Using ligand exchange reactions to control the coordination environment of Pt(II) acetylide complexes: applications to conjugated metallacyclynes

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Abstract

Ligand exchange of *cis*-bis(diphenylphosphino)ethylene (dppee) with *trans*-$(Ph_3P)_2Pt(C\equiv CR)_2$ easily generates the *cis*-complexes (dppee)$Pt(C\equiv CR)_2$ in 64–95% yield. This transformation is used to convert pyridine-containing macrocycle **7** to its *cis*-analogue **8** and the macrocyclic bipyridine analogue **10** to the unique macrocyclic ligand **11**. X-ray structural characterization of *trans*-complexes **5a** and **5b** and *cis*-complexes **6a** and **6b** are reported, as is the structure of the strained macrocycle **8**.
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1. Introduction

Platinum acetylide complexes such as **1** or **2** are readily available in high yields from the reaction of terminal acetylenes with *cis*- or *trans*-$(R_3P)_2PtCl_2$, respectively [1,2]. With non-chelating phosphine ligands, the stereochemistry of a *cis*-platinum center (**1**) can be achieved if the reaction temperature is kept low ($-10\ ^{\circ}$C). At higher temperatures, isomerization of the *cis*-$(R_3P)_2PtCl_2$ species to the thermodynamically more stable *trans*-complex effectively competes with alkynylation, affording the *trans*-product **2**. Chelating phosphines such as $Ph_2PCH_2CH_2CH_2PPh_2$ can prevent *cis*-*trans* isomerization to give *cis*-acetylides (**1**) [3]. In addition to small molecule complexes, these versatile alkynylation reactions have been exploited for the formation of carbon-rich oligomers [4], polymers [5], macrocycles [6,7], and supramolecular complexes [3]. Furthermore, the reductive elimination by *cis*-platinum-

complexes to generate butadiynes has recently been established, expanding the usefulness of complexes **1** [8].
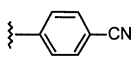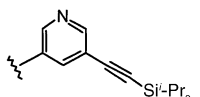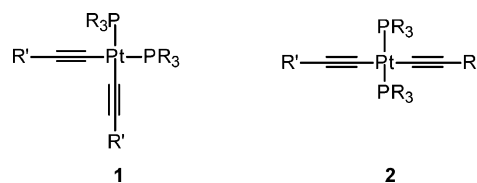

In the interest of generating varied supramolecular building blocks from common precursors, we targeted the conversion of *trans*-acetylides such as **2** to *cis*-acetylides **1** via ligand exchange. We communicate herein the results of this strategy, which has been successfully tested with simple molecular systems such as **5a–c** to generate the *cis*-derivatives **6a–c**. We then applied this methodology to the generation of a strained macrocycle **8** and to the conversion of the bifunctional macrocycle **10** to its *cis*-complex, **11**. The solid state characteristics of the *trans*- and *cis*-complexes are compared via an analysis of the X-ray crystal structures of the $L_2Pt(C\equiv CSi^iPr_3)_2$ and $L_2Pt(C\equiv C-p-CN-C_6H_4)_2$ derivatives **5a/6a** and **5b/6b**, respectively. A discussion of the solid–state structural features of the strained platinacycle **8** is also presented.

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Table 1
Yields and NMR spectroscopic data for compounds **5a–c** and **6a–c**

| Compound	R	5 Yield (%)	6 Yield (%)	5 δ ^{31}P NMR ($^1J_{P-Pt}$, Hz)	6 δ ^{31}P NMR ($^1J_{P-Pt}$, Hz)
a	$-Si^iPr_3$	78	95	21.1 (2719)	52.0 (2208)
b	⌇—⟨benzene⟩—CN	62	91	19.8 (2601)	53.9 (2276)
c	⌇—⟨pyridine⟩—C≡C—Si^iPr_3	76	64	19.9 (2607)	53.9 (2277)

2. Synthesis

trans-Platinum alkynyl complexes **5a–c** were prepared as shown in Scheme 1 [1,2]. The appropriate terminal acetylene **3a–c** was added to a degassed solution of $(PPh_3)_2PtCl_2$ **4** in Et_2NH. A catalytic amount of CuI was then added and the mixture was stirred at 50 °C for a period of 14 h. After work-up, the *trans*-$(PPh_3)_2Pt(C≡CR)_2$ complexes, **5a–c**, were all isolated as stable, colorless solids in good yield (see Table 1).

The *trans*-bis(alkynyl) complexes were easily converted to the *cis*-derivatives **6a–c** by treating a CH_2Cl_2 (or CD_2Cl_2) solution of the respective *trans*-complex (**5a–c**) with one equivalent of *cis*-1,2-bis(diphenylphosphino)ethylene (dppee). Analysis of the ^{31}P-NMR spectra of all of the *trans*-complexes **5a–c** shows a virtual triplet at ca. 20 ppm. Upon addition of the dppee (δ −22), a loss in intensity of the virtual triplet corresponding to **5a–c** is observed, concurrent with the growth of a new psuedo-triplet further downfield at ca. 54 ppm, attributed to **6a–c**. The dissociated triphenylphosphine is indicated by a resonance at −4 ppm. In addition to the deshielding of the phosphorus as the *trans*-bis(phosphino)-species is converted to a *cis*-derivative, a decrease in the phosphorus–Pt coupling is also observed, consistent with *cis*-bis(phosphino)–Pt derivatives [3]. The $^1J_{P-Pt}$ is ca. 2600–2700 Hz for the *trans*-bis(alkynyl) derivatives **5a–c**, whereas upon chelation of the dppee to form **6a–c**, $^1J_{P-Pt}$ is ca. 2200–2300 Hz. In all cases, the displacement of the triphenylphosphine appeared to be greater than 90% complete in less than 2 h, but the mixtures were left overnight to ensure complete reaction. Solvent removal and purification by

column chromatography (alumina) gave the *cis*-bis(alkynyl) complexes **6a–c** as stable solids in good to excellent yields. It is interesting to note that the *cis*-bis(alkynyl) complexes were consistently more soluble than the *trans*-analogues, significantly aiding their isolation and characterization.

