz).

Synthesis of ($^{t\mathrm{Bu}}$P(O)C)PtMe(CN*t*Bu) (2-CN*t*Bu). A solution of **2-L** in C$_6$D$_6$ (prepared as described above) was treated with 1 equiv. *tert*-butylisonitrile to generate (**2-CN*t*Bu**) in approximately 80% yield from **1** (^{1}H NMR integration *vs.* hexamethylbenzene internal standard). Analytically pure material was obtained by allowing the solvent to evaporate from an NMR sample then adding pentane to the residue and vigorously stirring the suspension before carefully removing the supernatant by pipette. X-ray quality crystals were obtained by slow evaporation of a benzene–pentane solution of ($^{t\mathrm{Bu}}$P(O)C)PtMe(CN*t*Bu). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K) δ 8.42 (d(d), 1H, $^3J_{\mathrm{Pt–H}}$ = 38 Hz), 8.34 (m, 1H), 6.82 (d(d), 1H), 1.29 (d, 18H, $^3J_{\mathrm{P–H}}$ = 15 Hz), 1.08 (d, 3H, $^3J_{\mathrm{P–H}}$ = 4 Hz, $^2J_{\mathrm{Pt–H}}$ = 54 Hz), 0.84 (s, 9H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz, 298 K) δ 176.3 (d, $^2J_{\mathrm{P–C}}$ = 13 Hz), 148.5 (d, $^3J_{\mathrm{P–C}}$ = 3 Hz, $^2J_{\mathrm{Pt–C}}$ = 38 Hz), 144.2, 142.6 (d, $^3J_{\mathrm{P–C}}$ = 10 Hz), 132.1, 119.4 ($^4J_{\mathrm{Pt–C}}$ = 29 Hz), 57.4, 40.1 (d, $^1J_{\mathrm{P–C}}$ = 28 Hz, $^2J_{\mathrm{Pt–C}}$ = 68 Hz), 29.9, 28.3 (d, $^2J_{\mathrm{P–C}}$ = 5 Hz, $^3J_{\mathrm{Pt–C}}$ = 18 Hz), −17.2 (d, $^2J_{\mathrm{P–C}}$ = 8 Hz, $^1J_{\mathrm{Pt–C}}$ = 406 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz, 298 K) δ 155 ($^1J_{\mathrm{Pt–P}}$ = 3452 Hz). Anal. Calcd For C$_{19}$H$_{33}$N$_2$OPPt: C, 42.93; H, 6.26: N, 5.27. Found: C, 42.82; H, 6.14; N, 5.21.

Thermolysis of ($^{t\mathrm{Bu}}$P(N–H)N)PtMe$_2$ (3) in C$_6$D$_6$ (or C$_6$H$_6$). In a typical experiment, a medium-walled NMR tube fitted with a ground glass joint was charged with **3** (1.0–10.0 mg, 0.0021–0.021 mmol) and hexamethylbenzene internal standard. C$_6$D$_6$ (or C$_6$H$_6$) (~0.4 mL) was added by vacuum transfer, the tube was flame sealed, and an initial ^{1}H NMR spectrum was recorded. The tube was then submerged in an oil bath at 100 °C for four days and was examined daily by ^{1}H NMR spectroscopy. During heating the solution changed from colorless to pale yellow.

Spectroscopic data for ($^{t\mathrm{Bu}}$P(N–H)N)PtMePh (4). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K) δ 8.46 (dd, 1H, $^3J_{\mathrm{Pt–H}}$ = 21 Hz), 8.10 (m, 2H), 7.47 (m, 2H), 7.23 (t, 1H), 6.76 (t, 1H), 5.87 (d, 1H), 5.72 (m, 1H), 4.59 (br), 1.60 (d, 3H, $^3J_{\mathrm{P–H}}$ = 6 Hz, $^2J_{\mathrm{Pt–H}}$ = 88 Hz), 1.13 (d, 18H, $^3J_{\mathrm{P–H}}$ = 14 Hz). ^{13}C chemical shifts obtained by HMQC (C$_6$D$_6$, ^{1}H: 500 MHz, ^{13}C: 126 MHz, 298 K) δ 150, 138, 137, 128, 123, 115, 109, 28, −23. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121 MHz, 298 K) δ 102.2 ($^1J_{\mathrm{Pt–P}}$ = 1980 Hz). ^{1}H NMR (pyridine-*d*$_5$, 500 MHz, 298 K) δ 8.54 (d, 1H), 7.43 (t, 1H), 7.06 (d, 1H), 6.24 (t, 1H), 4.97, 1.45 (d, 18H, $^3J_{\mathrm{P–H}}$ = 14 Hz), Pt–Me not observed in pyridine-*d*$_5$. ^{31}P{^{1}H} NMR (pyridine-*d*$_5$, 121 MHz, 298 K) δ 104.2 ($^1J_{\mathrm{Pt–P}}$ = 2018 Hz).

Generation and characterization of ($^{t\mathrm{Bu}}$P(N–H)C)PtMe(pyr-*d*$_5$) (5-pyr-*d*$_5$). Following the thermolysis of **3** (as described above) the volatiles were removed *in vacuo* and pyridine-*d*$_5$ was added by vacuum transfer. ^{1}H NMR (pyridine-*d*$_5$, 500 MHz, 298 K) δ 7.22 (observed by COSY), 7.01 (d, 1H), 5.85 (t(d), 1H), 4.97, 1.52 (d, 18H, $^3J_{\mathrm{P–H}}$ = 14 Hz), 0.87 (s, 3H, $^2J_{\mathrm{Pt–H}}$ = 69 Hz).[42] ^{31}P{^{1}H} NMR (pyridine-*d*$_5$, 121 MHz, 298 K) δ 87.1 ($^1J_{\mathrm{Pt–P}}$ = 3907 Hz).

