1024 *Organometallics* **2001,** *20,* 1024−1027

Toward Organometallic Polymers with High Directionality Containing Bis-*ortho*-Chelating Ligands

Stephan Back,[†,‡] Martin Albrecht,[†] Anthony L. Spek,[§] Gerd Rheinwald,[‡]
Heinrich Lang,*[,‡] and Gerard van Koten*[,†]

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, Technische Universität Chemnitz, Institut für Chemie, Lehrstuhl Anorganische Chemie, Strasse der Nationen 62, 09111 Chemnitz, Germany, and Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received July 24, 2000

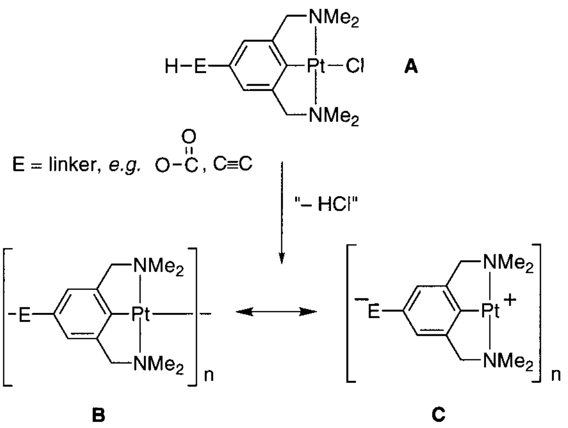
Summary: The preparation and structure of the rigid rod-like platinum monoacetylide $\{Pt\}C{\equiv}C\text{-}4\text{-}C_6H_2I\text{-}1\text{-}(CH_2NMe_2)_2\text{-}2,6)$ $(\{Pt\} = [Pt(C_6H_3\{Me_2NCH_2\}_2\text{-}2,6)])$ *are described. Its oxidative addition to* $Pd(dba)_2$ *yields a heterobinuclear* $\{Pt\}C{\equiv}C\{Pd\}I$ *complex* $(\{Pd\} = [Pd(-4\text{-}C_6H_2\{Me_2NCH_2\}_2\text{-}2,6)]^+)$*; this provides a new strategy for the controlled and stepwise construction of rigid rod-like metallopolymers.*

Introduction

The chemistry and coordination behavior of metal complexes of the monoanionic, potentially tridentate coordinating NCN pincer ligand system (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$)[1] and related tridentate phosphino or sulfido derivatives have been explored thoroughly for a large number of different metal ions.[2] This ligand is able to stabilize unusual oxidation states of group 10 metal centers, e.g., a Ni(III) center in the Kharasch addition reaction.[3] Moreover, the carbon-to-metal σ-bond in, for example, [PtCl(NCN)] (complex **1**; abbreviated as {Pt}Cl) has been shown to be stable toward hydrolysis by water and dilute acids.[4]

Functionalization of the pincer ligand at the *para*-position relative to the metal-bound carbon allows for the construction of macromolecules with more than one metal atom.[5] In addition, this approach provides access to hydrogen-bonded molecular structures exhibiting a directional vector imposed by the ligand architecture and the metal coordination geometry, e.g., using square-planar d^8 metal centers.[6] Such structures (cf. **A**, Scheme 1) may function as models for electronic conduction along π-conjugated organometallic chains[7] or as complexes with high hyperpolarizabilities,[8] since the metal center is held in direct proximity to the π-conjugated system owing to the rigid complexation by the NCN ligand.

Scheme 1



Self-condensation, i.e., formal loss of HCl from complexes of type **A**, can be considered a promising strategy to construct long-chain molecules (ideally polymers) which are bound either covalently (type **B**, Scheme 1) or via ionic interactions (type **C**). Related bimetallic complexes containing nondirectional bis-NCN type linkers between the metal centers were demonstrated to transmit electronic information along their π-conjugated organic systems.[5d,9]

---

* Corresponding authors. E-mail: g.vankoten@chem.uu.nl; heinrich.lang@chemie.tu-chemnitz.de.

[†] Debye Institute, Utrecht University.

[‡] Universität Chemnitz.

[§] Bijvoet Center, Utrecht University.

(1) (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751.

(2) For examples see: (a) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317. (b) Loeb, S. J.; Shimizu, G. K. H.; Wisner, J. H. *Organometallics* **1998**, *17*, 2324. (c) Vigalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 895.