All of the bis(alkynyl) complexes, **5a–c** and **6a–c**, were fully characterized using ^{1}H- and ^{13}C-NMR and IR spectroscopies, electrospray mass spectral analysis, and microanalysis, where possible. In addition to ^{31}P-NMR spectroscopy, convincing evidence for the conversion from *trans*- to *cis*-stereochemistry came from analysis of the ^{13}C-NMR spectra. In the *trans*-compounds **5a–c**, the σ-acetylide carbon ($L_2Pt(C≡CR)_2$) appears as a triplet (δ 128.9, 119.3 and 117.1, respectively) with a two-bond *cis*-coupling $^2J_{C-P} = 15$ Hz. Upon chelation of the dppee ligand, the two phosphorus nuclei are no longer magnetically equivalent, leading to a more complex splitting pattern. This carbon resonance appears as an apparent doublet of doublets at δ 125.0 and 112.3 for **6a** and **6b**, respectively [9]. The *cis*-coupling $^2J_{C-P}$ is still measured at 15 Hz in both cases, but the *trans*-$^2J_{C-P}$ coupling is significantly larger, ranging from 137 Hz for **6a** to 146 Hz for **6b** [3].

We next turned our attention toward the synthesis of strained macrocycle **8** (Scheme 2). Beginning with platinacycle **7** [6], treatment with one equivalent of dppee in CH_2Cl_2 leads to the formation of **8** in 87% isolated yield, subsequent to purification on an alumina column. This stable, bright yellow solid was fully characterized including single crystal X-ray analysis (vide infra). Like the acyclic complexes **6a–c**, the ^{31}P-NMR spectrum provides convincing evidence for the formation of **8**: a single resonance is observed at 51.7
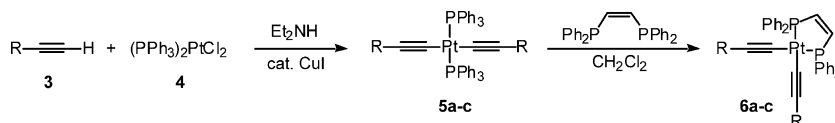
Scheme 1. Syntheses of *cis*- and *trans*-platinum bis(alkynyl) complexes.
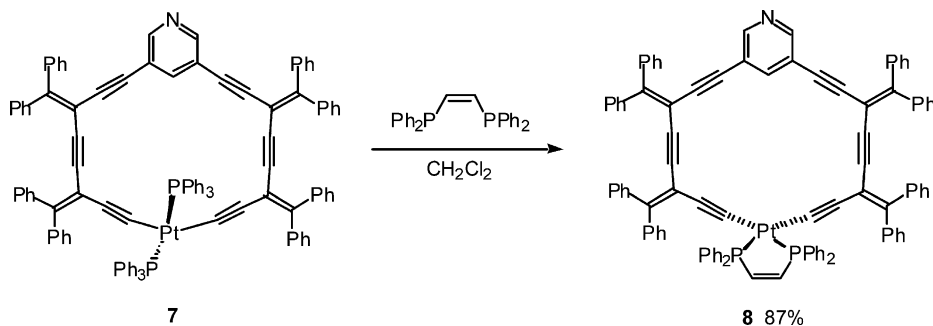
Scheme 2. Synthesis of strained *cis*-platinacycle **8**.

ppm with $^1J_{P-Pt} = 2267$ Hz. The ^{13}C-NMR spectrum (125 MHz) of **8** is consistent with that observed in the acyclic complexes and shows all 34 of the expected non-equivalent carbon resonances.

This methodology has also been applied toward the formation of a larger, bidentate, supramolecular building block, **11**, as described in Scheme 3 [10]. Pyridine-containing oligomer **9** [11] was desilylated using NaOH in THF–MeOH, and the deprotected oligomer was treated with **4** under high dilution conditions in the presence of a catalytic amount of CuI at 50 °C for 14 h. After workup and solvent removal, the large platina-cycle **10** was selectively precipitated out of a CH_2Cl_2–acetone solution, in a reasonable yield for a macro-cyclization [12]. This pale yellow solid, while quite stable, showed limited solubility (< 3 mg ml^{-1} in CH_2Cl_2), making purification by column chromatography impractical. This fact contributed to the lower isolated yield.

The ^{31}P-NMR spectrum of macrocycle **10** shows a single resonance at 18.0 ppm, consistent with the chemical shifts observed in the acyclic *trans*-acetylides. Due to the limited solubility of **10**, the signal/noise resolution of the spectrum was insufficient for observation of the expected Pt satellite peaks. The ^{13}C-NMR spectrum of compound **10** showed similarly poor signal/noise. While all of the 21 unique carbon resonances are discernible, the alkynyl quaternary carbon peaks are of especially low intensity, particularly those that are coupled to phosphorus. The most convincing evidence

for the formation of **10** comes from the ESI mass spectrum: a signal centered at *m/z* 2498.7 (100% intensity) corresponds to $[M+H^+]^+$, and the isotopic distribution of this signal is consistent with the calculated pattern for this complex [13].

The *trans*-platinacycle **10** was converted to the *cis*-derivative **11** by treating with dppee in CH_2Cl_2. After solvent removal, diethyl ether was used to extract out the triphenylphosphine produced by the reaction, leaving pure complex **11**, isolated in 71% yield. The ^{31}P-NMR spectrum shows a single resonance at δ 53.6 with $^1J_{P-Pt} = 2292$ Hz, which is consistent with the other *cis*-bis(alkynyl) species. Further support for the formation of **11** comes from ESI mass spectral analysis, which shows three significant signals at *m/z* 2281 (25%), 2265 (75%) and 2243 (100%) corresponding to $[M+K^+]^+$, $[M+Na^+]^+$ and $[M+H^+]^+$, respectively. Molecular modeling for platinacycle **11** suggest that the *syn*- and *anti*-conformations about platinum (*syn* conformation is shown in Scheme 3) should be easily interconverted in solution via bond rotation. Thus, it is unknown at present which conformation is preferred.

