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[12] Raman spectra of solid samples were measured on a Renishaw Raman Image Microscope System 2000: NaN_3: $\tilde{\nu}_s(N_3)$ 1361 cm^{-1}, $\tilde{\nu}_{as}(N_3)$ inactive; AgN_3: $\tilde{\nu}_s(N_3)$ 1338, $\tilde{\nu}_{as}(N_3)$ 2070 cm^{-1}; $AgN_3 \cdot 2AgNO_3$: $\nu_{as}(N_3)$ 2079, $\nu_s(N_3)$ 1330 cm^{-1}. The Raman spectrum of NaN_3 is consistent with $D_{\infty h}$ symmetry of the azide unit. However, the literature assignment of a linear and symmetrical structure for the azide unit in AgN_3[9] is at variance with the present data, which clearly indicate a linear and asymmetrical structure in both AgN_3 and $AgN_3 \cdot 2AgNO_3$.

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Inter- versus Intramolecular C–H Activation: Synthesis and Characterization of a Novel Platinum–Carbene Complex**

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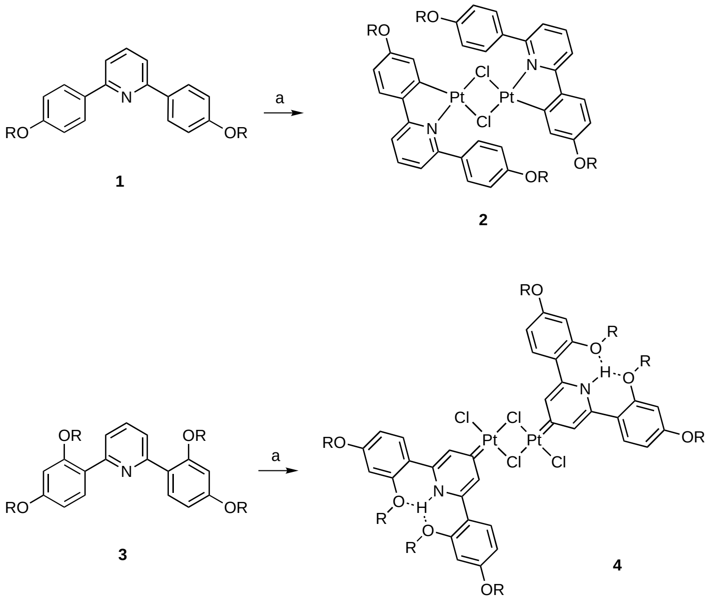
Cyclometalation is a reaction that has been both widely used[1, 2] and widely studied.[3, 4] Typically, the coordinating moiety within a ligand forms a bond to a metal center, and then intramolecular C–H activation takes place to yield a five- or six-membered chelate ring. In the course of our studies, we sought to synthesize a number of cycloplatinated species that would show novel mesogenic behavior. To this end, we have prepared a number of 2,6-disubstituted pyridines, such as **1** and **3** (Scheme 1), and allowed them to react with potassium tetrachloroplatinate under normal cycloplatination conditions.[5] When we used pyridine **1** we isolated the expected cycloplatinated product **2**, formed by coordination of the pyridine followed by intramolecular C–H activation, in high yield. However, when we used pyridine **3** we isolated a very different product. The only product isolated (indeed, the only product observed in the crude reaction mixture) was that which forms from the intermolecular activation of a C–H bond, that is, **4**. Complex **4** was isolated in reasonable yield and analyzed by ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction.



Scheme 1. Synthesis of **2** and **4**. a) $K_2[PtCl_4]$, acetic acid. $R = n\text{-}C_6H_{13}$.

The X-ray crystal structure of **4** shows a number of interesting features (Figure 1). A crystallographically imposed center of symmetry exists between the two platinum and two chlorine atoms (Cl1) to give a flat rectangle, with the other two chlorine atoms (Cl2) only 0.082(4) Å out of this plane. The nitrogen-containing ring is at an angle of 38.62(24)° to the plane defined by the Pt_2Cl_2 rectangle. Two extremes for the bonding of this organic fragment to this rectangle are illustrated in Scheme 2. The Pt–C bond length of 1.951(9) Å is very similar to the values observed for the Pt^0–carbene complex derived from 1,3-dimesitylimidazol-2-ylidene (1.959(8) and 1.942(8) Å).[6] It is also similar to the length of 1.973(11) Å for the cationic Pt^{IV}–carbene complex $[PtCl_2\{C(NHMe)(NHC_6H_4Cl)\}(PEt_3)_2]ClO_4$,[7] and significantly shorter than that in the non-carbene cycloplatinated species $[\{PtCl(tBu_2PCMe_2CH_2)\}_2]$ (2.062(6) Å)[8] or Pt^{II}–C_{aryl} single bond lengths of 1.98–2.02 Å in arylplatinum complexes.[9, 10] Two shorter Pt–C bonds have been reported: a bond length of 1.82(6) Å for the platinum–carbene complex $[\{PtCl(tBuCH_2COiPr)\}_2]$[11] (though given the relatively large estimated standard deviations associated with this measurement, this value is not significantly different from ours), and a