(3) See, for example: (a) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423. (b) Kleij, A. W.; Kleijn, H.; Jastrzebski, J. T. B. H.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 277.

(4) (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (b) Albrecht, M.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Chem. Eur J.* **2000**, *6*, 1431.

(5) (a) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659. (b) Davies, P. J.; Grove, D. M.; van Koten, G. *Organometallics* **1997**, *16*, 800. (c) Albrecht, M.; van Koten, G. *Adv. Mater.* **1999**, *11*, 171. (d) Lagunas, M. C.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Eur. J. Inorg. Chem.* **1998**, 163. (e) Steenwinkel, P.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 5647.

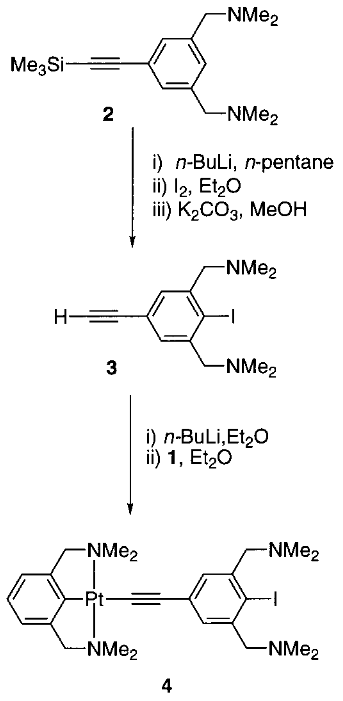
(6) (a) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, accepted. (b) Davies, P. J.; Veldman, N.; Grove, D. M.; Spek, A. L.; Lutz, B. T. G.; van Koten, G. *Angew. Chem.* **1996**, *108*, 2078; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1956. (c) James, S. L.; Verspui, G.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1996**, 1309.

(7) See for example: (a) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477. (b) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. (c) Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 99. (d) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775.

(8) (a) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (b) Sponsler, M. B. *Organometallics* **1995**, *14*, 1920.

10.1021/om000636z CCC: $20.00

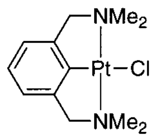
Scheme 2



Hitherto, only reports dealing with the preparation of symmetric, nondirectional organometallic polymers have appeared.[10] Moreover, to the best of our knowledge, direct approaches to well-defined oligomers or polymers of structural type **C** are not known. Therefore, we have developed a stepwise synthesis of such complexes having a directionality vector along the organometallic chain. Preliminary studies showed that the platinum–acetylide σ-bond in, for example, $\{Pt\}C{\equiv}CSiMe_3$ is easily cleaved in the presence of halide sources, such as $[CuCl]_n$ or $[N^nBu_4]Cl$.[11] Thus, the well-known Cu(I)-mediated reactions for the synthesis of Pt(II) acetylides[12] are not feasible options for the consecutive construction of type **B** structures. Hence, the synthesis of a NCN ligand system that includes two chemically different reactive sites was necessary in order to enable the easy and controlled chemoselective formation of type **B** structures.

Results and Discussion

Preparation and Solid State Structure of 4-Ethynyl-2,6-bis(dimethylamino)methyl-1-iodobenzene (3). C_6H_2I-1-$(CH_2NMe_2)_2$-2,6-$(C{\equiv}CH)$-4 (**3**) has been obtained by selective 4-lithiation of $C_6H_3(CH_2NMe_2)_2$-3,5-$(C{\equiv}CSiMe_3)$-1 (**2**), followed by titration of the resulting lithium derivative with an ethereal iodine solution and subsequent reaction with a solution of K_2CO_3 in MeOH (Scheme 2). The IR spectrum of **3** showed stretching vibrations ($\nu_{\equiv CH}$ = 3292 cm^{-1} and $\nu_{C\equiv C}$ = 2106 cm^{-1}) which are typical of phenylacetylene derivatives.[13]



1

Figure 1. Platinum pincer complex **1**.