3. X-ray crystallographic analyses

Single crystals of air stable solids **5a**, **5b**, **6a** and **6b** for crystallographic analysis were grown from solutions as described in the experimental section. Key crystallographic details can be found in Table 2, and ORTEP
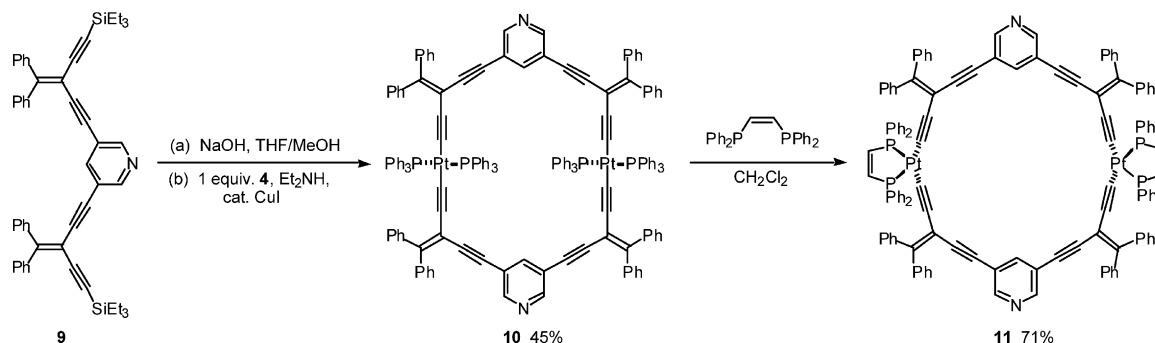

Scheme 3. Synthesis of *trans*-platinacycle **10** and *cis*-complex **11**.

Table 2
Crystallographic data for **5a**, **5b**, **6a**, **6b** and **8**

	5a	5b	6a	6b	8
Formula	$C_{58}H_{72}P_2PtSi_2$	$C_{56}H_{42}Cl_4N_2P_2Pt$	$C_{48}H_{64}P_2PtSi_2$	$C_{45}H_{32}Cl_2N_2P_2Pt$	$C_{103}H_{75}Cl_4NOP_2Pt$
Formula weight	1082.37	1141.75	954.20	928.66	1741.47
Crystal dimensions (mm³)	$0.40 \times 0.16 \times 0.08$	$0.44 \times 0.33 \times 0.07$	$0.46 \times 0.18 \times 0.12$	$0.41 \times 0.09 \times 0.06$	$0.49 \times 0.20 \times 0.19$
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$Pbca$ (no. 61)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Unit cell dimensions					
a (Å)	9.0547(6)	13.3751(7)	25.3967(10)	17.0043(8)	10.1674(4)
b (Å)	11.6651(8)	11.1464(6)	24.6617(10)	14.1145(7)	15.3820(6)
c (Å)	14.2860(10)	16.6531(9)	30.4032(13)	17.0083(8)	27.2200(12)
α (°)	67.069(1)	–	–	–	97.089(1)
β (°)	87.606(1)	94.9834(10)	–	103.8327(10)	98.465(1)
γ (°)	75.287(1)	–	–	–	99.225(1)
V (Å³)	1341.36(16)	2473.3(2)	19042.3(13)	3963.7(3)	4108.8(3)
Z	1	2	16	4	2
ρ_{calc} (g cm⁻³)	1.340	1.533	1.331	1.556	1.408
μ (mm⁻¹)	2.755	3.157	3.095	3.790	1.928
Reflections collected	8589	13590	126311	21725	25786
Independent reflections (R_{int})	5385 (0.0232)	5050 (0.0222)	19465 (0.0506)	8102 (0.0372)	16535 (0.0194)
Observed reflections [$F_o^2 \geq 2\sigma(F_o^2)$]	5376	4258	13174	6584	14840
Data/restraints/parameters	5385/6/376	5050/0/295	19465/3/947	8102/0/478	16535/2/1015
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0308	0.0329	0.0366	0.0280	0.0342
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0804	0.0947	0.0979	0.0659	0.0896

drawings are shown in Figs. 1–4. Selected bond lengths and angles for **5a**, **5b**, **6a** (two crystallographically independent molecules) and **6b** are summarized in Table 3 [14]. The only significant deviation in bond lengths between *cis*- and *trans*-derivatives is observed in the Pt–P bonds, which are consistently shorter for **6a** and **6b** than for **5a** and **5b**. The Pt–CC bond angles are typically linear, with the notable exception of **6b**, where a significant distortion occurs in the solid state and reduces these angles to 168.8(3) and 174.2(3)°. The ≡C–Pt–C≡ and P–Pt–P bond angles for **5a** and **5b** are all 180°. For complexes **6a** and **6b**, the P–Pt–P angles are quite consistent at 86° C, whereas the ≡C–Pt–C≡ bond angles vary from 89 to 95°.
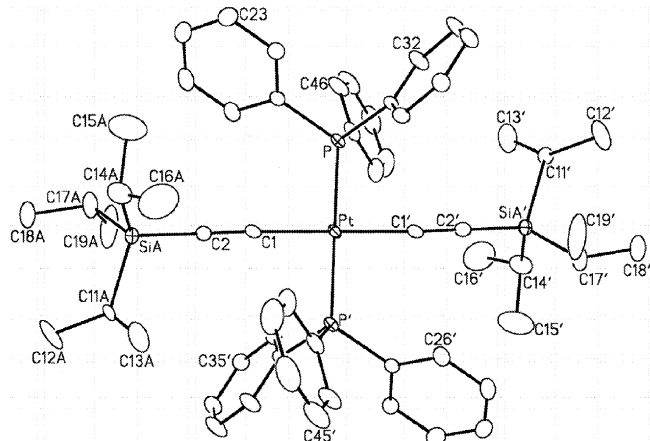
Single crystals of **8** were grown from a boiling 1,2-dichloroethane solution upon cooling and form a co–crystallite with two molecules of solvent. The solid-state structure confirms the heavily distorted and non-planar enyne framework, which would be expected due to the *cis*-platinum linkage. Overall, the main core of the macrocycle remains nearly planar, but then pivots dramatically at alkylidene carbons C(17) and C(23) to accommodate the square planar bonding to platinum. The bonding about platinum is quite similar to that observed for compounds **6**. The majority of the distortion and strain is therefore borne by the alkylidene and acetylene framework. Little bond angle distortion occurs at the alkylidene bond angles C(16)–C(17)–C(19) and C(22)–C(23)–C(25), which at 110.7(3) and 112.8(3)° are comparable to those of **7** (ca. 112.5°) [6]. In addition, the mean alkyne bond angle of 172.6° for **8** is only slightly less than that found for complex **7**
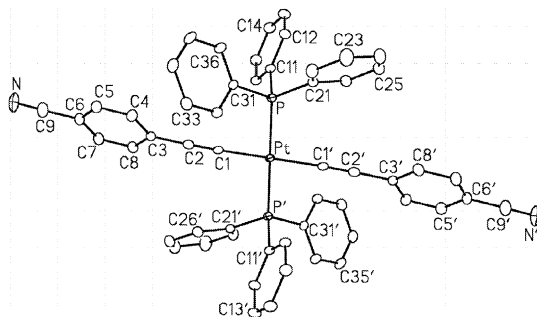