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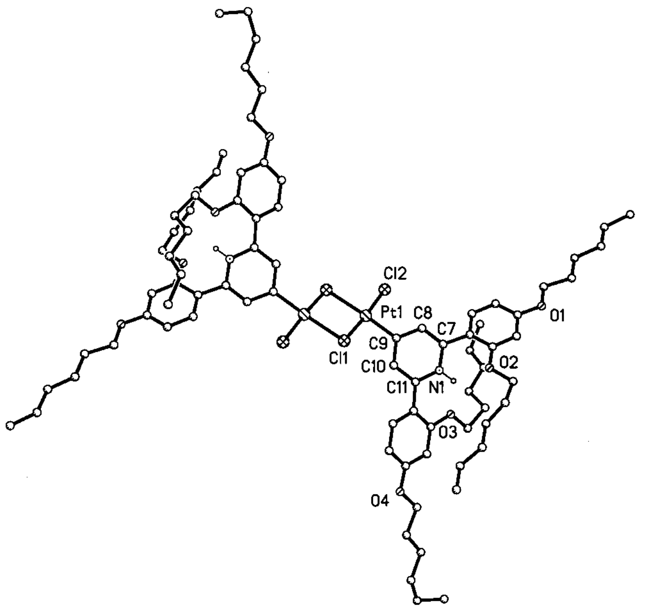
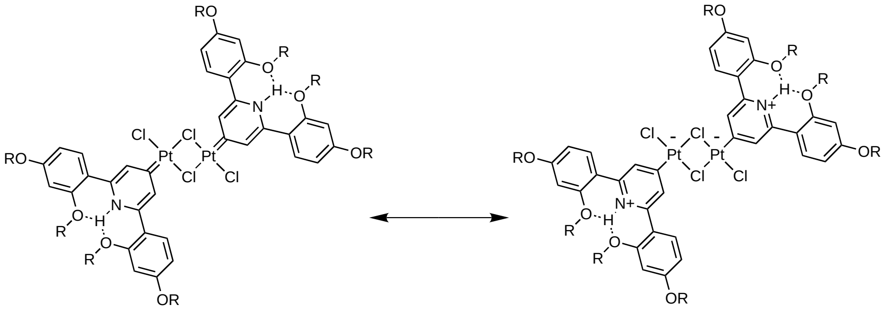


Figure 1. The crystal structure of **4**. Selected bond lengths [Å] and angles [°]: Pt1–C9 1.951(9), Pt1–Cl2 2.281(2), Pt1–Cl1 2.320(2), Pt1–Cl1′ 2.448(2), N1–C7 1.352(10), N1–C11 1.361(10), C7–C8 1.362(10), C8–C9 1.408(10), C9–C10 1.401(10), C10–C11 1.389(10); C9-Pt1-Cl2 91.2(3), C9-Pt1-Cl1 92.4(2), Cl2-Pt1-Cl1 175.86(8), C9-Pt1-Cl1′ 176.8(2), Cl2-Pt1-Cl1′ 91.56(7), Cl1-Pt1-Cl1′ 84.85(7), Pt1-Cl1-Pt1′ 95.155(7), C7-N1-C11 123.7(7), N1-C7-C8 119.0(8), C7-C8-C9 121.5(8), C10-C9-C8 116.6(7), C10-C9-Pt1 120.7(6), C8-C9-Pt1 122.6(6), C11-C10-C9 122.0(8), N1-C11-C10 117.1(8).



4 **5**

Scheme 2. The carbene **4** and the zwitterion **5** as possible formal structures. $R = n\text{-}C_6H_{13}$.

length of 1.90(1) Å for a sterically constrained Pt–C bond in an NCN tridentate donor.[12] Thus, the short C–Pt bond length would seem to suggest that a carbene structure—that is, **4**—is the correct representation of the structure. Further evidence for this form comes from the ^{13}C NMR spectrum, where a resonance at $\delta = 324.3$ indicates a carbene, and we can discount structure **5** as a possibility.