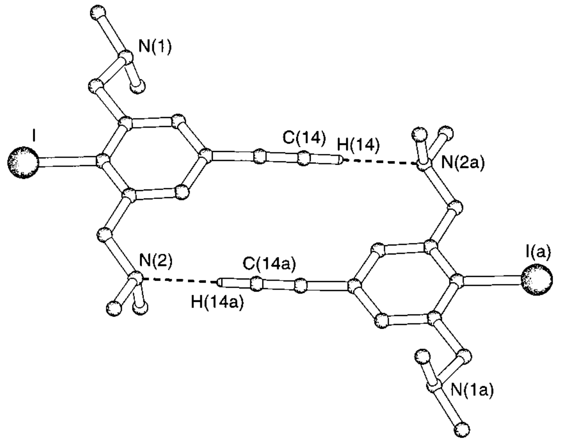


Figure 2. Molecular structure of **3** showing the presence of hydrogen-bonded molecular dimers in the solid state: C(14)–H(14) 0.950 Å, H(14)···N(2a) 2.401 Å, C(14)···N(2a) 3.296(3) Å; C(14)–H(14)···N(2a) 156.69°.

Orange-red crystals of **3** were grown by cooling a *n*-pentane solution of **3** to −30 °C. The molecular structure of **3** has been determined by single-crystal X-ray diffraction analysis.

The CH_2NMe_2 groups point away from the iodine, and the nitrogen lone pair of the NMe_2 group is directed toward the acetylenic proton of a coplanar neighboring molecule of **3** (Figure 2), suggesting intermolecular C–H···N hydrogen bonding (H(14)···N(2a) 2.401 Å, C(14)–H(14)···N(2a) 156.7°). The hydrogen-bonded dimeric units display a ladder-type orientation which is mediated by weak intermolecular halogen–halogen interactions (I···I 3.7273(11) Å). This I···I distance is shorter than the sum of the van der Waals radii (4.3 Å), but substantially longer than the bond distance in molecular iodine (2.66 Å) and corresponds well with the average value of the intermolecular I···I separation in crystalline I_2.[14] The packing motif of compound **3** is similar to that of 4-X-ethynylbenzene derivatives (X = Cl, Br, I).[15] All other structural details of molecule **3** are similar to those of iodo aryl compounds[16] and/or aromatic acetylenes reported earlier.[6,14,17]

Preparation and Structural Characterization of $\{Pt\}C{\equiv}C$-4-C_6H_2I-1-$(CH_2NMe_2)_2$-2,6 and Its Reac-

---

[9] Back, S.; Gossage, R. A.; Lang, H.; van Koten, G. *Eur. J. Inorg. Chem.* **2000**, 1457.

[10] See for example: (a) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319. (b) Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagihara, N. *J. Polymer Sci.* **1982**, *20*, 565. (c) Markwell, R. D.; Butler, I. S.; Kakkar, A. K.; Khan, M. S.; Al-Zakwani, Z. H.; Lewis, J. *Organometallics* **1996**, *15*, 2331. (d) Puddephatt, R. J. *Chem. Commun.* **1998**, 1055.

[11] Back, S.; Gossage, R. A.; Lutz, M.; del Río, I.; Spek, A. L.; Lang, H.; van Koten, G. *Organometallics* **2000**, *19*, 3296.

[12] (a) Cross, D. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987. (b) Porter, P. L.; Guha, S.; Kang, K.; Frazier, C. C. *Polymer* **1991**, *32*, 1756. (c) Osakada, K.; Sakata, R.; Yamamoto, T. *Organometallics* **1997**, *16*, 5354.

[13] See for example: (a) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489. (b) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

[14] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984.

[15] Weise, H.-C.; Boese, R.; Smith, H. L.; Haley, M. M. *Chem. Commun.* **1997**, 2403.

[16] Hinchcliff, A.; Munn, R. W.; Pritchard, R. G.; Spicer, C. J. *J. Mol. Struct.* **1985**, *130*, 93.

[17] García, J. G.; Asfaw, B.; Rodriguez, A.; Fronczek, F. *Acta Crystallogr.* **1998**, *C54*, 489, and references therein.