Fig. 1. Structure of *trans*-(Ph₃P)₂Pt(C≡CSiⁱPr₃)₂, **5a** (20% probability level).

Fig. 2. Structure of *trans*-(Ph₃P)₂Pt(C≡C–*p*–CN–C₆H₄)₂·(CH₂Cl₂)₂, **5b** (20% probability level, solvent omitted).
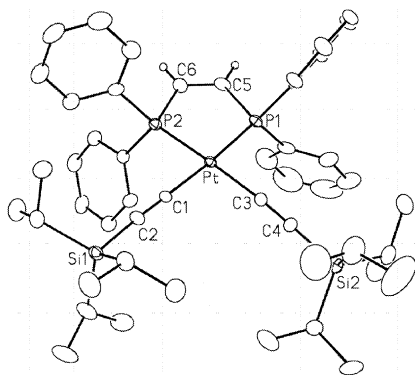
Fig. 3. Structure of *cis*-(dppee)Pt(C≡CSi^{i}Pr$_3$)$_2$·CH$_2$Cl$_2$, **6a** (20% probability level, solvent omitted).
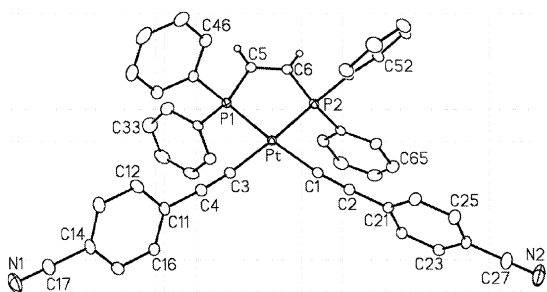

Fig. 4. Structure of *cis*-(dppee)Pt(C≡C–*p*–CN–C$_6$H$_4$)$_2$·CH$_2$Cl$_2$, **6b** (20% probability level, solvent omitted).
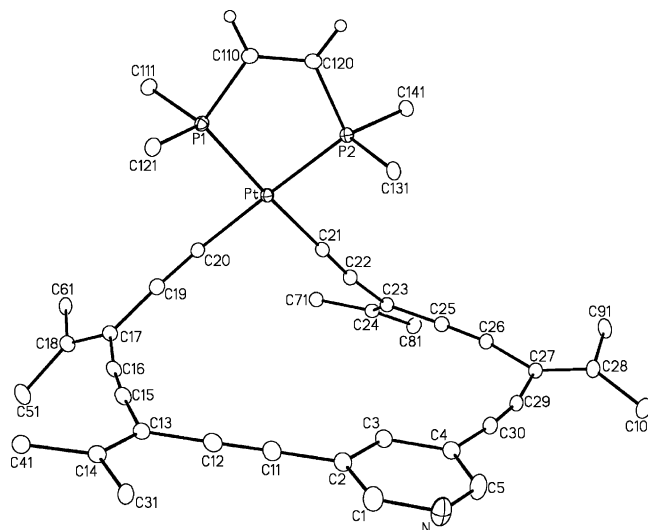

Fig. 5. Structure of **8**. Selected bond lengths (Å) and bond angles (°): Pt–P(1) 2.2686(8), Pt–P(2) 2.2711(8), P(1)–Pt–P(2) 85.61(3), P(1)–Pt–C(20) 92.30(9), P(1)–Pt–C(21) 174.62(9), P(2)–Pt–C(20) 172.76(9), P(2)–Pt–C(21) 93.65(9), C(20)–Pt–C(21) 89.07(13), C(2)–C(11)–C(12) 177.0(4), C(11)–C(12)–C(13) 178.9(4), C(13)–C(15)–C(16) 174.2(4), C(15)–C(16)–C(17) 172.3(3) C(17)–C(19)–C(20) 166.8(4), Pt–C(20)–C(19) 169.9(3), Pt–C(21)–C(22) 171.5(3), C(21)–C(22)–C(23) 173.8(4), C(23)–C(25)–C(26) 172.9(4), C(25)–C(26)–C(27) 171.1(4), C(27)–C(29)–C(30) 168.5(4), C(4)–C(30)–C(29) 174.5(4) (20% probability level; solvent and all but the *ispo* carbon atoms of the phenyl groups removed for clarity).

(173.8°) [6]. Thus, while platinacycle **8** appears to be much more strained than **7**, bond length analyses shows that this is not actually the case (Fig. 5).

In conclusion, *trans*-bis(acetylide) complexes of Pt(II) are easily converted to their *cis*-counterparts via ligand exchange with dppee. These reactions proceed easily at room temperature when triphenylphosphine is displaced from the *trans*-complex. The ability to form the strained macrocycle **8** gives an indication of a significant predisposition toward chelation versus bridging for the dppee ligand. Conversion of the platinacycle **10** to **11** demonstrates the potential usefulness of this exchange reaction for the formation of valuable supramolecular building blocks.