The proton attached to the nitrogen atom was inserted at a calculated position. The O3–N1 and O2–N1 distances are 2.622(9) and 2.720(8) Å, respectively. These distances are substantially shorter than the sum of the van der Waals radii of O and N (3.07 Å)[13] and thus confirm the presence of a hydrogen-bonding interaction. The O2–O3 distance, at 3.742(9) Å, is longer than the sum of the van der Waals radii, indicating no particular O–O interaction. One of the effects of this hydrogen bonding is to twist both of the phenyl rings to angles of 34.63(29)° (the ring to which O1 and O2 are attached) and 32.79(36)° (the ring to which O3 and O4 are attached) with respect to the nitrogen-containing ring, so that one oxygen atom is below the proton and one above. In the solution ^1H NMR spectrum this proton is very deshielded ($\delta = 12.77$). The positions of the two OR chains that are hydrogen bonded to this proton are locked in the solid state and remain locked in solution, as shown by the unusual proton resonances for these chains (for instance, the terminal methyl groups of these chains appear at $\delta = 0.69$ rather than at the more normal value of $\delta =$ 0.95 for the other chains).

The solution ^1H NMR spectrum of **3** shows no unusual features (in particular, the resonances for the two different OR chains are identical), indicating that there are no unexpected steric restrictions on the conformations. Indeed, our own preliminary studies show that pyridine **3** exhibits a perfectly normal coordination chemistry.[14] On mixing **3** with $K_2[PtCl_4]$ in solution, one would expect that **3** would initially coordinate to the platinum center through the nitrogen atom. Such a coordinated species then has C–H bonds in close proximity that can be activated in an intramolecular fashion, giving rise to a cyclometalated species. All else being equal, the relative reactivity of intramolecular activation, compared with intermolecular activation, based upon the effective concentration, has been estimated at a factor of 10.[3] Thus the exclusive formation of the carbene species that we observe implies that this formation must be a very favorable process, which is presumably assisted by the stabilization offered by the hydrogen-bonded proton. One other feature of complex **4** is its remarkably stability: it melts in air at 246 °C with no decomposition.

Experimental Section

2: 2,6-bis(4-*n*-hexyloxyphenyl)pyridine (**1**; 103 mg, 0.239 mmol) was added to a solution of $K_2[PtCl_4]$ (99 mg, 0.239 mmol) in acetic acid (400 mL). The mixture was stirred at 70 °C for 60 h. The solvent was removed, and the product washed with water. The product was dissolved in chloroform, filtered, washed with hexane, and crystallized from ethyl acetate. Yield: 100 mg (63 %, 0.075 mmol). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.71$ (4H, AA′XX′), 7.70 (2H, t, $^3J = 7.6$ Hz, pyridine), 7.36 (2H, dd, $^3J = 7.6$, $^4J = 1.2$ Hz, pyridine), 7.21 (2H, d, $^3J = 8.5$ Hz, cycloplatinated ring), 7.03 (2H, dd, $^3J = 7.6$, $^4J = 1.2$ Hz, pyridine ring), 6.91 (4H, AA′XX′), 6.60 (2H, dd, $^3J = 8.5$, $^4J = 2.3$ Hz, cycloplatinated ring), 6.46 (2H, d , $^4J =$ 2.3 Hz, cycloplatinated ring), 3.97 (6H, t, $^3J = 6.7$ Hz, OCH_2), 3.86 (6H, t, $^3J = 6.7$ Hz, OCH_2), 1.79 (8H, m, CH_2), 1.44 (24H, m, CH_2), 0.95 (6H, t, $^3J = 7.0$ Hz, CH_3), 0.91 (6H, t, $^3J = 7.0$ Hz, CH_3); elemental analysis: found (calcd): C 52.6 (52.7), H 5.5 (5.5), N 2.2 (2.1).

4: 2,6-bis(2,4-di-*n*-hexyloxyphenyl)pyridine (**3**; 159 mg, 0.260 mmol) was added to a solution of $K_2[PtCl_4]$ (108 mg, 0.260 mmol) in acetic acid (400 mL). The mixture was stirred at 70 °C for 60 h. The solvent was removed, and the product washed with water. The product was dissolved in chloroform, filtered, washed with hexane, and crystallized from acetone. Yield: 84 mg (36 %, 0.047 mmol). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta =$ 12.77 (2H, t, $^4J = 2.1$ Hz, NH), 8.03 (4H, d, $^4J = 2.1$ Hz, pyridine ring), 7.78 (4H, d, $^3J = 8.9$ Hz), 6.64 (4H, dd, $^3J = 8.9$, $^4J = 2.4$ Hz), 6.52 (4H, d, $^4J =$ 2.4 Hz), 4.00 (8H, t, $^3J = 6.4$ Hz, C4-OCH_2), 3.99 (8H, t, $^3J = 5.8$ Hz, C2-OCH_2), 1.80 (8H, m), 1.58 (8H, m), 1.44 (8H, m), 1.34 (24H, m), 1.15 (8H, m), 0.95 (20H, m, CH_2, CH_3 of the non-hydrogen-bonded chain), 0.69 (12H, t, CH_3 of the hydrogen-bonded chain); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 324.3$ (C attached to Pt).