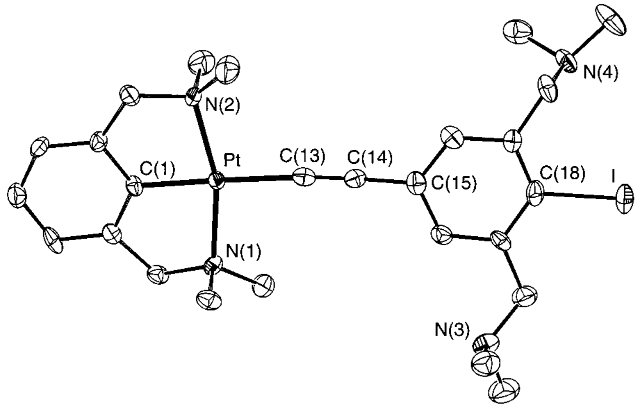
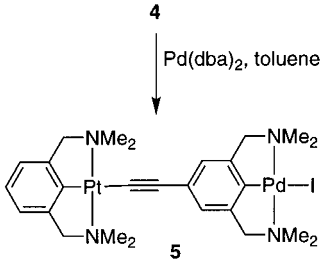


Figure 3. ORTEP view (50% probability) of the platinum acetylide **4** with the adopted numbering scheme. Selected bond distances (Å) and angles (deg): Pt−C(1) 1.942(7), Pt−C(13) 2.061(7), Pt−N(1) 2.077(5), Pt−N(2) 2.088(5), C(13)−C(14) 1.195(10), C(14)−C(15) 1.438(9), C(18)−I 2.118(7); C(1)−Pt−C(13) 178.3(3), C(1)−Pt−N(1) 81.6(3), C(1)−Pt−N(2) 80.9(3), N(1)−Pt−N(2) 162.5(2), N(1)−Pt−C(13) 96.8(2), N(2)−Pt−C(13) 100.7(3), Pt−C(13)−C(14) 170.6(7), C(13)−C(14)−C(15) 175.5(8).

tion with Pd(dba)$_2$. Selective deprotonation of the acetylenic moiety in the ligand precursor **3** without affecting the carbon−halide bond was accomplished by using *n*-BuLi at −78 °C (Scheme 2). The lithium acetylide was treated in situ with platinum complex {Pt}Cl (**1**), thus affording the rigid rod-like platinum acetylide [{Pt}C≡C-4-C_6H_2I-1-(CH_2NMe_2)$_2$-2,6] (**4**). All spectroscopic data (IR, ^{1}H NMR, ^{13}C{^{1}H} NMR) of **4** are in accordance with the proposed structure and compare well with the values recently reported for similar platinum-bound acetylides.[12]

By cooling a toluene solution of **4** to −30 °C, single crystals were obtained which were suitable for an X-ray crystal structure determination. The solid state structure of **4** is given in Figure 3. The platinum center is held in a distorted square-planar environment with the σ-acetylide ligand in a position *trans* to C_{ipso} of the η^3-*N*,*C*,*N* bonded aryldiamine ligand. This coordination geometry is typical for molecules containing a NCN−Pt entity.[4,6] The Pt−C(13) bond length of 2.061(7) Å is within the range of reported Pt σ-acetylide distances.[18] The C≡C triple bond (C(13)−C(14) 1.195(10) Å) is slightly longer than in the nonmetalated acetylene **3** (1.183(3) Å), which corresponds with a shift of the $\nu_{C\equiv C}$ stretching vibration band to lower wavenumbers (cf. Experimental Section). As expected, the π-conjugated organometallic system in **4** is nearly linearly arranged and therefore represents a rigid rod-like building block for the preparation of polymeric materials containing transition metals interconnected by directional linkers. The aromatic rings are tilted by only 12.9(3)° relative to each other, which is essential for electronic communication and a direct consequence of the acetylenic spacer. In bisaryl platinum systems, which lack such a C_2 fragment, this angle is typically larger than 75° and, therefore, any π-conjugation is interrupted. Interestingly, the C_{sp}−C_{sp^2} and C−I bond lengths (C(14)−C(15) 1.438(10) Å, C(18)−I 2.118(7) Å) are both very close to the values found in the metal-free acetylene **3**, suggesting a minimal influence of the platinum center on the carbon−iodide bond.