4. Experimental

4.1. General

Reagents were purchased reagent grade from commercial suppliers and used without further purification. Degassing of solvents was accomplished by vigorously bubbling N$_2$ through the solutions for greater than 45 min. All transmetallation reactions were performed in dry glassware under an inert atmosphere of N$_2$. Column chromatography: alumina oxide (neutral, Brockman 1, 150 mesh) from Aldrich Chemical Company Inc. Thin layer chromatography (TLC): aluminum sheets coated with alumina oxide N/UV$_{254}$ or plastic sheets coated with silica gel G UV$_{254}$ from Macherey–Nagel: visualization by UV light. M.p. Gallencamp apparatus; uncorrected. IR spectra: Nic–Plan IR microscope (as solids or cast from CH$_2$Cl$_2$, as noted). ^{1}H-, ^{13}C-, and ^{31}P-NMR: Varian Gemini 400 or 500 instruments at room temperature in CD$_2$Cl$_2$. ESIMS (m/z): micromass Zabspec oaTOF or PE Biosystems Mariner TOF instruments; solvents as noted.

4.2. *trans*-(Ph$_3$P)$_2$Pt(C≡CSi^{i}Pr$_3$)$_2$ (5a)

An excess of TIPS acetylene (112 mg, 0.615 mmol) was added to a degassed solution of **4** (114 mg, 0.144 mmol) in Et$_2$NH (50 ml). A catalytic amount of CuI (5 mg, 0.03 mmol) was added and the mixture was stirred at r.t. for 12 h and then heated to 50 °C for 4 h. Ether–CH$_2$Cl$_2$ (100 ml, 1:1 v/v) were added, and the resulting solution was washed with water (2 × 50 ml), sat. NH$_4$Cl (4 × 50 ml) and dried (MgSO$_4$). Solvent removal and subsequent precipitation from concentrated CH$_2$Cl$_2$ afforded **5a** (121 mg, 78%) as an off-white solid. M.p. 205 °C (dec.). R_f = 0.68 (hexanes–CH$_2$Cl$_2$ 2:1, alumina). IR (μscope) 3079, 3052, 2939, 2887, 2859, 2031, 1573, 1481 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.85–7.80 (m, 12H), 7.38–7.31 (m, 18H), 0.57 (d, J = 3.2 Hz, 36H),

Table 3
A comparison of selected bond lengths (Å) and bond angles (°) for **5a**, **5b**, **6a** and **6b**

	5a	5b	6a [b]	6a [c]	6b
Bond lengths					
Pt–C(1)	2.005(4)	2.024(4)	1.994(4)	2.014(5)	2.006(4)
Pt–C(3)	–	–	2.004(5)	2.011(5)	2.009(3)
C(1)–C(2)	1.207(6)	1.152(6)	1.219(6)	1.203(7)	1.212(5)
C(3)–C(4)	–	–	1.207(7)	1.213(7)	1.205(5)
Pt–P(1)	2.2973(8)	2.3161(10)	2.2622(12)	2.2587(13)	2.2583(9)
Pt–P(2)	–	–	2.2600(13)	2.2599(13)	2.2545(9)
Bond angles					
Pt–C(1)–C(2)	176.2(4)	176.2(4)	177.8(5)	177.7(5)	168.8(3)
Pt–C(3)–C(4)	–	–	176.2(5)	177.1(5)	174.2(3)
C(1)–C(2)–X	–[a]	173.8(5)	176.6(5)	178.5(5)	175.6(4)
C(3)–C(4)–X	–	–	178.4(5)	174.6(5)	176.0(4)
P–Pt–P	180.0	180.0	86.44(5)	86.18(5)	86.29(3)
≡C–Pt–C≡	180.0	180.0	88.77(18)	89.24(18)	95.32(14)
P–Pt–C(1) [or P(1)–Pt–C(1)]	93.75(10)	87.26(11)	176.48(14)	177.04(13)	174.36(10)
P–Pt–C(1′) [or P(2)–Pt–C(3)]	86.25(10)	92.74(11)	177.06(15)	177.42(14)	176.40(10)

[a] Positional disorder at Si precludes accurate determination.
[b] Crystallographically independent molecule A.
[c] Crystallographically independent molecule B.

0.37 (septet, $J = 7.3$ Hz, 6H); ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$, APT) δ 135.4 (psuedo-t, $^2J_{C-P} = 6.3$ Hz), 132.7 (psuedo-t, $^1J_{C-P} = 29$ Hz), 130.3, 128.9 (t, $^1J_{C-P} = 15$ Hz), 128.1 (psuedo-t, $^3J_{C-P} = 5.3$ Hz), 112.5, 18.8, 12.0; ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 21.2 (psuedo-t, $J_{P-Pt} = 2719$ Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) m/z 1082 ([M+H$^+$]$^+$, 14), 900 ([M–CCSi^{i}Pr$_3$+H$^+$]$^+$, 100); ES HRMS m/z Calc. for C$_{58}$H$_{73}$Si$_2$P$_2$Pt ([M+H$^+$]$^+$) 1082.4374, Found 1082.4373. Anal. Calc. for C$_{58}$H$_{72}$P$_2$PtSi$_2$: C, 64.36; H, 6.70. Found: C, 64.05; H, 6.64%. Single crystals for X-ray crystallography grown by slow evaporation from a CD$_2$Cl$_2$ solution at r.t.