Synthesis of ($^{t\mathrm{Bu}}$P(N)N)PtMe(pyr) (6). A 5.0 mL standard solution was prepared containing **3** (39.8 mg, 0.0861 mmol), pyridine (34.6 μL, 0.433 mmol, 5.0 equivalents compared to **3**), and dioxane as an internal standard (3.7 μL, 0.043 mmol) in C$_6$D$_6$. Four medium-walled NMR tubes fitted with Teflon stopcocks were each charged with 0.5 mL of this solution and additional pyridine (3.4 μL, 13.8 μL, and 31.1 μL) was added to three of the tubes (yielding 10, 25, and 50 equivalents of pyridine compared to **3**). Initial spectra were taken, showing shifts in the resonances for **3**, the most pronounced being a downfield shift for the N–H proton. The tubes were heated in a 100 °C oil bath for 3 days, yielding **6** (86–96% yield by ^{1}H NMR integration *versus* the dioxane standard). ^{1}H NMR for **6**: (C$_6$D$_6$, 300 MHz) δ 8.16 (dt, 6.64, 2H), 7.29 (d, 1H), 6.97 (q, 1H), 6.78 (dt, 1H), 6.63 (tt, 1H), 6.32 (dd, 2H), 5.67 (td, 1H), 1.61 (d, $^3J_{\mathrm{P–H}}$ = 13.4 Hz, 18H), 0.95 (d, $^3J_{\mathrm{P–H}}$ = 0.7 Hz, $^2J_{\mathrm{Pt–H}}$ = 69.9 Hz,

Table 1 Crystallographic data for **1**, **2-CN*t*Bu**, **3**, and **6**

Chemical reference	**1**	**2-CN*t*Bu**	**3**	**6**
Chemical formula	$C_{15}H_{28}NOPPt$	$C_{19}H_{33}N_2OPPt$	$C_{15}H_{29}N_2PPt$	$C_{39}H_{66}Cl_2N_6O_2P_2Pt_2$
Formula mass	464.44	531.53	463.46	1174.00
Temperature	100(2)	100(2) K	130(2) K	130(2) K
Wavelength	0.71073	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*21/*c*	$P2_1/n$	$P2_1/c$	*C*2/*c*
a/Å	14.183(4)	8.6571(12)	14.4311(4)	30.661(16)
b/Å	8.830(3)	13.566(2)	8.6437(2)	9.818(12)
c/Å	13.514(4)	18.381(3)	13.5536(3)	17.841(8)
α/°	90	90	90	90
β/°	95.220(13)	98.684(8)	95.8300(10)	122.137(13)
γ/°	90	90	90	90
Unit cell volume/Å^3	1685.4(8)	2133.9(5)	1681.91(7)	4548(6)
No. of formula units per unit cell, *Z*	4	4	4	4
Absorption coefficient, *μ*/mm^{-1}	8.414	6.658	8.428	6.372
No. of reflections measured	29 750	98 592	6896	7882
No. of independent reflections	5412	5412	4063	4116
R_{int}	0.1628	0.0796	0.0517	0.0720
Final R_1 values ($I > 2\sigma(I)$)	0.1115	0.0360	0.0384	0.0473
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.2314	0.0869	0.0788	0.0870
Final R_1 values (all data)	0.1469	0.0553	0.0537	0.0743
Final w$R(F^2)$ values (all data)	0.2456	0.0957	0.0836	0.0942
Goodness of fit on F^2	1.191	1.093	0.998	1.037
CCDC number	996399	996400	996401	996402

3H). ^{31}P NMR (C_6D_6, 121 MHz) δ 86.4 (s, $^1J_{P-Pt}$ = 3921 Hz). HMQC data (C_6D_6, ^{1}H: 500 MHz, ^{13}C: 125.7 MHz): δ 8.16, 150.8; 7.28, 115.8; 6.97, 136.0; 6.78, 143.9; 6.62, 136.7; 6.29, 125.5; 5.97, 105.7; 1.60, 28.7; 0.94, −21.3 (Pt*CH*$_3$ *trans* to N).

Crystallographic details

Parameters related to the structures for **1**, **2-CN*t*Bu**, **3**, and **6** are described in Table 1. The data for **1** and **2-CN*t*Bu** was integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker.[43] The data for **3** and **6** was integrated and scaled using DENZO-HKL Scalepack.[44] Solution by direct methods (SHELXS, SIR97[45]) produced a complete heavy atom phasing model consistent with the proposed structures. The structures were completed by difference Fourier synthesis with SHELXL97.[46,47] Scattering factors are from Waasmair and Kirfel.[48] Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–1.00 Å. Isotropic thermal parameters U_{eq} were fixed such that they were 1.2U_{eq} of their parent atom U_{eq} for CH's and 1.5U_{eq} of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

The structure of **1** was highly disordered. To test the disorder, a solution in P1 was attempted, which showed the same disorder with a Flack parameter of close to 0.5. The data was tested for twinning using Cell_Now[49] and by attempting to add a twin card to the shelex refinement. Some statistical improvement of the structure was achieved by leaving out a larger section of strongly disagreeing data, however, the remaining data is still 96.6% complete to 25 degrees in theta.

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