Scheme 3



Preparation of Binuclear {Pt}C≡C{Pd}I (5) ({Pd} = [Pd(−4-C_6H_2{CH_2NMe_2}$_2$-2,6)]$^+$). Treatment of the Pt−acetylide **4** with an equimolar amount of Pd(dba)$_2$[19] (dba = dibenzylideneacetone) at 25 °C leads to the insertion of a Pd atom into the C−I bond (Scheme 3).[3] Formation of the heterobimetallic complex {Pt}C≡C{Pd}I (**5**) ({Pd} = [Pd(−4-C_6H_2{CH_2NMe_2}$_2$-2,6)]$^+$) is indicated by ^{1}H NMR spectroscopy, which clearly reveals a downfield shift of the resonances of the protons of the CH_2NMe_2 groups upon coordination to the Pd(II) center. The singlets for the NMe_2 groups are located at 2.95 ppm in **5** (cf. 2.25 ppm in **4**), and the signal of the benzylic protons is shifted from 3.43 ppm (in **4**) to 3.91 ppm. Similar effects are also observed in the ^{13}C{^{1}H} NMR spectrum of **5**. The resonance of C(1) is diagnostic and shifts from 107.0 ppm (**4**, bound to iodide) to 160.7 ppm (**5**, bound to palladium). In the IR, the C≡C stretch vibration ($\nu_{C\equiv C}$ = 2075 cm^{-1}) in **5** is virtually identical with that observed for **4**.

Conclusions

The NCN-type ligand C_6H_2I-1-(CH_2NMe_2)$_2$-2,6-(C≡CH)-4 (**3**), containing two different reactive sites, has been synthesized. In the solid state, this molecule forms a β-type network stabilized by I···I interactions and C−H···N hydrogen bonding. The attachment of **3** to a {Pt} terminal unit leads to the formation of the rigid rod-like Pt−acetylide **4**. The crystal structure of this free NCN−Pt monoacetylide combines features of both NCN−Pt complexes as well as of other Pt−acetylide systems. The presence of a Pt center does not change the structural arrangement of the iodo−NCN fragment. Further, oxidative addition of **4** to a Pd(0) moiety yields the heterobinuclear Pt−Pd complex **5** and thus provides a good strategy for the controlled and stepwise construction of rigid rod-like metallopolymers.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by distillation from sodium/benzophenone ketyl; *n*-pentane was purified by distillation from CaH_2. All NMR spectra were recorded at 298 K (^{1}H NMR at 300 MHz, ^{13}C-{^{1}H} NMR at 75 MHz). Chemical shifts (δ) are reported in ppm (*J* in Hz) and referenced to $SiMe_4$. FAB mass spectra were recorded at the Department of Mass Spectrometry, Bijvoet Center, Utrecht University. Melting points are uncorrected. Microanalyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr, Germany.

---

[18] See for example: (a) Sebald, A.; Stader, C.; Wrackmeyer, B. *J. Organomet. Chem.* **1986**, *311*, 233. (b) Kowalski, M. H.; Arif, A. M.; Stang, P. J. *Organometallics* **1988**, *7*, 1227.

[19] Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 134.

The starting materials {Pt}Cl (**1**),[4] $Pd(dba)_2$,[19] and C_6H_3-$(CH_2NMe_2)_2$-2,6-($C\equiv CSiMe_3$)-4 (**2**)[6] were prepared according to published procedures. All other chemicals were obtained commercially and used as received.

C_6H_2I-1-$(CH_2NMe_2)_2$-2,6-($C\equiv CH$)-4 (3). To a *n*-pentane solution (150 mL) of **2** (2.17 g, 7.5 mmol) was added *n*-BuLi (1.6 molar in hexane, 6.1 mL, 9.8 mmol) at −78 °C. After gradual warming to 25 °C (12 h), the reaction mixture was concentrated and the residue dissolved in Et_2O (20 mL). An ethereal solution of I_2 (2.5 g, 9.8 mmol in 100 mL) was slowly added until a brown color persisted. The reaction mixture was extracted with aqueous HCl (10%, 4 × 10 mL). After washing with Et_2O (3 × 50 mL), the combined aqueous phases were basified to pH > 12 using a 5% NaOH solution and extracted with Et_2O (3 × 50 mL). The combined ethereal extracts were dried over $MgSO_4$ and filtered, and the Et_2O was evaporated in vacuo to yield a brown oil. This was transferred to a solution of K_2CO_3 in MeOH (1.0 g, 7.2 mmol, 100 mL). After stirring for 5 h at 25 °C, all volatiles were removed in vacuo, and the residue was extracted with *n*-pentane (3 × 50 mL). Evaporation of the combined extracts gave **3** (2.18 g, 85% yield based on **2**) as a brown oil, which solidified upon standing.