4.3. trans-(Ph₃P)₂Pt(C≡C–p-CN–C₆H₄) (5b)

TMS-protected ethynylbenzonitrile (60 mg, 0.30 mmol) was dissolved in THF–MeOH (20 ml) and treated with NaOH [15]. After stirring at r.t. for 1 h, ether (15 ml) was added and the resulting solution was washed with sat. NH$_4$Cl (2 × 15 ml), dried over MgSO$_4$ and the solvent was removed. The resulting deprotected alkyne was added, with no further purification, to a degassed solution of **4** (120 mg, 0.152 mmol) in Et$_2$NH (50 ml). A catalytic amount of CuI (5 mg, 0.03 mmol) was added and the mixture was stirred at 50 °C for 14 h. Ether–CH$_2$Cl$_2$ (100 ml, 1:1 v/v) were added, and the resulting solution was washed with water (2 × 50 ml), sat. NH$_4$Cl (4 × 50 ml) and dried (MgSO$_4$). Solvent removal and subsequent precipitation from concentrated CH$_2$Cl$_2$ afforded **5b** (90 mg, 62%) as an off-white solid. M.p. 228 °C (dec.). $R_f = 0.25$ (CH$_2$Cl$_2$, silica). IR (CH$_2$Cl$_2$, cast) 3053, 2223, 2105, 1595, 1495 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.80–7.75 (m, 12H), 7.47–7.38 (m, 18H), 7.19 (d, $J = 8.6$ Hz, 4H), 6.31 (d, $J = 8.6$

Hz, 4H); ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$, APT) δ 135.1 (psuedo-t, $^2J_{C-P} = 6.0$ Hz), 133.2 (t, $^4J_{C-P} = 1.3$ Hz), 131.3, 131.2 (t, $^5J_{C-P} = 1.3$ Hz), 131.1 (psuedo-t, $^1J_{C-P} = 29$ Hz), 130.9 (psuedo-t, $^4J_{C-P} = 1.0$ Hz), 128.3 (psuedo-t, $^3J_{C-P} = 5.4$ Hz), 119.6, 119.3 (t, $^2J_{C-P} = 15$ Hz), 112.8 (t, $^3J_{C-P} = 2.3$ Hz), 107.8; ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 19.8 (psuedo-t, $J_{P-Pt} = 2601$ Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) m/z 1004 ([M+H$^+$+MeOH]$^+$, 100); ES HRMS m/z Calc. for C$_{55}$H$_{43}$N$_2$OP$_2$Pt ([M+H$^+$+MeOH]$^+$) 1004.2494, Found 1004.2499. Anal. Calc. for C$_{54}$H$_{38}$N$_2$P$_2$Pt·CH$_2$Cl$_2$: C, 62.51; H, 3.81; N, 2.65. Found: C, 63.28; H, 3.64; N, 2.62%. Single crystals for X-ray crystallography were grown by layering a CH$_2$Cl$_2$ solution with hexanes and allowing slow diffusion at 4 °C.

4.4. trans-(Ph₃P)₂Pt(C≡Cpyr–meta-(C≡CSi^{i}Pr₃))₂ (5c)

3-(Trimethylsilylethynyl)-5-(triisopropylsilylethynyl)pyridine (28 mg, 0.079 mmol) was mono-deprotected by dissolving in THF–MeOH (20 ml) and treating with K$_2$CO$_3$ (10 mg). After stirring at r.t. for 2 h, ether (15 ml) was added and the resulting solution was washed with sat. NH$_4$Cl (2 × 15 ml), dried over MgSO$_4$ and the solvent was removed. The resulting deprotected alkyne was added, with no further purification, to a degassed solution of **4** (31 mg, 0.039 mmol) in Et$_2$NH (40 ml). A catalytic amount of CuI (3 mg, 0.02 mmol) was added and the mixture was stirred at 50 °C for 14 h. Ether–CH$_2$Cl$_2$ (100 ml, 1:1 v/v) were added, and the resulting solution was washed with water (2 × 50 ml), sat. NH$_4$Cl (4 × 50 ml) and dried (MgSO$_4$). Solvent removal and purification via column chromatography

(CH$_2$Cl$_2$, alumina) afforded **5c** (38 mg, 76%) as an off-white solid. M.p. 191 °C (dec.). R_f = 0.78 (CH$_2$Cl$_2$, alumina). IR (CH$_2$Cl$_2$, cast) 3056, 2942, 2864, 2155, 2106, 1573, 1463 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 8.17 (br d, 2H, J = 1.5 Hz), 7.82–7.77 (m, 12H), 7.47–7.40 (m, 20H), 6.50 (psuedo-t, 2H, J = 2.0 Hz); ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$, APT) δ 150.8, 148.2, 140.6, 135.3 (psuedo-t, $^2J_{C-P}$ = 6.0 Hz), 131.4 (psuedo-t, $^1J_{C-P}$ = 29 Hz), 131.0, 128.4 (psuedo-t, $^3J_{C-P}$ = 5.3 Hz), 124.5, 119.3, 117.1 (t, $^2J_{C-P}$ = 15 Hz), 109.0, 104.1, 93.9, 18.8, 11.7; ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 19.9 (psuedo-t, J_{P-Pt} = 2607 Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) m/z 1285.5 ([M+H$^+$]$^+$, 100).

4.5. cis-(dppee)Pt(C≡CSi^{i}Pr$_3$)$_2$ (6a)