Crystal data for **4**: $C_{82}H_{122}Cl_4N_2O_8Pt_2\cdot Me_2CO$, $M_r = 1853.93$, monoclinic, space group $C2/c$, $a = 32.261(2)$, $b = 15.7989(7)$, $c = 20.0825(9)$ Å, $\beta = 119.867(1)^\circ$, $V = 8876.4(7)$ Å^3, 180(2) K; final $R1$, $wR2$, and S values are 0.052, 0.084, and 1.013 for 454 parameters. Data were collected with a Siemens SMART CCD area-detector diffractometer. Refinement was by full-matrix least squares on F^2 for all data with SHELXL-96.[15] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101757. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Solid-Phase Synthesis and Encoding Strategies for Olefin Polymerization Catalyst Libraries **

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Although the application of combinatorial methods in the pharmaceutical industry is fast becoming an industrial standard for the discovery and optimization of novel drug-based molecules,[1] similar methods aimed towards the identification of new materials and catalysts remain in their infancy.[2] Recent reports have appeared describing the synthesis and screening of libraries of organometallic catalysts for examining a number of transformations.[3] The application of combinatorial methods aimed toward the discovery and optimization of olefin polymerization catalysts is an area that promises to be of major importance especially to the chemical industry, which produces approximately 46 million metric tons of polyolefins annually.[4]

Since most commercial-scale polyolefin processes employ supports with high surface areas for immobilizing olefin polymerization catalysts, it is somewhat surprising that few reports have appeared examining the use of polystyrene as a catalyst support.[5] Fréchet and co-workers have recently shown that suitably modified cross-linked polystyrene can function as an efficient activator for catalysts based on Group 4 metallocenes.[6] Polystyrene with low cross-linking not only acts as a more chemically compatible support relative to silica, but also provides a "solutionlike" environment that more closely resembles the environment in which homogeneous metallocene catalysts function. In addition, a plethora of solid-phase synthetic methodologies have appeared in recent years, providing a broad knowledge base which should facilitate efforts in the field of olefin polymerization catalysis.[7]

Recent reports have shown that certain catalysts based on complexes of late transition metals with diimines exhibit olefin polymerization activities comparable to those found for early transition metal single-site metallocene-based systems.[8] These systems offer advantages over their early transition metal counterparts in that they are easily synthesized and provide a broader range of functional-group compatabilities.[9] Herein we report the first example of a combinatorial approach to the parallel synthesis of a 1,2-diimine library complexed with Ni^{II} and Pd^{II} as olefin polymerization catalysts using 1% cross-linked polystyrene as a solid support. Specifically, a general synthetic methodology has been developed that allows for the parallel synthesis and screening of ethylene polymerization catalyst libraries in a spatially addressable format.[10] Furthermore, we have discovered that it is possible to apply chemical encoding techniques to these catalysts and distinguish catalyst performance trends. Since steric bulk on the aryl rings has been shown to play a dramatic role on polymer yield and molecular weight (M_w) for these catalytic systems, we chose to synthesize aryl-substituted 1,2-diimine complexes of Ni^{II} and Pd^{II} on 1% cross-linked polystyrene. In addition, we sought to examine how electronic perturbations may affect catalyst performance.

Our synthetic approach began with a regioselective alkylation of the unsymmetrical 1,2-diimine **1** with bromomethyl polystyrene (1.05 equiv of lithium diisopropylamide (LDA), 0°C, THF) to give the polystyrene-grafted 1,2-diimine ligand **2** (Scheme 1).[11] To incorporate a variety of functionalized aryl-substituted 1,2-diimines, a divergent approach was explored starting from diketone resin **3**, which was obtained in high yield (> 95% based on recovered 2,4,6-trimethylaniline) from the hydrolysis of 1,2-diimine resin **2** with oxalic acid in THF/H_2O (5/1 v/v) at 70°C for 12 h. This transformation was monitored by single-bead FT-IR spectroscopy ($\tilde{\nu} = 1635$ (C=N), 1712 cm^{-1} (C=O)).

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