Mp: 52 °C. IR (NaCl): 2106 cm^{-1} (s; $\nu_{C\equiv C}$), 3292 cm^{-1} (s; $\nu_{\equiv CH}$). ^1H NMR ($CDCl_3$): δ 2.31 (s, 12 H, NMe_2), 3.09 (s, 1 H, $\equiv CH$), 3.49 (s, 4 H, CH_2), 7.41 (s, 2 H, $C_{aryl}-H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 45.5 (NMe_2), 68.8 (CH_2), 77.8 ($C\equiv CH$), 83.0 ($C\equiv CH$), 121.5 (C_{aryl}), 131.5 (C_{aryl}), 132.1 ($C_{aryl}-H$), 142.3 (C_{aryl}). FAB-MS: *m*/*z* (rel int) 343 (100) $\{[M + H]^+\}$, 341 (40) $\{[M - H]^+\}$, 215 (40) $\{[M + H]^+ - HI\}$, 128 (30) $\{[HI]^+\}$ 58 (50) $\{[C_3H_8N]^+\}$. Anal. Calcd for $C_{14}H_{19}IN_4$ (342.22): C, 49.14; H, 5.60; N, 8.11. Found: C, 49.24; H, 5.63; N, 8.11.

{Pt}$C\equiv CC_6H_2I$-4-$(CH_2NMe_2)_2$-3,5 (4). To a Et_2O solution (150 mL) of $LiC\equiv CC_6H_2I$-4-$(CH_2NMe_2)_2$-3,5 (350 mg, 1.0 mmol) was added **1** (430 mg, 1.0 mmol) at −78 °C. After gradual warming to 25 °C and stirring for 24 h, all volatile materials were removed in vacuo. The resulting residue was extracted with *n*-pentane (5 × 40 mL), and the combined organic pahses were evaporated to dryness, affording **4** (290 mg, 40% yield based on **1**) as a brown solid.

Mp: 140 °C (dec). IR (KBr): 2076 cm^{-1} (s, $\nu_{C\equiv C}$). ^1H NMR ($CDCl_3$): δ 2.25 (s, 12 H, NMe_2), 3.21 (s, $^3J_{HPt} = 39.8$ Hz, 12 H, NMe_2), 3.43 (s, 4 H, CH_2), 4.11 (s, $^3J_{HPt} = 48$ Hz, 4 H, CH_2), 6.8−7.0 (m, 3 H, $C_{aryl}-H$), 6.89 (s, 2 H, $C_{aryl}-H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 45.6 (NMe_2), 56.0 (NMe_2), 69.1 (CH_2), 80.0 (CH_2), 103.3 ($PtC\equiv C$), 107.0 (C_{aryl}), 118.6 ($C_{aryl}-H$), 126.6 (C_{aryl}), 128.0 ($C_{aryl}-H$), 132.4 ($C_{aryl}-H$), 138.2 ($PtC\equiv C$), 141.1 (C_{aryl}), 146.1 (C_{aryl}), 166.6 (C_{aryl}). FAB-MS: *m*/*z* (rel int) 728 (20) $\{[M + H]^+\}$ 727 (15) M^+, 385 (90) $\{[C_{12}H_{19}N_2Pt]^+\}$, 343 (10) $\{[C_{14}H_{16}IN_2]^+\}$. Anal. Calcd for $C_{26}H_{37}IN_4Pt$ (727.60): C, 42.92; H, 5.13; N, 7.70. Found: C, 42.68; H, 5.26; N, 7.60.

{Pt}$C\equiv C${Pd}I (5). To a solution of **4** (70 mg, 0.1 mmol) in toluene (30 mL) was added $Pd(dba)_2$ (55 mg, 0.1 mmol) at 25 °C. After stirring for 48 h, all volatile materials were evaporated. The residue was successively washed with *n*-pentane (2 × 5 mL) and Et_2O (3 × 10 mL) and extracted with CH_2Cl_2 (5 × 10 mL). The combined CH_2Cl_2 extracts were filtered through a pad of Celite and concentrated to 5 mL. Addition of *n*-pentane (30 mL) resulted in a brownish precipitate. Drying in vacuo gave **5** (35 mg, 40% based on **4**).