cis-1,2-bis(Diphenylphosphino)ethylene (18 mg, 0.045 mmol) was added to a solution of **5a** (50 mg, 0.046 mmol) in CH$_2$Cl$_2$ (5 ml) and the mixture was stirred at r.t. for 14 h. Solvent removal followed by purification via column chromatography (hexanes–CH$_2$Cl$_2$ 2:1, alumina) afforded **6a** (42 mg, 95%) as a colorless solid. M.p. 250 °C (dec.). R_f = 0.68 (hexanes–CH$_2$Cl$_2$ 2:1, alumina). IR (CH$_2$Cl$_2$, cast) 2938, 2888, 2860, 2057, 1462, 1436 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.89–7.83 (m, 8H), 7.50–7.31 (m, 14H), 0.98–0.93 (m, 42H); ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$) δ 146.9 (psuedo-dd, $^1J_{C-P}$ = 48, $^2J_{C-P}$ = 26 Hz), 134.1–133.9 (m), 131.5, 130.3 (psuedo-dt, $^1J_{C-P}$ = 57, $^2J_{C-Pt}$ = 24 Hz), 129.2–129.1 (m), 125.0 (dd, $^2J_{C-P}$ = 137 Hz (trans), $^2J_{C-P}$ = 15 Hz (cis), 111.3–108.4 (psuedo-dt, $^3J_{C-P}$ = 30 Hz, $^2J_{C-Pt}$ = 273 Hz), 19.1, 12.3; ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 52.0 (psuedo-t, J_{P-Pt} = 2208 Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) m/z 976 ([M+Na$^+$]$^+$, 100), 955 ([M+H$^+$]$^+$, 37); ES HRMS m/z Calc. for C$_{48}$H$_{64}$NaSi$_2$P$_2$Pt ([M+Na$^+$]$^+$) 976.3562, Found 976.3560. Anal. Calc. for C$_{48}$H$_{64}$P$_2$PtSi$_2$·0.5H$_2$O: C, 59.85; H, 6.80. Found: C, 59.83; H, 6.61%. Single crystals for X-ray crystallography were grown by layering a CH$_2$Cl$_2$ solution with hexanes and allowing slow diffusion at 4 °C.

4.6. cis-(dppee)Pt(C≡C–p-CN–C$_6$H$_4$)$_2$ (6b)

cis-1,2-bis(Diphenylphosphino)ethylene (10 mg, 0.025 mmol) was added to a solution of **5b** (25 mg, 0.026 mmol) in CH$_2$Cl$_2$ (2 ml) and the mixture was stirred at r.t. for 14 h. Solvent removal followed by purification via column chromatography (CH$_2$Cl$_2$, alumina) afforded **6b** (20 mg, 91%) as a light brown solid. M.p. 164 °C (dec.). R_f = 0.70 (CH$_2$Cl$_2$, alumina). IR (CH$_2$Cl$_2$, cast) 3054, 2223, 2112, 1597, 1495, 1483 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.81–7.74 (m, 8H), 7.58–7.35 (m, 18H), 7.22 (d, J = 8.6 Hz, 4H); ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$) δ 146.7 (psuedo-dd, $^1J_{C-P}$ = 48 Hz, $^2J_{C-P}$ = 25 Hz), 133.6–133.3 (m), 132.6 (psuedo-t,

J_{C-Pt} = 270 Hz), 131.9, 131.8, 131.5 (psuedo-t, $^4J_{C-P}$ = 5 Hz), 129.9–129.1 (m, two coincident carbons), 119.4 112.3 (psuedo-dd, $^2J_{C-P}$ = 146 Hz (trans), $^2J_{C-P}$ = 15 Hz (cis)), 110.7 (psuedo-dt, $^3J_{C-P}$ = 31 Hz, $^2J_{C-Pt}$ = 308 Hz), 108.6; ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 53.93 (psuedo-t, J = 2276 Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) m/z 1710 ([2M+Na$^+$]$^+$, 61), 866 ([M+Na$^+$]$^+$, 30); ES HRMS m/z Calc. for C$_{44}$H$_{31}$N$_2$P$_2$Pt ([M+H]$^+$) 844.1610, Found 844.1613. Anal. Calc. for C$_{44}$H$_{30}$N$_2$P$_2$Pt·CH$_2$Cl$_2$: C, 58.20; H, 3.47; N, 3.01. Found: C, 58.13; H, 3.20; N, 2.96%. Single crystals for X-ray crystallography were grown by layering a CH$_2$Cl$_2$ solution with hexanes and allowing slow diffusion at 4 °C.

4.7. cis-(dppee)Pt(C≡Cpyr–meta-(C≡CSi^{i}Pr$_3$))$_2$ (6c)

cis-1,2-bis(Diphenylphosphino)ethylene (8 mg, 0.02 mmol) was added to a solution of **6a** (25 mg, 0.019 mmol) in CH$_2$Cl$_2$ (2 ml) and the mixture was stirred at r.t. for 2 h. Solvent removal followed by purification via gradient column chromatography (CH$_2$Cl$_2$ to CH$_2$Cl$_2$–acetone 5:1, alumina) afforded **6c** (14 mg, 64%) as a pale blue transparent solid. M.p. 93 °C. R_f = 0.20 (neat CH$_2$Cl$_2$, alumina). IR (CH$_2$Cl$_2$, cast) 2942, 2890, 2864, 2156, 2113, 1574, 1462 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 8.35 (br s, 2H), 8.26 (br s, 2H), 7.82–7.76 (m, 8H), 7.59–7.34 (m, 16H) 1.13–1.12 (m, 42 H); ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$) δ 151.1, 148.8, 146.8 (psuedo-dd, $^1J_{C-P}$ = 48 Hz, $^2J_{C-P}$ = 26 Hz), 140.6, 133.8–133.5 (m), 132.0, 130.0–129.2 (m, two coincident carbons), 124.1 119.8, 103.9, 94.5, 18.4, 11.7 (two carbons not observed); ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 53.9 (psuedo-t, J = 2277 Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) m/z 1179 ([M+Na$^+$]$^+$, 70), 1157 ([M+H$^+$]$^+$, 100);

4.8. cis-Macrocycle 8

cis-1,2-bis(Diphenylphosphino)ethylene (6 mg, 0.02 mmol) was added to a solution of platinacycle **7** (25 mg, 0.015 mmol) in CH$_2$Cl$_2$ (2 ml) and the mixture was stirred at r.t. for 14 h. Solvent removal followed by purification via column chromatography (hexanes–CH$_2$Cl$_2$ 1:2, alumina) afforded **8** (20 mg, 87%) as a bright yellow solid. M.p. 201 °C (dec.). R_f = 0.38 (hexanes–CH$_2$Cl$_2$ 1:2, alumina). IR (CH$_2$Cl$_2$, cast) 3053, 2157, 2093, 1658, 1597, 1486 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 8.12 (d, J = 2.0 Hz, 2H), 8.08 (t, J = 2.0 Hz, 1H), 7.85–7.78 (m, 8H), 7.50–7.00 (m, 54H); ^{13}C-NMR (125 MHz, CD$_2$Cl$_2$, APT) δ 153.8, 149.7, 148.7, 146.9 (psuedo-dd, $^1J_{C-P}$ = 48 Hz, $^2J_{C-P}$ = 26 Hz), 143.1, 142.1, 141.2, 140.9, 140.1, 133.9–133.7 (m), 131.6, 130.9 (two coincident carbons), 130.8, 130.4, 130.0 (psuedo-t, $^1J_{C-P}$ = 58 Hz), 129.3–129.2 (m), 129.0, 128.9, 128.1 (two coincident carbons), 127.9 (two

coincident carbons), 127.8, 127.6, 120.3, 112.1 (psuedo-dd, $^2J_{C-P} = 118$ Hz (*trans*), $^2J_{C-P} = 12$ Hz (*cis*)), 110.5 (psuedo-d, $^3J_{C-P} = 27$ Hz), 105.8, 102.9, 94.9, 93.9, 88.3, 88.2; ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 51.7 (psuedo-t, $J = 2267$ Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) *m/z* 1548 ([M + Na$^+$]$^+$, 100), 1525 ([M + H$^+$]$^+$, 64). Anal. Calc. for C$_{99}$H$_{65}$NP$_2$Pt: C, 77.94, H, 4.29, N, 0.92. Found: C, 77.75, H, 4.22, N, 0.95.

4.9. trans-Macrocycle 10

Oligomer **9** (62 mg, 0.082 mmol) was deprotected by dissolving in THF–MeOH (20 ml) and treating with saturated NaOH solution (3 ml) [11]. After stirring at r.t. for 4 h, ether (15 ml) was added and the resulting solution was washed with sat. NH$_4$Cl (2 × 15 ml), dried over MgSO$_4$ and the solvent was removed. The resulting deprotected alkyne was added, with no further purification, to a degassed solution of **4** (65 mg, 0.082 mmol) in Et$_2$NH (150 ml). A catalytic amount of CuI (5 mg, 0.03 mmol) was added and the mixture was stirred at 50 °C for 14 h. Ether–CH$_2$Cl$_2$ (150 ml, 1:1 v/v) were added, and the resulting solution was washed with water (2 × 50 ml), sat. NH$_4$Cl (4 × 50 ml) and dried (MgSO$_4$). Solvent removal (using no heat) followed by precipitation from CH$_2$Cl$_2$–acetone afforded **10** (45 mg, 45%) as a bright yellow solid. M.p. 166 °C (dec.). $R_f = 0.08$ (hexanes–CH$_2$Cl$_2$ 1:1, alumina). IR (CH$_2$Cl$_2$, cast) 3050, 2201, 2083, 1581, 1481 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.77 (d, 4H, $J = 2.0$ Hz), 7.65–7.59 (m, 24H), 7.42–7.37 (m, 12H), 7.35 (psuedo-t, 2H, $J = 2.0$ Hz), 7.31–6.82 (m, 64H); ^{13}C-NMR (125 MHz, CD$_2$Cl$_2$) δ 150.3, 149.1, 142.3, 140.6, 139.1, 135.4 (psuedo-t, $^2J_{C-P} = 6.2$ Hz), 131.2 (psuedo-t, $^1J_{C-P} = 29$ Hz), 130.9, 130.8, 130.4, 128.2 (psuedo-t, $^3J_{C-P} = 6.6$ Hz), 127.8 (two coincident carbons), 127.5, 127.2, 120.7, 118.9 (signal too weak to observe P or Pt coupling), 111.2 (signal too weak to observe P or Pt coupling), 105.9, 95.7, 85.5; ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 18.0 (coupling to Pt not observed due to poor signal/noise); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) *m/z* 2498.7 ([M + H$^+$]$^+$, 100).

4.10. cis-Macrocycle 11

cis-1,2-bis(Diphenylphosphino)ethylene (5 mg, 0.01 mmol) was added to a solution of **10** (16 mg, 0.0064 mmol) in CH$_2$Cl$_2$ (5 ml) and the mixture was stirred at r.t. for 14 h. Solvent reduction followed by washing with diethyl ether (2 × 2 ml) and subsequent filtration afforded **11** (10 mg, 71%) as a pale yellow solid. M.p. 160 °C (dec.). IR (CH$_2$Cl$_2$, cast) 3050, 2090, 1575, 1483 cm^{-1}; ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.95 (d, $J = 2$ Hz, 4H), 7.62–7.57 (m, 16H), 7.49–7.45 (m, 8H), 7.37–7.18 (m, 48H), 7.05 (psuedo-t, $J = 2.1$ Hz, 2H), 6.88–6.84 (m, 4H), 6.65–6.61 (m, 8H); ^{13}C-NMR (100 MHz, CD$_2$Cl$_2$) δ 151.6, 150.1, 141.9, 141.2, 139.6, 133.7–133.6

(m), 131.5, 130.8, 130.5, 129.7 (psuedo-t, $^1J_{C-P} = 57$ Hz), 129.1–129.0 (m), 127.9, 127.7, 127.4 (two coincident carbons), 119.9, 95.6, 85.8 (4 carbons not observed); ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$) δ 53.6 (psuedo-t, $J = 2292$ Hz); ESMS (NO$_2$Me–ClCH$_2$CH$_2$Cl) *m/z* 2265 ([M + Na$^+$]$^+$, 75), 2243 ([M + H$^+$]$^+$, 100).

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 210797–210801 for compounds **5a**, **5b**, **6a**, **6b** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[10] See, for example: K. Campbell, C.J. Kuehl, M.J. Ferguson, P.J. Stang, R.R. Tykwinski, J. Am. Chem. Soc. 124 (2002) 7266.

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[13] We attempted to improve the solubility of this complex through the use of Et$_3$P rather than Ph$_3$P ligands, but found that the resulting *trans*-acetylide complex (analogous to **10**) did not convert to *cis*-derivative upon reaction with dppee, presumably due to the reduced lability of the Et$_3$P ligand.

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