Mp: >200 °C. IR (KBr): 2075 cm^{-1} (s, $\nu_{C\equiv C}$). ^1H NMR (CD_2Cl_2): δ 2.95 (s, 12 H, NMe_2), 3.18 (s, $^3J_{HPt} = 38.2$ Hz, 12 H, NMe_2), 3.91 (s, 4 H, CH_2), 4.09 (s, $^3J_{HPt} = 46.5$ Hz, 4 H, CH_2), 6.8−7.0 (m, 3 H, $C_{aryl}-H$), 7.06 (s, 2 H, $C_{aryl}-H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 54.1 (NMe_2), 55.4 (NMe_2), 66.9 (CH_2), 80.0 (CH_2), 103.5 ($PtC\equiv C$), 117.8 ($C_{aryl}-H$), 124.7 (C_{aryl}), 127.5 ($C_{aryl}-H$), 131.4 ($C_{aryl}-H$), 137.4 ($PtC\equiv C$), 142.1 (C_{aryl}), 146.1 (C_{aryl}), 160.7 (C_{aryl}), 166.6 (C_{aryl}). FAB-MS: *m*/*z* (rel int) 833 (10) M^+, 448 (20) $\{[C_{14}H_{18}IN_2Pd]^+\}$, 385 (100) $\{[C_{12}H_{19}N_2Pt]^+\}$. Anal. Calcd for $C_{26}H_{37}IN_4PdPt$ (834.02): C, 37.44; H, 4.47; N, 6.72. Found: C, 36.98; H, 4.10; N, 6.38.

Table 1. Crystallographic Data for Complexes 3 and 4

	3	**4**
empirical formula	$C_{14}H_{19}IN_2$	$C_{26}H_{34}IN_4Pt$
fw	342.21	727.59
diffractometer	Enraf Nonius CAD4-T	Bruker SMART CCD
T/K	150	173
cryst syst	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
cryst size/mm	0.63 × 0.38 × 0.38	0.10 × 0.10 × 0.08
cryst color	orange-red	colorless
unit cell dimens		
a/Å	25.6646(10)	12.2857(7)
b/Å	5.8561(17)	11.7091(6)
c/Å	22.8571(18)	19.5948(10)
β/deg	121.537(5)	105.235(1)
V/Å^3	2927.9(9)	2719.7(3)
Z	8	4
D_{calc}/g cm^{-3}	1.553	1.777
μ/mm^{-1} (Mo Kα)	2.170	6.314
abs corr	PLATON (ABSPSI)	PLATON (DELABS)
transmn range	0.86−0.98	0.45−0.65
$(\sin \theta/\lambda)_{max}$/Å^{-1}	0.65	0.68
no. of reflns obsd, measd, unique	8450, 3382, 3011	11597, 6943, 4301
R_{int}	0.035	0.054
no. of params	154	297
R_1[a] obsd/all reflns	0.0219/0.0263	0.0451/0.1002
wR_2[b] all reflns	0.0543	0.0826
S	1.033	0.915
resid density/e Å^{-3}	−0.95 < 0.70	−2.33 < 1.15

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 2\sigma(I)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Single-Crystal X-ray Diffractions. X-ray data were collected on an Enraf-Nonius CAD4-T with rotating anode (**3**) or on a Bruker SMART CCD area detector (**4**), using monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data and details on data collection and refinement are given in Table 1. The structures were solved with Patterson methods (DIRDIF-97[20]) and refined against F^2 of all reflections (SHELXL-97[21]). Non-hydrogen atoms were refined freely with anisotropic displacement parameters, and hydrogen atoms were refined at calculated positions riding on their carrier atoms. Weights were introduced in the last refinement cycles. Neutral atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables of Crystallography*. All other calculations, graphical illustrations, and checking for higher symmetry were performed with the PLATON[22] package.

Acknowledgment. The authors are grateful to the Volkswagenstiftung and Utrecht University for financial support (1.5 year stay of S.B.). We would also like to thank Dr. I. del Río, Dr. R. A. Gossage, and Dr. J. Boersma for valuable discussions.

Supporting Information Available: Full listing of crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000636Z

---

(20) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1997.

(21) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

(22) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2000.